

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

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 $\beta(Q)$ 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-Beuche |
| | | 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 $\langle R^3 \rangle = (1 + (\sigma/R)^2)(1 + 2(\sigma/R)^2)R^3$. 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 $E+\delta$ 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 ! | $P(r) = [(Z+1)/(R_{\text{bar}}-R_1)]^{Z+1} r^Z \exp\{-(Z+1)/(R_{\text{bar}}-R_1).r\}/\Gamma(Z+1)$ |
| 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. R₁ 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 \bar{R} and σ/\bar{R} , 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 <i>continuous</i> , 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 | R_2-R_1 | where if $n < 0$ $R_B = R_2 + \Delta R$ |
| 3 | R_1 | $n > 0$ $R_B = R_1$ |
| 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 (<i>not</i> to be combined with spherical shells !) |
| 2 | R - 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 $F(Q) = F(Q) + (\Delta\rho)V \frac{2J_1(QR)}{QR}$ 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 |
| 2 | b - 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 ON or 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 (<i>not</i> to be combined with spherical shells ! - see notes in model 8) |
| 2 | R - radius |
| LTYP=71 | $\Delta\rho$ - Gaussian shell centred at $(a+b)/2$, with same material as rectangular shell from a to b . |
| 2 | b - 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 $t = \frac{(b-a)}{\sqrt{2\pi}} \frac{R_0^2 + (b-a)^2/12}{R_0^2 + t^2} \approx \frac{(b-a)}{\sqrt{2\pi}}$. 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 $\rho(r) = \Delta\rho \cdot \exp\{-(r-a)/L\}$ for $r \geq a$, for which LTYP=21 uses:

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

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 $\rho(r) = \Delta\rho \cdot \exp\{-(a-r)/L\}$, 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

```

```

1.000000 -1.000000 -1.000000 0.000000 (R1 = R3 - head - tail )
11 4 6 14 14 (
1.000000 -1.000000 0.000000 0.000000 ( R2 = R3 - tail )
11 8 6 13 13
1.000000 1.000000 0.000000 0.000000 ( R4 = R3 + head )
11 7 3 1 1
-1.000000 0.000000 0.000000 0.000000 ( (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 ... + G*Q**7

2 B

3 C

etc.....

8 G

LTYP=21 A I(Q)= A one record only version, to generate P(Q)=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) ≤ ABS(T), so if central Q values are at -Δ and +Δ 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(-Q²R²/3.0)

= 2 R Guinier radius

LTYP = 11 K= 2πS Porod surface with diffuse interface. Note an *infinite flat* sharp interface convoluted with a Gaussian has a sigmoidal profile which scatters exactly Q² times this. The inclusion of a Lorentz 1/Q² 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) + Kexp(-Q²σ²)/Q⁴

LTYP = 21 K= 2πS diffuse Porod surface with separate surface layer of different scattering length density.

= 22 Δ₁ Scattering length density difference (substrate - solvent)

= 23 σ₁ diffuseness of substrate.

= 24 Δ₂ Scattering length density difference (layer - solvent)

= 25 H thickness of layer

= 23 σ₂ additional diffuseness of layer. (Note that σ₂ is convoluted with σ₁ in the Δ₂² 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/Q² is required.)

$$I(Q) = I(Q) + \frac{K}{Q^4} \left((\Delta_1 - \Delta_2)^2 e^{-\sigma_1^2 Q^2} + \Delta_2^2 e^{-(\sigma_1^2 + \sigma_2^2) Q^2} + 2(\Delta_1 - \Delta_2) \Delta_2 \cos(QH) e^{-(2\sigma_1^2 + \sigma_2^2) Q^2 / 2} \right)$$

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.

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

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

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

LTYPE(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 (cm^{*-1})

MODEL 14

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

- LTYPE=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.

- LTYPE=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.

- LTYPE=21 $I(Q=0)$ exactly as for a Gaussian coil. **Worm- like chain**
- 22 n gives total chain length $L = n\lambda$
- 23 λ 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 $Q\lambda < 3.1$ 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 $R_G^2 = n\lambda^2/6$. 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 $Q\lambda < 9.4$ an analytical approximation of numerical results is used. For $Q\lambda < 13.4$ and $Q\lambda > 13.4$ 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 $\exp(-Rax^2Q^2/2)$ 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

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

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 $M = f \cdot M_{\text{arm}}$ 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.

$$\begin{aligned} \text{LTYP}=41 \quad Nf &\text{ - scale} \\ 42 \quad R_g &\text{ - radius of gyration} \\ 43 \quad (\alpha / Nf) &\text{ - relative scale of fractal term} \\ 44 \quad \xi &\text{ - exponential damping length in mass fractal} \\ 45 \quad \nu &= 1/(\mu + 1) \text{ - Flory exponent, } 3/5 \text{ in good solvent, } 1/2 \text{ in theta solvent (i.e. } \mu = 2/3 \text{ to } 1) \end{aligned}$$

$$P(Q) = Nf \left(\exp\{-Q^2 R_g^2 / 3\} + \frac{4\pi\alpha}{Q\xi(Nf)} \frac{\sin(\mu \tan^{-1}(Q\xi))}{(1 + Q^2 \xi^2)^{\mu/2}} \right)$$

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.

$$\begin{aligned} \text{LTYP}=51 \quad \text{scale} &= ??? \times \Delta\rho^2 & \text{needs checking - is probably as per LTYP=61 below !} \\ 2 \quad N &\text{ monomers per molecule} \\ 3 \quad a &= \text{length per monomer (} R_G^2 = Na^2/6 \text{)} \\ 4 \quad f &= \text{fraction of molecule of one scattering type} \\ 5 \quad \chi &= \text{interaction parameter (per monomer ?)} \end{aligned}$$

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

$$\begin{aligned} \text{LTYP}=61 \quad \text{scale} &= V\Delta\rho^2 \quad \text{where } V = \text{volume of whole molecule} = MW/(\rho_{\text{bulk}} \cdot N_A), \\ &\Delta\rho = \text{scattering length density difference.} \\ 2 \quad R_g &\text{ - radius of gyration of deuterated end of arm} \end{aligned}$$

- 3 $f_a = 4f_1 = \text{fraction of molecule deuterated}$
 4 $f_b = \text{fraction of molecule in backbone (or cross bar)} = f_3$
 5 $\chi = \text{interaction parameter (per monomer ?)}$

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:

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

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

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 - Dirac Worm - like chain. A.L.Kholodenko, (who asks that we call the model after Dirac, upon whose idea it is based) *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 $I(Q) \approx P_{WORM}(Q)P_{AXIAL}(Q)$. After slight rearrangement of the original equations (using $L = n\lambda$):

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

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

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

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

combinations of n and λ giving the expected contour length $L = n\lambda$, 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 W_{max} 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 $P_{AXIAL}(Q)$:

$$P_{AXIAL}(Q) = N(\rho_1 - \rho_3)^2 (AL)^2 \exp \left\{ -\frac{1}{2} Q^2 R_{AX}^2 \right\} \quad \text{where for a uniform scattering length density, in}$$

general, the mass per unit length $M_L = \frac{M}{LN_A}$ gives cross sectional area $A = \frac{M_L}{\rho_{BULK}}$. Specifically for a

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):

$$F_{AXIAL}(Q) = (\rho_1 - \rho_2)\pi R_1^2 L \frac{2J_1(QR_1)}{QR_1} + (\rho_2 - \rho_3)\pi R_2^2 L \frac{2J_1(QR_2)}{QR_2}, \quad P_{AXIAL}(Q) = NF_{AXIAL}(Q)^2$$

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.

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

$\phi = N.(2\pi R_{ax}^2 n\lambda)$. 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 = $(2\pi R_{ax}^2)SCALE_{FISH}/A$ 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 $L = n\lambda$

73 λ 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 λ); monodisperse if (σ/L_{MEAN}) < 0.01

Kholodenko –Dirac 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.

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

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

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

83 λ 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 λ , taken as monodisperse if (σ/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 LTYPE = 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. LTYPE = 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 $Q = Q_{\text{data}} + \text{RSCALE} \times Q_{\text{resol}}$ 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 !

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

21 $A/I(Q=0)$

31 $B/I(Q=0)$

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

$$\zeta^{-2} = \frac{\sqrt{B}}{2} + \frac{A}{4B} = \frac{1}{2} Q_M^2 (I_M / (I_M - I_0))^{1/2} - \frac{1}{2} Q_M^2$$

$$\left(\frac{2\pi}{d}\right)^2 = \frac{\sqrt{B}}{2} - \frac{A}{4B} = \frac{1}{2} Q_M^2 (I_M / (I_M - I_0))^{1/2} + \frac{1}{2} Q_M^2$$

$$I_0 = \frac{8\pi\phi(1-\phi)(\Delta\rho)^2}{\zeta((2\pi/d)^2 + \zeta^{-2})^2} = \frac{8\pi\phi(1-\phi)(\Delta\rho)^2}{\sqrt{2}Q_M^3 I_M} (I_M - I_0) \{(I_M / (I_M - I_0))^{1/2} - 1\}^{1/2}$$

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.)

| | | |
|----------|-------|--|
| LTYPE=11 | Iz | $I(Q) = 4\pi\langle\eta^2\rangle a_0^3 \{(1 + Q_0/Q)/(1 + a_0^2(Q+Q_0)^2)^2 +$ |
| 12 | Q_0 | $(1 - Q_0/Q)/(1 + a_0^2(Q-Q_0)^2)^2\}$ |
| 13 | a_0 | |

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

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 Iz approximately equal $I(Q=0)$.

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

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

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

MODEL 18

Rods (or discs) or oriented rods, of full length L and radius R . For N randomly oriented rods the form factor $P(Q)$ is: $P(Q) = N \int_0^{\pi/2} F^2(Q) \sin(\gamma) d\gamma$

where $F(Q) = (\Delta\rho)V \frac{\sin(\frac{1}{2}QL \cos \gamma)}{\frac{1}{2}QL \cos \gamma} \frac{2J_1(QR \sin \gamma)}{QR \sin \gamma}$ in which $J_1(x)$ 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)

LTYPE=1 or 11 SCALE - rigid, core/shell rod (or disc) with a shell at the end (LTYPE=1) or without a shell at the end (LTYPE =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 Ψ | 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.

$$P(Q) = \int_0^{2\pi} d\phi \int_0^\pi P_s(\theta, \phi, \Gamma) \left\{ F^2(Q, \gamma^+) + F^2(Q, \gamma^-) \right\} \sin(\theta) d\theta$$

where F(Q) is as above, $\cos \gamma^\pm = \sin \theta \cos \phi \cos \Psi \pm \cos \theta \sin \Psi$

and the rod orientation function is taken to be: $P_s(\theta, \phi, \Gamma) = \frac{(1 - \cos 2\phi_0)(1 + \sin^2 \theta \cos 2\phi_0)^{3/2}}{4\pi(1 - \sin^2 \theta \cos 2\phi_0 \cos 2(\phi - \phi_0))^2}$

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:

$$P(Q, \Psi = 90^\circ) = 2 \int_0^{\pi/2} \frac{(1 - \cos 2\phi_0)}{(1 - \sin^2 \theta \cos 2\phi_0)^{3/2}} F^2(Q) \sin \theta d\theta$$

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 $\beta(Q)$ 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:

$$P_{MS}(\theta, \phi, m) = P_{MS}(\theta, m) = \frac{e^{m \cos^2 \theta}}{4\pi \int_0^{\pi/2} e^{m \cos^2 \theta} \sin \theta d\theta} = \frac{e^{m \cos^2 \theta}}{4\pi \int_0^1 e^{mx^2} dx}$$

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 $\gamma = \theta$:

$$P(Q, \Psi = 90^\circ) = 4\pi \int_0^{\pi/2} P_{MS}(\theta, m) F^2(Q) \sin \theta d\theta$$

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 .

$$P(Q) = 4 \int_{\alpha=0}^{\pi/2} \int_{\beta=0}^{\pi/2} P_{MS}(\beta, m) F^2(Q, \gamma) d\beta d\alpha$$

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)

$$\text{LTYP}=1 \quad \text{SCALE} \quad I(Q) = I(Q) + \text{SCALE} \int_0^{\pi/2} \Phi^2(u) \sin(\alpha) d\alpha$$

$$=2 \quad A \quad \text{radius} \quad \text{where} \quad \Phi(u) = 3(\sin(u) - u \cos(u))/u^3$$

$$=3 \quad X \quad \text{axial ratio} \quad \text{and} \quad u = QA(\sin^2(\alpha) + X^2 \cos^2(\alpha))^{1/2}$$

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* x *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). The original equations are in J.B.Hayter & J.Penfold, Mol.Phys. 42 (1981)109-118; the "rescaling" is in J.P.Hansen & J.B.Hayter, Mol. Phys.46(1982)651; whilst the "penetrating background" is thought to have only appeared as an ORNL report involving Hayter. 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) $S(Q) + I0(crit)/(1+\zeta^2 Q^2)$

6 " " " ζ correlation length for critical scatter

$$AKK=1/r_D^2 \text{ where } r_D^2 = \epsilon_0 K_r RT / (2\rho N_A^2 e^2 I)$$

$$I = \text{ionic strength} = 0.5 \sum (m_+ z_+^2 + m_- z_-^2) \text{ where } m = \text{molality}$$

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

$$r_D^2 = (8.85 \times 10^{-12} \text{C}^2 \text{N}^{-1} \text{m}^{-2}) 78 (8.31 \text{JK}^{-1} \text{mol}^{-1}) (298 \text{K}) (10^{20} \text{\AA}^2 \text{m}^{-2})$$

$$2 (10^3 \text{kgm}^{-3}) (6.02 \times 10^{23} \text{mol}^{-1})^2 (1.6 \times 10^{-19} \text{C})^2 (0.1 \text{molkg}^{-1})$$

$$\text{so } r_D = 9.6 \text{\AA}, \text{ AKK} = 0.10 \text{ \AA}^{-1}$$

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 | $\eta_p V_T^2 (\rho_2 - \rho_3)^2$ | 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 $3j_1(u_1)/u_1$, 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 $[((\rho_1 - \rho_2) / (\rho_2 - \rho_3)) (R_1/R_2)^3]$ if LTYP(1)=11 $[((\rho_1 - \rho_2) / (\rho_2 - \rho_3)) X R_1^3 / ((R_1 + \delta)^2 (R_1 X + \delta))]$ | |

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

$$\begin{aligned}
 F(Q, \mu) &= V_{\text{core}}^3 (\rho_1 - \rho_2)^3 j_1(u_1)/u_1 + V_{\text{total}}^3 (\rho_2 - \rho_3)^3 j_1(u_2)/u_2 \\
 &= (4\pi/3)(\rho_2 - \rho_3) X R_2^3 [3j_1(u_2)/u_2 + 3(R_1/R_2)^3 ((\rho_1 - \rho_2) / (\rho_2 - \rho_3)) j_1(u_1)/u_1] \\
 \text{in which } u_1 &= Q.R_1 [(1 - \mu^2) + X^2 \mu^2]^{1/2} \\
 u_2 &= Q.R_2 [(1 - \mu^2) + X^2 \mu^2]^{1/2} \\
 j_1(u) &= (\sin(u) - u \cos(u)) / u^2
 \end{aligned}$$

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 $u_2 = Q [(1 - \mu^2)(R_1 + \delta)^2 + (R_1 X + \delta)^2 \mu^2]^{1/2}$

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-Beuche. (See MODEL 7 for a similar structure factor and MODEL 17 for the Debye term.)

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

| | | |
|---------|-------|--|
| 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-Beuche 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.Carlike, W.S.Howells & S.König, Physica B 182(1992)341-348.

| | | |
|----------|----------|--|
| LTYP= 11 | A | Lorentzian for inelastic neutrons: $I(Q) = I(Q) + A.W/\{ 2\pi ((E - \delta)^2 + (W/2)^2) \}$ |
| 12 | W | FWHM of peak |
| 13 | δ | shift in Q or E scale |

| | | |
|----------|-------|--|
| LTYP= 21 | SCALE | Gaussian peak $I(Q) = I(Q) + SCALE*\exp\{-0.5*((Q-Q_0)/\sigma)^2\}$ |
| 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 | $I(Q) = I(Q) + SCALE*\exp\{-0.5*[(Q-Q_0)/(\sigma + (\text{abs}(\sigma_2) + \sigma_3)(Q-Q_0))]^2\}$ |
| 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 | $I(Q) = I(Q) + SCALE.\exp\{ -\sigma^2/2\tau^2\}\exp\{ -(Q - Q_0)/\tau \}$ |

| | | |
|-----------|------------------------------------|--|
| 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 :

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

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:

$$\Psi(t) = (1-R) \frac{\alpha}{2} (\alpha t)^2 e^{-\alpha t} + R \frac{\alpha \beta}{2} \int_{t'=t}^{t'=\infty} (\alpha t')^2 e^{-\alpha t'} e^{-\beta(t-t')} dt'$$

$$\Psi(t) = (1-R) \frac{\alpha}{2} (\alpha t)^2 e^{-\alpha t} + \alpha R \frac{\alpha^2 \beta}{(\alpha - \beta)^3} [e^{-\beta t} - e^{-\alpha t} (1 + (\alpha - \beta)t + \frac{1}{2}(\alpha - \beta)^2 t^2)]$$

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

| | | |
|------------|-----------|---------------------------------------|
| LTYPE = 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:

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

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

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, LTYPE=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 !)

LTYPE(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

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

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.

LTYPE(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 diffusness | " | λ_1 core thickness | λ_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 | " | λ_2 shell or head group thickness | $(1/\kappa)$ exponential decay length for head group. |
| 5 | R σ Lorentz factor | (Ignored) | R σ | R σ |

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 λ_1 , the shell ρ_2 and thickness λ_2 , and the solvent ρ_3 . The total layer thickness is $\lambda_1 + 2\lambda_2$.

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:

$$f(Q) = \lambda_1 \frac{\sin(Q\lambda_1/2)}{Q\lambda_1/2} + 2\lambda_2 \frac{(\rho_2 - \rho_3)}{(\rho_1 - \rho_3)} \cos(Q(\lambda_1 + \lambda_2)/2) \frac{\sin(Q\lambda_2/2)}{Q\lambda_2/2}$$

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 λ_1 , of large radius R_{sphere} in a solvent ρ_3 ,

$$I(Q) \rightarrow \frac{8\pi(\rho_1 - \rho_3)^2 S}{Q^4} \sin^2(Q\lambda_1/2)$$

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} , λ_1 in $f(Q)$ and $(R\sigma)$ are in Å, 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) so that $\text{scale} = 10^{-32}\pi(\rho_1 - \rho_3)^2 S (R\sigma)^2 L^2$ with L in Å.

For an *oriented sheet*, $(R\sigma)=0$, where the scattering is in one direction in Q, one compares the scattering from an oriented disk of large radius R_{disk}

$$I(Q) \rightarrow N(\rho_1 - \rho_3)^2 V^2 \left(\frac{\sin(Q\lambda_1/2)}{Q\lambda_1/2} \right)^2$$

to obtain, for the most commonly used LTYP=1, $\text{scale}' = 10^{-24} \cdot \pi^2 \cdot (\rho_1 - \rho_3)^2 V \phi = 10^{-16} \cdot \pi^2 \cdot (\rho_1 - \rho_3)^2 L^2 S^2 / N$ [revised 8/13, was $10^{-16} \cdot (\rho_1 - \rho_3)^2 S^2 / N$, though now the π^2 is a little uncertain] 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} , $S = N \cdot \pi(R_{\text{disk}})^2 = \phi / (10^{-8} \lambda_1 [\text{\AA}])$ and $V = \pi(R_{\text{disk}})^2 \lambda_1$ is volume in \AA^3 . It seems that you can only determine S if you make a decision about some lateral dimension R_{disk} in order to calculate N or V, but that will then give a range of values to try to make consistent with S and ϕ .

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.

When random or oriented sheets are combined with model 29 below, S is the *total* area of sheet, (the area of stack times M layers), 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 λ_1 the \sin^2 term averages to 1/2 and we reach the normal "Porod" limit of

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

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):

$$f(Q)(\rho_1 - \rho_3) = (\rho_2 - \rho_3)(\lambda_1 + 2\lambda_2) \frac{\sin(Q(\lambda_1 + 2\lambda_2)/2)}{Q(\lambda_1 + 2\lambda_2)/2} + (\rho_1 - \rho_2)\lambda_1 \frac{\sin(Q\lambda_1/2)}{Q\lambda_1/2}$$

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):

$$f(Q) = \lambda_1 \frac{\sin(Q\lambda_1/2)}{Q\lambda_1/2} + \frac{2}{\kappa^2 + Q^2} \frac{(\rho_2 - \rho_3)}{(\rho_1 - \rho_3)} (\kappa \cos(Q\lambda_1/2) - Q \sin(Q\lambda_1/2))$$

If $x=0$ is at the centre of the core, then the scattering length density is ρ_1 to $x=\lambda_1/2$, and $\rho_2 \exp\{-\kappa(x - \lambda_1/2)\}$ 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. Note there are the same numbers of “layers” and “gaps”, so one face of the stack ends with a “gap”. (This and the absolute intensities were checked using data calculated for large radius multilammellar vesicles). 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 $R\sigma$ as per MODEL 28.

LTYP = 11 or 21 SCALE. When $\rho_3 = \rho_1$ and $(R\sigma)$ is large, then $SCALE = 10^{-32}\pi.S(R\sigma)^2$ similarly to MODEL 28 but ignoring the value of $\Delta\rho^2$ which is included below, though if ρ values are entered as say 6.35 for $6.35 \times 10^{10} \text{ cm}^{-1}$, then you need to include the 10^{20} thus $SCALE = 10^{-12}\pi.S(R\sigma)^2$. When ρ_1 is close to ρ_2 , say within ~10%, the same equation seems to approximately work, but for intermediate values there is a complex weighted average to be derived. In both cases the area of the stack is S divided by the number of layers M . [NOTE this indirectly includes the effective volume fraction of the “stack” relative to the third “background” phase – 8/13 - I don’t know what that meant!]

When $\rho_3 = \rho_1$ and $(R\sigma)=0$ for oriented stacks, $SCALE = 10^{-24} \cdot \pi^2 \cdot V \phi/L^2 = 10^{-16} \cdot \pi^2 \cdot S^2/N$; though again if ρ values are in units of 10^{10} cm^{-1} we need a factor of 10^{20} so $SCALE = 10^{-4} \cdot \pi^2 \cdot S^2/N$. As with Model 28, the factor π^2 was determined empirically by comparison of sheared disk data from Model 18, LTYP=21.

| | | |
|---|----------|---|
| 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. |
| <i>EITHER</i> 8 | $\sigma(X)$ | standard deviation of Gaussian distribution for X <i>OR</i> |
| <i>OR</i> 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 | $R\sigma$ | include ONLY if LTYP =21, multiplies I(Q) by Lorentz term, as for MODEL 28, pushes scattering up from Q^{-2} towards Q^{-4} at small Q. |

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

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) (2014) 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, $(R2-R1)=2*\lambda*R_{mid}$ (See example file in Appendix B) |
| NCON=4 | $V(J) = (1.0-V(K))*V(L)$ used for $R1=(1-\lambda)*R_{mid}$, $\lambda=(R2-R1)/(R1+R2)$ |
| 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 $V(J) = A*V(K) + B*V(L) + C*V(M) + D*V(N) + E*V(M) + F*V(O) + G*V(P)$
- 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 $V(J) = A \cdot V(K) / (B + C \cdot V(L))$ [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 $V(J) = \{V(K) - V(L)\} \cdot V(M) + \{V(N) - V(O)\} \cdot V(P) + \{V(Q) - V(R)\} \cdot V(S)$

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:

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

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.

LSOFILE (MODEL FILE) FORMAT

This file may contain a number of model descriptions and is read sequentially in the same way as the DATAFILE. If the model was generated using the FF command in the interactive FIT routine then it will contain exact parameter values to enable the calculation to be repeated at a later date. Estimated standard deviations are also included for reference, though these are not of course required as input. These and other **non-necessary parameters are included in brackets** below. Other control records decide the sort of fitting procedure to be followed and whether any of the parameters are fixed or constrained in some way.

Records for each model description, with their FORTRAN input formats and variable names are as follows:

- (i) (5(2X,I3)) NT number of title records (max 4)
 NP number of parameter records (max 64, 40 refining)
 (NS) number of data sets - see (v) (max 3)
 NC number of constrained parameters - see (vi) (max 6)
 NN number of numerical constants - see (vii) (max 24)

- (ii) (17(3X,I2)) IW weight function 0 - unit weights, 1- $1/(\text{error}^2)$, 2- $1/\text{data}$ (K1=0 or 1 or 2 in interactive FIT)
 IK type of fit 0 - normal least squares
 1 - Marquardt method (K2=0 or K2=1 in interactive FIT)
 IP 1- include predicate observations, 0- none
 MS miss data, use every MS'th point in earlier cycles of slow calculations (use K4=n in FIT).
 (IY) used internally 1- polydisperse refining

The following four integers were removed from the program in April 1993, when a more general set up for numerical integration schemes was introduced. So now use K6 = 1 or K7=1 to re-initialise all integration schemes. Nov. 2000 version introduced K8=1 to exclude $\beta(Q)$ correction to S(Q). For compatibility with older data sets this is ignored on input (FISH gives a reminder) so will have to be set again in FIT.

- (ignored - was METH was model 6 Q)
 (ignored - was METH2 was model 6 , R)
 (XB set 1 to exclude $\beta(Q)$ correction to S(Q))
 (ignored - was METHELL)
 (LS(1)...LS(4)) spare- used by POLCAL etc.
 (NPRED) number of predicate observations
 (NDAT) number of normal observations
 (NYC) cycle or iteration number
 (NPR) number of refining parameters

- (iii) (80A1) ((LCOM(I,J)),I=1,80),J=1,NT), NT title records

- (iv) (3I3,3A4,E14.6,E13.3,F6.1,E10.2) Model description records for each of NP

parameters, see next section for how to use them:

- (I) running number 1...NP on output
 LM(i) model number
 LTyp(i) parameter number
 LPAR(J,i),J=1,3 label for parameter
 V(i) value of parameter
 (ESD(i)) standard deviation on output
 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 $\sigma_r/rbar$.

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.