Application of the Indirect Transform Method to Obtaining Distance Distribution Functions of Extremely Large Colloids and Emulsions Using Small-Angle X-ray Scattering Data Obtained With a Bonse–Hart Instrument*

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Abstract

The indirect Fourier transform method for obtaining distance distribution functions and associated parameters from small-angle X-ray scattering data was adapted for studies of particles having radii of gyration up to 35000 Å and distance distribution functions extending up to 150 000 Å. Data were collected with a Bonse–Hart instrument. Distance distribution functions were obtained for materials of interest to petroleum production, including a powdered wax, a powdered asphaltene, a crude oil, and emulsions of dilute aqueous solutions of a partially hydrolyzed polyacrylamide polymer shaken with organic solvents.

Introduction

The distance distribution function is proportional to the number of pairs of difference electrons separated by a given distance which are found in the combination of two volume elements within the particle. It gives the maximum structural information without assumptions for small-angle X-ray scattering studies of non-crystalline and poorly crystalline materials. However, such functions often are not obtained, because direct Fourier transform methods and unsmearing corrections often require more precise data than can be obtained.

Glatter (1977a, b, 1979, 1980) has shown that an indirect Fourier transform method can be used to obtain the distance distribution function and several other parameters. Some advantages are that the demands for precise experimental data are not as severe as for most direct methods, that smearing corrections are made on exact spline functions rather than by unsmeared inexact experimental data, and that statistical errors in intensity data can be considered.

It was desired to study very large colloids, micelles and emulsions of interest to petroleum production, and such particles can have radii of gyration well in excess of 10 000 Å (Dwiggins, 1979). In this particle size range, both slit height and width smearing are important when a Bonse–Hart instrument is used. Although slit-height corrections are not necessary if average radii of gyration are obtained using the Guinier method, both corrections are necessary for more detailed studies. It was not possible to make both unsmeared corrections on the experimental data and also to use a direct Fourier transform method to obtain distance distribution functions, because the demands for precise data proved too severe. Thus, it was decided to see if Glatter's method could be adapted for the materials of interest using data collected with a Bonse–Hart instrument.

Theory

For details of the theory, the papers of Glatter (1977a, b, 1979, 1980) should be consulted. A few of the equations used in this study will be described.

The distance distribution function \( P(r) \) is approximated by

\[
P(r) = \sum_{\nu=1}^{N} c, \phi_{\nu}(r) \quad \text{for} \quad 0 \leq r \leq D,
\]

and by \( P(r) = 0 \) for \( D < r < \infty \). The \( \phi_{\nu}(r) \) functions are cubic B-spline functions (Greville, 1969) that can be calculated exactly, and the \( c, \) values are constants to be determined. \( r \) is the distance, and \( D \) is the maximum distance in any particle. The \( N \) usually must be 30 or less to avoid instability problems.

The intensity of scattering, \( I(h) \), is given by the expression

\[
I(h) = \sum_{\nu=1}^{N} c, F\{\phi_{\nu}(r)\}
\]

where \( h = 2\pi \sin \theta / \lambda_0 \), \( \theta \) is the Bragg angle (half the total scattering angle), and \( \lambda_0 \) is the reference wavelength of incident radiation. The term \( F \) is an operator that is the product of up to four other operators \( F_1F_2F_3F_4 \). The operator \( F_1 \) transforms from \( r \) space to \( h \) space, resulting in the intensity for ideal geometry. The operators \( F_2 \) to \( F_4 \) smear for slit height, slit width and wavelength polydispersity as necessary for a particular problem.

Two important points concerning these equations are that the constants \( c, \) are the same in both and that...
the operator $F$ is applied only to exactly known spline functions and not to inexact experimental data.

To solve for the $c_v$ values, the spline functions are generated and then transformed by operator $F$ as indicated in (2) for each value of $h$. Next, a standard variational method is used to give the best values of $c_v$, so that the sum of the squares of differences between $I(h)$ given by (2) and $I_{(h)}$ experimental intensity values, weighted for experimental precision, is a minimum subject to a single side condition necessary for stabilization. The side condition results in an undetermined Lagrange multiplier $\lambda$, and solutions for $c_v$ values are obtained for a series of $\lambda$ values. The inflection point in a plot of a stability function (Glatter, 1977b), calculated along with $c_v$ values, vs $\lambda$ is used to locate the proper $\lambda$ value and thus to allow selection of the corresponding $c_v$ values.

Once the $c_v$ values are obtained, several other parameters of interest can be obtained in addition to $P(r)$ given by (1).

The radius of gyration $R_0$ is given by

$$R_0^2 = \int_0^P r^2 P(r) dr/2 \int_0^P P(r) dr.$$  \hspace{1cm} (3)

The intensity $I_{(h)}$ for perfect collimation is given by

$$I_{(h)} = \sum_{v=1}^N c_v F_1(\phi, \sigma).$$  \hspace{1cm} (4)

It should be emphasized that the parameters $R_0$ and $I_{(h)}$ can be obtained accurately only after a satisfactory solution for $P(r)$ is found. This is opposite to the situation for direct Fourier transform methods when one must first obtain unsmeređe intensities and then determine $P(r)$.

Glatter’s derivations are based on a monodisperse particle. A polydisperse system presents no problems in obtaining $P(r)$ if it is understood that $P(r)$ is an average value for all of the particles, in analogy to the case for radial distribution functions obtained from high-angle X-ray data. If it is known that the particles are monodisperse, then shape information can be obtained as described by Glatter (1979). If it is known that the particles are of approximately the same shape, but have different sizes, then a particle size distribution function can be obtained (Glatter, 1980). However, if neither of these assumptions can be made, then only certain broad limits for the shape and size of the particles can be specified. This merely is the consequence of the well-known fact that unique three-dimensional structural data cannot be obtained from one-dimensional scattering data.

Calculation method

The computer program ITP-79 was obtained from Glatter (1980) along with excellent instructions. A few changes were necessary for its use with data collected at very low angles with the Bonse–Hart instrument.

The slit-height smearing correction breaks down for the Bonse–Hart instrument at very low angles. This is because the intensity pattern for the samples studied is confined to angles well under 100° 2θ, and the effective slit height of the Bonse–Hart instrument allows passage of angles up to several degrees. This problem is easily corrected. If experimental data are collected over an angular range sufficient to include most of the small-angle intensity, as was done in this investigation, then one can use for calculations a half-slit-height that is just slightly larger than necessary to allow passage of the maximum scattering angle of the experiment. The slit-height intensity profile is set equal to unity over this height range. A constant called $ZR$ in the computer program is set equal to zero. The mentioned procedure allows the Glatter slit-height smearing correction to be used without modification of the computer program and, in effect, allows the correction for infinite slit height to be made as is appropriate when the effective slit height of the instrument is much greater than the angular range of significant intensity of scattering (Kratky, Porod & Skala, 1960). Gravatt & Brady (1969) found the infinite-slit-height smearing correction appropriate for the Bonse–Hart unit.

The modified procedure for slit smearing was tested using another method. Firstly $P(r)$ was obtained for slit-height-smeared intensity test data using the Glatter method, including the modified slit-height smearing correction. Then $P(r)$ was determined by first slit-height unsmearing the test data using the method of Lin, von Bastian & Schmidt (1974) and then applying the Glatter method, without slit-height smearing. The values of $P(r)$ obtained by the two methods were sufficiently close.

Minor changes in input and output formats of Glatter’s program are necessary for the extreme values of $h$ and $R$ used; this becomes apparent the first time the program is used.

Experimental

The automated Bonse–Hart instrument used has been described (Dwiggins, 1978). A special method has been described that often must be used for measuring the absorption correction so that the background can be properly subtracted (Dwiggins, 1979). Special methods and precautions concerning sample preparation have been given by Dwiggins (1978, 1979).

To obtain the most precise data possible for the lowest scattering angles, both a blank curve and sample curve were obtained for each experiment. Intensity data were obtained at both negative and positive scattering angles in the region of the direct beam, and the zero-angle position was located so that the integrated intensity at negative angles equalled that at positive angles.

Very careful alignment of the stepping mechanism that drives the micrometer is necessary to prevent introduction of a wobble. The stepping motor rotates once for every 20° 2θ, and a wobble of this frequency will not be eliminated by either the Glatter treatment or curve smoothing at the very low angles measured.
Results and discussion

Fig. 1 gives the uncorrected experimental scattering curves for a powdered wax sample and for the empty sample cell. Even without making the absorption correction it is obvious that the intensity of scattering is an appreciable fraction of the transmitted beam intensity. About $10^{-3}$ attenuation of the direct X-ray beam was used to avoid non-linear response of the counting circuits. Points are not shown on the raw data curves in Fig. 1 because the high counting rates allow counting statistics with too little scatter to show on the curves. The angular steps were $0.1' 2\theta$.

The absorption correction method used (Dwiggins, 1979) works when different attenuation factors are used for the scattering curves for the sample and empty cell. Thus an attenuation coefficient of about $10^{-2}$ was used to collect data for all other samples to improve counting statistics and to avoid changing attenuation coefficients in a single run. The Glatter method does not require collection of data to extremely high values of $2\theta$, and there is a limit on the maximum angle to be used that depends on various parameters used in Glatter's treatment. Typical absorption-corrected curves have been given that show scatter of points after the absorption correction has been made (Dwiggins, 1979), and calculated absorption coefficients are also given. Absorption coefficients for samples studied in this work are of the same order.

The Glatter treatment requires calculation of a standard deviation for each scattering point. Because the background is significant, both the counting statistics for the sample and empty-cell scattering curves must be considered in calculation of the required standard deviations. The Glatter computer program does an elaborate statistical analysis of the data, and this is described in the instructions that come with the program. When the experimental precision is unsatisfactory the calculation of $P(r)$ usually fails because an inflection point in the stability plot cannot be located, and an unsatisfactory error band for the $P(r)$ curve is indicated.

Points are not shown on the $P(r)$ curves given in figures, because the Glatter method gives a smooth curve, and the points all lie on the curves for the scale of magnification used. In all cases 101 $r$ points were used. The values of $P(r)$ are on a relative basis. Glatter (1979) has published $P(r)$ curves and equations for particles of various shapes, and these are useful for comparison with experimental $P(r)$ curves.

In Fig. 2, results are given for powdered wax and Boscan asphaltene that were prepared in a manner described previously (Dwiggins, 1978, 1979). Because of the great contrast between the electron density of the particles and air, counting statistics were favorable. The wide $P(r)$ curves for both wax and asphaltene indicate that the particles depart considerably from monodisperse spheres, implying that there is either a great departure from spherical shape and/or a wide distribution in particle size, especially for the wax with the
very long tail at high values of $r$. Because both samples were ground and not sorted according to particle size, it is likely that the spread and tails of the $P(r)$ curves are caused more by a particle size distribution than by a departure from spherical shape.

Fig. 3 gives results for Red Wash crude oil that was stored at 278 K for a year. This oil has a very high wax content and colloids rich in wax. The counting statistics were acceptable, but not as favorable as for the powdered solids because of the lesser contrast in electron density. Although the $P(r)$ curve obtained is not that for a monodisperse sphere, it is much closer to one than are the curves obtained for the solids. Thus, there can be some departure of shape from a sphere and/or some size polydispersity.

Aqueous solutions of partially hydrolyzed polyacrylamide polymer, when carefully prepared to dissolve all of the polymer, show little small-angle scattering (Dwiggins, 1979). This polymer is used to increase the viscosity of aqueous solutions injected to increase petroleum production. It was found that aqueous solutions of this polymer shaken with a wide variety of organic solvents produced emulsions. These emulsions range from very unstable to rather stable ones that can stand for several months without complete phase separation. For polymer solutions containing less than two percent polymer, the solution was shaken with the desired organic solvent and allowed to stand for at least one day to allow any excess organic solvent to separate.

Fig. 4 gives the result for an emulsion of the polymer solution with hexadecane. The counting statistics were unfavorable, and the resulting $P(r)$ curve has considerable ripple that is not statistically significant. The particle size distribution has a very long tail, indicating very great deviation from spherical shape and/or a very great particle size range. Because the emulsion slowly separates over several weeks, indicating that some very large particles must be present, the large variation in particle size probably contributes more to the tail of $P(r)$ than does shape.

Fig. 5 gives the results from an emulsion of the polymer solution with ethylene bromide at two different times. The ethylene bromide gave good electron density contrast, allowing more favorable counting statistics than did the hexadecane. The $P(r)$ curve is lowered at higher $r$ values after time. This emulsion also slowly separates over a period of several weeks. Thus, the $P(r)$ curves as a function of time seem reasonable because they indicate that the emulsion is being depleted in larger particles as time passes. This would be expected because large particles should migrate faster toward the separated organic phase than do smaller particles.

**Conclusions**

The indirect transform method of Glatter can be used to obtain distance distribution functions to at least 150 000 Å in favorable cases. However the method cannot be used blindly, and one must be aware of the many factors that influence results.

Although only the final $P(r)$ curves are shown, each experiment required the calculation of many. Several parameters were varied to ensure convergence on the correct result. Two parameters that were varied, in addition to $z$, were $D$ and $N$. If there are convergence problems, often variation of the minimum and maximum values of $h$ used for calculations will indicate the portion of the intensity data that is causing problems. However, all values of $h$ must lie in a range that depends on various parameters used in the calculations and that can be calculated as described by Glatter. When a different type of instrument is used, the effects of slit height and width smearing should be examined carefully. Several hundred $P(r)$ calculations had to be made for model and experimental data to obtain the

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**Fig. 4.** Distance distribution function of an emulsion prepared by shaking hexadecane with a 1.78% solution of partially hydrolyzed polyacrylamide polymer in water. Intensity data were collected seven days after the emulsion was prepared, $R_o=22 000$ Å.

**Fig. 5.** Distance distribution function of emulsion prepared by shaking ethylene bromide with a 1.78% solution of partially hydrolyzed polyacrylamide polymer in water. (1) Intensity data collected one day after the emulsion was prepared, $R_o=35 000$ Å. (2) Intensity data collected 11 days after the emulsion was prepared, $R_o=23 000$ Å.
results reported here. However, automation of most data processing steps* allowed calculations in a reasonable time.

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* A computer program for processing raw intensity data to locate zero-angle positions of the intensity curves, to calculate the absorption correction, and to calculate the absorption-corrected intensity is available from the author. However, the program may require extensive modification for use with other equipment.

\textbf{References}