# Intense Pulsed Neutron Source

# POSY2
# A Users Guide

June 2004

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# Disclaimer

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# Acknowledgements

The current data analysis, fitting and plotting package, called POSYIDL2, is based on software originally written for IPNS using Interactive Data Language (IDL) from Research Systems, Inc. by Dr. Alan Munter.

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## ALL EMERGENCIES 911

# IPNS Operations

While the IPNS facility operates seven days a week, twenty four hours a day during normal operations, there are scheduled periods during oerations cycles when IPNS does not produce neutrons for users. These periods are as follows:

RCS maintanence checks:

Daily 9:00 A.M. - 9:15 A.M.

Accelerator machine research periods:

First Thursday of every run cycle 9:00 A.M. - 11:00 A.M.

Every Tuesday 9:00 A.M. - 3:00 P.M.

Moderator annealing:

Every Monday and Friday, 9:00 A.M. - 9:45 A.M.

Moderator gas exchange:

Every Tuesday, during machine research, 9:00 A.M. - 3:00 P.M.

No data will be collected during these periods. This is normal.

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# Setting Up and Starting Run Files

This Chapter describes how to set up and start a new run, or a sequence of new runs, stop an active run and schedule a run , or a sequence of runs. It is assumed that all run file set up will be done from the DEC Windows terminal (the big screen by the computer). In all instances, <cr> means carriage return.

NOTE: Pay particular attention to the setting up process: it contains several parts and is the most important part of the data collection process. Discuss the set up parameters beforehand, and decide on the final settings before you start setting up a run file.

## Opening the POSY Directory

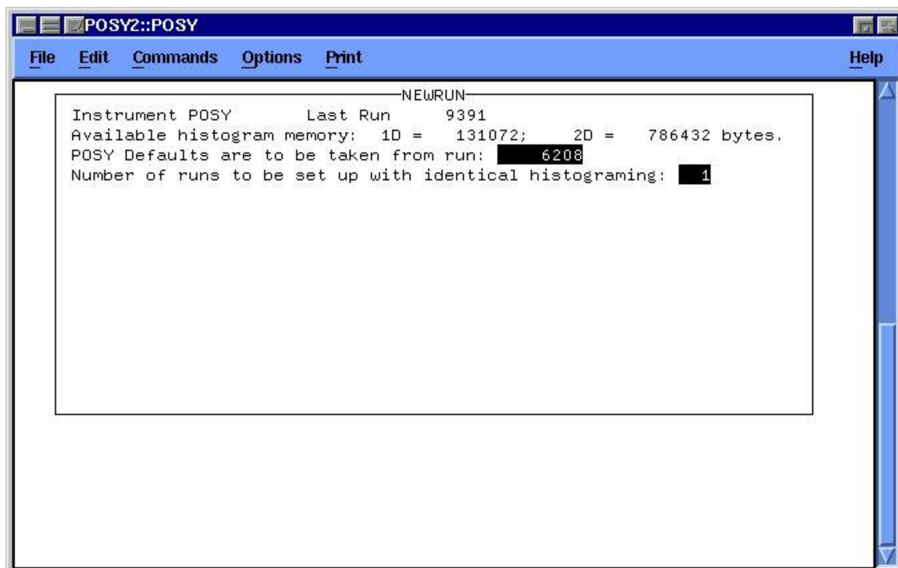
To move to the POSY directory, type SET DEF [POSY] <cr> (make sure there is a space between DEF and [POSY]). Other directories are: [POSY.DATA], where all the data is stored, and [POSY.POLYMER] which contains the programs that manually change sample settings such as temperature and angle.

## Defining a New Run

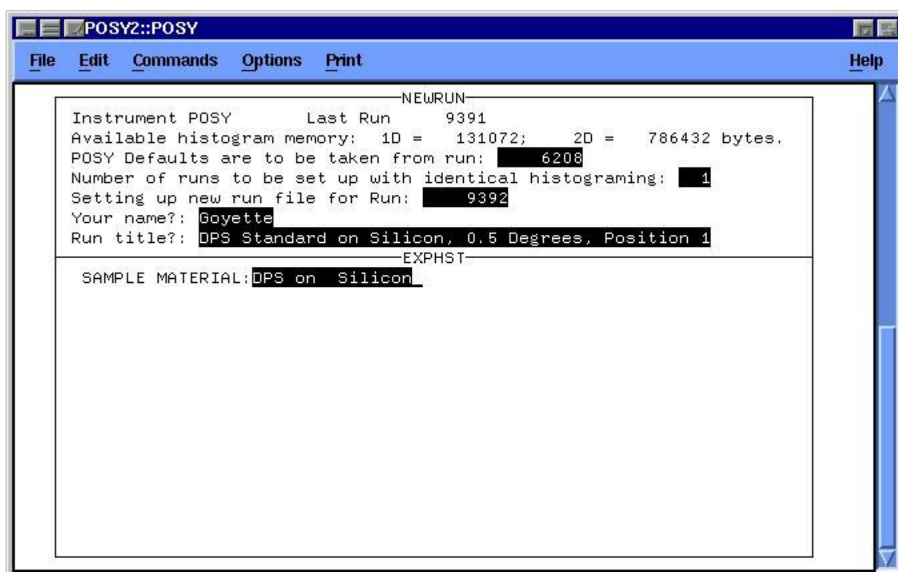
To define a new run , use the following procedure:

Type NEWRUN <cr>.

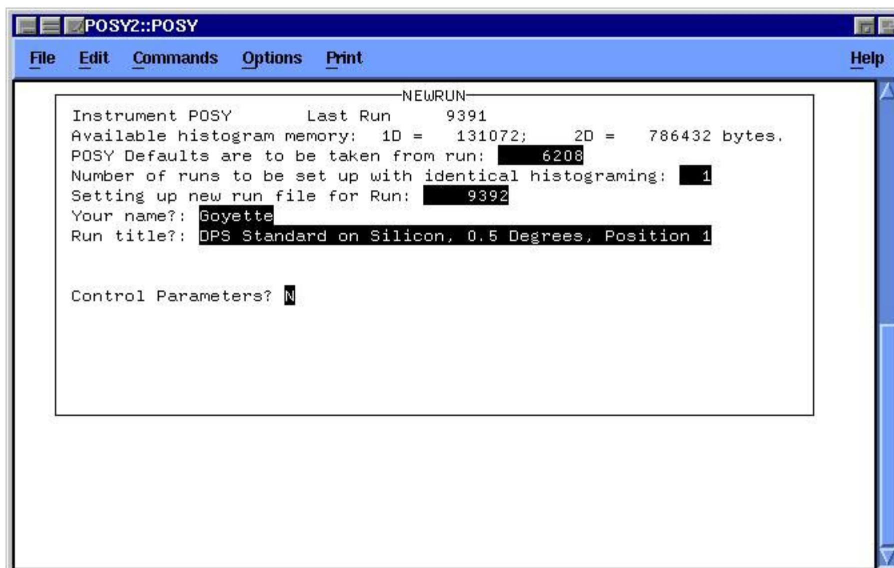
The MicroVax allows you to adjust the settings of the run by prompting you with a list of questions. Some of these settings have default values which will appear after the prompt in a black highlighted region. These should normally be accepted, by pressing the carriage return (<cr>). First, you will have to choose a run file from which to read the parameters for this run file:




Do not change the default run number without first consulting with a member of the POSY2 staff. You will also be asked how many runs to set up with identical histogramming. This number will usually be one. Setting up more than one run will be covered at the end of the chapter. Next you will be asked to supply some information on the new run:




After which you will be placed back in the main menu. Next you will have the option of changing some control parameters:



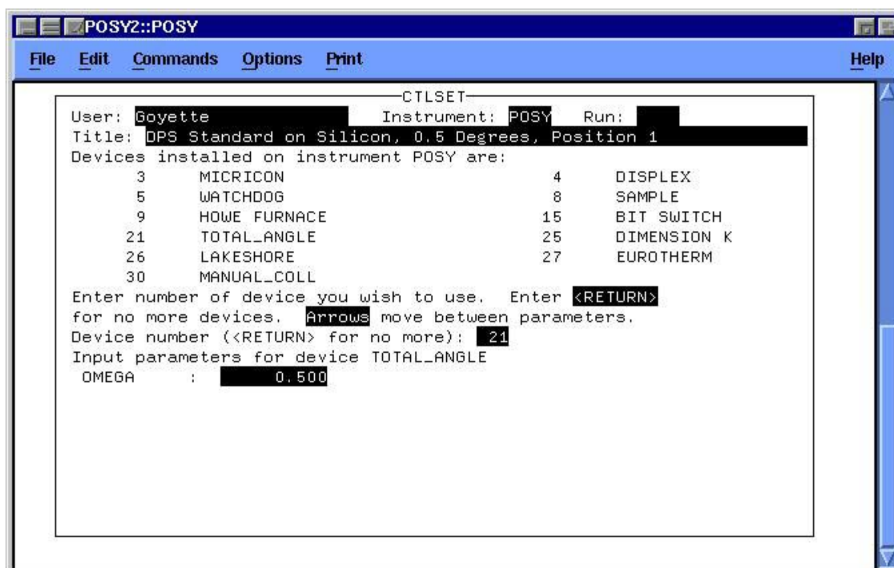

If you do not want to change any of the control parameters (for example, the angle) then enter a carriage return to complete the set up of the run.

# Changing Control Parameters

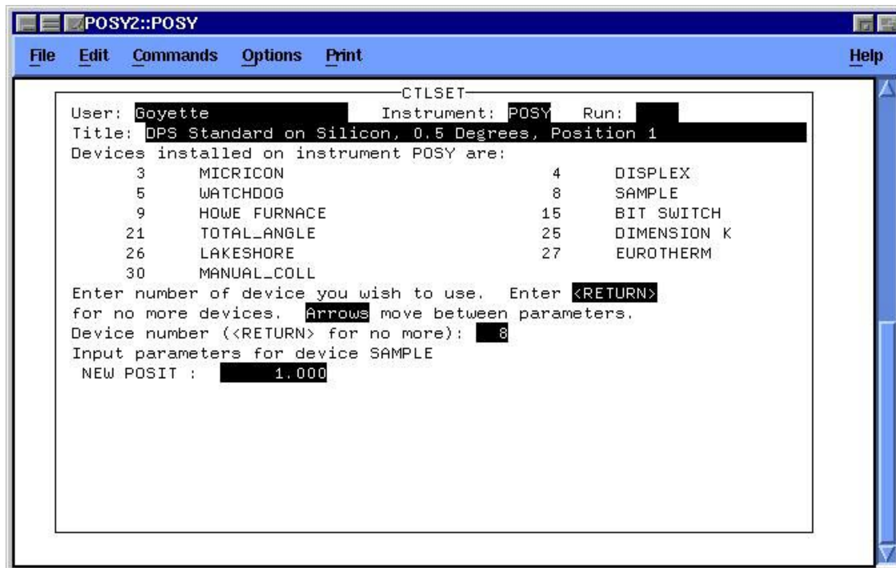
If you wish to change some control parameters, you should still be at the prompt :

```
Control Parameters:  {N}.
```

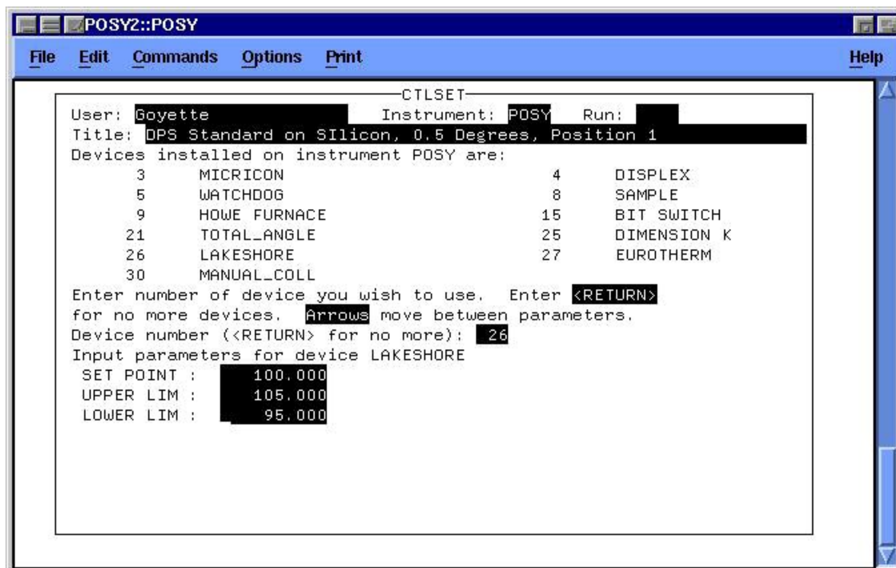
Type: Y <cr> . This will bring up an additional menu. Choosing the default setting of zero, or typing zero if the device is set to another number, will put you back to the Newrun menu. Currently, only Total_Angle, Lakeshore, Manual_coll and Sample are installed. To change the angle of the sample, choose Device Number 21:



Input the desired sample angle in degrees. When the run is started the computer will automatically set the sample angle and collimator positions. The sample changer can be pre-loaded with up to four different samples. Any one of the four samples may be chosen by specifying in which position the desired sample is located. To use the sample changer, choose Device Number 8:



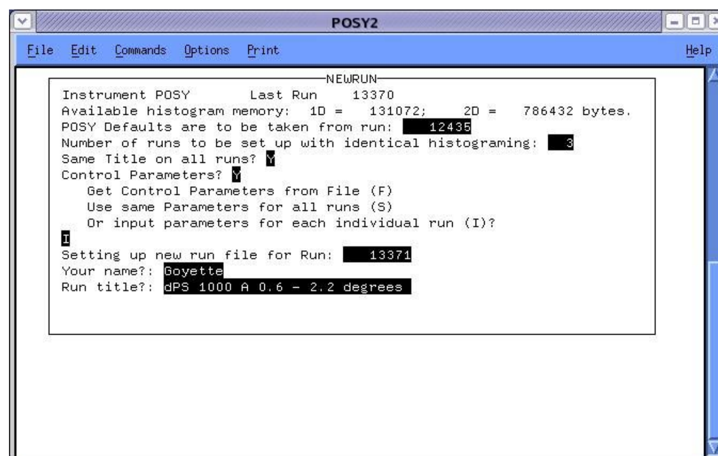

If you are using the in-situ sample heater, you may wish to set the sample temperature from the run file. To set the sample temperature, use device number 26 (Lakeshore):




Enter the desired set point at the prompt. This is the temperature the Lakeshore controller will hold. Next, enter an upper and a lower limit for the temperature. This is a temperature window that is acceptable to you for data collection. If the temperature moves out of this window, the runtime software will inhibit data collection until the temperature moves back into this window.

# Setting Up Multiple Runs

Setting up more than one run is similar to setting up runs one at a time. You will be asked some additional questions during the set up process:




Type in the number of runs you want to setup. You may use the same title on all runs, but remember to include additional information in the title so you can distinguish the difference between the runs. The runtime software will prepend your title with the phrase specifying what position the run has in the sequence (1 of 3, 2 of 3, 3 of 3). Select the default “Input parameters for each individual run” at the appropriate prompt. When it is time to enter control parameters, you will do so in the manner described earlier, except that the control parameter window will appear sequentially for each run you are setting up. For example, if you are setting up three run files, the control parameter window will appear, the title will be something like “1 of 3 dPS 1000A 0.6 - 2.2 Degrees”. You will enter control parameters in the usual way. When you are done with the first run file, the control parameter window will appear again, but this time the title will be “2 0f 3 dPS 1000A 0.6 - 2.2 Degrees”, and you will enter the control parameters for the second run file. This will repeat for the third run file. After all run files are setup, verify, schedule and start the runs in the usual manner.

# Checking Control Parameters

Before typing START, it would be wise to check the control parameters by using the command PRUN CONTROL RUN #.

When you use the Prun Control command, the computer will display all control parameters that were set for that run number. If you set the angle as a control parameter, the current angle and the angle that will be set for the next run will be displayed:

POSY2::POSY

File Edit Commands Options Print Help

```
POSY2_POSY> prun control 9392
 N32016 MICROPROCESSOR -  1 PROCESSORS

POSY RUN      9392:  Goyette
DPS Standard on Silicon, 0.5 Degrees, Position 1

Controlled Devices and Parameter Settings
 DEVICE:  TOTAL_ANGLE
OMEGA          0.500 UPSTR      2672.920 DNSTR      -279.120 OMEGA NOW     0.400
UPSTR NOW  2673.000 DNSTR NOW  -278.000 OMEGA LOW     0.000 UPSTR LOW    50.000
DNSTR LOW  -600.000 OMEGA HI       5.000 UPSTR HI   3500.000 DNSTR HI   3500.000
OMEGA STP      4.000 UPSTR STP      1.000 DNSTR STP      1.000 OMEGA BCK    50.000
UPSTR BCK     50.000 DNSTR BCK     50.000 OMEGA MOT      1.000 UPSTR MOT     2.000
DNSTR MOT      3.000
 DEVICE:  SAMPLE
NEW POSIT      1.000
POSY2_POSY>
```

Omega lists the angle for the new run, Omega Now lists the value prior to the new run. The data listed after Omega Now are low and high limits that can be set on the stepper. Similarly, Information on the settings for the upstream and downstream collimator slits are also given .  Information on sample position will also be displayed if sample position was set as a control parameter.

NOTE: PRUN CONTROL will only give information on the angle, collimator and sample position and temperature if they were set as control parameters. It will not give any information if the angle is set using the programs SETANG, SAMPLE or TEMTUR.

## Scheduling Runs

If you want to schedule a run to run for a set amount of time, use the schedule command:

SCHEDULE TIME(RUN#)/# OF PULSES <cr>

There are 108000 Pulses in one hour, so if you want a run to last one hour then use 108000P for # of pulses, and the number 1 for time. If you want a run to be 30 min., then use 54000P for # of pulses, and 1 for time. Lets say that you wanted to schedule three runs in a row, and that these runs have run #'s 500,501 and 502. Lets also assume that you want the first run to last two hour, the second run to last one-half hour, and the third run to last three-quarters of an hour. Your first schedule command would look like this:

SCHEDULE 2(500)/108000P <cr>

the second schedule command would look like:

SCHEDULE 1(501)/54000P <cr>

and the third schedule command would be:

SCHEDULE 3(502)/27000P <cr>.

Notice that for the third command, we have specified the number of pulses corresponding to one-quarter of an hour, but we have defined the time of the run to be three of these increments: three groups of pulses at 1/4 hour per group is 3/4 hour for run 502. You must set the parameters for each run using the NEWRUN command, before you can schedule the run. If you have not done this before, refer to the section on STARTING A NEW RUN. You may check the scheduling of a run using PRUN CONTROL. If you have scheduled more than one run and you want to check them all then use the same command, but list all the runs you want to check:

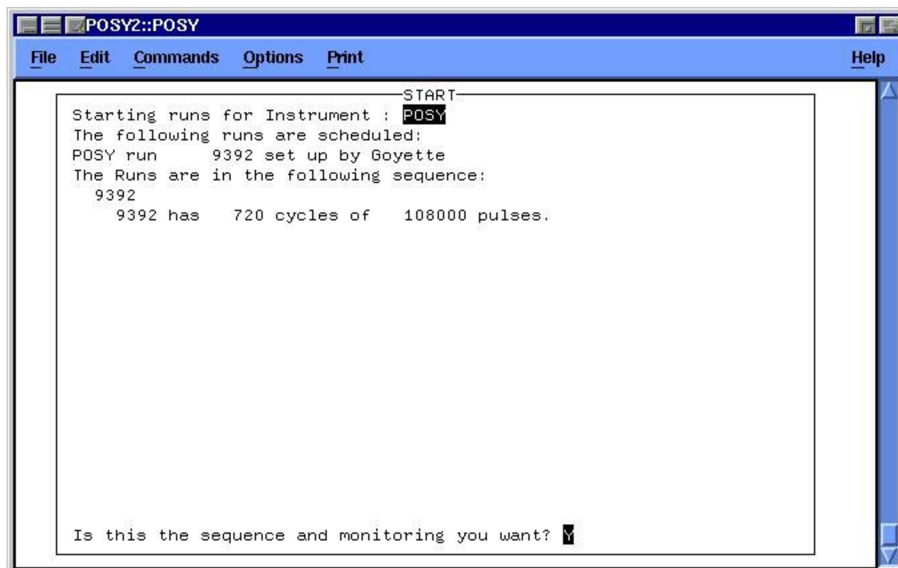
PRUN CONTROL 500,501,502 <cr>.

## Starting a Run

You may use the START command to start a run or a series of runs. To start run number 500 you would type:

START 500

You will be presented with the STARTRUN window:




Type Y at the prompt if the information is correct to start the run. Type N to re-enter the start command with the prper information.

You may also start a series of runs at the same time. For example, to start the example runs from before, you would type:

START 500,501,502 <cr>.

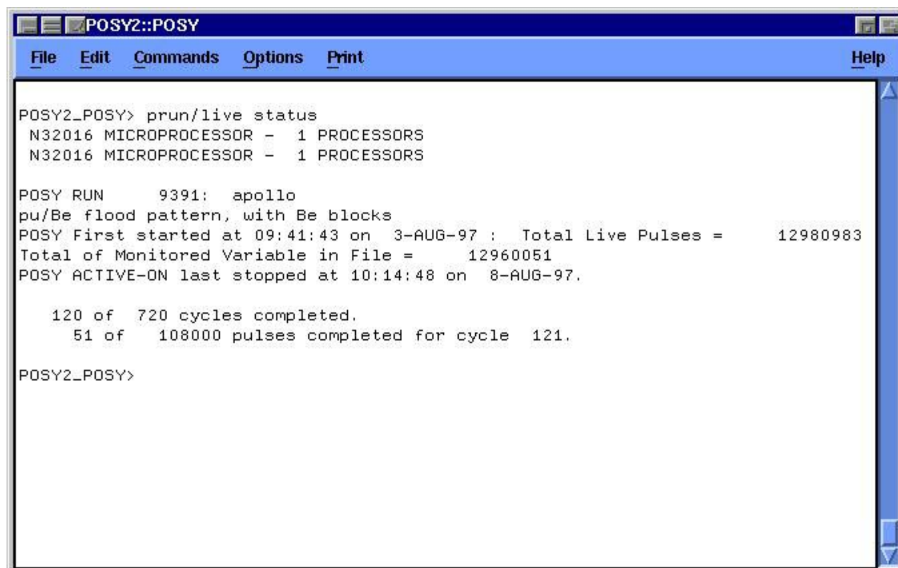
This command will start run 500 and run it for the scheduled amount of time. once run 500 is finished, 501 will start and run for its scheduled amount of time. Finally, run 502 will be started and will run for its scheduled time.

# Checking the Status of a Live Run

To determine whether a live run is active, or to determine the status of a run that is known to be live, use the command PRUN/LIVE STATUS.

POSY2_POSY> prun/live status

The computer will display information concerning the live run:




## Reading T0 Pulses Using RDP

You can monitor the number of T0 pulses that have been counted by typing the command RDP. The number of T0 pulses will be displayed:

```
POSY: NUMBER OF T0 PULSES=    107778
```

## Checking the angle using ANGCAL

The program ANGCAL is available to check the current angle setting and also to determine the correct position channel and collimation for any angle. To use this program type ANGCAL. You will be prompted:

```
CALIBRATE ANGLE (A) OR COLLIMATION (C) (DEFAULT=A):
```

Enter an A or return to check the angle. You will get another prompt:

```
PEAK CHANNEL NUMBER OR ANGLE :
```

You can enter an angle or a position channel. Any number greater than 3.0 is assumed to be a position channel. Any number less than or equal to 3.0 is assumed to be an angle. If you enter a position channel, the program will tell you the corresponding angle:

```
PEAK CHANNEL NUMBER OR ANGLE : 200
ANGLE =0.44741 DEGREES
```

If you enter an angle the program will tell you the corresponding position channel.

```
PEAK CHANNEL NUMBER OR ANGLE : 0.5
CHANNEL =195.58
```

To check the proper collimation for a specific angle, enter C at the initial prompt and then enter the desired angle at the appropriate prompt. You will be shown the correct collimation for both collimators:

```
ENTER DESIRED ANGLE : 0.5
UPSTREAM COLLIMATOR SETTING FOR 0.50 DEGREES IS 2634.
DOWNSTREAM COLLIMATOR SETTING FOR 0.50 DEGREES IS 2796.
```

Note: Collimation is normally determined automatically from the sample angle.

## Calibrating the Sample Angle

If after using ANGCAL you determine that the actual sample angle does not correspond to the angle recorded by the computer, you may correct the angle recorded by the computer using the following procedure. After running ANGCAL to determine the actual sample angle run SETANG and type C for Calibrate Angle. Enter the actual sample angle you determined using ANGCAL. Then type E for EXIT. Immediately re-run SETANG, and select P and enter the initially desired angle. Once the computer has finished changing the angle use the command @CLEARMEM to clear the live data memory. Recheck the sample angle using ANGCAL to verify that the sample angle is now calibrated.

Note: The @CLEARMEM command is very dangerous, as it will wipe all the live data memory. Do not type this command at any time other than at the very beginning of a run when you are calibrating the sample angle. If unsure, consult a member of the POSY2 staff.

## Changing the SampleAngle Using SETANG

The program SETANG is provided on the POSY2 system. It is used to change the sample position. To use this program, type SETANG. You will be prompted:

```
*** SETANG ***
 POSY USING TOTAL_ANGLE      -- DEVICE   21

THE ANGLE IS CURRENTLY  1.00 DEGREES.

ENTER NEW SAMPLE ANGLE (FULL AUTO) (P)
CHANGE LIMITS (L)
MOVE GONIOMETER MANUALLY (G)
```

```
MOVE COLLIMATORS MANUALLY (K)
MOVE TRANSLATION MANUALLY (T)
CALIBRATE ANGLE (C)
CHANGE OTHER PARAMETERS (O)
READ TRANSLATION POSITION (R)
EXIT PROGRAM (E)
ENTER CHOICE:
```

Enter the letter corresponding to the desired function and press <cr>. You will normally

enter P for ENTER NEW SAMPLE ANGLE (FULL AUTO). Once you have done so,enter the desired angle, followed by <cr>. FULL AUTO means that the collimation and sample translation will be determined automatically.

NOTE: It is possible to change the goniometer position, collimator positions or translation manually. This should not be attempted without first consulting a member of the POSY staff.

## Stopping a Run

If you wish to stop the run and save the data currently in the multibus memory, use the command:

STOPRUN <cr>.

To stop the run and not save the data in the multibus memory, use the command: QUITRUN <cr>. If you used QUITRUN by accident where you wanted to use STOPRUN , just type: START/RESTART RUN #, which will pick up where you left off when you quit, then use STOPRUN, which will save the data. START/RESTART will also allow you to resume data collection after system malfunctions, without loosing the data currently in the multibus memory. If you have stopped the run accidentally using the STOPRUN command, type START run#, where run# is the run you accidentally stopped. The computer will ask you if you wish to erase the data in the multibus memory. Type N for NO and the computer will start collecting data at the point where it left off when you typed stop. Normally, the data are stored in the multibus memory and every hour during an active run are written to the directory [POSY.DATA]. The computer will keep the latest three versions of the data set automatically. Every time the multibus memory is dumped to [POSY.DATA] the run file version will be updated.

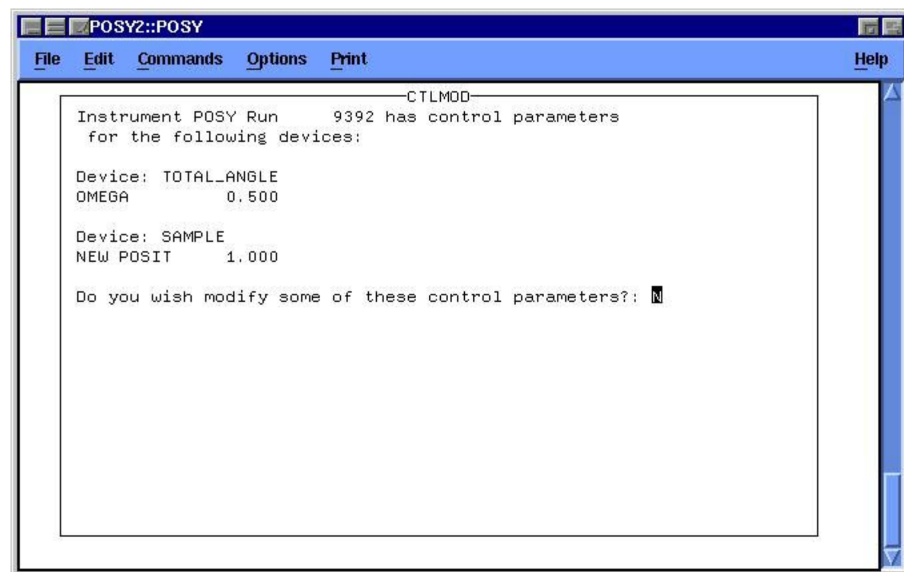
Remember: STOPRUN—saves data QUIT—does not save data

# Modifying Control Parameters in a Run File

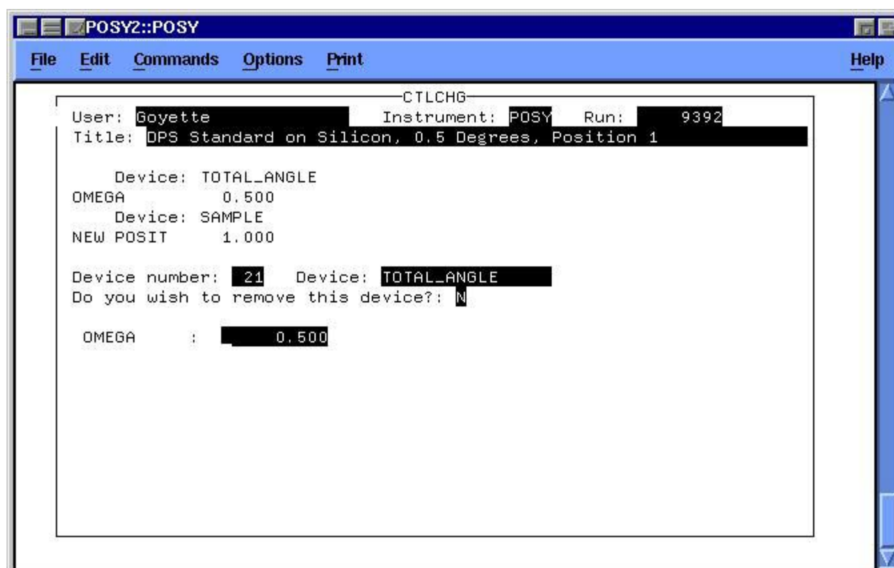
If, after completing the set up a run file, the modification or deletion of a control parameter in that run file is desired, use the command CTL:

POSY2_POSY> CTL run#

The program will display the control parameters that have been set for that run file. You have the option of changing the parameters that have been set or removing a control parameter completely. You do not have the option of adding a new control parameter.

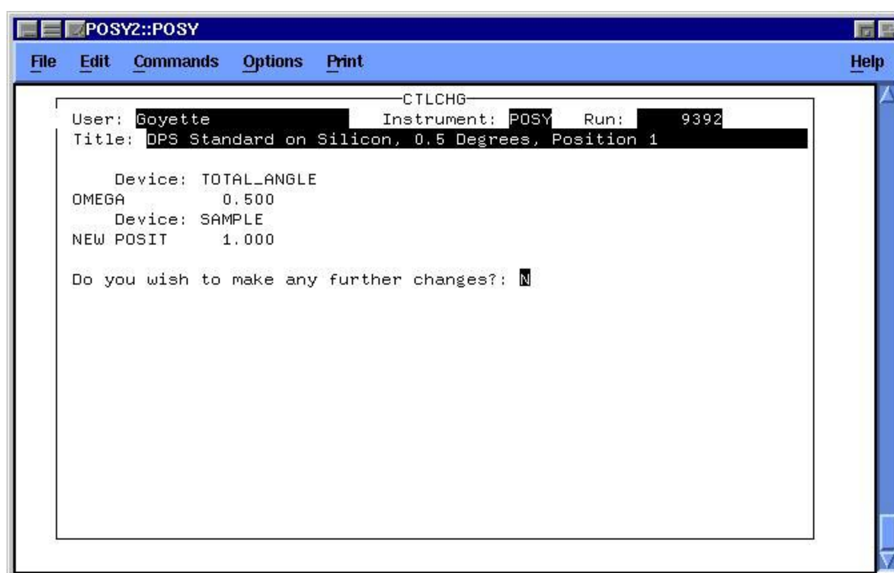



The program will go through each control parameter that has been set. It will first ask if you wish to remove the device:




If you answer yes, it will be removed completely. If you answer no, it will ask if you

wish to modify the value given for the device. Once the program has completed a device, it will move on to the next device where the process is repeated. When all parameters have been completed, the program will end.




If any modifications were made, you should check the new parameters by using PRUN CONTROL.

# Changing the Sample Position Using SAMPLE

The program SAMPLE is also provided on the POSY2 system. It is used to change the sample that will be in the beam. To use this program, type:

SAMPLE <cr>

you will be prompted:

```
POSY USING SAMPLE           - DEVICE    8
   *** SAMPLE ***
 NEW POSIT     {current position}
ENTER NEW POSITION (P), READ CURRENT POSITION (R),
 OR EXIT (E) ?    input <cr>
```

Input the desired sample position (any integer from 1 to 4) or <cr> to accept the current position.

## Changing the Sample Temperature Using TEMTUR

The program TEMTUR will allow you to change the sample temperature. To use it, type TEMTUR <cr>. You must specify which device to use. The only device installed on POSY2 is device 26 (Lakeshore). Specify device 26 at the prompt.

```
WHICH DEVICE DO YOU WANT?
   DEVICES AVAILABLE ARE:

     26     LAKESHORE
     27     EUROTHERM

   ENTER --> DEVICE NUMBER: 26
```

Now you will have the choice of entering the setpoint or changing other parameters.

```
S = ENTER SETPOINT AND LIMITS ONLY - DOWNLOAD ALL PA-
RAMETERS TO THE LAKESHORE CONTROLLER
C = CHANGE OTHER CONTROLLER PARAMETERS - NO DOWNLOADING
OF PARAMTERS - USE "S" ABOVE TO DOWNLOAD ALL PARAMETERS
TO THE LAKESHORE CONTROLLER
E = EXIT

ENTER --> S, C or E:
```

You should not attempt to change any other parameters without first consulting with a member of the POSY2 staff. Type S at the prompt to change the sample temperature. You will get the set point and limits prompt. Enter the desired sample temperature and limits. The default values are in parenthesis.

```
SET POINT ?          (     50.0 ) 100.0
UPPER LIMIT ?      (     55.0 ) 105.0
LOWER LIMIT ?        (     45.0 )  95.0
```

The program will show you the settings after you have entered them.

```
SET POINT 100.000 UPPER LIM 105.000 LOWER LIM 95.000
DELAY 1.000
CTL SENS    1.000 MEAS SENS   1.000 TUNE           2.000
GAIN  6.000
RESET           9.000 RATE          0.100 HEATE
3.000 RAMP  0.000
RAMP RATE   0.000
```

Make sure they are correct. The program will display a warning concerning the possible effects of downloading an incorrect temperature to the controller. If the values are not correct type E to exit and re-run TEMTUR to enter the correct values. If the values are correct type DOWNLOAD at the prompt.

```
E = Exit TEMTUR without downloading
DOWNLOAD = Continue and download controller parameters.


ENTER --> E or DOWNLOAD :
```

## Reading Sample Temperature Using RDT

You can monitor the sample temperature by typing the command RDT. You will receive a menu similar to the menu when using TEMTUR:

```
DEVICES AVAILABLE ARE:

  26     LAKESHORE
  27     EUROTHERM

ENTER --> DEVICE NUMBER: 26
```

Enter the device (usually 26) and the temperature will be displayed:

```
POSY LAKESHORE  CTL TEMP (1) =   190.00 : MEAS TEMP (1)
=   190.00
```

# Looking at the Data

This chapter describes methods by which you can look at live data as it is being collected, or at old data stored on the hard disk. Data may be viewed as a function of time of flight (which can be converted to wavelength), or as a function of position channel (which may be converted to angle). This chapter also describes how to obtain hard copies (printouts) of raw data.

## Intensity as a Function of Position

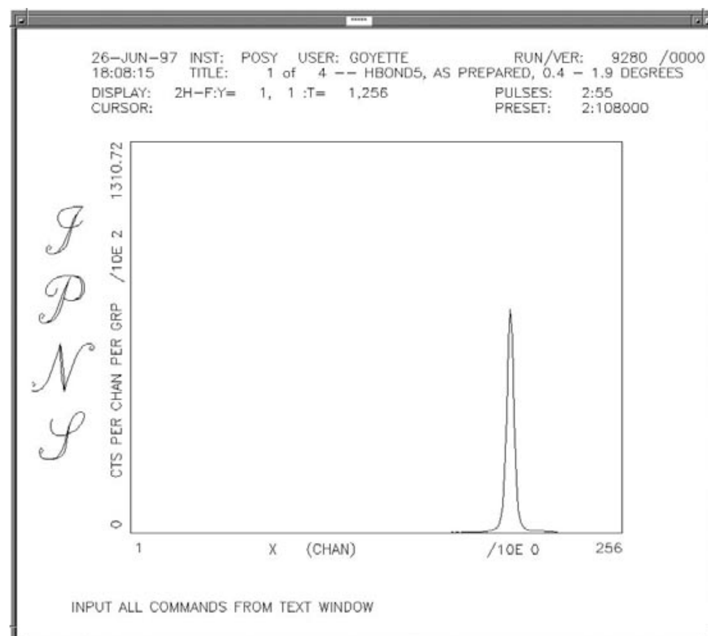
To view live data as a function of position channel for a particular time-of-flight, type:

TYP LH <cr> (stands for Live Histogram)

HST X <cr> (Histogram as a function of position channel X)

TPT time channel # (1-256) <cr>(time channel #corresponding to the time-of-flight of interest, it can be a number from 1 to 256)

DIS <cr> (to display a plot similar to the one below)




When a data display is active, placing the mouse arrow within the data display region will change the mouse arrow to a cursor (+). The cursor position is controlled by the mouse.

The cursor is useful in determining channel positions and intensities. Place the center of the + at the position of interest, and read the channel and intensity values from the screen.

To clear screen: Type: CVS <cr>

## Intensity as a Function of Time-of-Flight

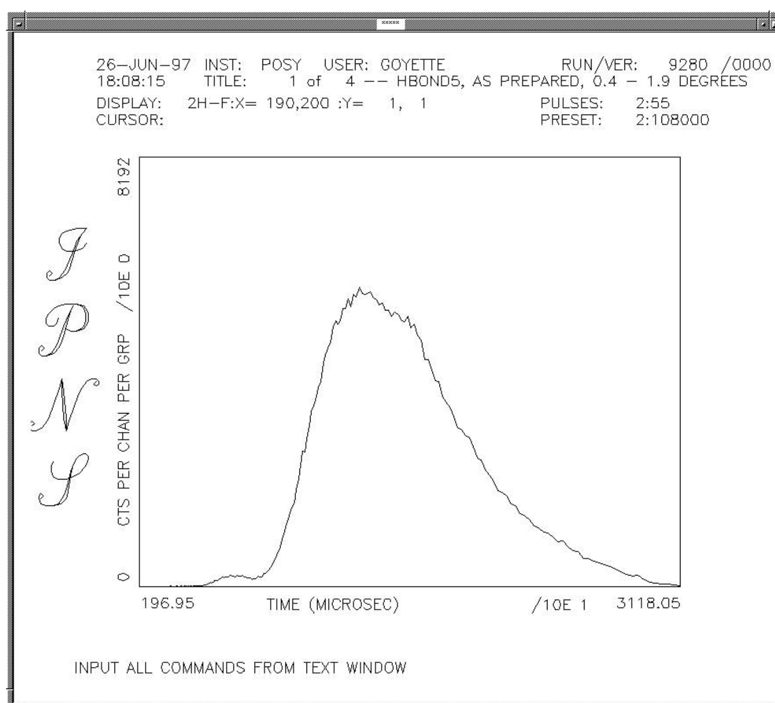
To view live data as a function of time-of-flight for a particular position channel, type:

TYP LH <cr> (if you have typed this already, you don't have to do it again)

HST T <cr> (histogram as a function of time-of-flight)

XPT POSITION CHANNEL # (1-256) <cr> (x position channel of interest, it also can be a number from 1 to 256)

DIS <cr> (to display a plot similar to the one below)




If you want a printed version of any of the plots that appear on the screen, type DPLOT PS <cr>. The data screen will disappear, and the computer will create a file labeled PGPLOT.PS. Wait about ten seconds and then type:

PRINT/QUEUE=LJ4MV_399 PGPLOT.PS <cr>

and a printed copy of the plot should appear on LJ4MV printer in Bldg. 399. There are several formats in which a plot can be saved (GIF, Post Script, Color Post Script, etc. Consult a member of the POSY2 Staff for more details.)

# Rescalling the X and Y Axis of Any Plot

To change the upper and lower limits on either the X or the Y axis use the following procedures:

## Changing the Y-Axis

The general commands to change the y-axis are these:

YMIN <cr> to change the minimum of the y-axis.

YMAX <cr> to change the maximum of the y-axis.

YSC <cr> to toggle between automatic and manual scaling.

The computer will indicate which mode you are in after you type YSC. To specify a YMAX and YMIN of your own, you must be in Manual scaling mode. DIS <cr> as always, to display the plot.

EXAMPLE: changing YMAX from the current value to 5000:

YMAX 5000 <cr>

YSC <cr> (to go into manual mode)

DIS <cr>

To return to the automatic scaling, just Type:

YSC <cr> (to go back to automatic scaling mode)

DIS <cr>

## Changing the X-Axis

To reset the min and max values for the x-axis, use the following command:

DX NEW XMIN NEW XMAX <cr>

Where NEW XMIN is the desired value of XMIN and NEW XMAX is the desired value for XMAX. EXAMPLE: changing XMIN to 40 and XMAX to 80:

DX 40 80 <cr>

DIS <cr>

To return to the original scaling for the x-axis, use the same command:

DX 1 256 <cr>

Remember that when you plot as a function of position channel you must specify the x-axis in position channels, and when you plot as a function of time-of-flight you must specify the x axis in microseconds. This means that when you switch from x to tof you must give the command

DX 3918 32063 <cr>

and when you switch from tof to x you must give the command

DX 1 256 <cr>.

## Integrating Over Several Channels

You may integrate over several position channels or time channels by specifying the inclusive range of channels when giving either the TPT command or the XPT command.

TPT Lower limit Upper limit (when integrating over time channels)

or XPT Lower limit Upper limit (when integrating over position channels)

For example, lets say you want to integrate from time channel 20 to time channel 105. You would type:

TPT 20 105 <cr>

and follow all other details from the first example in this chapter.

## Looking at Old Data

You can also look at data that was collected previously by using the RUNN command to recall a previous run along with the commands to display file data:

TYP FD or TYP FH <cr> (File Density, and File Histogram)

RUNN run# <cr>

DIS <cr>

The commands HST X and HST T may be used as with live runs.

## Looking at Monitor Data

Monitor data may be observed in the same way as detector data. The only difference is that you specify TYP L for live monitor data and TYP F for file monitor data.

## Reinitializing the Graphics Software

It is sometimes necessary to reinitialize the software that displays a plot on the VAX screen. When this is the case, simply type DINT, which will reinitialize the plotting package. If this does not work, type DINTALL. After this, you are ready for normal data display procedures.

# Operator Messages

Operator messages are sometimes displayed on the screen by the MicroVax in building 399. These are usually announced by a change of the screen to half black and half "normal". Initially, it may appear as if a serious system error has occurred; but this is not the case. Hold the CONTROL key down while pressing the F2 key, located at the upper left of the keyboard will switch back to the regular screen.

# Performing a Transmission Run

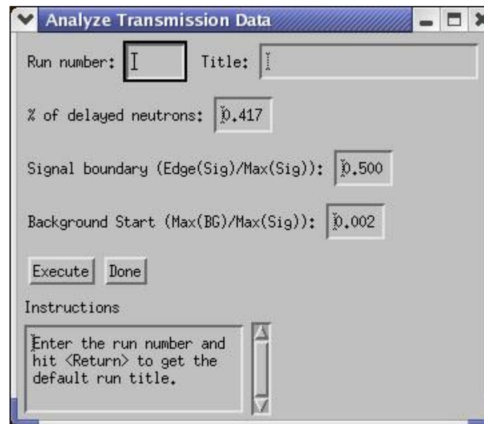
A transmission run should be performed after any change in the moderator has occurred. In addition, a transmission run should be performed after changes of or modifications to sample holders.

## Setting Up a Transmission Run

To perform a transmission run, remove the sample holder from the beam, if using the single sample holder, or rotate an empty sample position into the beam if using the sample changer. Close the slits on the variable slit mask until they are approximately one-third open, and place the variable slit mask in front of the reflected beam flight path. Next, retract the boron nitride mask that is inside the detector (consult a staff member to see how this is done). Finally, open the beam gate and then perform a new run as described in the next chapter. Once the transmission run has finished, replace the boron nitride mask back into the normal operating position.

### Processing a Transmission Run

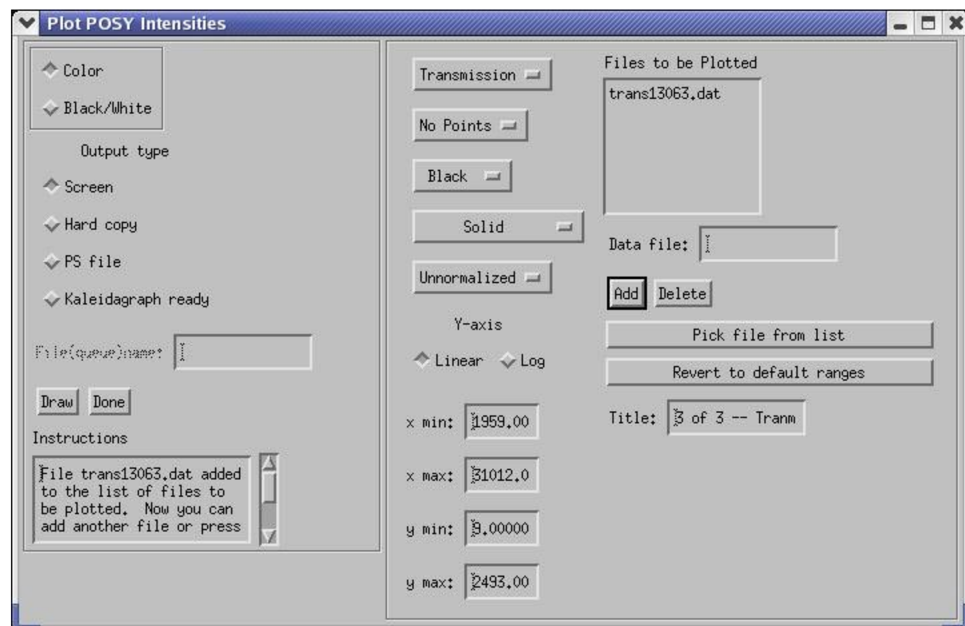
After the transmission run has finished, it may be analyzed and a TRANS.DAT file may be created by using the POSYIDL2 program. You can only use POSYIDL2 from an X-windows terminal. Different platforms use different programs, which must be configured properly to allow X Window connections. To use the POSYIDL2 program, log on to one of the IPNS LINUX systems where the POSY2 data is mounted using your LINUX username and password. If necessary, set your display variable to the IP address of the computer where you sitting. Then type POSYIDL2. Click the button labeled POSY2 in the window that appears. Your will be presented with the main POSY2IDL window. Select Analyzer Transmission Data from the Data Analysis menu. You will be presented with the Analyze Transmission Data window:



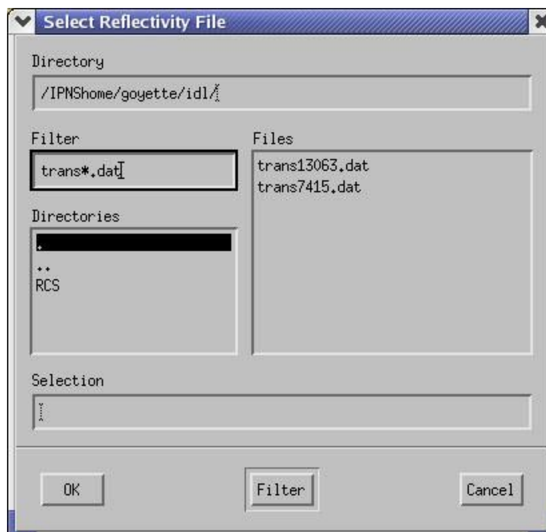

Type the run number of the run file you wish to analyze into the box labeled Run Number, and press return. You must press return from the Run Number box for the program to correctly read all the information from the run file. Once the run file has been read, the title box in the window will be filled automatically. You can modify the title or any of the other data in the window. When you are ready to write a TRANS.DAT file to disk, press the execute button: The instructions box will tell you when the TRANS.DAT file has been written. The instructions box will also contain messages on how to use the program.

## Plotting a Transmission Data File

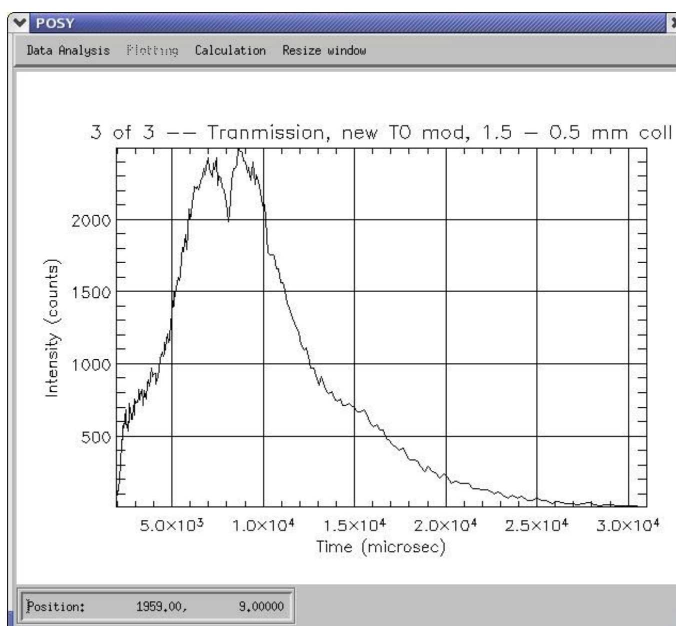
After generating a transmission data file (a TRANS.DAT file) you can plot the results to the screen or to a printer by using the POSYIDL program and selecting Analyzed Data from the Plotting Menu. You will get the following window:




Click on the topmost button on the left had side of the window and select Transmission. Type in the name of the file in the box labeled Data File and click the button labeled Add, or use the Pick From List button to see a list of files in the current directory:




You can change the directory in which you are looking by typing in the new directory path in the box labeled Path. You can also look at only some files by specifying a filter. Click on the file you want, and press the button labeled OK. The file you clicked on should show up in the Data file box. Click Add to add the file to the Files to be Plotted list. When you are in the Plot POSY Transmission Files window you can specify any combination of points, lines and error bars for the plotting of the data. You can also specify whether you want a color or black and white plot, and whether you want to plot to the screen, to a Post Script file or to a printer (Hard Copy). If you request that the plot be sent to a file, you will have to enter a file name into the box labeled file (queue) name. This box also stores the name of the queue to print to if you request that the plot be sent to a print queue. When you have made all the appropriate selections, press the draw button. The Instructions box will inform you when the plot is finished, and will offer instructions on how to use the program. If you have selected the screen as output, you will get back the main window which contains the plot:



When you are done viewing the transmission data file, click the Done box in the Plot POSY Transmission File window. This window will close, but the main window, which still contains the plot will remain.  This is normal.

# Data Analysis

This Chapter describes how to extract information from the raw data, analyze the raw data and display the results in several different forms. It is generally helpful to have a member of the POSY2 staff on hand at this point until some experience is obtained.

## Generating a Reflectivity File

Run files may be analyzed, and reflectivity files generated, using the POSYIDL2 program. POSYIDL2 can only be used from an X-window terminal. Refer to the chapter on Performing a Transmission Run for the procedure on how to bring up a POSYIDL2 window. Select Analyze Reflectivity Data from the Data Analysis menu. You will get the Analyze Experimental Data window:

Analyze experimental data
Run number:
Filename root: quartz
Transmission file: trans13063.dat
Select Transmission File
Title:
Delayed n %: 0.417000
Pick specular position
Left Bg Start: Left Bg End:
Right Bg Start: Right Bg End:
Signal Start: Signal End:
No monitor Use monitor
Execute Done
Instructions
Enter the run number and hit <Return>.

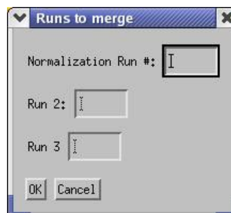
Type the run number in the box labeled Run Number, and press return. Remember that you must press return while you are in the Run Number box for the program to work correctly. Once the program has finished reading the run file, the Title box will contain the title of the run file. Specify the file name prefix (usually the users last name) in the box labeled Filename Root. The default transmission run data file will be displayed in the box labeled Transmission File. The transmission file can be changed, as can the title, by entering the appropriate box and typing in the new information. Also notice that after

the program had finished reading the run file, a position histogram of the run file appeared in the main window of POSYIDL. Once you have selected the appropriate transmission file, click the button labeled Pick Specular Position. Now click on the header of the main window (make sure you click on the header and not inside the plot area). Identify the specular position, and click on the center of the specular peak with the cursor. The program will determine the signal regions (highlighted in green) as well as the left and right background regions (highlighted in red). Move back to the Analyze Experimental Data window and you will notice that the values for signal and background region will now be displayed in the appropriate boxes. If you do not like these values, you may type in your own. In addition, if for some reason (such as you clicked in the plot window when you should have clicked on the header) the program found very bad values for the regions, you can have the program refind the signal and background regions by clicking the Find Specular Position button again. When everything is set correctly, press the button labeled Execute. A message will appear in the Instructions box when the reflectivity file is finished. The Instructions box will also contain instructions on how to use the program.

## Merging Reflectivity Files

You can merge up to four reflectivity files using the POSYIDL program. Select Merge Reflectivity Files from the Data Analysis menu. You will get the Merge Data Sets window:

Type in the appropriate User Name. Keep in mind that all the files you want to merge must begin with the user name you specify here. Click in the box labeled # of Runs, type in the number of runs you wish to merge and press return. Again, you must be in the # of Runs box when you press return. You will get the Runs to Merge window:

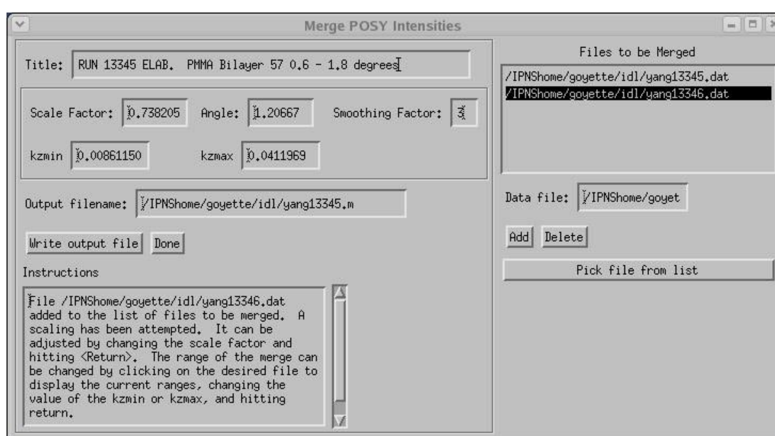



Type in the run numbers that you wish to merge, remembering that the first run number is the normalization run. Click the OK button, and you will return to the Merge Data Sets window. The title of the normalization run will be displayed in the title box. Use

the default values for Max dR/R and Max dKz or type in new values. When everything is ready click the Execute button to merge the files and generate a file that will have the name beginning with the username you entered, followed by the run number of the normalization run, and ending with a ".m" (goyette7621.m for example). In addition, a file will be written which is compatible with the data fitting program Parratt32. The naming convention above will be followed, but the file name will end with parr.dat (goyette7621parr.dat, to use the example given above). The ".dat" extension is required by parratt32.

## Manually Merging Reflectivity Files

The previous method of merging reflectivity files was totally automated, and will be appropriate for most data. If you prefer, you can manually merge reflectivity files using the POSYIDL program. Select Manually Merge Reflectivity Files from the Data Analysis menu. You will get the Merge Data Sets window:




Type in the name of the files to be merged in the box labeled Data File, or use the Pick From List button. Enter the data files one at a time and then press the button labeled ADD to add them to the list. Enter the files in order from lowest angle data file to highest angle data file. These data files must be .DAT files. As each file is entered, minimum and maximum values for $k_z$, scaling factor and angle will be automatically calculated for each file and displayed in the appropriate box. You can view this information for each reflectivity file by clicking on individual file names in the list. Values may be modified simply by typing in a new value in the appropriate box. As each file is entered into the list, it will be merged with the previous file. Adjust values of $k_{zmin}$ and $k_{zmax}$ until the plot has the desired appearance. Modifications to any $k_{zman}$, $k_{zmax}$, scaling factor and angle can be observed immediately in the plot window. Changes in dR/R and $dk_z$ will affect how densely populated the points are in the merged file. When a good merged is obtained, enter an output file name and click the button labeled Write Output File.

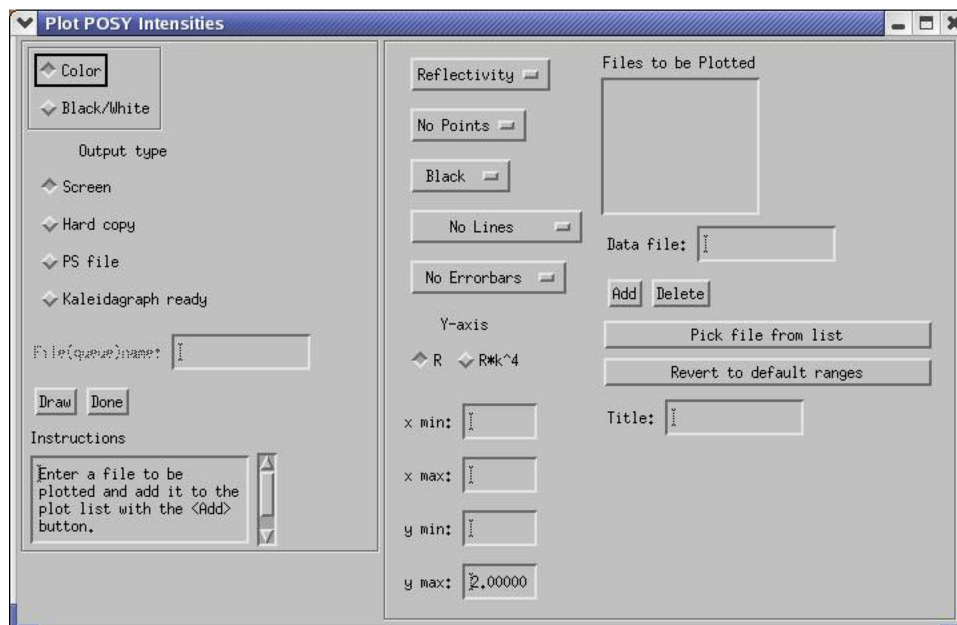
## Plotting Experimental Data

You can plot (to the screen, to a file or to a printer) reflectivity files (.DAT and .M files) and run files (.RUN files) using the POSYIDL program.

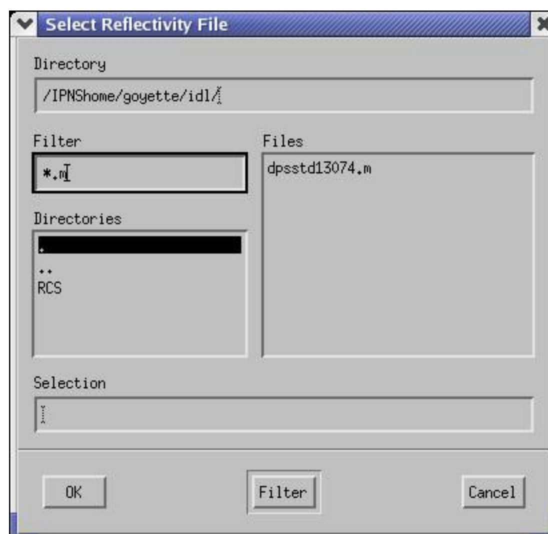
### Plotting Reflectivity Files

To plot a reflectivity file, select Reflectivity from the Plotting Menu. You will get the Plot

POSY Reflectivity File window:

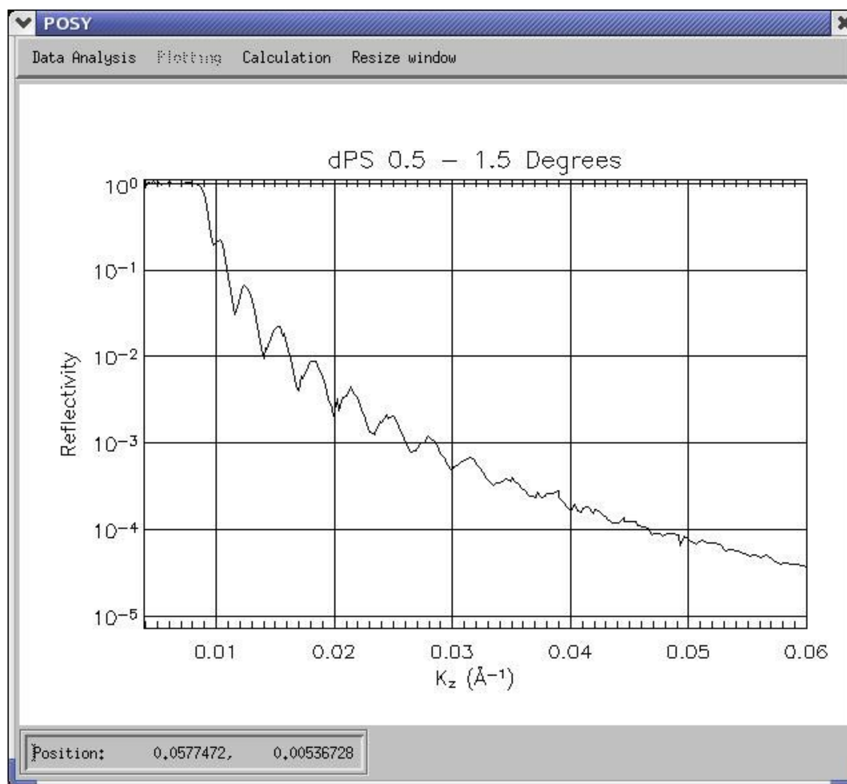



Click on the topmost button on the left had side of the window and select Reflectivity. As we did when we were plotting a transmission run, type in the name of the file in the box labeled Data File, or use the Pick From List button to see a list of files in the current directory:




You can change the directory you are looking in by typing in the new directory path in the box labeled Path. You can also look at only some files by specifying a filter. When you are in the Plot POSY Reflectivity Files window you can specify any combination of points, lines and error bars for the plotting of the data. You can also specify whether you want a color or black and white plot, and whether you want to plot to the screen, to a Post Script file, to a file that can be read easily by KaleidaGraph or to a printer. You can also specify whether you want to plot R, or Rk 4. When you have made all the appropriate selections, press the Draw button. The Instructions box will inform you when the plot is

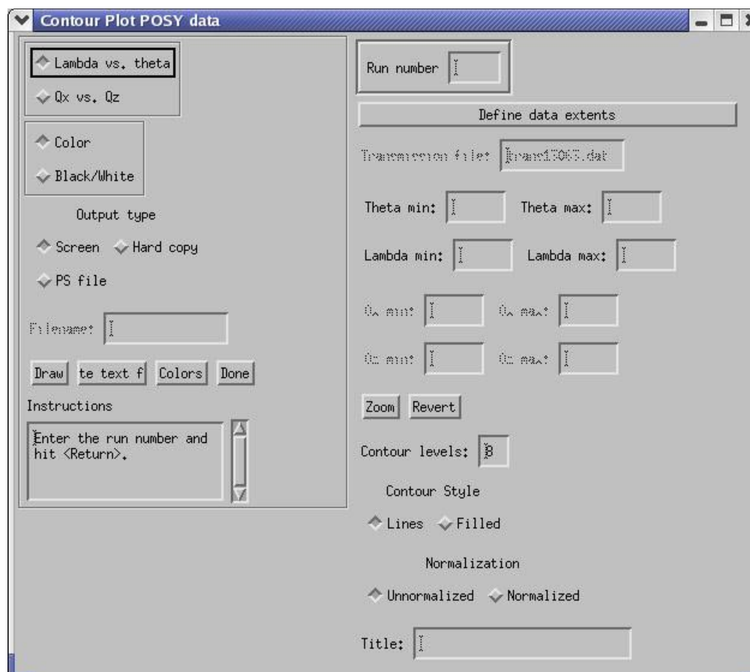
finished, and will offer instructions on how to use the program. If you have selected the screen as output, you will get back the main window which contains the plot:



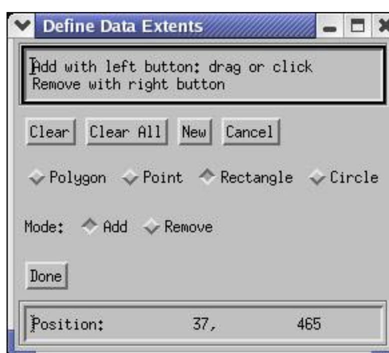

When you are done viewing the transmission data file, click the Done box in the Plot POSY Reflectivity File window. This window will close, but the main window, which still contains the plot will remain. This is normal.

### Plotting Contours of Run Files

You can generate contour plots of run files by using the POSYIDL program. Select contour from the Plotting menu. You will get the Contour Plot POSY Data window:

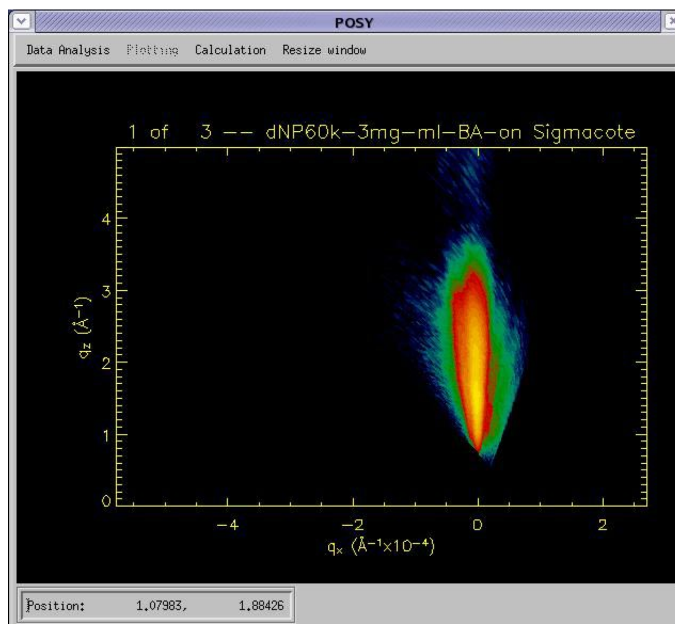



As always, type the run number in the box labeled Run Number and press return, making sure you press return while you are in the Run Number box. When the program has finished reading the run file, a plot of the data will appear in the main POSYIDL window. This plot is unlabeled and displayed only in channel numbers. To display the plot in theta and lamda, press the button labeled Define Data Extents. The Define Data Extents window will appear:




You will need this window in a moment. First, switch back to the main window which contains the unlabeled plot. Using the cursor click and drag a box around the data you wish to plot. Click DONE on the DEFINE DATA EXTENTS window once the box is correct. If the box is not right, redraw it. After you click Done, the define data extents window will come back again. Switch back to the plot window. Draw a box around the specular reflection just like you did for the data. Click done on the Define Data Extents window again. Then switch back to the Contour Plot POSY Data window and click the button labeled Draw. The plot in the main window will be expanded so that the range you selected with the cursor box will fill the plot window, and the axes will be labeled in theta and lamda. You may modify the contour to display in Q x and Q z instead of theta and lamda. You may also generate a color contour, where the contour levels are lines or

filled. Below is an example of a color contour, with filled contours, plotted as Qx -vs-Qz:




You may direct the output to the screen, to a printer or to a Post Script file. The contour may be normalized to a transmission run. The number of contour levels can be changed and you can always type in the data extents by hand if you would prefer to do so. When you are finished, press the button labeled Done on the Contour Plot POSY Data window. The window will disappear, and you will be back to the main POSYIDL window.

# Data Fitting and Modeling

This chapter describes how to create and modify data model files, generate calculated data sets, and compare them to experimental data sets using chi squared fitting. It is necessary for you to have some experience using the program LAYERS before using these fitting routines on your own. If you do not have the necessary experience, obtain the assistance of a member of the POSY2 staff to fit your data.

## Fitting Data Using LAYERS

The fitting routine LAYERS can be run from the POSYIDL program by selecting Layers from the Calculation pulldown menu. You will get the RUN Layers window:

Run LAYERS

Working directory:

Experimental Filename:

Kmin:

0.00100000

Kmax:

0.0200000

deltaK:

0.00015000

K step (deltaK/K):

0.0350000

Calculate Done

```
Scattering Density    Layer      Roughness
 R(b/v)     Im(b/v)    Thickness  Halfwidth    Tag
 (10**-12  cm/A**3)       (A)        (A)
0.034800 0.0000000  9999.000   10.000   0.000
```

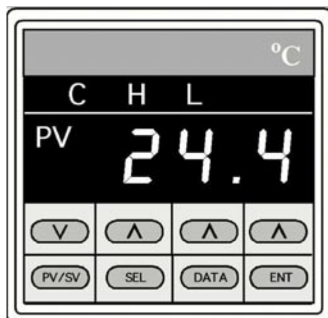
The program will automatically read the current PM.DAT file and display it in the text window. The values of Kmin, Kmax, deltaK and Kstep are displayed separate from the rest of the data in PM.DAT, but will still be written the old way when PM.DAT is

updated. Type in the experimental file name in the box labeled Experimental Filename. Make any desired modifications to the profile and press the button labeled Calculate. The PM.DAT file will automatically be saved, and the current Fortran version of LAYERS will be executed. The experimental data file and the calculated file will be displayed in the main POSYIDL window. As before, the experimental file will be plotted using the + symbol, while the calculated file will be plotted using a line.

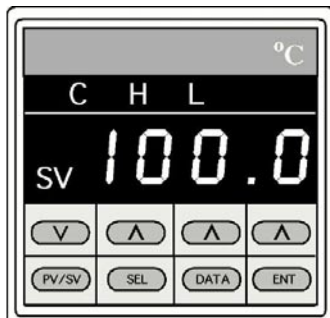
# Using the Annealing Oven

This chapter describes how to use the vacuum annealing oven, located in the POSY2 instrument area, to anneal samples. The annealing temperature is controlled using an Omega CN4400 PID controller. The temperature is monitored using a type "k" thermocouple, which is placed into the back of an aluminium cavity located inside the oven.

To use the annealing oven, allow for a two hour warm up period if the oven is off, or the desired set point differs from the current oven temperature by more that fifty degrees Celsius. If the oven is off, turn the oven on and wait for the temperature controller to start. Once the controller has started, the present temperature should be displayed (the PV light should be illimunated).




To display the current setpoint, press the button labeled PV/SV until the SV light is illuminated. To change the setpoint first press the button labeled PV/SV until the SV light is illuminated.



Press the up arrow key (^) of any digit to be set. The digit should blink on and off to indicate that it has been selected. Once the proper digit has been selected, press either the up arrow for that digit (^) or the down arror (v) (there is only one down arrow) until the desired value for that digit is displayed. Once that digit is correct, press the up arrow for the next digit to be set, and repeat the process. When all the digits display the desired values, press enter to store the setpoint. The digits will stop flashing when the setpoint is stored, and the oven will begin controlling using the new setpoint. Finally, press the button labeled PV/SV until the PV light is illuminated.

Note: There are only three up arrows but there can be four digits displayed in the setpoint value. While the two right most up arrows will only accept numbers ranging from 0 to 9, the leftmost up arrow will accept numbers from 0 to 24. This means that the maximum allowable temperature is 240 C.

# Neutron Reflection

The material in this chapter was taken from *Neutron Reflection Studies of Polymer-polymer Interfaces* , DG Bucknall and JS Higgins, in *Polymers and Surfaces. A Versatile Combination* ed H Hommel, Research Signpost 1998.

## Introduction to Reflection Theory

Polymer interfaces and surfaces are an area of study that has always been important since they impinge on all aspects of polymer science. The interfacial behaviour is fundamental to the bulk properties of the system, and consequently the applications of the polymers. For instance adhesion, miscibility, compatibilisation, welding, surface wetting, blend morphology, mechanical strength, etc, are all controlled by interfacial behaviour. The characterisation and understanding of these properties on a microscopic level are therefore of vital importance.

Numerous techniques have been applied to investigate the surface and interfacial behaviour of polymers. However, the accuracy demanded of the experimental data in order to obtain useful interfacial information requires specialist techniques and the associated equipment that goes with them. One technique which has seen an explosion in popularity within the polymer community over the last ten years is specular neutron reflectivity. The reasons for this popularity are partly to do with the development and advances in the reflectometers, but are mostly associated with the simple fact that neutron reflectivity is often the only technique that can answer the questions that are being posed by the polymer interface community. The wealth of information that can be obtained by a well designed experiment would have been difficult to comprehend ten years ago. The object of this contribution is to demonstrate the power of the technique and why it is worth going to one of the handful of neutron sources around the world where neutron reflectometers are operated.

Neutron reflection provides the composition variation normal to the surface of the polymer film, with an accuracy on a sub-nanometer length scale. This kind of information is also given by X-ray reflectivity and to some degree also by light ellipsometry, however the neutron scores over these other radiation sources in two important respects. Firstly, there is the favourable difference in scattering properties between elements and isotopes of elements. With X-rays contrast between different regions of the sample is provided by the electron density difference between molecules, whilst for light it is the refractive index. The analogue for neutrons is the neutron scattering cross section. Across the periodic table, this scattering cross section appears

to be not only of random magnitude, but also of sign and varies even between isotopes of a specific element. For the polymer scientist the neutron is of particular interest because hydrogen and deuterium have vastly different neutron cross sections. This means that with a little careful chemistry deuteration can open up a huge area of unique experimental possibilities.Deuteration is therefore an ideal labelling technique to highlight whole molecules or specific sections of the polymer and produce a large contrast variation with the normal hydrogenous molecules around it.

The second major advantage is that the neutron can penetrate through many engineering materials. This allows the use of neutrons in complex sample environments if the situation warrants it, without the worry of absorption, which is a major problem for light and X-ray techniques. The energies of the thermal neutrons used for reflectivity, make the technique non-destructive, allowing repetitive measurements on one sample to be made, for instance to look at changes after successive annealing processes. The neutrons do not require high vacuum containment which allows samples to be measured under normal atmospheric conditions. Because of these advantages there should be little wonder at the huge growth in the application of neutron reflectivity to the investigation of polymer interfaces and surfaces. However, it must always be remembered that although neutron reflectivity is an extremely powerful technique, it should be used in conjunction with other techniques to fully exploit its potential.

# Reflection Theory

It is the wave behaviour of neutrons that has allowed a close analogy with classical optics. With only a few minor modifications, neutron waves are able to reflect, refract and interfere following all the standard optical rules [1]. A full discussion of the theory of reflection is not appropriate at this point since this has been covered extensively in the literature [1,2]. However, it is necessary to include a brief description of the essential points since an understanding of them is vital in the interpretation of reflectivity data.

At this point it is necessary to define a few concepts. An interface is defined as the position between media of 2 different refractive indices. The neutron refractive index of medium j is given as:

$$n_j = 1 - \frac{\lambda^2 N_d b}{2\pi} + \frac{i\lambda N_d \sigma_a}{4\pi} \qquad (1)$$

where $N_d$ is the atomic number density, $b$ is the coherent scattering length, the product $N_d b = \rho_z$ is the scattering length density, $\sigma_a$ is the adsorption cross-section and $\lambda$ is the neutron wavelength. Strictly then the refractive index is a complex number. For most materials, however, with the exception of those containing the elements, Li, B, Cd, Sm, or Gd, the adsorption cross-section is effectively zero, i.e. $\sigma_a$ » 0, and therefore for most polymers Equation 1 reduces to:

$$n_j = 1 - \frac{\lambda^2 N_d b}{2\pi} = \frac{\lambda^2 \rho_z}{2\pi}$$

(2)

The neutron scattering length *b* is a nuclear property describing the interaction between the neutron and the atomic nucleus [3]. The value of *b* varies randomly across the periodic table and also between isotopes of the same element [4]. Here neutrons present a big advantage over other radiation such as light or X-rays, with isotopic substitution providing enhanced contrast between two otherwise equivalent species. The large difference in *b* between 1H and 2H (D) is of particular usefulness to the polymer scientist, as will be discussed in a little more detail later.

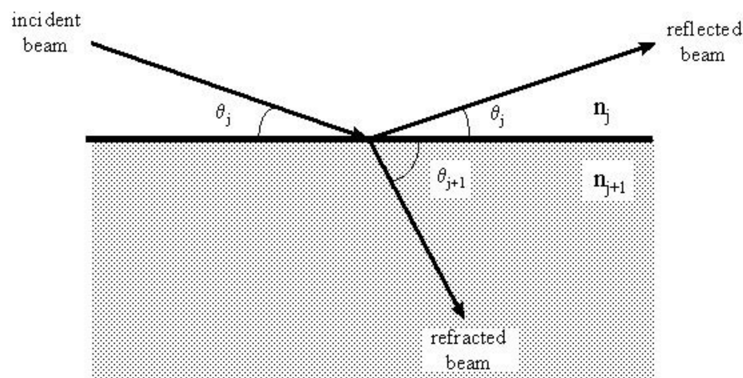



Figure 1: Schematic diagram of an incident neutron beam on a flat interface between two media, showing the reflected and refracted beams.

Figure 1 shows a neutron beam incident on an interface between two infinitely thick media with refractive indices $n_j$ and $n_{j+1}$, where the interface is also infinitely sharp. The beam can be either reflected, at an angle, $\theta_j$, equal to that of the incident beam, or refracted with an angle according to Snell's Law [5]:

$$n_j \cos\theta_j = n_{j+1} \cos\theta_j$$

(3)

Taking the case where the interface is between a vacuum, or essentially air, (j=0) and a liquid or solid (j+1=1), then $n_0$ is 1 and Equation 3 reduces to

$$\cos\theta_1 = n_1^{-1} \cos\theta_0$$

At a critical angle, $\theta_0=\theta_c$, the angle of refraction becomes zero ( $\theta_1= 0$) and thus $cos\theta_c=n_1$. For values of $\theta_0 < \theta_c$ total external reflection of the incident beam is observed with only an evanescent wave refracting into the sample. For values of $\theta_0 > \theta_c$ external reflection of the incident beam is accompanied by refraction into the sample.

The reflectivity of an incident beam on an infinitely sharp interface as described above is defined as the ratio of the reflected to incident beam energies [5]. A similar expression for the ratio of the refracted to incident beam energies defines the transmissivity, ***T***. The reflectivity has both parallel and perpendicular components with respect to the interface. It is only the perpendicular reflectivity component that is of importance to the specular reflection of neutrons, since is contains the information about the concentration-depth profile.

The perpendicular reflectivity, ***R***, is determined using the Fresnel reflection coefficient, $r_{j,j+1}$ , for the interface described in Figure 1, which is defined:

$$r_{j,j+1} = \frac{n_j \sin\theta - n_{j+1} \sin\theta_{j+1}}{n_j \sin\theta + n_{j+1} \sin\theta_{j+1}} \tag{4}$$

The reflectivity is then simply given by:

$$R = r_{j,j+1} r^*{}_{j,j+1} \tag{5}$$

where the asterisk (*) denotes the complex conjugate. Since there is no complex component to the reflectivity from most materials then this simplifies to:

$$R = r^2{}_{j,j+1}$$

The reflectivity from this sharp interface is characterised by the critical angle, $\theta_c$, indicated by the point at which the reflectivity drops from unity, and is often referred to as the critical edge. The wavelength at which this occurs is given by:

$$\theta_c \approx \lambda \left( \frac{Nb}{\pi} \right)^{0.5}$$

Since the neutron momentum transfer is related to the incident angle and wavelength by the relationship

$$q = 2k = \frac{4\pi}{\lambda} \sin\theta \tag{6}$$

it is also possible to derive $r_{j,j+1}$ and hence ***R*** in terms of $q$. Therefore, the reflection coefficients are given by:

$$r_{j,j+1} = \left( \frac{q_{z,j} - q_{z,j+1}}{q_{z,j} + q_{z,j+1}} \right)$$

(7)

where $q_{z,i}$ are the component of the momentum transfer perpendicular (normal) to the surface. Since:

$$q_{z,i} = 2\left( \frac{q_z^2}{4} - \frac{q_c^2}{4} \right)^{0.5}$$

where $q_z$ is defined by Equation 6, and $q_c$ is the critical value of $q_{z,i}$ below which total reflection occurs. Substituting Equation 7 into Equation 5 gives the reflectivity for a sharp interface between two bulk media as:

$$R(q) = \left[ \frac{1 - \left[ 1 - \left( q_c / q_z \right)^2 \right]^{1/2}}{1 + \left[ 1 - \left( q_c / q_z \right)^2 \right]^{1/2}} \right]^2$$

(8)

This is also known as the Fresnel reflectivity and is often denoted as $R_f$. A calculated Fresnel reflectivity is shown in Figure 2(a). The region of total reflection below $q_c$ is clearly visible. The drop off in reflectivity at $q_z > q_c$ can be shown to be proportional to $1/q_z^4$, at large values of $q_z$[2, 6] which is identical to the behaviour observed in systems which have infinitely sharp interfaces and scattering that obeys Porod's Law.

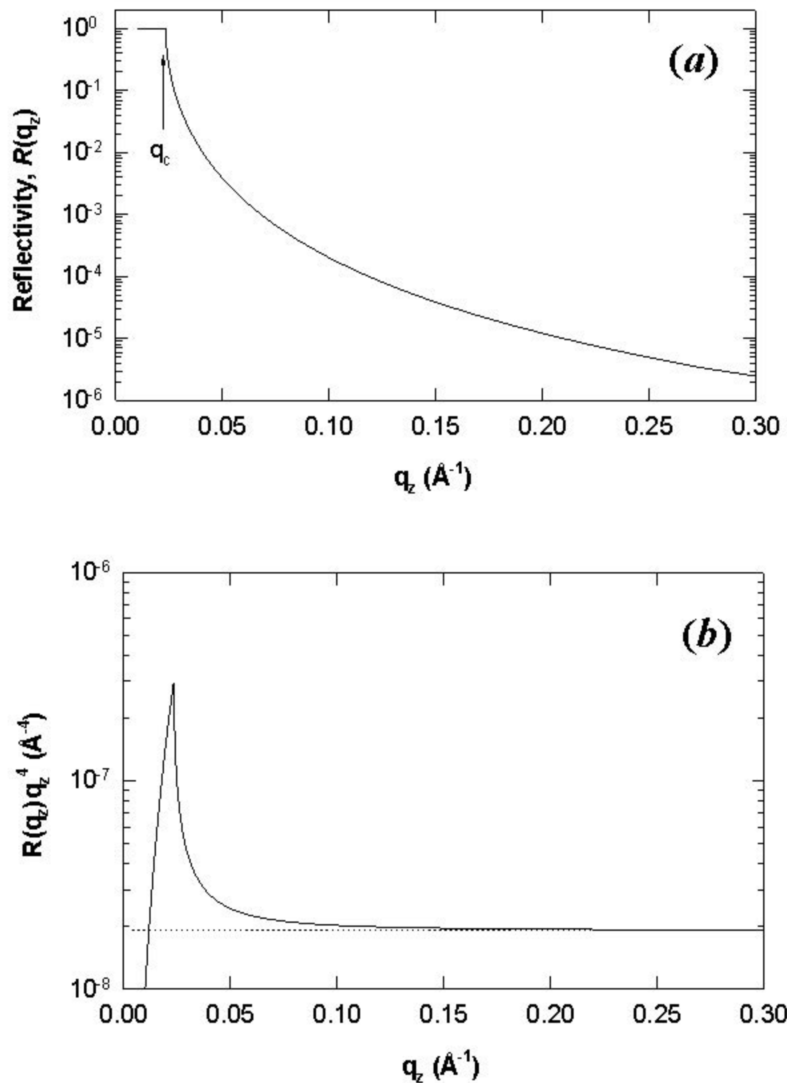



Figure 2: (a) Calculated Fresnel neutron reflectivity profile from an infinitely sharp interface between two media obtained from Equations 4 and 5 or 8. Total reflection (***R***= 1) occurs for $q_z \leq q_c$. (b) Reflectivity multiplied by $q_z^4$, showing the asymptotic limit reached at large values of $q_z$.

One interesting result is that the plot of $R(q_z)q_z^4$ asymptotes to a limiting value which is proportional to the square of the reflectance at the air-media interface.

With these equations in mind, the problem of a sample containing *m* discrete layers can now be addressed. The situation is shown in Figure 3, where the (*m* +1) layer is the substrate and 0 is defined as the medium surrounding the sample, i.e. air. The reflection coefficient for the sample is calculated by firstly considering the coefficient between the substrate and the bottom layer, $r_{m,m+1}$ ,i.e. between the ( *m*+1)$^{th}$ and *m*$^{th}$ layers, which is simply given by Equation 4 where $j=m$. The reflectivity coefficient between the ( *m*-1)$^{th}$ and *m*$^{th}$ is then given by:

$$r'_{m-1,m} = \frac{r_{m-1,m} - r_{m,m+1}\exp(2i\beta_m)}{1 + r_{m-1,m}r_{m,m+1}\exp(2i\beta_m)}$$

(9)

where $r_{m-1,m}$ is again given by Equation 4, and the prime ( ´) indicates that internal reflections have been taken into account, in this case between the *m-1,m* and *m,m+1* interfaces. A phase factor, $\beta_m$, has also been introduced and represents an optical path length term for the $m^{th}$ layer, such that:

$$\beta_m = \left(2\pi/\lambda\right) n_m d_m \sin\theta$$

where $n_m$ and $d_m$ are the refractive index and thickness respectively of layer *m*, and θ is the angle of incidence. The reflectance, $r'_{m-2,m-1}$ , is calculated in a similar way, and the process continued in a recursive method for each successive layer until the reflectivity coefficient for the top layer, $r'_{0,1}$ , is obtained. The reflectivity, ***R***, is then given by substituting $r'_{0,1}$ into Equation 5.

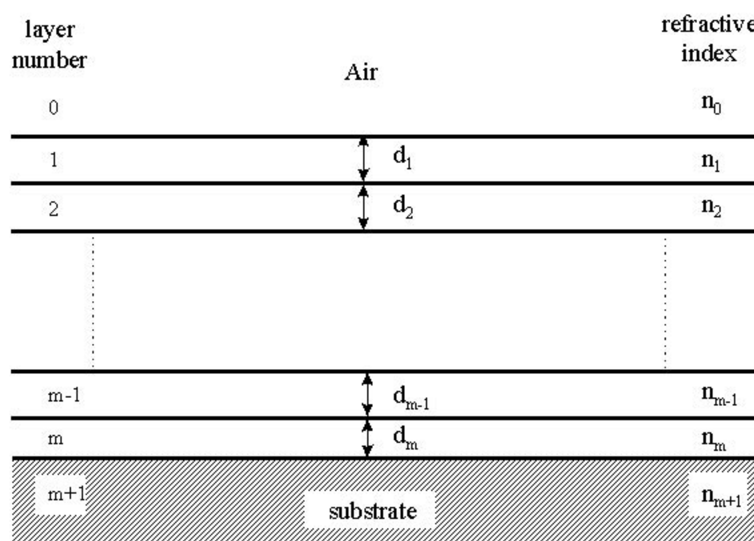



Figure 3: Schematic diagram of a sample composed of *m* discrete layers each with a thickness, $d_i$, and refractive index, $n_i$.

For a double layer sample Equation 9 can be applied together with Equation 5, to give the reflectivity profile shown in Figure 4( a) for a deuterated polystyrene (dPS) layer on a poly(methyl methacrylate) (PMMA) layer on a silicon substrate. The minima and maxima observed are characteristic of the layer thicknesses. When the neutron wavelength satisfies the Bragg condition $\lambda = 2d\sin\theta$, constructive interference occurs. This leads to $d_i = 2\pi/\Delta q_i$, where $\Delta q_i$ is the difference between successive minima. Therefore the high frequency interference fringes are from the thicker layer, in this case 600 nm, and the low frequency fringes from the thinner layer of 200 nm thick. The reflectivity in the $R_q^4$ versus *q* plot as in Figure 4( b) is seen to asymptote to a limiting value at high *q* values, which is proportional to the sum of the squares of the reflectances at each of the interfaces, given by:

$$Rq_z^4 = 16\pi^2 \sum_{i,j} \left( \rho_i^2 - \rho_j^2 \right) \tag{10}$$

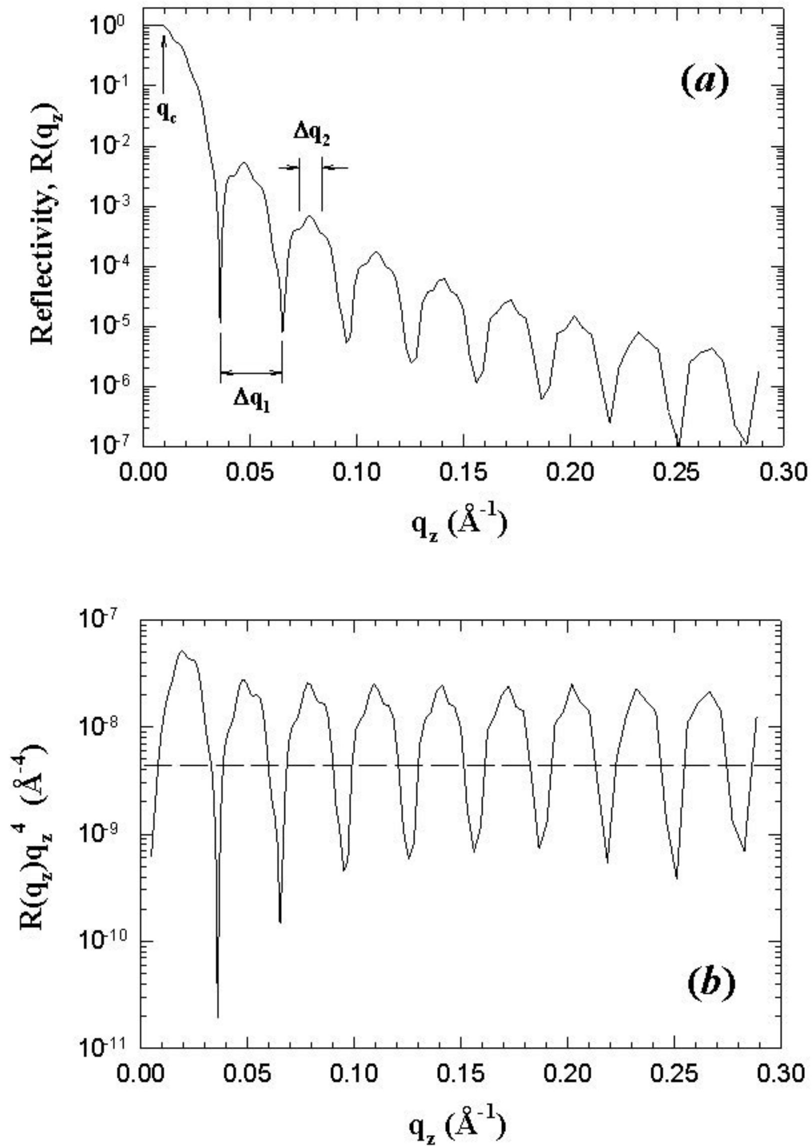



Figure 4: (a) Calculated reflectivity profile of a bilayer of dPS on PMMA on Si using Equation 5 and 9. ( b) Reflectivity plotted as $R_q^{\,4}$ versus $q$, showing that the reflectivity oscillates about an asymptotic value (dashed line).

This approach to calculating reflectivity is exact, but extending it to multilayer systems proves to be extremely cumbersome mathematically. For this reason many people have favoured a more general solution and perhaps the most versatile and widely used among these is that of Abeles [7]. This method defines a characteristic matrix for each discrete layer so that for the $m^{th}$ layer the corresponding matrix is:

$$c_m = \begin{bmatrix} \cos\beta_m & -(i/\kappa_m)\sin\beta_m \\ -i\kappa_m \sin\beta_m & \cos\beta_m \end{bmatrix} \quad (11)$$

where $\kappa_m = n_m sinq_m$ and $\beta_m$ has been defined above. Once matrices for each individual layer have been calculated, an overall sample matrix $M$ is defined as the product of the individual matrices, so that for a sample with $m$ layers as described in Figure 3 the resultant matrix is defined as:

$$M = \prod_{m=0}^{m} c_m = \begin{bmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{bmatrix} \quad (12)$$

The reflectivity is then simply related to the matrix elements from $M$ by the relationship:

$$\left| \frac{(M_{11} + M_{12}\kappa_{m+1})\kappa_0 - (M_{21} + M_{22})\kappa_{m+1}}{(M_{11} + M_{12}\kappa_{m+1})\kappa_0 + (M_{21} + M_{22})\kappa_{m+1}} \right|^2 \quad (13)$$

where $m+1$ denotes the substrate and $0$ the air. As can be seen this general solution lends itself very well to the use of computers. It is well suited to modelling the reflectivity profiles from samples with complex internal layer structure.

# Instrumentation

It is obvious from the definition of the momentum transfer $q$ (Equation 6) that reflectivity measurements as a function of $q$ can be achieved by varying either $q$ or $\lambda$. Fixed wavelength reactor sources using monochromatic beams therefore vary $q$ to give the required $q$ range, whereas pulsed neutron sources use a broad band or 'white' beam polychromatic beam and time-of-flight (TOF) to determine $\lambda$ at fixed $q$. Common to both methods of measurement however is a high degree of automation which is essential for accurate measurement of $R(q)$. Perhaps the major drawback to neutron reflectivity is the limited number of instruments around the world, which basically only reflects the small number of facilities. However, the number of instruments continues to grow.

This article is not meant to be a comprehensive review of instruments since this has been dealt with in depth in the literature (see for example References 8-17 with a good review by Russell [6] ). With two ways of producing neutrons there are basically two designs of reflectometer, each of which will be illustrated by describing typical instruments.

The CRISP reflectometer at the ISIS Facility at the Rutherford Appleton Laboratory is typical of a pulsed source time-of-flight (TOF) instrument. A schematic illustration of the major optical components is shown in Figure 5. The moderated neutrons pass through a double set of choppers, firstly, a disc chopper to select the wavelength range and then a prompt pulse suppressing nimonic chopper. The beam is coarsely collimated by neutron absorbing jaws before entering the experimental measurement area. Fine collimation is achieved by two slits before the sample which define the illuminated area and resolution at the sample position. The beam profile and intensity is monitored just before reaching the sample using a scintillator detector. Post sample the background noise is suppressed by two further slits or by a shielded nose cone. Reflection is detected either with a single or a position sensitive detector. CRISP views a liquid hydrogen moderator which gives a wavelength range of 0.5-6.5 Å, with the disc chopper working at 50 Hz. This range can be extended to 12 Å if the disc chopper is operated at 25 Hz, although this has the drawback of only collecting 1 in every 2 pulses of neutrons. The instrument has been designed to be able to measure liquid surfaces and therefore has a horizontal sample geometry and an inclined beam at 1.5° to the horizontal. At 50 Hz this angle yields a $q_z$ range of 0.05 to 0.65 Å$^{-1}$, which is optimised for liquid surface measurements. In this $q$ region the kinematic approximation is applicable and is widely utilised for analysis of monolayer structure at the air-water interface [18]. Computer controlled goniometers at the sample position allow movement of solid samples (or confined liquids) to angles other than the 1.5° specified by the instrument design geometry. For liquid surfaces accessing angles less than 1.5° to measure in a $q$ range lower than 0.05 Å$^{-1}$ , a super-mirror is inserted in the path of the beam. This super-mirror totally reflects all wavelengths greater that ~1.5 Å, and reduces the angle of incidence on the sample by where $q_{sm}$ is the angle of the super-mirror to the beam. CRISP like other pulsed neutron source reflectometers has a fixed wavelength range, therefore at each incident angle on the sample a limited $q$ range is obtained. The $q$ range can easily be extended by running 2 or more incident angles and combining the data [9]. The reflectivity profile at a fixed incident angle due to the polychromatic beam is therefore collected all at once, and the time required to measure the total spectrum is only limited by the statistics of the collected data.

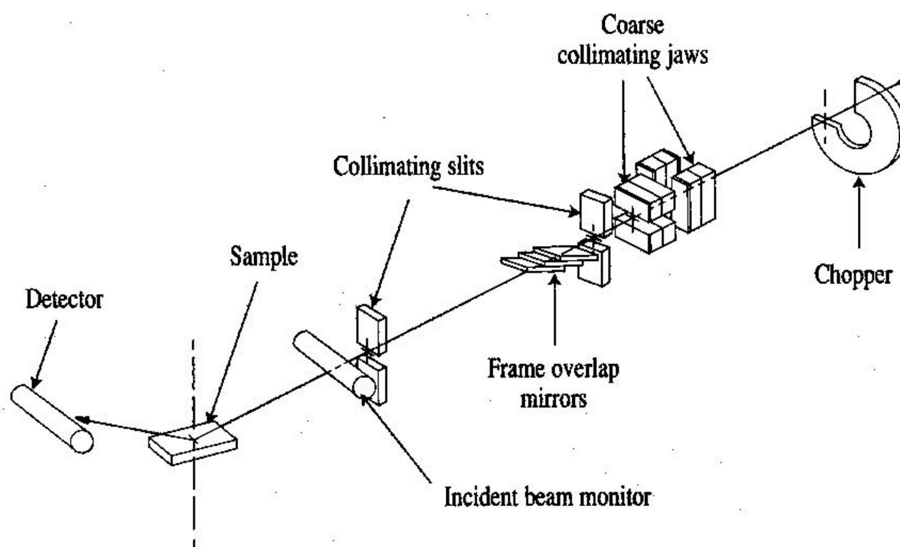



Figure 5: Schematic layout of the time-of-flight neutron reflectometer CRISP at the ISIS Facility, Rutherford Appleton Laboratory.

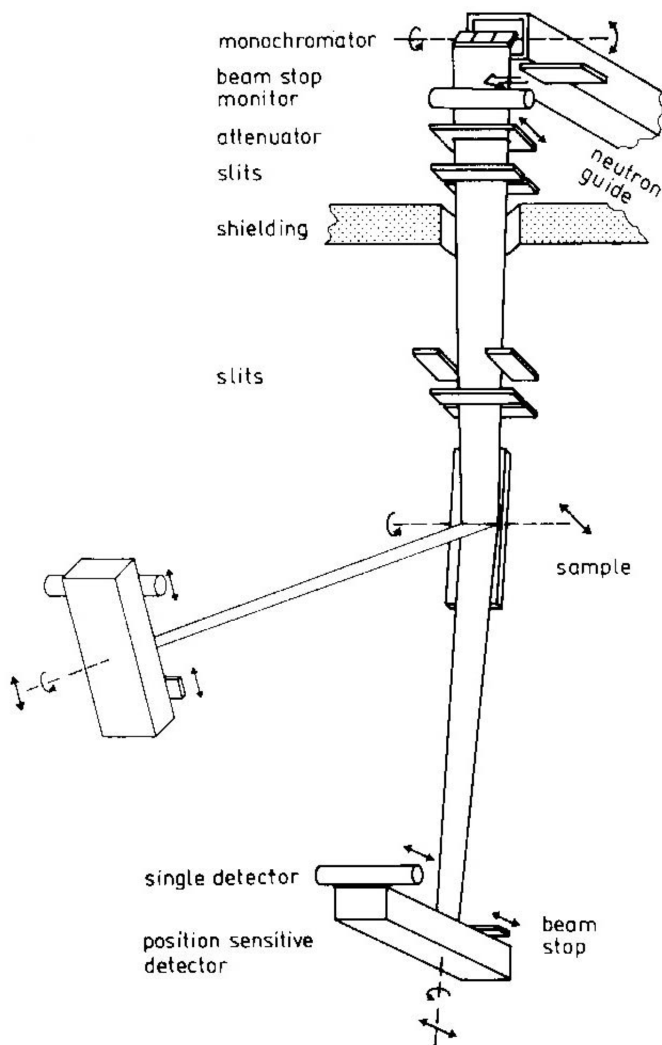



Figure 6: Schematic of the fixed wavelength neutron reflectometer Torema II at the GKSS.

By contrast reactor based reflectometers with fixed wavelength sources measure the reflectivity profile point-by-point in $q$ and hence in $2q$. This method of measurement is often called $q$ - $2q$ scans and is identical to the method employed by the closely related X-ray reflectometers. A typical example of a $q$ - $2q$ neutron reflectometer is Torema II at the GKSS research reactor, Hamburg, Germany (see Figure 6). Here moderated neutrons are focused using a monochromating graphite crystal to give a neutron wavelength of 0.43 nm. The beam flux is then monitored before attenuation and 3 variable slits define the beam on the sample. The sample is vertically mounted and is rotated at each angle of measurement ($q$). The position sensitive detector is rotated at each measurement point at twice the incident angle ($2q$). Due to the relatively high neutron flux at reactor sources, it is necessary at the lower incidence angles to attenuate the beam using plexiglass plates before the collimation to reduce the intensity reaching the sensitive detectors. A drawback of this technique is that both sample and detector must move with respect to the beam. This has a serious repercussion in that the illuminated area varies with rotation of the sample. This is not a problem if there are no lateral inhomogeneities, but can pose difficulties for data interpretation of the measured reflectivity profile if they do exist. On

the whole, many of the advantages or disadvantages regarding sample measurement are trivial and the real differences between instruments now seems to be the perception by the users as to speed of measurement. This is only related to the ‘brightness’ of the neutron source and not the reflectometer.

# Isotopic Substitution

| • Polymer | Abbreviation | $r_z$ (Å$^{-2}$) ´ $10^6$ | |
|---|---|---|---|
| | | hydrogenated | deuterated |
| • polystyrene | PS | +1.41 | +6.50 |
| • poly(methyl methacrylate) | PMMA | +1.10 | +7.22 |
| • polyethylene | PE | -0.33 | +8.24 |
| • poly(dimethylsiloxane) | PDMS | +0.06 | +5.04 |
| • polybutadiene | PB | +0.41 | +6.60 |

As mentioned before, one of the greatest assets available to neutron reflectivity and of course neutron scattering in general is the use of isotopic substitution for contrast enhancement. For the polymer scientist this is extremely important, because by substituting hydrogen for deuterium a vastly different scattering length density can be produced. This has enormous implications since by a very minor chemical alteration it is possible to contrast a molecule or even a part of a molecule from an environment. In Table 1 the scattering length densities for some common polymers are compared in their normal hydrogenous and deuterated forms using the equation:

$$\rho_z = \frac{\sum b_i D_m N_A}{M_m} \tag{14}$$

where $\sum b_i$ is the sum of the monomer atomic coherent scattering lengths, [4] $D_m$ is the bulk polymer density, $N_A$ is the Avogadro constant and $M_m$ is the monomer molar mass. The use of deuteration can be illustrated further by imagining a reflectivity experiment, for example polymer-polymer interdiffusion, where it is not possible to distinguish between the polymers using X-rays. If two different polymers are chosen their hydrogenous isotopic forms may have enough natural contrast to distinguish between them using neutrons. By comparison of the values in Table 1, however, it is seen that even in this case the differences are very small. Consider now the case of interdiffusion between layers of the same polymer, something which is of vital interest in all aspects of adhesion for example. Here there is no natural contrast and indeed the separate layers are totally identical and no distinction between the sample before and after annealing can be made. If however, one layer is made of deuterated polymer a large difference

is immediately introduced between it and the normal hydrogenous layer. When the layers interdiffuse the change in the interface from a sharp step to a diffuse profile can easily be followed. This deuteration scheme can also be applied to enhance the natural contrast between layers of two different species. Indeed it can be used in a whole host of experiments for example to look at molecules segregating to interfaces and surfaces, or even deuterating the ends of polymer chains to look at preferential adsorption. The use of such deuterated contrast enhancement seem endless and only limited by the ability of the synthetic chemists who provide the labelled polymers.

However, a cautionary note must be added. Although for the most part deuteration leaves a polymer with physically identical properties, for a few well studied examples deuteration can alter considerably the polymer behaviour, especially near phase transitions. Blends of some polymers have been shown to display upper critical solution temperatures contradicting the expected assumption that such isotopic blends form ideal mixtures [19-30]. The effect was first noted for isotopic mixtures of hydrocarbons [31], but has been observed for polystyrene (PS) [19, 22, 23, 26] polybutadiene (PB) [20] and poly(ethylenepropylene) (PEP) [25]. When annealed to equilibrium thin films of isotopic blends of these polymers have a non-homogeneous structure with the lower surface energy component preferentially segregating to the air-polymer and polymer-substrate interfaces. The segregation occurs due to a weakly unfavourable $\chi$ interaction parameter originating from the difference in polarizability between C-H and C-D bonds [22]. The effect is only observed however, if the relationship:

$$\chi < \frac{2}{N} \tag{15}$$

is satisfied, where $N$ is the degree of polymerisation. This means that isotopic segregation in these system is only evident if $N > 2/\chi$ and since $\chi$ is typically very small for hydrogenous-deuterated mixtures ( $\chi$ (h/d-PS) » $2\times10^{-4}$ [20] ) means that effectively $N$ must be very large. Although this segregation may in principle be a problem in practice it is not so, since careful use of deuteration and design of the experiment can eliminate the problem entirely.

# Data Analysis

Routine analysis of reflectivity data would ideally be solved by direct inversion of experimental data into either scattering length density, $r(z)$ , or even volume fraction, $f(z)$, profiles. Generally, this cannot be achieved due to the loss of phase information, making this closely related to the phaseless Fourier problem [32]. The analysis then becomes effectively the reverse situation, where reflectivities calculated from simulated $r(z)$ profiles are used in a comparative way to minimise deviations from the measured reflectivity.

For simple systems analytical expressions exist for calculating reflectivity profiles, using the relationships of Fresnel and Snell (see above). However, most real samples do not

typically conform to this simplistic ideal. Extracting the scattering length density profile from the reflectivity data, *R(q)* , becomes necessarily more complex. Because of the lack of phase information from measured reflectivity data it is not generally possible to directly obtain *r(z)* profiles by inversion of the *R(q)* curve. Analysis of the *R(q)* curves to give *r(z)* profiles is generally not unique in that it is possible that several different *r(z)* profiles are consistent with the experimental data given the experimental error and limited *q* range. There are essentially two methods of data analysis:

1. model fitting
2. approximations and free-form techniques.

These are briefly described below together with a review of theoretical work on inversion techniques which are still not widely applicable to real problems due to the limitation with regard to the lack of phase information.

It should be stressed that many of the problems associated with fitting reflectivity data such as uniqueness of fit can be alleviated by use of complementary techniques. In cases where such additional information is not available the careful design of the experiment becomes imperative, and labelling schemes must be extensively used. In general the more information acquired regarding the sample the easier the task of fitting the data.

## Model Fitting

The standard approach to reflectivity analysis is model fitting and refinement mostly using the matrix technique. In this method a functional form for *r(z)* is chosen on the basis of all known data about the system. This will include any complementary information from other reflectivity measurements and/or techniques. The resulting reflectivity profile assuming the *r(z)* model is computed using Equations 11, 12 & 13 and compared to the experimental data. The parameters of the model are then modified using least-squares or simplex fitting routines so that the deviations of the calculated and measured reflectivity profiles are minimised [33]. Clearly then this approach requires a significant amount of prior knowledge of the sample. This method works well when the system is quite well defined and therefore the initial model *r(z)* profile gives *R(q)* sufficiently close to the experimental data. This approach has the advantage that many of the other non-unique solutions for *r(z)* can be eliminated based on the expected physical properties of the system. However, many cases present themselves where no reasonable starting guess for *r(z)* exists, making the process of model fitting one of hard work and many intuitive guesses.

All the equations so far used to describe the reflectivity from specimens have been from infinitely sharp interfaces. However, no interface is infinitely sharp, but exhibits a gradient in density not only between the specimen and the surrounding media, i.e. the substrate or air, but also between consecutive layers of polymers. This may represent a diffuse interface between the polymers or even interfacial roughness or waviness. It is important to distinguish between these. Extensive treatment of interfacial roughness and waviness can be found in the literature [34-36]. The difference between roughness and waviness is evident in the *r(z)* profile projection over the neutron coherent length, $l_c$[6]. Long-range roughness or waviness of the interface over distances larger than, $l_c$, has an effect similar to that of a divergence of the incident beam. This can be seen as leading to a small curvature in the *r(z)* profile. Neutrons impinging on a rough interface, with

interfacial waviness smaller than $l_c$, have local angles of incident which vary greatly from the average. When projected onto a *r(z)* profile this gives a wider smooth transition between the two layers. In general, this leads to a reduction in the reflectivity arising from that interface. Névot and Croc [37] showed that for a Gaussian roughness at a bulk interface the Fresnel reflectivity is modified by an exponential factor:

$$R = R_f \exp\left(-q^2\sigma^2\right) \tag{16}$$

where σ is the standard deviation of the Gaussian function describing the roughness. Clearly, from this equation it can be seen that reflectivity is very sensitive to interfacial roughnesses. Large deviations from Fresnel reflectivity are expected even for small amounts of roughness. The treatment of roughness has been extended to thin layers by applying a similar Gaussian factor to the reflectivity coefficients of Equation 7 [38]:

$$r_{j,j+1} = \left(\frac{q_{z,j} - q_{z,j+1}}{q_{z,j} + q_{z,j+1}}\right)\exp\left(-\frac{q^2}{2}\sigma^2\right) \tag{17}$$

An alternative approach to introducing a diffuse interface between two bulk layers is to divide the interface into a number of discrete layers as shown in Figure 7. The change in concentration between each layer must be small enough that the calculated reflectivity profiles do not contain interference fringes associated with the arbitrary choice of histogram thicknesses.

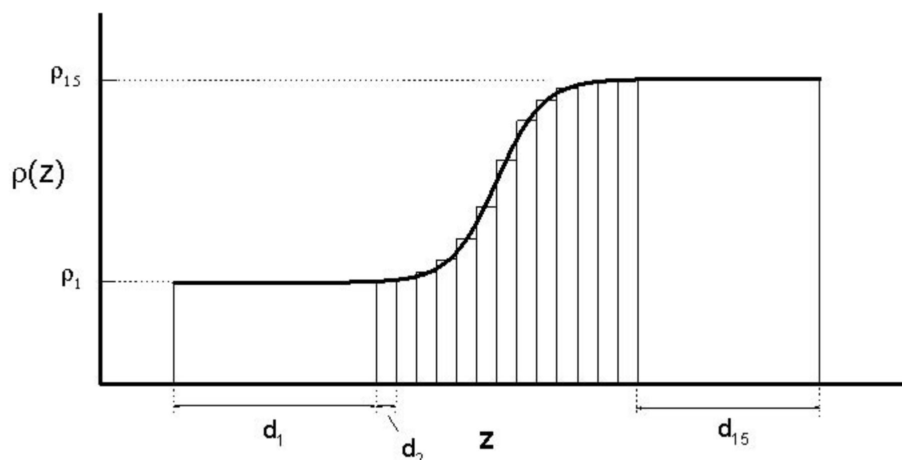



Figure 7: Schematic diagram to show how a diffuse interface, in this case a hyperbolic tangent function, between two polymers can be described by division of the system into histograms with discrete thicknesses, $d_i$, Associated with each layer is a specific scattering

length density, $r_i$.

## Maximum Entropy and Bayesian Analysis

Since generally the total thickness of the sample is known from other techniques it is possible to apply a free form solution. One approach is the simulated annealing procedure [39], where the total sample thickness is divided into a suitably large number of equally sized pixels. The problem then becomes one of statistically varying the values of $r_z$ in each pixel with certain restrictions concerning jump height and smoothness of curve. This method has the advantage that very little is assumed about the nature of the density profile. However, it does suffer from ambiguity since it is possible to produce a large number of satisfactory fits which are quite possibly meaningless. This problem can be reduced if a suitable starting situation is used. An alternative approach which has been gaining much interest and demonstrated considerable success especially among the polymer community is the maximum entropy (MaxEnt) technique of free form solutions [32, 40, 41]. This uses entropy as a regularising function when varying the value of $r_z$ in each of the pixels, which make up the model. A smoothing correlation function is applied to the values of $r_z$ between pixels removing physically meaningless small wavelength $r_z$ spikes which could occur with uncorrelated pixels. Codes now exists where very little prior knowledge is required other than total sample layer thickness and air and substrate scattering length densities. The program developed by Sivia [42] tries to fit at first one layer and then incrementally more layers to a *r(z)* model until a precision limit is reached in a $\chi^2$ fit of calculated and experimental *R(q)* . Clearly then these free-form solutions can prove very useful in interpreting data, but a cautionary note must be added that some of the results may still be meaningless.

From the reflectivity data, *R(q)* it is desired that the scattering length density profile, *r(z)*, can be inferred. This inference can be summarised mathematically by the conditional probability distribution function (PDF), prob[ r(z) ½R(q)], [32] where ‘ ½‘ means given. This means that with respect to the data, the best estimate of R(q) is given by the r(z) profile which maximises this PDF.

However, this PDF is an unknown, and to calculate it, it is necessary to apply Bayes’ Theorem. Bayes’ Theorem relates the unknown PDF to two others, one of which can be calculated and the other estimated.

prob[*r(z)* ½*R(q)*]  prob[*R(q)* ½*r(z)*]  prob[*r(z)*] (18)

Using Bayesian terminology the ‘prior’ PDF (prob[*r(z)*]) represents the state of knowledge about *r(z)* before measurement of the sample. The prior state of knowledge is that modified by the data through a ‘likelihood function’ (prob[*R(q)* ½*r(z)*]), which indicates how likely it is that the data set would have been obtained given a trial *r(z)* profile. To give the required PDF, called the ‘posterior’ PDF, the product of these ‘prior’ and ‘likelihood’ PDF’s are taken. This then represents the state of knowledge about the density profile after data have been collected.

It is unusual to be totally ignorant of prior knowledge about the sample, since information is usually available on the sample preparation, in addition to the possibility of being able to describe the *r(z)* profile by a histogram-like structure of ‘heights’ and ‘widths’. This additional prior knowledge allows the problem to be simplified further, and an estimate of the *r(z)* profile is then obtained by maximising the ‘posterior’ PDF, prob[{$d_i$,$r_i$}½*R(q)*,$r_s$],

where $d_i$ and $r_i$ are thicknesses and scattering length densities of each of the *M* layers describing *r(z)*, and $r_s$ is the substrate scattering length density. If the number of layers is known this is then a simple problem of parameter estimation. If, however, *M* is not known it is necessary to calculate the PDF prob[*M* ½*R(q)*, $r_s$] [32, 40].

## Speckle Holography and Other Techniques

Although the application of neutrons to the study of density profiles as a function of depth is now well established, the information obtained is often subject to questions of uniqueness. In fact it is quite possible that several different models adequately describe the same reflectivity profile. The experimental data hold vital information about layer thicknesses as well as interfacial and surface structure. As described above most work to date has involved fitting paramaterised models to the measured data. This is mostly successful, but can lead to the possibility of scientific prejudice leading to constraints of the model. To alleviate this problem, the ability to directly invert the reflectivity data to a density-depth profile would be most desirable. However, the lack of phase information in the reflectivity data prevents true inversion, and while several inversion methods can be applied they still rely on some knowledge of phase information. This is discussed in more detail in section 6.4. Two related approaches to reduce ambiguity of fits, speckle holography and use of magnetic substrates, are briefly described below.

To alleviate the ambiguity problems inherent in traditional reflectivity measurements, a novel approach is based on the holographic speckle imaging technique [43, 44] used in optical astronomy, which Sivia [32, 45] has called speckle holography. Assuming that the reflectivity is related to the derivative of the density profile ( *dr/dz* ) by a phaseless Fourier transform:

$$R(q) = \frac{(4\pi)^2}{q^4}\left|\int_{-\infty}^{+\infty}\frac{d\rho}{dz}e^{iqz}dz\right|^2 \tag{19}$$

then the autocorrelation function (ACF) of dr/dz is given by the Fourier transform of R(q)q 4:

$$ACF\left(\frac{d\rho}{dz}\right) = c\int_{-\infty}^{+\infty}R(q)q^4e^{-iqz}dq \tag{20}$$

where *c* is a constant. However, Sivia shows [32, 45] that autocorrelation functions are not unique unless there is a distant reference signal (see Figure 8). Such a reference signal can be introduced into a reflectivity sample by introducing a thick buffer layer between the real sample under investigation and the substrate. The *r(z)* discontinuity at the substrate-buffer layer interface then acts as the distant reference in the *dr/dz* plot. In practice, the reflectivity data plotted as $Rq^4$ versus *q* is Fourier transformed to give the autocorrelation function of *dr/dz* . The *r(z)* profile is then simply obtained by integration of the peaks in the ACF(*dr/dz*) profile. Although the Fourier approximation of Equation 19 is only strictly valid for $R(q) << 1$ and $q >> q_c$, this method at least in principle should distinguish between previously ambiguous solutions.

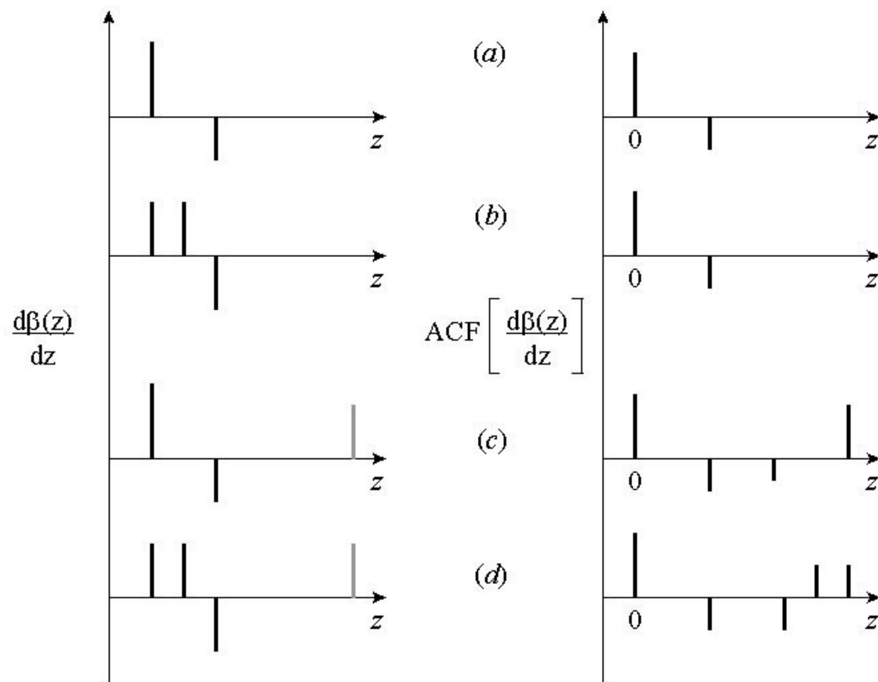



Figure 8: Derivatives of the scattering length density profiles ($d\beta/dz$) from 4 different samples, together with their autocorrelation functions (ACF($d\beta/dz$)). The values of $d\beta/dz$ in (a) and (c) and (b) and (d) are identical except for the inclusion of a reference point source on the right-hand side of (c) and (d). The inclusion of the reference source produces a scaled mirrored copy of the $d\beta/dz$ on the right-hand side of the ACF's (After References [32] and [45]).

Direct inversion of simulated data has shown that simultaneous use of X-ray and neutron reflectivity data on a sample with an additional artificial bilayer between the substrate and the film under investigation [46], can often eliminate ambiguities in data inversion [32]. This idea has been developed by Sanyal [47] for use with tuneable X-rays and the distorted-wave Born Approximation to successfully analyse synchrotron reflectivity data obtained from Langmuir-Blodgett films. The neutron equivalent has also been developed and is based on the use of polarised neutrons and magnetised substrates, to determine uniquely and unambiguously the density profile of thin non-magnetic films [48].

The essential requirement of this technique is to be able to measure the unknown non-magnetic film on two different substrates whose scattering-length densities can denoted by $r_1$and $r_2$. Using a magnetised substrate and polarised neutrons this condition is satisfied for the scattering-length densities of the parallel and anti-parallel spin components of the polarised neutrons. In this way two simultaneous experiments are being performed on the same film but effectively different substrates. The scattering-length densities of the magnetic substrate will then be given by either the sum or difference of the nuclear and magnetic components. Under these conditions the difference in the reflectivities for the two neutron spin states is given by:

$$\frac{\left(R_1(q)-R_2(q)\right)}{R(q)}=(\rho^2{}_1-\rho^2{}_2)+2(\rho_1-\rho_2)\mathrm{Re}\left[\int\frac{d\rho(z)}{dz}e^{iq'z}dz\right] \tag{21}$$

Where $z$ is the perpendicular distance to the surface, $R_i(q)$ are the reflectivities as a function of the neutron wavevector transfer, $q$, of the two spin states of the neutrons ($i=1,2$) and Fresnel reflectivity ($i= f$) and $q'$ is the average wavevector transfer measured in the film. In the simplest approximation $R_f(q)$ is given by $4\pi/q^4$. If Equation (21) is Fourier transformed, the derivative of the scattering length density, $dr(z)/dz$ , of the film is obtained directly and unambiguously:

$$\frac{1}{2\pi}\int\left(\frac{\left(R_1(q)-R_2(q)\right)}{R_f(q)}\right)e^{-iq'z}dz$$
$$=(\rho_1-\rho_2)\delta(0)+(\rho_1-\rho_2)\left[\frac{d\rho(z)}{dz}+\frac{d\rho(-z)}{dz}\right] \tag{22}$$

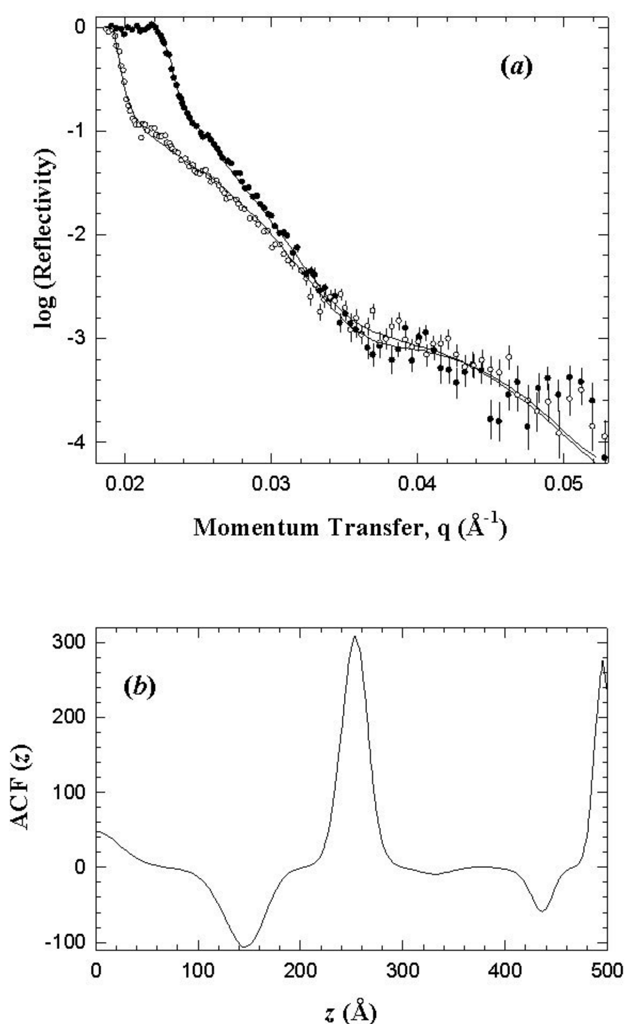



Figure 9: (a) Reflectivity curves of a dPS film on a nickel substrate measured using polarised neutrons with spins parallel (solid circles) and anti-parallel (open circles) to the magnetic field. ( b) Autocorrelation function (ACF) data obtained by applying Equation 22 to the data of ( a). The spike in the data at a z= 25 nm represents the thickness of the film.

The delta function, *d(0)*, arises from the interface between a substrate and the film deposited on it. Using polarised neutrons the reflectivities of $R_1(q)$ and $R_2(q)$ are obtained from the two spin states of the neutron when the sample is in a magnetic field. This technique is ideally suited to the study of polymer films, and preliminary experiments to demonstrate its effectiveness have been successfully demonstrated using a nickel substrate to determine the profile of a single dPS film, see Figure 9 [49]. Of course the technique is not restricted to single layers as demonstrated by the simulations of Sivia [48]. This study showed, however, that a perfectly sharp interface between the magnetic substrate and the non-magnetic film under investigation is vital for the distorted-wave Born Approximation to be valid.

# Inversion Techniques

The ideal situation for analysis of reflectivity data would be a direct inversion of the experimental data into a *r(z)* profile. However, a big obstacle to this becoming routine is the loss of phase information incurred due to the square term in the reflectivity coefficients $R(q)= ½r_{01½}^{2}$. Due to this, there are presently no valid analytic expressions relating *R(q)* to *r(z)* over the entire $q_z$ range of the reflectivity curve. However, in a limited number of cases direct inversion is possible. The kinematic approximation for example together with extensive deuteration schemes is very powerful for systems within the kinematic regime, i.e. in the limit of high $q$ ($q >> q_c$) and which are weakly reflecting ($R >> 1$). This limits the approach to systems which form very thin layers at bulk interfaces. The technique is well established therefore for the interpretation of reflectivity data of surfactants at the air-water interface (see for example references 18, 50, 51). The kinematic approximation has been applied to polymers adsorbed at the air-water interface [52] but is of limited use to most polymer systems.

True inversion as stated requires knowledge of not only the amplitude but also phase of the reflection coefficients, $r_{01}$. If these were known then in principle inversion of *R(q)* into *r(z)* profiles would be possible and practical algorithms exist. [53, 54]. However, in general, except in the cases discussed above, no phase information exists and methods to retrieve it from the measured reflectivity have been discussed on model simulated data in the literature [55-66]. However, many of these methods can yield numerous solutions for the phase, which then leads to non-unique inversion solutions. Extra data are then required to identify the correct solution, either by complementary depth profiling techniques [67, 68], or isotopic substitution methods [50, 51]. As seen above when placed on a magnetic reference substrate the reflectivity data from an unknown film which is non-magnetic can be inverted to *r(z)* with the use of polarised neutrons. Schemes for inverting the two spin states of the reflectivity data have been proposed by Sivia [48] and Majkrzak [69]. However these methods are based on the Born approximation which is valid only in the kinematic limit ($q >> q_c$). Independently de Haan [70] and Majkrzak [65, 71] both proposed essentially identical methods for retrieving exactly the amplitude and phase information of the reflection coefficient even in the dynamic regime ($q >> q_c$). This method uses a 'tuneable' reference layer beneath the unknown layer. The complex reflection coefficient of the unknown layer can be obtained unambiguously by measuring the sample with 3 spin states with respect to the magnetic reference layer [66].

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