REVIEWS OF MODERN PHYSICS VOLUME 31, NUMBER 4 OCTOBER, 1959

Anisotropic Light Scattering of Streaming Suspensions and Solutions

WILFRIED HELLER

Chemistry Department, Wayne State University, Detroit 1, Michigan

I. INTRODUCTION

In recent years considerable use has been made of light scattering for determining the shape of dissolved macromolecules and of dispersed colloidal particles. The favored method uses the variation of scattering with the angle of observation. The theories used are due to Gans[1] and Debye.[2] An alternative method is that of Krishnan.[3] Here, the relative intensities of the "four Krishnan components" of light scattered at 90° with respect to the primary beam are the experimental data. The former method uses incident natural light; the latter, incident plane polarized light. Both have in common the investigation of light scattering by systems with randomly oriented molecules or particles. There is no need for a review of either of these methods since several excellent summaries are already available.[4] A much neglected, yet more powerful and older third method, is due to Diesselhorst and Freundlich.[5] In this, the light scattering is observed subsequent to an orientation of the scattering bodies, e.g., by streaming. Such an orientation produces an anisotropy of light scattering: the scattered intensity varies with the orientation of the electric vector of the incident beam with respect to the morphologically extraordinary direction of the scattering bodies. This review is concerned with the three principal phenomena of anisotropic light scattering observed or to be expected: dityndallism, conservative dichroism, and "bidissymmetry."

II. METHODS AND PROBLEMS OF ORIENTATION

The necessary orientation of particles or molecules may be produced by streaming, or by an electric or magnetic field. Flow orientation is due exclusively to anisometric (nonspherical) shape and is therefore of primary interest here. It is "kinematic"—although the particles rotate continuously due to the velocity gradient q and to the rotatory Brownian movement, they spend most of their time in a position defined by the angle χ. This is the angle between the most probable direction of the longest dimension of the particles and the direction of the velocity gradient. If the particles or molecules are deformable, the phenomenon is complicated by dilation at an angle of 45° with respect to q and the direction of flow, and compression at an orthogonal angle. The direction of flow is generally referred to as the extraordinary direction e of the system. It will actually be an extraordinary direction only if $q \rightarrow \infty$, i.e., when the longest dimension of the particles is parallel to the direction of flow ($\chi = 90°$). If the particles are uniaxial, the direction of flow becomes then—according to the definition in crystal optics—the optic axis of the system and, therefore, the optically extraordinary direction.

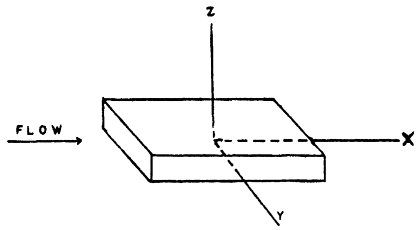
Magnetic and electric orientation are simpler in nature since the direction of orientation always coincides with the direction of the field or with the direction normal to it. The degree of orientation is governed here by the torque acting upon the particles and the superimposed randomizing effect of the rotatory Brownian movement. Complications arise from the fact that magnetic and electric orientation may be due to both anisometry and intrinsic (magnetic or electric) anisotropy. Since the orienting torque due to anisometry is generally very weak the orientation is, in general, mainly due to a permanent or induced magnetic or electric dipole. The existence of the two torques can lead to considerable complication if they are orthogonal. The orientation may then change direction with field strength, temperature, or frequency. Some of the resulting optical complications are described in detail elsewhere.[6] Of particular interest is the application of alternating magnetic[7] or electric[8] fields. Whenever magnetic orientation is applicable, it deserves preference over electric orientation because of a variety of possible secondary complications of the latter.[8]

III. DITYNDALLISM

1. Classical Experiments and Definitions

Dityndallism was discovered by Diesselhorst and Freundlich[5] on various streaming colloidal solutions.

[1] R. Gans in *Handbuch der Experimentalphysik* (Akademische Verlagsgesellschaft, Leipzig, 1928), Vol. 19, p. 34; Ann. Physik **62**, 331 (1920).
[2] P. Debye, lecture given at the Polytechnic Institute of Brooklyn, Brooklyn, New York (November 25, 1944).
[3] R. S. Krishnan, Proc. Indian Acad. Sci. **A1**, 211 (1934) and numerous later papers by this author and his associates.
[4] See, e.g., H. C. van de Hulst, *Light Scattering by Small Particles* (John Wiley & Sons, Inc., New York, 1957).
[5] H. Diesselhorst and H. Freundlich, Physik. Z. **16**, 422 (1915); **17**, 117 (1916).
[6] W. Heller, "Nouvelles recherches sur les propriétés magnéto-optiques des solutions colloidales" in *Actualités sci. et ind.* (Hermann et Cie., editors, Paris, 1939), Vol. 806.
[7] Selected references may be found in W. Heller, *Kolloidphysik des Eisenoxydsols*; in Abegg-Koppel, *Handbuch der anorganischen Chemie* (S. Hirzel, Leipzig, 1934), Vol. 4, Chap. 3, p. 2B.
[8] W. Heller, Revs. Modern Phys. **14**, 390 (1942).



DIRECTION OF PRIMARY BEAM	DIRECTION OF ELECTRIC VECTOR	DIRECTION OF OBSERVATION	SCATTERED RELATIVE INTENSITY RODS	SCATTERED RELATIVE INTENSITY PLATES
X	Y	Z	●	○
X	Z	Y	●	●
Z	X	Y	○	○
Z	Y	X	●	○
Y	Z	X	●	●
Y	X	Z	○	○

FIG. 1. Dityndallism produced by flow orientation of colloidal rods and plates. ●, scattered intensity is strong. ○, scattered intensity is weak.

Figure 1 illustrates their procedure and results. The colloidal solution flows through a rectangular cell in the x direction. The principal velocity gradient is in the z direction and a secondary gradient is in the y direction. Consequently, rod-like particles will, at a sufficiently high velocity gradient, direct their morphologically extraordinary direction, i.e., the major axis, preferentially toward x, while disk-like particles will direct theirs, the shortest dimension, preferentially toward z. The direction of the linearly polarized beam and of its electric vector and the direction of observation (always perpendicular to the incident beam) are varied to the fullest possible extent.

The black and white disks indicate that the observed scattered intensity is weak or strong, respectively.[9] It follows that, for one particle, the intensity of light scattered at 90° with respect to the incident beam is strongest if the electric vector is perpendicular to the plane of observation and parallel to the largest dimension of the particle. The laterally observed Tyndall beam of a dispersed system of oriented rods has therefore maximal intensity if the electric vector of the incident beam vibrates, for $q \rightarrow \infty$, parallel to the direction of flow and has minimal intensity for the orthogonal direction of vibration. This effect, called "dityndallism,"[10a] could be defined in analogy to birefringence and dichroism by

$$(D_o)_\theta = (I_e - I_o), \tag{1}$$

where I is the intensity of light scattered at an angle θ, per unit solid angle, per unit volume of unit concentration, and per unit intensity of the incident beam, and o refers to the ordinary direction of the system. The usefulness of this definition is limited, however, since $(I_e - I_o)$ may be finite also in the unoriented system. An alternate definition,

$$(D)_\theta = (I_e' - I_e'') - (I_o' - I_o'') = \Delta I_e - \Delta I_o, \tag{1a}$$

therefore may be introduced as preferable. The superscripts $'$ and $''$ refer to the oriented and unoriented system, respectively. For practical work, definition (1a) may be expressed in terms of more convenient intensity ratios.[10b]

Flow dityndallism is an exclusive form effect only if produced by deformation of isotropic fluid material (e.g., emulsion droplets) or by orientation of anisometric intrinsically isotropic bodies. Anisometric bodies are rarely intrinsically isotropic. In general, therefore, an intrinsic dityndallism of equal or opposite sign will be superimposed upon the form dityndallism. A quantitative differentiation between the two effects should be possible by varying the refractive index of the medium.

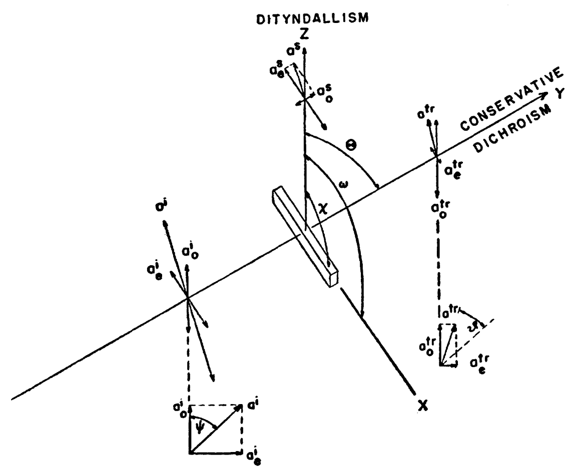


FIG. 2. Geometrical definitions pertinent to flow dityndallism and conservative flow dichroism.

2. Physical Optics of Dityndallism

The physical optics of dityndallism is somewhat intricate. This is discussed with the aid of Fig. 2, where the principal drawing is in perspective, while two auxiliary drawings pertain to the xz plane viewed in the direction of the light source. The symbols x, y, and z indicate the direction of flow of the primary beam and

[9] A quantitative investigation can be expected to show that there are four different intensities for platelets and three for rodlets.

[10a] H. Zocher, Kolloid Z. **37**, 336 (1925).

[10b] M. Nakagaki and W. Heller, J. Polymer Sci. (June, 1959).

of the velocity gradient, respectively. The angle χ between the major axis of the rod-like particle considered and the velocity gradient is, for simplicity, assumed to be 90°. This corresponds to $q \rightarrow \infty$. The angle between the electric vector of the incident beam and the yz plane is ψ, that between the vector of the scattered beam—or of the scattered component considered—and the xz plane is ψ' (symbol not shown in Fig. 2). The angle between the variable plane of observation and the direction of flow is ω, that between the direction of observation and the direction of the primary beam is θ.

Consider first the situation pictured in Fig. 2, in which $\theta=\omega=\chi=90°$ and let the angle ψ be 90° and 0° in two *consecutive* measurements. The amplitude of the component of the incident beam vibrating in the extraordinary direction $a_e{}^i$ gives rise to an amplitude of the scattered component $a_e{}^s$, and, in the more general case, of a component $a_o{}^{s\prime}$. The latter is not considered in the drawing. Similarly, $a_o{}^s$ (and a neglected component $a_e{}^{s\prime}$) will result from $a_o{}^i$.[11] Since $a_e{}^s \neq a_o{}^s$, the consecutively determined amplitudes of the components of the transmitted beam, $a_e{}^{tr} \neq a_o{}^{tr}$. Next assume that $\theta=\omega=\chi=90°$, but $(0° \neq \psi \neq 90°)$. The scattering process is then equivalent to that expected for two coherent components with the amplitudes $a_e{}^i$ and $a_o{}^i$. Consequently, the scattered linearly polarized beam, of amplitude a^s, resulting from their interference, vibrates at an angle $\psi' \neq \psi$. Measurement of the dityndallism is therefore reduced to a single measurement, that of the angle ψ' for which the scattered intensity transmitted through an analyzer is maximal.[12] The difference between ψ and ψ' reaches a maximum when $\psi=45°$.

When $\theta=90°$, $\omega \neq 90°$, $\chi=90°$ (and $0° \neq \psi \neq 90°$), the scattered beam is elliptically polarized, the ellipticity being due to phase differences between the orthogonal coherent components of wavelets of scattered light originating in different volume elements of the particle. The situation is the same when $\theta=\omega=90°$, $\psi=0°$, but $\chi \neq 90°$.

This discussion allows one to anticipate a few physical phenomena which have yet to be verified experimentally. It should be possible to determine χ by rotating the direction of observation, in the xz plane, to the particular $\omega \neq 90°$ value at which the ellipticity vanishes, i.e., at which the scattered beam represents linearly polarized light. The rate of change of the state of polarization during this rotation should vary with the shape of the particles. This should provide an auxiliary method for the determination of shapes. Assume that the proper ω value yielding linearly polarized light is found: a transition from $\theta=90°$ to $\theta \neq 90°$ will then also produce ellipticity and the rate of its change with θ also should vary with the dimensions of the particles or molecules.

The case may arise that ellipticity is observed even for $\theta=\omega=90°$, $\chi=90°$, and $0° \neq \psi \neq 90°$. This would be indicative of intrinsic anisotropy and the degree of ellipticity would be indicative of the magnitude of intrinsic anisotropy. Ellipticity would be due here to the difference in retardation of the orthogonal components of scattered light within the scattered particle by virtue of differences in its refractive indices parallel and perpendicular to the rod axis. This effect would represent the true complement, in the scattering process, to intrinsic birefringence.

3. Theory of Dityndallism

The theory of dityndallism is concerned with the scattering process of nonspherical particles and with the distribution function of their principal axes. The latter was treated first by Langevin[13] for the relatively simple case of magnetic (or electric) orientation. This theory yields the relationship

$$(\mu_e-\mu_u)(\mu_u-\mu_o)=2.0, \tag{2}$$

where the subscript u refers to the unoriented system and μ is the refractive index. The relationship should, of course, hold also for turbidity and true absorption. It was verified for the former effect.[14] The distribution function for electric orientation of flexible macromolecules was derived, more recently, by Isihara.[15] The more complicated case of flow orientation of rigid spheroids has been treated by Boeder[16] and, more rigorously, by Peterlin and Stuart.[17] Finally, the distribution function for the end-to-end distance of flow deformed molecules has been developed recently.[18]

The theory of anisotropic scattering for the case in which intrinsically isotropic and rigid anisometric particles are small compared to the wavelength of the incident beam is implicitly contained in an early treatment by Rayleigh.[19] A recent extension of this theory by A. F. Stevenson includes the dimensions commonly encountered with proteins and synthetic macromolecules. This theory will be published in the near future.

[11] Owing to the interference of each of the two disregarded components with the respective coherent orthogonal components, a linearly polarized beam results in each instance which vibrates in reality at an angle $\psi' \neq 0°$ and $\psi' \neq 90°$, respectively. It is surprising that in depolarization measurements on resting solutions by Krishnan's method no attention has been paid either to the existence of these two linearly polarized scattered beams or to their measurement.

[12] Similarly V_v+V_h and H_v+H_h could be determined in one measurement and the four "Krishnan-components" V_v, V_h, H_v, and H_h in two measurements instead of the four generally used in depolarization measurements on unoriented systems.

[13] P. Langevin, Radium **7**, 249 (1910).

[14] W. Heller and G. Quimfe, Phys. Rev. **61**, 382 (1942).

[15] Isihara, Koyama, Yamada, and Nihioka, J. Polymer Sci. **17**, 341 (1955); see also C. Wippler; J. Polymer Sci. **23**, 199 (1957).

[16] P. Boeder, Z. Physik **75**, 258 (1932).

[17] A. Peterlin and H. A. Stuart, *Hand- und Jahrbuch d. Chem. Physik*, A. Eucken and K. L. Wolff, editors (Akademische Verlagagesellschaft, Leipzig, 1943), Vol. VIII, Sec. IB.

[18] Peterlin, Heller, and Nakagaki, J. Chem. Phys. **28**, 470 (1958).

[19] Lord Rayleigh, Phil. Mag. **41**, 447 (1871); **44**, 28 (1897).

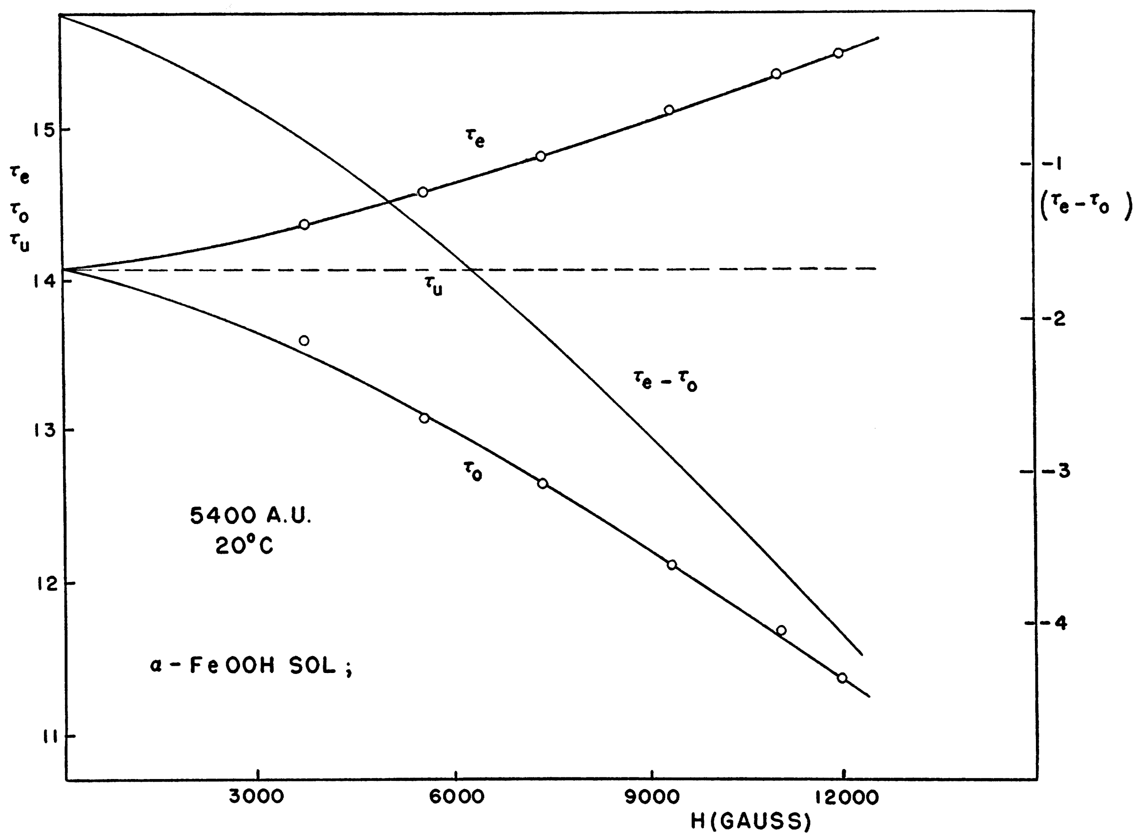


FIG. 3. Conservative magnetic dichroism of an α-FeOOH-sol.

The treatment of anisotropic light scattering to be expected from random coils deformed by flow is difficult, and suitable approximations are therefore necessary. Exploratory investigations to that effect have been published elsewhere.[20,10b]

IV. THE CONSERVATIVE DICHROISM

1. Definitions and Methods of Measurement

Figure 2 shows that the turbidity τ of a dispersed system of oriented anisometric particles varies with the direction of the electric vector of the incident linearly polarized beam. Consequently, the difference $(\tau_e - \tau_o) \neq 0$.[21] The existence of this effect was explicitly proved only rather recently.[6] It was subsequently designated as "conservative" dichroism.[22] This effect, like dityndallism, is primarily an effect of anisometry, but again the intrinsic anisotropy may make a contribution of equal or opposite sign. If the form effect predominates, then the sign of the total effect immediately indicates the orientation of the longest particle dimension with respect to the extraordinary direction. In order to evaluate the relative contribution of the intrinsic effect, one can—as with birefringence—eliminate the form effect by suitably varying the refractive index of the medium.[23]

Investigation of the conservative dichroism requires that one work in a spectral range of negligible absorption. Otherwise, the effect observed is complex in nature because of the simultaneous presence of true dichroism which is due to a difference in the extinction coefficients ϵ_e and ϵ_o. The two effects are physically not separable.

The theory of conservative dichroism, like that of dityndallism, is implicitly contained in the paper by Rayleigh[19] when the particles are small compared to the wavelength. The theory for larger particles is, at present, under preparation. The latter case is of far greater importance since the smallness of the turbidity in systems with very small particles makes it difficult

[20] A. F. Stevenson and H. L. Bhatnagar, J. Chem. Phys. **29**, 1336 (1958).

[21] "Turbidity rations" may often be easier to obtain or may convey supplemental information. Thus, the ratios τ_e/τ_u or τ_o/τ_u, where *u* refers to the unoriented system, give the turbidity of the oriented system, for the particular direction of the electric vector, relative to that of the isotropic unoriented system.

[22] See reference 11 in Heller, Quimfe, and Yeou-Ta, Phys. Rev. **62**, 479 (1942).

[23] Results by A. Piekara and W. Heller (to be published).

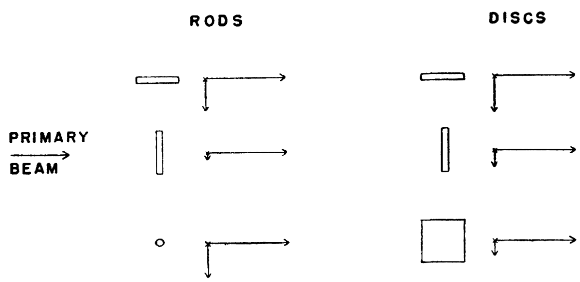


FIG. 4. Anisotropic interference of light scattered by oriented rods and plates not small compared to the wavelength of the incident beam.

to obtain a reliable turbidity difference $(\tau_e - \tau_o)$. Although the attractive feature of conservative dichroism, like that of dityndallism, is primarily the possibility of obtaining numerical data on the dimensions of nonspherical bodies, other applications also are interesting: one can easily obtain semiquantitative information on changes in size, shape, and structure of aggregates formed during coagulation of anisometric particles.[24] Furthermore, the mechanism and kinetics of sol-gel transformation and the change in rotatory mobility of particles during this process can be studied successfully.[25]

Several methods are available for experimental determination of $(\tau_e - \tau_0)$. First, by conventional spectrophotometric procedure τ_e and τ_0 may be measured in succession. The plane of polarization is rotated, between measurements, by 90° and the oriented system and the reference medium (solvent) are brought into the light path consecutively. In the case of magnetic orientation, one may use a split beam of orthogonally polarized components, each of which traverses one compartment of a twin cell filled with the oriented system and solvent, respectively. The second measurement is made after rotating the twin cell by 180° about an axis perpendicular to the field and incident twin beam.[26] Figure 3 shows the magnetic conservative dichroism thus obtained in an old colloidal solution of FeOOH.[27] (The results, to which the true dichroism makes a negligible contribution at 5400 a.u. show immediately that the plate-like particles of submicroscopic size orient themselves parallel to the lines of force.) These two methods give τ_u, in addition to τ_e and τ_o. This is not the case for the third method, which is the fastest, and also the most sensitive if the effects are small. Here, $\psi = 45°$ (Fig. 2). The conservative dichroism then produces a rotation of the plane of polarization ϑ[28] from which $(\tau_e - \tau_o)$ is easily derived.[29]

V. BIDISSYMMETRY IN UNPOLARIZED LIGHT

The rods and disks, shown schematically in Fig. 4 in the three possible orientations with respect to an incident unpolarized beam, lead to radiation diagrams of which two vectors are shown schematically in each case: the radius vector at 90° and that at 0° with respect to the direction of the primary beam. The former vector applies to observation in the plane of the paper. The reduction, by interference, in the intensity of laterally scattered light is more pronounced if the longest direction of the particle is perpendicular to the primary beam and is directed towards the observer. Again, a differentiation between rods and disks should be possible, although the quantitative differences in the optical effects can be expected to be smaller than for incident polarized light.[30] Intrinsic anisotropy also makes a contribution here, since interference varies with the refractive index.

Of particular interest is the fact that here light scattering exhibits a twofold dissymmetry. This is shown schematically in Fig. 5. The cross sections of the schematic radiation diagrams of spheres, random coils, or randomly oriented nonspherical bodies (left) and of oriented nonspherical bodies or deformed random coils

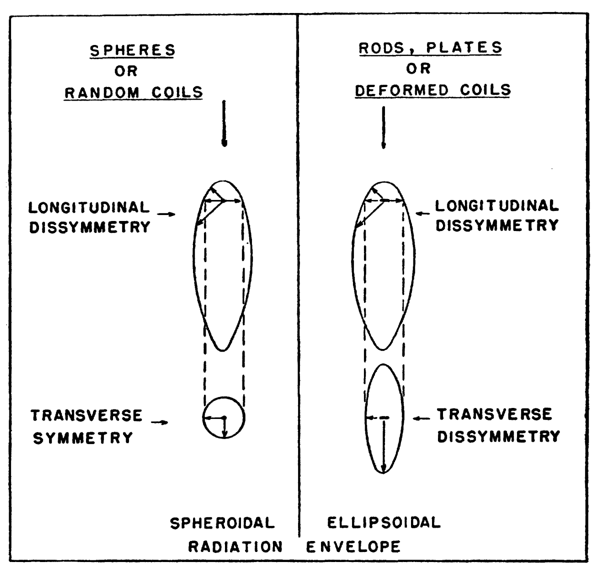


FIG. 5. Conventional dissymmetry (left) and bidissymmetry on orientation or deformation (right).

[24] W. Heller, J. Phys. Chem. **41**, 1041 (1937).

[25] W. Heller and G. Quimfe, Compt. rend. **205**, 1152, 1394 (1937); **207**, 157 (1938).

[26] The apparatus constructed and used for this purpose has been described briefly elsewhere[14] and will be discussed in detail in a separate publication.

[27] Details are given in the M. S. thesis of G. Quimfe, Faculté des Sciences, University of Paris (1938).

[28] The superficial similarity with rotation due to rotatory power has led a few authors to confuse dichroism with optical rotation. Rotation of the polarizer allows a very easy differentiation between the two effects.

[29] W. Heller and H. Zocher, Z. physik. Chem. (Leipzig) **A164**, 55 (1933).

[30] If interference in the forward direction cannot be neglected—nearly microscopic particle size or large refractive index difference between particles and medium—all three configurations of both rods and disks will lead to different scattering intensities.

(right), not negligibly small compared to the wavelength, are given by the upper drawings for the direction of the primary beam indicated by the top arrows. The cross sections of the diagrams in the lower pair of drawings apply to incidence of the primary beam perpendicular to the plane of the paper. The radiation diagram on the left exhibits merely the well-known "longitudinal" dissymmetry, while that on the right has, in addition, a "transverse" dissymmetry. Light scattering is here therefore "bidissymmetrical". The dityndallism in polarized light also exhibits bidissymmetry, but its features are more complicated.

While significant details of the scattering process are lost when unpolarized light is used, the resulting greater simplicity of the phenomena allows simplification of both the optical theory and the apparatus. One may, therefore, consider approximating treatments which would fail for polarized light. Thus, Debye's "interference" treatment[2] was used in order to establish the theory of bidissymmetry expected for flow deformed random coils.[18] This theory allows one to derive, from the bidissymmetry, important information on molecular parameters which cannot be obtained easily by any other means.