

Evaluation of Light-Scattering and Small-Angle X-Ray Techniques Using Dilute Dispersions of Uniform Polystyrene Latices

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INTRODUCTION

Monodisperse polystyrene latices have been extremely useful in studies of both theoretical and practical nature. Several investigations on the optical properties of these materials have been published. Dandliker¹ applied the Mie² theory and deduced the particle size from both the particle molecular weight and the first minimum in the angular intensity (first order interference pattern). Billmeyer³ evaluated the size of a relatively small polystyrene latex using an interesting transmission technique. Tabibian, Heller, and Epel,⁴ and also Kerker and Matijevic,⁵ have applied the Mie theory to a number of polystyrene and polyvinyltoluene latices. LaMer and co-workers⁶⁻¹² have confirmed in broad outline that the Mie theory correctly predicts the behavior of aerosols and hydrosols. Using colloidal sulfur sols,¹³ and later polystyrene latices,¹⁴ LaMer and co-workers have studied in some detail the appearance of the higher order Tyndall spectra. Bateman, Wenéck, and Eshler¹⁵ have tested the Mie theory for a wide range of particle sizes using polystyrene latices.

In general, most of these papers are concerned with a more or less rigorous proof of the Mie theory, or to check the accuracy of the light-scattering equipment. Most light-scattering investigators are more familiar with the simpler Debye¹⁶ and Zimm¹⁷ methods of treating data. The present investigation was undertaken in an attempt to evaluate further the results of previous light-scattering studies in these laboratories on small gels present in cellulose acetates.^{18,19} These gels, when dispersed in acetone, appear to consist largely of nearly monodisperse spherical or potato shaped objects of about 0.3-0.4- μ in diameter.

The work was subsequently extended to evaluate the utility of several scattering equations in the literature, both in the field of light scattering and small-angle x-ray scattering. One of the purposes of this paper, therefore, will be to estimate the applicability of these light-scattering techniques to colloidal systems having sizes near the wavelength of light when only moderate accuracy is required.

EXPERIMENTAL PROCEDURES

Samples and Dispersion Preparation

Several samples of nearly monodisperse, spherical polystyrene latices were kindly made available to us by Dr. John W. Vanderhoff of The Dow Chemical Company. The sample designations and the average size deduced by electron microscopy at the Dow Physical Research Laboratory are shown in Table I.

TABLE I
Characterization of the Polystyrene Latices

Designation	Diameter, μ
LS-040-A	0.088
LS-055-A	0.188
LS-057-A	0.264
LS-061-A	0.365
LS-063-A	0.557
LS-066-A	0.814
LS-067-A	1.171

All samples were diluted volumetrically with distilled water, and the exact concentrations were determined by dry weight analysis. The dispersions were then passed through a 15- μ sintered glass filter to remove dust before optical readings were made.

Instrumentation

Two instruments were utilized in this investigation: a Brice-Phoenix Model 1000-D light-scattering machine and a Beckman ratio recording spectrophotometer (DK-2). The former was employed for the angular work. Its lineup and calibration are described in a previous publication.¹⁸ All measurements were made with 5461 Å light at 20°–135°. The Beckman spectrophotometer was used for the transmission studies. The wavelength range 365–700 m μ was investigated. Matched 10 cm. cells were employed throughout this part of the investigation. No modifications were made to this equipment to improve the alignment of the light beams or to remove the small-angle scattering of the samples.

THEORY

In order to estimate independently particle molecular weights, sphere diameters, and surface areas, several light-scattering and x-ray formulations were applied to the experimental data. The pertinent equations will be discussed below.

Debye Light-Scattering Formulation

The weight-average particle molecular weight M_w (the weight in grams of a mole of spheres) and the z -average diameter D_z may be evaluated by

using the theory developed by Debye¹⁶ and Zimm.¹⁷ Essentially the procedure calls for a double extrapolation to zero angle and zero concentration of a plot Hc/τ vs. $\sin^2(\theta/2) + kc$. The value M is then given by:

$$1/M_w = H^c/\tau_{c=0, \theta=0} \quad (1)$$

and D_z is determined by:

$$D_z^2 = 5(\lambda')^2 (\text{slope})/4\pi^2 (\text{intercept}) \quad (2)$$

where

$$H = 32\pi^3 n_0^2 (dn/dc)^2 / 3\lambda^4 N \quad (3)$$

and λ and λ' are the wavelengths of the light in vacuum and in the solution, respectively; N is Avogadro's number, n_0 is the refractive index of the solvent, and dn/dc is the rate of change in refractive index of the solution caused by changing the solute concentration. The value for H at 5461 Å. was taken to be 6.74×10^{-6} , as calculated by Billmeyer,³ for the purposes of this investigation. The turbidity τ was evaluated for each concentration c for a series of angles θ . The (slope) and (intercept) values refer to the slope and intercept obtained by plotting $(H^c/\tau)_{c=0}$ vs. $\sin^2(\theta/2)$.

The molecular weight as calculated by eq. (1) is subject to corrections due to depolarization. There are two cases to be considered: molecular depolarization and geometrical depolarization. The first case has been considered by Cabannes.²⁰ His solution to this problem is well known. Generally, the correction for depolarization due to anisotropic molecules is of the order of a few per cent or less, and may often be neglected. The second case is important in large particles, and comes about because of refraction effects. Use of the Cabannes correction factor for eq. (1) when most of the depolarization is geometrically caused will result in a serious over-correction of the molecular weight.²¹ The correction for this formulation [eq. (1)] is not known. When geometrical depolarization is encountered, the Mie theory must be employed.

The angular scattering pattern of monodisperse spheres having diameters the size of the wavelength of the light or larger will exhibit maxima and minima. If it can be assumed that the refractive index of the spheres is near that of the solvent, Debye's equations for scattering from spheres may be used. In one form, these may be written:¹⁸

$$\lambda'/D = k' \sin(\theta/2) \quad (4)$$

where D is the diameter and k' will assume values near $4/3$, 1, and $4/5$ for the first minimum, first maximum, and second minimum of the scattering intensity appearing at angle θ , respectively. When these maxima and minima appear they are sensitive indicators of monodisperse spheres.

Transmission Techniques

Using transmission techniques, the turbidity is defined by:

$$I = I_0 e^{-\tau x} \quad (5)$$

where I/I_0 is the fraction of light passing through a cell of thickness x . The wavelength dependence of the turbidity is given by Rayleigh's law:²²

$$\tau = k\lambda^a \quad (6)$$

where a has the limiting value of -4 when the particles are much smaller than the wavelength of the light. As the particle size approaches that of the wavelength of light, the value of a has the value^{8,23} of about -2 . This theory has been expanded upon by Billmeyer³ and by Doty and Steiner.²⁴ For very large monodisperse spheres the wavelength dependence of the turbidity goes through a maximum, which may be used to estimate the diameter of the particles.²⁵

Adaptation of Small-Angle X-Ray Equations

Two methods of analysis normally applied to the evaluation of particle sizes by small-angle x-ray techniques were also employed in evaluating the sizes of the spheres. Shull and Roess²⁶ have presented a theory which is applicable to Maxwellian size distributions of particles. The equations, as presented by Guinier,²⁷ may be written:

$$\log \tau = \text{constant} - (n + 4)/2 \log (h^2 + 3/r_0^2) \quad (7)$$

where r_0 and n are experimental numbers and $h = (4\pi \sin \theta)/\lambda$. $\log \tau$ is plotted versus $\log [h^2 + (3/r_0^2)]$, different values of $3/r_0^2$ being chosen, until a straight line is obtained. The slope of this straight line then defines the value of n . The arithmetic mean of the diameters is then given by

$$D = (20/3)^{1/2} [\Gamma(n/2 + 1)/\Gamma(n/2 + 1/2)] r_0 \quad (8)$$

which equates the value r_0 to the diameter through the use of the gamma functions of n . The factor $(20/3)^{1/2}$ is to convert radii of gyration in the original equation to the equivalent sphere diameter.²⁸

Debye, Anderson, and Brumberger²⁹ published a very interesting theory useful for evaluation of void surface areas in porous materials. The principle employed in the computation of the surface area is the evaluation of the probability that a measuring rod of arbitrary length, randomly placed in the medium, will have its ends in the two different phases (i.e., solid vs. pore space). Extensive use is made of an exponential correlation function.

According to Debye,³⁰ this theory can also be applied to dilute dispersions such as considered in this paper. The specific surface S_{sp} (in square meters per gram) is defined by

$$S_{sp} = 4\phi(1 - \phi)/d_{pb} \times 10^4 \quad (9)$$

where the void fraction, ϕ , is replaced by the volume fraction of the dispersed phase:

$$\phi = V_{ps}/(V_w + V_{ps}) \quad (10)$$

where V_{ps} and V_w are the volumes of polystyrene and water per cubic centimeter, respectively. The parameter d_B is the bulk density, and b is defined by the relation:

$$b = (\lambda'/2\pi) (\text{slope/intercept})^{1/2} \quad (11)$$

where the slope and intercept values are obtained by plotting $\tau^{-1/2}$ versus $4 \sin^2 (\theta/2)$ (this last term equals θ^2 for small angles) and extrapolating to $\theta = 0^\circ$, in a similar manner as considered for eq. (2).

RESULTS

Debye Light-Scattering Parameters

The results of the treatments developed by Debye will be presented first. Figure 1 shows a Zimm plot of the small-angle data (20° – 70°) obtained from measurements on the 0.365μ diameter (Dow) latex. Equation (1), unfortunately, cannot be applied to Figure 1 because of the unusually high value of the depolarization encountered for this system, 0.723. Depolarizations of this magnitude have been observed earlier,¹ and are due to the geometrical depolarization discussed above.

Figure 2 illustrates the minimum in scattering intensity at 105° obtained from the zero concentration portion of the complete angle Zimm plot. By application of eq. (4) a diameter of 0.39μ can be deduced. Also illustrated in Figure 2 is the initial slope from which D_z may be calculated. The value

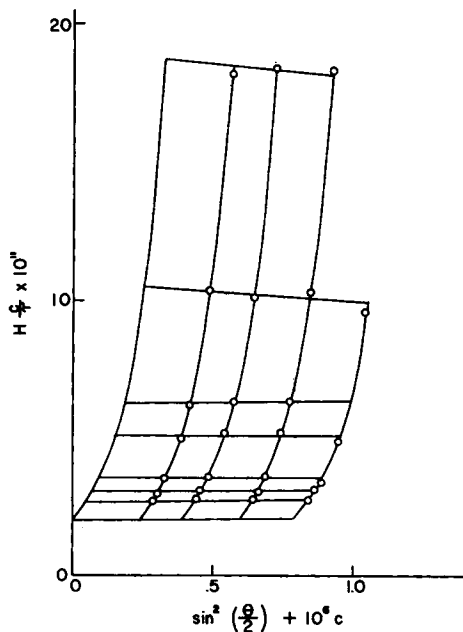


Fig. 1. Evaluation of low-angle data, Dow LS-061-A.

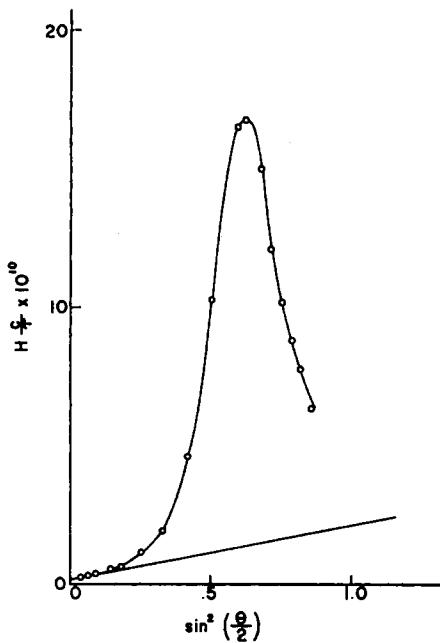


Fig. 2. Zero concentration line and limiting angle line, Dow LS-061-A.

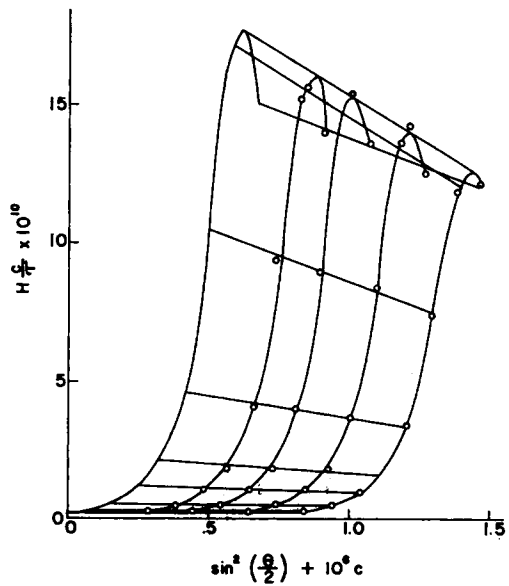


Fig. 3. Zimm plot illustration of the maximum at 105° , Dow LS-061-A.

obtained from eq. (2), however, is unrealistically high, also due to geometrical depolarization. Figure 3, based on the same data as used in Figures 1 and 2, contains a wider angle Zimm plot than Figure 1, and illustrates the maximum as a function of concentration. The complete Zimm plot is not shown because the sharp minimum in scattering intensity at 105° creates a difficult-to-draw effect.

Figure 4 illustrates the zero concentration line of the Zimm plot obtained from light-scattering observations on the 0.557μ (Dow) latex. The appearance of multiple minima and maxima in the pattern can be noted. The diameter of these spheres may be estimated from each of these.

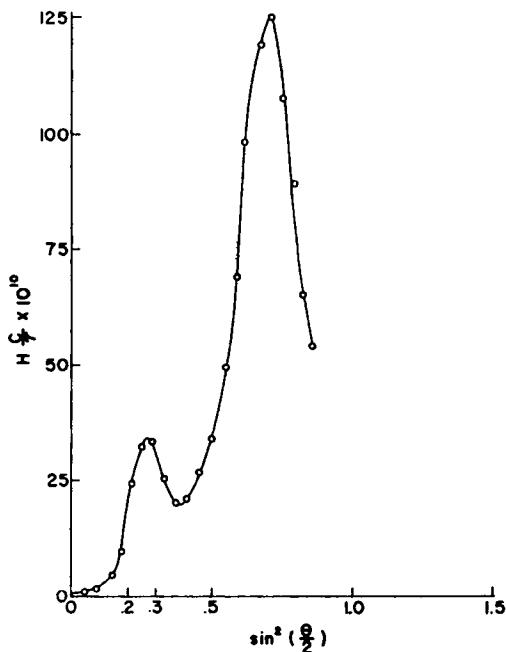


Fig. 4. Zero concentration line Zimm plot of the Dow LS-063-A (0.557μ) latex.

A similar study was carried out on latex LS-O57-A (0.264μ). The Zimm plot was without maxima or minima. A summary of the light-scattering results obtained using the above formulations is shown in Table II. It is observed that the M_w and D_z values are fairly reasonable for the 0.264μ size latex. For the larger sized latices, the M_w and D_z values are unrealistic, and are not shown in Table II. However, at this size the maxima and minima have appeared, and reasonable calculations can be made with eq. (4).

The principal error introduced in these calculations is probably the assumption that the refractive index of the latex is close to that of the dispersing fluid, water.^{1,31} The phase shift of the light resulting from this difference is not accounted for by the above theories.

TABLE II
Evaluation of Latices Using Approximate Light-Scattering Formulations

Parameter	Latex designation		
	LS-057-A	LS-061-A	LS-063-A
Electron microscope diameter, μ	0.264	0.365	0.557
Shull and Roess D , μ	0.273	0.385	0.619
D_w (from M_w), μ	0.22	—	—
D_z , μ	0.24	—	—
D (1st min.), μ	—	0.394	0.590
D (1st max.), μ	—	—	0.661
D (2nd min.), μ	—	—	0.620

The values obtained from the maxima and minima data are considerably better although all of these results are slightly high. These values also could be further improved by taking into account the actual refractive index difference.¹

Shull and Roess Formulation

The two small-angle x-ray theories investigated and adapted to optical light-scattering produced very interesting results. Application of the Shull and Roess formulation to the 0.365μ latex is illustrated in Figure 5. Here $\alpha = 3/r_0^2$. In Figure 5 $\log(\tau/Hc)$ at zero concentration was plotted vs. $\log(h^2 + \alpha)$ until a straight line was obtained, in this case at $\alpha = 2000$.

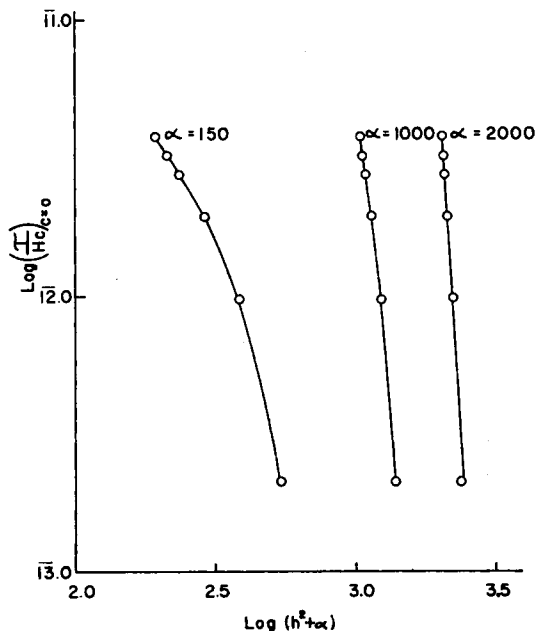


Fig. 5. Application of the Shull and Roess formula, Dow LS-061-A.

Log (τ/Hc) at zero concentration was used so that interparticle interference would be eliminated. The resulting diameters calculated by use of eqs. (7) and (8) are shown in Table II. It was further found that small errors in α and hence n caused by not having a straight line tended to be self-compensating. For the smaller angles (20° - 70°) normally used in light scattering, this method apparently gives very nearly the correct answer for moderate-sized particles.

Debye Surface Area Evaluation

The evaluation of surface areas by using the method developed by Debye²⁹ for small-angle x-ray scattering was also of interest. As mentioned above, this theory should also be useful for visible light-scattering problems. It is of considerable interest to have an independent measure of the surface area of colloidal objects, as well as mass and diameter, in order to more completely evaluate the shape of such materials.

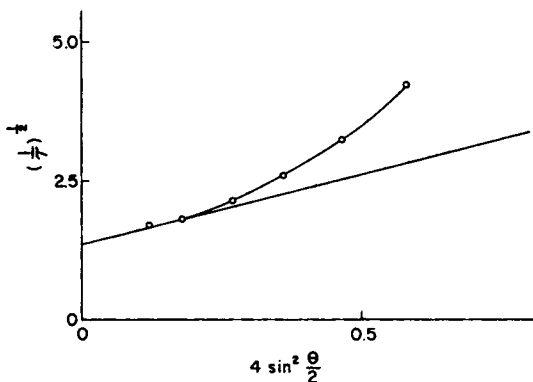


Fig. 6. A plot of $\tau^{-1/2}$ vs. $4 \sin^2(\theta)$ to determine surface areas by the Debye method. Sample LS-063-A (0.557μ , Dow). $C = 2.58 \times 10^{-6}$ g./ml.

In contrast with the above methods in which an extrapolation to zero concentration was involved, the measurement of surface areas was carried out using a finite concentration. A plot of $\tau^{-1/2}$ versus $4 \sin^2(\theta/2)$ is shown in Figure 6. The resulting experimental surface areas obtained through the application of eqs. (9) to (11) are compared with those com-

TABLE III

Surface Areas Obtained by Debye's Equations Compared with Surface Areas Determined Geometrically

Sample	c, g./ml.	Surface areas, m. ² /g. H ₂ O	
		Experimental	Calculated
LS-057-A (0.264 μ)	1.19×10^{-6}	12.1×10^{-6}	2.6×10^{-6}
LS-061-A (0.365 μ)	5.94×10^{-7}	36.6×10^{-6}	9.3×10^{-6}
LS-063-A (0.557 μ)	2.58×10^{-6}	12.9×10^{-6}	2.5×10^{-6}

puted from the concentration and the known diameter (electron microscopy) in Table III. In each case, it is observed that the experimental value is four or five times larger than that estimated from the known concentration and diameter of the spheres. The cause of this discrepancy is not known but may be in part due to the relatively large difference in refractive index between solvent and dispersed phase.

Light-Scattering Studies by Transmission

The lattices were also examined by transmission techniques as described above. One concentration of each latex was examined for each sample. The results for five of the samples are shown in Figure 7. The optical density, O.D., of the samples is related to the turbidity τ by the relationship $\tau = (0.2303) 0.2$, where 10 cm. cells are employed. Some results that were obtained from this experiment were as follows:

(1) A plot of $\log \tau$ vs. $\log \lambda$ as suggested by eq. (6) yielded straight lines for the smaller-sized particles. As the particle size is allowed to increase, the value of the slope gradually becomes less negative. The values of the Rayleigh slopes obtained from such plots are tabulated in Table IV.

(2) As noted in Figure 7, the largest particle size exhibits a maximum in its O.D. at 472 m μ . According to Heller's²⁵ work, the maximum should occur at 651 m μ , assuming that the ratio of the refractive indices of the polystyrene and water is near 1.20. The experimental maximum predicts a

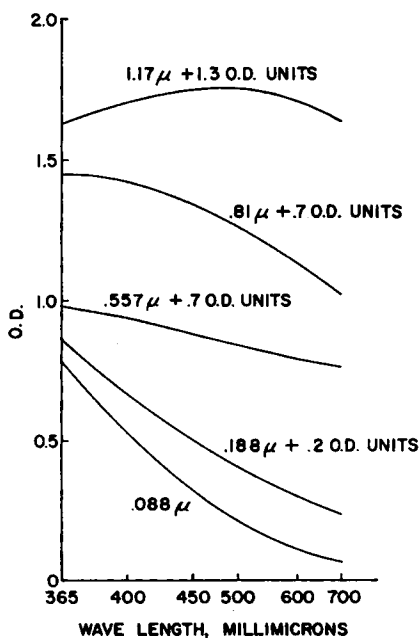


Fig. 7. Transmission patterns of the polystyrene lattices as a function of wavelength. Note artificial vertical displacements on some of the curves.

diameter of 0.85μ according to Heller's theory, as compared with the actual size of 1.17μ . Much of the error may be due to the relatively large amount of scattered light that is recorded as "transmitted" by the Beckman equipment.³²

(3). The precision in the measurement of a in eq. (6) is about ± 0.1 unit. The slope of the smallest latex, of course, cannot be more negative than -4.0 .

TABLE IV
Rayleigh Slopes Obtained by Application of Eq. (6)

Latex diameter, μ	Slope a , eq. (7)
0.088	-4.1
0.188	-3.2
0.264	-2.9
0.365	-2.5
0.557	-2.2
0.814	curve
1.17	curve

DISCUSSION

The main purpose of carrying out this investigation was to test the validity of several approximate light and x-ray scattering relationships outside the range of their normal application. With this in mind, the following conclusions can be drawn.

(1) If highly accurate results are required, most of the methods considered above are somewhat inadequate, depending on the size of the spheres relative to the wavelength of the light and the difference in refractive indices between the dispersed and dispersing phases. The Debye surface area treatment shows a constant error which the writer cannot explain. For approximate results, or for relative evaluations, however, these equations may still prove useful.

(2) The maxima and minima in the angular light-scattering pattern, and the Shull and Roess formulations are probably the best guides to the actual particle size in the range where the particles are somewhat larger than the wavelength of the light.

It should be re-emphasized that much better results can be obtained by use of more exact theories such as developed by Mie. However, many interesting systems are difficult to evaluate using this theory. It is desirable to have an indication of the usefulness and expected errors in applying simple relationships to previously uncharacterized colloids. Since much of the present treatment is applicable to general colloidal systems, it is hoped that this paper may contribute toward this end.

Note Added in Proof. Since this work was completed, an advance has been made in the computation of surface areas by the Debye method. Caul-

field and Ullman^{23,24} have shown that, if one knows he has spheres, the correct diameter is given by:

$$D = 2(10)^{1/2}b \quad (12)$$

from which the surface area may be computed. This correction leads to the values shown in Table V.

TABLE V
Sphere Diameters by Caulfield and Ullman's Modified Debye Treatment

Dow diameter, u	b, u	$2(10)^{1/2}b$
0.264	3.75×10^{-2}	0.238
0.365	6.17×10^{-2}	0.392
0.557	7.59×10^{-2}	0.480

It is observed that the recomputed diameters will give nearly the correct surface areas. It is of some value to note that these diameters are considerably more accurate than the Zimm plot values. This may, in part, be due to the square root plot involved.

The writer wishes to thank Miss Barbara Franklin for diligently carrying out the experimental phases of this work.

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Synopsis

Several light- and x-ray-scattering formulations were evaluated using polystyrene spheres having diameters near the wavelength of the employed light. While some error in the dimensions calculated using these equations is both expected and found, it is shown that these methods may still be useful for approximate or relative results. One of the purposes of this paper will be to estimate the applicability of these light-scattering techniques to colloidal systems having sizes near the wavelength of light when only moderate accuracy is required. It is shown that the better diameter estimations are obtained by using (1) the maxima and minima that appear in the angular light-scattering pattern, or (2) the Shull and Roess formulation adopted from small-angle x-ray theory

Résumé

Plusieurs formules de diffusion de lumière et de rayons- ont été envisagées en utilisant des sphères de polystyrène ayant des diamètres proches de la longueur d'onde de la lumière employée. Puisqu'une certaine erreur dans les dimensions calculées en employant ces équations est à la fois attendue et trouvée, on a montré que ces méthodes peuvent encore être employées pour des résultats approximatifs ou relatifs. Un des buts de cet article sera d'estimer l'applicabilité de ces techniques de diffusion lumineuse aux systèmes colloïdaux ayant des dimensions proches de la longueur d'onde de la lumière lorsqu'une modeste précision est seulement demandée. On a montré que de meilleures estimations de diamètre ont été obtenues en employant les maximum et minimum qui apparaissent dans le modèle angulaire de diffusion lumineuse ou la formule de Shull et Roess adaptée à partir de la théorie des rayons-X à faible angle.

Zusammenfassung

Einige Licht- und Röntgenstreuungsverfahren wurden unter Verwendung von Polystyrolkugeln mit Durchmessern in der Nähe der Wellenlänge des verwendeten Lichts erprobt. Ein gewisser Fehlerbereich bei den mit den angegebenen Beziehungen berechneten Dimensionen ist zwar zu erwarten und wird auch gefunden, doch zeigt es sich, dass diese Verfahren für Näherungs- oder Vergleichszwecke brauchbar sind. Einer der Zwecke der vorliegenden Arbeit ist es zu zeigen, wie weit diese Lichtstreuungsverfahren auf kolloide Systeme mit Teilchengrößen in der Nähe der Lichtwellenlänge anwendbar sind, wenn nur eine mässige Genauigkeit erforderlich ist. Es wird gezeigt, dass bessere Werte für den Durchmesser bei (1) Benützung der Maxima und Minima in der Winkelabhängigkeit der Streulichtintensität oder (2) der aus der Theorie der Röntgenkleinwinkelstreuung übernommenen Formulierung von Shull und Roess erhalten werden.

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