LIGHT SCATTERING. XXII.*

USE OF THE FORWARD ANGLE DISSYMMETRY METHOD FOR THE DETERMINATION OF THE PARTICLE SIZE IN SYSTEMS OF UNKNOWN CONCENTRATION

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The applicability of the forward angle dissymmetry method modified for the determination of the size of spherical particles in monodisperse systems of unknown concentration has been analyzed. It has been demonstrated on samples of polystyrene latex (particle size 200 to 300 nm), that the results obtained by this method are fairly accurate and reproducible, the measurements themselves being very simple and fast. A discussion of the course of the corresponding scattering functions (explicitly tabulated for practical purposes) and the experimental data made it possible to specify the advantages and limitations of the individual modifications of the method. Two quotients were suggested for a preliminary evaluation of the polydisperse latexes: *a*) ratio of the mean particle sizes established at two wavelengths, and *b*) ratio of the average particle sizes determined at two pairs of angles of observation — both of them for unpolarized, vertically and horizontally polarized light.

In systematical investigations of the light scattering methods suitable for the study of the properties of particles whose concentration is either unknown or difficult to determine, we have obtained good results with the so-called ratio methods[1]. Their advantage consists in that the results obtained are to a large extent independent of the conditions of measurement: by establishing ratios of two values of a given function (obtained at two values of the parameter), or two conjugated functions (at a given value of the parameter), elimination of most of the correction and normalization factors is achieved. In the transmission functions of the type $\tau = f(L)$ (where τ is turbidity and L is the characteristic particle size), it is virtually only the wavelength that can serve as the parameter. On the contrary, in the case of the transverse methods, both the wavelength and the angle of observation or the polarization of light can be selected. The dissymmetry method is best known of all; the dissymmetry z being as a rule defined by the relationship $z = i_\theta / i_{180-\theta}$, where i is the intensity of the scattered light and θ is the angle of observation. The other two methods used, that is, "scattering ratio" (ratio of the intensities of scattered light with the primary beam polarized horizontally and vertically) and "depolarization method" (ratio of the intensities of the horizontally and vertically polarized components of the scattered light with an unpolarized primary

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beam) are equivalent, as long as the system contains perfectly transparent and isotropic particles[2]. The individual methods described above can be combined with each other, thus increasing their applicability and accuracy, as well as the reliability of measurements.

The method investigated here is a certain analogy of the dissymmetry method, which can be applied within the range of sizes of particles whose radiation envelope has lost its symmetry, but so far has got no maxima. On overpassing the critical size (which also depends on the relative refractive index and shape of the particles), the first maximum appears on the radiation envelope; with further increase in the particle size the maximum is gradually shifted from large angles to small ones ($180 \rightarrow \rightarrow 0°$), which is accompanied by in appearance of further maxima and minima. For this reason, the usual dissymmetry method ($z = i_{45}/i_{135}$) was originally replaced by its modification ($z = i_{45}/i_{90}$). However, Maron and Pierce[3] have shown recently that the method involving two close angles (with a difference of 10 or 15°) is clearly more advantageous; they called it the "forward angle ratio" method (FAR). We have slightly modified the FAR method with respect to the experience obtained to date with the ratio methods, and adjusted it for the determinations of the size and concentration of spherical particles in systems having an insufficiently defined composition. The applicability of the method (called here the forward angle dissymmetry method) has been verified by an analysis of its possibilities and limitations, and also by comparing the data obtained on a model system by light scattering and electron microscopy.

EXPERIMENTAL

Samples: Polystyrene latex (Kaučuk, Kralupy n. Vlt.) served as a model system. The characteristics of the individual samples are given in Table I. The original concentrates were diluted so as to preclude virtually the danger of multiple scattering. Since an addition of pure distilled water might disturb the stability of latexes, the samples were diluted with a solution of the stabilizer supplied by the manufacturer. The relative concentration of the basic sample was regarded as equal to unity; the concentration scale was prepared by gradual dilution of samples to yield a half, a quarter, or an eighth part of the basic concentration. The diluent was purified by pressure filtration through a G 5 fritted disc; of the latex samples, only the basic one was purified, using partial sedimentation. The samples for electron microscopy were taken directly from cells used in the light scattering measurements.

Light scattering: Measurements were carried out on a Sophica apparatus at angles 30, 45, 60, 90, and 150°, the wavelength being 436 and 546 nm; the primary beam was unpolarized or polarized vertically and horizontally. For control purposes, the values of reduced intensities were also determined (against a benzene and a glass standard); since, however, it was the aim of the measurement to demonstrate the suitability of the method for the determination of the size and concentration of particles in insufficiently defined systems, only relative values are introduced each time. (The ratios of two quantities have of course an absolute validity). The data obtained were treated and evaluated on the basis of Mie's theory; to this purpose, the necessary tables and graphs were prepared (*cf.*[4]).

TABLE I

Electron Microscopic Determinations of the Particle Sizes of Polystyrene Latexes (Samples A—D)

Sample	d, mm	D_p, mm	σ	σ/D_p	L_{em}, nm	L_{em}, nm[a]
A	21·076	1·3036	0·0443	0·0340	206 ± 7·0	214
B	20·474	1·5174	0·0321	0·0212	247 ± 5·2	247
C	20·201	1·6068	0·0239	0·0149	265 ± 3·9	268
D	20·832	1·8041	0·0279	0·0154	289 ± 4·5	300

D_p is the latex particle size, d is the period distance in a standard grating (read on a photographic plate); σ is the standard deviation of the D_p values; σ/D_p gives the stability of the assembly; L_{em} is the actual particle size of latexes determined in the present work; [a] the particle size given by the producer of latexes.

Electron microscopy: The specimens for electron microscopy were treated by the common replica technique. At the same time, a replica of the grating having a known period distance was also prepared. The photographic plates thus obtained were measured with an Abbé comparator (Zeiss, Jena). Several hundreds of particles were measured in each sample. The data were then compared with those obtained by the light scattering method.

RESULTS AND DISCUSSION

Forward Angle Dissymmetry Method

As has been said above, the method used by the author is an adapted FAR method (Maron and Pierce[3]) for the determination of the number and size of particles, especially in systems whose composition is not known. As long as our results are identical with those obtained by these authors, they are mentioned only briefly; a broader explanation is offered in those cases only when the findings and aspects under consideration are original, or the points of view are different.

In contrast with the classical definition of dissymmetry, $z = i_\theta/i_{180-\theta}$, let us define forward angle dissymmetry $\zeta = i_{\theta 1}/i_{\theta_2}$, where $\theta_2 - \theta_1 = 10$ or $15°$, both angles lying within the range $\theta < 90°$. In the case under consideration, we measured the forward angle dissymmetry values ζ_u, ζ_v, ζ_h at angles 30/45 and 45/60 and two wavelengths, 436 and 546 nm; the indexes u, v, h refer to the unpolarized and vertically or horizontally polarized beam of primary light, respectively. If we express i_θ in terms of the Mie theory and use the corresponding tables[4], we can easily obtain the necessary data for constructing the dependences $\zeta = f(\alpha)$ or $\zeta = f(L)$, where $\alpha = \pi L/\lambda$ (L being the diameter of a spherical particle, and λ being the wavelength of light in the given medium). The values thus obtained for the relative refractive index $m = 1·05$; $1·10$; $1·15$; $1·20$ and for the interval of the values $\alpha = \langle 0·2\,(0·2)\,10·0 \rangle$

are summarized in Tables II and III. Using these data, it is easy to construct graphs suitable for practical uses (ζ as functions $L(436)$ and $L(546)$). The limit values of ζ for $\alpha = 0$ are defined as follows:

	30/45	45/60
$\lim_{\alpha=0} \zeta_u = (1 + \cos^2 \theta_1)/(1 + \cos^2 \theta_2)$	7/6	6/5
$\lim_{\alpha=0} \zeta_v = 1$	1	1
$\lim_{\alpha=0} \zeta_h = \cos^2 \theta_1/\cos^2 \theta_2$	3/2	2

The character of the curves $\zeta = f(\alpha)$ allows an approximate linear numerical interpolation inside the individual intervals, almost as far as the first maximum, which is shifted to higher α values than it is observed with other methods. The first maximum ζ_u^I (but also ζ_v^I and ζ_h^I) lies approximately at $\alpha \approx 5{\cdot}6; 5{\cdot}6; 5{\cdot}4; 5{\cdot}2$ (for $\theta_1/\theta_2 = 30/45$) and $\alpha \approx 4{\cdot}4; 4{\cdot}2; 4{\cdot}0; 4{\cdot}0$ (for $\theta_1/\theta_2 = 45/60$) for $m = 1{\cdot}05; 1{\cdot}10; 1{\cdot}15; 1{\cdot}20$. For the values of maxima it holds: $\zeta_v^I > \zeta_u^I > \zeta_h^I$, and further $\zeta^I(30/45) > \zeta^I(45/60) > > \zeta^I(60/75)$ (which can be illustrated by data in Tables II–IV).

In the case of strictly monodisperse systems the particle sizes can in principle be determined also for α values higher than those corresponding to the first maximum of the dependence $\zeta = f(\alpha)$. To this purpose, measurements at two wavelengths are used, namely, at 436 and 546 nm. We discern two cases: *a*) Function $\zeta = f(\alpha)$ is bi-valued for the dissymmetry values measured: if $\zeta_{436} > \zeta_{546}$, then we have here the ascending part of the curve; in the opposite case, the part under consideration is the descending one (both ζ_{436} and ζ_{546} must of course lie on the same side of the peak). *b*) Function $\zeta = f(\alpha)$ is multi-valued: the analysis is possible in exceptional cases only, taking into account *a*) and the magnitude of ζ at 30/45 and 45/60, or the values ζ_u, ζ_v, ζ_h.

Determination of the particle size in polydisperse systems (or, more exactly, determination of the size distribution) is generally not an easy task. A certain hope of success may arise with systems having particle sizes much smaller than it would correspond to ζ_{max}, provided that the distribution function is known, or a justified assumption as to its character can be made, and if several pairs of angles of wavelengths are used for the determination of ζ. In the case of slightly polydisperse systems, dependences strictly valid for monodisperse systems can be used for an estimation or approximate determination of an average particles size; however, the conclusions arrived at ought to be verified by using another independent method.

A considerable advantage of the method described above consists in the comparatively very small dependence of the initial course of the function $\zeta = f(\alpha)$ on the relative refractive index, m (*cf.*[3] and Tables II and III), which allows an investigation even of such systems in which an exact determination of m would be difficult, if not impossible.

Determination of the Size of Latex Particles

To estimate the objectivity of the particle size determination by light scattering methods, polystyrene latex is used as a rule, and a new (or adapted) method is usually tested by comparing it with the electron microscopic data.

The electron microscopic determinations of the size of latex particles were carried out on samples A – D, taken directly from the measuring cells; it was therefore possible to consider some changes that might occur owing to the dilution of the samples. The magnitude of the particle images recorded on the photographic plates was compared with the periodic distance on the standard grating. The results were treated statistically (from several hundreds of measurements) and summarized in Table I. The dilution of original samples did not lead to any conclusive changes in the average particle size. The degree of polydispersity of the particles can be estimated on the basis of the magnitude of the standard deviation σ: polydispersity increases in the series of samples C, D, B, A. In the case of sample A there was a clear tendency toward aggregation of the individual latex particles; as to the other samples, the association of particles was less pronounced.

The forward angle dissymmetry values, ζ, were determined for two pairs of angles (30/45 and 45/60) and for two wavelengths (436 and 546 nm), unpolarized (u) or polarized vertically (v) or horizontally (h). Although the results obtained are in a fairly good agreement with the electron microscopic data (Table V), there are still some deviations and tendencies which we shall try to explain below.

Let us first admit that the data obtained are correct as far as the experimental procedure itself is concerned (preparation of the sample, measurement of the intensities of the scattered light and extrapolation of the dissymmetry values to zero concentration). If we now write down quotients $L(546)/L(436)$ and $L(30/45)/L(45/60)$ for unpolarized (u), vertically (v) or horizontally (h) polarized light, we can imagine to what extent the differences observed are random or regular (Table VI). It is easy to see, in the case of quotients $L(546)/(436)$, that the values of $L(546)$ are almost in all cases clearly higher than $L(436)$. At the same time, the quotient for sample A has practically always substantially higher value than for the other samples. The quotient $L(30/45)/L(45/60)$, too, behaves in a similar way. Although in the case of samples B, C, and D its values are slightly more different from 1·00 in comparison with the values of the quotient $L(546)/L(436)$, the difference from sample A is still pronounced. The quotients of the individual samples remain comparatively constant, which indicates a non-random, physical nature of the differences observed in the particle sizes determined by different methods.

Table II

Values of the Function $\zeta = f(\alpha)$ for the Pair of Angles $\theta_1/\theta_2 = 30/45$; Relative Refractive Index $m = 1{\cdot}05$; $1{\cdot}10$; $1{\cdot}15$; $1{\cdot}20$; Unpolarized (u), Vertically (v) and Horizontally (h) Polarized Primary Beam

α	1·05			1·10			1·15			1·20		
	u	v	h	u	v	h	u	v	h	u	v	h
0·2	1·1696	1·0026	1·5037	1·1696	1·0026	1·5035	1·1696	1·0027	1·5033	1·1696	1·0027	1·5032
0·4	1·1785	1·0104	1·5147	1·1785	1·0105	1·5140	1·1785	1·0106	1·5133	1·1785	1·0107	1·5126
0·6	1·1936	1·0234	1·5333	1·1934	1·0298	1·5315	1·1933	1·0239	1·5299	1·1932	1·0242	1·5282
0·8	1·2150	1·0421	1·5596	1·2146	1·0424	1·5562	1·2142	1·0428	1·5530	1·2139	1·0432	1·5496
1·0	1·2434	1·0669	1·5942	1·2426	1·0673	1·5887	1·2418	1·0678	1·5830	1·2412	1·0685	1·5774
1·2	1·2794	1·0984	1·6381	1·2783	1·0992	1·6295	1·2746	1·1002	1·6207	1·2762	1·1014	1·6117
1·4	1·3242	1·1376	1·6922	1·3231	1·1394	1·6799	1·3218	1·1414	1·6671	1·3207	1·1438	1·6538
1·6	1·3791	1·1859	1·7584	1·3782	1·1893	1·7414	1·3774	1·1933	1·7235	1·3766	1·1979	1·7043
1·8	1·4457	1·2446	1·8381	1·4456	1·2505	1·8156	1·4455	1·2574	1·7913	1·4445	1·2652	1·7649
2·0	1·5259	1·3152	1·9338	1·5269	1·3246	1·9047	1·5274	1·3350	1·8729	1·5271	1·3462	1·8383
2·2	1·6220	1·4000	2·0486	1·6243	1·4134	2·0121	1·6254	1·4276	1·9727	1·6254	1·4420	1·9316
2·4	1·7373	1·5019	2·1866	1·7414	1·5199	2·1431	1·7442	1·5385	2·0983	1·7465	1·5574	2·0553
2·6	1·8767	1·6247	2·3540	1·8843	1·6492	2·3050	1·8920	1·6752	2·2591	1·9016	1·7031	2·2204
2·8	2·0466	1·7743	2·5589	2·0615	1·8092	2·5075	2·0793	1·8481	2·4643	2·1031	1·8935	2·4323
3·0	2·2567	1·9593	2·8124	2·2842	2·0107	2·7615	2·3183	2·0710	2·7215	2·3609	2·1438	2·6904
3·2	2·5191	2·1907	3·1283	2·5660	2·2671	3·0795	2·6210	2·3577	3·0387	2·6805	2·4629	2·9973
3·4	2·8512	2·5067	3·5266	2·9243	2·5958	3·4785	3·0019	2·7236	3·4302	3·0481	2·8602	3·3733
3·6	3·2769	2·8613	4·0345	3·3839	3·0205	3·9850	3·4875	3·1937	3·9262	3·5788	3·3703	3·8601
3·8	3·8329	3·3557	4·6934	3·9864	3·5810	4·6420	4·1302	3·8222	4·5755	4·2703	4·0842	4·5108
4·0	4·5779	4·0208	5·5709	4·8033	4·3491	5·5192	5·0234	4·7169	5·4477	5·2658	5·1725	5·3777
4·2	5·6114	4·9485	6·7762	5·9601	5·4559	6·7284	6·3171	6·0705	6·6372	6·7066	6·8903	6·5091
4·4	7·1115	6·3050	8·5025	7·6776	7·1442	8·4533	8·2440	8·2138	8·2799	8·7418	9·5741	7·9652
4·6	9·4094	8·4148	11·104	10·361	9·8870	11·006	11·167	11·738	10·569	11·541	13·710	9·8136
4·8	13·231	11·966	15·287	14·934	14·705	14·925	15·649	17·807	13·728	15·197	20·052	12·001
5·0	20·207	18·650	22·598	23·850	24·069	21·082	22·253	28·583	17·761	19·009	28·286	14·054

TABLE II
(*Continued*)

α	1·05			1·10			1·15			1·20		
	u	v	h	u	v	h	u	v	h	u	v	h
5·2	34·903	33·530	36·810	36·700	44·412	30·414	29·812	44·496	21·744	20·476	31·755	14·936
5·4	72·577	76·904	67·778	57·376	84·705	41·515	32·188	49·282	23·278	17·742	24·501	13·849
5·6	177·53	248·18	130·83	63·013	93·288	45·658	25·590	32·823	20·658	12·958	15·136	11·328
5·8	194·45	240·21	152·15	41·742	47·674	36·487	16·844	18·085	15·698	8·7452	8·8817	8·6163
6·0	73·815	69·561	79·877	23·008	22·351	23·806	10·609	10·182	11·093	5·8383	5·3226	6·4143
6·2	30·736	26·903	37·291	13·052	11·782	14·853	6·8248	6·0938	7·7622	4·0129	3·3852	4·7840
6·4	15·530	13·311	19·513	7·9235	6·8823	9·5090	4·5683	3·8766	4·5172	2·8729	2·3129	3·5833
6·6	8·9081	7·5709	11·338	5·1042	4·3209	6·3370	3·1787	2·6014	3·9916	2·1235	1·6629	2·7063
6·8	5·5339	4·6775	7·0917	3·4356	2·8487	4·3700	2·2809	1·8149	2·9365	1·6135	1·2251	2·1006
7·0	3·6103	3·0351	4·6525	2·3816	1·9362	3·0887	1·6812	1·2982	2·2132	1·2876	0·9336	1·7271
7·2	2·4182	2·0191	3·1363	1·6830	1·3369	2·2262	1·2872	0·9556	1·7409	1·1255	0·7827	1·5442
7·4	1·6318	1·3492	2·1359	1·2113	0·9317	1·6429	1·0551	1·7502	1·4645	1·1177	0·7808	1·5144
7·6	1·0907	0·8874	1·4494	0·9014	0·6634	1·2621	0·9642	0·6705	1·3480	1·2641	0·9494	1·6136
7·8	0·7121	0·5632	0·9716	0·7216	0·5060	1·0408	1·0142	0·7242	1·3764	1·5823	1·3312	1·8364
8·0	0·4537	0·3407	0·6476	0·6636	0·4551	0·9632	1·2307	0·9503	1·5581	2·0962	1·9771	2·2040
8·2	0·2986	0·2066	0·4541	0·7473	0·5333	1·0475	1·6725	1·4328	1·9282	2·8653	2·9776	2·7751
8·4	0·2543	0·1686	0·3960	1·0340	0·8092	1·3252	2·4443	2·3296	2·5540	4·0494	4·6378	3·6331
8·6	0·3640	0·2681	0·5183	1·6579	1·4413	1·9162	3·7331	3·9651	3·5398	5·8738	7·6223	4·8227
8·8	0·7434	0·6169	0·9391	2·8907	2·7882	2·9996	5·8227	7·0099	4·9941	8·2687	12·298	6·2250
9·0	1·6817	1·5069	1·9365	5·2649	5·7026	4·8716	8·8615	12·276	6·8988	10·309	16·363	7·4541
9·2	3·9495	3·7784	4·1758	9·6088	12·081	7·8501	12·047	18·190	8·8800	10·790	15·991	8·0553
9·4	9·8309	10·324	9·2861	15·908	23·156	11·730	13·538	19·389	10·216	9·7031	12·386	7·9212
9·6	25·801	32·549	20·514	20·031	28·641	14·914	12·707	15·909	10·427	8·0898	8·9782	7·3374
9·8	51·218	75·676	36·476	18·572	22·349	15·543	8·2009	11·872	9·7251	6·7632	6·8860	6·4400
10·0	43·334	48·738	38·045	13·123	15·493	14·020	6·9958	8·9023	8·6429	5·8733	5·7604	5·9960

To allow a comparison of the values and course of functions, the tabular data are given with a considerably higher accuracy and for a broader range of the α values than needed for practical purposes.

TABLE III

Values of the Function $\zeta = f(\alpha)$ for the Pair of Angles $\theta_1/\theta_2 = 45/60$; Relative Refractive Index $m = 1{\cdot}05$; $1{\cdot}10$; $1{\cdot}15$; $1{\cdot}20$; Unpolarized (u) Vertically (v) and Horizontally (h) Polarized Primary Beam

α	1·05			1·10			1·15			1·20		
	u	v	h	u	v	h	u	v	h	u	v	h
0·2	1·2040	1·0034	2·0062	1·2041	1·0034	2·0058	1·2041	1·0034	2·0053	1·2041	1·0035	2·0048
0·4	1·2162	1·0135	2·0250	1·2162	1·0137	2·0231	1·2163	1·0139	2·0211	1·2164	1·0140	2·0192
0·6	1·2367	1·0308	2·0566	1·2318	1·0311	2·0520	1·2369	1·0314	2·0474	1·2371	1·0317	2·0427
0·8	1·2663	1·0557	2·1018	1·2663	1·0561	2·0931	1·2663	1·0565	2·0840	1·2664	1·0571	2·0751
1·0	1·3059	1·0890	2·1620	1·3059	1·0897	2·1469	1·3058	1·0904	2·1316	1·3058	1·0912	2·1161
1·2	1·3574	1·1323	2·2391	1·3574	1·1336	2·2152	1·3574	1·1350	2·1908	1·3577	1·1367	2·1661
1·4	1·4230	1·1877	2·3360	1·4235	1·1902	2·3000	1·4245	1·1934	2·2632	1·4256	1·1970	2·2253
1·6	1·5058	1·2578	2·4565	1·5082	1·2632	2·4047	1·5109	1·2696	2·3508	1·5140	1·2770	2·2947
1·8	1·6100	1·3462	2·6059	1·6156	1·3565	2·5334	1·6214	1·3684	2·4569	1·6271	1·3819	2·3764
2·0	1·7413	1·4580	2·7922	1·7515	1·4754	2·6928	1·7609	1·4948	2·5881	1·7688	1·5161	2·4790
2·2	1·9073	1·5997	3·0259	1·9232	1·6266	2·8937	1·9364	1·6555	2·7573	1·9454	1·6856	2·6201
2·4	2·1198	1·7815	3·3245	2·1433	1·8213	3·1548	2·1618	1·8628	2·9869	2·1744	1·9049	2·8296
2·6	2·3975	2·0194	3·7152	2·4339	2·0788	3·5050	2·4640	2·1411	3·3091	2·4911	2·2072	3·1395
2·8	2·7715	2·3406	4·2411	2·8328	2·4342	3·9873	2·8918	2·5383	3·7648	2·9565	2·6601	3·5839
3·0	3·2964	2·7924	4·9732	3·4081	2·9521	4·6657	3·5263	3·1434	4·4002	3·6606	3·3856	4·1762
3·2	4·0708	3·4632	6·0338	4·4307	3·7555	5·6381	4·5024	4·1243	5·2686	4·7215	4·6002	4·9099
3·4	5·2908	4·5310	7·6507	5·6872	5·0979	7·0649	6·0503	5·8231	6·4368	6·2848	6·7072	5·7762
3·6	7·3962	6·4069	10·292	8·1334	7·5912	9·2222	8·5886	9·0590	7·9846	8·5320	10·602	6·7519
3·8	11·565	10·248	15·056	12·870	13·070	12·559	12·847	16·197	9·8903	11·353	18·073	7·6678
4·0	21·914	20·545	24·871	22·987	28·843	17·417	18·453	32·216	11·595	12·565	23·808	8·0193
4·2	59·100	68·811	47·360	37·830	72·906	21·833	17·970	31·423	11·551	9·2473	12·551	7·2108
4·4	128·13	226·86	73·177	25·799	33·646	19·269	9·8419	10·739	8·956	5·1021	4·7688	5·4588
4·6	30·199	26·978	37·695	9·5324	8·5491	11·296	4·4627	3·7089	5·670	2·6986	2·0232	3·6756
4·8	7·9908	6·4792	12·871	2·8193	2·8451	5·5764	2·1018	1·7807	3·310	1·4925	0·9480	2·3995
5·0	2·7612	2·1631	4·8006	1·5310	1·0821	2·7220	1·0012	0·6516	1·9624	0·9072	0·4923	1·6497

TABLE III
(*Continued*)

α	1·05			1·10			1·15			1·20		
	u	v	h	u	v	h	u	v	h	u	v	h
5·2	1·0313	0·7748	1·9071	0·6835	0·4211	1·3949	0·6209	0·3208	1·2781	0·6719	0·3411	1·2832
5·4	0·3638	0·2481	0·7537	0·3528	0·1744	0·8087	0·4442	0·2372	0·9925	0·6581	0·3721	1·1803
5·6	0·1195	0·0619	0·3101	0·2670	0·1343	0·6165	0·4884	0·3114	0·9663	0·8186	0·5540	1·2739
5·8	0·0941	0·1054	0·2269	0·3617	0·2368	0·6789	0·6868	0·5298	1·1410	1·1764	0·9419	1·5380
6·0	0·2272	0·1758	0·3893	0·6176	0·4834	0·9567	1·1484	0·9483	1·2509	1·8112	1·6847	1·9769
6·2	0·5289	0·4429	0·7913	1·1030	0·9367	1·4741	1·8733	1·7237	2·1075	2·8436	3·0518	2·6238
6·4	1·0765	0·9276	1·5120	1·9532	1·7682	2·3234	3·1304	3·2168	3·0193	4·4407	5·5820	3·5261
6·6	2·0705	1·8203	2·7596	3·5231	3·4193	3·7000	5·3333	6·3312	4·3647	6·7663	10·469	4·6747
6·8	4·0291	3·6341	5·0222	6·6492	7·1824	5·9466	9·0291	13·405	6·1875	9·3799	18·026	5·8589
7·0	8·5107	8·0480	9·5006	13·141	17·449	9·4416	13·550	25·973	8·1415	10·342	19·060	6·5976
7·2	21·314	22·736	19·159	23·468	42·828	13·730	14·651	25·463	9·2688	8·7578	12·317	6·4725
7·4	62·312	97·323	37·961	25·031	39·272	16·050	11·215	14·080	8·8081	6·3657	7·1822	5·6187
7·6	68·668	89·912	48·470	15·983	17·433	14·196	7·4349	7·6007	7·2287	4·3919	4·2625	4·5454
7·8	26·985	24·759	31·996	9·2384	8·5656	10·454	4·8587	4·4442	5·4993	3·0393	2·6245	3·6182
8·0	12·302	10·452	17·677	5·6135	4·8572	7·2312	3·2633	2·7709	4·1172	2·2031	1·7303	2·9264
8·2	6·7605	5·6138	10·322	3·6133	3·0089	5·0038	2·2900	1·8270	3·1384	1·7059	1·2483	2·4205
8·4	4·1478	3·4083	6·4708	2·4393	1·9660	3·5444	1·5886	1·2732	2·4662	1·3966	0·9664	2·0386
8·6	2·7051	2·2041	4·2655	1·7078	1·3291	2·5863	1·3139	0·9308	2·0001	1·1981	0·7837	1·7563
8·8	1·8176	1·4648	2·8970	1·2324	0·9162	1·9453	1·0734	0·7076	1·6805	1·1088	0·6943	1·5901
9·0	1·2279	0·9721	1·9921	0·9152	0·6354	1·5144	0·9494	0·5814	1·4924	1·1797	0·7677	1·5792
9·2	0·8138	0·6233	1·3658	0·7165	0·4411	1·2461	0·9807	0·6002	1·4567	1·5128	1·1848	1·7704
9·4	0·5158	0·3680	0·9269	0·6524	0·3712	1·1450	1·2708	0·9176	1·6222	2·2982	2·4580	2·2030
9·6	0·3196	0·1938	0·6497	0·8209	0·5142	1·2717	2·0186	1·9670	2·0569	3·6902	5·6005	2·8631
9·8	0·2768	0·1473	0·5882	1·5225	1·2551	1·7557	4·5762	4·8213	2·8072	5·2032	9·3742	3·5972
10·0	0·6162	0·4514	0·9585	3·2539	7·1818	2·7775	6·3406	9·1239	3·7734	5·8218	9·3626	4·1268

To allow a comparison of the values and course of functions, the tabular data are given with a considerable higher accuracy and for a broader range of the α values than needed for practical purposes.

TABLE IV

Values of the Function $\zeta = f(\alpha)$ for the Pair of Angles $\theta_1/\theta_2 = 60/75$; Relative Refractive Index $m = 1{\cdot}05$; $1{\cdot}10$; $1{\cdot}15$; $1{\cdot}20$; Unpolarized (u), Vertically (v) and Horizontally (h) Polarized Primary Beam

α	1·05			1·10			1·15			1·20		
	u	v	h	u	v	h	u	v	h	u	v	h
0·2	1·1761	1·0039	3·7441	1·1762	1·0040	3·7416	1·1763	1·0040	3·7391	1·1763	1·0040	3·7364
0·4	1·1901	1·0158	3·7803	1·1904	1·0160	3·7703	1·1908	1·0162	3·7600	1·1912	1·0165	3·7492
0·6	1·2140	1·0360	3·8417	1·2228	1·0364	3·8177	1·2154	1·0368	3·7932	1·2162	1·0372	3·7688
0·8	1·2489	1·0656	3·9296	1·2500	1·0661	3·8834	1·2512	1·0667	3·8374	1·2524	1·0674	3·7912
1·0	1·2965	1·1059	4·0457	1·2981	1·1067	3·9671	1·3000	1·1076	3·8892	1·3021	1·1088	3·8120
1·2	1·3592	1·1592	4·1940	1·3623	1·1608	4·0687	1·3657	1·1627	3·9453	1·3693	1·1649	3·8241
1·4	1·4417	1·2292	4·3797	1·4475	1·2328	4·1881	1·4540	1·2370	4·0011	1·4611	1·2420	3·8183
1·6	1·5497	1·3209	4·6109	1·5611	1·3291	4·3271	1·5737	1·3385	4·0530	1·5875	1·3496	3·7887
1·8	1·6927	1·4425	4·9006	1·7138	1·4591	4·4911	1·7365	1·4782	4·1043	1·7604	1·5004	3·7410
2·0	1·8840	1·6058	5·2698	1·9201	1·6366	4·6942	1·9572	1·6718	4·1699	1·9924	1·7115	3·6998
2·2	2·1458	1·8301	5·7566	2·2039	1·8839	4·9640	2·2556	1·9436	4·2808	2·3010	2·0080	3·7046
2·4	2·5172	2·1499	6·4242	2·6073	2·2417	5·3461	2·6807	2·3403	4·4780	2·7262	2·4428	3·7948
2·6	3·0745	2·6333	7·3880	3·2172	2·7955	5·9082	3·3203	2·9696	4·8043	3·3714	3·1542	4·0000
2·8	3·9886	3·4345	8·8627	4·2695	3·7571	6·7392	4·4026	4·1228	5·2892	4·4731	4·5466	4·3249
3·0	5·7152	4·9772	11·280	6·2212	5·7702	7·9305		6·7637	5·9045		8·0241	4·7006

To allow a comparison of the values and course of functions the tabular data are given with a considerably higher accuracy than needed for practical purposes.

Before discussing the conclusions, let us try to find out to which extent the above assumption is warranted: *1.* In the first place, the individual samples can be more or less polydisperse, which has already been indicated by the electron microscopic measurement. The polydispersity can be either primary (the individual particles are not monodisperse) or secondary (particles form larger aggregates). Both these tendencies were observed in the electron microscopic measurements: the former is determined by different values of the standard deviation (Table I), the latter is

TABLE V

Determination of the Latex Particle Sizes (L, nm) of Samples A–D by the Forward Angle Dissymmetry Method (Two Independent Series of Measurements)

λ_0	$L(\zeta_u)$		$L(\zeta_v)$		$L(\zeta_h)$	
	30/45	45/60	30/45	45/60	30/45	45/60
			Sample A (L_{em} = 206 nm)			
436	284	230	279	227	290	249
	287	230	280	226	292	236
546	340	276	334	258	356	298
	338	269	335	255	355	286
			Sample B (L_{em} = 247 nm)			
436	256	249	249	243	249	238
	253	251	250	244	246	240
546	256	249	262	242	257	238
	253	251	250	242	249	243
			Sample C (L_{em} = 265 nm)			
436	268	256	259	253	256	242
	261	262	265	257	249	246
546	268	256	270	253	269	241
	268	266	257	262	273	255
			Sample D (L_{em} = 289 nm)			
436	289	283	284	277	283	276
	289	287	287	280	281	277
546	289	284	283	279	282	276
	284	286	287	278	283	277

L_{em} is the particle size determined by electron microscopy, L is the particle size determined by the forward angle dissymmetry method ζ_u, ζ_v and ζ_h, using light having the wavelength λ_0 (*in vacuo*) and at angle ratios $\theta_1/\theta_2 = 30/45$ and $45/60$. The ζ values were extrapolated to $x \rightarrow 0$ (where x is the relative concentration of particles).

TABLE VI

Quotients $L(546)/L(436)$ and $L(30/45)/L(45/60)$ for Latex Samples A–D

$L(546)_u/L(436)_u$		$L(546)_v/L(436)_v$		$L(546)_h/L(436)_h$		$L(30/45)_u/L(45/60)_u$		$L(30/45)_v/L(45/60)_v$		$L(30/45)_h/L(45/60)_h$	
30/45	45/60	30/45	45/60	30/45	45/60	436	546	436	546	436	546
Sample A (206 nm)											
1·20	1·20	1·20	1·14	1·23	1·20	1·23	1·23	1·23	1·29	1·26	1·19
1·18	1·17	1·20	1·12	1·22	1·21	1·25	1·25	1·24	1·31	1·24	1·24
Sample B (247 nm)											
1·00	1·00	1·05	1·00	1·03	1·00	1·03	1·03	1·02	1·08	1·05	1·08
1·00	1·00	1·00	0·99	1·01	1·01	1·09	1·01	1·02	1·03	1·02	1·02
Sample C (265 nm)											
1·00	1·04	1·04	1·00	1·05	1·00	1·05	1·05	1·02	1·07	1·06	1·12
1·03	1·00	0·97	1·02	1·09	1·03	1·00	1·00	1·03	0·98	1·01	1·07
Sample D (289 nm)											
1·00	1·00	1·00	1·01	1·00	1·00	1·02	1·02	1·03	1·01	1·02	1·02
0·98	1·00	1·00	0·99	1·00	1·00	1·00	0·99	1·02	1·03	1·01	1·02

The forward angle dissymmetry values were measured in unpolarized (u), vertically (v) and horizontally (h) polarized primary beam, the wavelength of which was 436 or 546 nm, at two pairs of angles 30/45 and 45/60.

corroborated by the fact that the scattering data (Tables V and VI) indicate a substantially higher degree of polydispersity of sample A than it would correspond to the respective standard deviation. *2.* An important factor can also be seen in the preparation of samples having required concentrations (purification and dilution of samples). The purification of samples is generally difficult; in principle, only large particles that may be present can be removed (if sedimentation fractionation is not used). The samples should be diluted using a solution of stabilizer having the necessary concentration; not even in this case, however, is it possible to be sure that the aggregates that may be present in the solution have disintegrated into individual particles. *3.* An extrapolation of the dissymmetry values, ζ, to infinite dilution has proved to be absolutely necessary, owing to their pronounced concentration dependence. Maron and Pierce[3] have shown that its slope increases with increasing particle size (the dependence becomes curved above 700 nm). The dependences obtained in our case were mostly linear; their slope $k = \partial\zeta/\partial x$ (where x is relative concentration) were negative in all cases (Table VII), which is in agreement with observations made by Maron and Pierce[3] (their ratio X being a reciprocal value of our dissymmetry ζ). An analysis of our data enables us to state some other findings: *a*) The k values are considerably smaller in virtually all cases for λ_0 546 nm than for λ_0 436. *b*) With the exception of sample A, the k values are considerably smaller for the pair of angles 30/45 than for 45/60 (for λ_0 546 nm the difference is not sufficiently conclusive, since the k values are very small in this case – with the exception of k_h, which, however, shows that the above statement is justified). *c*) The k_v values are in all cases substantially smaller than k_h; the experimental data (Table VII) confirm that $k_u \approx \frac{1}{2}(k_v + k_h)$. *d*) The k_h values are generally very high – such a great concentration dependence seems rather unexpected. If the slope k was the only measure for the accuracy of determination of $\lim_{x \to 0} \zeta$, then measurements carried out in vertically polarized light, λ_0 546 nm, and at the pair of angles 30/45 can be considered optimum; and measurements in horizontally polarized light, λ_0 436 nm, and at the pair of angles 45/60 are then the least advantageous. The actual situation, however, is slightly more complicated: the accuracy of determination is also governed by some other factors, both experimental and theoretical (for instance, the presence of large foreign particles, geometric parameters of the apparatus and cell, steepness of the corresponding scattering function *etc.*), which must always be weighed individually and complexly.

Returning to the results presented in Table V, we can say that the forward angle dissymmetry method reflects physical facts, although in a limited way, and rather in tendencies than in detail. It can be expected, in accordance with the Mie theory, that for a perfectly monodisperse system this method will provide identical dissymmetry values (and thus particle sizes), be it that they were obtained at various wavelengths, various pairs of angles, or various polarization of light. Small and regular

TABLE VII

Relative Slopes, k, of the Function $\zeta = f(x)$

Pair of angles	λ_0, nm	k_u	k_v	k_h	$\frac{k_v + k_h}{2}$
		Sample A (L_{em} = 206 nm)			
30/45	436	−0·22	−0·16	−0·29	−0·23
		−0·17	−0·13	−0·35	−0·24
	546	−0·07	−0·07	−0·18	−0·12
		−0·07	−0·07	−0·18	−0·12
45/60	436	−0·15	−0·10	−0·44	−0·27
		−0·15	−0·14	−0·37	−0·25
	546	−0·08	−0·04	−0·25	−0·14
		−0·09	−0·06	−0·20	−0·13
		Sample B (L_{em} = 247 nm)			
30/45	436	−0·15	−0·12	−0·18	−0·15
		−0·16	−0·09	−0·20	−0·14
	546	−0·07	−0·04	−0·08	−0·06
		−0·05	−0·04	−0·06	−0·05
45/60	436	−0·22	−0·16	−0·37	−0·26
		−0·22	−0·16	−0·37	−0·26
	546	−0·06	−0·04	−0·14	−0·09
		−0·05	−0·05	−0·16	−0·10
		Sample C (L_{em} = 265 nm)			
30/45	436	—	—	−0·43	—
		−0·34	−0·26	−0·60	−0·43
	546	−0·17	−0·12	−0·20	−0·16
		−0·13	−0·05	−0·21	−0·13
45/60	436	—	−0·44	—	—
		−0·57	—	−0·83	(−0·63)
	546	—	−0·14	—	—
		−0·15	−0·16	−0·38	−0·27
		Sample D (L_{em} = 289 nm)			
30/45	436	−0·28	−0·18	−0·33	−0·26
		−0·26	−0·20	−0·36	−0·28
	546	−0·07	−0·04	−0·09	−0·06
		−0·08	−0·06	−0·10	−0·08
45/60	436	−0·48	−0·45	—	—
		−0·57	−0·39	−0·74	−0·56
	546	−0·11	−0·06	—	—
		−0·12	−0·09	−0·25	−0·17

Owing to the different actual values of the relative concentration x of the individual samples A—D, only slopes k corresponding to a given sample can be compared with each other (and not those of different samples). Meaning of quantities: $k_u = \partial\zeta_u/\partial x$; $k_v = \partial\zeta_v/\partial x$; $k_h = \partial\zeta_h/\partial x$; ζ forward angle dissymmetry; λ_0 light wavelength (*in vacuo*).

deviations of the L values from the L_{em} value of samples B to D indicate a low degree of polydispersity of their particles in accordance with the results of electron microscopic measurements (Table V). In the case of these, almost monodisperse systems the forward angle dissymmetry method yields comparatively good results, even if the concentration of particles in the system is unknown. As soon as the particle size has been determined, their concentration, too, can be measured easily: the experimentally determined reduced intensity value (best for $\theta = 90°$) is compared with the tabular data on specific intensity for the respective value of L; the constant of proportionality represents the concentration in question.

It is justified to expect, with respect to the character of the scattering functions, that the polydisperse samples will exhibit considerable deviations, both between the values of L and L_{em} and between themselves. Such behaviour was in fact observed with sample A, which moreover shows a clear tendency toward aggregation of particles (judging by the electron microscopic pictures). In the case of polydisperse samples, therefore, the L values obtained for a longer wavelength, λ_0, and for the pair of smaller angles will in general be clearly higher; this finding also corroborates the observations made by Maron and Pierce[3]. All the L values established for the sample A, too, were much higher than L_{em} (in accordance with the assumption of the secondary aggregation of particles). The fact that also smaller values of L than average[3] were found could be explained, if we remember that the resulting dissymmetry, ζ, is not a sum of the contributions of the components $x_j\zeta_j$, but that $\zeta = \sum x_j(i_{\theta_1})_j : : \sum x_j(i_{\theta_2})_j$; here, it will be necessary to wait for a detailed analysis of behaviour of the scattering functions.

For a preliminary evaluation of polydispersity, the quotients defined in Table VI would be of advantage. The values of both the angular and wavelength quationts for samples B and D are close to unity; for the polydisperse sample A they lie between 1·20 and 1·25. So long as the theoretical correlation function between the quotient values and the distribution function are not known, they can be used in those polydisperse systems only which have been tested by means of another, more laborious method (such as electron microscopy, sedimentation analysis, *etc.*)

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REFERENCES

1. Sedláček B.: This Journal *32*, 1374 (1967); *32*, 1595 (1967).
2. Heller W., Pangonis W. J., Economou N. A.: J. Chem. Phys. *34*, 971 (1961).
3. Maron S. H., Pierce P. E.: J. Polymer Sci. C *27*, 183 (1969).
4. Pangonis W. J., Heller W.: *Angular Scattering Functions for Spherical Particles*. Wayne State University Press, Detroit 1960.

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