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Small-Angle X-Ray Scattering Determination of Particle-Diameter Distributions in Polydisperse Suspensions of Spherical Particles*†

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A scheme is developed for using small-angle x-ray-scattering data to find the distribution of the particle diameters in dilute colloidal suspensions of noninteracting spherical particles. No assumptions need to be made about the form of the distribution function. An investigation is made of the errors likely to be introduced in the numerical operations on the data. The method was tested on theoretical scattering curves for which the calculations could be done both numerically and analytically. After these tests showed the feasibility of the calculation, diameter distributions were computed from the x-ray small-angle scattering data from some polydisperse colloidal samples composed of spherical particles. The results suggest that this technique may often be a useful procedure for analysis of small-angle x-ray-scattering data.

INTRODUCTION

IT is often of interest to know the distribution of particle diameters in colloidal suspensions. Several attempts have been made to determine this distribution by small-angle x-ray scattering. Hosemann,[1] Shull and Roess,[2] and Roess and Shull[3] devised schemes whereby the distribution function could be found by comparing experimental small-angle x-ray scattering data with plots of theoretical scattering curves calculated by assuming reasonable forms for the single-particle scattering curve and the particle-diameter distribution functions. This technique is not always a sensitive method of deciding between different diameter distributions, since very different diameter distribution functions can often yield remarkably similar scattering curves. The method also has the disadvantage of requiring assumptions about the form of the distribution function.

Several authors have described methods of finding the distribution function. Roess[4] showed that for a polydisperse sample of independent spherical particles, the diameter distribution could be obtained from an integral transform of the scattered intensity. In order to ensure convergence, Roess had to leave his results in a form that is often inconvenient to apply to experimental curves. Riseman[5] independently developed an essentially equivalent procedure for finding the diameter distribution function from the scattering data from polydisperse assemblies of spherical particles, and Luzzati[6] briefly outlined a technique for calculating the distribution of particle diameters in a polydisperse sample containing particles of the same shape. Neither

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† A more detailed decription of this investigation is given in a thesis submitted by J. H. Letcher in 1963 in partial fulfillment of the requirements for the Ph.D. degree at the University of Missouri.
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1 R. Hosemann, Kolloid-Z. **117**, 13 (1959).
2 C. G. Shull and L. C. Roess, J. Appl. Phys. **18**, 295 (1947).
3 L. C. Roess and C. G. Shull, J. Appl. Phys. **18**, 308 (1947).
4 L. C. Roess, J. Chem. Phys. **14**, 695 (1946).
5 J. Riseman, Acta Cryst. **5**, 193 (1952).
6 V. Luzzati, Acta Cryst. **10**, 33 (1957).

Roess, Riseman, nor Luzzati attempted to analyze experimental scattering curves.

In this paper the diameter distribution for noninteracting assemblies of spherical particles is expressed as an integral transform of the scattered intensity. The transform can be conveniently evaluated by numerical techniques. The practicality of the method is tested on theoretical scattering curves which can be evaluated both analytically and numerically. The procedure is then applied to some experimental scattering curves.

THEORY

General Theory of Scattering from Polydisperse Systems

Guinier *et al.*[7] show that the relationship between the average relative intensity $\langle F_a^2(h)\rangle$ of the small-angle x-ray-scattering from a single randomly oriented particle of uniform electron density and with the single-particle characteristic function $\gamma_0(r/a)$ is given by the expression

$$\langle F_a^2(h)\rangle=\delta^2 V\int_0^a \gamma_0(r/a)\left(\frac{\sin hr}{hr}\right)4\pi r^2 dr, \qquad (1)$$

where a is the maximum particle diameter (that is, the length of the longest straight line that can be inscribed in the particle), δ is the difference between the electron density within the particle and the electron density of its homogeneous environment, V is the volume of the particle, h is the reduced scattering angle $4\pi\lambda^{-1}\sin(\theta/2)$, λ is the x-ray wavelength, and θ is the scattering angle.

For a polydisperse assembly of randomly oriented independent particles let $\rho(a)$ be the probability that the x ray is scattered by a particle of maximum diameter a. Let $\rho(a)$ be normalized so that

$$\int_0^\infty \rho(a)da=1.$$

Then the scattered intensity $F^2(h)$ from a polydisperse sample in which all particles scatter independently and have random orientation will be given by:

$$\langle F^2(h)\rangle=\int_0^\infty da\rho(a)\langle F_a^2(h)\rangle.$$

For the polydisperse assembly a characteristic function $\gamma(r)$ may be defined so that

$$\langle F^2(h)\rangle=\delta^2\bar{V}\int_0^\infty dr\gamma(r)4\pi r^2\left(\frac{\sin hr}{hr}\right), \qquad (2)$$

where the volume of a particle with maximum diameter a is $V_0 a^3$,

$$\gamma(r)=\frac{V_0}{\bar{V}}\int_r^\infty daa^3\rho(a)\gamma_0(r/a),$$

and $\bar{V}$, the average particle volume, is given by the expression

$$\bar{V}=V_0\int_0^\infty \rho(a)a^3da.$$

By Fourier inversion of Eq. (2)

$$\gamma(r)=\frac{1}{2\pi^2\delta^2\bar{V}}\int_0^\infty dh\left(\frac{\sin hr}{hr}\right)h^2F^2(h).$$

This equation is now put into a different form in order to allow the first three derivatives of $\gamma(r)$ to be computed by differentiation of the integrand. Rearrangement gives

$$\gamma(r)=1-r\frac{C}{8\pi\delta^2\bar{V}}+\frac{1}{2\pi^2\delta^2\bar{V}}\int_0^\infty dh\left[\frac{h^4F^2(h)-C}{h^2}\right]\cdot\left(\frac{\sin hr}{hr}-1\right),$$

where

$$C=\lim_{h\to\infty} h^4F^2(h).$$

Then

$$\gamma''(r)=\frac{1}{2\pi^2\delta^2\bar{V}}\int_0^\infty dh[h^4F^2(h)-C]\frac{d^2}{d(hr)^2}\left[\frac{\sin hr}{hr}\right] \qquad (3)$$

and

$$\gamma''(0)=\frac{-1}{6\pi^2\delta^2\bar{V}}\int_0^\infty dh[h^4F^2(h)-C]. \qquad (4)$$

The Particle-Diameter Distribution Function for Spheres

So far in this development, no restriction has been made on particle shape. If we limit the discussion to the scattering from assemblies of spherical particles, then[7]

$$\gamma_0(r/a)=1-(3r/2a)+(r^3/2a^3)$$

and

$$\gamma(r)=\frac{\pi}{6\bar{V}}\int_r^\infty daa^3\rho(a)\left(1-\frac{3r}{2a}+\frac{r^3}{2a^3}\right).$$

A consequence of Eq. (23) of Chap. II of Ref. 7 is that for $r\geq a$, $\gamma_0(r/a)=\gamma_0'(r/a)=0$. Therefore

$$\rho(r)=-\frac{2\bar{V}}{\pi}\frac{d}{dr}\frac{\gamma''(r)}{r}.$$

If

$$\int_0^\infty \rho(a)da$$

[7] A. Guinier *et al.*, *Small Angle Scattering of X-rays* (John Wiley & Sons, Inc., New York, 1955), pp. 12–19.

exists for assemblies of spherical particles, then $\gamma''(0)$ is zero, because

$$\gamma''(r)=\frac{\pi r}{2\bar{V}}\int_r^\infty da\rho(a).$$

(Note that this notation uses r as a particle diameter, not a radius.) By Eq. (3)

$$\rho(r)=\frac{1}{\pi^3\delta^2 r^2}\int_0^\infty dh[h^4F^2(h)-C]\alpha(hr), \quad (5)$$

where

$$\alpha(hr)=\left[\cos hr\left(1-\frac{8}{\rho^2r^2}\right)-\frac{4\sin hr}{hr}\left(1-\frac{2}{h^2r^2}\right)\right].$$

Equation (5) gives the particle-diameter distribution function in terms of an integral that can be handled by numerical techniques. This expression has the distinct advantage that no numerical differentiation is necessary.

Computer Calculations

If Eq. (5) is to be used to derive the particle-diameter distribution function, the sample must satisfy three conditions. First, it must contain only spherical particles. Second, the scattering curve must be free of interparticle effects. Third, the outer part of the scattering curve must be proportional to h^{-4}, so that the integral in Eq. (5) will converge.

A computer program was written to accept experimental $F^2(h)$ data for scattering angles from 1 to 50 mrad in steps of 1 mrad. The computer evaluated the integral

$$\rho_0(r)=\frac{1}{\pi^3r^2}\int_0^{h_{\max}}[h^4F^2(h)-C]\alpha(hr)dh, \quad (6)$$

where $h_{\max}=4\pi\lambda^{-1}\sin(\theta_{\max}/2)$, and $\theta_{\max}$ is the largest angle at which experimental data are available. In Eq. (5), the quantity $\beta(h)=[h^4F^2(h)-C]$ was assumed to take the form $Ah^{-2}+Bh^{-4}$ for $\theta\geq\theta_{\max}$, with the constants A and B being determined from the experimental data. [The asymptotic behavior of $F^2(h)$ suggests that this form of $\beta(h)$ is physically reasonable.] This procedure permitted evaluation of the integral in Eq. (5) for $h\geq h_{\max}$. Allowance for the contribution of h values greater than $h_{\max}$ will be referred to as "correction for termination error."

It can be shown that

$$\frac{1}{\pi^3r^2}\int_{h_{\max}}^\infty[Ah^{-2}+Bh^{-4}]\alpha(hr)dh=\frac{1}{\pi^3r^2}[A\cdot r\cdot D_a(h_{\max}\cdot r)+B\cdot r^3\cdot D_b(h_{\max}\cdot r)], \quad (7)$$

where

$$D_a(x)=2\frac{\sin x}{x^4}-2\frac{\cos x}{x^3}-\frac{\sin x}{x^2} \quad (8)$$

and

$$D_b(x)=\frac{4\sin x}{3x^6}-\frac{4\cos x}{3x^5}-\frac{2\sin x}{3x^4}+\frac{\cos x}{9x^3}-\frac{\sin x}{18x^2}-\frac{\cos x}{18x}-\frac{Si(x)}{18}+\frac{\pi}{36}, \quad (9)$$

$$Si(x)=\int_0^x\frac{\sin x dx}{x}.$$

A numerical listing of these functions is avaliable from the authors.

For the test functions, the constants A and B were calculated by simultaneous solution of the equations $\beta(h_i)=Ah_i^{-2}+\beta h_i^{-4}$ for two values of h. Tests showed that the results were insensitive to the choice of the values of h_i.

A different method was employed to determine A and B for experimental curves, for which the value of C was not known. One would expect that at $h=h_{\max}$, the function $\beta(h)=[h^4F^2(h)-C]$ would be continuous and have a continuous slope. Also, as $\gamma''(0)=0$, the integral in Eq. (4) must vanish. From this condition and the requirement that $\gamma(r)$ and $\gamma'(r)$ must be continuous at $h_{\max}$, the constants A, B, and C can be determined from the relations

$$0=\int_0^{h_{\max}}dhh^4F^2(h)-Ch_{\max}+A(h_{\max})^{-1}+\tfrac{1}{3}B(h_{\max})^{-3}, \quad (10)$$

$$(h_{\max})^4F^2(h_{\max})=A(h_{\max})^{-2}+B(h_{\max})^{-4}+C, \quad (11)$$

$$x^4F^2(x)=Ax^{-2}+Bx^{-4}+C, \quad (12)$$

where $x=h_{\max}-\epsilon$, and ϵ is a small number.

From Eqs. (10), (11), and (12),

$$A=E_1(x^4-h_{\max}{}^4)-E_2(x^4+3h_{\max}{}^4)+4E_3h_{\max}{}^4, \quad (13)$$

$$B=E_1(x^2h_{\max}{}^4-h_{\max}{}^2x^4)+3E_2(h_{\max}{}^2x^4+h_{\max}{}^4x^2)-6E_3h_{\max}{}^6, \quad (14)$$

$$C=E_1(h_{\max}{}^2-x^2)+E_2(x^2-3h_{\max}{}^2)+2E_3h_{\max}{}^2, \quad (15)$$

where

$$E_1=-3E_0h_{\max}{}^3\int_0^{h_{\max}}dhh^4F^2(h),$$

$$E_0=[2h_{\max}{}^2x^4+4h_{\max}{}^4x^2-6h_{\max}{}^6]^{-1},$$

$$E_2=E_0h_{\max}{}^8F^2(h_{\max}),\quad\text{and}\quad E_3=E_0x^8F^2(x).$$

The Test Functions

In order to test the results of the $\rho(r)$ program for systematic errors in the experimental data and to check the accuracy of the numerical methods in the $\rho(r)$ program, theoretical intensity functions were used that

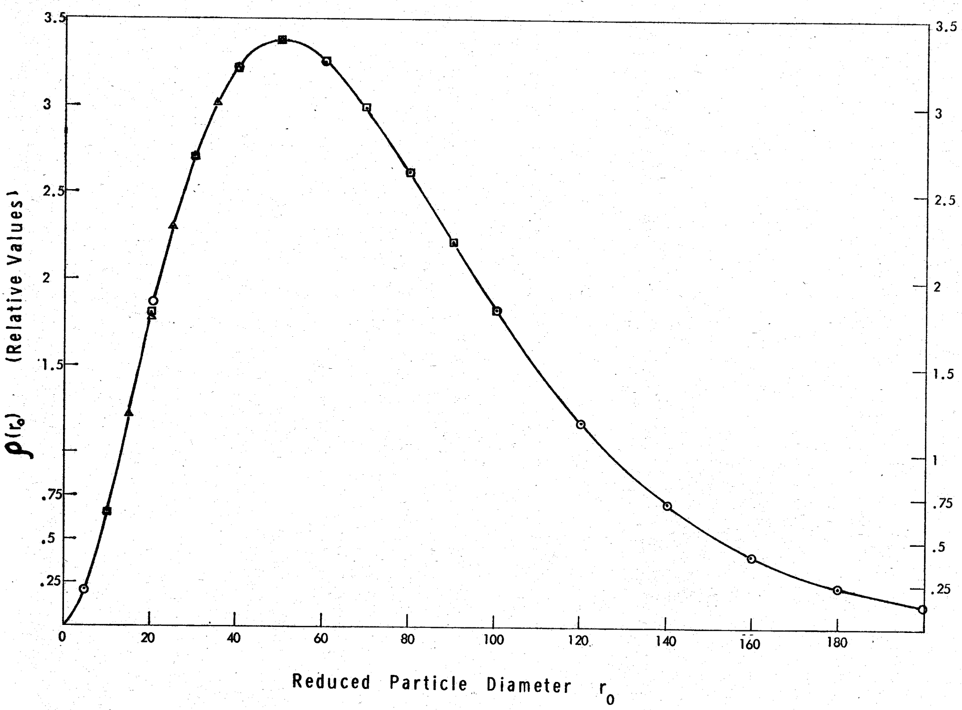

FIG. 1. Relative values of the diameter distribution for the $F_2{}^2(h)$ test functions. Triangles, squares, and circles denote test functions with D_{max} values of 200, 100, and 50 Å, respectively. The abscissa shows the reduced particle diameter $r_0=50(D_{max})^{-1}r$, with r being expressed in angstroms.

were known to yield given particle-diameter distribution functions. If[8]

$$\rho(r)=[a^{n+7}/(n+6)!]r^ne^{(-ar/2)}, \qquad (16)$$

where $n=0, 1, 2, \cdots$, then

$$F_n{}^2(h)=I_n(h)=\frac{a^{n+7}(-1)^n}{(n+6)!}\frac{\partial^n}{\partial a^n}\times\left[720a^{-7}\left(1+\frac{x^2}{5}\right)(1+x^2)^{-3}\right], \qquad (17)$$

where $x=2h/a$. Therefore for $n=0$,

$$h^4F_0{}^2(h)-C=h^4\left(1+\frac{4h^2}{5a^2}\right)\left(1+\frac{4h^2}{a^2}\right)^{-3}-\frac{a^4}{80}, \qquad (18)$$

and for $n=2$

$$h^4F_2{}^2(h)-C=\frac{h^4}{70}(C_1y^{-5}+C_2y^{-4}+C_3y^{-3}+C_4y^{-2})-\frac{C_4a^4}{1120},$$

where

$$y=(1+4h^2/a^2), \quad C_1=48, \quad C_2=12, \quad C_3=7, \quad C_4=3.$$

Diameter-distribution functions were calculated with the functions $F_0{}^2(h)$ and $F_2{}^2(h)$ for several values of the constant a. When $n=0$, $\rho(r)=k_0e^{-ar/2}$, where k_0 is the normalizing constant. For $n=2$, $\rho(r)$ has a maximum at $r=4/a=D_{max}$, and $\rho(r)$ curves were computed for the a values 0.002, 0.004, 0.008, 0.02, 0.04, 0.08, and 0.16 Å^{-1}, yielding maxima in the calculated $\rho(r)$ curves at 2000, 1000, 500, 200, 100, 50, and 25 Å, respectively. The results of these calculations are given in Fig. 1. After the curves had been corrected for termination error by the scheme outlined previously, at no point was the error greater than 0.1%. Figure 2 shows the contribution of each term in the termination error when $\rho(r)$ is calculated from the test function $F_2{}^2(h)$. When diameter distributions were calculated with this function with incorrect values of C_1 and C_2, there was little change noticeable in the plots of the test function, but at small r, a large error was generated in $\rho(r)$. In the $F_2{}^2(h)$ test functions, termination error is extremely large at small r, and this error accounts for the large fluctuations in $\rho(r)$, as in this range of r, $\rho(r)$ is the small difference between two large quantities.

For the calculations with the test functions, the differences between the computed and the expected results were in all instances less than 0.5% and in most cases were under 0.1%. The termination errors were greatest at small r and decreased for increasing r. The values obtained for A and B were found to be quite insensitive to the choice of ϵ, and the change of ϵ never produced errors as large as 0.2% in the calculated values of $\rho(r)$.

The Effect of Systematic and Random Errors in the Input Data

In the evaluation of the merit of this method of determining $\rho(r)$, the question arises concerning the sensitivity of the calculation to various types of errors. The effect of a random error in the experimental data

[8] P. W. Schmidt, Acta Cryst. 11, 674 (1958).

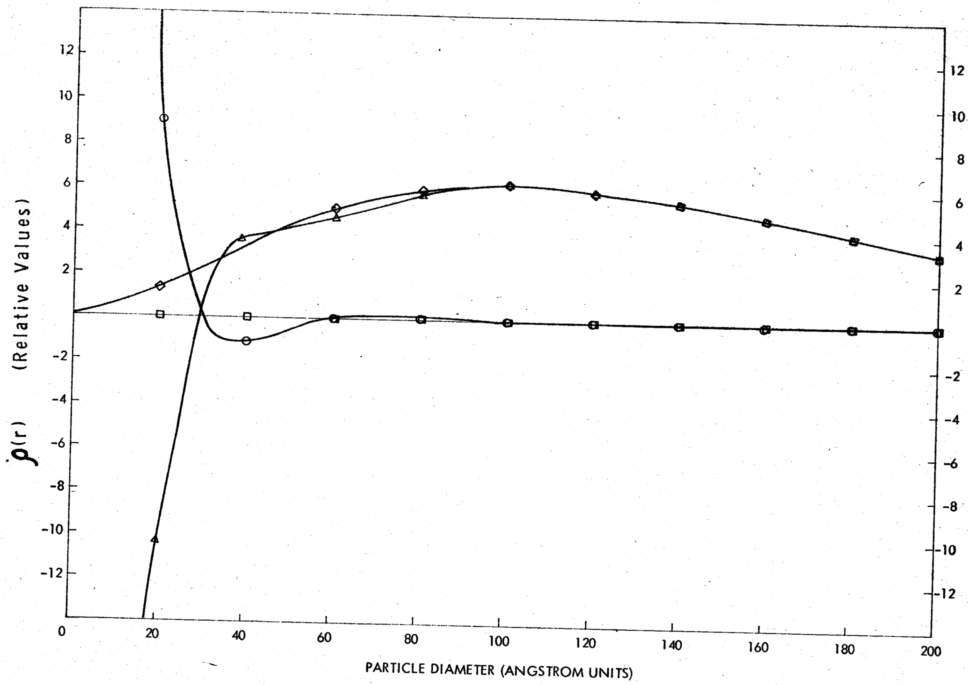

FIG. 2. The effects of termination error on the relative values of the diameter distribution function $\rho(r)$ for the $F_2^2(h)$ test function with $D_{max}=100$ Å. The values of $\rho(r)$ before and after correction for termination error are indicated by triangles and diamonds, respectively, and the termination error terms in Eq. (7) proportional to $D_a(h_{max}\cdot r)$ and $D_b(h_{max}\cdot r)$ are shown, respectively, by circles and squares. The termination error from $D_b(h_{max}\cdot r)$ can be seen to be negligible for $r\geq 20$ Å.

was tested by introducing a random error in $F^2(h)$ by defining an "incorrect" value $F_s^2(h)$ by the relation $F_s^2(h)=F^2(h)[1+(N-4.5)\sigma]$. The number σ determined the magnitude of the random error, and N is a different random number for each value of h. When $\sigma=0.005$, the maximum fluctuation between values of $F_s^2(h)$ is 4.5% of $F^2(h)$. Values of σ producing 0.9%, 2.7%, and 4.5% maximum fluctuation were used with each of four test functions. For $r>80$ Å, the change in the computed values of $\rho(r)$ was negligible even with 4.5% fluctuation, and the error grew as r decreased.

It was found with the $F_2^2(h)$ test functions that the relative effect of random errors at a given r value decreased as D_{max} decreased. For example, for $D_{max}=25$ Å, there were negligible errors in $\rho(r)$, but for $D_{max}=1000$ Å, the random errors in the test function caused errors greater than those shown in Fig. 3, for which D_{max} is 200 Å. Different sets of random numbers were

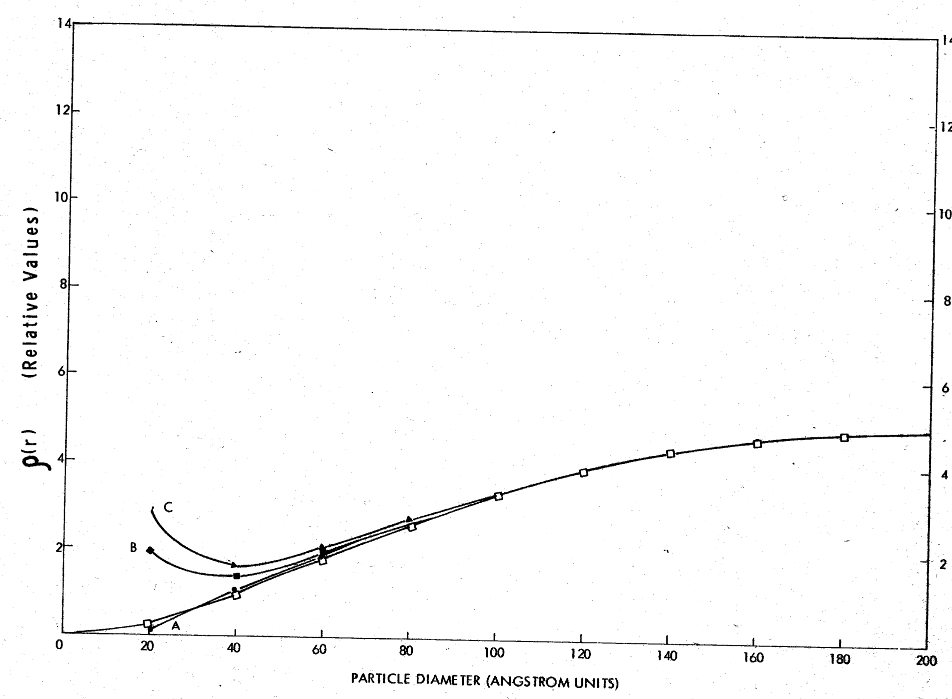

FIG. 3. The effect of random errors on the relative values of $\rho(r)$ computed from the $F_2^2(h)$ test function with $D_{max}=200$ Å. Open squares show $\rho(r)$ for no random error, and the $\rho(r)$ curves for maximum fluctuations of 0.9%, 2.7%, and 4.5% are indicated, respectively, by curves A, B, and C.

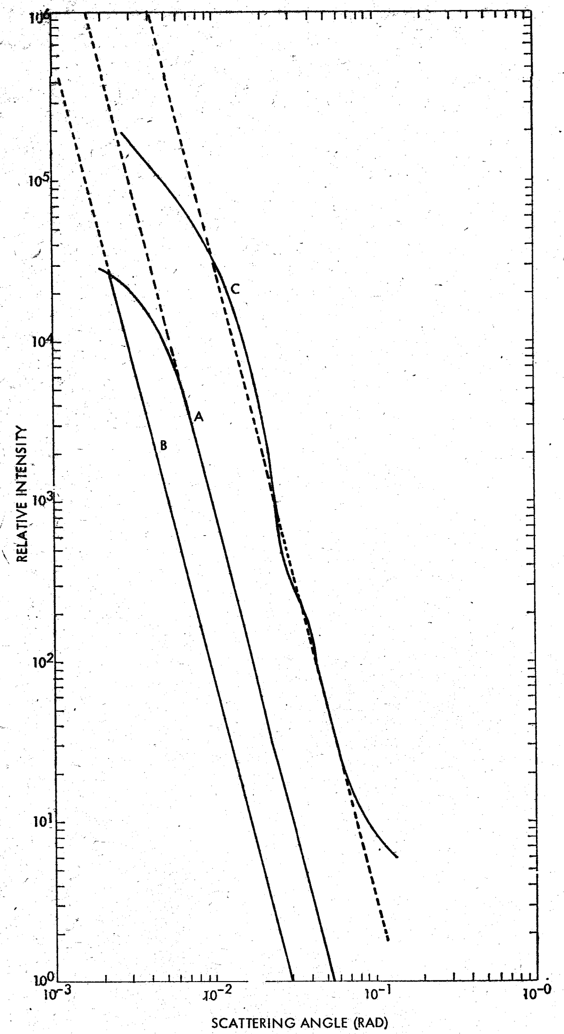

FIG. 4. The corrected x-ray scattering curves for the Ludox samples. Curves A, B, and C represent Ludox III, Ludox II, and Ludox I, respectively.

used with several of the test functions, in order to rule out the possibility of an anomalous situation occurring because of a given combination of random numbers. For all sets of random numbers, the relative errors were comparable.

The introduction of a random error in the angular range of the test function which would correspond to experimental data showed that a large error in $\rho(r)$ would result if and only if the sum of the termination-error terms were large with respect to the original computed value of

$$\rho_0(r)=\frac{1}{\pi^3 r^2}\int_0^{h_{\max}}[h^4F^2(h)-C]\alpha(hr)dh.$$

A systematic continuous error such as misdefining C_1 and C_2 in computing the test function $F_2{}^2(h)$ had the same effect as a random error; i.e., large variations in $\rho(r)$ can be produced at small r, with the magnitude of the error decreasing or r becomes larger.

Analysis of Experimental Scattering Curves

The scattering curves for three experimental samples,[9,10] which will be referred to as Ludox I, Ludox II, and Ludox III are shown in Fig. 4. The data were corrected for slit-height collimation effects and for all background except the scattering from the solvent water. The outer parts of all the curves are proportional to h^{-4}. The effects of interparticle interference were eliminated by diluting the suspensions until the shape of the scattering curve was unchanged when the concentration was further reduced by a factor of two.

The Ludox II sample was unsuitable for the $\rho(r)$ calculation, since the scattering curve was proportional to h^{-4} over the entire range of the experimental data, and thus no information was available about the inner part of the scattering curve. This behavior was due to the relatively large average particle diameter (about 1000 Å) in this sample.

For the other two samples, the $\rho(r)$ curves are shown in Figs. 5 and 6. For both samples the calculations were done for three different values of ϵ. The computed diameter distributions were found to be quite insensitive to the choice of ϵ. For the $\rho(r)$ curves in Figs. 5 and 6, the ϵ values were chosen to make the slope of the $F^2(h)$ curve as nearly continuous as possible at $h=h_{\max}$.

The $\rho(r)$ plots were not normalized, since normalization would require assumptions about the number of particles with diameters greater than 300 Å. For these samples, computations of $\rho(r)$ for $r>200$ Å are probably not reliable because they depend too strongly on the values of $F_2{}^2(h)$ at small h, where the data are quite uncertain.

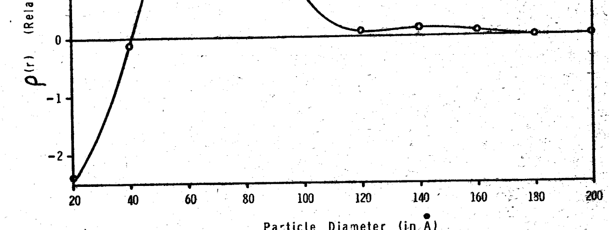

FIG. 5. Relative values of $\rho(r)$ for Ludox I.

[9] The Ludox samples studied were Ludox I: SM Colloida Silica No. 3397-66 Du Pont Chemical Corporation, Ludox II 100 μm Silica Sol No. 2692-125 Du Pont Chemical Corporation All scattering curves were obtained on an apparatus describe elsewhere [H. D. Bale, Ph.D. thesis, University of Missour (1959)] and were corrected for slit collimation error by the tech nique of Schmidt and Hight [P. W. Schmidt, and R. Hight Acta Cryst. 13, 480 (1960)].

[10] The Ludox III data were obtained by R. Hight [thesi University of Missouri (1962)].

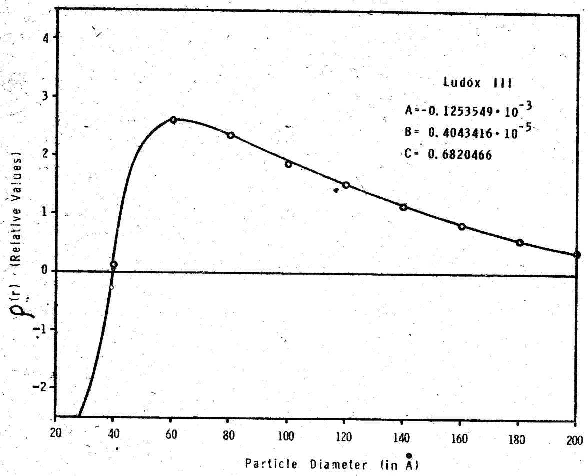

FIG. 6. Relative values of $\rho(r)$ for Ludox III.

The values of $\rho(r)$ for $r=20$ Å are not significant because they are sensitive to errors of all types. For the Ludox samples, the sources of these errors could not be located. The results of the error studies on the test functions suggest that the Ludox I and III $\rho(r)$ values should be meaningful for $r \geq 40$ Å.

In Ludox I, the most probable particle diameter was found to be 70 Å. This result is in good agreement with the mean particle diameter of 70 Å given by the manufacturer.

For Ludox III, the most probable diameter was found to be about 55 Å, but the distribution of diameters was found to be very broad, extending to much larger values of r. This distribution is not inconsistent with the manufacturer's value of 140 Å for the mean particle diameter.

DISCUSSION

The results of the computations of $\rho(r)$ for the test functions and the Ludox samples suggest that this method may be useful procedure for interpretation of small angle x-ray scattering data. A final judgment about the method, however, will have to wait until $\rho(r)$ has been computed for a number of experimental scattering curves. Further tests are now in progress.

Equation (5) can also be applied to suspensions of particles which are not spherical. In this case, the resulting $\rho(r)$ curves represent the diameter distribution of the sample composed of spherical particles that would produce the observed scattering. If the particles in the experimental sample are nearly spherical, one might expect that the computed $\rho(r)$ curve would ordinarily be a reasonable approximation to the diameter distribution actually present in the sample. Care must be taken in using this procedure, however, since certain scattering curves may not be obtainable from any reasonable distribution of spherical diameters. Attempts to apply Eq. (5) to these scattering curves would not lead to meaningful results. Suggestions of this effect were obtained in computation of the $\rho(r)$ from the scattering curves from two polydisperse thoria sols, which electron micrographs showed were composed of particles shaped approximately like cubes.

The computed $\rho(r)$ curves represent the diameter distribution that would produce the observed scattering if the sample particles had uniform electron density. Because the assumption of uniform electron density neglects the atomic and molecular structure, for small r the calculated diameter distributions might not represent the actual diameter distributions in the sample.

Under quite general conditions[11] the constant A can be shown to be always positive. Therefore, it should always be positive when it is obtained in a computation of $\rho(r)$ from an experimental curve. For the two Ludox samples, however, the values of A were negative. At present, no explanation can be given for this result.

The studies of the test functions indicate that termination errors generate only a small error in $\rho(r)$ when $r \geq 40$ Å, if the data are known in the angular range where the scattering is proportional to h^{-4}. Unfortunately, however, experimental data are often uncertain in this region, and these errors may limit the accuracy with which the constants A, B, and C, and thus, $\rho(r)$ may be determined.

In a study of polydisperse sols, the parameters usually measured, such as average specific surface or molecular weight, represent averages which give little information about the deviations from average values. The diameter distribution function should provide useful information about the distribution of particle dimensions, and with this information a more complete description of the sample will be possible than would otherwise be obtained.

ACKNOWLEDGMENTS

The authors would like to express their appreciation to the Monsanto Company for use of their computer facilities for part of the calculations, to Dr. John Bugosh and his assoliates at Du Pont Chemical Corporation Laboratories for donating the Ludox samples, and to Oscar Roloff and Harry E. Dey for assistance in construction of the x-ray scattering apparatus.

[11] P. W. Schmidt and O. L. Brill (unpublished research).