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# Theoretical Investigations on the Light Scattering of Colloidal Spheres. IV. Specific Turbidities in the Lower Microscopic Range and Fine Structure Phenomena\*

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(Received February 27, 1958)

Additional calculations were carried out on the scattering cross sections of spheres and the specific turbidities of their dispersed systems using again the Mie theory. The parameters considered were  $\alpha = 7.0$  (0.2) 25.6 and  $m = 1.05$  (0.05) 1.30. The close spacing of the  $\alpha$  values allowed the detection of a fine structure of regular period in the  $(\tau/c)_0(\alpha)$  curves and related curves. The fine structure is explained as the result of interferences of secondary magnitude.

**C**ALCULATIONS<sup>1</sup> of  $R$ ,  $K$ , and  $(\tau/c)_0$ ,<sup>†</sup> by means of the Mie theory, on the light scattering of spheres covering, in general,  $\alpha = 0.2-15.0$ , have now been extended to  $\alpha = 25.6$ , corresponding to a particle diameter of 3.34 microns if  $\lambda_0 = 5460.73$  a.u. In addition, the  $\alpha$  range from 7.0 to 15.0 has now been considered in  $\Delta\alpha$  steps of 0.2 instead of 1.0. The microscopic dimensions now covered in detail for  $m = 1.05$  (0.05) 1.30 are frequently encountered in the microscopic "tail" of size distribution curves obtained in strongly heterodisperse colloidal systems. The supplemental data are therefore required for faithful derivations of distribution curves by means of light scattering methods currently in use in this laboratory.<sup>‡</sup> They also open up the possibility of accurate size determinations and of rapid and convenient indirect counts of spherical or nearly spherical cells, bacteria, and microorganisms of suitable size in dilute suspensions.

## RESULTS

### 1. Numerical Data

Table I gives the scattering cross sections  $R$  for the standard conditions specified previously.<sup>1</sup> The specific turbidities,  $(\tau/c)_0$  and the scattering coefficients are easily derived from Table I. The data, computed with the IBM 650 processing machine, duplicated a series of data obtained previously with the UDEC digital computer for integer  $\alpha$  values  $> 6.0$ . Comparison of the duplicated data showed that the present data contain in general four significant figures.

### 2. Fine Structure of $R(\alpha)$ , $K(\alpha)$ , and $(\tau/c)_0(\alpha)$ Curves

It had previously been noted<sup>1</sup> that the  $(\tau/c)_0$  curves exhibit near the first maximum a series of indentations which are more pronounced the larger  $m$ . A numerical analysis showed them to be present throughout the entire  $(\tau/c)_0(\alpha)$  range, with the exception of the Rayleigh range, although they may be far too small

TABLE I. Scattering cross section  $R \times 10^{10}$  cm<sup>2</sup> (calculated for  $\lambda = 4093.57$  a.u. [ $\lambda_0 = 5460.73$  Å] in water at 20°C).

$\alpha \backslash m$	1.05	1.10	1.15	1.20	1.25	1.30
7.2	17.421	67.173	136.47		252.64	264.06
7.4	19.458	74.593	150.39		269.22	280.98
7.6	21.661	82.575	165.12		288.05	294.43
7.8	24.036	91.153	180.56		306.99	300.79
8.2	29.348	110.14	213.97		337.77	320.84
8.4	32.310	120.57	231.96		354.72	332.73
8.6	35.489	131.63	250.65		373.07	334.29
8.8	38.893	143.36	270.04		387.80	333.61
9.2	46.398	168.84	311.54		411.22	352.96
9.4	50.517	182.66	333.40		427.34	350.79
9.6	54.895	197.23	355.68		440.75	342.13
9.8	59.544	212.54	378.54		447.28	343.56
10.2	69.707	245.31	426.84		463.92	354.46
10.4	75.238	262.82	451.81		476.19	339.98
10.6	81.077	281.14	476.97		479.94	334.10
10.8	87.229	300.25	502.58		478.41	348.31
11.2	100.53	340.83	555.62		492.19	338.17
11.4	107.70	362.29	582.41		495.40	327.13
11.6	115.25	384.52	609.28		489.02	342.51
11.8	123.17	407.51	636.61		485.17	359.15
12.2	140.15	455.93	691.90		497.46	337.38
12.4	149.22	481.39	718.95		489.29	353.72
12.6	158.72	507.60	746.03		479.35	386.27
12.8	168.64	534.49	773.66		482.79	386.82
13.2	189.81	590.49	828.20		488.65	394.33
13.4	201.07	619.70	854.05		475.29	444.85
13.6	212.78	649.67	879.93		474.16	461.01
13.8	224.97	680.27	906.28		490.97	457.33
14.2	250.81	743.43	956.53		485.69	537.28
14.4	264.49	776.07	979.87		480.83	573.42
14.6	278.67	809.34	1003.4		501.06	578.56
14.8	293.39	843.15	1027.2		522.76	589.89
15.2	324.42	912.58	1069.6		515.72	716.02
15.4	340.75	948.22	1089.3	751.67	536.24	732.23
15.6	357.64	984.31	1109.6	743.29	575.13	739.21
15.8	375.11	1020.7	1129.6	739.04	587.62	801.58
16.0	393.15	1057.6	1146.9	744.90	586.72	875.70
16.2	411.81	1095.0	1161.9	749.45	605.77	901.02
16.4	431.06	1132.9	1177.1	742.24	658.88	902.63
16.6	450.89	1171.2	1193.4	733.20	692.39	948.26
16.8	471.33	1209.6	1208.5	736.57	698.59	1035.8
17.0	492.37	1248.2	1220.1	748.66	714.60	1064.7
17.2	514.08	1287.1	1229.7	749.92	772.91	1059.6
17.4	536.43	1326.5	1240.6	740.72	832.22	1081.3
17.6	559.43	1365.9	1252.4	739.87	850.26	1176.2
17.8	583.09	1405.4	1261.7	756.50	863.44	1202.0
18.0	607.37	1445.0	1267.3	771.60	915.29	1192.7
18.2	632.31	1484.8	1272.4	769.61	997.26	1186.3
18.4	657.95	1524.6	1279.7	766.73	1031.6	1277.0
18.6	684.26	1564.3	1287.0	783.62	1044.2	1293.9
18.8	711.27	1603.9	1290.2	813.39	1082.7	1289.0
19.0	738.98	1643.4	1290.4	826.28	1174.7	1255.1
19.2	767.39	1683.0	1292.3	825.87	1227.8	1326.2
19.4	796.48	1722.4	1297.2	839.80	1241.6	1334.7

\* This work was supported by the Office of Naval Research.

<sup>1</sup> W. Heller and W. J. Pangonis, J. Chem. Phys. **26**, 498 (1957).

<sup>†</sup> These and other symbols have been defined previously (see reference 1).

<sup>‡</sup> To be published elsewhere.

TABLE I.—Continued

$\alpha \backslash m$	1.05	1.10	1.15	1.20	1.25	1.30
19.6	826.28	1761.4	1300.4	879.65	1264.2	1342.4
19.8	856.79	1800.1	1298.4	914.54	1348.2	1286.1
20.0	888.02	1838.5	1295.2	924.21	1423.1	1325.7
20.2	919.98	1876.9	1295.9	934.74	1439.6	1336.6
20.4	952.69	1914.8	1299.2	974.85	1444.7	1359.1
20.6	986.12	1952.2	1298.7	1031.8	1503.3	1287.5
20.8	1020.3	1989.1	1293.5	1061.9	1598.5	1294.6
21.0	1055.2	2025.6	1290.1	1074.2	1620.2	1322.2
21.2	1090.8	2061.7	1292.2	1107.1	1610.5	1354.4
21.4	1127.2	2097.1	1294.6	1175.3	1634.3	1280.0
21.6	1164.3	2131.8	1291.4	1232.3	1734.4	1262.5
21.8	1202.2	2165.9	1285.9	1254.7	1763.9	1317.2
22.0	1240.9	2199.7	1286.0	1280.0	1748.0	1344.0
22.2	1280.3	2232.8	1291.7	1344.7	1737.8	1291.1
22.4	1320.4	2264.9	1294.2	1426.8	1816.4	1260.1
22.6	1361.3	2296.0	1290.3	1468.2	1860.6	1348.8
22.8	1402.9	2326.6	1288.3	1489.2	1846.7	1349.2
23.0	1445.3	2356.7	1295.3	1539.2	1808.0	1344.9
23.2	1488.5	2386.0	1305.8	1632.9	1845.6	1310.5
23.4	1532.5	2414.1	1309.4	1702.1	1914.5	1436.0
23.6	1577.2	2441.1	1308.5	1726.4	1903.4	1401.6
23.8	1622.6	2467.5	1314.5	1757.5	1846.0	1459.3
24.0	1668.8	2493.4	1330.9	1840.3	1839.7	1425.3
24.2	1715.7	2518.1	1346.0	1937.0	1930.2	1567.7
24.4	1763.4	2541.6	1352.1	1976.0	1918.4	1525.2
24.6	1811.9	2564.0	1358.6	1992.9	1863.4	1644.7
24.8	1861.0	2586.0	1377.3	2048.1	1820.0	1605.3
25.0	1911.0	2607.3	1403.9	2155.0	1903.2	1724.9
25.2	1961.6	2627.2	1422.9	2218.3	1901.9	1718.3
25.4	2013.0	2645.6	1433.9	2229.7	1874.2	1893.8
25.6	2065.1	2663.2	1452.3	2254.0	1804.9	1841.2

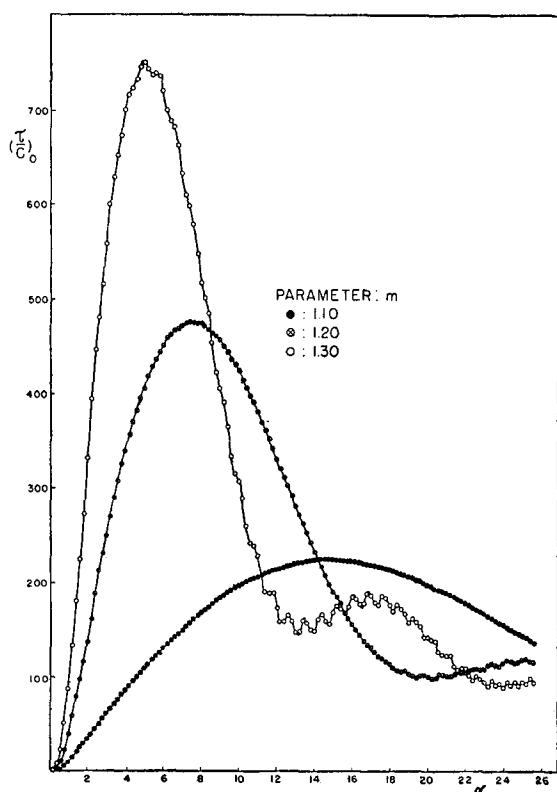


FIG. 1. The specific turbidity of aqueous dispersed systems of colloidal and microscopic spheres, calculated for a vacuum wavelength,  $\lambda_0$ , of 5460.73 Å and water at 25.00°C as the medium. The concentration,  $c$ , refers to 0.01 volume fractions.

to be detected in graphs. An extension, in Fig. 1, of the earlier  $(\tau/c)_0(\alpha)$  curves, for three representative  $m$  values shows these indentations to be particularly pronounced after passage of the first turbidity minimum if  $m=1.30$ . A detailed consideration, of the latter  $\alpha$  range, shows now that these indentations are not irregular fluctuations as assumed by previous authors, who noted them in favorable sections of  $K(\alpha)$  plots,<sup>2</sup> but are oscillations of surprisingly regular period. The distance between the secondary turbidity minima (and also that between the secondary turbidity maxima), expressed in terms of  $\Delta\alpha$ , is  $0.85 \pm 0.05$  from  $\alpha=19$  down to  $\alpha=11.5$ . Analysis of the first primary turbidity maximum shows that this period is numerically maintained down to an  $\alpha$  value as small as 4.5. § Except for a possible uncertainty of 10%, the period of 0.85 found for  $m=1.30$  applies also to  $m=1.20$  and  $m=1.25$ . Thus, it seems that the period of oscilla-

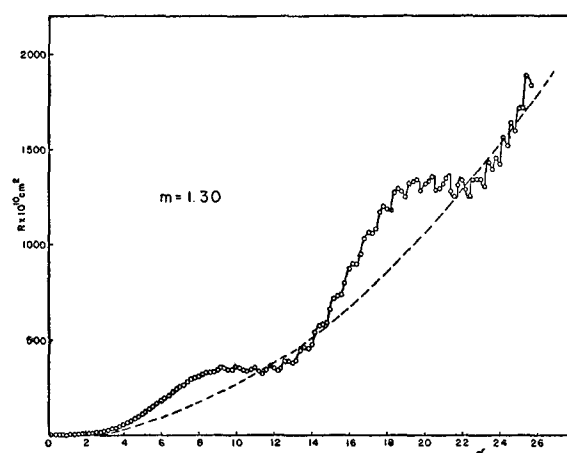


FIG. 2. Primary and secondary oscillations in the variation, with  $\alpha$ , of the scattering cross section (total radiation) of one sphere. Dotted curve is approximating relation, strictly valid as  $\alpha \rightarrow \infty$ :  $R = (\lambda^2/2\pi)\alpha^2$ , where  $\lambda$  is the wavelength in the medium.

tion is, in a good approximation, independent of  $m$ , while its amplitude increases at a given  $\alpha$  rapidly with  $m$ . The only complication in this relatively simple picture is the fact that the period is 0.4 rather than  $0.85 \pm 0.05$  at  $\alpha$  values  $> 22.0$ , subsequent to a transition period between  $\alpha=19.5$  and  $\alpha=22.0$ , where an unequivocal determination of the period is not possible. This complication occurs only for  $m=1.30$  within the  $\alpha$  ranges considered. In spite of the apparent conclusiveness of the graph it is not possible, however, to assert that such a more or less sudden increase in the frequency of oscillation takes place above a critical  $\alpha$  value or range of  $\alpha$  values. For, it would be perfectly possible to satisfy all data by a period of about 0.4 even within those lower  $\alpha$  ranges where the visually obvious period is about 0.8. A definite decision between

<sup>2</sup> See, e.g., H. G. Houghton and W. R. Chalker, J. Opt. Soc. Am. **39**, 955 (1949).

§ The graphical analysis is obviously not precise enough to exclude a systematic minor variation in period with  $\alpha$ .

the existing alternative could be made only on the basis of computations for very narrow  $\Delta\alpha$  intervals of 0.05 within a trial range, say between 13.1 and 13.9. Such computations are not available at present.

Attempts at explaining the fine structure of the  $(\tau/c)_0(\alpha)$  curve, must necessarily be based upon the behavior of the  $R(\alpha)$  curves which show an equivalent fine structure.  $R$  increases with  $\alpha^6$  as  $\alpha \rightarrow 0$  and with  $\alpha^2$  as  $\alpha \rightarrow \infty$ .<sup>3</sup> This over-all decrease in the slope of the  $R(\alpha)$  curve with increasing  $\alpha$  is not continuous but oscillatory, as evident from Fig. 2 in which the limiting  $R(\alpha)$  curve, reached at  $\alpha \rightarrow \infty$ , is dotted for  $m=1.30$ . These major oscillations can be interpreted as the result of periodic variations in the interference between

the scattered radiation and the incident radiation, a factor neglected in the treatments by Rayleigh-Gans and Debye. The fine structure superimposed upon these major oscillations may be interpreted, in a first approximation, as the result of periodically varying interferences within the scattered radiation itself, keeping in mind that a differentiation between the two interference phenomena is allowed only in a first approximation. The fine structure would therefore be related to the maxima and minima observed in lateral scattering. One should, therefore, expect a simple relationship between the period of the strongly pronounced lateral maxima and minima and that of the comparatively very weak secondary maxima and minima in the  $R(\alpha)$  and  $(\tau/c)_0$  curves.

<sup>3</sup> Reference 1, page 502.

## Neighbor Interactions and Internal Rotations in Polymer Molecules. I. Stereospecific Structure and Average Dimensions

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(Received March 10, 1958)

The skeletal bonds of vinylic polymer molecules are classified as (+) bonds and (−) bonds according to the arrangement of the side groups relative to the bonds. The detailed structure of isotactic and syndiotactic polymers is characterized by the different regularities of arrangement of these two bond types along the molecular chain. Symmetry properties of (+) and (−) bonds, and of (+)(+), (−)(−), and (−)(+) bond pairs, are discussed. These lead to relations between the average values of functions of the internal-rotation angles of the various bond-pairs.

The end-to-end distance of isotactic and syndiotactic molecules is expressed in terms of bond lengths, bond angles, and internal rotation angles of the skeletal bonds, using methods of matrix algebra. The mean-square end-to-end distance  $\langle h^2 \rangle$  of these molecules is determined by certain averages of trigonometric functions of the internal rotation angles enclosed between neighboring skeletal bond pairs. The averages depend on the energy of interaction of neighboring side groups as well as on the internal interactions within the skeletal bonds, and are different in the isotactic and syndiotactic molecules.

### I. INTRODUCTION

IN 1932 Eyring<sup>1</sup> suggested a solution of the problem of calculating the mean-square end-to-end distance  $\langle h^2 \rangle$  of polymer molecules as a function of bond lengths, bond angles, and internal rotations. Eyring's method has since been improved and extended by many authors.<sup>2-12</sup>

<sup>1</sup> H. Eyring, *Phys. Rev.* **39**, 746 (1932).

<sup>2</sup> S. E. Bresler and J. Frenkel, *Acta Physicochimica U.S.S.R.* **11**, 485 (1939).

<sup>3</sup> J. Frenkel, *Kinetic Theory of Liquids* (Oxford University Press, New York, 1946).

<sup>4</sup> C. Sadron, *J. chim. phys.* **43**, 12 (1946); **44**, 22 (1947).

<sup>5</sup> H. Kuhn, *J. Chem. Phys.* **15**, 843 (1947).

<sup>6</sup> P. Debye, Lecture at High Polymer Conference, Strasbourg, November, 1946.

<sup>7</sup> M. H. Benoit, *J. chim. phys.* **44**, 18 (1947); *J. Polymer Sci.*, **3**, 376 (1948).

<sup>8</sup> W. J. Taylor, *J. Chem. Phys.* **15**, 412 (1947); **16**, 257 (1948).

<sup>9</sup> M. V. Volkenshtein and O. B. Ptitsyn, *Doklady Akad. Nauk S.S.S.R.* **78**, 657 (1951); *Zhur. Fiz. Khim.* **26**, 1061 (1952).

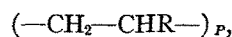
<sup>10</sup> (a) T. M. Birshtein and O. B. Ptitsyn, *Zhur. Fiz. Khim.* **26**, 1215 (1952); (b) **28**, 213 (1954).

<sup>11</sup> R. A. Sack, *J. Chem. Phys.* **25**, 1087 (1956).

<sup>12</sup> I. Eliezer and H. J. G. Hayman, *J. Polymer Sci.* **23**, 387 (1957).

One of the main purposes of the various extensions was to calculate the dependence of  $\langle h^2 \rangle$  on the interactions between the groups connected by the skeletal bonds. These interactions were usually represented for each bond by a potential of hindered rotation of that bond, and were assumed to be independent of the state of internal rotation of other bonds. In other words, the rotation of each bond, though hindered by interactions within the bond was assumed to be independent of the state of rotation of its neighbors.

There are, however, many cases, where the above approximation does not seem sufficient, because rotations of adjacent bonds may be interdependent to a significant extent. In all polymers of the type



there are states of minimum potential of hindered rotation for which the neighboring R groups may come as close together as 2.5 Å. If, for example, the R groups repel each other strongly at such a distance, the probability of such states is reduced considerably, and other