

THE "FISH" REFERENCE MANUAL
(DATA FITTING PROGRAM FOR SMALL-ANGLE DIFFRACTION etc.)

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INTRODUCTION

This report describes the data fitting program FISH, written by R.K.Heenan. The program is best suited to the fitting of a curve with a relatively large number of data points by a model with a few parameters. There are presently some eighty available models, mostly concerned with the fitting of small angle diffraction data, though others such as polynomial fitting and peak fitting are of more general use, as are the graphics routines.

The mathematical model used to fit the data and the values of the parameters in a model may be changed interactively by the user. This is in contrast to most "least squares packages" where a model routine has to be compiled and linked by the user with a standard library. Complete model descriptions or previously saved sets of parameter values may be recalled from a file at any time. Any set of results may be written out to file. All actions of the user are recorded in a monitor file, which may later be sent to a printer for closer examination. Values of parameters may be fixed, tied together or constrained as the iterative fit proceeds.

A simple graphics interface allows plots of the results. The FISH program is designed to be easily portable from one computer to another. The FISH2 program first released in Oct. 1999 runs under VMS, Windows and Unix, using PGPLOT graphics routines. (FISH3 with a graphical user interface in IDL is under development for VMS and Windows.)

A typical run of the program uses READ or READ3 open a data file, the user selecting a workspace (data set or memory) numbered 1 to 24, to store the data. The command FIT then enters the set up routine for data fitting. A "model file" is read containing previously set up model descriptions, one of which is selected for use. Data set numbers are then chosen for the observed, calculated, background and other necessary data stores (such as polydispersity, structure factor etc.). The interactive FIT routine itself may then be started. The RUN command causes a single cycle of least squares fitting to be done. PP for Print Parameters will then display the results. After STOP to leave the interactive routine and returning to the main program a LIST command may be used to save calculated data sets in a file. Detail information on each of these stages and on the format of the various files is given below. An example interactive session is included as Appendix D.

ACKNOWLEDGEMENTS

A number of contributors are thanked for allowing inclusion of their own routines or for making modifications or additions to some parts of the code. These include C.Fagotti, J.Penfold, J.Hayter, A.Mackie, A.North, W.S.Howells and H.Stanley. Major contributions are acknowledged in the FORTRAN code and in the appropriate parts of this manual. References to formulae in the scientific literature are given where relevant. These should be consulted for the limitations and interpretation of the theories applied.

FITTING METHODS

Fitting is by a standard iterative linear least squares method, involving computation of first derivatives of each calculated data point with respect to each parameter in the model. Derivatives are calculated analytically in easier cases, else from the result of a small numerical shift in one direction (the user may adjust the size of these shifts). Convergence may often be improved by applying less than the computed least squares shifts. This may be done via the "partial shift" associated with each parameter, the value of which in the program also determines whether a parameter is refining or not (ON or OFF) or whether it is tied to another parameter (> 0 , $= 0$, or -1 respectively). Calculated shifts are often too large due to ignoring higher derivatives. If not "damped" down in some way dramatic oscillations in parameter values may occur and the fit then only converges if just one or two parameters are adjusted at a time. The rate of convergence is often best when multiplying calculated shifts by a partial shift of about 0.4.

A variation of damping procedure is offered by the "Marquardt method" in which diagonal elements of the least squares matrix are multiplied by $(1+l)$, where l starts large and is recomputed at each cycle to obtain optimum convergence. (Consult standard texts on fitting procedures). This has the effect of forcing the fit along the line of steepest descent when it is a long way from convergence, gradually moving back to the more tortuous least squares route, which is at right angles to this direction, as l decreases. In this method the goodness of fit is forced to always improve but there is no guarantee of finding even a local minimum. Runs with test data shows that the Marquardt method may not converge to the true least squares minimum where that minimum is not well defined (which is usually why one tries to use it). A parameter search and/or different starting points should be used to give some idea of parameter correlation. Large values in the least squares correlation matrix itself (use command CC to see this) will also indicate a poorly determined fit. Note that when using the Marquardt method the estimated standard deviations of the parameters become unreasonably small - run one cycle of normal least squares before recording their values.

(To use the Marquardt method enter K2=1 and initialise CON(1) for l by entering N1= 1; to return to least squares enter K2=0.)

Some more detailed notes on least squares and Marquardt fitting are given in Appendix E.

If these methods fail then "predicate observations" may provide an alternative to simply leaving some parameters at fixed values. An expected value of a parameter is included in the fit as a data item with a carefully assigned weight. This is explained further under "MODEL 5" below, and has proven particularly useful in the field of molecular structure determination where a bond length may be allowed to "float" about its chemically expected value.

Data points to be fitted may be given unit weights (use $K1=0$) or weighted as $1/E^2$ ($K1=1$) or as $1/data$ ($K1=2$, for where $E = \sqrt{data}$), where errors E are read in with the data. If you have no errors, and the usual $K1=1$ is present in the most model file, then FISH will complain about "zero weights", you will then have to set either $K1=0$ or $K1=1$. $K1$ is the first control parameter on the second line of the model file (more later or see LSQ model file format on p43).

Some experiments have been made with a maximum entropy weights scheme for particle size distributions, this requires further development.

SOME PROGRAM PHILOSOPHY

The main sections of the program are each controlled by a simple command language; if you are stuck simply type HELP or H for a list of relevant commands.

Data are stored in "sets" which are given a number (1-9), these are similar in concept to (but considerably predate !) "workspaces" in the ISIS GENIE program. Arithmetic manipulation of these sets is catered for, however more complex operations are best done elsewhere such as in specific raw data reduction codes or in the GENIE program. For those not familiar with GENIE these workspaces are simply data storage arrays. The model description used to calculate each point in such an array is analogous to a list of sequential instructions given to a programmable calculator. However FISH does pre-search the model description for special cases, such as polydisperse particles, which require initialisation.

Since the initial use was to process small angle X-ray data from a linear position sensitive detector all data sets may be stored with "left" and "right" sides with Q or radius respectively descending and ascending in value. Raw PSD data may then be "centred" and adjusted before binning into Q . The data files allow for NCH data points, using points NC1 to NC2 on the "left" and NC3 to NC4 on the "right". Thus poor data at the ends of the usual ascending Q range may simply be ignored, but kept in the file, by setting $NC3 > 1$ and $NC4 < NCH$ (see the DATAFILE definition section).

More detail comments on programming styles are made in the section "Making changes to the program".

HOW TO GET STARTED- the FISHPREF.TXT file

A file FISHPREF.TXT will be needed in your working directory, as illustrated below. A typical model file LSINP.DAT and an example of FISHPREF.TXT and distributed with the program download. (FISHPREF.TXT provides a simple way to keep the operation of FISH2 the same on any platform, by avoiding the use of system variables.)

```
! tshi FISHPREF.TXT file needs to be in your working directory
! lines with exclamation mark are comments and are ignored
! Need system type VAX (for vms) or WIN (for Win95 or WNT) or LNX (for any linux and unix)
WIN
! Need "source directory" for FISH's command definition files
! ( which are called FCOMMAIN.TXT, FCOMPLT.TXT and FHELPFIT.TXT )
C:\FISH2\
!
! then the directory for logging file FISHLOG.LIS and
! graphics plot files ( scratch area on vax)
C:\FISH2\WORK\
!
! and finally the directory and name of the LSQFILE containing models
! file ( you can call it any name you choose.)
C:\FISH2\WORK\lsinp.dat
! Inside FISH use SET to switch to another file.
```

Run the executable, then use READ *filename*, or READ3 *filename* command in the main routine to get the input data, then try FIT. Follow through the items 1 to 3 in the FIT control section menu, to decide which set to fit and which sets will store the calculated data, etc. Then proceed into the FIT interactive commands section. Study the example session at

the end of this manual. Use of an existing LSQFILE model file (usually stored as LSINP.DAT) will be a great help as actual examples are easiest to follow.

FORTRAN FILES TO BE ASSIGNED

There are several files required by or generated by FISH, these can be changed from inside the program using SETUP in the main program. They are summarised in the table below. Files may be called by any appropriate name, but will be referred to by the names in the table below throughout this manual.

Fortran stream number	File name in this manual	Purpose	Present default name
INPUT			
	FISHPREF.TXT	Defines important directories and initial name of LSQFILE	FISHPREF.TXT
1	DATAFILE	Actual data e.g. I _{obs} (Q)	nnnn.Q
3	LSQFILE	Least squares model description(s)	LSINP.DAT
OUTPUT			
2	MONITOR	To record what you did	MON.LIS
4	NEWDATA	Modified or calculated data. FISH will prompt for a file name.	FOR004.DAT
8	NEWLSQ	Modified or new model descriptions e.g. to save latest parameter values. FISH will prompt for a file name.	FOR008.DAT
graphics		graphical output, default postscript	FISHPLOT.PS

In addition there are three text files which define the command names and minimum abbreviations for the main program, the PLOT routine and the interactive FIT routine. NOTE that the MON.LIS file can become quite large, you may need to purge or delete it regularly.

COMMANDS IN THE MAIN CONTROL ROUTINE

These are the commands available on first entering FISH. Most people will only need to use READ, FIT, LIST, PLOT, INDEX, STOP and possibly RANGE. The minimum numbers of characters for an acceptable abbreviation are underlined. Input strings are converted internally to uppercase, up to the first space (so that case sensitive file names in Unix are preserved). The Nov. 2000 version allows spaces in filenames (for Windows).

HELP

Lists the entire detailed help file.

H

Lists command names only.

READ-DATA *[filename]*

for ASCII (normal character) files in standard DATAFILE format. Uses DATIN routine and channel 1. Filename is optional, if missing the file previously set up will be used, as files may contain many sets of data.

READ3 or **R3** *filename*

for ASCII (normal character) 3 column Q, Intensity, Error file with a single data set in Fortran free format.

READ2 or **R2** *filename*

for ASCII (normal character) 2 column Q, Intensity (without Errors) file with a single data set in Fortran free format. If fitting you may need to use switch K1=2 or K1=1 to set least squares weights.

RNLS filename

for standard ILL data file with Q, Intensity, Error.

OTOKO filename

attempts to read OTOKO binary format Xray file, NOT quite working ?, only works on WINDOWS, please consult RKH if you need to import such data.

GETWIR

for BINARY linear data input, old Daresbury SAXS format in file [RKH.DL]Snnnn.FV4, where nnnn is input run number.

LIST

to list data set to monitor file (for printer) or to write out an ASCII data set to the NEWDATA file, in which case new title records will be asked for. (The output ASCII file, default FOR004.DAT, may be read into a GENIE workspace by COLETTE command OLD.)

INDEX

show details of the sets you have stored.

ARITHMETIC

add, subtract, divide, scale, normalise data sets.

QBIN - for processing raw linear detector data.

First enters the RANGE routine, calculates Q values for set I and will rebin into set J, if J non-zero. Assumes that raw data channels are equi-spaced, will ask for camera distance, detector element spacing and incident X-ray or neutron wavelength. (Enter a negative Q BIN DELTA Q value to jump back to main routine if things go wrong.)

CENTRE - helps to find middle of Daresbury SAXS data set,

asks for pixel range L1,L2 to left of beam stop and a guess for mid-point. The mid-point is entered multiplied by 10, to give the nearest 0.1 division. Then it sums $(N(R)-N(L))^{*2}$ over R corresponding to $L=L1,L2$ where N(i) is the count per channel. A small range of mid-points is chosen, the "best" may be at the minimum sum. Use with care and plot results to test !!!

L-R

Put Left-Right differences for a Daresbury SAXS set into another data set, e.g. ready to plot. Results are placed on the left side for the full range over which left and right sides overlap. If data is in Q then a linear interpolation is done on the right side to force Q values to match the left side.

RANGE n

Allows removal of points at the ends of the range of data set n. e.g. to use points 10 to 70 in a set with normal ascending Q enter 0 0 0 10 70

PLOT

Enters longwinded, complicated, but very flexible plot routine. First you will need to set up a list of sets to plot, several can be placed on the same axes. If in doubt about optional parameters enter zeroes to get default action. PLOT has its own command language and help facility as detailed below.

FIT

Enters least squares model-fitting program via the FIT menu. This has its own interactive language and HELP command. A large number of models are available. See separate sections below. It is possible to fit more than one linear data set simultaneously with overlapping parameters.

SETUP

Allows new input or output files, so there is no need to exit the program to switch to another data file. Enter zero to just list currently opened files.

STOP

Use this for a graceful exit from the program, don't forget to PRINT MON.LIS to the printer if the monitor might contain useful information. It should provide a record of what you did on the screen. Tidy up any output files, note that on a VAX their names default to FOR00n.DAT, where n is a channel number, if they were not assigned elsewhere.

QUIT

Same as STOP

COMMANDS FOR THE PLOTTING ROUTINE

These commands are available after giving PLOT in the main program, note that a completely new command language is then in use. The input here is extremely tedious, however complicated overlaid plots may easily be built up using a variety of graph markers. To get into this routine use PLOT in the main routine. To generate a plot a recipe has to be set up, by READ, with a list of which work spaces are to be plotted and with which symbols. (i.e. you have to know in advance exactly which sets you want to plot as later overlays are not possible at present.) This recipe is preserved upon subsequent calls to PLOT (use LIST to see it), so if you wish to change any of the workspaces a repeat plot can be made without having to re-do a READ. A SCREEN or FILE command will then produce the plot to the appropriate device.

NOTE the PLOT command in the interactive FIT routine becomes PICT and PLOT then enters a high speed routine to show OBS, CALC and OBS-CALC for the present cycle of refinement. This does however redefine the plot recipe ! Skip the rest of this section if you are only interested in doing simple fits. You may however need to use this routine to plot say a polydispersity function or to change axis types (e.g. PICT, LOGLOG, STOP from FIT interactive commands to start Log(Y) vs. Log(x) plots).

HELP

Full help instructions.

H

Quick list, or H Command for information on any Command.

SYMBOL

lists standard line and symbol types

READ

Asks for a list of curves (sets) to be drawn, all on same axes with different symbols or line types for each. (do SYMBOL for more information) You will be asked for:

(a) (I1) Number of curves (up to 9)

(b) for each curve:

(i) (5I1) LTYPE - see below, line type e.g. solid or symbols

LSYMBOL - see below, marker type e.g. cross or asterix

IFOLD =1 to fold about centre

IEB =n to add error bars of $\pm n * E(i)$

I_NUM_NOT_Q=1 to plot against channel rather than Q

e.g. for + signs with error bars enter 5301

(ii) if data has left and right sides, (2I1) LTYPE, LSYM for the left side data

(iii) YSHIFT - added to Y values at plot time

line types LTYP are: 1 - straight line segments,
 2 - smooth curve(local polynomials) 3 - dashed, 4 - dotted
 5 - use symbols of type LSYM as specified by :
 LSYM= 1 - up triangle, 2 - down triangle, 3 - +, 4 - X, 5 - square,
 6 - diamond, 7 - circle, 8 - *

NOTE: Some symbol or line type options may not be implemented on particular computers.
 For symbols on a solid curve, enter the set twice, once as solid, again with symbols. If in doubt about any values leave zero to get defaults.

LIST

Gives details on data sets chosen by READ

SCREEN

Draw on screen, the LOCAXIS routine will ask about the axis ranges - dependant upon local installation, then you will get the plot !

FILE

Plot to a file. (The default postscript type can at present only be changed from PLOT in the FIT routine).

INDEX

Usual master index of all sets in memory.

STOP

Returns to calling routine.

LINEAR

use Y against X values just as supplied.

LOG

use LOG(Y) against X, or use before other plot types to return to base 10 logs.

LOGLOG

use LOG(Y) against LOG(X) (or LN(Y) against LN(X) if first issue a LN command).

LN

choose LN(Y) against X, or use before other plot types to switch to natural (base e) logarithms.

GUINIER

LOG(Y) against X^{**2} , uses log to base 10 unless you have previously issued a LN command.

ZIMM

1/Y against X^{**2} .

RODS

LOG(Y*X) against X^{**2} for thin rods.

SHEETS

LOG(Y*(X^{**2})) against X^{**2} .

USER

choose your own transformations. These are of the form $(X^{**i})(Y^{**j})\text{LOG}(X^{**k})(Y^{**l})$ where i,j,k,l may be defined differently for both X and Y axes.

FIT n m

straight lines to be fit to sets n to m, will ask for X range for each set, where the units of X may be the originals, as transformed or as channel number. Will turn "off" the fit if one is already "on". Use LIST to see the gradient etc. but after first doing a SCREEN or FILE command to see the plot.

FIT ROUTINE - MAIN MENU

This menu appears after issuing FIT in the main program, it guides the set up needed before entering the interactive fit routine. Normal usage involves first READING some experimental data in the main routine, then enter FIT, and work through options 1, 2 and 3 in this menu.

1 - Read model file.

This reads the LSQFILE of model descriptions, enter 1 when you reach the appropriate model.

2 - Choose OBS,CALC etc.

First asks how many data set you want to fit - normally just 1, for multi-data sets fits the model must be specifically designed with this in mind.

Follow the instructions given to choose workspace numbers to be used for the OBServed data, the CALCulated data, BKG for experimental background (model 3), POLY polydispersity function (model 6) and WRK to store scaled background (models 3 and/or 4) etc.

If in doubt enter 1 2 3 4 5 6 7 8 9 assuming your data is in workspace 1, but in theory leave a zero for a set not required e.g. 1 2 0 0 3 0 4 5. Missing a space or entering zero for a workspace that is actually required may result in the program stopping with a subscript out of range error. You may have to re-enter option 2 after replacing one model by another using option 1 if extra workspaces are required or if new data with a different number of points has been READ in.

For multiple data set models you may skip missing sets by entering -1 for OBS. e.g. if the model has core, shell & drop contrasts but you only want to input and fit core and drop, then say you have 3 sets to fit, but enter say 1, -1 and 2 in the OBS column.

3 - Enter fit routine

Goes into the interactive fitting routine, see the next section.

4 - Calculate only or set Q.

Used instead of option 2 if there is no experimental data and you wish to do a calculation only.

5 - Index

As usual, helps if you have forgotten which sets are in use.

6 - Return

Goes back to the main control routine.

31- Enters derivative test routine TESTER.

32- Enters derivative shift and integration scheme set up routine DELSET

FIT ROUTINE COMMANDS - INTERACTIVE LEAST SQUARES FITTING

This routine is reached from the FIT routine main menu, option 3, above. A highly abbreviated command language is used here due to the large number of times each command is used. To start with try out the commands P, PP, RUN, n=r (e.g. 1=123.45), n=ON (e.g. 1=ON=0.5), n=OFF.

Parameters are in array V(i), commands below may have ranges n,m where n and m are integers. If m is not present then m=n by default. Real number r does not need a decimal point, but no E+0n allowed (yet).

R or RUN	do one cycle of calculation.
ST or STOP or RE or RETURN	return to calling routine.
n m or n,m or n.m	prints values of V(n) to V(m) on screen.
n=r	sets value of V(n) to real number r
n,m=ON	sets status of V(n) to V(m) to ON by setting partial shifts to 1.0
n,m=ON=r	additionally resets partial shift to value r (e.g. use 0.4) which multiplies calculated shifts, reduces oscillations in many cases.
n,m=OFF	sets status of V(n) to V(m) to OFF by setting partial shifts to 0.0
ON or OFF	changes status of whole fit <u>regardless</u> of partial shifts (NOTE: OFF followed by ON zeroes all the calculated shifts, before they are applied, useful if something has gone wrong.)
n,m=TIE	turns back on constraints turned off by setting partial shift to -1.0.
P	Prints all V(i) parameter values on screen (same as 1,99)
PP	Prints all Parameter information to screen, including titles, constraints etc.
PF	Print to File, lists all data and correlation matrix to MONITOR file.
FF	Fill File writes current model and parameter values to file NEWLSQ (default FOR008.DAT).
TT	Terminal Table, lists OBS,CALC data etc. to screen.
CC	prints least squares Correlation Coefficient matrix on screen.
PS or S	" data Sets in use
PC or C	" Constraint relations
PN or N	" Numerical constants, CON(1) is Marquardt lambda
PT or T or PK or K	prints control records and titles
Sn,m or Cn,m or Nn,m	prints a range of the above
Cn= or Tn=	will invite a replacement for a constraint or title
Pn,m=	" " " " " parameter records to change or construct a model, (regret no insert instruction).
Nn=r	resets constant n, e.g. N1=1.0 for Marquardt l, N4 for Dr, N5 for R _{max}
Kn=i	" control flag n, e.g. K2=1 for Marquardt method, K2=0 least squares, K5=1 to re-initialise numerical integration schemes.
IN or INDEX	usual index of data sets
PICT	enters normal long-winded plot routine e.g. PICT, LOGLOG, STOP to switch PLOT to log-log axes.
PLOT	special plot for least squares data -see note below.
H or HELP	prints a shortened version of this section on screen.

Most sensible combinations of command and range are allowed.

Notes on PLOT command inside FIT which rather cryptically asks:

PLOT CONTROLS IDEV=0-EXIT, 1-plot, 2-save file, 3-new screen, 4-new file type

error bars are IEB*sigma

IPW=1 adds scaled wts

IDEL spreads graphs apart (IDEL=2 is default)',

ITXT = 0 table in file, 1 no table, 2-both, 3-screen only',

IDEV,IEB,IPW,IDEL,ITXT = (511)

Note this expects a string up to 5 characters long, but giving just 11 will give IDEV=1, IEB=1 to get a plot with error bars on the screen.

Answering just 2 will give IDEV=2 to save the plot previously drawn to screen in a file, default postscript.

Answering 3 may be used to change the default screen type, or 4 to change the default hard copy file type (e.g. for /CGML to get a file that may be incorporated into WORD, or /GIF). The latter two options also prompt for new values of the default line-width, character size and marker size so that plots may be further customised. The hard copy file also contains a table of parameters. Parameter ITXT can add this table to the screen version (e.g. if you need to make a screen dump) or remove it from the hardcopy by using say 11002 or 11001 respectively.

The upper trace in the plot is the observed data (+ markers with added error bars if IEB=1), the lower trace is the difference OBS-CALC, with error bars (if IEB=1).

If you have asked to store P(Q), S(Q) or $\beta(Q)$ you will be prompted to over plot these, enter 1 for solid line, 3 for dashed, 5n where n=1 to 6 for different marker types. S(Q) and $\beta(Q)$ will be rescaled to suit the plot axes.

ABSOLUTE INTENSITIES

The "scale" parameters for each model have a physical significance when the input data is in absolute units. The formulae supplied should enable them to be understood. Unfortunately it was not convenient to use an entirely consistent basis for all of them. Some scale factors may not be in their most familiar form e.g. by having a particle volume included or removed. This may avoid a divide by zero possibility at R=0 or reduce parameter correlation by making the scale constant independent of particle size. The polydisperse spheres distribution are all normalised to total volume, allowing change from one distribution to another with minimal parameter shifts and also the possibility of fixing the total volume fraction at a known value.

In general for neutron small angle scattering the probability of scattering per unit solid angle per unit thickness of sample, in cm^{-1} , is

$$d\Sigma(Q)/d\Omega = N(\Delta\rho)^2V^2P(Q)$$

where there are N particles cm^{-3} (typically 10^{16}) of volume V and particle form factor P(Q) is normalised such that P(Q=0)=1.0. $\Delta\rho$ is the scattering length density difference between two phases for which

$$\rho = \sum_i n_i b_i \cdot \rho_{\text{bulk}} \cdot N_A / MW \quad \text{where } b_i \text{ is a scattering length in cm.}$$

$$\begin{aligned} \text{e.g. for D}_2\text{O} \quad \rho &= (2*0.667 + 0.580) \times 10^{-12} \text{cm} \times 1.1 \text{g.cm}^{-3} \times 6.02 \times 10^{23} \text{mol}^{-1} / 18 \text{g.mol}^{-1} \\ &= 6.4 \times 10^{10} \text{cm}^{-2} \end{aligned}$$

If $\Delta\rho$ is entered in units of 10^{10}cm^{-2} then the scale factors given below for each model are multiplied by 10^{20} and they then generally all work without underflow or overflow occurring in the FORTRAN programs. Molecular dimensions R are assumed in \AA ($= 10^{-10} \text{m} = 0.1 \text{nm}$) and scattering vector Q in \AA^{-1} throughout.

For X-ray scattering ρ may be most easily expressed in electrons per unit volume, calculated from atomic numbers and molar volumes. The probability of scattering by one electron then needs to be included,

$I/I_0 = e^4 (2 - 2\sin^2(2\theta)) / (m^2 c^4) \sim 7.94 \times 10^{-26} \text{cm}^2$ at small angles. The actual "cross section" units for X-rays should be carefully checked for a given instrument, one may for example have to divide by the sample-detector distance squared in order to get counts per unit area detector per unit volume of sample or possibly have to allow for sample thickness or incident beam monitor somewhere.

LSQFILE MODEL DESCRIPTIONS AND CALCULATION METHODS

Each model description contains NT title records, NP parameters, NS data set information records, NC constraints and an array of NN numerical constants. This section of the manual concerns the NP parameter records (type (iv) in the LSQFILE format later) which tell FORTRAN routines DERIV and CALCQ in FISH how to calculate an I(Q) array. In most cases the list of records are scanned in order for each point in the Q array. For more complex cases involving, for example, integration over a particle size distribution, the list is first analysed by the program to decide on the method of computation.

Several models are usually combined together to generate the complete calculated data I(Q). For example we may start with MODEL 1 for a spherical particle, multiply by MODEL 22 for a hard sphere structure factor, add MODEL 3 for a background, and finish with MODEL 99 (which is always required). Consulting the detail descriptions of each model below it will be seen that this takes NP = 2 + 2 + 3 + 1 = 8 records altogether. If there are two separate sizes of spherical particle then the two records for MODEL 1 may be repeated with a different scale factor and radius for the second particle. Given that there are some 45 different models, many of which can be repeated, and numerous constraints to tie parameters together, there are an almost infinite number of overall models possible. Some examples are given at Appendix B. The LSINP.DAT file that you may have available will only have a selection of possibilities. You should feel free to edit it to form new combinations of models.

Most sensible combinations of model are allowed, there are some limitations such as using polydisperse spheres or Hayter-Penfold S(Q) only once per data set to be fitted due to various initialisation checks. (If MODEL 88 is used to fit more than one data set then the initialisation is repeated each cycle before each new set.) The program will not always complain if asked to do something impossible or inconsistent - the user should check that the calculated I(Q) is reasonable. In extreme cases it may be necessary to study the workings of the program or to write a separate program to generate test data.

A model may be altered or even read in from the terminal by the Pn,m= interactive command in the FIT routine. Most models require a series of records in a specified order, the control numbers LTYP(i) decide what they do, the character string labels are left free to the user to annotate. The LTYP value on the first record of a group describing a model has particular significance. It is often denoted LTYP(1) in the descriptions below. For many models LTYP(1) may be 1, 11, 21, 31 each of which specifies a different sub-model. NOTE we are not referring to the first of the NP parameter records, but to the first record for a particular model. In general please include as many records for each model as are described in the manual (even if some are labelled "spare" or are not used by a particular sub-model). The LTYP(i) numbers on records after the first in a model do not need the extra multiples of 10 (except as stated below, e.g. for MODEL 16, LTYP(1)=11), this helps to switch rapidly between sub-models by a single Pn= command.

Several terms in the scattering cross section are actually summed simultaneously as I(Q) is generated. These are combined on reaching the MODEL 99 record or some other appropriate instruction - such as to "square" or to multiply by an S(Q) structure factor. Most of the complications arise when dealing with the form factor F²(Q) for polydisperse spheres or an anisotropic particle which then has to be multiplied by a structure factor S(Q). Skip this next part if you are not concerned with such systems:

The structure factor for polydisperse or asymmetric particles has to be corrected by a ratio β(Q) to obtain an effective structure factor, still assuming no preferential interactions of any one particle with another, (J.B.Hayter & J.Penfold Colloid Polymer Sci. 261(1983)1022; M.Kotlarchyk & S-H Chen, J.Chem.Phys. 79(1983)2461-2469):

$$S'(Q) = 1 + \beta(Q)(S(Q) - 1)$$

In the notation used internally by FISH:

$$\beta(Q) = F(Q)^2 / (\text{SUMX} \cdot P(Q)) = \langle |F(Q)|^2 \rangle / \langle F(Q) \rangle^2$$

At each addition to the intensity the program accumulates:

$$P(Q) = P(Q) + \text{"scale"} \cdot F^2(Q)$$

$$F(Q) = F(Q) + \text{"scale"} \cdot F(Q)$$

$$\text{SUMX} = \text{SUMX} + \text{"scale"}$$

$$I(Q) = I(Q) + \text{"scale"} \cdot F^2(Q)$$

IMPORTANT NOTE - this simplified methodology is ONLY correct for simple cases, such as polydisperse spheres or a system all of rods or all of ellipses. It will not work for mixtures of different shapes, or mixtures of the same shapes but different contrasts. To calculate β(Q) properly FISH would need to store separately both the number densities of each type of particle and their contrasts. The averages need to distinguish a small number of particles with large contrast from a large number of particles with small contrast which would otherwise contribute the same to I(Q).

On reaching an S(Q) model both S(Q) and $\beta(Q)$ are computed and I(Q) is multiplied by the corrected S'(Q):

$$I(Q) = I(Q) \times S'(Q)$$

In each model below calculation of $\beta(Q)$ is mentioned where relevant. The FIT ROUTINE - MAIN CONTROLS menu option 2 allows the original functions S(Q) and P(Q) to be stored in workspaces, enabling them to be added to plots or written out to file. You will of course be expected to have provided workspaces for $\beta(Q)$ and S'(Q) when needed.

NEW (Nov. 2000) - the $\beta(Q)$ correction to S(Q) may be turned off with the switch K8=1.

WHAT FISH DOES - A SUMMARY OF THE MODELS AVAILABLE

The models here are grouped in the table below by functionality rather than in their (largely historical) numerical order

MODEL (LM)	L TYP	Models in FISH
		PARTICLE FORM FACTORS
1	1	Spherical particle - simple monodisperse solid sphere
12	1	Guinier radius (direct fit, useful to include flat background)
10 or 8	1	Spherical shell, sharp step (repeat for multiple shells)
10 or 8	11	Spherical shell, linear, diffuse step
10 or 8	21	Spherical shell, decreasing exponential, to infinity
10 or 8	31	Spherical shell, decreasing exponential, truncated
10 or 8	41	Spherical shell, increasing exponential from R=0
10 or 8	51	Spherical shell, increasing exponential, from previous R
9	1	square operation, use after model 8 monodisperse shells
18	1	Rod/disc - rigid, monodisperse, randomly oriented, core/shell, with shell at ends (useful for core/shell disc)
18	11	Rod/disc - rigid, randomly oriented, core/shell, without shell at ends (useful for hollow cylinder)
18	21 & 31	Rods, as above, oriented in shear flow, Hayter & Penfold, fit to 1d averaged wedges of 2d data.
18	41 & 51	Rods, as above, nematic "Maier-Saupe, DeGennes" distribution.
18	61 & 71	Rods, as above, nematic "Maier-Saupe, DeGennes" distribution, viewed end-on.
1	11	"end on" view of a monodisperse cylinder
10 or 8	61	End-on view of mono/polydisperse fixed rod, multi-shell, sharp step
21	1	Solid ellipsoid, use model 24 instead.
24	1	Ellipsoid, core/shell with outer/inner radius ratio constant
24	11	Ellipsoid, core/shell with constant thickness shell
24	21 & 31	Ellipsoids as above, but with molecular constraints for surfactant micelles.

		POLYDISPERSITY used with Model 10
1	21	Polydisperse solid spheres - analytic equations for Schultz distribution
6	11	Schultz distribution (all model 6 use numerical integration)
6	21	symmetric parabola
6	31	triangular decreasing
6	41	concave decreasing
6	51	flat "hat"
6	1	cubic polynomial
6	61	alternative cubic polynomial
6	71	stick model (for bimodal)
6	81	power law between R1 & R2
6	91	log-normal distribution
5	1	test of a maximum entropy condition on polydispersity
		PARTICLE STRUCTURE FACTORS
7	1	Critical scattering "attractive" S(Q)
19	1	Correlation hole S(Q)
22	1	Hard sphere S(Q)
22	11	Hard sphere S(Q) with attractive/repulsive square well
23	1	Hayter-Penfold charged sphere S(Q) (using their routines)
25	1	as model 23, with additional critical scattering term.
11	21	P(Q) = Constant (useful for fitting just S(Q))
		POLYMERS
14	1	Debye Gaussian coil - for polymers
14	11	Polydisperse Debye Gaussian coil
14	21	attempt at Kratky-Porod worm-like persistence chain, (14 - 71 is better)
14	31	Benoit f-branched star Debye coil
14	41	Dozier star polymer
14	51	Leibler diblock copolymer
14	61	H-shaped copolymer with deuterated tips (D.J.Read)
14	71	Kholodenko worm – mono/polydisperse with Guinier Raxial
14	81	Kholodenko worm – mono/polydisperse with core/shell rod
		SURFACES, SHEETS & FRACTALS
20	1	Q**n term (compare LM=11)
12	11	Porod surface, with optional diffuse interface
12	21	Porod surface, with diffuse layer of different scattering density.
26	1	Surface fractal form factor
13	1	Volume fractal S(Q)

26	11	Andrew Allen, "cement" surface fractal
13	11	Andrew Allen "cement" volume fractal
28	1 & 11	Polydisperse sheet, with Lorentz "waviness"
28	21	Core/shell sheet, with Lorentz "waviness"
28	31	Core/exponential shell sheet, with Lorentz "waviness"
29	1	One dimensional paracrystalline stack, Kotlarchyk & Ritzau. (useful even for a bilayer)
29	11	Wenig & Bramer, flat, 3 phase paracrystal, allows gaps between stacks to have different scattering densities
		GENERIC GELS & 2 PHASE MODELS
16	1 & 11	Teubner & Strey 2 phase "peak"
17	11	Debye random 2 phase
27	1	Gels - Lorentzian plus Debye-Bueche
		PEAK FITTING
27	21	Gaussian peak
27	71	Stretched Gaussian peak (as used for LOQ resolution)
27	31	Voigt peak (Gaussian convoluted with Lorentzian)
27	51	Gaussian peak, going to exponential, with continuous first derivative.
27	61	Ikeda-Carpenter equation for neutron moderator time distributions
27	81	Gaussian convoluted by exponential
		QUASIELASTIC
4	11	"Vanadium" resolution function for neutron quasielastic scattering
11	31	Delta function, as alternative to LM=4, LTYP=11 for quasielastic data.
27	11	Lorentzian, for quasielastic neutrons
		GENERAL
2	1	does nothing - allows parameters to be introduced into constraints
3	11	Simple flat background (note background is stored separately and is not resolution smeared)
3	1	Quadratic background
11	1	General polynomial to order 7
4	1	Scaled subtraction of a "background" data set.
11	21	$P(Q) = \text{Constant}$ (useful for fitting just $S(Q)$)
15	21 & 31	Resolution smearing by a constant width Gaussian
15	41	Resolution smearing by input curve
15	51,61 & 71	Resolution smearing, estimated for LOQ at ISIS
5	-n	Predicate observation - allows weighting of parameters towards "known" values, see manual.
88	0 or n	Allows multiple data sets, following lines are for all (0) or just set n.
99	1	ALWAYS needed to end the calculation

MODEL 1

Solid particles, analytic equations for sphere, "end view" of cylinder, and Schulz polydisperse spheres:

LTYP = 1, Small angle scatter from a spherical particle of radius r. Each size of particle in a mixture of sizes requires two records:

LTYP=1 A scale = $I(Q=0) = 10^{-24} N(\Delta\rho)^2 V^2$

LTYP=2 r radius

where N particles.cm⁻³ have volume $V=4\pi R^3/3 \text{ \AA}^3$ and scattering length density difference is in cm⁻² (see above).

Together these do $F = 3 * [(\sin(Qr) - Qr \cos(Qr)) / (Qr)^3]$

$P(Q) = P(Q) + A * F^2$

$F(Q) = F(Q) + A * F$ (note this has A not A^{1/2} see IMPORTANT NOTE above.)

"End on" view of a cylinder of radius r (compare model 8, LTYP = 61)

LTYP=11 A scale

LTYP=12 r radius

Analytic equations for Schultz distribution, from M.Kotlarchyk & S-H Chen, J.Chem.Phys. 79(1983)2461-2469 (following others), after rearrangement to avoid overflows with small σ , and re-scaling the Schultz to per unit volume (similar to Model 6 below) so that "scale" varies little with changes in σ/R and is proportional to total dispersed volume (integrated over the polydispersity). Note volume mean radius (needed for $\phi = NV$) is given by $\langle R^3 \rangle = (1 + \sigma/R)(1 + 2\sigma/R)R^3$. e.g. for number mean $R = 50 \text{ \AA}$ and $\sigma/R = 0.2$, volume mean $\langle R^3 \rangle^{1/3} = 51.97 \text{ \AA}$, i.e. larger due to the asymmetric size distribution. This makes a considerable difference to the scaling due to the dependence of $I(Q=0)$ on $\sim V^2$. $F(Q)$ is computed as above for inclusion in a $\beta(Q)$ correction done by a following $S(Q)$. Note this model will not store polydispersity separately as done for the numerical integration in Model 6. The main purpose of this model is to add "extra" scattering, such as a "magnetic core", to other more complex models.

LTYP=21 A scale = $10^{-24} \phi (\Delta\rho)^2$ where $\Delta\rho$ is in units of cm⁻² and ϕ is total volume fraction, summed over the polydispersity.

LTYP=22 R mean radius

LTYP=23 σ/R polydispersity

MODEL 2

Does nothing ! The parameter entered here is normally used in constraints, e.g. for a shell thickness in polydisperse spheres.

MODEL 3

A quadratic (e.g. for a background) is ADDED into the calculated data set (at model 99). This is also added into workspace WRK, as defined in option 2 of "fit routine main controls" (see model 11 for a general polynomial fit not stored in WRK). Note the addition is done AFTER any structure factor multiplication, squaring operations or resolution smearing of $I(Q)$ regardless of where the records appear in the file. (NOTE the PLOT command gives an option to subtract WRK(Q) from both OBS and CALC before producing the plot.)

LTYP=1 A $WRK(Q) = WRK(Q) + A + B * Q + C * Q ** 2$

2 B

3 C

LTYP=11 A short version for a flat background, saving two records, $WRK(Q) = WRK(Q) + A$

MODEL 4

Add an experimental or otherwise calculated background to the calculated set. This "background" is input as set BKG in the FIT control section, the scaled data is added into set WRK (together with any model 3 background) so may be subtracted in plots or investigated separately. Note the addition is done AFTER any structure factor, squaring or smearing on I(Q) regardless of where the records appear in the deck.

LTYP=1 A scale parameter (which may be refined) $WRK(Q)=WRK(Q)+ A*data(Q,BKG)$

The LTYP = 11,12 model uses data stored in set 9 (hardwired at present, see IV= 9 lines in code, and MODEL 15, LTYP = 41) to add an "elastic line" for quasi-elastic neutron data. The elastic line, being itself the resolution function does not need to be smeared, so is put into the "background" here. At I(Q=E) we have $I(E) = I(E) + A*CUBIC(RESOL(E + \delta))$ where function CUBIC is a Lagrange cubic interpolation through a group of the nearest 4 points, that here returns zero if E+ δ is outside the range of the data stored in set 9, (as defined by NC3(9) to NC4(9)). i.e. the supplied resolution data must be reasonably smooth, in similar bins to the data being fit, and cover positive and negative Q values, though it may cover less range than the actual data.

LTYP=11 A scale parameter (which may be refined) - special model for vanadium resolution function.
12 δ shift δ (which may be refined)

MODEL 5

Used to enter "predicate observations", these are NOT part of the computation of I(Q) and are simply extra items of experimental data. The idea is simple, one includes a guessed value of a parameter as a data item with a weight based on its expected uncertainty. This is more flexible than fixing a parameter at some arbitrary value as the value may still move in the least squares fit. The method has proven very useful for underdetermined molecular structures in gas electron diffraction and microwave spectroscopy where some bond lengths are well known to always fall within certain tolerances.(The primary reference is L.S.Bartell, D.J.Romenesko and T.C.Wong in "Molecular Structure by Diffraction Methods" eds. GA.Sim and L.E.Sutton, (Specialist Periodical Reports), The Chemical Society, London, Vol.3,(1975), Part I, Chapter 4.)

NOTE- control flag IP=K3 on record (ii) decides whether predicate observations are to be included in a fit regardless of whether these entries have non-zero weights.

Two records are needed for each predicate observation:

Either (i) simple type :

LTYP= -J guessed value for parameter J in the model
 -J weight for this observation

Or (ii) a special type, for use with polydisperse small angle scatter :

LTYP=1 Guess for V_0
 2 Weight " "
 3 Guess for $\sigma(r)/rbar$
 4 Weight " " "
 5 Guess for entropy term (a big number)
 6 Weight for " "

Entropy here is an experimental use of the maximum entropy method, to help with polydisperse problems.

$$\text{entropy} = -\int P(r)\log_e(P(r)/B) dr$$

where estimator B is CON(7)=N7 and P(r) integrates to unity.

MODEL 6

Used alone this allows for polydisperse solid spherical particles, in combination with MODEL 10 polydisperse core/shell or multilayer particles are calculated.. A number of choices of particle size distribution are allowed, decided upon by the value of LTYP(1) on the first of at least four records required. Some experimentation is required to find a model that will converge, the small and large particle limits correspond to extreme high and low Q data respectively which are usually poorly defined. Predicate observations (see model 5) with high weights may help to restrain polynomial coefficients as will application of small partial shifts. It is recommended to refine a flat background addition to I(Q), checking that its value remains sensible compared to expected systematic errors or incoherent background.

If the particle size distribution is P(R) then, unless otherwise specified, R is automatically restricted to a range where P(R)>0 and R< Rmax where Rmax is stored as CON(5), which is N5 in the interactive routine. The step size in R is CON(4) or N4, which is used:

- (a) during an initial search to check Rmin and/or Rmax values
- (b) when storing P(R) in set POL, which may later be written out or plotted. (Note that this is despite the fact that the numerical integrals may be performed by a quadrature method that does not actually use this array.)
- (c) as the R interval for Simpson's rule integrations.

REMEMBER TO SET R SEARCH STEP SIZE and Rmax!! (e.g. do N4=2.0 N5=1000.)

Moments and averages of P(r) are calculated numerically, **you will be prompted for a choice of numerical integration method** on starting a calculation (or do K5 = 1 to be prompted again). Integration schemes available are 4,10,48 or 64 point Gaussian quadrature, two more general 10 point quadratures (see C.G.Harris & W.A.B.Evans International J. Computer Math. B6(1977)219-222) and finally Simpson's rule. In general the higher number methods produce the best results, and with modern computers are not unduly slow. A Gaussian quadrature is like Simpson's rule except that the points used are not equally spaced. For functions that are well described by a polynomial a quadrature method is more efficient. See Appendix F if you are not familiar with numerical integration methods.

Until Feb 2002 the values of radii in MODEL 10 were left at the values last used by the numerical integration for MODEL 6, i.e. the maximum values included, so to see the "mean" you had to look at MODEL 6, not the MODEL 10 line with PSHIFT = -2.0. Since FEB 2002 the constraints routines are called one more time after the calculations, with R = Rbar, so that MODEL 10 radii are now printed out at their mean values.

Remember also to set CON(7) for entropy estimator B if it is needed. When using Model 6 some informative print out will appear which includes the *numerically computed* values of average radius Rbar, $\sigma(R)/Rbar$ etc.; check that these are what you expect ! (if not examine the parameter values and check N5 & N4).

Model 6 may at present only be used once in the whole fit (you could add a previously calculated polydisperse set using MODEL 4 or for solid particles use MODEL 1 - LTYP=21).

On the first record of each sub-model below "scale" = $10^{-24} \phi (\Delta\rho)^2$ where $\Delta\rho$ is scattering length density difference in cm^{-2} . ϕ = volume fraction = $\sum N_i V_i$, i.e. the polydispersity function is normalised to unit volume. If model 6 is combined with model 10 and $\Delta\rho$ for model 10 is entered in units of 10^{-10}cm^{-2} then the model 6 "scale" = $10^{-4} \phi$

LTYP=11	Scale	Modified Schultz distribution
12	R_{bar} mean radius	
13	R_1 offset, usually zero !	$P(r) = [(Z+1)/(R_{\text{bar}}-R_1)]^{Z+1} r^Z \exp\{- (Z+1)/(R_{\text{bar}}-R_1) \cdot r\} / \Gamma(Z+1)$
14	$\sigma/(R_{\text{bar}}-R_1)$	where $r = R - R_1$ and $\sigma = (R_{\text{bar}}-R_1)/(Z+1)^{1/2}$

At σ goes to zero the Schultz distribution tends to a delta function, at small σ a Gaussian, and for large σ becomes skewed to larger sizes similar to a log-normal. The main advantage of the Schultz form is in

having an analytic solution for $F(Q)$ - see Kotlarchyk & Chen mentioned above, though it is actually simpler in practise to perform numerical calculations as here. This is still tricky as Z can be large causing underflow and overflow problems. The calculation is made stable by taking logarithms and by using an asymptotic form of the gamma function $\Gamma(Z+1)$ at large Z . The model tends not to converge unless the starting parameters are very close to the final answer. NOTE the Schultz distribution $P(r)$ is significant down to $r=0$ when σ is large. R_1 optionally allows the whole distribution to be shifted, so $P(r)=0$ for $r < R_1$.

LTYP=91	Scale		Log-normal distribution
92	R_{bar}	mean radius	
93	R_1		$P(r) = \exp\{-0.5(\log(r) - \mu)^2 / (\sigma^2)\} / (\sigma \sqrt{2\pi})^{1/2}$
94	$\sigma/(R_{\text{bar}}-R_1)$		where $r = R - R_1$ and $(R_{\text{bar}}-R_1) = \exp\{\mu + 0.5\sigma^2\}$

This also produces a size distribution skewed to higher r , the median is $\exp\{\mu\}$. Some physical significance may be attributed given a system which is randomly subdivided into smaller pieces. The model here is characterised by R_{bar} and σ/R_{bar} , with an optional shift of the whole distribution by R_1 . The definition of a "log-normal" $P(r)$ seems to vary a little from one reference to another.

The next four model types allow the r range to be directly adjusted (see constraints for how to tie R_1 and (R_2-R_1) to fit R_{mid} and λ) :

LTYP=21		Symmetric parabola	$P(r) = 4A(r-R_1)(r-R_2)/(R_1-R_2)^2$
LTYP=31		Triangular decreasing	$P(r) = A(R_2-r)/(R_2-R_1)$
LTYP=41		Concave decreasing parabola	$P(r) = A(R_2-r)^2/(R_2-R_1)$
LTYP=51		Constant	$P(r) = A$ for $R_1 \leq r \leq R_2$

These four simple functions for $P(r)$ all require four records:

LTYP=21 or 31 or 41 or 51	Scale	
22 etc.		R_2-R_1
23		R_1
24		spare, but must be included

Several other shapes or definitions of polydisperse particle distributions are available:

LTYP=1	A	Polynomial for polydispersity
2	B	$P(r) = A + B*r + C*r^2 + D*r^3$
3	C	
4	D	
LTYP=61	A	Modified polynomial for polydispersity
62	B	$P(r)=A +ABr +ABCr^2 +ABCDr^3$
63	C	scaling is easier but terms stop after a zero coefficient.
64	D	
LTYP=71	Scale	"Stick model" or "free form" polydispersity
72 C1		$P(r)$ is interpolated by a 4 point cubic polynomial
73 R1		through sticks of height C_n at position R_n . At least
72 C2		fours sticks are required with r values increasing
73 R2		but not necessarily at equal intervals. This copes

72 C3 with a "bimodal" particle size distribution.
 73 R3 N.B. $P(r)$ is *continuous*, but is set zero when the cubic interpolation is less
 72 C4 than zero. Negative values of C_n affect shape of adjacent positive regions
 73 R4 so leave them in ! May need a dozen or more sticks with the first and
 72 etc. last set to zero. Start with the other C_i equal. Scale parameter is as per
 usual, $P(r)$ is normalised to give correct volume as per Schultz etc.

LTYP=81 Scale polydispersity $P(r) = (\text{abs}(r - R_B))^{|n|}$
 2 R2-R1 where if $n < 0$ $R_B = R2 + \Delta R$
 3 R1 $n > 0$ $R_B = R1$
 4 n and $\Delta R = N4 = \text{CON}(4)$

This is the same as LTYP=41 if $n=-2$, but gives flexibility to change the degree of asymmetry in the size distribution.

MODEL 7

Critical scattering structure factor- this MULTIPLIES all previously summed terms in $I(Q)$. Preceding derivatives of $I(Q)$ are also appropriately treated. (For a similar form factor see MODEL 27.)

LTYP=1 κ - kappa $S(Q) = 1 + \kappa / (1 + \zeta^2 Q^2)$
 2 ζ - zeta, correlation length $I(Q) = I(Q) * S(Q)$

MODEL 8

Monodisperse spherical particle with "multi-shell" contrast profile. Compare MODEL 1 where $|F(Q,R)|^2$ is summed, here we sum $F(Q)$ and then use MODEL 9 to square to get $I(Q)$. (This model must usually be first in the deck and must have all its pairs of $\Delta\rho$ and R records adjacent. Consult the FORTRAN code if you really need to use it elsewhere, as it may not do what you want.) See MODEL 10 for more details of LTYP=11,21,31,41,51 or 71, which are complex, as they are a THREE parameter model involving the preceding radius also !

ALSO, LTYP = 6, monodisperse core/shell rods seen "end - on" (compare model 18).

LTYP=1 $\Delta\rho$ - contrast ($F(Q)$ as per (10-2) below)
 2 a - radius
 LTYP=11 $\Delta\rho$ - contrast "fuzzy" shell, linearly increasing or decreasing, from previous radius.
 2 b - radius
 LTYP=21 $\Delta\rho$ - exponential shell, downhill to infinity, from previous radius a
 2 $a + 3.5L$ radius defining exponential decay.
 LTYP=31 $\Delta\rho$ - exponential shell, downhill, cut at $a + 3.5L$, from previous radius a
 2 $a + 3.5L$ radius defining exponential decay and cut off.
 LTYP=41 $\Delta\rho$ - exponential shell, uphill, from radius zero.
 2 $3.5L$ defining exponent L
 LTYP=51 $\Delta\rho$ - exponential shell, uphill, cut at $(a - 3.5L)$, from previous radius $(a - 3.5L)$
 2 a radius defining exponent L .
 LTYP=61 $\Delta\rho$ - contrast, end-on view of a rod (*not* to be combined with spherical shells !)

$2R$ - radius

For an “end - on” view of a rod we have in the equations of model 18, $\theta = \phi = \pi/2$, so $\cos(\gamma) = 0$, $\sin(\gamma) = 1$.

so here we do $F(Q) = F(Q) + (\Delta r)V \frac{2J_1(QR)}{QR}$ where the latter term tends to unity as Q goes to zero.

Note that though the shape of the scattering does not depend on rod length L , it still affects the absolute intensity through $V = \pi R^2 L$. Here we use $L = 1$, so the “scale” for model 9 is multiplied by L^2 . For a general discussion, including the interparticle structure factor for packed rods see: G.Oster & D.P.Riley, Acta.Cryst. 5(1952)272-276.

LTYP=71 $\Delta\rho$ - Gaussian shell centred at $(a+b)/2$ - see notes in model 10

$2b$ - radius

MODEL 9

Square operation, used immediately after MODEL 8.

LTYP=1 scale = $N \times 10^{-48}$ $I(Q) = \text{scale} * F(Q)^2$
 where there are N particles cm^{-3} and $\Delta\rho$ in model 8 is in cm^{-2}

MODEL 10

"Multi-shell" contrast for use with polydispersity MODEL 6, parameters are the same as for MODEL 8, a pair of records for each step in the contrast profile.

NOTE- the square operation is handled automatically so, unlike MODEL 8, a MODEL 9 record is NOT required. You will be prompted for a choice of a quadrature method of integration (or do K5 = -11).

NOTE- the program needs to know which radius in the contrast is polydisperse. This is done by setting one partial shift PS(j) to -2.0 where j corresponds to an R record. (Do not turn this ONor OFF !) Other radii in the profile may be kept fixed or may be constrained in the usual way, most often tied to the PS(j)=-2 parameter.

NOTE- until Feb 2002 the values of radii in MODEL 10 were left at the values last used by the numerical integration for MODEL 6, i.e. the maximum values included, so to see the "mean" you had to look at MODEL 6, not the MODEL 10 line with PSHIFT = -2.0. Since FEB 2002 the constraints routines are called one more time after the calculations, with $R = Rbar$, so that MODEL 10 radii are now printed out at their mean values.

NOTE that the LTYP=11,21,31,41,51 & 71 cases are THREE parameter functions, depending on two radii a and b and a contrast step. The least squares derivative calculations modify that already calculated for the “previous” radius. In equations below $c = (b-a)$ An example below shows how to use such models.

LTYP=1 $\Delta\rho$ contrast (see (10-2) below)
 2 a - radius
 LTYP=11 $\Delta\rho$ - contrast “fuzzy” shell, linearly increasing or decreasing, from previous radius a .
 2 b - radius
 (shell volume, increasing is $\pi c(6a^2 + 8ac + 3c^2)/3$, decreasing is $\pi c(6a^2 + 4ac + c^2)/3$)
 LTYP=21 $\Delta\rho$ - exponential shell, downhill to infinity, from previous radius a [ALL EXPONENTIAL SHELLS
 2 $b = a + 3.5L$ radius defining exponential decay. NEED CORRECTION !]
 LTYP=31 $\Delta\rho$ - exponential shell, downhill, cut at $a + 3.5L$, from previous radius a
 2 $b = a + 3.5L$ radius defining exponential decay and cut off.
 (shell volume is $4\pi L \{ a^2 + 2aL + 2L^2 - \exp(-c/L)(b^2 + 2bL + 2L^2) \}$)
 LTYP=41 $\Delta\rho$ - exponential shell, uphill, from radius zero.

- 2 3.5L defining exponent L
- LTYP=51 $\Delta\rho$ - exponential shell, uphill, cut at $(a - 3.5L)$, from previous radius $b = (a - 3.5L)$
- 2 a radius defining exponent L. (Beware a and b are now opposite way around !)
(shell volume is $4\pi L\{a^2 - 2aL + 2L^2 - \exp(-c/L)(b^2 - 2bL + 2L^2)\}$)
- LTYP=61 $\Delta\rho$ - contrast, end-on view of a rod (*not* to be combined with spherical shells ! - see notes in model 8)
 $2R$ - radius
- LTYP=71 $\Delta\rho$ - Gaussian shell centred at $(a+b)/2$, with same material as rectangular shell from a to b .
 $2b$ - radius

The single particle form factor $P(Q)$ is $F(Q)^2$ where for a spherically symmetric particle of scattering length density $\rho(r)$ at radius r we have:

$$F(Q) = 4\pi \int_0^\infty r^2 \rho(r) \frac{\sin(Qr)}{Qr} dr \quad (10-1)$$

When $\rho(r)$ takes a complex form, as for LTYP= 11,21,...51, this Fourier integral may be split into a sum of terms for each step or feature. For a vertical step of upwards of $\Delta\rho$ at radius a , as in the sharp interface model, LTYP=1

$$F(Q) = -4\pi\Delta\rho(\sin(Qa) - Qa.\cos(Qa)) / Q^3 \quad (10-2)$$

If $\rho(r)$ increases linearly from zero to $\Delta\rho$ between radii a and b , for LTYP=11, then:

$$F(Q) = 4\pi\Delta\rho \{ 2(\cos(Qa) - \cos(Qb)) + Qa.\sin(Qa) - Qb.\sin(Qb) \} / (Q^4(b-a)) \quad (10-3)$$

To model a more diffuse boundary Gradzielski et al (M.Gradzielski, D.Langevin,L.Magid, R.Strey, J.Phys.Chem,99(1995)13232-13238) used a symmetrical Gaussian distribution for $\rho(r)$, which after approximating the lower integration limit of (10-1) to $-\infty$ gives an analytic equation for $F(Q)$, used for LTYP=71,

$$F(Q) = 4\pi\Delta\rho.(b-a)\exp\{-Q^2t^2/2\}(R_0\sin(QR_0) + Qt^2\cos(QR_0))/Q$$

where $R_0 = (a+b)/2$ and the Gaussian $\rho(r) = \Delta\rho\exp\{-(r-R_0)^2/2t^2\}$ is normalised to have the same amount of material as the spherical shell between a and b by $t = \frac{(b-a)R_0^2 + (b-a)^2/12}{\sqrt{2\pi}R_0^2 + t^2} \approx \frac{(b-a)}{\sqrt{2\pi}}$. The approximate t is the exact value for a

flat sheet, which FISH uses as a starting value and iterates twice (the first time with $2t^2$ in the denominator which speeds convergence). The approximate t is assumed in analytic derivatives. Unfortunately the Gaussian shell is only realistic for a well matched “shell” contrast, and, since the integral for a “half Gaussian” appears not to be analytic, may not easily be applied to “core” or “droplet” contrasts.

An alternative form, useful particularly in the polymer field, would be for $\rho(r)$ to decrease exponentially (“downhill”) from a value $\Delta\rho$ at $r = a$ to zero at infinity as $\rho(r) = \Delta\rho.\exp\{-(r-a)/L\}$ for $r \geq a$, for which LTYP=21 uses:

$$F(Q) = \frac{4\pi.\Delta\rho}{Q^3(Q^2L^2 + 1)} \left(Qa(hQL\sin(Qa) - \cos(Qa)) + \frac{(1 + 3Q^2L^2)\sin(Qa) + 2hQ^3L^3\cos(Qa)}{(Q^2L^2 + 1)} \right) \quad (10-4)$$

where constant $h = +1$. [THIS IS WRONG & NEEDS CORRECTING IN FISH – RKH 03/2004]

For LTYP=31 the exponential is truncated by a small vertical step to zero at $R = (a + 3.5L)$, by automatically adding a term (10-2) for the step, at the same time subtracting the remainder of the exponential from $R = (a + 3.5L)$ to infinity.

If the exponential in $\rho(r)$ instead increases (“uphill”) from zero at minus infinity to $\Delta\rho$ at $r = a$ according to $\rho(r) = \Delta\rho.\exp\{-(a-r)/L\}$, then $h = -1$ in equation (10-4). Again by adding and subtracting appropriate terms it is possible to truncate $\rho(r)$ at $R = 0$ for LTYP=41 or $R = (a - 3.5L) > 0$ for LTYP=51

Equations (10-2) to (10-4) were derived by RKH (the latter two for the first time ?), and their results were extensively checked by numerical Fourier transforms of trial profiles, against both FISH output and a separate program which expressed the equations in different ways. Thus they are believed to be correct !

NOTE the SANS for a parabolic profile (as for a “polymer brush” on a flat surface) at a spherical interface appears not to have an analytic solution, but may be approximated by a series of linear segments of LTYP=11 with appropriate constraints. For the brush case $\rho(r) = (1 - (r-a)/c)^{1/2}$ and the exact shell volume is $8\pi c(35a^2 + 28ac + 8c^2)/105$, whilst for a concave profile $\rho(r) = ((r-a)/c - 1)^2$ and the shell volume is $4\pi c(10a^2 + 5ac + c^2)/30$.

NOTE To generate a desired contrast profile it may be necessary to use some "dummy" shells. The example below is for a linear ramp up, a flat top, and a linear ramp down, as might be used for a hollow shell, vesicle, structure:

```

T 1 P 15 S 1 C 4 N 5
W 1 K 0 IP 0 MS 1 IY 1 -6 -6 11 0 61 10 4
SCHULTZ POLYDISPERSE 3 SHELL SPHERE LINEAR/FLAT/LINEAR - FOR VESICLES
1 10 1 rh2-rh1=0 0.000000E+00 0.000E+00 0.0 0.00E+00
2 10 2 R1 3.100000E+02 0.000E+00 -1.0 0.00E+00
3 10 11 rh2-rh3 6.000000E+00 0.000E+00 0.0 0.00E+00
4 10 2 R2 3.250000E+02 0.000E+00 -1.0 0.00E+00
5 10 1 rh3-rh4=0 0.000000E+00 0.000E+00 0.0 0.00E+00
6 10 2 R3 3.500000E+02 0.000E+00 -2.0 0.00E+00
7 10 11 rh4-rh5 -6.000000E+00 0.000E+00 -1.0 0.00E+00
8 10 2 R4 3.650000E+02 0.000E+00 -1.0 0.00E+00
9 6 11 SCHULTZ SCA 5.000000E-06 2.283E-07 1.0 1.36E-08
10 6 12 RBAR 3.000000E+02 9.083E+00 1.0 7.94E-01
11 6 13 R0-SHIFT 0.000000E+00 0.000E+00 0.0 0.00E+00
12 6 14 SIG/(RB-R0) 2.000000E-01 0.000E+00 0.0 0.00E+00
13 8 2 head 1.500000E+01 0.000E+00 0.0 0.00E+00
14 8 2 tail 2.500000E+01 1.244E+00 1.0 2.08E-02
15 99 1 FINISH 1.000000E+00 0.000E+00 0.0 0.00E+00
1 1 c18e12e17 CALC 2 BKG 0 POL 3 SSE= 8.816E+03
11 2 6 13 14
1.00000 -1.00000 -1.00000 0.00000 (R1 = R3 - head - tail)
11 4 6 14 14(
1.00000 -1.00000 0.00000 0.00000 (R2 = R3 - tail)
11 8 6 13 13
1.00000 1.00000 0.00000 0.00000 (R4 = R3 + head)
11 7 3 1 1
-1.00000 0.00000 0.00000 0.00000 ( rh4-rh5) = - (rh2-rh1) )
1.000E+00 3.282E-06 2.000E-01 4.000E+00 2.000E+03

```

The shells defined by parameters 1 & 2 and 5 & 6, with zero contrast, are needed for the following LTYP=11 shells. The polydisperse radius is parameter 6, marked by the -2.0 in the partial shifts column. The other radii are all tied to it by constraints.

MODEL 11

General polynomial fit (see also MODEL 20) or generate a constant in $P(Q)$, or a "delta" function at the origin.

LTYP=1 A $I(Q) = I(Q) + A + B*Q + C*Q^{**2} + D*Q^{**4} \dots + G*Q^{**7}$

2 B

3 C

etc.....

8 G

LTYP=21 A $I(Q) = A$ one record only version, to generate $P(Q) = \text{constant}$, is useful before a multiplicative $S(Q)$ which needs to be refined or tested.

LTYP=31 A

32 T tolerance (may not be refined)

Defines a "delta function" at $Q = 0$ intended for

inelastic data, (but is replaced by MODEL 4, LTYP = 11), does $I(Q) = I(Q) + A/(2T)$ when $ABS(Q) \leq ABS(T)$, so if central Q values are at $-\Delta$ and $+\Delta$ where Δ is a little less than T the area of the delta function is 1.0

MODEL 12

Guinier radius (LTYP=1) or diffuse Porod interface (LTYP=11) or diffuse Porod interface with a diffuse coating of thickness H.

LTYP = 1	A	scale (analogous to model 1)	$I(Q) = I(Q) + A \exp(-Q^2 R^2 / 3.0)$
= 2	R	Guinier radius	
LTYP = 11	$K = 2\pi S$	Porod surface with diffuse interface. Note an <i>infinite flat</i> sharp interface convoluted with a Gaussian has a sigmoidal profile which scatters exactly Q^2 times this. The inclusion of a Lorentz $1/Q^2$ term for a randomly oriented flat surface involves some approximations for real surfaces, which require further investigation (RKH 2/4/98).	
= 12	σ		$I(Q) = I(Q) + K \exp(-Q^2 \sigma^2) / Q^4$
LTYP = 21	$K = 2\pi S$	diffuse Porod surface with separate surface layer of different scattering length density.	
= 22	Δ_1	Scattering length density difference (<i>substrate - solvent</i>)	
= 23	σ_1	diffuseness of substrate.	
= 24	Δ_2	Scattering length density difference (<i>layer - solvent</i>)	
= 25	H	thickness of <i>layer</i>	
= 23	σ_2	additional diffuseness of <i>layer</i> . (Note that σ_2 is convoluted with σ_1 in the Δ_2^2 term.)	

The scattering equation was derived (RKH 19/3/98) from the shell/core/shell flat sheet case (see MODEL 28, LTYP=21) convoluted with Gaussian functions, by letting the core thickness tend to infinity. FISH uses analytic derivatives. (Some further investigation of the validity of the Lorentz $1/Q^2$ is required.)

$$I(Q) = I(Q) + \frac{K}{Q^4} \left((\Delta_1 - \Delta_2)^2 e^{-s_1^2 Q^2} + \Delta_2^2 e^{-(s_1^2 + s_2^2) Q^2} + 2(\Delta_1 - \Delta_2) \Delta_2 \cos(QH) e^{-(2s_1^2 + s_2^2) Q^2 / 2} \right)$$

MODEL 13

Structure factor for volume fractals, in Teixeira formulation J.Appl.Cryst. 21(88)781-785, where "normalisation" R^{*d} matches Kjems and Sinha's $C/(d-1)$. The Q^{*d} dependence is for the range $1/\zeta < Q < 1/R$. Compare MODEL 26 the form factor for surface fractals.

$$S(Q) = 1 + (QR)^{-d} d\Gamma(d-1) (1 + (Q\zeta)^{-2})^{(1-d)/2} \sin\{(d-1)\text{atan}(Q\zeta)\}$$

$$I(Q) = I(Q) * S'(Q)$$

LTYP=1	d - fractal dimension, 2 to 3
2	ζ - aggregate size
3	R - particle radius (for normalisation assuming aggregates of spheres).

LTYP(1)=11 adds 4 extra records for Andrew Allen's cements etc. model, see A.J.Allen, J.Appl.Cryst. 24(91)624-634 and Harwell Report MPD/NBS/361 (but beware typos. in the equations). NOTE this is then a structure factor * form factor !

14	$\Delta\rho$ (in $1.0e10\text{cm}^{*-2}$)
15	f - overall vol fraction of fractal phase
16	f_L - local volume fraction
17	S - rough (max) surface area ($\text{cm}^* -1$)

MODEL 14

Gaussian coil for monodisperse (LTYP(1)=1) or polydisperse (LTYP(1)=11) polymers (e.g. for partially deuterated polystyrene), for a wormlike chain (LTYP=21, or better LTYP=71 & 81), for a Star polymer according to Benoit (LTYP=31) or Dozier (LTYP=41). Generally no calc of $\beta(Q)$ except for LTYP = 71 & 81.

LTYP=1	$I(Q=0)=I_0$	Debye Gaussian coil	$I(Q) = I(Q) + I_0 \cdot 2(y-1+\exp(-y)) / y^2$
2	R_g radius of gyration		where $y = (QR_g)^2$

For a dilute solution $I_0 = \phi V (\Delta\rho)^2$ where V is the volume of polymer in one scattering object (the coil) and $\Delta\rho$ is in cm^{-2} . $\phi = c/d$ and $V = M / (d \cdot N_A)$, where c is the concentration of polymer ($\text{g} \cdot \text{cm}^{-3}$), of molecular weight M ($\text{g} \cdot \text{mol}^{-1}$) and density d ($\text{g} \cdot \text{cm}^{-3}$).

For a blend of volume fraction X of d- and h- polymers $I_0 = X(1-X) \cdot V(\Delta\rho)^2$. Corrections are possible for differences in density and molecular weight of the d- and h- polymers, see e.g. G.D.Wignall & F.S.Bates, *J.Appl.Cryst.* 20(1987)28-40 and references there in.

LTYP=11	I_0	Polydisperse Gaussian coil	$I(Q) = I(Q) + I_0 \cdot 2(y - 1 + (1 + Uy)^{-1/U}) / ((1 + U)y^2)$
12	R_g radius of gyration		where $y = (QR_g)^2 / (1 + 2U)$
13	U index of polydispersity, assuming Schultz distribution,		$U = 1 - M_W / M_N$

Note the program takes $|U|$ to avoid numerical problems and if $|U| < 0.01$ reverts to the monodisperse model.

LTYP=21	$I(Q=0)$ exactly as for a Gaussian coil.	Worm-like chain
---------	------------------------------------------	------------------------

22 n gives total chain length $L = n \ell$

23 ℓ statistical chain element length

24 R_{ax} cross sectional radius of gyration of the chain, assuming a Gaussian scattering density distribution.

25 U index of polydispersity, as above.

This is based on the Kratky-Porod worm-like persistence chain model of M.Ragnetti & R.C.Oberthur, *Colloid & Polymer Sci.* 264(1986)32-45. See also R.G.Kirste & R.C.Oberthur in Glatter & Kratky "Small Angle X-ray Scattering", 1982, p407-411. The latter reference should be studied carefully before using this model. Note that separate equations are used in different parts of the Q range, there may be "transitions" visible at some of the junctions, which are not smoothed or blended here.

For $Q\ell < 3.1$ the Debye Gaussian coil is modified by additional terms to become the form factor of a worm-like chain of Sharp & Bloomfield. The radius of gyration of the coil is given by $R_G^2 = n\ell^2/6$. This part is reported accurate to better than 1% for $n > 10$. The higher Q parts are valid only for an infinite chain, say $n > 50$ (see Fig. 8 in the Glatter & Kratky article) and rely on calculations of Des Cloiseaux for an infinite thin chain. For $Q\ell < 9.4$ an analytical approximation of numerical results is used. For $Q\ell < 13.4$ and $Q\ell > 13.4$ further analytical approximations to a damped oscillation proposed by Des Cloiseaux are used. (These latter two equations had incorrect Q dependencies, so were corrected - confirmation of this else where has not yet been found.)

All four terms are multiplied by $\exp(-R_{ax}^2 Q^2 / 2)$ to allow for the thickness of the chain (note the $1/Q$ for a long rod is already there), which is assumed to have a Gaussian scattering density profile (see Glatter & Kratky p415, eqn 53). Polydispersity U is approximately corrected for by multiplying by the ratio of the polydisperse to monodisperse Gaussian coils given above.

When LTYP=31 we have the **Benoit** extension of the Debye equation for an **f-branched star polymer**. The theory assumes that the monomer-monomer distribution is independent of whether the chain joining them passes through a branch point. For further discussion and a case of star branched PE in the melt, see J.C.Horton, G.L.Squires, A.T.Boothroyd, L.J.Fetters, A.R.Rennie, C.J.Glinka & R.A.Robinson, *Macromolecules* 22(1989)681-686; the original reference is H.Benoit, *J.Polym.Sci.* 11(1953)507

LTYP=31	$I(Q=0)=I_0$		$I(Q) = I(Q) + I_0 \cdot 2(y-1+\exp(-y) + (f-1)(1-\exp(-y))^2/2) / fy^2$
32	R_g radius of gyration		where $y = f(QR_g)^2 / (3f-2)$
33	f the number of branches.		Note when $f=1$ the Debye coil equation is obtained.

At small Q , the Guinier term is identical to a Gaussian coil of radius R_g (i.e. independent of f) and so $I(Q=0)$ is the same as $LTYP=1$ with $M = f \cdot M_{arm}$ where M_{arm} is the molecular weight of a single arm.

The Benoit equation does not work for some (or all ?) star polymers in solution where strong interparticle and osmotic effects occur even well below c^* . **Dozier et.al.** propose a "functional description" which combines a Guinier radius of the whole star at low Q with a power law "mass correlation" function within the star (note similarities with volume fractal in MODEL 13). A number of scaling relationships should exist between the various molecular parameters, consult - W.D.Dozier, J.S.Huang & L.J.Fetters, *Macromolecules* **24**(1991)2810-2814; also D.Richter, O.Jucknischke, L.Willner, L.J.Fetters, M.Lin, J.S.Huang, J.Roovers, C.Toporovski & L.L.Zhou, *J.de Physique IV, Colloque C8*, **3**(1993)1-12.

- LTYP=41 Nf - scale
 42 R_g - radius of gyration
 43 (α / Nf) - relative scale of fractal term
 44 ξ - exponential damping length in mass fractal
 45 $\nu = 1/(\mu + 1)$ - Flory exponent, 3/5 in good solvent, 1/2 in theta solvent (i.e. $\mu = 2/3$ to 1)

$$P(Q) = Nf \left(\exp\{-Q^2 R_g^2 / 3\} + \frac{4pa}{Qx(Nf)} \frac{\sin(m \tan^{-1}(Qx))}{(1 + Q^2 x^2)^{m/2}} \right)$$

Note this model has NOT been programmed with the usual attention to overflow problems at extremes of Q etc. so use it with care !

Scattering from **diblock copolymer** L.Leibler, *Macromolecules* **13**(1980)1602-1607, eq IV-2 to IV-8.

- LTYP=51 scale = ??? x $\Delta\rho^2$ needs checking - is probably as per LTYP=61 below !
 2 N monomers per molecule
 3 a = length per monomer ($R_G^2 = Na^2/6$)
 4 f = fraction of molecule of one scattering type
 5 χ = interaction parameter (per monomer ?)

Scattering from **H-shaped polymer**, with deuterated tips (a development of Leibler's diblock copolymer).

- LTYP=61 scale = $V\Delta\rho^2$ where V = volume of whole molecule = $MW/(\rho_{bulk} \cdot N_A)$,
 $\Delta\rho$ = scattering length density difference.
 2 R_g - radius of gyration of deuterated end of arm
 3 $f_a = 4f_1$ = fraction of molecule deuterated
 4 f_b = fraction of molecule in backbone (or cross bar) = f_3
 5 χ = interaction parameter (per monomer ?)

Scattering from H-shaped molecule with deuterated tips, see D.J.Read, *Macromolecules* **31**(1998)899-911, noting that M in equation (68) should be number of monomers z_i in each section of the molecule. The general form of the equation for an incompressible system is:

$$S_{inc}(Q) = N(b_D - b_H)^2 \frac{S_{DD}S_{HH} - S_{DH}^2}{S_{DD} + S_{HH} + 2S_{DH}} = N(b_D - b_H)^2 S^*(z_i, QR_{Gi}) = V\Delta\rho^2 S^*(f_i, QR_{Gi})$$

$$I(Q) = \left(\frac{1}{S_{inc}(Q)} - 2c \right)^{-1}$$

where there are N polymer molecules per unit volume and the b_x are scattering lengths of monomers. It is more convenient to work in scattering length densities and fractions of the molecule in each part, f_1 for one deuterated tip, f_2 for the remainder of each arm, and f_3 for the cross-bar. The R_G of parts 2 & 3 are scaled as for Gaussian coils i.e. $R_{G2} = R_{G1} \sqrt{(f_2/f_1)}$ etc.

Kholodenko Worm-like chain. A.L.Kholodenko, *Macromolecules* **26**(1993)4179-4183, for an example of its use see P.Hickl, M.Ballauf, U.Scherf, K.Mullen & P.Lindner *Macromolecules* **30**(1997)273-279.

For long thin rods $I(Q) \sim P_{WORM}(Q)P_{AXIAL}(Q)$. After slight rearrangement of the original equations (using $L = n\ell$):

$$P_{WORM}(Q) = \frac{2}{3n} \int_0^{3n} \left(1 - \frac{y}{3n}\right) f(y) dy \quad [6/1/03 \text{ corrected sign of } 2^{\text{nd}} \text{ term}] \text{ where for}$$

$$Q \leq \frac{3}{\ell} \quad f(y) = \frac{\sinh(Ey)}{E \sinh(y)} \quad E = \left[1 - \left(\frac{Q\ell}{3}\right)^2\right]^{1/2}$$

$$Q > \frac{3}{\ell} \quad f(y) = \frac{\sin(Fy)}{F \sinh(y)} \quad F = \left[\left(\frac{Q\ell}{3}\right)^2 - 1\right]^{1/2} \quad [\text{it really is sin not sinh!}]$$

These equations go smoothly between Gaussian coil, Q^{-1} and Q^{-2} behaviour for appropriate values of n and ℓ . For large $n\ell$ as expected at higher Q , $P_{WORM} \rightarrow \frac{P}{QL}$. Trial and error will be required for different

combinations of n and ℓ giving the expected contour length $L = n\ell$, especially if the fit is "stuck" in one of the limiting forms. Check the value of the SCALE parameter to find a "best fit". The model will ask for two numerical integration schemes, the first for $P_{ROD}(Q)$ and the second for the polydispersity in L . You will also be asked for Wmax to determine the maximum L to be included.

The code in FISH carefully allows for the low Q limits and for potential numerical over flow or under flow situations. The Schultz distribution used here is *not* stored in the POL workspace (nor pre-processed by POLSET) thus this model may be repeated or even added to polydisperse spheres. $\beta(Q)$ corrections are calculated.

LTYP=71 has a radial Guinier form for $P_{AXIAL}(Q)$:

$$P_{AXIAL}(Q) = N(\mathbf{r}_1 - \mathbf{r}_3)^2 (AL)^2 \exp\left[-\frac{1}{2}Q^2 R_{AX}^2\right] \quad \text{where for a uniform scattering length density, in general, the mass per unit length } M_L = \frac{M}{LN_A} \text{ gives cross sectional area } A = \frac{M_L}{\rho_{BULK}}$$

uniform cylinder $A = 2\pi R_{AX}^2$, though the following model might then be more appropriate. The scaling here may be presented with various other molecular parameters using the equations in Model 14 LTYP=1, especially if the Q^{-1} limit of $P_{WORM}(Q)$ is included.

LTYP=81 has an axial core/shell cylinder for which (c.f. model 8, LTYP=61):

$$F_{AXIAL}(Q) = (\mathbf{r}_1 - \mathbf{r}_2) \rho R_1^2 L \frac{2J_1(QR_1)}{QR_1} + (\mathbf{r}_2 - \mathbf{r}_3) \rho R_2^2 L \frac{2J_1(QR_2)}{QR_2}, \quad P_{AXIAL}(Q) = NF_{AXIAL}(Q)^2$$

For numerical convenience FISH calculates SCALE x (V.P(Q)) in order to make the fitted SCALE either constant or to vary more slowly with changing shape of the worm.

LTYP=71 SCALE = $10^{-24} \phi (\rho_1 - \rho_3)^2$ where for N worms per unit volume, core volume fraction

$\phi = N \cdot (2\pi R_{AX}^2 n \ell)$. NOTE - since we do not know M_L , FISH assumes R_{AX} is for a cylinder, for which $R = \sqrt{2} R_{AX}$. If you do know M_L , then calculate the proper SCALE = $(2\pi R_{AX}^2) \text{SCALE}_{FISH} / A$ where A is the cross sectional area described above. As usual ρ_1 & ρ_3 are scattering length densities in cm^{-1} for the worm and solvent, molecular dimensions are in \AA , $I(Q)$ in cm^{-1} and Q in \AA^{-1} . NOTE this is NOT the same

SCALE as the normal rod model 18 1, this choice makes it simpler to add a "wet shell" to a known "dry core".

72 n gives total mean chain contour length $L = n\ell$

73 ℓ statistical chain element length (Kuhn length) = 2 x (persistence length).

74 R_{ax} cross sectional radius of gyration of the chain, assuming a Gaussian scattering density distribution. If $R_{ax} < 1.0 \text{ \AA}$ the cross sectional term is set to 1.0, giving just the infinitely thin worm.

75 not used.

76 not used.

77 polydispersity (σ/L_{MEAN}) in chain length (with fixed ℓ); monodisperse if $(\sigma/L_{MEAN}) < 0.01$

Kholodenko worm-like chain with core/shell cylinder. Beware this model has a lot of parameters, whole families of best fits may exist even with ideal data.

$$LTYP=81 \quad SCALE = 10^{-24} \phi_{CORE} (\rho_1 - \rho_3)^2$$

$$\text{where for } N \text{ worms per unit volume, } \phi_{CORE} = N \cdot (\pi R_1^2 n \ell)$$

82 n gives total mean chain length $L = n\ell$

83 ℓ statistical chain element length (Kuhn length) = 2 x (persistence length).

84 R_1 radius of core.

85 DELR shell thickness such that outer radius $R_2 = R_1 + DELR$

86 CONTRAST = $(\rho_2 - \rho_3)/(\rho_1 - \rho_3)$, where ρ_1, ρ_2, ρ_3 are for core, shell & solvent. NOTE again that

this is NOT the same as rod model 18 1, and that for a hollow shell the value here becomes infinite. In practise try using some large number like 100 or 1000 for a hollow worm.

87 (σ/L_{MEAN}) polydispersity in chain length, for a Schultz distribution of contour lengths with fixed ℓ ,

taken as monodisperse if $(\sigma/L_{MEAN}) < 0.01$

MODEL 15

Smearing for instrument resolution. This is normally done AFTER all other calculations, before the MODEL 99 record. Partial shift PS(i) has no effect for this model, which cannot be refined, except by trial and error adjustment of RSCALE Both the calculated data and its derivatives in the least squares are smeared.

Except for LTYP = 41 the resolution function is divided into NSIMP intervals over ± 3.5 standard deviations and Simpson's rule is used to convolute the calculated intensity I(Q) (but not the background in WRK). The data and its derivatives are required at NSIMP Q values for each point in the data. These are found either by interpolation of local cubic functions through groups of 4 points in I(Q) or more slowly by exact calculation. Outside of the original Q range exact calculations are always made for I(Q) and its derivatives as the local cubic may not extrapolate well. NSIMP must be an odd number > 5 , e.g. 21 The main FIT MENU option 2 allows the unsmeared data to be stored in a separate data set. LTYP = 41 uses a supplied resolution function (e.g. vanadium data for quasi-elastic scattering).

NOTE set RSCALE to zero to turn off the smearing.

LTYP = 1	RSCALE	Gaussian resolution function estimated for typical LOQ conditions
2	NSIMP	(using old LETI detector and $\lambda=2-10\text{\AA}$), width is multiplied by RSCALE.
LTYP=11	RSCALE	as above, but exact calc at all points instead of cubic interpolation.

12	NSIMP	(this is the best option to try first, use RSCALE = 1.0, NSIMP = 21.0)
LTYP=21	RESOL	Constant resolution of FWHM= RESOL, note RESOL=2.35 σ
22	NSIMP	
LTYP=31	RESOL	as above, but exact calc at all points instead of cubic interpolation.
32	NSIMP	
LTYP=41	RSCALE	Uses resolution curve stored in set 9 (hard wired as IV = 9 in code), assumed on
42	not used	bins smaller or roughly equal to those of the data. The function may be
broadened		

or narrowed by a factor RSCALE. In a loop over $Q = Q_{data} + RSCALE \times Q_{resol}$ the calculated $I(Q)$ is interpolated by a local Lagrange cubic function, and the convolution summed by the trapezium rule. The resolution data is used over the range determined by NC3(9) to NC4(9).

LTYP=51	RSCALE	Resolution function estimated (Apr 96) for LOQ ORDELA detector, $\lambda = 2.2-10 \text{ \AA}$. Uses a Gaussian “stretched” in tails (see model 27, LTYP=71) parametrised by fits to LOQ data simulated at selected Q values. Resolution is multiplied by abs(RSCALE). Negative RSCALE uses cubic interpolation except at ends of Q range, positive RSCALE uses exact calculation at all points.
52	NSIMP	
LTYP=61	RSCALE	as above, LOQ ORDELA detector $\lambda = 6-10 \text{ \AA}$, these needs redoing for “new” Ordela multi-wire detector () which has better resolution – meanwhile try say RSCALE = 0.8
62	NSIMP	
LTYP=71	RSCALE	as above, LOQ High Angle Bank - initial estimate - $\lambda = 2.2-10 \text{ \AA}$.
72	NSIMP	

LTYP=51,61,71 assumes a sample diameter of 8 mm. Approximate values of abs(RSCALE) to suit other beam diameters, are given in the table below, based on comparisons of simpler calculations of mean FWHM. RSCALE varies in a roughly linear fashion with Q.

Sample diameter =	10 mm	12 mm	14 mm
ORDELA low Q	1.045	1.105	1.17
“ high Q	1.035	1.085	1.14
HAB low Q	1.060	1.13	1.21
“ high Q	1.035	1.08	1.13

MODEL 16

Teubner and Strey (J.Chem.Phys. 87(87)3195) (no calc of $\beta(Q)$) This assumes $g(r) = (d/2\pi r) \exp\{-r/\zeta\} \sin(2\pi r/d)$ i.e. a sinusoidally varying domain scattering length density with the oscillations damped out by a correlation length ζ . No deductions may be made about the three dimensional nature of the structure involved. The model will "fit" a wide range of interacting particles or bicontinuous/porous structures as long as the diffraction pattern has a fairly broad peak.

LTYP=1	$I(Q=0) = I_0$	$I(Q) = I(Q) + I_0 / [(1 - I_0/I_m) \cdot \{ (Q^2/Q_m^2 - 1)^2 + I_0/I_m \}]$
2	$I(\text{maximum}) = I_m$	
3	$Q(\text{peak}) = Q_m$	see below to relate these to d and ζ

Teubner and Strey, second form, this is one place where LTYP must be correct on all three records !

$$\begin{aligned} \text{LTYP}=11 & \quad 1/I(Q=0) I(Q) = I(Q) + I(Q=0) / [1 + A.Q^2 + B.Q^4] \\ 21 & \quad A/I(Q=0) \\ 31 & \quad B/I(Q=0) \end{aligned}$$

Teubner & Strey correlation length z and domain size d are given by:

$$\begin{aligned} z^{-2} &= \frac{\sqrt{B}}{2} + \frac{A}{4B} = \frac{1}{2} Q_M^2 (I_M / (I_M - I_0))^{1/2} - \frac{1}{2} Q_M^2 \\ \left(\frac{2p}{d}\right)^2 &= \frac{\sqrt{B}}{2} - \frac{A}{4B} = \frac{1}{2} Q_M^2 (I_M / (I_M - I_0))^{1/2} + \frac{1}{2} Q_M^2 \\ I_0 &= \frac{8p\phi(1-\phi)(\Delta r)^2}{z((2p/d)^2 + z^{-2})^2} = \frac{8p\phi(1-\phi)(\Delta r)^2}{\sqrt{2} Q_M^3 I_M} (I_M - I_0) \{ (I_M / (I_M - I_0))^{1/2} - 1 \}^{1/2} \end{aligned}$$

where ϕ and $(1-\phi)$ are the volume fractions of the phases. Note that in the limit $k \rightarrow 0$ the Debye model (see below) is obtained and $\zeta = a_0$, however Q_m becomes imaginary so model 17 must be used instead.

MODEL 17

Debye random two phase / Wang et.al. The Debye model for random two phase structure has $g(r) = \exp\{-r/a_0\}$ which gives $A = 2a_0^2$, $B = a_0^4$ in the T&S second form above. It is also a special case of a model proposed by Z.-Y.Wang, M.Konno & S.Saito, J.Chem.Phys. 90(1989)1281-1284, using $g(r) = \exp\{-r/a_0\} \cos(Q_0 r)$. (The full model appears similar to one of the terms in the Cahn-Hilliard scheme for spinodal decomposition.)

$$\begin{aligned} \text{LTYP}=11 & \quad I_z & \quad I(Q) = 4\pi \langle \eta^2 \rangle a_0^3 \{ (1 + Q_0/Q) / (1 + a_0^2(Q+Q_0)^2)^2 + \\ & & \quad (1 - Q_0/Q) / (1 + a_0^2(Q-Q_0)^2)^2 \} \\ 12 Q_0 & & \\ 13 & \quad a_0 & \end{aligned}$$

$$\text{Correlation length } \zeta = a_0 / (1 + a_0^2 Q_0^2)$$

The $I(Q)$ above is as given in the original paper, in which it is noted that $I(Q)$ can tend to go negative at low Q ! Only in some cases does I_z approximately equal $I(Q=0)$.

$$I_z = 8\pi \langle \eta^2 \rangle a_0^3 / (1 + a_0^2 Q_0^2)$$

Set $Q_0=0$ to obtain the exact result for the Debye model (also see MODEL 27, LTYP=1) for which

$$I(Q) = I(0) / (1 + a_0^2 Q^2)^2 \text{ and } I(0) = I_z = 8\pi \phi(1-\phi)(\Delta\rho)^2 a_0^3$$

MODEL 18

Rods (or discs) or oriented rods, of full length L and radius R . For N randomly oriented rods the form

$$\text{factor } P(Q) \text{ is: } P(Q) = N \int_0^{p/2} F^2(Q) \sin(g) dg$$

$$\text{where } F(Q) = (\Delta r) V \frac{\sin(\frac{1}{2} QL \cos g)}{\frac{1}{2} QL \cos g} \frac{2 J_1(QR \sin g)}{QR \sin g} \text{ in which } J_1(x) \text{ is the first order Bessel}$$

function of the first kind, $V = \pi R^2 L$ and we must integrate numerically over angle γ between the Q vector and the axis of the rod. FISH will prompt for a choice of integration scheme (or do $K5 = 1$), see notes on model 6.

Note that $F(Q=0) = (\Delta\rho)V$ and that further similar terms may be added to $F(Q)$ for “core plus shell” systems. (See I.Livesey, J.Chem.Soc. Faraday Trans 2, 83(1987)1445-1452)

- LTYP=1 or 11 SCALE - rigid, core/shell rod (or disc) with a shell at the end (LTYP=1) or without a shell at the end (LTYP =11) of the rod.
- 2 R - radius (NOTE this is the OUTER radius for core/shell cases, NOT the inner one.)
- 3 LENGTH
- 4 DR - shell thickness
- 5 CONTRAST = $(\rho_1 - \rho_2)/(\rho_2 - \rho_3)$
where ρ_1 is for inner region, ρ_2 for outer region and ρ_3 for the solvent.

Set DR and/or CONTRAST to zero for a uniform rod. For a hollow cylinder CONTRAST = -1. See also CONSTRAINTS 17 &18.

SCALE = $10^{-24} \phi (\rho_2 - \rho_3)^2$ where ϕ = volume fraction, scattering length density ρ is in units of cm^{-2} , and rod radius R and LENGTH are assumed to be in Å. SCALE is thus invariant for a given system and consistent with the approach used for polydisperse spherical particles. SCALE has the same meaning for both uniform solid and core/shell rods, but note that it depends on the *shell* scattering length density, so it will vary if CONTRAST is adjusted !

(Before Aug 96, earlier in the TEST version,, SCALE = $10^{-48} N(\rho_2 - \rho_3)^2 = 10^{-24} (\rho_2 - \rho_3)^2 \phi (\pi R^2 L)$ where there are N cylinders per cm^3 .. Defined in this way SCALE changes rapidly with the dimensions L and R of the cylinder which was not good for the fitting procedures. Prior to March 93, LTYP=1 had no shell at the end and LTYP =11 did not exist.)

(Ratio $\beta(Q)$ is calculated, so this $P(Q)$ may be combined with a structure factor. Between Aug 96 and Nov 2000 this was however not calculated correctly, due to a mistake in the scaling of $F(Q)$, which made $S'(Q)$ very small.)

- LTYP= 21 or 31 SCALE = $10^{-24} \Phi (\rho_2 - \rho_3)^2$ Rigid rods, with or without end-cap, oriented by shear flow.
- 2 R outer radius, defining volume fraction $\Phi = N\pi R^2 L$
- 3 L Length of rod.
- 4 DR shell thickness
- 5 CONTRAST = $(\rho_1 - \rho_2)/(\rho_2 - \rho_3)$, as for LTYP=1,11
- 6 $\Gamma = G/D_r$ Ratio of shear gradient G to rotational diffusion constant D_r , see constraint 14.
- 7 Ψ angle of Q to flow direction (degrees)
- 8 $d\Psi$ If $d\Psi > 0$ then the program will also integrate over $(\Psi - d\Psi)$ to $(\Psi + d\Psi)$

This follows exactly J.B.Hayter & J.Penfold, J.Chem.Phys. 88(1984)4589-4593 for Couette flow where the neutron beam passes twice through the sample.

$$P(Q) = \int_0^{2\pi} d\mathbf{f} \int_0^{\pi} P_s(\mathbf{q}, \mathbf{f}, \Gamma) \left\{ F^2(Q, \mathbf{g}^+) + F^2(Q, \mathbf{g}^-) \right\} \sin(\mathbf{q}) d\mathbf{q}$$

where $F(Q)$ is as above, $\cos \mathbf{g}^{\pm} = \sin \mathbf{q} \cos \mathbf{f} \cos \Psi \pm \cos \mathbf{q} \sin \Psi$

and the rod orientation function is taken to be: $P_s(\mathbf{q}, \mathbf{f}, \Gamma) = \frac{(1 - \cos 2\mathbf{f}_0)(1 + \sin^2 \mathbf{q} \cos 2\mathbf{f}_0)^{3/2}}{4\mathbf{p}(1 - \sin^2 \mathbf{q} \cos 2\mathbf{f}_0 \cos 2(\mathbf{f} - \mathbf{f}_0))^2}$

in which $2\phi_0 = \text{atan}(8/\Gamma)$ and $F(Q)$ is as given above. Note that if $G = \Gamma = 0$ then $2\phi_0 = \pi/2$ and $P_s(\theta, \phi, \Gamma) = 1/(4\pi)$. As G increases the angular distribution narrows and the most probable angle moves towards the flow direction, but never reaches it due to the effects of rotational diffusion, e.g. at $\Gamma = 10$, $2\phi_0 = 0.2148\pi$.

When $\Psi = 90^\circ$ (Q is roughly perpendicular to the rod axis) we have $\gamma^+ = \theta$ and $\gamma^- = (\pi - \theta)$ so the integrals and range of integration simplify to:

$$P(Q, \Psi = 90^\circ) = 2 \int_0^{p/2} \frac{(1 - \cos 2f_0)}{(1 - \sin^2 q \cos 2f_0)^{3/2}} F^2(Q) \sin q dq$$

Some experimentation with the numerical integration schemes used in FISH will be required, especially if L/R is large, and Γ is large. Automatic integration routines are little use for the $d\theta$ integral as the functions oscillate rapidly, a Simpson rule of at least 359 points seems best. The $d\phi$ integral seems to behave well with an adaptive Gauss/Kronrod rule. If the $d\Psi$ integration is used at all, a 4 point Gaussian quadrature should suffice, except perhaps at very small Q and large Γ when more points might be better. Except at $\Psi = 90^\circ$ the calculations are VERY slow, the Q range and number of data points should be restricted. Use $K4 = n$ to include only every n'th point in the least squares. The rod length determined depends very much on the constraint applied to Γ via an approximation for D_r (see constraint 14). It is possible in FISH to fit say $\Psi = 0$ and $\Psi = 90$ data sets simultaneously, with Γ constrained to the applied shear gradient and the viscosity of the solvent. The program will run faster if the slow $\Psi=0$ calculation is first in the model parameters, so the derivatives calculated for the larger number of tied ($PS(i) = -1$) parameters in the second data set will be for a faster $\Psi=90$ case (- else wise turn OFF tied parameters in the second set if they are not actually adjusting, use $n=TIE$ to reintroduce a constraint).

(NOTE At present only $F^2(Q)$ and not $F(Q)$ is calculated, so ratio $b(Q)$ to modify any $S(Q)$ is **not** applied)

LTYP= 41 or 51 Maier-Saupe “nematic phase” distribution of rigid rods, with or without end-cap.

2 - 8 As for sheared rods above.

Using the same coordinate system, the orientation function $P_S(\theta, \phi, \Gamma)$ above becomes $P_{MS}(\theta, m)$ where the distribution of angles of the rod to the vertical θ is given by:

$$P_{MS}(\mathbf{q}, \mathbf{f}, m) = P_{MS}(\mathbf{q}, m) = \frac{e^{m \cos^2 q}}{4p \int_0^{p/2} e^{m \cos^2 q} \sin q dq} = \frac{e^{m \cos^2 q}}{4p \int_0^1 e^{mx^2} dx}$$

where all angles ϕ are equally likely. The larger the value of m the greater the degree of orientation, numerically a maximum of $m \sim 50$ is possible, whilst $m < 0.1$ gives an almost random distribution.

The lack of ϕ dependence allows simplification of the integral for $P(Q)$ when $\Psi = 90^\circ$, Q is parallel to the average rod axis (i.e. the opposite to the sheared rods above !) and $\gamma = \theta$:

$$P(Q, \Psi = 90^\circ) = 4p \int_0^{p/2} P_{MS}(\mathbf{q}, m) F^2(Q) \sin q dq$$

The Maier-Saupe distribution is used for a nematic liquid crystal by F.Hardouin, Gsigaud, M.F.Achard, A.Brulet, J.P.Cotton, D.Y.Yoon, V.Percec & M.Kawasumi, *Macromolecules* **28**(1995)5427-5433, though their equation (9) for $P(Q, \Psi=0)$ is wrong ! They cite the Maier-Saupe distribution as being from P.G.DeGennes, “The Physics of Liquid Crystals”, Oxford Press, 1974, p43. The latter mistakenly relates the normalising integral in the denominator of P_{MS} to an error function. Note that m is a positive number, not negative.

LTYP= 61 or 71 “End - on view” of Maier-Saupe distribution of rigid rods, with or without end-cap.

2 - 8 As for sheared rods above.

In the Hayter-Penfold coordinates (the beam goes along y, the vertical is z, Q is in the x-z plane) we now define the Maier-Saupe distribution for angle β between the rod axis and the y direction, and angle α between the rod axis and the x-z plane. As before the angle between the rod axis and Q is γ , but now $\cos \gamma = \sin \beta (\cos \Psi \cos \alpha - \sin \Psi \sin \alpha) = \sin \beta \cos(\Psi - \alpha)$, so that the scattering is, as expected, independent of Ψ .

$$P(Q) = 4 \int_{a=0}^{p/2} \int_{b=0}^{p/2} P_{MS}(\mathbf{b}, m) F^2(Q, \mathbf{g}) db da$$

Note the LTYP=7 & 8 lines are still needed, the value of Ψ is ignored (set zero internally), though an integration will be carried out if $d\Psi \neq 0$.

When m is very small $P(Q)$ is almost the same as for the previous model, with m small also, and of course the same as for LTYP=1 or 11 the randomly oriented rod. When m or Γ is very large, the rod radius very large and the rod length small, then any of the oriented rod model results may be compared with model 28 for thin interfaces.

MODEL 19

Correlation hole structure factor. This assumes $g(r)=0$ for $r<h$ and $g(r)=1$ for $r>h$, an exclusion volume of radius h about some object, as proposed by deGennes.

LTYP=1	Hole volume fraction η	$S(Q) = 1 + 3\eta[Qh\cos(Qh) - \sin(Qh)]/(Qh)^3$
2	Hole radius h	$I(Q) = I(Q)*S'(Q)$

MODEL 20

$I(Q) = I(Q) + A*Q^N$ where A and N may be determined, useful to add in a Q^{-4} background etc. (see also MODEL 11). Uses FORTRAN for $Q**N$, so N must be valid for $**$ operation.

LTYP=1	A
=2	N

MODEL 21 (Compare MODEL 24)

Ellipsoid of revolution of radii A , A , and $C=X*A$. This requires a numerical integration for $I(Q)$

LTYP=1	SCALE	$I(Q) = I(Q) + SCALE \int_0^{p/2} \Phi^2(u) \sin(a) da$
=2	A radius	where $\Phi(u) = 3(\sin(u) - u.\cos(u))/u^3$
=3	X axial ratio	and $u = QA(\sin^2(\alpha) + X^2\cos^2(\alpha))^{1/2}$

Alternatively change the variable to $\mu=\cos(\alpha)$ and integrate from zero to one. (calculates $\beta(Q)$ so can use with structure factor).

MODEL 22

Hard sphere structure factor, Percus-Yevick equation, as solved analytically by N.W.Ashcroft and J.Lekner, Phys.Rev. 145(1966)83-90, multiplies previous $I(Q)$. Note first peak is at approx $Q=3.5/R$.

LTYP= 1	ETA	volume fraction of dispersed spheres
= 2	R	radius of hard spheres.

Hard sphere with square well, according to R.V.Sharma & K.C.Sharma, Physica A89(1977)213-218. How this relates to the "Baxter sticky hard sphere" $S(Q)$ (of later date) I am not sure as I have not been able to find the actual equations for the latter. [Thanks to R.Triolo for pointing out the Sharma paper and cross checking results here.]

LTYP= 11	ETA	volume fraction of dispersed spheres
= 12	R	radius of hard spheres.
= 13	eps/kT	depth of square well, attractive is negative.
= 14	lambda	square well extends to $\lambda \times \text{diameter}$

MODELS 23 & 25

Structure factor for charged spheres. MODEL 25 has an extra two records to add in a critical scattering term (note not same as model 7 as the extra +1 there is avoided). If $LTYP(1) = 1$ the Hayter-Penfold one component macroion (OCM), RMSA, model is used (with penetrating background), J.P.Hansen & J.B.Hayter, Mol. Phys.46(1982)651, J.B.Hayter & J.Penfold, Mol.Phys. 42 (1981)109-118. Thanks are due to

J.Penfold for allowing his code to be included directly in FISH and to C.Fagotti for implementing it and re-parametrising the equations. LTYP(1) = 11 gives the GOCM model of L.Belloni, J.Chem.Phys 85(1986)519

LTYP=1 or 11 Sphere radius

2 Q charge (electrons) per sphere

3 AKK inverse Debye screening length (Å⁻¹)

4 ETA volume fraction

5 (model 25 only) I0(crit) S(Q) + I0(crit)/(1+ζ²Q²)

6 " " " ζ correlation length for critical scatter

AKK=1/r_D where r_D² = ε₀K_TRT/(2ρN_A²e²I)

I= ionic strength = 0.5 Σ(m₊z₊² + m₋z₋²) where m = molality

e.g. for a 1:1 electrolyte, I=m, at 0.1 molal in water at 25°C, relative permittivity K_T=78

r_D² = (8.85x10⁻¹²C²N⁻¹m⁻²) 78 (8.31JK⁻¹mol⁻¹)(298K)(10²⁰Å²m⁻²)

2 (10³kgm⁻³) (6.02x10²³mol⁻¹)² (1.6x10⁻¹⁹C)² (0.1molkg⁻¹)

so r_D = 9.6Å, AKK= 0.10 Å⁻¹

MODEL 24

Two shell ellipsoid (compare MODEL 21) If the LTYP(1) = 1 then (outer radius / inner radius) is constant at all points; for LTYP(1) = 11 the outer shell has a constant thickness of δ. LTYP(1) = 21 or 31 are specially constrained cases of LTYP(1) = 1 or 11 respectively, used by C.Fagotti for swollen micellar systems. In these cases simple physical parameters are used, via the CON(i) array to compute the scattering, see Appendix C. Note you will be prompted for a choice of numerical integration method, see notes on model 6.

LTYP=1,11,21,31 SCALE n_p V_T²(ρ₂-ρ₃)² NOTE this is for the OUTER step !!

2 R1 inner radii are R1 : R1 : X.R1

3 X X=1 for sphere, X < 1 for oblate, X > 1 for prolate

4 R2 (if LTYP=1), δ (if LTYP=11)

5 coefficient of 3j₁(u₁)/u₁, NOTE this is not tied to the other parameters in any way :
(but see CONSTRAINTS 15, 16 & 17 which will do this for LTYP(1)=11)

if LTYP(1)=1 [((ρ₁ - ρ₂) / (ρ₂ - ρ₃))(R₁/R₂)³]

if LTYP(1)=11 [((ρ₁ - ρ₂) / (ρ₂ - ρ₃))XR₁³ / ((R₁+δ)²(R₁X+δ))]

We need: $I(Q) = I(Q) + n_p \int_0^1 F^2(Q, \mathbf{m}) d\mathbf{m}$ where:

$$F(Q, \mu) = V_{\text{core}} 3(\rho_1 - \rho_2)^3 j_1(u_1)/u_1 + V_{\text{total}} 3(\rho_2 - \rho_3)^3 j_1(u_2)/u_2$$

$$= (4\pi/3)(\rho_2 - \rho_3)XR_2^3 [3j_1(u_2)/u_2 + 3(R_1/R_2)^3 (\rho_1 - \rho_2) / (\rho_2 - \rho_3) j_1(u_1)/u_1]$$

in which $u_1 = Q.R_1 [(1-\mu^2) + X^2\mu^2]^{1/2}$

$$u_2 = Q.R_2 [(1-\mu^2) + X^2\mu^2]^{1/2}$$

$$j_1(u) = (\sin(u) - u \cdot \cos(u)) / u^2$$

and ρ_1, ρ_2, ρ_3 are the scattering length densities of the core, outer shell and solvent respectively.

For LTYP(1)=11

$$F(Q, \mu) = (4\pi/3)(\rho_2 - \rho_3)(R_1 + \delta)^2 (R_1 X + \delta) [3j_1(u_2)/u_2 + \{(\rho_1 - \rho_2) / (\rho_2 - \rho_3)\} (R_1^3 X / ((R_1 + \delta)^2 (R_1 X + \delta))) 3j_1(u_1)/u_1]$$

where u_1 is as before and $u_2 = Q \cdot [(1 - \mu^2)(R_1 + \delta)^2 + (R_1 X + \delta)^2 \mu^2]^{1/2}$

MODEL 26

Approximate form factor for surface fractals, see e.g. Teixeira J. Appl. Cryst. 21(88)781-785 or Schmidt et al. J. Chem. Phys. 90(89)5016-5023, derived in H.D. Bale & P.W. Schmidt, Phys. Rev. Letts. 53(84)596-599. This is only for $Q \gg 1/\zeta$ where ζ is the average pore or object size. Compare MODEL 13 for volume fractals.

$$I(Q) = I(Q) + \pi \Delta \rho^2 S \Gamma(5 - d_s) \sin\{(d_s - 1)\pi/2\} Q^{-(6 - d_s)}$$

LTYP=1 scale

2 d_s surface fractal dimension, for smooth surface to rough surface, $2 < d_s < 3$, scattering at high Q goes approximately as Q^{-4} to Q^{-3}

For $d_s=2$ the Porod limit is reached and $\text{scale} = \pi 10^{-32} (\Delta \rho)^2 S$ with $\Delta \rho$ in cm^{-2} and surface area per unit volume, S , in cm^{-1} [The meaning of S for higher values of d_s is not clear ???] A diffuse interface may have a steeper gradient than Q^{-4} , see the modified Porod of MODEL 12.

LTYP=11	S/V in cm^{-1}	Andrew Allen version, see MODEL 13
12	D	Fractal dimension
13	$\Delta \rho$	in 10^{10}cm^{-2} (NOTE - won't adjust independently of S/V)
14	ζ	

MODEL 27

"Peaks" and network functions - Lorentzian plus Debye-Bueche; Lorentzian for quasi-elastic neutrons, Gaussian function, Voigt (Gaussian convoluted with a Lorentzian), Gaussian to exponential, Ikeda-Carpenter moderator function, and Gaussian convoluted with an exponential.

LTYP=1 Gel networks etc., as proposed for aqueous gelatin by I. Pezron *et al.* Polymer 32(1991)3201-3210. Lorentzian plus Debye-Bueche. (See MODEL 7 for a similar structure factor and MODEL 17 for the Debye term.)

$$I(Q) = I(Q) + I_1 / (1 + Q^2 \xi^2) + I_2 / (1 + Q^2 a^2)^2$$

LTYP= 1	I1	$I(Q=0)$ Lorentzian term
2	ξ	screening length for a semi-dilute solution $c > c^*$, in a good solvent is the average mesh size of a transient network.
3	I2	$I(Q=0)$ Debye-Bueche term (compare notes on MODEL 17).
4	a	decay length for inhomogeneities of correlation function $\gamma(r) = \exp(-r/a)$

LTYP = 11 has a Lorentzian for quasi-elastic neutron scattering, for which see also MODELS 4, 11 & 15 and compare the methods in D.S. Sivia, C.J. Carlile, W.S. Howells & S. König, Physica B 182(1992)341-348.

LTYP= 11	A	Lorentzian for inelastic neutrons: $I(Q) = I(Q) + A \cdot W / \{2\pi((E - \delta)^2 + (W/2)^2)\}$
12	W	FWHM of peak

13	δ	shift in Q or E scale
LTYP=21	SCALE	Gaussian peak $I(Q) = I(Q) + \text{SCALE} \cdot \exp\{-0.5 \cdot ((Q-Q_0)/\sigma)^2\}$
22	W	FWHM of peak. Standard deviation $\sigma = \max(W/\sqrt{2 \ln(2)}, 1.0e-12)$
23	Q_0	peak position
LTYP=71, "Stretched Gaussian peak, as for LTYP =21, except extra terms added, as used for empirical fitting of LOQ resolution function.		
LTYP=71	SCALE	$I(Q) = I(Q) + \text{SCALE} \cdot \exp\{-0.5 \cdot [(Q-Q_0)/(\sigma + (\text{abs}(\sigma_2) + \sigma_3)(Q-Q_0))]^2\}$
72	W	approximate FWHM of peak, $\sigma = \max(W/\sqrt{2 \ln(2)}, 1.0e-12)$
73	Q_0	peak position
74	σ_2	symmetric stretch of tail
75	σ_3	asymmetric stretch of tail
LTYP=31	SCALE	Voigt function, Gaussian convoluted with a Lorentzian
32	σ	Computed from real part of complex error function,
33	γ	see source code from W.I.F.David.
33	Q_0	peak position
LTYP=51	SCALE	Gaussian going over to exponential, with continuous first derivative
52	W	As LTYP=21 when $(Q - Q_0) < \sigma^2/\tau$
53	Q_0	when $(Q - Q_0) > \sigma^2/\tau$ then:
53	τ	$I(Q) = I(Q) + \text{SCALE} \cdot \exp\{\sigma^2/2\tau^2\} \exp\{-(Q - Q_0)/\tau\}$
LTYP=61	SCALE	Ikeda-Carpenter equation for moderator time distributions.
62	$\Sigma/\lambda = 2.5277842\alpha$,	where Σ is in cm^{-1} and wavelength λ in Angstrom
63	t_0	time origin offset, times assumed in μsec ,
64	$1/\beta$	
65	R,	fraction in storage term, $0 \leq R \leq 1$

Ikeda & Carpenter (Nucl.Instrs. & Meths. A239(1985)536-544) first note that for high energy neutrons, from an hydrogenous moderator the time distribution should approximate to the chi-squared distribution expected for neutrons in an infinite medium of free protons at rest, with no adsorption :

$$f(v, t) = \frac{\Sigma v}{2} (\Sigma v t)^2 \exp(-\Sigma v t) \quad (t > 0)$$

where v is the neutron speed and Σ is the neutron scattering cross section. At short times this predicts a universal shape for the neutron pulse if time is scaled by v . At long times their experimental observations suggested a decay time independent of neutron wavelength, as might be expected for the moderation process. A fraction R of the neutrons are convoluted with an exponential of decay time $1/\beta$ to give a neutron pulse shape that is the sum of "slowing down" and "storage" terms:

$$\Psi(t) = (1 - R) \frac{a}{2} (at)^2 e^{-at} + R \frac{ab}{2} \int_{t'=t}^{t'=\infty} (at')^2 e^{-at'} e^{-b(t-t')} dt'$$

$$\Psi(t) = (1 - R) \frac{a}{2} (at)^2 e^{-at} + aR \frac{a^2 b}{(a - b)^3} [e^{-bt} - e^{-at} (1 + (a - b)t + \frac{1}{2}(a - b)^2 t^2)]$$

where $\int_0^{\infty} \Psi(t) dt = 1$ and $\alpha = v\Sigma$.

LTYP = 81	SCALE	Gaussian convoluted by an exponential
82	σ	
83	Q_0	
84	$1/\beta$	

A Gaussian $\exp\{-0.5*((Q-Q_0)/\sigma)^2\}/(2\pi)^{0.5}\sigma$ is convoluted with an exponential $\beta\exp\{-\beta Q\}$, where both functions are normalised to unity, to give:

$$I(Q) = I(Q) + \frac{b}{2} \exp\left(\frac{1}{2}(b\mathbf{s})^2 - b(Q - Q_0)\right) \operatorname{erfc}\left(\frac{1}{\sqrt{2}}\left(b\mathbf{s} - \frac{(Q - Q_0)}{s}\right)\right)$$

$$\text{where } \operatorname{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-x^2} dx$$

See J.M.Carpenter, R.A.Robinson, A.D.Taylor & D.J.Picton, Nucl.Instr. & Methods A234(1985)542-551 for use of a pair of these terms to model the fast & slow components of pulsed source diffractions peaks (compare the Ikeda-Carpenter equations above), where Q is then actually of course time.

MODEL 28

Form factors for scattering from a thin interface, which may be used either alone, or in conjunction with Model 29 for a one dimensional para-crystalline stack. (The separation of form factor P(Q) and structure factor S(Q) allows details of interfacial structure to be included. An “all-in-one” approach is included as MODEL 29, LTYP=11 which allows a third, background, phase of different scattering density, but assumes sharp interfaces to the layers.). Some of the models here are mathematically closely related to those used for polymers at large radius interfaces (RKH still to investigate the links here !)

LTYP(1)=1, 21 and 31 have a Lorentz factor to approximately allow for a small Gaussian distribution of surface normals around the Q vector. Following Appendix A of N.T.Skipper, A.K.Soper & J.D.C.McConnell, J.Chem.Phys. 94(1991)5751-5760 we multiply by

$$L_N(Q) = \frac{1}{1 + \frac{1}{2}Q^2(R\mathbf{s})^2}$$

When $R\sigma$ is very large this corresponds to the Q^{-2} Lorentz factor used by Kotlarchyk et.al. following M.Shibayama & T.Hashimoto, Macromols. 19(1986)740-749 as an approximation for randomly oriented stacks. When $R\sigma = 0$ the Q vector is always normal to the surface, i.e. the interface is perfectly flat. In practise the $R\sigma$ term is always significant and the theoretical Q^{-2} behaviour of the form factor for a flat sheet is rarely seen.

LTYP(1)= 1 or 11 (which is now redundant, just set $R\sigma = 0$) has a rectangular profile of mean thickness L, with a Schultz polydispersity characterised by width $\sigma(L)/L$. This is convoluted with a Gaussian $\exp(-z^2/2\sigma^2)$ to allow for interfacial diffuseness $t = (2\pi)^{1/2}\sigma$. See M.Kotlarchyk & S.M.Ritzau, J.Appl.Cryst. 24(1991)753-758 [assumed factor of 4 missing in eqn 17].

NOTE that the scaling constant is as for LTYP=21 below, *but* is multiplied by L^2 where L is the layer thickness in Å.

NOTE that even modest values of t cause the form factor (on a log plot) to fall off rapidly at high Q.

	LTYP(1)= 1	11	21	31
n1	scale' = scale.L ²	as for LTYP=1	scale	scale
2	t interface diffuseness	"	ℓ_1 core thickness	ℓ_1 core thickness
3	L layer thickness	"	$(\rho_2 - \rho_3)/(\rho_1 - \rho_3)$	$(\rho_2 - \rho_3)/(\rho_1 - \rho_3)$
4	$\sigma(L)/L$ layer polydispersity	"	ℓ_2 shell or head group thickness	(1/ κ) exponential decay length for head group.

5	Rσ Lorentz factor	(Ignored)	Rσ	Rσ
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LTYP(1)=21 is a monodisperse symmetrical shell/core/shell layer, where we assume here the core has scattering length density ρ_1 and thickness ℓ_1 , the shell ρ_2 and thickness ℓ_2 , and the solvent ρ_3 . The total layer thickness is $\ell_1 + 2\ell_2$.

We take the $I(Q) = I(Q) + \text{scale} \cdot L_N(Q) \cdot f^2(Q)$ where (M.Kotlarchyk, E.Y.Sheu & M.Capel, Phys.Rev.A46(1992)928-939. checked by RKH) we find:

$$f(Q) = \ell_1 \frac{\sin(Q\ell_1/2)}{Q\ell_1/2} + 2\ell_2 \frac{(\mathbf{r}_2 - \mathbf{r}_3)}{(\mathbf{r}_1 - \mathbf{r}_3)} \cos(Q(\ell_1 + \ell_2)/2) \frac{\sin(Q\ell_2/2)}{Q\ell_2/2}$$

For a *randomly oriented sheet*, as for a *vesicle* of large radius, we compare the scattering from a thin spherical shell of scattering length density ρ_1 and thickness ℓ_1 , of large radius R_{sphere} in a solvent ρ_3 ,

$$I(Q) \rightarrow \frac{8\rho(\mathbf{r}_1 - \mathbf{r}_3)^2 S}{Q^4} \sin^2(Q\ell_1/2)$$

to derive: $\text{scale} = 10^{-32} \pi (\rho_1 - \rho_3)^2 S (R\sigma)^2$. where the scattering length densities are in cm^{-2} , ℓ_1 in $f(Q)$ and $(R\sigma)$ are in \AA , and S is the area of sheet per unit volume of sample in cm^{-1} . [$S = N \cdot 4\pi (R_{\text{sphere}})^2$] NOTE an extra factor of L^2 is needed in the scale for LTYP=1 or 11 (as per table above).

When combined with model 29 below, S is the *total* area of sheet, so for a multilamellar vesicle, the scale factor increases in proportion to the number of layers for a constant number of particles N , or remains roughly constant for a fixed amount of material in the layers. !

(Note - in the limit of large ℓ_1 the \sin^2 term averages to 1/2 and we reach the normal ‘‘Porod’’ limit of

$$I(Q) \rightarrow 2\pi S' (\rho_1 - \rho_3)^2 / Q^4 \quad \text{where} \quad S' = 2S \quad \text{since we count both surfaces of the sheet !}$$

For ‘‘large’’ randomly oriented multi-layer stacks (e.g. starch granules ?) this should still be the correct form of the scale factor (CHECK).

For an *oriented sheet*, where the scattering is in one direction in Q , one compares the scattering from an oriented disk of large radius R_{disk}

$$I(Q) \rightarrow N (\mathbf{r}_1 - \mathbf{r}_3)^2 V^2 \left(\frac{\sin(Q\ell_1/2)}{Q\ell_1/2} \right)^2$$

to obtain: $\text{scale} = 10^{-16} \cdot (\rho_1 - \rho_3)^2 S^2 / N$ where the scattering length densities are in cm^{-1} , N is the ‘‘number of particles per unit volume’’ in cm^{-1} , S is the surface area of sheet per unit volume of sample in cm^{-1} [$S = N \cdot \pi (R_{\text{disk}})^2$] Note that for a truly infinite sheet, $S = N \cdot (1\text{cm})^2 = \phi / (10^{-8} \ell_1 (\text{\AA}))$. This scale factor works seems to work reasonably well in practise, despite the fact that $(R\sigma)$ in $L_N(Q)$ may become quite large, when for an infinite, flat sheet it should be zero.

The ‘‘scale’’ factors given here have been tested numerically by fitting hollow sphere, multi-layer vesicle and oriented disk data generated by other FISH models.

Note that the way the ‘‘shell’’ has been programmed here, to simplify the scale parameter, causes difficulties when $\rho_1 = \rho_3$ and we must use the equivalent equation (RKH has not coded this - yet):

$$f(Q)(\mathbf{r}_1 - \mathbf{r}_3) = (\mathbf{r}_2 - \mathbf{r}_3)(\ell_1 + 2\ell_2) \frac{\sin(Q(\ell_1 + 2\ell_2)/2)}{Q(\ell_1 + 2\ell_2)/2} + (\mathbf{r}_1 - \mathbf{r}_2)\ell_1 \frac{\sin(Q\ell_1/2)}{Q\ell_1/2}$$

LTYP(1)=31 monodisperse shell/core/shell, a rectangular core with exponentially decaying shell, characterised by decay length $(1/\kappa)$ for which RKH has derived (typo in last term corrected 21/10/03):

$$f(Q) = \ell_1 \frac{\sin(Q\ell_1/2)}{Q\ell_1/2} + \frac{2}{\mathbf{k}^2 + Q^2} \frac{(\mathbf{r}_2 - \mathbf{r}_3)}{(\mathbf{r}_1 - \mathbf{r}_3)} (\mathbf{k} \cos(Q\ell_1/2) - Q \sin(Q\ell_1/2))$$

If $x=0$ is at the centre of the core, then the scattering length density is ρ_1 to $x = \ell/2$, and $\rho_2 \exp\{-\kappa(x - \ell/2)\}$ for larger x . Thus it is sensible, but not actually necessary, to have $\rho_2 = \rho_1$.

MODEL 29

One dimensional paracrystalline stack models. Paracrystal models assume a particular type of disorder of lattice planes, in that successive plane spacings are chosen at random from a distribution function (usually Gaussian). Though nearest neighbour relationships may be physically reasonable, longer range correlations may not actually be representative of real structures. The mathematics tends to produce oscillations at small Q , which may be smeared out to some extent by using an instrument resolution function.

LTYP=1 Structure factor $S(Q)$ for a one dimensional para crystal (normally to be used with MODEL 28). See M.Kotlarchyk & S.M.Ritzau, *J.Appl.Cryst.* 24(1991)753-758. NOTE that the $1/Q^2$ Lorentz factor is included in MODEL 28. $I(Q) = I(Q) * S'(Q)$ where $S'(Q)$ is in equations (9)-(12) of the paper referenced.

LTYP = 1 M number of layers in the stack.
 2 D mean distance apart - plane spacing.
 3 $\sigma(D)/D$ Gaussian distribution in plane positions (Hosemann g-factor).
 4 spare (not used, but need to include)

LTYP = 11 or 21 Three phase model of W.Wenig & R.Bramer, *Colloid & Polymer Science*, 256(1978)125-132 using the method and notation of I.H.Hall, E.A.Mahmoud, P.D.Carr & Y.D.Geng, *Colloid & Polymer Science*, 265(1987)383-393. (with some corrections for typographic errors re-checked by RKH, see comments in subroutine PARA3, and thanks to P.Jenkins & T.Waigh for copies of these papers and their routine DALLFIT). The model has separate probability distributions for the layers and for the gaps in the paracrystalline stack. Scattered intensity is then derived in terms of the one dimensional Fourier transforms of the two distributions. Layers and gaps are assumed infinite, parallel, flat sheets with sharp interfaces. The stack may be immersed in a background medium of separate scattering density. When $\rho_3 = \rho_1$ numerical results are almost identical for comparable cases to those of MODEL 28 coupled to MODEL 29, LTYP=1. The LTYP=21 version multiplies by a Lorentz term with Rs as per MODEL 28.

LTYP = 11 or 21 SCALE as per MODEL 28, ignoring the $\Delta\rho^2$ which is included below. NOTE this indirectly includes the effective volume fraction of the "stack" relative to the third "background" phase

 2 M number of layers in the stack. (This is converted to INTEGER if either "top hat" distribution is used below, as the equation then involves (negative number)^M. M will probably then need to be adjusted by trial and error.)

 3 ρ_2 scattering density of layers in stack

 4 Y mean thickness of layers

EITHER 5 $\sigma(Y)$ standard deviation of Gaussian distribution for Y

OR 15 $\delta(Y)$ width of "top hat", rectangular distribution for Y

 6 ρ_1 scattering density of "gaps" in stack

 7 $D = X + Y$ mean d-spacing, where X = mean thickness of gaps.

EITHER 8 $\sigma(X)$ standard deviation of Gaussian distribution for X *OR*

OR 18 $\delta(X)$ width of "top hat", rectangular distribution for X

 9 ρ_3 scattering density of background medium. Set $\rho_3 = \rho_1$ if the background is not different.

NOTE the equations, are not symmetrical, so do not set it to ρ_2 !!

(10 Rs) include ONLY if LTYP =21, multiplies $I(Q)$ by Lorentz term, as for MODEL 28,

 pushes scattering up from Q^{-2} to Q^{-4} at small Q .

MODEL 88

Allows simultaneous fitting of more than one data set. e.g. with different scale factors but the same model. LTYP=n means that following records apply only to the n'th data set in the fit, until the next 88 record (n = 1, 2, or 3; not the workspace number). Use 88 0, i.e. LTYP=0 to return to normal "al sets" usage. This will allow say a different scale factor and background for a simultaneous fit to two or three data sets, whilst sharing other model parameters. In many cases additional constraints will be needed.

MODEL 99

The final scale to stop the calculation, ALWAYS required. The accumulated intensity is multiplied by a final overall scale factor (useful to correct the units) and stored away. NOTE be careful not to have more than one scaling parameter refining at a time !

LTYP=1

SCALE

Calc(Q) = SCALE * [I(Q) + WRK(Q)] where WRK(Q) contains the background
- see MODELS 3 & 4.

CONSTRAINTS BETWEEN PARAMETERS

Parameters in a fit or calculation may be tied together in various ways. The pair of control records needed for each constraint may be read from an LSQFILE or else the same information supplied interactively in the FIT routine by the Cn= command. Simple linear or multiplicative constraints are fully programmed already, other constraint types would need to be added by the user into the FORTRAN routines CONTIE, CONOP and CONDER. Such a case might be for complex geometric constraints within a molecular structure. The normally available cases allow one for example to refine a multi-shell small angle scattering profile where certain shell widths are fixed relative to each other, see the example included at MODEL 10.

NOTE- for a constraint to become operative the partial shift PS(J) for V(J) must be set to -1.0 To turn on a constraint that has been turned off (by n=OFF) use n=TIE. To fix the value of a "tied" parameter, it may only be necessary to fix the parameter(s) to which it is tied.

BEWARE - some of the later constraints NCON >14, may not be coded on all platforms - no error messages are given, so CHECK that the constraints are operating !

The records needed in the LSQFILE are:

(vi) (a) (20I4) NCON decides the type of constraint relationship

J, K, L, M integers decide which parameters are involved.

(b) (8F10.0) A,B,C,D numerical constants

(this record is always expected, even if no constants are required by the constraint)

The types of constraint available are:

NCON=1 $V(J) = A*V(K) + B*V(L) + C$

NCON=2 $V(J) = V(K)*V(L)$

NCON=3 $V(J) = 2.0*V(K)*V(L)$ used for, MODEL 6, $(R2-R1)=2*\lambda*Rmid$
(See example file in Appendix B)

NCON=4 $V(J) = (1.0-V(K))*V(L)$ used for $R1=(1-\lambda)*Rmid$, $\lambda=(R2-R1)/(R1+R2)$

NCON=5 $V(J) = A*V(K)*V(L)**B + C*V(M) + D$

NCON=6 $V(J) = [A + B*V(K)*V(L)**C]**D$

NCON=7 $V(J) = [(A + B*V(K))*V(L) + C*V(M)]**D$

NCON=8 $V(J) = V(K)*(A*V(L) + B) + C*V(M) + D$

NCON=9 $V(J) = A*(B*V(K) + C)**D$

NCON=10 $V(J) = [[A*(V(K) + B*V(L))**C]*V(M)]**D$

NCON=11 $V(J) = A*V(K) + B*V(L) + C*V(M) + D*V(N) + E$

(Earlier versions of FISH had one less term here, but old models are converted automatically on input)

NCON=12 $V(J) = (1.0 - V(K)) * (V(L) - V(M))$

NCON=13 $V(J) = V(K) - V(L) + V(M) * [V(N) - V(K)] + V(O) * [V(L) - V(P)]$

used for scattering length density difference where given relative concentrations of core and/or solvent penetrate a shell, (needs a dummy model 2 parameter for "zero" for only core or solvent case).

NCON=14 Constraint for sheared rods, see model 18. Parameter numbers J, K, L, M are respectively for Γ , rod radius R, shear gradient G (in sec^{-1}) and η/T = viscosity/temperature (for which Penfold et.al. use 3×10^{-5} for D_2O). G and η/T should be given as model 2 parameters, so for example an "effective viscosity" η/T may be refined within some physically reasonable limits. Rod length L and shell thickness DR are assumed to be $V(K+1)$ and $V(K+2)$. The constraint sets $\Gamma = G/D_r$, where rotational diffusion constant D_r is approximated by $D_r = 3k_B(s-t)/(8\pi\eta/T)L^3$ in which $s = \log_e(L/R)$ and $t = 1.57 - 7.0*(0.28 - 1/s)^2$. The approximation is only good for large values of L/R, when $s > 2$. For numerical stability FISH keeps $s \geq 2$ at all times.

NCON=15 Constrain parameter J = shell thickness δ , for core/shell ellipse MODEL 24, by solving a cubic equation for δ . Parameters K & L are $y = (\text{Volume of "dry" shell/ volume of core})$ & $f = \text{fraction of solvent in shell}$. (Note this also uses parameters (J-1) and (J-2) for axial ratio X and inner radius.) Usually you will also need constraint 16.

NCON=16 Constrain parameter J = contrast term, for core/shell ellipse, MODEL 24

Parameters K, L, M, N, O are respectively $y = (\text{Volume of "dry" shell/ volume of core})$; $f = \text{fraction of solvent in shell}$; scattering length densities of core; dry shell; and solvent. (also uses (J-2) and (J-3) for axial ratio X and inner radius.). Values of V_{core} , V_{total} and ρ_2 are stored in CON(9), CON(10) and CON(11). See also NCON=21. BEWARE do not let shell disappear, as "contrast" becomes infinite giving divide by zero !

NCON=17 Constrain parameter J = new scale factor for further data sets of core/shell ellipse or core/shell rod, MODELS 24 or 18. Parameters K, L, M, N,O,P are respectively: first scale factor; $f = \text{fraction of solvent in shell}$; scattering length densities of first shell, first solvent, new shell, new solvent.

NCON=18 Constrain parameter J = contrast for core/shell rod, MODEL 18, with solvent in shell.

Parameters K, L, M, N, are respectively: $f = \text{fraction of solvent in shell}$; scattering length densities of core; dry shell; and solvent. In this case divide by zeroes are tested and trapped.

NCON=19 $V(J) = A * V(K) + B * V(L) + C * V(M) + D * V(N) + E * V(O) + F * V(P)$

NCON=20 "Hedgehog " constraint for contrast steps in a stretched out "polymer" shell (R.K.Heenan 22/7/98).

If the shell is composed of cylindrical spines normal to the core surface then the scattering length density as a function of particle radius R falls off from the core/shell boundary as $1/R^2$. More generally if we propose a $1/R^h$ fall off then h may vary continuously from $h = -2$, the Hedgehog case, to a uniform shell $h = 0$. (Note $h > 0$ is meaningless !) If the profile is approximated by a series of n linear sections (using MODEL 10, LTYP=11) then the contrast steps go as: $(\rho_i - \rho_j) = (\rho_1 - \rho_n)(R_i^h - R_j^h)R_1^{-h}$

In the constraint J,K,L,M,N & O are respectively for $(\rho_i - \rho_j)$, R_1 , R_i , R_j , $\Delta\rho = (\rho_1 - \rho_n)$, and h . To finish the series R_j for the last *vertical* step (which may be large) R_j must point to a zero (usually an extra MODEL 2 line) and then we set $1/\text{zero}$ to zero. Note that these constraints must come *after* the ones defining the set of radii R_i to be used. It is up to the user to keep the value of h in a valid range! (Bugs in derivatives fixed Nov 2005.)

NCON=21 Same as NCON=16, contrast for core/shell ellipse, but ignores V(K), allowing a free choice of shell thickness.

NCON=22 $V(J) = A * V(K) / (B + C * V(L))$ [used in double constraint for co-surfactant in shell]

NCON=23 Part of multiple constraints for oil & drug partitioning between core & shell of microemulsion, needs 8 parameters & 4 constants (consult RKH).

NCON=24 For core/shell/shell with polydisperse outer radius R3 & multiplicative constraints for R1 & R2. Finds $R1/R3 = V(J)$ and $R2/R3 = V(K)$ for uniform, fuzzy & exponential shells (model 10 1 or 10 11 or 10 21 or 10 31) given $V(\text{dry shell})/V_{\text{core}}$, X1 solvent fraction at R1, X2 solvent fraction at R2 and Y1 = fraction of shell (e.g. polymer) in first shell (params L,M,N,O respectively) given V(P) is R1, V(P+2) is R2 and V(P+4) is R3. (uses iterative method after solving exactly for two uniform shells - consult RKH if in doubt or fails to work, added 8/2/2002, small bug fixed 29/10/02).

NCON=25 $V(J) = \{V(K) - V(L)\} * V(M) + \{V(N) - V(O)\} * V(P) + \{V(Q) - V(R)\} * V(S)$

METHOD- the least squares procedure requires the derivative of each calculated data point with respect to each refining parameter. If a particular parameter is constrained to others, then the derivatives for those others need to be modified by routine CONDER which does:

$$\partial I(Q) / \partial V(i) = \partial I(Q) / \partial V(i) + [\partial V(J) / \partial V(i)] * [\partial I(Q) / \partial V(J)] \quad \text{for } i = K, L, M \dots$$

See Appendix E for further details. Note if you are careful, constraints may be nested, the derivative modifications are done in reverse order to allow for this.

MAKING CHANGES TO THE PROGRAM

Addition of new models requires changing routines DERIV and CALCQ in FISHMODEL.FOR and routine DELSET in FISH4. To understand how they work first study routine CALCQ which calculates I(Q) for a given Q. Routine DERIV is more complex in that it calculates both I(Q) and its derivatives with respect to refining parameters $dI(Q)/dV(J)$. Wherever possible analytic expressions for derivatives are used, if this is not suitable then routine DELSET chooses the size of shifts for numerical calculation of the derivatives. Options 31 and 32 in the FIT menu provide a useful route to help debug a new model or to test the calculation of derivatives. For complex models it is advisable to write a separate program to generate some test data. Graphics control is again long-winded but calls to local graphics routines are made ONLY by the routines LOCDEV, LOCAXIS, LOCGRAPH and LOCLIN. These may easily be rewritten to suit a particular computer system.

Fortran CHARACTER variables are so far only used in a few places for filenames.

The program is split into a number of files at present, on some computers a library structure might be more appropriate.

FISH1.FOR contains the main control routine, input of DATAFILE and simple processing of sets - QBIN, CENTRE, ARITH etc. Has the SET routine which opens/closes data files and BLOCK DATA section.

FISH2 contains graphics routines that call ONLY the routines in FISHGRAPH.

FISHGRAPH has locally specific graphics routines. At RAL these now use UNIRAS, including a routine to write an abbreviated parameter table alongside a plot which may then be sent to a laser printer file.

FISH3 has a second plot routine, for the least squares, plus some odds and ends.

FISH4 file has the entire least squares fitting procedure with its FIT menu and interactive control routine TALK, also the constraints routines and derivative set up routine DELSET.

FISHMODEL has the calculation routines DERIV and CALCQ containing the models.

FISHSMEAR tackles smearing to allow for instrument resolution, MODEL 15.

FISH5 contains only routines concerned with polydisperse small angle scattering including quadrature routines for numerical integration.

FISH6 has routines peculiar to UEA & FRI Norwich for Vonk desmearing and some colloid calculations, it is not required by other people.

FISH7 has the Hayter-Penfold and other charged particle structure factor routines.

NOTE not all occurrences of a particular common block are identical, a list of parameters in one routine will frequently become an array in another routine, nor are they all the same lengths.

Three "text" files are also required their location being determined in FISHPREF.TXT. These files both define the commands used and contain the on-line HELP comments.

FISH_COMMANDS_MAIN.TXT text file to define command language for main program

FISH_COMMANDS_PLOT.TXT " " " " " " " " FISH2 plotting

FISH_HELP_FIT.TXT help file for FIT routine commands in FISH4, the actual commands are defined by BLOCK DATA section. in FISH1, and are difficult to add to or alter !

Since FISH2 of Oct 1999 all dependence on external mathematical libraries such as NAG, for either mathematical functions or numerical integration has been removed. For detailed acknowledgements of the routines adopted or adapted for FISH see the Fortran source code.

PLANNED CHANGES, KNOWN BUGS

If RANGE is used to reduce the number of points being fitted the plot routines sometimes do not compensate properly and plot data previously stored in the excluded part of the array - please report any instance of this !

July 96 - Note that FISH's calculation of $\beta(Q)$ to correct $S(Q)$ is rather limited in its applicability, see notes on page 10.

Summer 97 - In some cases SMEARING does not work when refining - the shifts seem wrong, could be numerical integration problems at high Q ????. Needs test for other models.

LOQ & FISH DATAFILE DEFINITION

Each data set in FISH has arrays Q, C and E for ordinate, abscissa and error respectively. The READ3 and READ2 commands will read more general data, one set per file. The LOQ & FISH file data format described below allows many sets of data per file. The READ command in the main control section will read them sequentially, asking whether to skip or not until the correct one is found. The file may also be rewound. The file description was written with cards in mind (are you old enough to know about these?) so is tightly formatted. However **the main data format is actually read in**, as a Fortran format as so almost any sensible ASCII character file from some other source can be read by the addition of five header records, skipping original header/footer lines as necessary.

Record Format Contents

(a) (20A4) Title (include a date !)

(b) (20A4) second title

(c) (6I5) NCH number of channels (data) (max 512)

NC1 Number of first good data point

NC2 last good point before beam stop

NMC centre TIMES TEN (so accurate to 0.1 channel)

NC3 first good point after beam stop

NC4 last good point after beam stop

NOTE - for normal, ascending Q only use NC1=NC2=NMC=0

NOTE - NCH does not have to equal NC4, "poor" data from the ends of the range may be carried around indefinitely, left in or out as desired by altering the NC's

(d) (4I10) NSUM if ≤ 0 total sum over NC1-NC2 plus NC3-NC4 stored here

which if this is $> 10^{**8}$, then is divided by 10^{**6} .

(IC(I),I=1,3) monitor counts

(You can use these four numbers for anything you like, they were originally used for Daresbury X-ray data monitor counters.)

(e)(I2,1X,19A4) IFLAG =1 only C(i=1,NCH) data array to be read

=2 only (Q(i),C(i), i=1,NCH) coordinate and data arrays to be read

=3 (Q(i),C(i),E(i), i=1,NCH) coordinate, data and error arrays to be read

(FMT(I),I=1,19) character string containing data format

This record might be: 3 (2(F12.7,2E17.5))

(f) (FMT)- using fortran format as read at (e) Actual data.

PS(i) "partial shift" this is

0.0 if parameter is fixed

>0.0 if parameter is refining, calculated shifts are multiplied by this value
- helps convergence in poorly conditioned cases.

-1.0 if parameter is constrained or tied.

-2.0 for the polydisperse radius in a complex contrast, see MODEL 10.

(v) NS records are skipped on input, have details of data sets on output

(vi) NC constraint records - see section above on CONSTRAINTS.

(vii) (8E10.3) (CON(I),I=1,NN) NN numerical constants:

CON(1) for MARQUARDT fit lambda, λ parameter .

CON(2) & CON(3) used by MODEL 5 for V_0 and $\sigma_T/rbar$.

CON(4) & CON(5) used by MODEL 6 for Δr in Simpson rule integration and as an upper limit for particle radius, r_{max} NOTE remember to set these if using MODEL 6 polydispersity !

CON(6) & CON(7) used by models 5 & 6 for calculated entropy and estimator B - see MODEL 5.

APPENDIX A - AN EXAMPLE DATA FILE

The file below was written out by COLETTE ready for input to FISH, it has been reduced to 6 data points, the third record has been edited by the user so that only points 2-4 are to be used in FISH. The 3 in the fifth record shows that Q, I(Q) & error(Q) are expected, using the format shown.

```

LOQ Wed 18-MAY-1988 15:21 SAMPLE: 714 EMPTY CAN: 749
lambda 2.20 10.00 Phi -90. > 90. deg Radii 35.0 335.
      0 6 0 0 0 2 4
      0 0 0 0
3 (F12.5,2E16.6)
      0.00562 1.664269E+01 1.182694E-01
      0.00607 1.018861E+01 6.170455E-01
      0.00655 4.091472E+00 3.789476E-01
      0.00707 4.746222E+00 4.646616E-01
      0.00865 6.092464E+00 2.959473E-01
      0.00947 8.743887E+00 2.343611E-01

```

APPENDIX B - AN EXAMPLE MODEL FILE - LSINP.DAT

This example file contains three separate models: (i) a single spherical particle plus background, note that only the constant term in the cubic background is being used to give a flat background addition.

(ii) polydisperse spheres with $R^{-1.5}$ size distribution defined by Rmid= 60 and width lambda =0.5. The lambda and R-MID parameters 5 & 6 do not do anything directly so are MODEL 2; they are related to R1 and R2 via the two constraints. Again a flat background is included.

(iii) similar polydisperse spheres interacting via a hard spheres structure factor. The hard sphere radius and volume fraction have partial shifts of 0.4 in order to damp their changes. Instrument resolution smearing is also added. The label field is entirely optional, the calculation is controlled by the MODEL and LTYP numbers in the second and third columns.

As a reminder the main columns are (note the running count number is ignored on input):

Running count	Model number	LTYP(i)	Label	Parameter Value V()	ESD	Partial shift	Calc shift
i						On/Off	
I3	I3	I3	A12	E14.6	E13.3	F6.1	E10.2
T 1 P	6 S	0 C	0 N	0			
W 1 K	0 IP	1 MS	1 IY	1 Q	7 R	7	6 1
SINGLE SPHERE PLUS BKG							
1 1	1 C1			1.842795E-04	5.014E-06	1.0	4.96E-08
2 1	2 R1			1.000000E 02	0.000E+00	1.0	0.00E+00
3 3	1 BKG	A		9.848869E-02	1.601E-02	1.0	2.20E-05
4 3	2	B*Q		0.000000E+00	0.000E+00	0.0	0.00E+00
5 3	3	C*Q**2		0.000000E+00	0.000E+00	0.0	0.00E+00
6 99	1	SCALE		1.000000E+00	0.000E+00	0.0	0.00E+00
T 1 P	10 S	1 C	2 N	5			
W 1 K	0 IP	1 MS	1 IY	1 Q	7 R	7	6 1

```

POLY DISP SPHERES PLUS BKG      CONSTRAINED TO FIT RM AND LAM
1  6 81 R**N VOL      1.842795E-04    5.014E-06    1.0  4.96E-08
2  6  2 R2-R1      7.326303E+01    0.000E+00   -1.0  0.00E+00
3  6  3 R1      2.997124E+01    0.000E+00   -1.0  0.00E+00
4  6  4 N      -1.500000E+00    0.000E+00    0.0  0.00E+00
5  2  1 LAMBDA      5.000000E-01    0.000E+00    0.0  0.00E+00
6  2  2   R-MID      6.000000E+01    4.136E-01    1.0  2.46E-03
7  3  1 BKG A      9.848869E-02    1.601E-02    1.0  2.20E-05
8  3  2   B*Q      0.000000E+00    0.000E+00    0.0  0.00E+00
9  3  3   C*Q**2      0.000000E+00    0.000E+00    0.0  0.00E+00
10 99 1   SCALE      1.000000E+00    0.000E+00    0.0  0.00E+00
   1  1 2114.SUB      CALC 2 BKG 3 POL 4   SSE= 3.898E+01
   3  2  5  6  0
   0.00000  0.00000  0.00000  0.00000
   4  3  5  6  0
   0.00000  0.00000  0.00000  0.00000
1.000E-01 1.843E-04 3.112E-01 2.000E+00 1.032E+02
T  1 P 14 S  1 C  2 N  5
W  1 K  0 IP 1 MS 1 IY 1 Q  7 R  7  6  1
(POLY DISP SPHERES)*HSS(Q)      CONSTRAINED TO FIT RM AND LAM
1  6 81 R**N VOL      1.842795E-04    5.014E-06    1.0  4.96E-08
2  6  2 R2-R1      7.326303E+01    0.000E+00   -1.0  0.00E+00
3  6  3 R1      2.997124E+01    0.000E+00   -1.0  0.00E+00
4  6  4 N      -1.500000E+00    0.000E+00    0.0  0.00E+00
5  2  1 LAMBDA      5.500000E-01    0.000E+00    0.0  0.00E+00
6  2  2   R-MID      6.660275E+01    4.136E-01    1.0  2.46E-03
7 22  1 HS S(Q) VOL      1.854555E-01    1.444E-02    0.4 -4.55E-05
8 22  2 SPH RADIUS      1.351837E+02    2.197E+00    0.4  2.26E-01
9  3  1 BKG A      9.848869E-02    1.601E-02    1.0  2.20E-05
10  3  2   B*Q      0.000000E+00    0.000E+00    0.0  0.00E+00
11  3  3   C*Q**2      0.000000E+00    0.000E+00    0.0  0.00E+00
12 15  1 SMEAR      1.000000E+00    0.000E+00    0.0  0.00E+00
13 15  2 NSIMP      2.100000E+01    0.000E+00    0.0  0.00E+00
14 99 1   SCALE      1.000000E+00    0.000E+00    0.0  0.00E+00
   1  1 2114.SUB      CALC 2 BKG 3 POL 4   SSE= 3.898E+01
   3  2  5  6  0
   0.00000  0.00000  0.00000  0.00000
   4  3  5  6  0
   0.00000  0.00000  0.00000  0.00000
1.000E-01 1.843E-04 3.112E-01 2.000E+00 1.032E+02

```

APPENDIX C - SPECIAL MODELS FOR 2-SHELL ELLIPSOID

MODEL 24 with **LTYPE(1)=21** or **31** are for swollen micellar systems with either constant ratios of inner and outer radii or constant outer shell thickness respectively. The standard model is entirely reparametrised using most of the numerical constant **CON()** array to store physical parameters. [Note this precludes the use of polydisperse spheres or other models using the **CON()** array, though the **CON()** here could easily be moved if required.]

The model assumes a surfactant micelle in water where the surfactant has a hydrocarbon tail. The head group/water interface may be "staggered", thereby including some of the surfactant tails in the "head group" region. This is controlled by **ALF**. One terminal **CH₃** group is always assumed to be in the core (compare **CON(2&3)** with **CON(15&16)**. Oil may be added to the core region via **CON(22-24)**.

LTYP=21 or 31 SCALE
 2 AGG aggregation number, number of surfactant molecules per micelle
 3 X axial ratio (if LTYP(1)=21) is not used if LTYP(1)=31 when shell thickness δ is
 calculated
 in CON(19) [Check this, I'm not sure !]

4 Charge

5 ALF fraction of CH₂ chain groups in core (α)

SCALE = $(\rho_2 - \rho_3)^2 v_T^2 N$ where number density of micelles $N = [\text{conc-cmc}] N_A / (\text{agg. no.})$
 and SCALE has units of cm^{-1} . The fitted value of this parameter should agree with the
 expected value in CON(17), if all the conversions to absolute units are correct !

This model makes extensive use of the numerical constants array, so it may be incompatible
 with some other models.

CON(1)=N1 Marquardt lambda, as usual
 2 CH₃ volume, \AA^3
 3 Σ bi CH₃, in units of 10^{-12}cm
 4 head group volume, \AA^3
 5 Σ bi headgroup, scattering length in units of 10^{-12}cm
 6 hydration number headgroup
 7 counterion volume, \AA^3
 8 Σ bi counterion, in units of 10^{-12}cm
 9 counterion hydration number
 10 solvent volume, \AA^3
 11 Σ bi solvent, in units of 10^{-12}cm
 12 scattering length density of solvent, $\rho_3, \text{\AA}^{-2}$
 13 [conc-cmc] surfactant, mol/litre
 14 NA, Avogadro's number. $10^{-19} = 6.0235 \times 10^4$
 15 $(\text{CH}_2)_{m-1}$ volume, \AA^3
 16 Σ bi " in units of 10^{-12}cm

17 expected scale in cm^{-1} 17-21 are calculated by the program
 18 R1, \AA
 19 R2 or δ
 20 $\rho_1, \text{\AA}^{-2}$

21 ρ_2

22 [oil], concentration of solubilised oil, mol/litre,
 note N_{oil} per micelle = aggregation number.[oil]/[conc-cmc]

23 oil volume, \AA^3

24 Σ bi oil, cm

These parameters are used by routine AGGRE to calculate the normal parameters to pass to the routines for two-shell ellipsoids ELLSH1 and ELLSH2.

Guides to use: ALWAYS check CON(17)-CON(21) to see if their values are reasonable.

CON(17) should agree (say within 20%) with the refining SCALE parameter, assuming the absolute units are correct.

CON(18), R1 or R1.X, should be less than the fully stretched tail, unless extra oil is present.

The calculation proceeds by calculating the volume of the inner core:

$$V_1 = (V_{CH3} + ALF.V_{CH2(m-1)}).AGG$$

Inner radius $R_1 = (3V_1/4\pi X)^{1/3}$

Total volume of a micelle $V_T = [V_{chain} + V_{head\ group} + V_{ion} +$

$V_{solvent} \cdot (\text{hydration number of head group} + \text{hydration number of ion})].AGG -$

$(V_{ion} + V_{solvent} \cdot (\text{hydration number ion})).CHARGE$

The value of R2 (LTYP(1)=21) is given by $V_T = (4\pi/3)R_2^3 X$

Shell thickness δ (LTYP(1)=31) is given by $V_T = (4\pi/3)(R_1 + \delta)^2(R_1 X + \delta)$ so δ is the only positive solution of:

$$\delta^3 + R(X+2)\delta^2 + R^2(2X+1)\delta - 3(V_T - V_1)/4\pi = 0$$

Knowing V_1 and V_2 and the scattering lengths the program calculates ρ_1 and ρ_2 and the coefficient of $j_1(u_1)/u_1$. Adding oil makes the above equations a little more complicated.

APPENDIX D - AN EXAMPLE INTERACTIVE SESSION

Input typed by the user is underlined, text in [square brackets] are explanatory comments added later.

\$@runfish

Welcome to the FISH data analysis program, enter HELP
 after Command> if you are lost.

 please type commands using only UPPER CASE

Command> READ 2658.Q

 [start sequential reading of data file]

DATA INPUT ROUTINE, READS FROM FORTRAN STREAM NO. 1

UP TO 9 SETS ("WORKSPACES") MAY BE USED

ENTER 0 (RETURN) TO IGNORE, OVERWRITES PREVIOUS SET OF SAME NO.

91 TO REWIND, 99 TO STOP, 95 TO SEARCH

LOQ Mon 22-MAY-1989 16:42SAMPLE: 2658 EMPTY CAN: 2646

Lambda 2.00 10.00 Phi -90. > 90. deg Radii 35.0 335.0

SAVE AS SET NO. = ? 1

[lets keep this data as set number 1]

ENTER LOCAL LABEL FOR THIS SET (A11)= 2658

3 (F12.5,2E16.6)

LOQ Mon 22-MAY-1989 16:42SAMPLE: 2658 EMPTY CAN: 2646

Lambda 2.00 10.00 Phi -90. > 90. deg Radii 35.0 335.0

SAVE AS SET NO. = ? 99 [get out of the input loop]

[lets try to fit the data ...]

Command> FIT

1-READ MODEL FILE 4-CALC ONLY, CHOOSE Q

2-CHOOSE OBS,CALC SETS ETC. 5-INDEX

3-ENTER FIT ROUTINE 6-RETURN TO MAIN ROUTINE

1

[start to read model file LSINP.DAT]

LSQIN READS MODEL DESCRIPTION FILE FROM FORTRAN STREAM 3

ENTER 0-TO IGNORE, 1-USE THIS MODEL, 9-REWIND

Gaussian coil [prints first 4 record of each model in file]

for polymers

1 14 1 Const 3.500000E+02 0.000E+00 0.4 0.00E+00

2 14 2 Rg 7.500000E+01 0.000E+00 0.4 0.00E+00

3 3 1 BKG A 5.000000E+00 0.000E+00 0.4 0.00E+00

4 3 2 B*Q 0.000000E+00 0.000E+00 0.0 0.00E+00

USE= [pressed return to enter zero, and read next model]

SINGLE SPHERE PLUS BKG

1 1 1 C1 1.842795E-04 5.014E-06 1.0 0.00E+00

2 1 2 R1 1.000000E+02 0.000E+00 1.0 0.00E+00

3 3 1 BKG A 9.848869E-02 1.601E-02 1.0 0.00E+00

4 3 2 B*Q 0.000000E+00 0.000E+00 0.0 0.00E+00

USE=0

POLY DISP SPHERES PLUS BKG CONSTRAINED TO FIT RM AND LAM

1 6 81 R**N VOL 1.842795E-04 5.014E-06 1.0 0.00E+00

2 6 2 R2-R1 7.326303E+01 0.000E+00 -1.0 0.00E+00

3 6 3 R1 2.997124E+01 0.000E+00 -1.0 0.00E+00

4 6 4 N -1.500000E+00 0.000E+00 0.0 0.00E+00

USE=1 [use this model and get out of input loop]

1-READ MODEL FILE 4-CALC ONLY, CHOOSE Q

2-CHOOSE OBS,CALC SETS ETC. 5-INDEX

3-ENTER FIT ROUTINE 6-RETURN TO MAIN ROUTINE

2

[now proceed around the main fit menu]

NO. OF SETS OF DATA TO FIT (MAX 3, (I1)) = 1

ENTER DATA SET numbers for:

OBS observations i.e. data to be fitted.

CALC for results of model calculation.

BKG if you are about to use experimental

subtraction, model 4, (WORK is ALSO

required !)

POLY is needed for polydispersity e.g. for

model 6

WORK is for polynomial background, model 3,
and/or observed background model 4, which
are not smeared so are kept separate.
UNSMEARED optional to save unsmeared when
smearing.
P(Q) optional to save form factor separately.
S(Q) optional to save structure factor
separately.
BETA(Q) optional beta ratio for polydisperse.
DEBUG(Q) optional for anything else !
Enter zeroes (spaces) for sets not required.

OBS, CALC, BKGD, POLY, WORK, UMSMEARED, P(Q), S(Q), BETA(Q), BUG(Q)
ENTER SET NUMBERS FOR EACH (10I1)
1203456780 [decides which data set to fit and where to store the output]

```
REFINING  1 SETS  OBS CAL BKG PLY WRK USM  PQ  SQ BET  DBG
          2658          1  2  0  3  4  5  6  7  8  0
1-READ MODEL FILE              4-CALC ONLY, CHOOSE Q
2-CHOOSE OBS,CALC SETS ETC.    5-INDEX
3-ENTER FIT ROUTINE           6-RETURN TO MAIN ROUTINE
```

3
FITTING/CALCULATION ROUTINE, TYPE PP TO SEE THE MODEL,
RUN TO CALCULATE, HELP FOR A LIST OF COMMANDS

>

PP [look at whole model]

```
T  1 P 10 S  1 C  2 N  5
W  1 K  0 IP 1 MS 1 IY 1 Q -6 R -6 -11 -11  1  0  2  0  0
0  0
```

```
POLY DISP SPHERES PLUS BKG  CONSTRAINED TO FIT RM AND LAM
1  6 81 R**N VOL      1.842795E-04  5.014E-06  1.0  0.00E+00
2  6  2 R2-R1        7.326303E+01  0.000E+00 -1.0  0.00E+00
3  6  3 R1           2.997124E+01  0.000E+00 -1.0  0.00E+00
4  6  4 N            -1.500000E+00  0.000E+00  0.0  0.00E+00
5  2  1 LAMBDA       5.000000E-01  0.000E+00  0.0  0.00E+00
6  2  2 R-MID        6.000000E+01  4.136E-01  1.0  0.00E+00
7  3  1 BKG A        9.848869E-02  1.601E-02  1.0  0.00E+00
8  3  2 B*Q          0.000000E+00  0.000E+00  0.0  0.00E+00
9  3  3 C*Q**2       0.000000E+00  0.000E+00  0.0  0.00E+00
10 99 1 SCALE        1.000000E+00  0.000E+00  0.0  0.00E+00
```

```
1  1 2658          CALC 2 BKG 0 POL 3  SSE= 0.000E+00
```

```
CONSTRAINT  1 TYPE  3 USE= 1
```

```
V(  2 ) = 2.0* V(  5 ) * V(  6 )  R2-R1=2*L *RM
```

```
CONSTRAINT  2 TYPE  4 USE= 1
```

```
V(  3 ) = (1.0- V(  5 ) ) * V(  6 )  R1=(1-L)*RM
```

```
1.000E-01 1.843E-04 3.112E-01 2.000E+00 1.032E+02
```

>R [R for RUN to start fitting, FISH first asks for
integration scheme numbers, we enter -11 to test]

```
INTEGRATION SCHEME FOR I(Q) K6 =  (*)
```

```
( 0-7, -VE TO LIST WEIGHTS, -11 TO TEST ALL, SET K6<0 TO GET HERE )
```

-11

TEST AT Q= ? (*)

.1

	Method	F**2(Q)	F(Q)	SUMX
0	SIMPSON	2.284441E+13	-8.243047E+07	1.210804E+04
1	GAUSS 4	1.850529E+13	-8.009058E+07	1.210425E+04
2	GAUSS 10	2.285260E+13	-8.242504E+07	1.210481E+04
3	RT+LN 10	2.285226E+13	-8.242519E+07	1.210481E+04
4	GEN 10	2.279486E+13	-8.242452E+07	1.210480E+04
5	GAUSS 16	2.285261E+13	-8.242503E+07	1.210481E+04
6	GAUSS 32	2.285261E+13	-8.242500E+07	1.210481E+04
7	GAUSS 64	2.285261E+13	-8.242500E+07	1.210481E+04

INTEGRATION SCHEME FOR I(Q) K6 = (*)

(0-7, -VE TO LIST WEIGHTS, -11 TO TEST ALL, SET K6<0 TO GET HERE)

7

INTEGRATION SCHEME FOR MOMENTS OF P(R), K7= (*)

-11

	Method	V=	SIG*2=	1.7402E+02	RBAR=	4.7706E+01
0	SIMPSON	6.8530E+09				
		ENT=	3.8283E+00			
1	GAUSS 4	6.8504E+09		1.7389E+02	4.7704E+01	
		ENT=	1.0824E+00			
2	GAUSS 10	6.8529E+09		1.7402E+02	4.7706E+01	
		ENT=	1.9536E+00			
3	RT+LN 10	6.8529E+09		1.7402E+02	4.7706E+01	
		ENT=	1.7930E+00			
4	GEN 10	6.8529E+09		1.7402E+02	4.7706E+01	
		ENT=	1.5818E+00			
5	GAUSS 16	6.8529E+09		1.7402E+02	4.7706E+01	
		ENT=	2.4080E+00			
6	GAUSS 32	6.8529E+09		1.7402E+02	4.7706E+01	
		ENT=	3.0869E+00			
7	GAUSS 64	6.8529E+09		1.7402E+02	4.7706E+01	
		ENT=	3.7725E+00			

INTEGRATION SCHEME FOR MOMENTS OF P(R), K7= (*)

7

[now it continues with proper calc]

POLYDISPERSE R= 3.00E+01 TO 9.00E+01 N= 1 TO 31

DR=N(4)= 2.00E+00 RMAX=N(5)= 9.00E+01

PMIN= 3.803E-14 PMAX= 1.250E-11 ENT= 3.773E+00 B=N(7)= 0.000E+00

VNORM= 1.84280E-04 SIG(R)/RB= 2.7652E-01 SIG**2= 1.7402E+02

RBAR= 4.7706E+01 AREA P(R)= 3.2551E-10

WEIGHT FUNCTION TYPE (K1=) 1, IF K1=1, WTS = 1/SIGMA**2 , OTHERWISE

UNIT

WTS

CYC 1 49 DATA+ 0 PRED, 3 PAR SWSE= 9.256E+03 XDWE= 9.171E+03 VAR=

1.928E+02

>1 6

[look at first 6 parameters]

1	6	81	R**N VOL	1.842795E-04	1.789E-04	1.0	-8.65E-05
2	6	2	R2-R1	6.000000E+01	0.000E+00	-1.0	0.00E+00
3	6	3	R1	3.000000E+01	0.000E+00	-1.0	0.00E+00
4	6	4	N	-1.500000E+00	0.000E+00	0.0	0.00E+00
5	2	1	LAMBDA	5.000000E-01	0.000E+00	0.0	0.00E+00
6	2	2	R-MID	6.000000E+01	1.238E+01	1.0	2.57E+01

>R

[run another cycle]

POLYDISPERSE R= 4.28E+01 TO 1.28E+02 N= 1 TO 43
 DR=N(4)= 2.00E+00 RMAX=N(5)= 1.28E+02
 PMIN= 7.315E-15 PMAX= 1.656E-12 ENT= 3.765E+00 B=N(7)= 0.000E+00
 VNORM= 9.77584E-05 SIG(R)/RB= 2.7495E-01 SIG**2= 3.4823E+02
 RBAR= 6.7872E+01 AREA P(R)= 6.0102E-11
 CYC 2 49 DATA+ 0 PRED, 3 PAR SWSE= 1.068E+04 XDWE= 1.060E+04 VAR=
 2.226E+02 [fit even worse]

>P

1	6	81	R**N VOL	9.775841E-05	2.330E-04	1.0	9.46E-04
2	6	2	R2-R1	8.566107E+01	0.000E+00	-1.0	0.00E+00
3	6	3	R1	4.283054E+01	0.000E+00	-1.0	0.00E+00
4	6	4	N	-1.500000E+00	0.000E+00	0.0	0.00E+00
5	2	1	LAMBDA	5.000000E-01	0.000E+00	0.0	0.00E+00
6	2	2	R-MID	8.566107E+01	3.213E+01	1.0	-8.31E+01
7	3	1	BKG A	1.364664E+00	6.109E-01	1.0	4.34E-02
8	3	2	B*Q	0.000000E+00	0.000E+00	0.0	0.00E+00
9	3	3	C*Q**2	0.000000E+00	0.000E+00	0.0	0.00E+00
10	99	1	SCALE	1.000000E+00	0.000E+00	0.0	0.00E+00

> 6=F=0.4 [damp down shifts on V6 and V1 as they are moving too much]

6	2	2	R-MID	8.566107E+01	3.213E+01	0.4	-8.31E+01
---	---	---	-------	--------------	-----------	-----	-----------

> 1=N=0.4

1	6	81	R**N VOL	9.775841E-05	2.330E-04	0.4	9.46E-04
---	---	----	----------	--------------	-----------	-----	----------

>R

POLYDISPERSE R= 2.62E+01 TO 7.86E+01 N= 1 TO 27
 DR=N(4)= 2.00E+00 RMAX=N(5)= 7.86E+01
 PMIN= 2.675E-13 PMAX= 5.451E-11 ENT= 3.776E+00 B=N(7)= 0.000E+00
 VNORM= 4.75972E-04 SIG(R)/RB= 2.7726E-01 SIG**2= 1.3389E+02
 RBAR= 4.1735E+01 AREA P(R)= 1.2544E-09
 CYC 3 49 DATA+ 0 PRED, 3 PAR SWSE= 3.971E+03 XDWE= 3.355E+03 VAR=
 8.273E+01

>1 7

1	6	81	R**N VOL	4.759722E-04	1.121E-04	0.4	-5.99E-04
2	6	2	R2-R1	5.240216E+01	0.000E+00	-1.0	0.00E+00
3	6	3	R1	2.620108E+01	0.000E+00	-1.0	0.00E+00
4	6	4	N	-1.500000E+00	0.000E+00	0.0	0.00E+00
5	2	1	LAMBDA	5.000000E-01	0.000E+00	0.0	0.00E+00
6	2	2	R-MID	5.240216E+01	2.821E+00	0.4	1.28E+01
7	3	1	BKG A	1.408045E+00	3.879E-01	1.0	3.27E-02

>R

POLYDISPERSE R= 2.88E+01 TO 8.63E+01 N= 1 TO 29
 DR=N(4)= 2.00E+00 RMAX=N(5)= 8.63E+01
 PMIN= 1.426E-13 PMAX= 1.888E-11 ENT= 3.774E+00 B=N(7)= 0.000E+00
 VNORM= 2.36320E-04 SIG(R)/RB= 2.7674E-01 SIG**2= 1.6032E+02
 RBAR= 4.5753E+01 AREA P(R)= 4.7304E-10
 CYC 4 49 DATA+ 0 PRED, 3 PAR SWSE= 3.888E+03 XDWE= 3.723E+03 VAR=
 8.099E+01

> PLOT

[still getting nowhere, do a plot to see fit]

PLOT CONTROLS IDEV= 0-EXIT, 1-screen, 2-file
 error bars are IEB*sigma (ONLY USE ON LINEAR PLOT)

IPW=1 adds scaled wts

IDEL spreads graphs apart (IDEL=2 is default)

IDEV,IEB,IPW,IDEL = (5I1)

11

OVER-PLOT P(Q) ? (LTYP,LSYM (2I1)) [return to enter zero]
 OVER-PLOT RESCALED S(Q) ? (LTYP,LSYM (2I1))
 OVER-PLOT RESCALED BETA(Q) ? (LTYP,LSYM (2I1))
 SUBTRACT BACKGROUND ("WRK",MODELS 3&4) ? (ANS 1)

	AUTO	CHOICE
X1	0.000E+00	0.000E+00
X2	2.258E-01	2.258E-01
Y1	-7.411E+02	-7.411E+02
Y2	8.725E+02	8.725E+02

AXES 1-AUTO, 2-U CHOOSE, 3-USE CHOICE, 0-RETURN ? 1
 TITLE ? [return to enter zero]

[you may be asked to check plot device type, plot appears on screen, lousy fit to data, try another model]

PLOT CONTROLS IDEV= 0-EXIT, 1-screen, 2-file
 error bars are IEB*sigma (ONLY USE ON LINEAR PLOT)
 IPW=1 adds scaled wts
 IDEL spreads graphs apart (IDEL=2 is default)
 IDEV,IEB,IPW,IDEL = (5I1) [return to get out of plot]

TALK ROUTINE

>STOP

DID YOU REMEMBER TO PF AND FF ? ,NOW SAVE CALC SETS

1-READ MODEL FILE	4-CALC ONLY, CHOOSE Q
2-CHOOSE OBS,CALC SETS ETC.	5-INDEX
3-ENTER FIT ROUTINE	6-RETURN TO MAIN ROUTINE

1 [continue reading model file]

LSQIN READS MODEL DESCRIPTION FILE FROM FORTRAN STREAM 3

ENTER 0-TO IGNORE, 1-USE THIS MODEL, 9-REWIND

(POLY DISP SPHERES)*HSS(Q)		CONSTRAINED TO FIT RM AND LAM			
1	6 81 R**N VOL	1.842795E-04	5.014E-06	1.0	-2.22E-04
2	6 2 R2-R1	7.326303E+01	0.000E+00	-1.0	0.00E+00
3	6 3 R1	2.997124E+01	0.000E+00	-1.0	0.00E+00
4	6 4 N	-1.500000E+00	0.000E+00	0.0	0.00E+00

USE=1 [use this one, same as before but with hard sphere structure factor added]

1-READ MODEL FILE	4-CALC ONLY, CHOOSE Q
2-CHOOSE OBS,CALC SETS ETC.	5-INDEX
3-ENTER FIT ROUTINE	6-RETURN TO MAIN ROUTINE

3

>P

1	6 81 R**N VOL	1.842795E-04	5.014E-06	1.0	-2.22E-04
2	6 2 R2-R1	7.326303E+01	0.000E+00	-1.0	0.00E+00
3	6 3 R1	2.997124E+01	0.000E+00	-1.0	0.00E+00
4	6 4 N	-1.500000E+00	0.000E+00	0.0	0.00E+00
5	2 1 LAMBDA	5.500000E-01	0.000E+00	0.0	0.00E+00
6	2 2 R-MID	6.660275E+01	4.136E-01	1.0	2.30E+01
7	22 1 HS S(Q) VOL	1.854555E-01	1.444E-02	1.0	-6.66E-02
8	22 2 SPH RADIUS	1.351837E+02	2.197E+00	0.4	0.00E+00
9	3 1 BKG A	9.848869E-02	1.601E-02	1.0	0.00E+00

```

10 3 2      B*Q      0.000000E+00    0.000E+00    0.0  0.00E+00
11 3 3      C*Q**2   0.000000E+00    0.000E+00    0.0  0.00E+00
12 15 1  SMEAR      1.000000E+00    0.000E+00    0.0  0.00E+00
13 15 2  NSIMP      2.100000E+01    0.000E+00    0.0  0.00E+00
14 99 1      SCALE    1.000000E+00    0.000E+00    0.0  0.00E+00

```

> OFF [trick to zero the shifts column]

> ON

> R

```

POLYDISPERSE R= 3.00E+01 TO 1.03E+02 N= 1 TO 37
DR=N(4)= 2.00E+00 RMAX=N(5)= 1.03E+02
PMIN= 3.686E-14 PMAX= 7.843E-12 ENT= 3.768E+00 B=N(7)= 0.000E+00
VNORM= 1.84280E-04 SIG(R)/RB= 3.1124E-01 SIG**2= 2.5661E+02
RBAR= 5.1469E+01 AREA P(R)= 2.4582E-10
SMEARING ROUTINE CALLED

```

NPSMEAR,NSHAPE,SCALE,NSIMP = 12 0 1.000 21

NOTE for debug purposes, non-smear calc is in SET 5

CYC 5 49 DATA+ 0 PRED, 5 PAR SWSE= 9.930E+03 XDWE= 9.916E+03 VAR= 2.159E+02

> 1 9

```

1 6 81 R**N VOL      1.842795E-04    2.491E-04    1.0  1.32E-04
2 6 2 R2-R1          7.326303E+01    0.000E+00   -1.0  0.00E+00
3 6 3 R1              2.997124E+01    0.000E+00   -1.0  0.00E+00
4 6 4 N               -1.500000E+00    0.000E+00    0.0  0.00E+00
5 2 1 LAMBDA          5.500000E-01    0.000E+00    0.0  0.00E+00
6 2 2 R-MID           6.660275E+01    1.813E+01    1.0  1.40E+01
7 22 1 HS S(Q) VOL    1.854555E-01    7.833E-01    1.0 -2.72E-01
8 22 2 SPH RADIUS     1.351837E+02    1.690E+02    0.4 -4.32E+01
9 3 1 BKG A           9.848869E-02    6.262E-01    1.0  1.21E+00

```

> R

```

POLYDISPERSE R= 3.63E+01 TO 1.25E+02 N= 1 TO 45
DR=N(4)= 2.00E+00 RMAX=N(5)= 1.25E+02
PMIN= 1.665E-14 PMAX= 6.382E-12 ENT= 3.764E+00 B=N(7)= 0.000E+00
VNORM= 3.15856E-04 SIG(R)/RB= 3.1045E-01 SIG**2= 3.7255E+02
RBAR= 6.2173E+01 AREA P(R)= 2.3933E-10
SMEARING ROUTINE CALLED

```

NPSMEAR,NSHAPE,SCALE,NSIMP = 12 0 1.000 21

NOTE for debug purposes, non-smear calc is in SET 5

CYC 6 49 DATA+ 0 PRED, 5 PAR SWSE= 3.126E+03 XDWE= 3.080E+03 VAR= 6.795E+01

> 1 9

```

1 6 81 R**N VOL      3.158562E-04    1.902E-04    1.0  5.24E-04
2 6 2 R2-R1          8.866681E+01    0.000E+00   -1.0  0.00E+00
3 6 3 R1              3.627278E+01    0.000E+00   -1.0  0.00E+00
4 6 4 N               -1.500000E+00    0.000E+00    0.0  0.00E+00
5 2 1 LAMBDA          5.500000E-01    0.000E+00    0.0  0.00E+00
6 2 2 R-MID           8.060619E+01    9.750E+00    1.0 -1.46E+01
7 22 1 HS S(Q) VOL    -8.685419E-02    1.518E-01    1.0  1.32E-01
8 22 2 SPH RADIUS     1.179190E+02    1.564E+02    0.4  5.50E+01
9 3 1 BKG A           1.306350E+00    3.447E-01    1.0  2.15E-02

```

> R

```

POLYDISPERSE R= 2.97E+01 TO 1.02E+02 N= 1 TO 37

```

DR=N(4)= 2.00E+00 RMAX=N(5)= 1.02E+02
 PMIN= 1.232E-13 PMAX= 3.711E-11 ENT= 3.768E+00 B=N(7)= 0.000E+00
 VNORM= 8.40031E-04 SIG(R)/RB= 3.1128E-01 SIG**2= 2.5185E+02
 RBAR= 5.0983E+01 AREA P(R)= 1.1528E-09
 SMEARING ROUTINE CALLED

NPSMEAR,NSHAPE,SCALE,NSIMP = 12 0 1.000 21
 NOTE for debug purposes, non-smearred calc is in SET 5
 CYC 7 49 DATA+ 0 PRED, 5 PAR SWSE= 8.133E+03 XDWE= 8.118E+03 VAR=
 1.768E+02

> 1 9 [the fit OUGHT to converge as XDWE is same as SWSE]
 1 6 81 R**N VOL 8.400314E-04 2.212E-04 1.0 -5.39E-04
 2 6 2 R2-R1 7.256344E+01 0.000E+00 -1.0 0.00E+00
 3 6 3 R1 2.968504E+01 0.000E+00 -1.0 0.00E+00
 4 6 4 N -1.500000E+00 0.000E+00 0.0 0.00E+00
 5 2 1 LAMBDA 5.500000E-01 0.000E+00 0.0 0.00E+00
 6 2 2 R-MID 6.596676E+01 3.524E+00 1.0 3.24E+00
 7 22 1 HS S(Q) VOL 4.478095E-02 1.780E-01 1.0 2.13E-02
 8 22 2 SPH RADIUS 1.399234E+02 2.009E+02 0.4 -5.90E+01
 9 3 1 BKG A 1.327847E+00 5.664E-01 1.0 -2.61E-02

> 1=N=.5 [damp down V1 which is oscillating]
 1 6 81 R**N VOL 8.400314E-04 2.212E-04 0.5 -5.39E-04

> R
 POLYDISPERSE R= 3.11E+01 TO 1.07E+02 N= 1 TO 39
 DR=N(4)= 2.00E+00 RMAX=N(5)= 1.07E+02
 PMIN= 4.870E-14 PMAX= 2.092E-11 ENT= 3.767E+00 B=N(7)= 0.000E+00
 VNORM= 5.70646E-04 SIG(R)/RB= 3.1107E-01 SIG**2= 2.7650E+02
 RBAR= 5.3456E+01 AREA P(R)= 6.7962E-10
 SMEARING ROUTINE CALLED

NPSMEAR,NSHAPE,SCALE,NSIMP = 12 0 1.000 21
 NOTE for debug purposes, non-smearred calc is in SET 5
 CYC 8 49 DATA+ 0 PRED, 5 PAR SWSE= 2.685E+02 XDWE= 2.487E+02 VAR=
 5.836E+00

> 1 9
 1 6 81 R**N VOL 5.706458E-04 4.494E-05 0.5 -1.47E-04
 2 6 2 R2-R1 7.612236E+01 0.000E+00 -1.0 0.00E+00
 3 6 3 R1 3.114096E+01 0.000E+00 -1.0 0.00E+00
 4 6 4 N -1.500000E+00 0.000E+00 0.0 0.00E+00
 5 2 1 LAMBDA 5.500000E-01 0.000E+00 0.0 0.00E+00
 6 2 2 R-MID 6.920214E+01 1.101E+00 1.0 2.25E+00
 7 22 1 HS S(Q) VOL 6.605905E-02 3.671E-02 1.0 4.61E-02
 8 22 2 SPH RADIUS 1.163301E+02 2.390E+01 0.4 3.97E+00
 9 3 1 BKG A 1.301789E+00 1.027E-01 1.0 -2.45E-03

> R
 POLYDISPERSE R= 3.22E+01 TO 1.11E+02 N= 1 TO 40
 DR=N(4)= 2.00E+00 RMAX=N(5)= 1.11E+02
 PMIN= 4.823E-14 PMAX= 1.610E-11 ENT= 3.766E+00 B=N(7)= 0.000E+00
 VNORM= 4.97388E-04 SIG(R)/RB= 3.1093E-01 SIG**2= 2.9429E+02
 RBAR= 5.5172E+01 AREA P(R)= 5.3890E-10
 SMEARING ROUTINE CALLED

NPSMEAR,NSHAPE,SCALE,NSIMP = 12 0 1.000 21

NOTE for debug purposes, non-smearred calc is in SET 5
 CYC 9 49 DATA+ 0 PRED, 5 PAR SWSE= 6.053E+01 XDWE= 4.033E+01 VAR=
 1.316E+00

> 1
 1 6 81 R**N VOL 4.973885E-04 2.178E-05 0.5 1.52E-05

> R
 POLYDISPERSE R= 3.23E+01 TO 1.11E+02 N= 1 TO 40
 DR=N(4)= 2.00E+00 RMAX=N(5)= 1.11E+02
 PMIN= 5.800E-14 PMAX= 1.606E-11 ENT= 3.766E+00 B=N(7)= 0.000E+00
 VNORM= 5.05004E-04 SIG(R)/RB= 3.1091E-01 SIG**2= 2.9691E+02
 RBAR= 5.5421E+01 AREA P(R)= 5.3984E-10
 SMEARING ROUTINE CALLED

NPSMEAR,NSHAPE,SCALE,NSIMP = 12 0 1.000 21

NOTE for debug purposes, non-smearred calc is in SET 5
 CYC 10 49 DATA+ 0 PRED, 5 PAR SWSE= 4.341E+01 XDWE= 2.320E+01 VAR=
 9.438E-01

> 1=N
 1 6 81 R**N VOL 5.050041E-04 1.850E-05 1.0 2.03E-05

> R
 POLYDISPERSE R= 3.23E+01 TO 1.11E+02 N= 1 TO 40
 DR=N(4)= 2.00E+00 RMAX=N(5)= 1.11E+02
 PMIN= 6.004E-14 PMAX= 1.672E-11 ENT= 3.766E+00 B=N(7)= 0.000E+00
 VNORM= 5.25346E-04 SIG(R)/RB= 3.1091E-01 SIG**2= 2.9683E+02
 RBAR= 5.5413E+01 AREA P(R)= 5.6182E-10
 SMEARING ROUTINE CALLED

NPSMEAR,NSHAPE,SCALE,NSIMP = 12 0 1.000 21

NOTE for debug purposes, non-smearred calc is in SET 5
 CYC 11 49 DATA+ 0 PRED, 5 PAR SWSE= 2.022E+01 XDWE= 8.952E-03 VAR=
 4.396E-01

> R
 POLYDISPERSE R= 3.23E+01 TO 1.11E+02 N= 1 TO 40
 DR=N(4)= 2.00E+00 RMAX=N(5)= 1.11E+02
 PMIN= 5.997E-14 PMAX= 1.671E-11 ENT= 3.766E+00 B=N(7)= 0.000E+00
 VNORM= 5.24995E-04 SIG(R)/RB= 3.1091E-01 SIG**2= 2.9682E+02
 RBAR= 5.5412E+01 AREA P(R)= 5.6147E-10
 SMEARING ROUTINE CALLED

NPSMEAR,NSHAPE,SCALE,NSIMP = 12 0 1.000 21

NOTE for debug purposes, non-smearred calc is in SET 5
 CYC 12 49 DATA+ 0 PRED, 5 PAR SWSE= 2.021E+01 XDWE= 3.490E-04 VAR=
 4.394E-01

> R
 POLYDISPERSE R= 3.23E+01 TO 1.11E+02 N= 1 TO 40
 DR=N(4)= 2.00E+00 RMAX=N(5)= 1.11E+02
 PMIN= 5.998E-14 PMAX= 1.670E-11 ENT= 3.766E+00 B=N(7)= 0.000E+00
 VNORM= 5.24919E-04 SIG(R)/RB= 3.1091E-01 SIG**2= 2.9682E+02
 RBAR= 5.5413E+01 AREA P(R)= 5.6137E-10
 SMEARING ROUTINE CALLED

NPSMEAR,NSHAPE,SCALE,NSIMP = 12 0 1.000 21

NOTE for debug purposes, non-smearred calc is in SET 5
 CYC 13 49 DATA+ 0 PRED, 5 PAR SWSE= 2.021E+01 XDWE= 3.399E-04 VAR=

4.394E-01

> PP [fit converged, XDWE is small compared to SWSE]
 T 1 P 14 S 1 C 2 N 5
 W 1 K 0 IP 1 MS 1 IY 1 Q 7 R 7 6 1 1 0 2 0 49
 13 5

(POLY DISP SPHERES)*HSS(Q) CONSTRAINED TO FIT RM AND LAM

1	6	81	R**N VOL	5.249193E-04	1.261E-05	1.0	7.24E-08
2	6	2	R2-R1	7.893859E+01	0.000E+00	-1.0	0.00E+00
3	6	3	R1	3.229306E+01	0.000E+00	-1.0	0.00E+00
4	6	4	N	-1.500000E+00	0.000E+00	0.0	0.00E+00
5	2	1	LAMBDA	5.500000E-01	0.000E+00	0.0	0.00E+00
6	2	2	R-MID	7.176235E+01	3.436E-01	1.0	-1.19E-03
7	22	1	HS S(Q) VOL	1.150149E-01	1.060E-02	1.0	4.80E-05
8	22	2	SPH RADIUS	1.183947E+02	3.820E+00	0.4	8.52E-02
9	3	1	BKG A	1.297392E+00	2.811E-02	1.0	-4.03E-06
10	3	2	B*Q	0.000000E+00	0.000E+00	0.0	0.00E+00
11	3	3	C*Q**2	0.000000E+00	0.000E+00	0.0	0.00E+00
12	15	1	SMEAR	1.000000E+00	0.000E+00	0.0	0.00E+00
13	15	2	NSIMP	2.100000E+01	0.000E+00	0.0	0.00E+00
14	99	1	SCALE	1.000000E+00	0.000E+00	0.0	0.00E+00

1 1 2658 CALC 2 BKG 0 POL 3 SSE= 2.021E+01

CONSTRAINT 1 TYPE 3 USE= 1
 V(2) = 2.0* V(5) * V(6) R2-R1=2*L *RM

CONSTRAINT 2 TYPE 4 USE= 1
 V(3) = (1.0- V(5)) * V(6) R1=(1-L)*RM

1.000E-01 5.249E-04 3.109E-01 2.000E+00 1.112E+02

> PLOT

PLOT CONTROLS IDEV= 0-EXIT, 1-screen, 2-file
 error bars are IEB*sigma (ONLY USE ON LINEAR PLOT)
 IPW=1 adds scaled wts

IDEL spreads graphs apart (IDEL=2 is default)

IDEV,IEB,IPW,IDEL = (5I1) 11 [to screen with errors]
 OVER-PLOT P(Q) ? (LTYP,LSYM (2I1)) 1 [solid line]
 OVER-PLOT RESCALED S(Q) ? (LTYP,LSYM (2I1)) 54 [xxx]
 OVER-PLOT RESCALED BETA(Q) ? (LTYP,LSYM (2I1)) 3 [dashed]
 SUBTRACT BACKGROUND ("WRK",MODELS 3&4) ? (ANS 1) 0

AUTO CHOICE
 X1 0.000E+00 0.000E+00
 X2 2.258E-01 2.258E-01
 Y1 -2.900E+02-7.411E+02
 Y2 8.620E+02 8.725E+02

AXES 1-AUTO, 2-U CHOOSE, 3-USE CHOICE, 0-RETURN ? 1

TITLE ?

EXAMPLE FIT TO RUN 2658 WITH POLYDISP INTERACTING SPHERES

[plot 1 appears here]

S(Q) * 5.00E+02 + 0.000E+00 [rescale and shift used to overplot S(Q) on same axes]

BETA(Q) * 5.00E+02 + 0.000E+00

PLOT CONTROLS IDEV= 0-EXIT, 1-screen, 2-file
 error bars are IEB*sigma (ONLY USE ON LINEAR PLOT)
 IPW=1 adds scaled wts
 IDEL spreads graphs apart (IDEL=2 is default)
 IDEV,IEB,IPW,IDEL = (5I1) [return to leave plot]

TALK ROUTINE

> STOP [go back to FIT menu]
 DID YOU REMEMBER TO PF AND FF ? ,NOW SAVE CALC SETS

1-READ MODEL FILE 4-CALC ONLY, CHOOSE Q
 2-CHOOSE OBS,CALC SETS ETC. 5-INDEX
 3-ENTER FIT ROUTINE 6-RETURN TO MAIN ROUTINE
6 [go back to main program]

Command> LIST

WRITE SET I TO DATA FILE (J=1), MONITOR(J=2) OR TO
 SCREEN(J=0) I,J=? (2I1) 21 [save calculated I(Q) in a file]

SET(2) CAL

OLD TITLES:

CAL
 CAL

TITLE:

26-MAY-89 09:24:22 CAL
 CAL

0-CONTINUE, 1-CHANGE TITLES, 2-RETURN ? 1
 ENTER TWO TITLE RECORDS (14A4, 20A4) :

FIT TO 2658.Q
second title line

TITLE:

26-MAY-89 09:24:22 FIT TO 2658.Q

0-CONTINUE, 1-CHANGE TITLES, 2-RETURN ? 0

Command> PLOT [use the long plot routine to draw the P(R) in set 3]

Welcome to the PLOT routine, enter HELP after

Plot> if you are lost

Plot> READ

HOW MANY CURVES ? (I1) 1

FOR EACH CURVE TO BE DRAWN ENTER ON THREE LINES :

SET NUMBER (I1)

LTYPE,LSYMBOL,IFOLD,IEB,INUM-NOT-Q (5I1)

Y SHIFT (F12)

CURVE 1 SET ? (I1) 3

LT LSY IFLD IEB INNQ (5I1) 1

YSHIFT 0.0

Plot> SCREEN

AUTO CHOICE

X1 0.000E+00 0.000E+00

X2 1.103E+02 2.258E-01

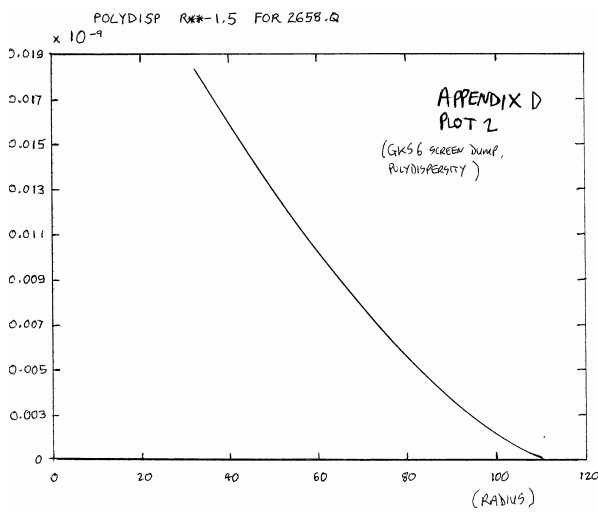
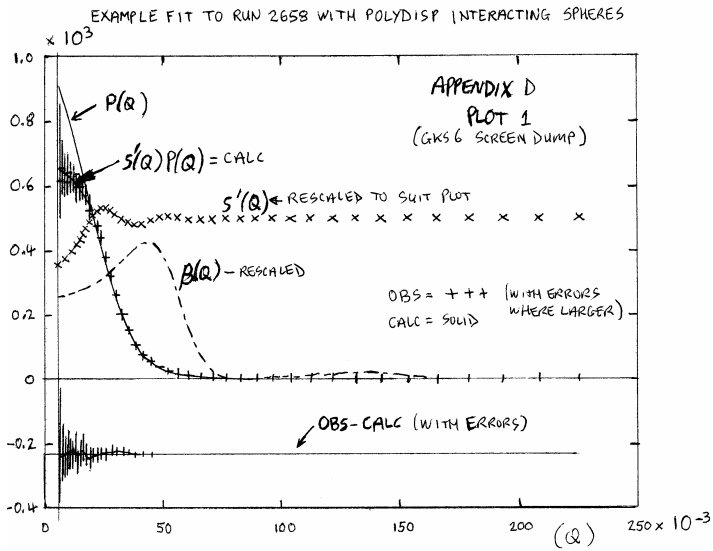
Y1 1.200E-13-7.411E+02
 Y2 1.734E-11 8.725E+02

AXES 1-AUTO, 2-U CHOOSE, 3-USE CHOICE, 0-RETURN ? 1
 TITLE ?

POLYDISP R**=-1.5 FOR 2658.Q

[plot 2 appears here]

Plot> STOP
 Command> STOP
 FORTRAN STOP
 \$
 \$ [returns to VMS operating system]



Appendix E - Least Squares and Marquardt Fits

General non-linear least squares fitting, of the sort required for most SANS data, relies on some understanding of statistical distributions, estimation of functions and solving a set of equations (matrix inversion). Thus the subject usually appears towards the end of text books on “numerical methods” ! All that I can do here is try to portray very briefly the route that is followed. Chapter 15 of “Numerical Recipes” gives a very much more rigorous account. [“Numerical Recipes in FORTRAN, The art of scientific computing”, W.H.Press, S.A.Teukolsky, W.T.Vetterling & B.P.Flannery, Cambridge University Press, 2nd Edition, 1992, reprinted 1994. Other versions of the book & software CD are available for Pascal, C, & Basic.]

Suppose our data are y_i where $i = 1$ to N at points x_i - these could be SANS intensities at N values of scattering vector Q value.

Let the parameters in our model be a_j where $j = 1$ to M

Calculated data points are $CALC_i = \text{function}(x_i, a_1, a_2, \dots, a_M)$

Define a “merit function”

$$c^2 = \sum_{i=1}^N \left(\frac{y_i - CALC_i}{\sigma_i} \right)^2 \quad (1)$$

If the errors (standard deviations) on data σ_i are *independent* and have a *normal (Gaussian) distribution* then statistical theories tell us that the minimum in χ^2 is the “most likely” solution and to expect that $\chi^2/(N-M) \sim 1$.

(A normal distribution is within $\pm 2\sigma$ 68% of the time, $\pm 3\sigma$ 95% of the time. The “Poisson distribution” for neutron counts has a broader tail for small counts. Since the merit function is then not quite correct, “outliers” can be a problem, set their W_i to zero ??)

At the minimum of χ^2 its derivative with respect to each of the parameters a_j will be zero:

$$\frac{\partial(c^2)}{\partial a_j} = 0 \text{ gives } M \text{ equations } \sum_i W_i (y_i - CALC_i) \frac{\partial CALC_i}{\partial a_j} = 0 \quad (2)$$

Where weights $W_i = 1/\sigma_i^2$

For the simplest case the model is “linear” in the parameters, each of which is just a scale factor in front of some mathematical function (which itself may be very non-linear) so that:

$$CALC_i = \sum_{k=1}^M a_k Fun_k(x_i) = \sum_{k=1}^M a_k D_{ik} \quad (3)$$

Note though that each “basis function” is actually just the derivative D_{ij} of the calculated model for that parameter:

$$D_{ij} = \frac{\partial CALC_i}{\partial a_j} = Fun_j(x_i) \quad (4)$$

In the linear case the set of equations (2) can be solved exactly to give the parameter values a_j . We will now however make the equations slightly more complicated by anticipating the method for the more general “non-linear” case !

Assume the present parameters a_j^{now} give $CALC_i^{\text{now}}$ with differences $E_i = (y_i - CALC_i^{\text{now}})$

We need to shift the parameters to $a_j = a_j^{\text{now}} + \Delta a_j$ to give the best (or at least a smaller) value of χ^2 . Since the problem is linear, we can use (3) to write

$$CALC_i = CALC_i^{now} + \sum_k \Delta a_k D_{ik} \quad (5)$$

which is substituted into (2) to give a set of M equations:

$$\sum_i W_i \left(E_i - \sum_k \Delta a_k D_{ik} \right) D_{ij} = 0 \quad (6)$$

The equations are easier to manipulate in matrix form as:

$$\Delta a (D^T W D) - D^T W E = 0$$

which may be rearranged to give the desired a column of parameter shifts Δa as a product of a square “least squares matrix” and a column matrix :

$$\Delta a = (D^T W D)^{-1} (D^T W E) \quad (7)$$

Δa is a column vector of M rows, derivative matrix D has N rows x M columns, weights W_{ii} are a diagonal N x N, and differences E is a column of N rows. Superscripts “T” mean transpose (i.e. $D_{ij}^T = D_{ji}$) and “-1” means the matrix inverse.

[If you are not familiar with this kind of notation just concentrate on the meaning of the results ! If an example might also help, then for the case of just two parameter and 3 data points, the simultaneous equations to be solved to find shifts $a = \mathbf{D}a_1$ & $b = \mathbf{D}a_2$ are:

$$\begin{aligned} a(W_1 D_{1a}^2 + W_2 D_{2a}^2 + W_3 D_{3a}^2) + b(W_1 D_{1a} D_{1b} + W_2 D_{2a} D_{2b} + W_3 D_{3a} D_{3b}) - (W_1 D_{1a} E_1 + W_2 D_{2a} E_2 + W_3 D_{3a} E_3) &= 0 \\ a(W_1 D_{1a} D_{1b} + W_2 D_{2a} D_{2b} + W_3 D_{3a} D_{3b}) + b(W_1 D_{1b}^2 + W_2 D_{2b}^2 + W_3 D_{3b}^2) - (W_1 D_{1b} E_1 + W_2 D_{2b} E_2 + W_3 D_{3b} E_3) &= 0 \end{aligned}$$

In a “linear case” (such as a polynomial or straight line fit) Δa gives an immediate and exact solution, even with zero starting parameters.

For a “non-linear” case (as almost all SANS) equations (3) to (5) are only *approximately* true, so the solution must be iterated. Note that the derivatives D_{ij} are now no longer constant at each Q value, so they must be recalculated for each iteration.

Fortunately it can be shown that ignoring the second derivatives in (3) is not detrimental, since they are usually small and statistically they should tend to cancel out when summed over the data. Nor does this have an effect on the location of the χ^2 minimum, only on the route taken to reach it.

It is a remarkable fact that the least squares method works at all for the “non-linear” cases found in SANS !

M x M matrix $C = (D^T W D)^{-1}$ is the variance-covariance matrix, its diagonal elements are $C_{jj} = \sigma_j^2$ the square of the *statistical* standard deviation for each parameter a_j - *assuming* the conditions mentioned above on σ_i for the data are valid ! Effects of systematic errors, such as imperfect data treatment, or say Q resolution not explicitly included in the model must be considered separately !

Frequently the parameter “errors” obtained for SANS data are unrealistically small, as some trial and error adjustments and common sense will easily show. Off-diagonal elements C_{ij} give the correlation coefficients between parameters, which are helpful to identify poor parametrisation of a model.

Note there is no standard notation for the different matrices (e.g. derivatives D are sometimes called J for Jacobian). In some applications it may be useful to include off-diagonal elements in the weight matrix W to allow for “correlation” between data points. This can help to give more realistic error estimates.

Practical results

All that is needed for least squares fits are (a) routines to calculate the model CALC and its derivatives D for a given set of parameters and Q values and (b) a routine to invert a symmetric matrix (i.e. to solve a set of equations).

Derivative D_{ij} may be calculated numerically (but less reliably) by simply shifting the value of a parameter a_j temporarily by a small amount δ and calling the model routine again:

$$D_{ij} \approx \frac{1}{\delta} \left(\text{CALC}(x_i, a_1, a_2, \dots, (a_j + \delta), \dots, a_n) - \text{CALC}(x_i, a_1, a_2, \dots, a_j, \dots, a_n) \right)$$

The “non-linear” nature of most SANS problems requires that the least squares solutions are iterated. In a well behaved system each iteration gets closer to the χ^2 minimum. When χ^2 ceases to improve further the fit has “converged”. Alas not all systems are “well behaved”, so we must learn some ways to cope !

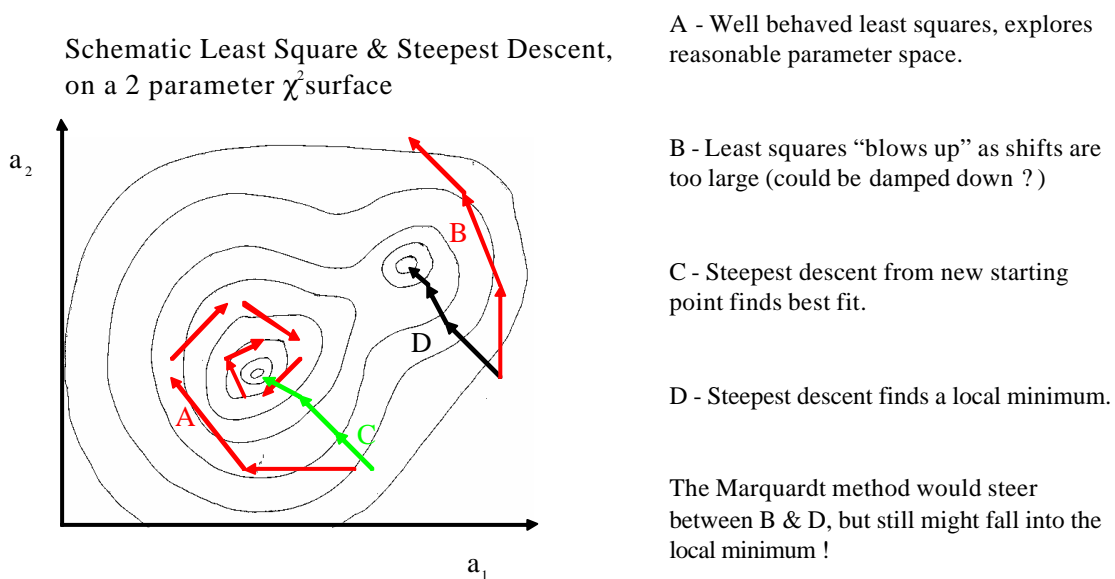
Steepest Descent & the Marquardt method

If the χ^2 merit function (1) is not well approximated by a quadratic near its minimum then the iterative least squares solution may not work.

Some oscillatory behaviour of given Δa_j between iterations may be *damped* down by applying only a fraction of the calculated shifts. Worse behaviour might require some time consuming trial & error on key parameters.

Following the “steepest descent” gradient of the χ^2 surface may be an alternative route to the desired minimum. Least squares tends to spiral down at right angles to the steepest descent of the χ^2 surface, thereby exploring more parameter space and being less likely to become stuck in a local minimum, but often in badly behaved cases “blowing up” altogether.

Marquardt (using an idea of Levenberg) noted a simple connection between the least squares and steepest descent routes. Replacing $(D^T D)$ by a constant diagonal gives the steepest descent route. By multiplying the diagonal elements of $(D^T D)$ by $(1+\lambda)$ where λ is small for least squares or large for steepest descent gives a route that varies between the two extremes.



The Marquardt recipe:

- (i) start with a modest $\lambda \sim 1$,
- (ii) compute D (and save it) and χ^2
- (iii) calculate parameter shifts using (7) with diagonal elements of (D^TWD) multiplied by $(1+\lambda)$
- (iv) compute new parameters and their χ^2
- (v) if fit has converged, or too many iterations, stop !
- (vi) if fit improves, keep new parameters, divide λ by 10 and return to (ii)
- (vii) if fit worsens, multiply λ by 10, return to (iii) (no new computation of D)

NOTE - to obtain the proper error estimates σ_j on parameters a_j set $\lambda=0$ for a final calculation.

The fit is guaranteed to improve, if only slowly, but not (in poorly behaved cases) to find a global minimum for χ^2 as the steepest descent route can become stuck in a "local minimum". It may be important, as with ordinary least squares, to try to find the solution again from slightly different starting points.

CONSTRAINTS

In many cases physical constraints and prior knowledge (e.g. shell to core molar volume ratio, consideration of fully extended surfactant tail lengths) may be required to locate *physically meaningful* parameters from amongst whole families of possible numerical solutions.

Absolute intensities are also vital either by constraining scale parameters to known volume fractions or concentrations or, where samples or intensities are less well known, by checking that fitted scale parameters are *consistent* with sample compositions.

If one parameter is constrained to another, then one could rewrite the model with one less parameter. This is not of course very convenient, so it is better to write the model with the maximum likely number of parameters that could be adjusted or investigated.

If parameter a_j is a function $f(a_k)$ of parameter a_k the model routine will give $\frac{\mathcal{I}CALC_i}{\mathcal{I}a_j}$ so the least squares

calculation has to add an extra term to $\frac{\mathcal{I}CALC_i}{\mathcal{I}a_k}$ by:

$$\frac{\mathcal{I}CALC_i}{\mathcal{I}a_k} = \frac{\mathcal{I}CALC_i}{\mathcal{I}a_k} + \frac{\mathcal{I}CALC_i}{\mathcal{I}a_j} \frac{\mathcal{I}a_j}{\mathcal{I}a_k} = \frac{\mathcal{I}CALC_i}{\mathcal{I}a_k} + \frac{\mathcal{I}CALC_i}{\mathcal{I}a_j} \frac{f'(a_k)}{\mathcal{I}a_k}$$

The FISH program will do this for a variety of pre-programmed constraint functions.

Appendix F - NUMERICAL INTEGRATION - GAUSSIAN QUADRATURES

Calculation of SANS intensities (and their derivatives) frequently requires some numerical integration, for example to sum over a polydisperse particle size, or in the form factors for monodisperse rods (discs) or ellipsoids.

Most of us will be familiar with the “trapezium rule” for integrating N data points, equally spaced h apart. Apart from the weights of $\frac{1}{2}$ on the first and last points, this is just “adding up the data”.

$$\int_{x_1}^{x_N} y(x)dx \approx h \left[\frac{1}{2} y_1 + y_2 + y_3 + \dots + y_{N-1} + \frac{1}{2} y_N \right] \quad (1)$$

Simpson’s rule gives a better answer with the same points but different weights as it is equivalent to fitting a cubic equation through adjacent groups of three points.

$$\int_{x_1}^{x_N} y(x)dx \approx \frac{h}{3} \left[y_1 + 4y_2 + 2y_3 + 4y_4 \dots + 2y_{N-2} + 4y_{N-1} + y_N \right] \quad (2)$$

Removing the restriction on the points being *equally* spaced allows use of much more efficient “quadrature methods”, which use a table of specially chosen x values (abscissae) and weights for the y values at those points. Since we are integrating the *model* function, the non-equally spaced points pose no problem! By some clever mathematics we may for example use a “10 point Gaussian quadrature” to integrate a function as if it were fitted by a 10th order polynomial, or say a 64 point quadrature for an order 64 polynomial. The coefficients for a 10 point “Gauss-Legendre” quadrature are illustrated below. Note that though for symmetry the integration interval is here -1 to $+1$ the abscissae and weights can easily be rescaled to suit a given range.

$$\begin{aligned} \int_{-1}^{+1} y(x)dx \approx & 0.06667(y(-0.9739) + y(+0.9739)) + 0.14945(y(-0.8651) + y(+0.8651)) + \\ & + 0.21909(y(-0.6794) + y(+0.6794)) + 0.26923(y(-0.4334) + y(+0.4334)) + \\ & + 0.29552(y(-0.1489) + y(+0.1489)) \end{aligned} \quad (3)$$

IF the function $y(x)$ is *well* approximated by a polynomial then the resulting integral will be more accurate than say using Simpson’s rule with many more points, and hence the fitting program will run more quickly. The abscissae in a Gaussian quadrature are grouped more closely towards the ends of the integration range.

(Actual integrations need the abscissae and weights to many more decimal places than illustrated in (3) above. Originally one looked them up in tables, but nowadays simple iterative routines are available to calculate them as needed. The precision of the computer becomes important for higher orders of quadrature.)

With modern computers the choice of integration scheme only makes a significant difference in speed for multi-dimensional integrals, such as for “oriented rods”. In this latter case one must however be careful as the form factor for long, thin rods has strong oscillations for which Gaussian quadrature does not work well and Simpson’s Rule is more appropriate for parts of the integration. It is advisable in any circumstance to test different integration schemes quite carefully, with increasing numbers of points to ensure that they converge adequately for a particular problem.

A full discussion of numerical integration methods (e.g. Chapter 4 in Numerical Recipes) focuses on issues such as estimation of accuracy and effects of singularities in the function. Certain functional singularities can be included in the quadrature, so that one “fits” say a polynomial times an exponential. These give rise to whole families of quadratures in addition to the usual “polynomial” Gauss-Legendre, such as Gauss-Chebyshev, Gauss-Laguerre, Gauss-Hermite and Gauss-Jacobi.

One advantage of the simple “trapezium rule” equation (1) is that it may efficiently be extended to include extra points between those of the previous set of points, to give an iterative answer with easily assessed “accuracy”. (Various library routines are available in this area.)

The Gaussian quadrature method does not have this property, increasing the number of points results in a completely new set of abscissae and weights. The Gauss-Kronrod method is an “adaptive” integration scheme which expands the Gauss-Legendre polynomials in an optimal way, re-using results of the previous iteration. It uses a sequence of N points such as $N=10, 21, 43, 87$. Such “adaptive” schemes usually require to be given both an absolute and relative error expected for the result of the integration in order to know when to stop !