Small Angle Scattering data analysis for dense polydisperse systems: the FLAC program

Flavio Carsughì¹, Achille Giacometti² and Domenico Gazzillo³

¹Facoltà di Agraria, Università di Ancona and INFM Unità di Ancona, Via Brecce Bianche, I-60131 Ancona, Italy
²Dipartimento di Scienze Ambientali, Università di Venezia, and INFM Unità di Venezia, S.Marta 2137, I-30123, Venezia, Italy
³Dipartimento di Chimica Fisica, Università di Venezia, and INFM Unità di Venezia, S.Marta 2137, I-30123, Venezia, Italy

Abstract

FLAC is a program to calculate the small-angle neutron scattering intensity of highly packed polydisperse systems of neutral or charged hard spheres within the Percus-Yevick and the Mean Spherical Approximation closures, respectively. The polydisperse system is defined by a size distribution function and the macro-particles have hard sphere radii which may differ from the size of their scattering cores. With FLAC, one can either simulate scattering intensities or fit experimental small angle neutron scattering data. In output scattering intensities, structure factors and pair correlation functions are provided. Smearing effects due to instrumental resolution, vertical slit, primary beam width and multiple scattering effects are also included on the basis of the existing theories. Possible form factors are those of filled or two-shell spheres.

PROGRAM SUMMARY

Title of program: FLAC

Catalogue identifier:

Program obtainable from: CPC Program Library, Queen’s University of Belfast, N. Ireland

Computer: Digital Workstation AU 433 (128 Mb RAM), Pentium I MMX 200 MHz (64 Mb RAM), Macintosh Powerbook G3 400 MHz (192 Mb RAM)
Operating systems: Digital UNIX 4.0E, Windows NT service pack 4, Mac OS 9.0.2

Programming language: Fortran 77

Memory required to execute with typical data: 640 kwords

No. of bits in a word: 32

No. of lines in distributed program, included test data, etc.: 6873; of which 1304 are routines of the Harwell Subroutine Library (HSL) library and their use must be acknowledged in any paper publishing results obtained by FLAC. The entire code must be linked with the International Mathematical Statistical Libraries (IMSL) library. An example of the input file flac.dat is also available (94 lines) together with 11 files *.com where common definitions are found (331 lines) and a file (flac.par) containing the parameters used for dimensioning the arrays (7 lines).

Additional keywords: Small-Angle Scattering, Hard Spheres, Polydispersity, Percus-Yevick, Mean Spherical Approximation.

Nature of physical problem: The problem is the calculation of the Scattering Cross Section in Small-Angle Scattering of polydisperse neutral and charged hard spheres. Both dense or dilute systems are considered.

Method of solution: The algorithms implemented here are obtained by solving the Orstein-Zernike integral equations within the Percus-Yevick or mean spherical approximation closures for neutral or charged hard spheres, respectively [1,2].

Restriction on the complexity of the problem: Only hard sphere (neutral or charged) potentials are used.

Typical running time: A test run considers 200 points for defining the size distribution function and calculates the Scattering Cross Section over $2^{13}$ points, without any smearing effects. For neutral hard spheres, on a DIGITAL Workstation AU 433 this test takes 7.7 s, while on the Macintosh and on the PC 26.1 and 49.6 s, respectively. On including instrumental smearing considering only one experimental configuration (by convoluting over 11 points) the CPU time on the DIGITAL Workstation AU 433 increases up to 46.8 s; if multiple scattering correction is also taken into account (by using $2^{7}$ points for the 2D
Fourier transform), the CPU time is 47.3 s. Furthermore, the addition of a vertical slit (sampled by $2^6$ points) requires 270.1 s of CPU time. For charged hard spheres, the calculation without any correction takes 12.1 s of CPU time.

References

[1] A.Vrij, J. Chem. Phys. 69, 1742 (1978); 71, 3267 (1979).
[2] D. Gazzillo, A. Giacometti and F. Carsughii, J. Chem. Phys. 107, 10141 (1997).

LONG WRITE-UP

1 Small Angle Scattering

Small Angle Scattering (SAS) is sensitive to the presence of structural and chemical inhomogeneities inside the systems, which behave as scattering entities. Here and in the program, we shall refer to these entities as *scattering particles* whenever they do not bear a charge and *macroions* otherwise. In the latter case a set of smaller scattering cores (*counterions* with opposite charge) are clearly present to satisfy electroneutrality.

Polydispersity means that the particles are not all identical but their size, charge or other properties exhibit a large variety of values (a phenomenon commonly found, for instance, in colloidal and micellar suspensions). Hence in presence of polydispersity SAS intensity may greatly differ from that of monodisperse systems. The aim of the present paper is to present a code (FLAC) which can be used in the analysis of experimental data of small-angle neutron scattering from polydisperse systems. The FLAC program provides the scattering functions from polydisperse fluids of neutral [1] or charged hard spheres [2], based on the analytical solutions of the Ornstein-Zernike (OZ) integral equations within the Percus-Yevick (PY) or the mean spherical approximation (MSA) closures, respectively [3]. For the sake of clarity and in order to be self-contained, general formulas appearing in the SAS theories will now be briefly recalled.

1.1 General Equations for polydisperse systems

The most general expression of the SAS is [4]

$$\frac{d\Sigma}{d\Omega}(\mathbf{q}) = \frac{1}{V} \left\langle \left| \int_V d\mathbf{r} \rho(\mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}} \right|^2 \right\rangle.$$  \hspace{1cm} (1)
Here \( \frac{d\Sigma}{d\Omega}(q) \) is the macroscopic differential coherent Scattering Cross Section (SCS) as a function of the exchanged wave vector \( q \), whose magnitude is defined by

\[
q = \frac{4\pi}{\lambda} \sin \theta
\]  

(2)

where \( \lambda \) is the neutron wavelength and \( 2\theta \) the full scattering angle. In Eq. 1, the integral is extended over the total sample volume \( V \), \( r \) is the position vector and \( \rho(r) \) the local scattering length density. For X-rays, the scattering length density is replaced by the electron density, leaving the general formalism unchanged. The angular brackets \( \langle \cdots \rangle \) represent an ensemble average over all possible positions and orientations of the particles in the system.

In the absence of long range order, the scattering length density can be thought as having a uniform value \( \rho_0 \) on which fluctuations \( \delta \rho(r) \) are superimposed. The distribution of scattering material inside a particle of species \( i \) is then defined by its form factor

\[
B_i(q) = \frac{1}{f_i} \int_{V_i} d\mathbf{r} \, \delta \rho(\mathbf{r}) \, e^{i\mathbf{q} \cdot \mathbf{r}},
\]

(3)

where

\[
f_i = \int_{V_i} d\mathbf{r} \, \delta \rho(\mathbf{r})
\]

(4)

is the scattering amplitude at zero-angle, and \( V_i \) is the volume of the scattering core (i.e. the subregion of a macroparticle which contains the scattering material: nuclei, etc.). Often it proves convenient to combine Eq. 3 and 4 as

\[
F_i(q) = f_i B_i(q).
\]

Let us assume that the polydisperse system can be regarded as a mixture with \( p \) components. By introducing an effective form factor \( P(q) \) as

\[
P(q) = \sum_{i=1}^{p} n_i f_i^2 |B_i(q)|^2,
\]

(5)

one can also define an effective structure factor \( S(q) \) of the mixture by rewriting Eq. 1 in the form

\[
\frac{d\Sigma}{d\Omega}(q) = P(q) S(q).
\]

(6)
Here, \( P(q) \) accounts for the distribution of scattering matter inside the particles, while \( S(q) \) is related to the particle-particle interactions and the resultant equilibrium structure of the system, and it is defined through Eq. (6).

### 1.2 Isotropy

If the particle-particle interactions are spherically symmetric (homogeneous and isotropic fluids), then the SCS can be cast into the Fournet-Vrij's form [1]:

\[
\frac{d\Sigma}{d\Omega}(q) = \sum_{i=1}^{p} n_i f_i^2 \left[ \left\langle |B_i(q)|^2 \right\rangle_\omega - \left| \left\langle B_i(q) \right\rangle_\omega \right|^2 \right] 
+ \sum_{i,j=1}^{p} \sqrt{n_i n_j} f_i f_j \left\langle B_i(q) \right\rangle_\omega \left\langle B_j^*(q) \right\rangle_\omega S_{ij}(q),
\]

where \( n_i \) is the number density of species \( i \) and the brackets \( \langle \cdots \rangle_\omega \) represent angular averages (this formula being still valid in case of non-spherically symmetric particles). The \( S_{ij}(q) \) are the Ashcroft-Langreth partial structure factors [5], defined by

\[
S_{ij}(q) = \delta_{ij} + \sqrt{n_i n_j} \tilde{h}_{ij}(q),
\]

where \( \delta_{ij} \) is the Kronecker delta and \( \tilde{h}_{ij}(q) \) is the three-dimensional Fourier transform of the total correlation function \( h_{ij}(r) \), which can be obtained by solving the OZ integral equations of the liquid state [3].

The first term on the rhs of Eq. 7 is called the “incoherent” part, and the remainder the “coherent” one. The incoherent part vanishes if the distribution of scattering matter is spherosymmetric and in this case

\[
\left\langle B_i(q) \right\rangle_\omega = \left\langle B_i^*(q) \right\rangle_\omega \equiv B_i(q)
\]

### 1.3 Two-Phase Model

Fortunately, for most of the investigated systems the particles are formed by a single type of uniform scattering material (first phase = solute) and are embedded in a uniform medium (second phase = solvent for a solution, or matrix for an alloy). In this case, \( \delta \rho(r) \) in Eq. 3 can be replaced by \( \Delta \rho = \rho_p - \rho_o \), where \( \rho_p \) and \( \rho_o \) are the scattering length density of the scattering particles and the embedding medium, respectively.
Thus the zero-angle scattering amplitude (Eq.4) is given by

\[ f_i = \Delta \rho \, V_i \quad (10) \]

and the form factor \( B_i(q) \) (Eq. 3) becomes

\[ B_i(q) = \frac{1}{V_i} \int \frac{d^3r}{V_i} \, e^{i\mathbf{q} \cdot \mathbf{r}} \quad (11) \]

### 1.4 Spherical scattering cores

In this case, Eq. 7 takes the simple form

\[ \frac{d\Sigma}{d\Omega}(q) = (\Delta \rho)^2 \sum_{i,j=1}^{p} \sqrt{n_i n_j} \, V_i \, V_j \, B_i(q) \, B_j(q) \, S_{ij}(q) \quad (12) \]

Then the effective structure factor can be expressed in terms of partial structure factors as

\[ S(q) = \frac{\sum_{i,j=1}^{p} \sqrt{n_i n_j} \, F_i(q) \, F_j(q) \, S_{ij}(q)}{\sum_{i=1}^{p} \, n_i \, F_i^2(q)} \quad (13) \]

The \( B_i(q) \) can be calculated analytically with the result

\[ B_i^*(q, R_i) = 3 \frac{j_1(q R_i)}{q R_i}, \quad (14) \]

where \( R_i \) is the scattering core radius of a particle of species \( i \), and \( j_1(x) \equiv (\sin x - x \cos x)/x^2 \) is the first-order spherical Bessel function. In general, \( R_i \leq R^H_i \), with \( R^H_i \) being the hard sphere radius of the \( i \)-th particle. Clearly, \( F_i^*(q, R_i) = \Delta \rho \, V_i \, B_i^*(q, R_i) \).

### 1.5 Hollow spheres

In the case of micelles or in the presence of a depletion zone around a precipitate, the scattering particles can be thought as a two-shell spheres, characterized by an inner core and an outer shell with different scattering length (or electron) densities. Even in this case the form factor \( F_i(q) \) has a relatively simple form

\[ F_i(q, R_{i1}, R_{i2}) = (\rho_1 - \rho_2) V_{i1} \, B_i^*(q, R_{i1}) + (\rho_2 - \rho_0) V_{i2} \, B_i^*(q, R_{i2}), \quad (15) \]
where \( R_{i1} \) and \( R_{i2} \) are the radii of the inner and outer shell, respectively, \( V_{im} \equiv 4\pi R_{im}^3/3 \) \((m = 1, 2)\) and \( \rho_0 \), \( \rho_1 \) and \( \rho_2 \) are the scattering length (or electron) density of the solvent, of the inner and the outer shell, respectively.

1.6 Smearing effects

Experimental data are in general plagued by several effects which might affect the scattering intensity, as compared to the theoretical one, and hence may lead to an incorrect interpretation. Most of them have been well studied and the way of controlling them is now well established. The instrumental resolution (i.e. the incident radiation wavelength spread, the finite collimation and the detector resolution) together with the radial average of the SAS data performed when isotropic data are collected on a 2D detector can be computed following the recipe given in Ref. [6], where each effect is described by a gaussian contribution, which is also used to model the primary beam for the beam width effect [4]. The vertical slit effect is also taken into account in the calculation, as described in Ref. [4]; this correction becomes relevant for slit systems and double crystal diffractometers. Finally, possible corrections due to multiple scattering are also calculated using the MUX routine [7], which is based on the theory developed in Ref. [8]. Since SAS experiments are performed with more instrumental configurations in order to scan the largest possible \( q \) range, up to three different setups are considered during smearing of the scattering intensities.

1.7 Backgrounds

Two different types of background are considered in FLAC. A flat incoherent one, like a plateau on which the small angle scattering intensity is superimposed, and the Porod one. The latter is due to the asymptotic scattering of large inhomogeneities and can be approximated as [4]

\[
\frac{d\Sigma^{\text{Porod}}}{d\Omega}(q) \approx k_P \ q^{-4}
\]

where \( k_P \) is the Porod constant.
2 Interparticle potential

As often reported in the literature (see e.g. Ref. [9]), the hard sphere radius \( R_{HS}^i \) of a particle need not coincide with the radius \( R_i \) of its scattering core. To include this possibility, the ratio \( s \equiv R_{HS}^i / R_i \) can be tuned in the program.

### 2.1 Neutral hard spheres

For neutral hard spheres, the interparticle potential \( V_{ij}(r) \) is described as

\[
V_{ij}(r) = \begin{cases} 
+\infty & \text{for } r < R_{ij}^{HS} \\
0 & \text{for } r > R_{ij}^{HS}
\end{cases}
\] (17)

where \( R_{ij}^{HS} \equiv (R_{HS}^i + R_{HS}^j) \). The OZ equations for an hard sphere mixture can be solved by using the PY closure. A closed-form for the SAS intensity for polydisperse hard sphere fluids was obtained by Vrij [1]. Our code for this part is constructed along the lines of that reference.

### 2.2 Charged hard spheres

In the case of charged hard spheres, the interparticle potential \( V_{ij}(r) \) takes the following form

\[
V_{ij}(r) = \begin{cases} 
+\infty & \text{for } r < R_{ij}^{HS} \\
e^2 z_i z_j / (\varepsilon r) & \text{for } r > R_{ij}^{HS}
\end{cases}
\] (18)

where Coulombic (attractive and repulsive) interactions are added to the previous neutral case, \( e \) being the elementary charge, \( z_i \) the valence of the \( i \)-th species and \( \varepsilon \) the dielectric constant of the solvent. This potential defines the Primitive Model of ionic fluids [3]. The MSA analytical solution of the OZ equations for this model allows to write a closed-form for the SAS intensity of polydisperse ionic fluids [2]. We assume that polydispersity is associated to macroions, whereas counterions are monodisperse. The electroneutrality condition, necessary to have a stable system, then reads:

\[
\sum_{i=1}^{p} n_i z_i + n_c z_c = 0,
\] (19)
where $n_c$ and $z_c$ are the number density and charge of the counterions, respectively.

3 Program description

3.1 General

The FLAC program is able to calculate the SCS of neutral or charged polydisperse hard spheres. In both cases FLAC also provides the result corresponding to non-interacting spheres (i.e. $P(q)$). The scattering density can correspond either to a filled or to a two-shell hollow sphere. These models are suitable for a large variety of physical systems, among which colloids and mycelles.

FLAC can work in two different modes: 1) it can provide the theoretical calculation of the scattering function, given a set of $q$ (experimental or simulated) values; 2) it can fit experimental data by using the two models described above.

The first mode is particularly useful to gauge the input parameters as a starting point for the fit. This is governed by the $ifit$ flag and it will described in detail below.

The filenames to be used are handled in the subroutine $file\_name$ and the proper input data are read by using the subroutine $read\_data$. Subsequently, the subroutine $control$ checks the consistency of the input values. If required, the definition of the smearing effects is worked out before the start of the calculation of the SCS in the $fres\_prep$ subroutine. The VA05AD routine of the Harwell Subroutine Library (HSL) [10] needs the definition of the functional to be minimized in the $calfnf$ subroutine and the statistical errors are estimated in the $kovafd$ routine developed at the Institut für Festkörperforschung of the Forschungszentrum Jülich, Germany. In input FLAC requires a set of physical parameters (average size of the particles, volume fraction, etc) plus the parameters of the distribution. In addition to the two parameters of the distributions considered here (Gaussian, Schulz, Weibull and log-normal) a parameter for the normalization is also required. We remark, however, that these three parameters are actually computed in terms of the above physical parameters. For each $q$ value, the intensity is calculated by using the subroutine $intensity$, where the proper model is selected. At this stage, the Porod background is considered. In sequence, the corrections due to instrumental smearing effects, vertical slit and multiple scattering are performed. Since a flat background does not alter any of the previous corrections, the incoherent background is added at the final stage. During the fit, a file called $*.int$ (see
below) is output at each iteration, for a clearer control of the convergence of the numerical procedure. Upon convergence, FLAC estimates the errors in the physical quantities and reorganizes the data for the output files.

3.2 Input/Output description

At the initial stage FLAC requires a filename interactively and then it sets up input and output filenames by appending the proper extension to this filename. A short description of each extension is reported below along with the meaning of all the files. We note that only the *.dat (containing the various parameters) is strictly necessary for running FLAC, the experimental data in *.ex1, *.ex2 and *.ex3 being necessary only in the case of fit. In this case the three files refer to experimental data obtained at three different experimental configurations that are then assembled together into a single array. All the other output files are created by FLAC.

The quantities contained in each file are organized in columns whose labels are reported in brackets (used here for clarity and not appearing in the file) and have their meaning written underneath.

**Input files:**

*dat*: general input data

*ex1, ex2, ex3*: experimental data (Q I E) of data collected in different instrumental configurations. This file is required only in case of fit.

Q: Scattering vector \( q \) (Å\(^{-1}\))
I: Experimental intensity (cm\(^{-1}\))
E: Experimental uncertainty (cm\(^{-1}\))

**Output files:**

*res*: General results

*int*: Calculated quantities (Q E D C B A)

A: Theoretical model + Porod background + instrumental resolution (cm\(^{-1}\))
B: A + slit effect (cm\(^{-1}\))
C: B + incoherent background (cm\(^{-1}\))
D: C + multiple scattering (cm\(^{-1}\))
E: D + random error (simulation) / experimental data (fit) (cm\(^{-1}\))
Q: Scattering vector \( q \) (Å\(^{-1}\))

*teo*: Calculated quantities (Q D C B A)
A: Effective structure factor
B: Effective form factor (cm$^{-1}$)
C: Theoretical model (cm$^{-1}$)
D: C + Porod background (cm$^{-1}$)
Q: Scattering vector $q$ (Å$^{-1}$)

gen: Calculated quantities on different $q$ range than the experimental one ($Q_{calc}$ C B A). This file is generated only in case of fit.
A: Effective structure factor
B: Effective form factor (cm$^{-1}$)
C: Theoretical model (cm$^{-1}$)
Q: Scattering vector $q_{calc}$ (Å$^{-1}$)

fon: Backgrounds (Q P F)
F: Flat incoherent background (cm$^{-1}$)
P: Porod background (cm$^{-1}$)
Q: Scattering vector $q_{calc}$ (Å$^{-1}$)

nr: Scattering particles (or scattering cores) and hard sphere size distributions (R A B D M N)
R: Scattering particle radius (Å)
A: Scattering particle size distribution (cm$^{-4}$)
B: Error of A (cm$^{-4}$)
D: Hard sphere diameter (Å)
M: Hard sphere size distribution (cm$^{-4}$)
N: Error of M (cm$^{-4}$)

gr: Pair correlation function (R G)
R: Distance from the center of a particle (Å)
G: Pair correlation function

We note that at the beginning of the calculation FLAC transforms all dimensional quantities in suitable powers of Å so that all calculations are performed in such units. In the final output all quantities are then restored to their original more convenient units.

3.3 Detailed description

All relevant parameters are to be specified in *.dat file. First, the spatial range ($r_{min}$ and $r_{max}$) of the size distribution function associated to polydispersity and its number of points (num_points_int) are required. For simplicity, the number of input points is given in powers of 2 throughout the code. Hence, for instance, $2^{\text{num\_points\_int}}$ is the actual number of points of the distribution function. The mesh size in reciprocal space $\Delta q$ is computed from the range extension ($q_{min}$ and $q_{max}$) and the corresponding number of points (num_points).
The instrumental resolution (for wavelength band and finite collimation), detector, radial average and beam width effects are controlled by separate flags: ires1, ires2, ires3, ires4 and ires5, respectively. The number of points for the convolution (nfold), the radii of source (r1) and the sample (r2) slits, source-sample (r11) and sample-detector (r12) distances, the wavelength (rlam) and its band (dlam), the spatial resolution of the detector (rdet), the sampling used for radial average (rrav), the FWHM of the primary beam (sbeam) and the total number of experimental configurations nconf have to be provided and they will be used only if these corrections are considered in the calculation. Note that r11 and r12 are arrays because of the different experimental configurations (maximum 3) considered in this analysis. For the vertical slit, the flag (isl), the number of points (nsl) used and the maximum q value (tmax) are considered as input parameters. The correction for multiple scattering is controlled by a flag (ims), and it requires the sample thickness (thick) and the number of points to be used for the 2D Fourier transform (nft); for this calculation, FLAC is exploiting the IMSL routines [11].

The data for the fitting routine (VAO5AD) of the HSL are also input parameters: the step increment (h), the maximum excursion (dmax) and the accuracy (acc) of the numerical calculation can be gauged at will. Moreover, the maximum number of iterations (maxfun) as well as the output form (iprint) can be also varied (in this last option, a customized option for a better visualization of the evolution of the fit parameters, is also possible). In the general part of the input data, one finds the main flag (ifit), which discriminates between the simulation of a theoretical curve or the fit of an actual set of experimental data (ifit = 1). In the first case the theoretical scattering functions are provided either for a generic range of q (ifit = 2) or for a specific set of experimental q values (ifit = 0). This latter case is particularly useful to find a proper starting set of parameters for the best fit analysis.

For both the fit and the simulation of experimental data, one should define the first (n1) and the last point (n2) of each experimental scattering intensity file to be used and another flag indicating whether the experimental data also include the experimental uncertainty (ierr). Note that also n1 and n2 are arrays like r11 and r12. For simulated data, a random error can be introduced in the calculated intensity and err_int is the bandwidth where the intensity can be randomly shifted using a uniform random number generator controlled by the input variable iseed. A weighted fit can be chosen with ipes as well as the backgrounds (flat and Porod ones), which are regulated by two flags: ifin and ipor, respectively. The flat background can be considered as it stands or it may take into account the volume fraction of the scattering particles; this case is particularly useful for highly concentrated systems.

The choice of the size distribution function (idist) allows four different functions: Gaussian, Schulz, Weibull and log-normal. Calculations for concentrated
or dilute systems can be controlled by the inter flag. The form factors of the scattering particles can be chosen between the one- and two-shell spheres by iff. For charged hard spheres, the counterions charge \( z_c \) and the Bjerrum length \( L_B \) defined by

\[
L_B = \frac{e^2}{k_B T \varepsilon}
\]

are to be given. Here \( k_B \) is the Boltzmann constant, \( T \) the absolute temperature, \( e \) the unit charge and \( \varepsilon \) the dielectric constant.

Finally a set of \( n \leq 13 \) physical parameters are provided for the calculation, each one with its own flag, describing whether its value is kept pinned to that given in the input data file (corresponding flag=0 ), left free for the optimization (corresponding flag = 1) or fixed to a value given in an external file \(*.res\) produced as output by FLAC (corresponding flag = 2). These parameters are the volume fraction \( x_f \), the average radius \( x_c \) of the scattering particles (in the case of a two-shell sphere, this correspond to the outer shell radius) and the dispersion \( x_d \) of the particle size; for monodisperse systems \( x_d \) must be set to 0. A condition we have used in our calculation is that the hard sphere radius must be larger or equal to the outer dimension of the scattering particle; \( x_s \geq 1 \) then represents the ratio between the hard sphere radius and the outer dimension of the scattering particles. The Porod constant \( x_p \) and the flat background \( x_{fo} \) are required and might also be optimized. The differences of scattering length densities between the outer and inner shell \( x_b \), between the outer shell and the solvent for the scattering particles (macroions) \( x_{con} \) and between the counterions and the solvent \( x_{con1} \) are also necessary for the calculation. The thickness of the outer shell for two-shell spheres is set by the variable \( x_a \) and \( x_z \) represents the charge associated to the macroions with sizes equal to the average of the distribution. Finally, a scaling factor \( x_k \) is necessary when data are not available in absolute units. At the end of the input file, the name of the external file where some data have to be used is also requested. All the input data are tested for non-appropriate values.

All adopted distribution functions depend upon three parameters. For three distributions (Gaussian, Schulz and log-normal), they can be analytically computed from the knowledge of the volume fraction, the mean radius and the polydispersity index (dispersion) which is a measure of the strength of polydispersity and whose definition can be found in Ref [12]. In the Weibull case, the lack of a one-to-one correspondence in the analytical expression enforces a numerical self-consistent procedure. All the \( n \) physical parameters to be optimized are constraint to be positive, apart from \( x_s \) which must be larger than 1 and \( x_b \) which can assume all real values. In the case of charged hard spheres, the population of counterions is determined by the electroneutrality condition and the value of the screening parameter \( \Gamma \) is computed iteratively using Eq. 50 of
The coherent transmission factor $T_{\text{coh}}$ is calculated by estimating the theoretical scattering cross section over a very wide interval in the $q$ space

$$T_{\text{coh}} = \exp \left\{ -D \left[ \frac{\lambda^2}{2\pi} \int dq \, q \, \frac{d\Sigma}{d\Omega}(q) \right] \right\},$$

where $D$ is the sample thickness and the term between square brackets represents the macroscopic coherent scattering cross section $\Sigma$ under the approximation of isotropic scattering, i.e. the integral of the differential one over the solid angle. This transmission factor is an indicator of the multiple scattering probability: the higher $T_{\text{coh}}$, the smaller is the multiple scattering probability. This effect is incorporated in FLAC, by the use of the MUX routine [7]. The output of the routine is adapted to the experimental $q$ grid by using linear interpolation, with the exclusion of the last point which is obtained by extrapolation. The structure factor for a system containing monodisperse counterions and macroions can also be computed with the charged monodisperse option. In this case the scattering is reduced to the sum of 4 terms, corresponding to a $2 \times 2$ matrix.

The average pair correlation function $g(r)$ is calculated by using the real space mesh size $\Delta r$ determined directly from the one in reciprocal space by using the standard relation $\Delta r = \pi/(N \, \Delta q)$, where $N$ is the number of points $\text{num\_points}$, and it exploits a standard Fast Fourier Transform (FFT) algorithm.

### 3.4 Compilation

FLAC must be placed in the same directory of the files containing the parameters (flac.par) and the common definitions (distribution.com, flag.com, general.com, ggc.com, intensity.com, library.com, names.com, parameters.com, points.com, quantities.com and smearing.com) and it must be linked with IMSL library [11].

### 4 Experiment

In order to illustrate the practical use of FLAC, we provide, along with the code, a set of so far unpublished experimental data collected, by us, at the point geometry KWSI diffractometer at the FZJ in Jülich, Germany, on silica particles in hydrogenated water. Samples have been prepared from commercial...
Ludox HS30 at the nominal volume concentration of 16.5%. The measurements have been performed by using 4.56 Å neutrons with a wavelength band of about 20% and the data have been collected with three different experimental configurations, i.e. sample-to-detector and collimation distance equal to 14, 4 and 1.2 m, in order to investigate the largest possible q range [13]. The samples were contained in quartz cell of 2 mm thickness, the multiple scattering being then not negligible. Hence, we have performed the data analysis by using the neutral one-level hard sphere model with 6 free parameters, i.e. the volume fraction, the average radius, the dispersion of the size distribution function, the hard sphere factor, the incoherent background and the contrast. The Weibull size distribution function has been selected in the present case. We have optimized the free parameters by including in the calculation also the smearing due to the wavelength band, different finite collimations and multiple scattering. In Fig.1, experimental data collected at three different instrumental configurations are depicted together with the theoretical scattering cross section, the incoherent scattering, the effective form factor and the smeared scattering cross section. Error bars are smaller than the size of the symbols and hence are not displayed. The agreement between experimental data and calculated cross section is excellent and the physical parameters shown in Tab. 1 are well representative of the system. The coherent transmission $T_{\text{coherent}}$ is relatively high, showing that the coherent multiple scattering does not play a major role in this sample. A nominal value of the scattering contrast of commercial Ludox HS30 has been estimated to be about $4 \times 10^{10}$ cm$^{-2}$, in good agreement with our optimized value.

**Acknowledgments**

The Italian MURST (Ministero dell’Università e della Ricerca Scientifica e Tecnologica), the INFN (Istituto Nazionale per la Fisica della Materia) are gratefully acknowledged for financial support. We thank Raffaele Della Valle for a critical reading of the manuscript. The authors are indebted to the HSL management for the free use of the routines, and to the computing group of the Institut für Festkörperforschung of the Forschungszentrum Jülich, Germany, for their assistance during the preparation of this work. The DuPont Company is also gratefully acknowledged for providing the Ludox HS30 material.

**References**

[1] A. Vrij, J. Chem. Phys. 69, 1742 (1978); 71, 3267 (1979).

[2] D. Gazzillo, A. Giacometti and F. Carsughi, J. Chem. Phys. 107, 10141 (1997).

[3] J. P. Hansen and I. R. McDonald, *The Theory of Simple Liquids*, Academic Press, London (1986).
[4] O. Glatter, in *Small Angle X-ray Scattering*, Eds. O. Glatter and O. Kratky, Academic Press, London (1982).

[5] N.W. Ashcroft and D.C. Langreth, Phys. Rev. 156, 685 (1967).

[6] J. S. Pedersen, D. Posselt and K. Mortensen, J. Appl. Cryst. 23, 321 (1990).

[7] M. Monkenbusch, J. Appl. Cryst. 24, 955 (1991).

[8] J. Schelten and W. Schmatz, J. Appl. Cryst. 13, 385 (1980).

[9] J. S. Pedersen, Phys. Rev. B47, 657 (1993).

[10] Harwell Subroutine Library, Release 11, AEA Technology (1993).

[11] IMSL, Fortran routines, Visual Numeric (1994).

[12] B. D’Aguanno and R. Klein, J. Chem. Soc. Faraday Trans. 87, 379 (1991).

[13] F. Carsughi, A. Giacometti and D. Gazzillo unpublished.
FIGURE CAPTIONS

Fig.1: Best fit of commercial Ludox HS30 with neutral one-level hard sphere. The experimental data collected at 14, 4 and 1.2 m are shown together with the theoretical intensity, the effective form factor, the incoherent background and the best fit obtained by smearing for the wavelength band, the finite collimation at different instrumental configurations and the multiple scattering.
Table 1

Physical parameters obtained by the best fit with a Weibull size distribution function of the commercial Ludox HS30. The parameters optimized by the best fit procedures are: $C_v$ the volume fraction, $\bar{R}$ the average radius, $\xi$ the dispersion of the size distribution function, $HS$ the ratio of the radii of the hard sphere and the scattering particle, $IB$ the incoherent background, $\Delta \rho$ the scattering contrast. Moreover, $N_p$ the scattering particle density and $S_p$ the specific surface are then calculated. The coherent transmission $T_{\text{coherent}}$ is also estimated.

| Parameter | Unit | Value |
|-----------|------|-------|
| $C_v$     | (%)  | 20.3±0.7 |
| $\bar{R}$ | (Å)  | 81.1±0.7 |
| $\xi$     | (%)  | 20.7±0.7 |
| $HS$      |      | 1.22±0.01 |
| $IB$      | (cm$^{-1}$) | 0.954±0.003 |
| $\Delta \rho$ | (cm$^{-2}$) | 3.43±0.05·10$^{10}$ |
| $N_p$     | (cm$^{-3}$) | 8.1±0.3·10$^{16}$ |
| $S_p$     | (cm$^{-1}$) | 6.9±0.3·10$^{5}$ |
| $T_{\text{coherent}}$ | (%) | 92.9 |
