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Structure and interaction in dense colloidal systems: evaluation of scattering data by the generalized indirect Fourier transformation method

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Abstract

The generalized indirect Fourier transformation (GIFT) technique is a versatile tool for the evaluation of small angle scattering data. It does not depend on models for the size and shape of the particles and requires model assumptions only for the interaction effects that are typically not as sensitive to the details of the assumptions. We review here the development of the technique from its inception, focusing on the included interaction models for hard, charged and attractive spheres, and lamellae. A considerable number of applications has also been reported ranging from surfactants, emulsions, microemulsions, food science, and ceramics to melts and block-copolymers.

1. Introduction

Small angle scattering of x-rays (Guinier 1939) and neutrons is an important tool for the investigations of structures (Guinier and Fournet 1955, Glatter and Kratky 1982, Feigin and Svergun 1987, Lindner and Zemb 1991, 2002, Brumberger 1995) in fields of research like life sciences, soft condensed matter and nanotechnology. Static light scattering is similar to these techniques in many aspects of theory and applications (van de Hulst 1981, Lindner and Zemb 1991, 2002). Therefore, it is of great interest to have good experimental equipment as well as powerful evaluation techniques for measured scattering data. Special care must be taken to consider the interaction effects during evaluation, because intra- and inter-particle effects influence the measured scattering patterns. The latter cannot be neglected unless the measured sample is very dilute. Dilution, however, can be technically impossible or may change the intra-particle structure, as in self-assembled systems (Kotlarchyk *et al* 1983). Evaluation techniques are needed that can handle interaction effects while simultaneously obtaining information on the individual particles.

In general the evaluation techniques can be distinguished into two groups: the approximation by predefined models for the particles on the one hand, and the model independent transformation of the scattering data into real space analogues on the other hand.

Model approximation starts with assumptions on the shape, internal structure and interactions of the particles. These assumptions are translated into mathematical expressions that describe the scattering behaviour of such a system. Finally, some parameters are varied to minimize differences between the model and the actual measured data. For a review on such model approximations see Pedersen (1997 or 2002). A comparison between model free and model based scattering data interpretation can be found in Pedersen (1999).

The transformation techniques typically aim at the pair distance distribution function (PDDF, $p(r)$) of the particles, which is related to the scattering intensity $I(q)$ by (Porod 1948)

$$I(q) = 4\pi \int_0^\infty p(r) \frac{\sin qr}{qr} dr \quad (1)$$

where q is the magnitude of the scattering vector. It is related to the scattering angle θ and the wavelength λ via $q = (4\pi/\lambda) \sin(\theta/2)$. Basically, $p(r)$ contains the same information as $I(q)$ since it is a unique transformation, but it has the advantage of being in real space, i.e. information on the structures can be read directly from the PDDF (Glatter 1979). It is also often simpler to identify the reason for differences between the actual PDDF and the PDDF calculated for a model than interpreting the discrepancies in reciprocal space. The design of realistic models is thereby facilitated.

The indirect Fourier transformation (IFT) technique (Glatter 1977a, 1977b, 1980a, 1980b, Moore 1980, Svergun *et al* 1988, Hansen and Pedersen 1991) is the method of choice to obtain the PDDF. It requires a minimum of *a priori* knowledge of the system, which can be of great value for an unbiased interpretation of the data. The model free approach is of limited value with regard to interacting systems, since in this case the model free PDDF contains the inter-particle contribution as well as the intra-particle contributions. This combination of features is often difficult to interpret, and makes a separation of intra- and inter-particle effects desirable, where the PDDF is just the transformed intra-particle component of the scattering curve. Such a $p(r)$ function could be interpreted in the same way as one obtained for dilute, non-interacting particles. Additionally, the separated inter-particle effects contain important, quantitative information about the system.

The generalized indirect Fourier transformation (GIFT) technique is such an extension of the IFT to take interaction effects into account. We want to review the development of this technique since its first introduction in 1997 (Brunner-Popela and Glatter 1997). The basic principle of the IFT will be recapitulated in section 2.1 as far as it is necessary to understand the GIFT, which will be presented in section 2.2. Section 3 will deal with models for interactions that are currently implemented in our GIFT software package. Applications will be discussed in section 4, and conclusions as well as the further directions of development will be given in section 5.

2. Principle

2.1. Indirect Fourier transformation

Following Glatter (1977a, 1977b) the IFT is based on one important assumption, namely that the $p(r)$ function can be represented as a sum of N basis functions $\varphi_\nu(r)$ up to a maximum dimension D_{\max} , as long as the basis functions are selected reasonably. Cubic B -splines have shown to be well suited for this task. These basis functions are Fourier transformed (Fourier 1808) by

$$\psi_\nu(q) = 4\pi \int_0^\infty \varphi_\nu(r) \frac{\sin qr}{qr} dr \quad (2)$$

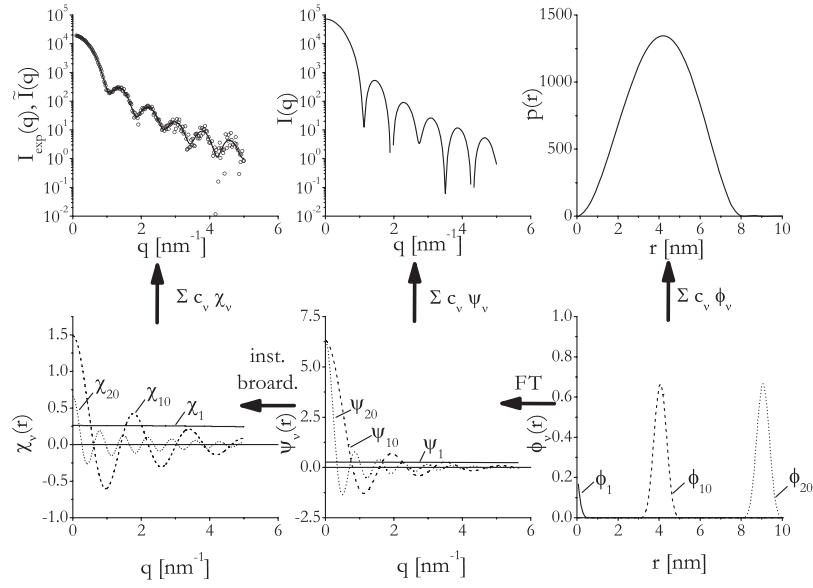


Figure 1. The direct way to obtain the PDDF (top right) function from the experimental $I_{\text{exp}}(q)$ (top left) would be to calculate a desmeared scattering curve (top centre) and to Fourier transform it. The difficulties of computing an adequate desmeared scattering curve and termination effect of the Fourier transformation inhibit this way. The IFT starts with a set of cubic B -splines (bottom right). They are Fourier transformed (bottom centre) and convoluted with instrumental broadening curves (bottom left). These transformed broadened splines are then approximated to the scattering curve. Since all transformations that are applied are linear, the coefficients obtained for the approximation can be used for the splines as well, resulting in the PDDF.

which is analogous to equation (1), where $p(r)$ is replaced with $\varphi_v(r)$. The sum of the transformed functions $\psi_v(q)$ represents the scattering intensity $I(q)$ measured with a theoretically perfect instrument. Instrumental broadening effects can be considered by smearing the functions $\psi_v(q)$, which results in a new set of functions $\chi_v(q)$. $\tilde{I}(q)$, the sum of these functions, can represent the actual measured scattering curve $I_{\text{exp}}(q)$. Therefore,

$$\begin{aligned}
 p(r) &= \sum_{v=1}^N c_v \varphi_v(r) \\
 I(q) &= \sum_{v=1}^N c_v \psi_v(q) \\
 I_{\text{exp}}(q) &\approx \tilde{I}(q) = \sum_{v=1}^N c_v \chi_v(q).
 \end{aligned} \tag{3}$$

The Fourier transformation resulting in $\psi_v(q)$ and the smearing transformations resulting in $\chi_v(q)$ are linear transformations, which guarantees that the factors c_v are the same for all the sums in equation (3). Therefore, it should be sufficient to solve the linear equation system linking $I_{\text{exp}}(q)$ in the measured q -range to the functions $\chi_v(q)$ to obtain the factors c_v , which define the function $\tilde{I}(q)$. These factors c_v can be used directly to calculate the desmeared scattering curve $I(q)$ and the PDDF from the sets of basis functions $\psi_v(q)$ and $\varphi_v(r)$ (figure 1). The corresponding condition for the equation system should be to minimize

the mean deviation L

$$L = \frac{1}{M} \sum_{i=1}^M \sqrt{\frac{\left(I_{\text{exp}}(q_i) - \sum_{v=1}^N c_v \chi_v(q_i)\right)^2}{\sigma^2(q_i)}} \quad (4)$$

where M is the number of measured points in the scattering curve and σ is the standard deviation of the experimental data points.

A modification of the equation system is necessary because it is a so-called ‘ill posed problem’, i.e. experimental uncertainties and the truncation of the scattering curve at low and high q values cause the obtained $p(r)$ function to oscillate around the true solution. If one links the value c_v to the coefficients of the neighbouring basis functions c_{v-1} and c_{v+1} in a way that a side condition should minimize the function

$$N_{c'} = \sum_{v=1}^{N-1} (c_{v+1} - c_v)^2 \quad (5)$$

simultaneously with condition (4), one can eliminate these oscillations. Therefore, one has to solve the problem

$$(L + \lambda N_{c'}) = \min \quad (6)$$

where the Lagrange multiplier λ determines the relative importance of the side condition. The correct Lagrange multiplier λ_{opt} can be determined by a Lagrange multiplier variation. L is low and $N_{c'}$ is nearly constant for the Lagrange multipliers close to λ_{opt} (Glatter 1977a, 1977b). It should be noted that the experimental uncertainty of a constant background can be handled in terms of a delta function added to the splines at $r = 0$ (Hansen and Pedersen 1991).

The solution of the stabilized equation system results not only in the PDDF, but it contains also the desmearing of the experimental scattering curve. This is the case since the sum of $c_v \psi_v(q)$ is the scattering curve $I(q)$ without any instrumental broadening effects.

It should be mentioned that the cross section $I_c(q) \propto I(q)/q$ and thickness $I_t(q) \propto I(q)/q^2$ functions of cylinders and lamellae can also be used for the IFT. There, the $\sin(qr)/(qr)$ function in equation (1) is replaced by a zeroth order Bessel function $J_0(qr)$ for cylinders and by $\cos(qr)$ for lamellae. The procedure thereafter is the same as for particulate systems and results in a cross section $p_c(r)$ or a thickness $p_t(r)$ function that can be interpreted in the same way as a standard PDDF (Glatter 1980b).

Another special case includes size distributions. In the case of polydisperse particles the measured intensity is the average of the different sizes weighted by the amount of the individual size relative to the other sizes. In this case the $\sin(qr)/(qr)$ term in equation (1) is replaced in general by the theoretical form factor of a sphere (Lord Rayleigh 1911) and instead of a $p(r)$ function one calculates the size distribution $D(r)$. The basic idea of equations (3) is retained, and it is only $D(r)$ instead of $p(r)$ that is represented by the set of splines (Glatter 1980a). Essentially, not only spheres, but also any shape of particles defined by a single size parameter r could be handled in the same way.

2.2. Generalized indirect Fourier transformation

The generalized indirect Fourier transformation is based on the IFT and on the relation (Zernike and Prins 1927, Brunner-Popela and Glatter 1997)

$$I(q) \propto P(q)S(q) \quad (7)$$

where $P(q)$ is the form factor that comprises the intra-particle effects and $S(q)$ is the structure factor that takes the interaction effects into account. Strictly speaking this relation is only true for spherical, monodisperse particles, or for lamellae, but it can also be used for polydisperse and elongated particles up to certain limits (see section 3.1).

The structure factor $S(q)$ is 1 for dilute systems. Deviations from 1 build up with concentration and strength of interactions and typically the parameters describing $S(q)$ are defined better if the interactions are stronger. The concentration limit, where $S(q)$ starts to become important, depends on the type of interaction and is for example much higher for hard spheres than for charged spheres.

In most cases the inter-particle structures are on longer length scales compared to the individual particle. Therefore, deviations from 1 in $S(q)$ are most pronounced at low q -values. If $2\pi/\sigma \ll q_{\min}$, where σ is the particle diameter and q_{\min} the smallest scattering vector measured, one can ignore $S(q)$ in most cases. Additionally, if the overall contrast of the particles is low, $P(q)$ is small at low q and consequently $S(q)$ is also not very accessible, because it mostly contributes where the measured signal is weak due to the product in equation (7). This can happen for example in small angle x-ray scattering on micelles where the hydrophobic core and the hydrophilic shell can have oppositely signed contrasts to the solute leading to $P(0)$ close to zero. To summarize, $S(q)$ has a weak effect on dilute as well as on some low contrast systems. Otherwise, it is important to take the interaction effects into account.

The relation (7) contains a product of two functions that are unknown. Therefore, the transformation into real space results cannot be performed with the same degree of model-free assumptions as in the case of an IFT. Consequently, it is necessary to assume a model for either $P(q)$ or $S(q)$. The idea of GIFT is to calculate $S(q)$ from a model, which allows one to compute a model free $p(r)$ via $P(q)$ using the standard IFT procedure.

In detail, GIFT calculates $S(q)$ from a model using a set of parameters d_j . The Fourier transformed basis functions $\psi_v(q)$ are multiplied by this $S(q)$, resulting in a new set of basis functions $\overline{\psi}_v(q)$. These new basis functions are smeared in the same way as in the case of IFT, and the calculation of the solution coefficients c_v is performed as was implemented in section 2.1. The relations used are

$$\begin{aligned}
 p(r) &= \sum_{v=1}^N c_v \varphi_v(r) \\
 P(q) &= \sum_{v=1}^N c_v \psi_v(q) \\
 I(q) &= \sum_{v=1}^N c_v \overline{\psi}_v(q) = S(q) \sum_{v=1}^N c_v \psi_v(q) \\
 I_{\text{exp}}(q) &\approx \tilde{I}(q) = \sum_{v=1}^N c_v \chi_v(q).
 \end{aligned} \tag{8}$$

The only question remaining after having decided on a model for $S(q)$ is the selection of the correct parameters d_j that describe the interactions. This is done by variation of the parameters d_j until the mean deviation L reaches the global minimum within the parameter hyperspace. There is no mathematical proof that there exists a global minimum or that this global minimum corresponds to the correct parameters d_j , but simulations (Brunner-Popela and Glatter 1997) and experimental results of known PDDFs (Brunner-Popela *et al* 1999, Lindner *et al* 2001) show that in general the structure factor parameters can be determined by finding the global minimum. Trivial exceptions to this rule are models in which different

sets of parameters d_j result in quasi-identical curves $S(q)$. In this case the mean deviation is the same for all the identical structure factors, and physical meaningful values of d_j must be determined in some other way. Nevertheless, as long as no other parameter set produces a lower mean deviation, the calculation of $p(r)$ and $P(q)$ will result in the correct curves (Fritz *et al* 2000).

The determination of the parameters c_v and d_j can no longer be done by a set of linear equations because of the product in equation (7) and the non-linearity of $S(q)$ in its parameters (Brunner-Popela and Glatter 1997). The selection of the best method to solve the non-linear least squares problem is essential, because the solution can be found only in an iterative way forcing the algorithm to be efficient with regard to computation time and reliable in finding the global minimum. Taylor expansion, gradient search, and the Marquardt algorithm (Bevington and Robinson 1992) are possible solutions to the problem, but sometimes they fail to find the global minimum and result in a local one for the d_j -values (Brunner-Popela and Glatter 1997, Brunner-Popela 1998, Bergmann *et al* 2000). Grid search (Bevington and Robinson 1992) is reliable, but hardly practicable due to its long calculation time. The Boltzmann simplex simulated annealing (BSSA) algorithm by Press and co-workers (Press *et al* 1992) is able to find the global minimum reliably within a reasonable amount of time (Bergmann *et al* 2000). A genetic algorithm (Charbonneau 1995) gave similar results to the ones obtained for the BSSA algorithm. It seems that the exact shape of the hypersurface determines which of the two algorithms finds the global minimum faster, and no general rule can be given as to whether the BSSA or the genetic algorithm should be preferred. We decided to use the BSSA algorithm as our standard.

Finally, it is necessary to state that the introduction of a model for $S(q)$ has effects on the nature of the resulting PDDF. The PDDF obtained for IFT is largely model free, except for the selection of the maximum dimension D_{\max} . In GIFT, the model for $S(q)$ influences the Fourier transformed basis functions and thereby the solution coefficients c_v . This effect is desirable because it eliminates the interaction effects from the $p(r)$ function, but on the other hand, it introduces a certain model dependence in the PDDF. This model dependence is still much weaker than in the cases where models for $P(q)$ are used to describe the size, shape and internal structure of the particles studied. The necessary *a priori* knowledge about the form factor is still kept at a minimum.

Figure 2 shows the effect of including the $S(q)$ in the indirect Fourier transformation. The PDDF of the simple IFT calculation shows strong oscillations that make it difficult to interpret the curve. The separation of $I(q)$ into $P(q)$ and $S(q)$ leads to a PDDF that shows only one peak that is slightly asymmetric to the left-hand side and the oscillations are eliminated. Such a curve can be interpreted easily in terms of a slightly elliptical homogeneous particle (Fritz and Bergmann 2004).

In general, the interpretation of such PDDFs can then be done in the standard way (Glatter 1979). If the particles are inhomogeneous, one can try to deconvolute the PDDF (Glatter 1981), which will result in the scattering length density profile. If the deconvolution does not work properly, it is a strong indication that the particle shape deviates considerably from spherical symmetry. In such cases, it is possible to interpret the PDDF by designing corresponding models (Fritz and Bergmann 2004).

3. Structure factor models

The previous section has shown that the models for the structure factor are crucial for a GIFT evaluation. In general such $S(q)$ models are based on an interaction potential between the particles and the Ornstein–Zernike equation (Ornstein and Zernike 1914) that links the direct

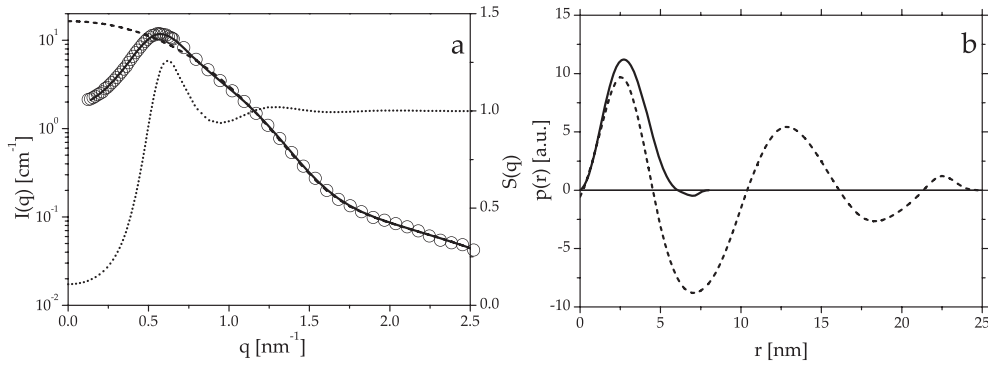


Figure 2. GIFT evaluation of SANS data of 5% CTAB in 10 mM KCl. (a) Separation of $P(q)$ (dashed) and $S(q)$ (dotted). The solid line is the product $P(q) \times S(q)$ including instrumental broadening effects. (b) The PDDF obtained by the GIFT calculation (solid) compared to the standard IFT one, where structure factor contributions have been ignored (dashed). For details of the experiment and sample see Fritz *et al* (2000).

correlations between particle positions to the total correlation function including indirect correlations. Solving the Ornstein–Zernike equation requires an additional closure relation that determines how the correlation functions depend on the interaction potential (Klein and D’Aguanno 1996). Correspondingly, the selection of the correct interaction potential is crucial for a GIFT calculation. Additionally, there is no closure relation that is best under all of the circumstances and therefore structure factor models based on several different closure relations have been implemented for each interaction potential in the GIFT.

3.1. Hard spheres

The hard sphere potential is simply zero if the particles do not overlap, and infinity if they do overlap. It leads to structures that are only controlled by the excluded volume effect. The Ornstein–Zernike equation can be solved analytically for such spheres using the Percus–Yevick closure relation (Percus and Yevick 1958). The resulting structure factor depends on radius R and volume fraction ϕ . This model was modified to include polydispersity using a simple distribution function that can be defined by one width parameter p around a centre radius R_{ave} . Then x_α is the fraction of particles having a radius R_α (Brunner-Popela and Glatter 1997). A set of structure factors $S_\alpha(q, R_\alpha, \phi)$ is calculated and their average is computed as

$$S^{\text{ave}}(q, R_{\text{ave}}, \phi, p) = \sum_{\alpha} x_{\alpha} S_{\alpha}(q, R_{\alpha}, \phi). \quad (9)$$

The resulting $S^{\text{ave}}(q, R_{\text{ave}}, \phi, p)$ is a crude but simple and fast model. Taking into account that many potentials behave similarly to effective hard spheres (Barker and Henderson 1967) it can be used even for non-hard sphere interaction potentials. This does not only hold true for deviations from hard spheres but also for deviations from perfect spherical symmetry. Additionally, S^{ave} for highly polydisperse systems looks similar to the structure factor of slender rods (van der Schoot 1992, Weyerich *et al* 1999). Therefore, it can be used to evaluate scattering data of interacting elongated particles up to a certain degree.

A different approach to treat polydispersity has been also implemented, namely the ‘effective’ structure factor $S^{\text{eff}}(q)$ (Salgi and Rajagopalan 1993, Pusey *et al* 1982). It is based on the extensive calculation of the scattering intensity of the interacting m -component system

that is divided by the average form factor of the particles

$$S^{\text{eff}}(q) = \frac{\sum_{\alpha,\beta=1}^m f_{\alpha} f_{\beta} B_{\alpha}(q) B_{\beta}(q) S_{\alpha\beta}(q)}{\sum_{\alpha=1}^m x_{\alpha} f_{\alpha}^2 B_{\alpha}^2(q)} \quad (10)$$

where f_{α} is the form amplitude of species α at $q = 0$ and $B_{\alpha}(q)$ the corresponding normalized form amplitude. $S_{\alpha\beta}(q)$ is the partial structure factor. The better treatment of polydispersity effects should lead to better results during GIFT evaluation, especially if the particles are inhomogeneous, which influences $B_{\alpha}(q)$. Simulations of polydisperse spheres show that the resulting PDDF is hardly influenced by the choice of S^{ave} or S^{eff} (Weyerich *et al* 1999). Better structure factor parameters, especially the polydispersity, were obtained for S^{eff} .

3.2. Charged spheres

Charge effects can be treated by three different structure factor models (Fritz *et al* 2000) that are all based on a Yukawa type (v^{Yuk}) (Yukawa 1935) interaction potential:

$$v^{\text{Yuk}}(r) = \frac{Z^2 e_0^2}{4\pi\epsilon\epsilon_0 r} \frac{e^{-\kappa(r-\sigma)}}{(1 + \kappa\sigma/2)^2} \quad (11)$$

where Z is the charge in electron charges e_0 , ϵ is the dielectric constant, ϵ_0 the permittivity of vacuum, κ the Debye screening parameter, σ the particle diameter, and r the centre to centre distance of the particles.

The structure factor models differ in the closure relation used, namely the rescaled mean spherical approximation (RMSA) (Hayter and Penfold 1981, Hansen and Hayter 1982), the hypernetted chain (HNC) (van Leeuwen *et al* 1959), and the Rogers–Young (RY) (Rogers and Young 1984) closure relations. RMSA is based on an analytical solution and is correspondingly fast to calculate. The HNC and RY closures are both calculated numerically (Klein and D’Aguanno 1996). The evaluation of the Rogers–Young closure relation can especially lead to long calculation times, but the obtained structure factors describe the structure thermodynamically consistent.

Simulations and evaluations of SANS data of well defined test samples showed that PDDFs were of comparable quality for all three structure factor models used. The parameters for the structure factor are also similar for all models, where the rescaled mean spherical approximation showed the greatest differences compared to the other two closure relations. Since the rescaled mean spherical approximation is an analytical solution and therefore numerically fast, it seems best for a quick evaluation. The HNC closure seems to be a reasonable choice for a standard GIFT evaluation, since it balances calculation speed and accuracy, while the RY approximation is rather time consuming even on current desktop computers. The quality of the results obtained for the RMSA and especially HNC closures shows that the RY calculation is only necessary if details of the structure factor parameters are of interest (Fritz *et al* 2000).

It is impossible to determine all of the parameters of the interaction potential simultaneously from scattering data, and only Z , σ and the volume fraction can be varied during a GIFT calculation. Even then, it is necessary to use a two-step approach to determine all three of the parameters from scattering data unless prior knowledge is available since an increase in radius and volume fraction can mimic the effect of higher charge. If no prior knowledge is available a first calculation leads to a separation of the form and structure factors, where the parameters for the interaction potential are most likely incorrect. The PDDF is always obtained correctly and can be used to estimate σ . This value of σ can be kept constant in a second run to obtain the correct volume fraction and charge (Fritz *et al* 2000).

3.3. Attractive spheres

Attractive interactions have been implemented in GIFT (Innerlohinger *et al* 2004) by two potentials, the square well and the depletion potential. The square well potential is a simple constant reduction of the interaction energy in a zone close to a particle. Basically, this model can also be used to describe simple repulsive interactions since an increase in energy, instead of the reduction, results in a square well potential. The depletion attraction is caused by the change in osmotic pressure of a non-adsorbing polymer or by the presence of other colloidal particles (Asakura and Oosawa 1954, 1958, Vrij 1976). It can be approximated in the range $\sigma < r < \sigma + d$ by Bergholtz *et al* (2003)

$$v^{\text{dep}}(r) = -\phi_p^{(R)} k_B T \frac{3(1+\xi)}{2\xi^3} \left(\frac{r}{\sigma} - 1 - \xi \right) \quad (12)$$

where σ is the diameter of the large particles and d the diameter of the small particles or the radius of gyration of the polymers. $\xi = d/\sigma$ is a size ratio, $\phi_p^{(R)}$ is the volume fraction of the small particles, and r is the centre to centre distance of the colloids, while $k_B T$ is the Boltzmann constant times the absolute temperature. The volume fraction $\phi_p^{(R)}$ is the volume of the small particles relative to the free volume, i.e. the total volume minus the volume of the large particles and their depletion zones, which can be calculated from the volume fraction of the large particles and the size ratio (Lekkerkerker *et al* 1992).

As in the case of charged spheres, there are several closure relations that have different benefits and drawbacks. The relations used for these potentials in GIFT are the Percus–Yevick closure, the soft core mean sphere approximation (SMSA) (Chihara 1973, Madden and Rice 1980) and the thermodynamically consistent mixture of HNC and SMSA closures, known as the HMSA closure (Zerah and Hansen 1986). The PY solution is fast and robust, but only correct if the interactions are not too strong and if the range of the potential is short. The SMSA closure is optimized for short-range repulsion combined with long-range attraction, but also deviates systematically for strongly correlated systems. In these cases the HMSA closure must be used, but just as in the RY closure for charged spheres, calculations are slow, and under some conditions, no consistent solution can be found. This numerical instability seems to be worse for depletion potentials than for square well potentials. Therefore, the depletion potential can be used within the framework of the GIFT, only combined with the PY and SMSA closures.

The parameters used to describe the interaction effects are, in the case of depletion interaction, the volume fraction of both types of colloids, the diameter σ and the size ratio ξ . Volume fraction, diameter, well width and well depth are the four parameters needed for square well interaction. Similar to charged spheres, the parameters can be quasi-linearly dependent and thereby impeding unambiguous determination of the parameter values (Innerlohinger *et al* 2004). Imposing constraints onto the accessible parameter space is one way to circumvent this problem. Typically the volume fraction can be estimated from the particle concentration and can be kept constant during the calculation. Another possibility is to use a low concentration measurement to obtain $P(q)$, where $S(q) \approx 1$. Only the parameters for $S(q)$ are varied then, while $P(q)$ is kept constant (Innerlohinger *et al* 2004). Strictly speaking this procedure corresponds to pure model approximation and should not be termed ‘GIFT’ any more.

3.4. Lamellae

Lamellae show great differences in geometry compared to the spheres discussed so far. In most cases they form stacks that are theoretically infinite in two dimensions and show

considerable variation in composition in the third dimension. This variation in the third dimension within one lamella can be sufficiently described by a thickness PDDF $p_t(r)$, which we have described in section 2.1. The Fourier transform of $p_t(r)$ is the thickness form factor $P_t(q)$. Except for this change of focus in the form factor the GIFT stays the same (i.e. $I(q)$ is replaced by $I_t(q)$ and $P(q)$ by $P_t(q)$ in equation (7)). We want to stress that in order to obtain this $I_t(q)$ function we have to use the relation $I(q) = I_t(q) \cdot q^{-2}$ and that the splines building up $p_t(r)$ are transformed by a cosine transformation and not by a $\sin(x)/x$ transformation as in the globular case.

The structure factor of lamellae can be described in combination with the GIFT in two ways (Frühwirth *et al* 2004), namely the modified Caillé theory MCT (Caillé 1972, Nallet *et al* 1993) and the paracrystalline theory PT (Hosemann and Bagchi 1964, Guinier 1994). The structure factor models were further modified according to Pabst *et al* (2000) by the addition of a diffuse background. Highly defective or unstacked lamellae, for example in single lamellar vesicles, can cause such contributions to the scattering intensity $I(q)$ that are scattering but hardly affected by the typical effects of $S(q)$ that were observed for other lamellae in the sample. Therefore

$$I_t(q) \propto P_t(q) (S(q) + N_{\text{diff}}) \quad (13)$$

where N_{diff} is related to the number of unaligned lamellae.

'Polydispersity' was a second modification added to $S(q)$ calculated from both theories, MCT and PT (Frühwirth *et al* 2004). If the number of lamellae within a single stack is low, $S(q)$ shows strong oscillations at low q , which are unobserved in experiments. These artefacts are eliminated by calculating a series of structure factors with different numbers of lamellae within the stack. The $S(q)$ is the average of these structure factors weighted by a Gaussian distribution. The mean deviation of the distribution was calculated as the square root of the number of lamellae within the stack in order to keep the number of free parameters constant. The parameters used to describe the structure factor $S(q)$ are therefore the number of layers, layer spacing, layer flexibility or disorder, and N_{diff} .

The $S(q)$ models are implemented in the GIFT technique in such a way that it is possible to use the original versions of structure factors from MCT and PT as well as the structure factors including one or both modifications.

3.5. Other models

The current version of the GIFT software contains three further models for $S(q)$, namely a model for fractal aggregates S^{frac} , a model for fluctuations close to the critical point S^{crit} and a model for polydisperse cylinders S^{cyl} .

The model S^{frac} is taken from the work performed by Teixeira (1988) and takes into account the power law linking the scattering intensity to the fractal dimension. In many cases the power law is unobserved at large q -values because of the finite size of the individual particles within the aggregate. This effect is included by a cut-off length ξ , which has to be translated into a meaningful parameter for each individual situation. The model is rather simple and neglects important aspects of the non-fractal local structure in the vicinity of a particle (Dimon *et al* 1986).

The structure factor close to a critical point S^{crit} can be described by a modified Ornstein-Zernicke form (Kotlarchyk *et al* 1983). The parameters used are the osmotic compressibility and the length of the critical fluctuations.

Finally, the model for slender cylinders that are polydisperse in length by van der Schoot (1992) was implemented. This structure factor model, however, has been hardly tested up to now in combination with the GIFT technique.

4. Applications

4.1. Surfactant systems

4.1.1. C_iE_j systems. Most of the GIFT applications that have been published up to now are concerned with surfactant systems or other self-assembled structures. The reason for this is simply the fact that the structure of such self-assembled systems can be a function of concentration. This behaviour does not allow dilution series to minimize particle interactions. Even the first application of GIFT (Brunner-Popela *et al* 1999) was concerned with the solutions of the nonionic surfactant $C_{12}E_5$ in D_2O and microemulsions formed by this surfactant with n-octane. The focus of this work was mostly on the technical aspects of comparing applications of S^{ave} with S^{eff} . It is also shown that neglecting interaction effects in IFT can lead to PDDFs that look like the ones of spheres while the actual structure is elongated.

Glatter *et al* (2000) extended the work to different C_iE_j surfactant solutions, studying their behaviour close to the critical point. Combining small angle neutron scattering with depolarized dynamic light scattering and ultra low shear viscosimetry, they investigated whether the micelles form associates due to attractive interactions or elongate when approaching the critical temperature. Evaluations were performed based on S^{ave} and S^{crit} . All of the systems studied showed a sphere to rod transition at all of the concentrations studied. Attractive interactions are an additional effect close to the critical point, and so the micelles demonstrate elongation and association.

The commercial surfactant Brij 35 is chemically similar to the pure C_iE_j surfactants with an average composition $C_{12}E_{23}$. It was studied by Tomšič *et al* (2004) in an aqueous solution and dissolved in various simple alcohols as well as in ternary water/alcohol/Brij 35 compositions. In the utilization of S^{ave} it was shown that the Brij/water system contains globular micelles that elongate at concentrations above 15%. Solutions in alcohols resulted in mostly un-aggregated Brij, while some large structures were also present.

The $C_{12}E_5$ /n-octane/water microemulsion system aforementioned was also investigated by Freiburger *et al* (2006) using the different structure factor models for hard spheres. They focused on the limits of the hard sphere model and tested it on the bi-continuous structures of the one-phase channel.

4.1.2. Other ethyleneoxide systems. The C_i part of these non-ionic surfactants can be replaced by cholesteryl ethers, resulting in molecules with a bulky, non-flexible hydrophobic part. Sato *et al* (2004) investigated systems with 10 and 15 ethyleneoxide groups in the headgroups of the molecules. According to the GIFT analysis using the hard sphere interaction potential, the longer hydrophilic chain induced formation of globular micelles, while the shorter chain resulted in slightly elongated structures. The size and shape of the micelles do not change over a wide range of concentrations up to 20 wt%. The polydispersity of the elongated micelles is higher compared to the globular micelles.

Another surfactant with a headgroup based on ethyleneoxide is Tween 40 (polyoxyethylene sorbitan monopalmitate). Microemulsions of this surfactant with water, isopropyl myristate and Imwitor 308 (glyceryl caprylate) were studied by Podlogar *et al* (2004). The structures change from elongated to globular with the addition of water. The structure factor parameters obtained show a much lower volume fraction than expected from the composition, indicating that the structures observed do not represent the complete Tween/Imwitor content added. The increase in polydispersity with observed elongation corresponds to earlier findings by Weyerich *et al* (1999).

4.1.3. Block copolymer solutions. Polyethyleneoxide blocks are also an important component of many block-copolymer systems that have been studied with GIFT. Park and Char (2004) studied the gelation of poly (DL-lactic acid-co-glycolic acid) flanked by two polyethyleneoxide blocks. SANS data were evaluated with S^{ave} and could be interpreted well in terms of a spherical model.

Similar block-copolymer systems where the central block is made of polypropyleneoxide, known as pluronics (BASF) or synperonics (ICI) are more common. Lindner *et al* (2003) investigated the micellar glass formed by the pluronic P94. Small angle x-ray scattering data were evaluated using S^{ave} in a concentration regime from 1 wt% up to 20 wt%. The micelles formed are globular and do not show any significant change in size and shape over the entire concentration range. The interaction radii correspond well to the radii obtained from the $p(r)$ function and the polydispersity is low. Additionally, one could observe the typical effect for many systems whose hydrophilic blocks are based on ethylene oxide, namely a much higher hard sphere volume fraction compared to the weight fraction. This is due to the steric interactions caused by the ethylene oxide chains mimicking larger hard spheres. The relation between this higher effective volume fraction and the actual weight fraction was found to be 2.1 for all of the concentrations of P94 investigated, which can be interpreted as swelling of the ethylene oxide chains with water.

Jansson *et al* (2005) have analysed small angle x-ray scattering data of mixtures of the pluronic P123 with the cationic surfactant cetyltrimethylammonium chloride (CTAC). They found a gradual decrease of P123 micelle size with CTAC addition, followed by a bidisperse state of small particles and micelles, and finally P123 molecules solubilized by CTAC. Low concentrations were evaluated using S^{ave} , since none of the models for the interaction potential was correct due to the mixture of charge repulsion and steric stabilization. The effective hard sphere model used resulted in PDDF that showed a decrease of micelle diameter from 21 to 17 nm. At high CTAC concentration a Yukawa potential with HNC closure was used successfully.

4.1.4. Charged micelles. Solutions of cetyltrimethylammonium bromide (CTAB) in KCl and KBr were evaluated by Fritz and co-workers (Fritz *et al* 2000, Fritz and Bergmann 2004) using the three structure factor models for charged spheres. The aim of these investigations was to test the structure factor models for charged spheres and to use the CTAB micelle as a well-characterized model for inhomogeneous spheres.

Mixtures of anionic (sodium oleate) and cationic (trimethylammonium family C_n TAB) show the formation of wormlike micelles (Raghavan *et al* 2002). The GIFT technique was used as a method with few model assumptions to check if the model of cylindrical micelles is appropriate for such systems. S^{ave} was used to model the interaction effects instead of the models based on a Yukawa type potential, since it is suited best to compensate for the deviations from spherical symmetry by increased polydispersity and since only qualitative trends can be read from the parameters once the system is truly cylindrical.

Sodium dodecyl sulfate micelles show also cylindrical growth, if *p*-toluidine hydrochloride is added as hydrophobic salt (Hassan *et al* 2003). All three models for Yukawa-type interaction potentials were used and showed comparable results for the initial state of globular micelles without any salt addition. Further calculations were therefore performed using only the RMSA closure. Salt addition led to an increase in length of the structures, which could be followed by the PDDF and the structure factor parameters.

CTAB micelles doped with increasing levels of 4-ethylphenol show also a transition from spherical micelles to elongated wormlike micelles (Singh *et al* 2004). Further addition of the dopant leads to the formation of vesicles coexisting with few cylinders. The structure factor

of a Yukawa type interaction potential in combination with the HNC closure can be used to describe the interaction effects present in this system.

Šegota *et al* (2001) investigated the micelles formed by sodium 4-(1-pentylheptyl) benzenesulphonate in water. Using S^{ave} and the structure factor model for charged spheres using the HNC closure they found inhomogeneous oblate structures with a maximum dimension of 10–12 nm. The PDDFs obtained for the two models are in good agreement.

4.1.5. Other micellar systems. Stradner *et al* (2000) used GIFT to check the structures formed in aqueous alkyl polyglucoside solutions on the addition of hexanol. They found a sphere to rod transition that was then studied in detail with the appropriate models.

Structures formed by the synthetic phospholipide OMGPC at higher concentrations were investigated by Orthaber and Glatter (2000). The main aim of these experiments was to prove that the globular core-shell structures that are formed at a low concentration are not concentration dependent. The structure factor model used was S^{ave} .

Fullerenes that have been made water soluble by six sulfobutoxypentyl arms form rodlike aggregates with an aggregation number of about 32 (Lin *et al* 2004). The authors verify their model based on the mean spherical approximation by comparing it to the $p(r)$ function obtained from GIFT.

4.1.6. Food grade systems. GIFT has been used for several applications related to food grade surfactant systems. Glatter *et al* (2001) determined the structures formed by sugar-esters in n-tetradecane and 1-butanol. The micelles change their shape up to 10 wt% sugar-ester, but stay globular with increasing aggregation number at larger concentrations. Water addition leads to swelling. Comparing the PDDFs obtained under different contrast conditions with the interaction radii shows that the hydrophobic tails interpenetrate to a large extent.

Different five-component food grade oil in water nonionic microemulsions (de Campo *et al* 2004, Yaghmur *et al* 2004) based on *R*(+)-limonene, ethanol, and water were also studied with small angle x-ray and neutron scattering. The surfactants used were the nonionic Brij 96v, Tween 60, and Tween 80; further components were glycerol or propylene glycol. The size, shape and internal composition of the structures formed along the different dilution lines could be followed well, if the scattering data were evaluated using S^{ave} .

4.1.7. Lamellar structures. Frühwirth *et al* (2004) used multilamellar vesicles of 1, 2-Dipalmitoyl-*sn*-glycero-3-phosphocholine to show the applicability of the models for lamellar stacks incorporated in the GIFT technique. Increasing temperature led to a decrease in bilayer thickness and an increase in Caillé parameter. The $p_l(r)$ function obtained was in good agreement with molecular dynamics simulations (Schmelter 2002).

4.2. Other applications

4.2.1. Combination with other methods. Determination of molecular weight is a common task of small angle scattering since this quantity is directly proportional to the forward scattering intensity. This relationship is only fulfilled if interaction effects can be neglected. As soon as the concentration is within the semi-dilute regime, the structure factor considerably decreases or increases the intensity. Dilution is often impossible, since it might change for example the aggregation number and thereby the molecular weight. Using GIFT to separate $P(q)$ from $S(q)$ allows one to use only $P(q)$ to reliably determine the molecular weight (Orthaber *et al* 2000).

The $p(r)$ function can be deconvoluted into a scattering length density profile, if the system is highly symmetric (Glatter 1981). A combination of intra- and inter-particle effects within the PDDF inhibits the determination of density profiles. Mittelbach and Glatter (1998) could show that deconvolution of PDDFs obtained via the GIFT result in reasonable profiles, since interaction effects have been eliminated by the structure factor.

4.2.2. Emulsions. Emulsions of micrometre size were measured by Lindner *et al* (2001) using static light scattering. They found a good agreement between the volume fraction obtained from S^{ave} and the oil concentration used for preparation. The interaction radius does not correspond as well to half of the maximum dimension as seen from the PDDF, since the interaction is dominated by the average size while the maximum dimension is determined by the largest particle within the ensemble. The polydispersity as obtained by the structure factor was found to increase slightly with concentration.

Innerlohinger *et al* (2004) have used silicone oil emulsions to test the attractive structure factor models that they have implemented in the GIFT. Depletion interaction was induced by Triton X-100 micelles and latex particles. The parameters of emulsion droplet size, size of the small particles and the volume fractions of large and small particles were regained well from the GIFT analysis.

Later on, Innerlohinger *et al* (2006) used a concentration series of such a silicone oil emulsion to compare results from static light scattering and ultra small angle neutron scattering. GIFT worked well for both techniques, and it could be shown that multiple scattering and instrumental smearing effects can be handled for such systems.

4.2.3. Inorganic materials. The surface charge of 3-(trimethoxysilyl) propyl methacrylate coated Stöber silica particles was investigated by Maranzano *et al* (2000) using various techniques. One of these methods was SANS in combination with direct model approximation and GIFT. The effective charge was determined assuming a Yukawa type potential in combination with the HNC closure relation.

Charge stabilized colloidal particles can be destabilized by increasing the salt concentration or changing the pH towards the isoelectric point. Wyss *et al* (2004) used this effect caused by enzymatic activities to cast green-bodies, which can then be sintered to result in the desired ceramics. They followed the destabilization and aggregation process by small angle light scattering and quantified the strength of the attraction between the particles by approximating the interaction potential with a square well potential in combination with the HMSA closure relation. The data are also compared with theoretical DLVO calculations.

Christoforides *et al* (2002) used the averaged hard sphere structure factor model to analyse the scattering data of controlled pore glasses. The evaluation results in parameters for porosity (from volume fraction), polydispersity and the size of the solid entities from the hard sphere radius. The authors used the version of the indirect Fourier transformation that leads to a size distribution $D(r)$, which allowed for the determination of the pore radii. The related Vycor glass produced similar results.

4.2.4. Organic materials. Micelles formed in asymmetric poly(ethylenepropylene-*b*-dimethylsiloxane) diblockcopolymers melts were investigated by Wang *et al* (2002) using small angle x-ray and neutron scattering. Using GIFT in combination with S^{ave} showed that the micelle remain unchanged in size while heating but their number density decreases gradually.

5. Conclusions and directions

Although many models for interactions have been implemented in GIFT, this type of development is unfinished. Even spherical particles, which have been covered the best up to now, show a great number of interactions that are unimplemented such as steric interactions, or soft, deformable cores. In particular, most types of deviations from spherical symmetry have hardly been touched upon. A structure factor model for hexagonally ordered cylindrical structures, similar to the structure factors of lamellae, is currently being developed. The description of semi-dilute cylindrical or elongated structures will be another future step. Finally, it might be interesting to use a kind of inverse approach, where the form factor is kept constant and the interaction potential for the structure factor is described with only few model assumptions. Another approach that is currently studied is to take a model for $P(q)$, but to describe the Fourier transformed structure factor, namely the pair correlation $g(r)$, in terms of splines, following the ideas of IFT.

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