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The Origin and the Complications of Electric Double Refraction and of Electric Dichroism in Dilute Dispersed Systems

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UNLIKE the Kerr effect in homogeneous systems, the electric double refraction in dispersed systems[1] may exhibit a very complex character; for example, the sign may change with field strength, electric frequency or the concentration of the dispersed phase. This paper is an attempt to review and to clarify the present situation and thus to open the way for a useful application of electro-optical anisotropy in colloidal research. Only phenomena in dilute dispersed systems (less than 1 g of dispersed phase per liter dispersed system) shall be discussed in the present paper.

I. ELEMENTARY COMPLICATIONS

1. Static Field

a. The Kerr Effect

The individual particles in dilute dispersed systems have, in zero electric field, complete freedom of rotation and translation ("independent" particles). Polarized by a homogeneous external field, independent electrically anisotropic particles are subjected to a torque that aims at directing the axis of maximum polarization parallel to the lines of force. If there is a permanent moment, a torque will act to orient the dipole axis in the right direction parallel to the field. In either case, the torque increases in direct proportion with the volume of the particles[2] and with the square of the field strength E. The double refraction resulting from orientation of the dispersed phase is given by

$$(n_{\parallel}-n_{\perp})=\frac{\delta\lambda_0 a_t}{d2\pi a_p}=\frac{\Delta a_t}{d a_p}=B\lambda_0 E^2=KE^2. \quad (1)$$

Here B is the Kerr constant; K the "absolute" Kerr constant; λ_0 the optical wave-length in vacuum; δ the phase difference; Δ the path difference; d the layer thickness; a_p the volume of the dispersed phase; a_t the volume of the dispersed system. For optically uniaxial particles, n_e may be either parallel or perpendicular to the electro-optically extraordinary $n_{\parallel}$.[3] The term $n_{\parallel}$ will be n_γ if orientation is due to anisotropy of an induced moment provided the optical dispersion is normal in the spectral region considered. If orientation is due to a permanent moment, $n_{\parallel}$ may be either n_γ or n_α.

A perfect orientation will finally be approached as E increases. Above a certain field range $\sim E_x$, a decrease of the exponent in Eq. (1) will therefore become measurable. The disorienting Brownian movement, and consequently, $\sim E_x$ decrease with increasing particle volume. Whereas for molecules of normal diameter (<10A) Eq. (1) may hold beyond 44,000 volts/cm (7), it may not hold beyond 50 volts/cm for particles 1000A in diameter, if we take Björnståhl's experiments in gold sols (4) as a guide. For particles of equal volume, the field strengths of the range $\sim E_x$ should be higher the weaker the electric anisotropy. The value of $\sim E_x$ could, therefore, be used as a criterion for electrical and structural anisotropy of colloidal particles of known volume.[4] A second, better known

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[1] This effect is the electric analog to the magnetic Majorana phenomenon, whereas the Kerr effect in homogeneous systems is the electric analog to the magnetic Cotton-Mouton effect. In dispersed systems of microscopic particles, it was first observed by Kerr (1) and later investigated by Chaudier (2). (Numbers in parentheses refer to bibliography at end of article.) In colloidal dispersions, it was first observed by Diesselhorst, Freundlich, and Leonhardt (3) and later was studied by Björnståhl (4). Since the effect in colloidal dispersion may only in part, or not at all, be a Kerr effect, the summary term "Diesselhorst-Freundlich" effect had been proposed (5).

[2] It is, therefore, not surprising that the Kerr constant in colloidal dispersions may be enormous (6), possibly 10^6 times as large as for nitrobenzene. If the size differences were taken into account, a "volume independent" Kerr constant would be of equal order of magnitude.

[3] The habit of choosing n_e-n_0 as symbols for double refraction in dispersed systems is not advisable. These symbols should be reserved for the anisotropy of the individual particles. Instead of $(n_{\parallel}-n_{\perp})$, (n_l-n_t) may be used (l = longitudinal, t = transverse to the direction of the field).

[4] Only the analogous $\sim H_x$ (of magnetic double refraction) has been used so far in this sense (8).

criterion is of course the magnitude of the Kerr constant.

b. *Electro-osmotic and Electrophoretic Double Refraction*

The external electric field leads to electro-osmosis if the surface of the walls of the trough has a potential ζ_w with respect to the interior of the medium.[5] It leads to electrophoresis if the surface of the dispersed particles has a potential ζ_p with respect to the interior of the medium. Either phenomenon may conceivably lead to orientation of anisometric particles, but only electrophoresis can be expected to lead to an orientation large enough to produce a measurable double refraction.

Electro-osmotic double refraction would be comparable to hydrodynamic double refraction (streaming double refraction) as observed in streaming dispersed systems. Hydrodynamic double refraction is due to orienting velocity gradients dv/dx and dv/dy perpendicular to the direction of flow z. Electro-osmosis of the rate u_E in a closed rectangular trough leads to a flow of the medium of dispersion[6] of the rate $v_{mE}=u_E$ near the walls, $v_{mE}=0$ at an intermediate level, and $v_{mE}=-0.5u_E$ at the center of the trough. The velocity gradients are a parabolic function of x and y, like the gradients in a mechanically produced flow through open rectangular tubes. (In both instances, the gradients are zero in the center and maximum near the walls.) For velocity gradients as low as those involved here, hydrodynamic double refraction is proportional to the velocity gradient perpendicular to the direction of observation[7] perpendicular to z. By taking into account that

$$u_E=uE=\frac{\zeta_w\epsilon_m}{4\pi\eta}E, \tag{2}$$

where u is the rate of electro-osmotic flow per unit field strength; ϵ_m is dielectric constant of the medium; η is its frictional constant;[8] we have

$$(n_{||}-n_{\perp})_{\perp yz}=K_1(dv_m/dy)E=K_1'E, \tag{3}$$

$$(n_{||}-n_{\perp})_{\perp xz}=K_{1a}(dv_m/dx)E=K'_{1a}E. \tag{3a}$$

If the dimensions of the trough in the directions x and y, are equal, $K_1'=K'_{1a}$. Both K_1' and K'_{1a} would become larger the smaller the respective dimensions of the trough. The longest axis of electro-osmotically oriented particles would not be parallel z, but inclined towards it, possibly as much as 45°. Electro-osmotic double refraction would obviously be zero in the center of the trough and it would reach its largest value near the walls. But even there it should be very weak unless very narrow troughs and very strong fields are used. If we consider, for example, a trough 0.5 cm wide perpendicular to z and the direction of observation, and a field of 100 v/cm, the velocity gradient will nowhere, except for a microscopic strip near the walls, exceed 10^{-1} second, if u has the order of magnitude 10^{-4} (cm^2 sec.$^{-1}$ volt^{-1}). For such velocity gradients, hydrodynamic double refraction is mostly undetectable. The hypothesis (9) that "electrophoretic currents" may be responsible for double refraction, has therefore hardly practical significance.

Electrophoresis of the rate

$$v_{pE}=v_pE=\frac{\zeta_p\cdot\epsilon_m}{4\pi\eta}E, \tag{4}$$

where v_p is the electric mobility per unit field strength,[9] leads to a displacement $v_{pE}t$ ($t=$time) of the particles relative to the medium. This displacement,[10] obviously independent of x, y,

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[5] The term "medium" comprises here all truly dissolved substances.

[6] The primary phenomenon of electro-osmosis in aqueous dispersed systems, is an electric transport of ions tangentially to the walls of the trough. An inseparable secondary phenomenon is the dragging along, with the ions and at the same rate, of the water molecules. If the walls consist of glass, and the medium of water, the walls will take on a negative charge, due to transition of Na ions into the medium. They and the water molecules will then migrate towards the cathode, under the influence of an external electric field.

[7] This theoretically supported regularity has mostly been studied for circular laminary flow [see bibliography in (10)]; but it is known also for linear laminary flow (11).

[8] For the derivation of relations (2) and (4) see reference (12) in the bibliography.

[9] The factor (4) presupposes here that the particles are non-conductors. Usually, $\zeta_p\neq\zeta_w$. Under appropriate conditions $\zeta_w=0$ whereas $\zeta_p\neq0$ or vice versa. Only if the surface layers on particles and walls of trough are identical, e.g., after coating with the same protein, $\zeta_p=\zeta_w$ (and $u=v_p$).

[10] The absolute displacement $v_p't$ depends of course on v_m and, consequently on x and y. The unit $v_p'=v_p$ at the level where $v_m=0$.

dv_m/dx, and dv_m/dy, may lead to an orientation and to "electrophoretic" double refraction. This double refraction would be comparable to that produced by settling of anisometric particles under the influence of gravitational or centrifugal acceleration, but it would not be comparable to the streaming double refraction with which it is generally compared.[11]

$$(n_{\parallel} - n_{\perp})_{\perp xz \text{ and } \perp yz} = K_2 \frac{\zeta_p \epsilon_m}{4\pi\eta} E = K_2' E. \qquad (5)$$

The constants K_1, K_{1a}, and K_2 depend on the optical wave-length λ_0, on the volume and form factor f (length/width) of the particles, on $(n_e - n_o)$, and also on the refractive index of the medium n_m, in case of morphic double refraction (see III, 1).

Contrary to electro-osmotic double refraction, electrophoretic double refraction would be equally strong in the center and at the walls of the trough. Direction of orientation and direction of flow would be parallel. The magnitude of electrophoretic double refraction should vary strongly with v_p according to the above relation.[12] For an estimate of the average magnitude, suppose $v_p = 1 \times 10^{-4}$ cm/sec./v/cm. The particles will require 1.6 minutes in order to displace themselves by 1 cm relative to the medium in a field of 100 v/cm. This is comparable to the rate of gravitational settling of fine microscopic particles. Procopiu (13) observed during such settling and in zero field double refractions which, expressed in terms of phase differences, reached values of $10^{-2}\pi$ (settling metal powders of unknown concentration). Values approaching $10^{-1}\pi$ were found in suspensions of very strongly anisometric tartrazine crystals (14) again in zero field and for an approximate concentration of 1 g tartrazine per liter suspension. Electrophoretic double refraction may therefore reach measurable values already in fairly weak fields, and moderate values in high fields. On the other hand, the torque acting upon the particles is so weak, because of the slow rate of displacement, that electrophoretic double refraction cannot play a predominant role if the particles are electrically anisotropic. Thus, it is not possible either to maintain the hypothesis that the strong electric double refraction in V_2O_5 sols is merely an effect of electrophoresis (15), or to follow the suggestion that complications in the sign of double refraction in these sols are due to a competition between a true electric and an electrophoretic[13] double refraction (16).

The experimental identification of electrophoretic double refraction may be impossible unless an alternating field is used (see below). A slight tendency of a Kerr effect towards saturation may, after a brief validity of Eq. (1) in weak fields, lead to an extensive quasi-linear variation of double refraction with E. Neither may the increase of K_2' with v_p be always a conclusive criterion. If Kerr effect and electrophoretic double refraction are superimposed the co-existence of the two effects may be detectable if $\sim E_x$ is not within the range of very weak fields. Below the range $\sim E_x$

$$(n_{\parallel} - n_{\perp}) = E(KE \pm K_2'). \qquad (6)$$

Figure 1 gives several theoretical curves for the double refractions discussed so far. They are conceived for uniaxial positive rods.

c. *Double Refraction Due to "Morphic" Orientation*

Anisometry (anisotropy of shape) may lead to orientation in a homogeneous magnetic field; rods will be oriented parallel to the field if they are paramagnetic with respect to the medium, perpendicular if they are diamagnetic by comparison (18). In analogy, one must assume for

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[11] Electrophoretic orientation is due to the displacement of the particles relative to the medium. Its rate has no gradient. No flow of the medium is required. Hydrodynamic orientation is due to the velocity gradient in the streaming medium.

[12] $v_p = 0$ at the isoelectric point of protein solutions. Electrophoretic double refraction of proteins should, therefore, disappear for a certain *p*H. This phenomenon could be used for determining curves of electric mobility electro-optically whenever electrophoretic double refraction forms a significant part of the electro-optical effect. (The Kerr effect should be independent of the *p*H except near the isoelectric point where aggregation phenomena are conceivable.) This possibility could, in some instances, be interesting because only a small volume, possibly less than 1 cc, is needed.

[13] The lath-like colloidal crystals of V_2O_5 (form factor: $\sim$30) have a strong electric anisotropy. Ketelaar (17) calculated the following dielectric constants from x-ray data: ϵ_γ : 3.10; ϵ_β : 2.30; ϵ_α : 2.18.

rods a tendency to parallel orientation in the electric field if their dielectric constant, ϵ_p, is larger than ϵ_m, and a tendency to perpendicular orientation if ϵ_m is larger.[14] The torque is proportional to $(\epsilon_p - \epsilon_m)$, but exceedingly weak unless this difference is considerable. If the particles are ultramicroscopic, i.e., if there is a pronounced Brownian movement, an actual orientation, due to anisometry, and a double refraction [which would follow relation (1)] are therefore unlikely unless the particles are strongly "parelectric."[15] Microscopic particles, however, may orient themselves without this pre-condition provided they are electrically almost isotropic.

d. Double Refraction Due to an Orientation Caused by Polarization of the Electrostatic Double Layer

Colloidal particles are usually surrounded by an electrostatic double layer. An inner layer of ions, bound at the surface of the particles by preferential adsorption or created in the surface by dissociation, is surrounded by a diffuse outer layer of ions of opposite sign. In an electric field, a disturbance of the symmetry of charge distribution in inner and outer layer is conceivable, as pointed out particularly by Bikermann (19). It would lead to the formation of a diffuse dipole. This concept seems to be supported by the fact (20) that the dielectric constant of colloidal solutions may increase with ζ_p.

The diffuse dipole should create an orienting torque if the particles are anisometric. The dipole would be strongest if formed parallel to the longest dimension of the particles. This in itself would lead to a tendency of the particles to orient themselves parallel to the direction of the electric field. Such an orientation has been assumed by Errera, Overbeek, and Sack (22). Such an argumentation can only be correct, however, if the elastic resistance towards deformation of the double layer is isotropic. This is most doubtful, since the charge density of the double layer around anisometric particles is known to be anisotropic. The electric energy required for displacing an ion parallel to the long axis of rodlike particles will, therefore, be different from the electric energy required for an equal displacement perpendicular to the rod axis. It is most likely smaller in the latter instance. This could possibly lead to a tendency of anisometric particles to orient themselves perpendicular to the direction of the field.

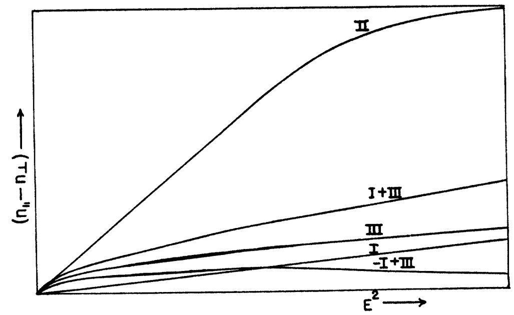

FIG. 1. Variation of double refraction with field strength (uniaxial positive rods). I. Kerr effect obeying Eq. (1); orientation ‖ lines of force. II. Kerr effect reaching saturation at moderate field strength; volume of particles is twice that in (I); orientation ‖. III. Electrophoretic double refraction; orientation ‖.

It has been assumed (19, 22) that electric double refraction may be due to the above type of orientation. However, no definite statement is possible at the present time as to whether or not the torque resulting from the deformation of the double layer is strong enough to lead to an actual orientation. A double refraction due to such an orientation, like electrophoretic double refraction, should vary in magnitude with ζ_p, hence, with the strength and concentration of the ions present in the medium, and it should vary with the effective thickness of the double layer, i.e., with the charge density. Such regularities, if found, would form a possible, but not necessarily conclusive, criterion for this type of double refraction.

2. Alternating Field

Electric double refraction will generally be investigated in an alternating field, in order to exclude electrolytic polarization and a possible coagulating influence of electrolysis. Application of an alternating field introduces also a series of additional features of decisive analytical im-

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[14] Procopiu (13) and with him Marshall (21) and Errera, Overbeek, and Sack (22) assume that morphic orientation is always parallel to the field.

[15] Actual orientation due to anisometry seems to have been proved in the magnetic field (23). Dispersed in water, strongly paramagnetic goethite crystals orient themselves perpendicular to the field by intrinsic anisotropy, but parallel if morphic anisotropy predominates.

TABLE I. Critical frequencies in liquids of dipolar molecules.

Liquid	$(\nu_0-\Delta\nu)_{20°}$	$\nu_{0\ 20°}$	$(\nu_0+\Delta\nu')_{20°}$
	Dipole ‖ axis of maximum polarization		
benzene	$>6\cdot10^8$	—	—
toluene	$>6\cdot10^8$	—	—
water	$\sim1\cdot10^9$	$2.4\cdot10^{10}$ (calc.)	$<4\cdot10^{12}$ $>8\cdot10^{10}$
	Dipole ⊥ axis of maximum polarization		
chloroform (24)*	$>1\cdot10^8$		
bromoform (24)*	$>2\cdot10^8$		
ethylether (24)*	$>1\cdot10^8$		
methyl alcohol	$\sim9\cdot10^9$		
ethyl alcohol	$\sim3\cdot10^8$		
n-amyl alcohol	$\sim1\cdot10^8$		
glycerol	$<\ 10^8>10^5$		
octyl alcohol (25)*	—	$\sim9.4\cdot10^6$	—
rosin (26)*	—	—	$<6\cdot10^1$
rosin (26)*; 70°C;	$>6\cdot10^1$	—	—

* Electro-optical data.

portance as regards the nature of electric double refraction.

a. The Kerr Effect

Orientation by a permanent moment.—Reversal of the field changes the direction of the orienting force for permanent dipoles, but not for induced dipoles. They will, therefore, behave distinctly different from each other in an alternating field. We consider permanent dipoles first. They will above a certain frequency become unable to "follow" the field; above this frequency, the degree of statistical orientation will be less than in the static field. Double refraction will, therefore, measurably decrease above a certain experimentally defined frequency[16] $(\nu_0-\Delta\nu)$—the experimental start of "anomalous" electric dispersion. In addition to the scarce optical data available, Table I contains some values of $(\nu_0-\Delta\nu)$ determined from the electric dispersion of ϵ in dipolar liquids (the frequency above which ϵ begins falling off measurably towards its optical value is obviously nearly equivalent with $(\nu_0-\Delta\nu)$). According to the data available, it is in general $>10^8$ cycles/sec.,[17] excepting for very viscous liquids and liquids with very large molecules.

Numerically better defined is the "critical" frequency ν_0. It is 2π times the reciprocal value of the "relaxation time" of orientation τ_0, i.e., of the time elapsed since removing the external field until the orientation, imposed by the field, has fallen to $1/e$ of its earlier value. The frequency ν_0 can be calculated, for spherical particles, from the Einstein-Debye relation given in references 27 and 28.

$$\nu_0=\frac{\omega_0}{2\pi}=\frac{kT}{8\pi^2\eta r^3}, \tag{7}$$

ω: the angular frequency, in radian/sec.; k: Boltzmann's constant; T: absolute temperature; r: radius of the particle; η: frictional constant. In Fig. 2 radii of colloidal dimensions are given for spheres dispersed in water. The value of ν_0 for anisometric particles will always be smaller than for spherical particles of equal volume. Figure 3 gives the correction factor

$$a=\frac{\nu_0 \text{ anisometric}}{\nu_0 \text{ isometric}}$$

for form factors up to 100. Equations are used that Perrin (29) derived for prolate and oblate spheroids, in extension of Debye's theory.

The theory is conceived for independent molecules. It can therefore be applied quantitatively only to dilute gases, but not to liquids where overlapping of the particle fields, association phenomena, and distribution function complicate matters. The disperse phase in dilute dispersed systems should, however, fulfill fairly well the requirements of the theory. Only two

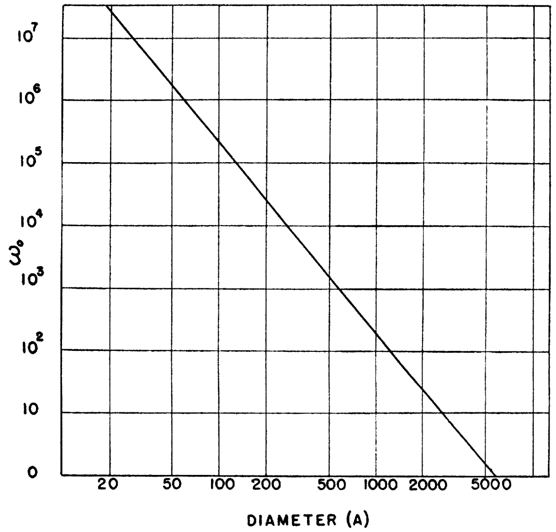

FIG. 2. ω_0 of colloidal dipoles (spheres; viscosity of H_2O; 18°C).

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[16] The magnitude of $\Delta\nu$ depends on the sensitivity of the apparatus used for measuring double refraction.

[17] The term "frequency" shall mean cycles/sec. (ν), when not specified.

curves on the electric dispersion of electric double refraction in dilute dispersed systems have been compiled up to date (V_2O_5 sols, benzopurpurine sols), both by Errera, Overbeek, and Sack (22). Both systems were apparently heterodispersed. A definite test of the theory is, therefore, not possible as yet. From Figs. 2 and 3 one would expect anomalous electric dispersion to be apparent at frequencies $\lessgtr 10^5$ cycles/sec. for ultramicroscopic particles $\gtrless 100$A in diameter, when dispersed in water. A quantitative validity of the theory in dilute dispersed systems would open a new way for determining the size of dipolar colloidal crystals and the molecular weight of dipolar colloidal molecules. Of particular interest would be the possibility of determining molecular weights of several monodispersed components present simultaneously in a dispersed system of proteins. A mere qualitative identification of components would be possible even without validity of Eq. (7).

An experimental frequency $(\nu_0+\Delta\nu')$ should exist for which the Kerr effect due to a permanent moment vanishes. Like $(\nu_0-\Delta\nu)$, its value would be entirely dependent on the sensitivity of the optical method, for, the double refraction declines asymptotically. The frequency $(\nu_0+\Delta\nu')$ would signify the experimental end of anomalous electric dispersion.

In heterodispersd systems, $(\nu_0-\Delta\nu)$ will be determined by the largest particles and $(\nu_0+\Delta\nu')$ by the smallest particles. The range $(\nu_0-\Delta\nu \rightarrow \nu_0+\Delta\nu')$ will, therefore, be larger in heterodispersed systems and it will increase with the degree of heterodispersion. This range could, therefore, become a valuable indicator of existence and magnitude of heterodispersion. Since only the effects of the smallest particles will be observed close to $(\nu_0+\Delta\nu')$, one would, in addition, have a means of isolating their optical effects. The optical effects of the largest particles, on the other hand, could be isolated, to a large extent, by measuring the double refraction exhibited in weak fields at frequencies $\ll \nu_0$. [This possibility has been used so far only in the static magnetic field (30).]

The anomalous "Debye-dispersion" within the range $(\Delta\nu+\Delta\nu')$ should be characterized by a continuous decline of double refraction along a smooth curve. Actually, irregularities may disturb this steady decline; near ν_0 resonance vibrations of the permanent dipole occur leading to electrical absorption [see the discussion in (35)]. Bands of electrical absorption are usually found in liquids between 10^8 and 10^9 cycles/sec. (35). While this second type of anomalous electric dispersion will hardly have to be taken into account for the effects of dispersed particles of ultramicroscopic size, it may enter in the electro-optical effects of the medium of dispersion.

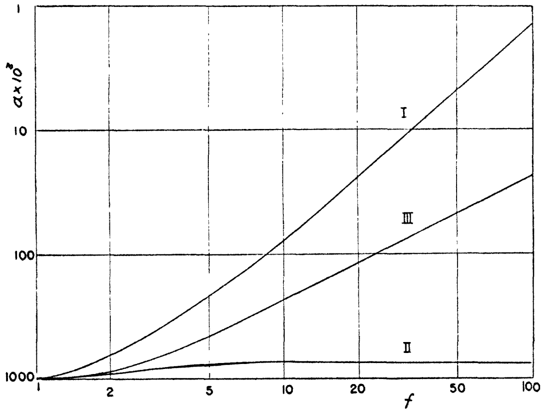

FIG. 3. Correction factor for calculating ω_0 of anisometric particles. $\alpha = \nu_0$ anisometric/ν_0 isometric; f: form factor (length/width). I. Rods (prolate spheroids); dipole axis $\parallel$ rod axis; II. Rods; dipole axis $\perp$ rod axis; III. Disks (oblate spheroids); dipole axis $\parallel$ or $\perp$ disk axis (the curve applies strictly only to a dipole $\parallel$ disk axis; the correction factor is slightly less than 10 percent higher if the dipole axis is $\perp$ disk axis).

Another more significant complication may arise[18] if a colloidal particle does not represent a single dipole but a conglomerate of dipoles. If these dipoles are distributed at random within the colloidal particle, they may be lined up under the influence of the electric field. In such a case, it would be impossible to deduce the size of the colloidal particle from the relaxation time of the electric double refraction.

Orientation by an induced moment.—If the particles are oriented by an induced moment, they will, above a certain frequency, no longer be able to reach during one-half of the period the same state of statistical orientation that is characteristic for the same effective field strength in the static field. This state will be reached only after more than one field pulsation. Electro-optically, this will result in an inability of the

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[18] According to an interesting, unpublished theory of H. Sack (now at Cornell University, Ithaca, New York).

double refraction to vary between its maximum value and zero (twice during one period). One might introduce the term "characteristic" frequency ν_c, which would be defined as the frequency that permits the orientation to decline only to $1/e$ of its maximum value. This frequency ν_c would be related to a relaxation time τ_c in a similar way as ν_0 is related to τ_0. From the experimental point of view, the frequencies $(\nu_c-\Delta\nu)$ and $(\nu_c+\Delta\nu')$, where $\Delta\nu$ and $\Delta\nu'$ are defined by the sensitivity of the optical method, would be significant. Above $(\nu_c-\Delta\nu)$, a measurable double refraction would subsist when the elongation of electrical vibration passes through zero; above $(\nu_c+\Delta\nu')$ the variation of double refraction would become unmeasurably small, i.e., it would appear quasistatic. The frequency range $(\Delta\nu+\Delta\nu')$ would represent the range within which the respective system loses its ability to act as a light shutter. Contrary to ν_0 of permanent dipoles, ν_c[19] of induced dipoles would not signify the existence of anomalous electric dispersion. The quasistatic double refraction should have the same order of magnitude as the double refraction in the static field, and it should keep it with rising frequency up to nearly optical frequencies.

Beams (24) found for the non-polar CS_2 an electro-optical relaxation time greater than 3×10^{-9} sec. Therefore, in ordinary liquids, $\nu_c>10^8$. In very viscous liquids and particularly in dispersed systems of colloidal particles, however, the characteristic frequency may come within reach of frequencies that are easily accessible. This concept is supported by early experiments by Tieri (31) and by Corbino (28) on the double refraction of iron oxide sols in oscillating magnetic fields. Up to a frequency of at least 1.5×10^3 cycles/sec., the double refraction was still able to vibrate between its maximum value and zero.[20] At a frequency of 6×10^5 discharges/sec., through a solenoid, the negative double refraction, apparently due to an induced magnetic moment (30), reached a final constant value after several consecutive field impulses had acted upon the dispersed system. In these particular solutions, therefore, ν_c lay apparently between 10^3 and 10^5 cycles/sec. Only very recently the analogous phenomenon in the electric field has been observed; according to Müller (34), suspensions of bentonite may cease to act as light shutters at frequencies as low as 10^2 cycles/sec., a phenomenon which can now be explained on the basis of the above concept.

Orientation by permanent and induced moment.—The dispersion of a complex Kerr effect in case of cooperation or competition of permanent and induced moment can easily be anticipated. In case of cooperation, double refraction will show anomalous Debye-dispersion at intermediate frequencies, and level off to a constant final value at higher frequencies. If the permanent moment is perpendicular to the axis of maximum induced polarization, the Kerr effect may change sign at the same intermediate frequencies. This effect has been observed by Raman and Sirkar (25) on octyl alcohol. An analog is possibly the change of sign, at 3×10^7 cycles/sec., observed by Errera, Overbeek, and Sack (22) in benzopurpurine sols.

Particular cases of anomalous electric dispersion.—Beside the Debye dispersion and the anomalous dispersion due to resonance vibrations, a third type of anomalous electric dispersion of electric double refraction is conceivable if the disperse phase consists of piezoelectric crystals. In such crystals, resonance vibrations of still somewhat problematic nature may occur at fairly moderate frequencies. In the case best studied, that of Seignette salt (Rochelle salt) (36, 37), the resonance vibrations occur between 10^3 and 10^6 cycles/sec., the exact frequency range depending on field strength and on temperature. The resulting anomalous dispersion of the dielectric constant is very similar to the anomalous dispersion of the refractive index at optical frequencies (Fig. 7). Dispersed systems of piezoelectric crystals have not been investigated as yet. But it can be anticipated that the electric double refraction in such systems would exhibit a strongly anomalous dispersion at

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[19] ν_c would under equal conditions be slightly higher than ν_0 of permanent dipoles. If a field is applied to particles of statistical distribution, particles that are accidentally parallel to the field, are already in their position of minimum potential energy. But only half of the permanent dipoles, oriented accidentally parallel, are in the same state.

[20] Corbino's results have been successfully duplicated and extended by Errera, Oostveen, and Sack (32) (maximum frequency: 50 cycles/sec.). Ewell (33) was the first to use oscillating fields for quantitative experiments on dispersed systems (magnetic field).

moderate frequencies. Even a change of sign of the effect with rising frequency is not inconceivable.

There is a slight probability that the very anomalous dispersion of electric double refraction in V_2O_5 sols may in part be due to anomalies of this kind. According to Errera (38), these sols have an extraordinarily high dielectric constant; a sol containing, e.g., 60 mg V_2O_5 per liter gave an $\epsilon = 567$. Its value varied with the field strength and it reached a maximum value between 2.4×10^3 and 4.2×10^3 cycles/sec. From his data, Errera calculated for colloidal V_2O_5 crystals a dipolar moment ~ 200 times larger than that of water. On the other hand, Ketelaar (17) concluded from his x-ray data that there cannot possibly be any strong dipolar moment. This author obtains for the mean static ϵ of the colloidal crystals a value of ~ 2.5. Since the results of both authors are undoubtedly correct, there seems to be an enormous discrepancy between the static dielectric constant and the constant determined in oscillating fields.

An "accidental" anomalous dispersion of electric double refraction, due to turbulence, is also conceivable. It will be briefly discussed under Section 2*b*.

b. The Electrophoretic Double Refraction

Electrophoretic double refraction should be governed by the moment of inertia, as in the static field, and, in addition, by the amplitude of longitudinal translatory oscillation relative to the medium, and by the hydrodynamics of oscillating flow.

Translatory oscillation of colloidal particles was first observed and extensively studied, by means of the ultramicroscope, by Cotton and Mouton (39). Ag particles, point-like in the static field, appeared like rods in the alternating field.[21] The length of the "rods" decreased with increasing frequency. On the basis of

$$A' = Ev'_p\sqrt{2}/\pi\nu, \tag{8}$$

where A' is the distance between the extreme positions of the particle = length of the "rod"; E is the effective field strength in v/cm; v_p' is the rate of absolute displacement of the particles at a given level, Cotton and Mouton found that Ag particles traveled about 10 percent slower in the alternating field (A' was 7μ instead of the calculated 8μ). The translatory oscillation was always in phase with the field (determined stroboscopically), and it could be detected, though only indirectly, at frequencies as high as 1.28×10^3 cycles/sec.

For the magnitude of double refraction, not A' but the relative displacement A of the particles during one-half period of the field, is important. A certain minimum relative displacement A_0 is obviously necessary in order to bring about a finite orientation. A decreases with E[22] and with increasing ν. Coordinated to A_0 should, therefore, be a critically low field strength E_0 (zero in the static field) and a critically high frequency ν_0'. Below E_0 no double refraction should occur; between $E_0 + \Delta E$ a quasiparabolic variation of double refraction with E may be observed (omitted in Fig. 5); beyond $E_0 + \Delta E$ Eq. (5) should be fulfilled. In short one has

$$v_{p_{E_0}} = v_{p_0} = 2A_0\nu, \tag{9}$$

$$E_0 = \frac{8A_0\pi\eta\nu}{\zeta_p \cdot \epsilon_m}, \tag{10}$$

$$\nu_0' = \frac{E\zeta_p\epsilon_m}{8A_0\pi\eta} = \frac{v_p}{2A_0}, \tag{10a}$$

$$(n_{\parallel} - n_{\perp}) = K_2(v_p - v_{p_0}) = \frac{K_2\zeta_p\epsilon_m}{4\pi\eta}(E - E_0)$$

$$= K_2\left[\frac{\zeta_p\epsilon_m E}{4\pi\eta} - 2A_0\nu\right]. \tag{5a}$$

The situation is illustrated in Figs. 4 and 5. The magnitude of A_0, E_0, and ν_0' will, under otherwise identical conditions, depend on the form factor of the particles, and on the moment of inertia (form factor and size). If the variation of A_0 with form factor and size were known, one would obviously have a new method for determining the length of ultramicroscopic

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[21] The "rods" were longest in the center of the trough, and present also near the walls. But at intermediate levels, the particles remained point-like. Since there is no comment on this phenomenon, observed again recently (40), it may be mentioned that it is bound to occur when $u > v_p$. v_p' has then opposite sign in the center and at the walls and it is zero at an intermediate level. If $u = v_p$, $v_p' = 0$ at the walls and it increases steadily towards the center (continuous increase in the length of the rods towards the center). If $u = 0$, $v_p' = v_p$; the rods would then have the same length everywhere. The alternating field could therefore be used for determining the relative importance and magnitude of electro-osmosis during electrophoresis.

[22] E shall here always signify "effective" field strength.

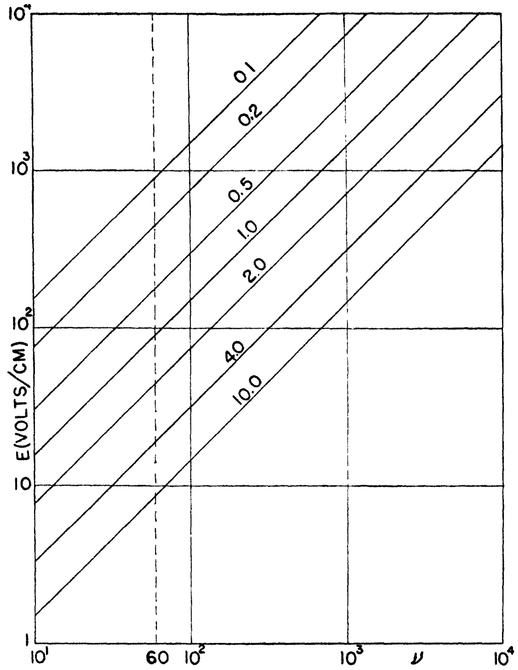

FIG. 4. E_0 of electrophoretic double refraction in alternating field. A_0: $1.5 \cdot 10^{-4}$ cm; parameter; $v_p \cdot 10^4$.

particles electro-optically, on the basis of Eq. (10) or (10a), provided the observed double refraction is electrophoretic. For an estimate of the highest ν_0' up to which electrophoretic double refraction is conceivable, one can, expressing A_0 in terms of the length l of the particle, assume that A_0 is certainly not smaller than $0.1l$. (An argument in favor of $A_0 = 3l$ in certain cases will be found below.) For particles 1000A long and for $v_p = 1 \times 10^{-4}$, one obtains $\nu_0 = 10^4$ in a field of 100 effective v/cm, and $\nu_0 = 10^5$ in a field of 1000 v/cm. Electrophoretic double refraction is, therefore, likely to cease at moderate frequencies[23] except for the application of unusually high fields.[24]

A second factor that may keep ν_0' at fairly moderate values is turbulence. Even in the static field electrophoretic displacement of particles relative to the medium should be accompanied by slight turbulence, on the periphery of the particles.[25] The periodic reversal of the direction of electro-osmotic and electrophoretic flow in the alternating field is likely to amplify such turbulence. In fact, Cotton and Mouton (39) observed in an alternating field of 1280 cycles/sec. a rapid turbulent movement of the liquid around air bubbles that were present in the sample. One could also interpret as an effect of turbulence their above-quoted result which needs to be verified on a more quantitative basis that the electric mobility in the alternating field is slightly smaller than in the static field.

Turbulence originating from electrophoresis would hamper also an orientation due to electric anisotropy. If turbulence did increase with the frequency (up to a maximum value, above which it should decrease again because of the finally infinitesimal value of A and A', it might conceivably cause an "anomalous" dispersion of the Kerr effect due to an anisotropy of the induced moment.

While it may be difficult to identify electrophoretic double refraction in the static field (see Section I, 1, *b*), the alternating field should provide a sufficient number of additional criteria to make a decision possible. They are: (*a*) the existence of E_0; (*b*) its increase with ν; (*c*) its decrease with increasing v_p.

Dilute suspensions of the rodlike tobacco mosaic virus and of the aucuba mosaic virus exhibit a positive electric double refraction (41) indicating an orientation parallel to the field.[26] The effect which thus fulfills the elementary requirement of electrophoretic double refraction, varies strictly linearly with the field strength as

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[23] Reversal of the field does not change the direction of the orienting torque, for electrophoretic orientation. The decline of electrophoretic double refraction with increasing ν would, therefore, be accompanied by an approach of a quasistatic effect. A quasistatic effect should actually be found in absence of Brownian movement, i.e., for microscopic particles, and within the whole range of frequencies for which electrophoretic orientation occurs. Because of the decrease of A with increasing frequency, this quasistatic effect should disappear above ν_0'. A quantitative oscillographic analysis should therefore allow one to distinguish between such a quasistatic effect and the quasistatic effect discussed in the section "Orientation by an induced moment."

[24] Quincke (42) sending the discharge of 3 Leyden jars through a dispersed system of microscopic particles, observed an A' of 0.5 mm.

[25] This possibility has not been taken into account as yet in the electrokinetic literature. The fact that v_p of microscopic particles, in a static field, seems to be fairly independant of their shape (12) does not necessarily exclude the possibility of turbulence and, implicitly, of shape playing a role in electrophoresis of ultramicroscopic particles.

[26] This can be concluded from the positive sign of hydrodynamic double refraction and also from Lauffer's result (43) that the double refraction of tobacco mosaic virus is morphic (see Section III, 1). The latter result, unnecessarily criticized (9), is conclusive though a completion of the data would be desirable.

required by Eq. (5a).[27] In addition, two of the above postulated regularities, (*a*) and (*c*) are fulfilled. They are compiled in Table II since they seem to have escaped attention. From various methods (summarized in reference (45) of the bibliography), one obtains for tobacco mosaic virus the mean data: l: ~5500A; f: ~50. From these data and from E_0 at $pH = 5.1$ (Table II), one obtains[28] $A_0 \sim 3l$. This value appears reasonable enough to lend further support to the concept that double refraction is here electrophoretic. A definite statement is not possible however since the frequency had not been varied in Lauffer's experiments (60 cycles/sec. had been used). Consequently, a test of the most important argument (*b*) is not possible. An argument, however of inconclusive nature, against electrophoretic double refraction, could be the fact that the slope of the curves does not vary distinctly with v_p (Table II).[29]

The electric double refraction of V_2O_5 sols, positive for all frequencies (parallel orientation of the lathlike rods) shows a slight minimum at 3×10^3 cycles/sec. (22). Electrophoretic double refraction, disappearing at this frequency may be responsible for the minimum. The form factor of the colloidal crystals is so high that an electrophoretic effect superimposed upon a far stronger Kerr effect is in fact most likely. [Ketelaar gives for particles in fresh sols the dimensions: ~150A, ~20A, <10A (f: >15) and for particles in sols aged for several years: ~1000A, ~100A, ~30A (f: ~30).] There are, however, still other possibilities as regards the explanation of the minimum.

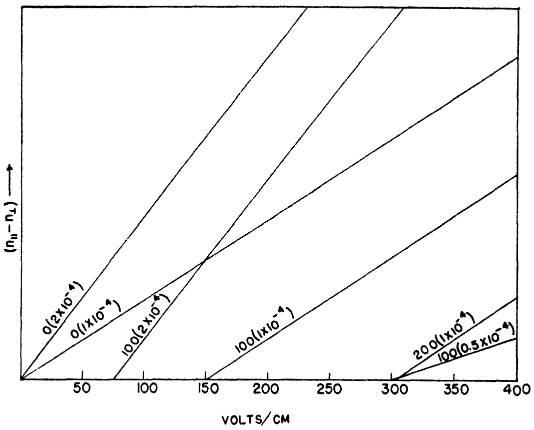

FIG. 5. Electrophoretic double refraction in alternating field. Length of particle: 5500A; f: >15; parameters: cycles/sec.; (v_p).

c. Double Refraction Due to an Orientation Caused by Polarization of the Electrostatic Double Layer

Double refraction due to this hypothetical orientation should be governed by the inertia of deformation of the double layer. Assuming an ionic displacement of 100A as the necessary minimum for effective polarization of the double layer around ultramicroscopic particles, one would obtain, for 100 v/cm and for water as a medium, a "critical" frequency of $<10^5$ cycles/sec. The relaxation of the double layer and, consequently, the double refraction should follow the laws governing the relaxation of an elastically deformed body. Applying Maxwell's theory of relaxation, one would conclude that the relaxa-

TABLE II. The apparent relationship between electric mobility of tobacco mosaic virus particles and E_0 of the electric double refraction in their suspensions. The validity range of Eq. (5). (An analysis of results obtained by M. A. Lauffer (41).)

g virus per liter	pH	$v_p(44)$ $\times 10^4$	E_0 (v/cm) (60 cycles/sec.)	Validity range of Eq. (5) (v/cm)	Relative slope of the linear $(n_{\parallel} - n_{\perp})f(E)$-function
			Tobacco mosaic virus		
0.9	6.4	<3.6 >2.0	~40	~70–~330	100
1.9	5.1	1.98	~100	~150–~360	80
			Aucuba mosaic virus		
1.7	6.7	<3.9 >2.1	~110	~150– >400	100
1.7	5.2	2.1	~170	~250–~370	106

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[27] Lauffer's statement that the positive effect, attributed to a dipole orientation, varies with the second power of the field strength, disagrees with his experimental findings in dilute suspensions.

[28] If we assume that v_p, at equal pH, and A_0 are the same for aucuba mosaic virus, in a first approximation, the length of this virus can be calculated from the electro-optical data, if we assume again that the double refraction is electrophoretic. One obtains 9900A at pH 5.2 and between 6400 and 11900A at pH 6.7.

[29] The only alternative to electrophoretic double refraction would be a double refraction due to the orientation of permanent dipoles, the dipole being located parallel to the long axis of the virus. For, the optical isotropy of the virus implies that there is no anisotropy of induced polarization. This alternate concept encounters difficulties, however. On the basis of Figs. 2 and 3 one calculates a critical frequency of ~2 cycles/sec. If the form factor were not 50 as assumed (45), but 5, the critical frequency would be ~100 cycles/sec., making this alternate explanation more likely. A completion of the experimental data, by varying the frequency, appears therefore imperative.

tion time of double refraction should vary with the field strength. Discovery of such an effect would be a criterion for the existence of this hypothetical electro-optical effect. Another criterion should exist; the oscillation of the deformed double layer should lead to a diffuse electric absorption near the "critical" frequency ν_0''. Errera, Overbeek, and Sack (22) believe that anomalies in the electric dispersion of double refraction in V_2O_5 sols can be explained by assuming an orientation by deformation of the double layer.

d. The Electric Dispersion of Double Refraction in Presence of Several Effects

If several or all effects are involved, the electric dispersion of $(n_{\parallel} - n_{\perp})$ may be quite complicated. Table III gives the sign of the various elements. It is assumed that neither electrical nor optical resonance vibrations nor morphic double refraction (see Section III) interfere with the sign of the elements, and that the Kerr effect of the medium of dispersion is negligible by comparison.[30] As to the sign of double refraction resulting from deformation of the double layer, it is assumed that the torque due to such a deformation leads to an orientation of anisometric particles perpendicular to the direction of the field. This concept, like the opposite one forwarded by Errera, Overbeek, and Sack, is merely a hypothesis, however; no definite pronouncement is possible at the present time (see the discussion in Section I, 1, *d*). Depending on the relative magnitude of the various torques involved, orientation and double refraction may have the same sign at all frequencies (then maxima and minima may occur) or they may change sign with rising frequency. The latter is likely only for the cases *C* and *D*.

TABLE III. The sign of various effects possibly involved in complex electrical dispersion of electric double refraction of monodisperse systems. Assumptions: rodlike particles; $n^2 = \epsilon$; (neither electrical nor optical absorption). The particles are uniaxial positive: *A*; *C*; uniaxial negative: *B*; *D*; the permanent dipole is parallel to the axis of maximum induced polarization: *A*; *B*; $\perp$: *C*; *D*.

Orientation is due to:	*A*	*B**	*C*	*D**	Measurable double refraction should disappear at the frequency (cycles/sec.)
Anisotropy of induced moment	+	+	+	+	$<10^{13}$
Permanent moment	+	+	−	−	$<10^8$
Electrophoresis	+	−	+	−	$<10^5$
Deformation of the double layer	(−)	(+)	(−)	(+)	$<10^5$
Anisometric shape	−	+	−	+	$<10^{13}$

* In case of predominant "morphic double refraction," all signs will be inversed.

In case of complicated electrical dispersion, it may be necessary to complete the double refraction data by other data before an unequivocal interpretation can be reached.[31] Only the most obvious possibilities shall be briefly mentioned. The sign of hydrodynamic double refraction may be used for determining the direction of orientation of the particles.[32] If a change in the direction of orientation, e.g., with rising frequency, is suspected, a direct ultramicroscopic observation is advisable. Both questions, direction of orientation and change in the direction of orientation, can be answered in a far simpler and conclusive manner, if the dispersed system exhibits a conservative dichroism (see Section IV). If the origin of an anomalous electric dispersion is in doubt, a stroboscopic (oscillographic) analysis as to whether the double refraction is quasistatic, or partly or wholly varying with the field, may be of decisive importance.[33] In some instances, a comparison of the dispersion of double refraction with the dispersion of the dielectric constant $(\epsilon_p + \epsilon_m)$ of the dispersed system may be useful,

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[30] If the particles have only a weak electrical or optical anisotropy the Kerr effect of the medium may become a major complicating factor. This will be true particularly if the colloidal particles are strongly soluble in the medium (as V_2O_5, and still far more benzopurpurine). Then the effects of colloidal crystals may be superimposed by pronounced effects of a molecular solution of the same compound; and the two effects may not have the same sign. Even electrolytes dissolved in the medium may play a role. Björnståhl found (4) that a solution of 0.5 millimoles of NaCl per liter water had a Kerr effect more than seven times larger than pure water. At a potential difference of 100 v, this electrolyte effect was about $\frac{1}{6}$ as strong as and of opposite sign than the effect of a gold sol.

[31] Therefore, it is not possible as yet to interpret unequivocally the electric dispersion of electric double refraction in V_2O_5 sols and in benzopurpurine sols.

[32] On this basis, it was possible above to conclude that the rods of tobacco mosaic virus are, in dilute suspensions, oriented parallel to the field. A highly sensitive and extremely simple apparatus for qualitative determination of hydrodynamic double refraction has been constructed by this author [described in (46)] which may be useful for such supplemental experiments.

[33] As an example, Müller's interesting result (34) that a part of the double refraction in bentonite suspensions, observed at moderate frequencies, does not vary with the field, shows that a Kerr effect due to anisotropy of the induced moment must have been involved.

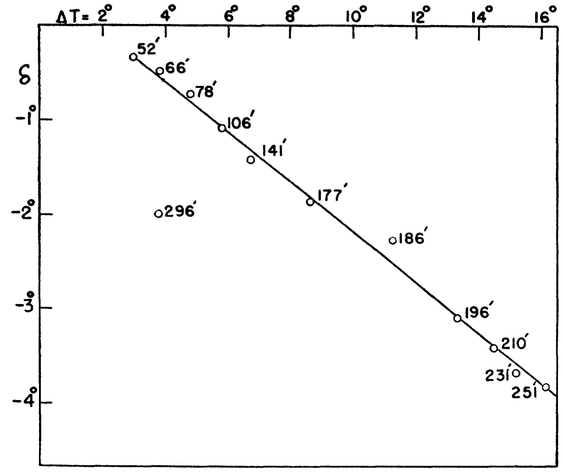

FIG. 6. Double refraction by convection in V_2O_5 sols. ΔT: Temperature difference (T_0: 21.5° C); the numbers give the time (minutes) elapsed since start of irradiation; irradiation was stopped after 251 minutes; thickness of layer: 0.281 cm; 6200A; 0.64 g V_2O_5 per liter sol.

although the contribution of ϵ_p to $(\epsilon_p+\epsilon_m)$ will mostly be very small. If the disperse phase is obtainable in macroscopic specimens, the direct determination of the dispersion of ϵ_p' may be more valuable. A comparison of both ϵ_p and ϵ_p' dispersions would possibly permit a definite conclusion regarding the interference of double layer deformation in electric double refraction.

II. ACCIDENTAL COMPLICATIONS

1. Orientation by Convection

Anisometric particles may orient themselves in the direction of vertical convection if thermal differences are allowed to develop in the sample. (This is almost unavoidable in the region of high field strengths.) Depending on the direction of the field, this orientation may be parallel or perpendicular to the field, and it may consequently either weaken or amplify a non-accidental double refraction observed horizontally.[34] Such double refraction has been described so far only for V_2O_5 sols where it interferes with both magnetic (47) and electric (22) double refraction. Figure 6 shows on the example of V_2O_5 sols the remarkable magnitude of double refraction by convection if the thermal differences are increased strongly by local irradiation. It should be easy to recognize such double refraction provided the direction of observation is horizontal; for, it should persist in zero field until thermal equilibrium is reestablished.

2. Orientation by Sedimentation

If the anisometric particles are nearly microscopic, they may be oriented during settling, as observed first by Meslin (48). This orientation like electrophoretic orientation is due to a displacement of the particles relative to the medium. The resulting double refraction interfered slightly in Procopiu's studies on the electric double refraction of coarse suspensions (13). If the form factor of the microscopic particles is very high, a major interference is conceivable.

3. Orientation in the Inhomogeneous Field

Anisometric particles will orient themselves parallel in an inhomogeneous field if $\epsilon_p > \epsilon_m$, and perpendicular if $\epsilon_p < \epsilon_m$. Contrary to the situation in the homogeneous field, the torque, increasing with the field gradient, may here reach considerable values. A field, quasi-homogeneous for very small ultramicroscopic particles, may be inhomogeneous for large ultramicroscopic particles. The direction of orientation may therefore be different for small and large particles, i.e., qualitative complications in the double refraction of heterodispersed systems may result. It is therefore essential to make sure of the homogeneity of the field. It is not inconceivable that some of the complications recorded in literature were due to an inhomogeneity of the field. In fact, with the exception of Errera, Overbeek, and Sack (22)—who made a thorough study on the topography of the field used—none of the more recent authors makes any statements as to whether or not the fields used were perfectly homogeneous.

Inhomogeneity of the field may lead to a further complication, which, however, it should be easy to detect. Particles will be thrown out of the field of maximum strength, if $\epsilon_p < \epsilon_m$ and they

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[34] If convection weakens a non-accidental double refraction, even a change in sign of the observed double refraction, e.g., with rising E, is conceivable (convection is likely to increase with E). Or, the variation of $(n_{\parallel}-n_{\perp})$ with E may show "hysteresis." For vertical observation, e.g., if a polarizing microscope is used, convection will always weaken a non-accidental double refraction, but it cannot lead to a change in sign. Accidental maxima or saturation with rising E may result.

will be concentrated in the field of maximum strength if $\epsilon_p > \epsilon_m$. The electric double refraction will consequently vary with time.

4. Deformation in the Inhomogeneous Field

The latter phenomenon, establishment of a concentration gradient in an inhomogeneous field, will occur of course also if the particles are spherical. If such spherical particles are liquid, their directed translation may be supplemented by deformation.[35] The deforming action of the inhomogeneous field should be stronger the larger the drops. Observations by Büchner (49) can be explained on this basis[36] and they seem to support our concept. The deformation should lead to a new type of electric double refraction (that may be called "electromorphic" double refraction). It should occur only within a restricted area of the field, and it should vary with the refractive index of the medium like ordinary morphic double refraction (see Section III, 1). Its sign should depend on the direction of deformation (parallel or perpendicular to the field). An oil emulsion in water, for example, should exhibit a double refraction opposite in sign to the double refraction exhibited by a water emulsion in oil.[36a]

5. Accidental Increase with Time of Double Refraction in the Homogeneous Field

Even though the optically studied central part of the field may be homogeneous, inhomogeneities in the outer parts of the sample may lead to an increase (or decrease, respectively) of colloid concentration, and, therefore, of double refraction in the central part. Up to the present, it has been found and investigated only in the magnetic field (50), but it should occur also in the electric field. It is, implicitly, accompanied, by hysteresis phenomena in the variation of $(n_{\parallel} - n_{\perp})$ with field strength, and it may be the cause of a "pseudo-inertia" of double refraction (see Table IV).[37]

III. OTHER COMPLICATIONS

1. Competition Between Intrinsic and Morphic Double Refraction

Maxwell showed (52) that a stratified system consisting of two electrically isotropic components should be electrically anisotropic. Extending this concept,[38] Wiener postulated optical anisotropy of a stratified system consisting of two optically isotropic components provided the period of stratification is small as compared to the optical wave-length (53) (morphic double refraction or "Wiener double refraction"). This condition is fulfilled if dispersed anisometric ultramicroscopic particles are oriented. The direction of the orienting force forms the symmetry axis of the morphically anisotropic dispersed system, and it is therefore equivalent to the optical axis of an uniaxial crystal.[39] Morphic

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[35] Liquid particles should also exhibit electrostriction. Double refraction would be affected only quantitatively by this phenomenon.

[36] Büchner observed that macroscopic sol droplets when immersed in electrolyte solutions become deformed parallel or perpendicular to the field depending on the conductance of drop and medium. Not considering the possibility of inhomogeneities of the field, Büchner made "surface charges" responsible. The fact that Bungenberg de Jong (51) sought the effect in vain in emulsions of microscopic droplets, in an apparently homogeneous field, favors the new explanation.

[36a] In a very particular case, that of Hg emulsions, an effective deformation may also occur in the homogeneous field, due to electrocapillary phenomena. Double refraction has actually been observed in such emulsions, by Björnståhl (4) and Procopiu (13). The effect varied linearly with E.

[37] Table IV shows the magnitude and the reversibility of the increase of magnetic double refraction in a homogeneous magnetic field ($\alpha-$FeOOH sol; average diameter of particles: ~1000A; pole diameter: 10 mm; pole distance: 8 mm; cross section of optically studied central field: 1 mm²). The increase of $(n_{\parallel} - n_{\perp})$ with time was pronounced only in high fields. Sols with identical particles of smaller size (~100A) did not show any increase at any field strength. There, the Brownian movement apparently neutralized the effect of directed translation. The increase of the effect, usually not exceeding eight percent, took not more than 1–3 minutes. Switching from high fields to weak fields, which produced double refraction but no increase, showed that it took up to 35 minutes or even more before the concentration gradient, and with it the excess double refraction, had disappeared. The relaxation of double refraction upon removing the field took always less than one second. If a sol was very sensitive, a "magnetic coagulation" resulted from the increase in concentration in the field (30). A band of coagulate was then formed at intermediate height, which outlined fairly sharply the contours of the field.

[38] This basis of Wiener's theory is little known. It is not mentioned in the better known monographs on morphic double refraction, such as the monograph by Ambronn-Frey (54).

[39] Optically biaxial systems should be obtainable if the three dimensions of the particles are unequal and if two degrees of freedom of rotation are restricted. It should be possible to verify this easily for morphic hydrodynamic double refraction of morphically appropriate particles, simply by making the velocity gradients dv/dx and dv/dy perpendicular to the direction of flow z strongly unequal.

double refraction is positive if the longest dimension of the particles is parallel (or if the shortest dimension is perpendicular) to the symmetry axis of the system. In the inverse case, the double refraction is negative.[40] [This holds only for particles without complex refractive index in the spectral region considered (56).] The morphic double refraction of anisometric particles of any shape, oriented by streaming, is consequently always positive, whereas it may be either positive or negative in case of electric or magnetic orientation.

If the anisometric particles have an anisotropic structure, the observed double refraction will consist of both intrinsic and morphic double refraction of either equal or opposite sign. For examples the former holds for V_2O_5 sols, the latter for benzopurpurine sols. A competition of the two double refractions will not lead to qualitative electro-optical complications if the dispersed system is monodispersed, and contains particles of the same shape and of equal intrinsic anisotropy,[41] unless the optical wave-length (see below) or the medium of dispersion[42] are changed. In heterodispersed systems, however, the double refraction may change its sign with rising field strength and with rising frequency, e.g., because the morphic double refraction may increase with the size of ultramicroscopic particles[43] more than the intrinsic double refraction. In weak fields only the largest particles are oriented, at high frequencies only the smallest particles are oriented. Hence, morphic double refraction may determine the sign of electric double refraction in weak fields and at low frequencies, whereas intrinsic double refraction may predominate in high fields and for high frequencies. A change of sign in transverse magnetic double refraction with increasing field strength, due to such a competition, has been observed in suspensions of tartrazine (14).

TABLE IV. The migration of colloidal particles into the homogeneous field. (α-FeOOH sol obtained from $Fe(CO)_5$; 5 months old; 1.370 g Fe/liter sol; 6200A; 0.281 cm.)

Days elapsed since sample had been brought into apparatus	0	1	3	5	7
Phase difference for 8700 Gauss; before action of high field	6°15′	6°10′	6°13′	6°12′	6°15′
Phase difference for 8700 Gauss; after a 10-minute action of 28,000 Gauss	6°36′	6°34′	6°42′	6°32′	6°37′
Temperature (±0.025°)	19.90°	20.10°	20.05°	19.85°	19.95

Prior to attempting an explanation of complicated electro-optical properties in not strictly monodispersed systems, it is, therefore, impera-

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[40] According to Wiener and Ambronn and Frey, one distinguishes between positive morphic double refraction of rods and negative morphic double refraction of disks. This definition presupposes that in the former case the arrangement has nematic symmetry, in the latter case smectic symmetry. Though this is most likely in case of spontaneous formation of anisotropic structures, it may be otherwise, as already pointed out by Frey (55). This is particularly true for dispersed systems of independent particles, where the morphically distinguished axis of the particles may be parallel or perpendicular to the symmetry axis of the morphically anisotropic dispersed system. Our new, more general definition of the sign of morphic double refraction, implicit in the old one, may, therefore, be preferable.

[41] Bradfield and Zocher (57) found that bentonite suspensions may show positive or negative hydrodynamic double refraction depending on origin and treatment of the samples. No explanation has been attempted. Since it is not very likely, though not impossible, that the sign of intrinsic anisotropy changes with the treatment, a competition between the two double refractions may be responsible. The plate-like stratified bentonite crystals swell noticeably, the degree depending on the nature and concentration of electrolytes in the medium, and depending also on the natural composition of the sample. Swelling might lead to a decrease of intrinsic anisotropy in excess of the simultaneous decrease of morphic double refraction. A change of sign of the total double refraction with progressing swelling is therefore conceivable. On the same basis, very interesting quantitative variations of the electric double refraction in bentonite sols, observed by Marshall (21) (a study apparently overlooked by more recent authors) can be explained. The double refraction varied strongly with the strength of the ions present in the medium as one would expect if swelling were responsible. Marshall considers the possibility of anisotropic coagulation. An anisotropic coagulation leads, however, to some typical variations in double refraction (58) which seem to be absent in the present case.

[42] Morphic double refraction, like light diffraction (and, implicitly, light depolarization) disappears evidently if the dispersed system becomes optically homogeneous, i.e., if the refractive indices of particles and medium become equal. Introduced by Ambronn (54), the technique of varying the medium has, therefore, become a most important tool for recognizing the nature of double refraction.

[43] If the particles are negligibly small as compared to the wave-length, the theory requires that morphic double refraction be independent of particle size. For ultramicroscopic particles, however, morphic double refraction seems to increase with size (13, 59). This, of course, may be due rather to an increase of the form factor with size; anisotropic anisometric crystals are known to exhibit an anisotropy of growth. In addition, and excepting amicronic crystals, larger crystals are more likely than smaller ones to be intrinsically heterogeneous. Intrinsic heterogeneity is often not accompanied by morphic irregularity, a fact well known in mineralogy. A quartz mineral, for example, may have the perfect shape of a single crystal, although it may represent a conglomerate of single crystals.

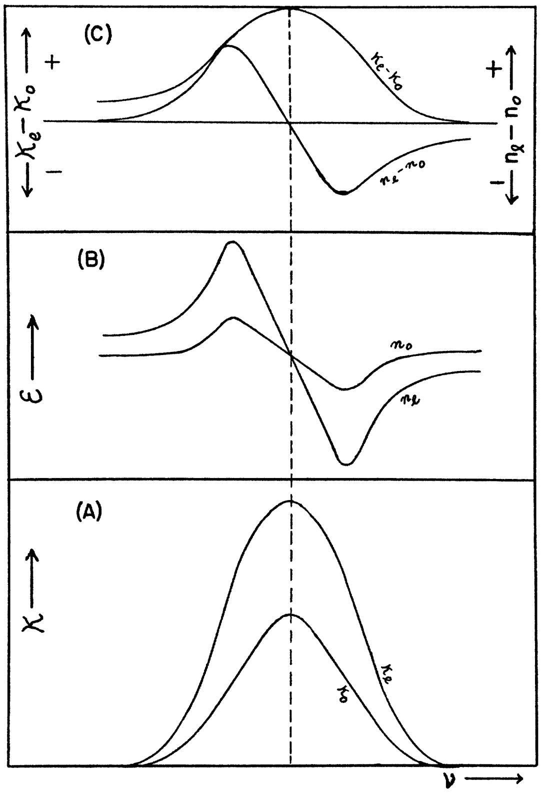

FIG. 7. Anomalous optical dispersion (uniaxial particles). *A*: the absorption coefficients; *B*: the refractive indices (the epsilon should be deleted and *n* substituted); *C*: consumptive dichroism and intrinsic double refraction.

tive to determine whether or not the two double refractions have opposite sign.

3. Anomalous Optical Dispersion

If the particles absorb light selectively in the spectral region considered, the optical dispersion of intrinsic double refraction will be anomalous. The situation is illustrated, in Fig. 7, for optically uniaxial particles. In dispersed systems of such particles, the electric double refraction $(n_{\parallel} - n_{\perp})$ will evidently show the same behavior as $(n_e - n_0)$ of the individual particles. It will change sign at the optical frequency for which absorption and dichroism are maximum.[44] It is consequently obvious that in the region of anomalous optical dispersion the sign of $(n_e - n_0)$ cannot be taken as a criterion for the direction of maximum polarization induced at non-optical frequencies. This criterion is only valid if $\epsilon = n^2$. Still less appropriate is the use of the sign of $(n_{\parallel} - n_{\perp})$ as a criterion in the above sense, since here, in addition, a morphic double refraction may invalidate the argumentation. Such an argument has been used for interpreting the nature of electric double refraction in V_2O_5 sols and in benzopurpurine sols. The particles of both sols however show in the visible an anomalous dispersion. Benzopurpurine sols, for example, which have been investigated by Wereide (62) and by Errera, Overbeek, and Sack (22), were found to exhibit a negative electric double refraction. It is certain that positive double refraction would be found instead, if the experiments were conducted at a wave-length $\lesssim 4500$A. While a negative sign of electric double refraction, in a region where $n^2 = \epsilon$, indicates conclusively (in absence of predominating morphic double refraction) that the orientation is due to a permanent dipole, no such conclusion is, therefore, possible in the region of anomalous optical dispersion.

It has become probable that the optical dispersion and, with it, the wave-length of inversion are shifted[45] noticeably towards longer waves as the size of the particles increases from amicronic towards microscopic dimensions (60). This change may be due to a change in the Lorenz-Lorentz force with size. In a heterodispersed system, small particles may show for example positive intrinsic double refraction whereas larger particles are for the same wave-length negatively birefringent. A

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[44] This relationship between linear double refraction and linear dichroism is in colloid literature mostly described under the name of "Zocher's rule" (65). It may be mentioned that Cotton was the first to draw attention to the fact that double refraction ought to change sign when the absorption is maximum. Cotton discussed the effects of circular anisotropy, circular double refraction (rotatory power), and circular dichroism (Cotton effect) (64), whereas Zocher discussed the corresponding effects of linear anisotropy.

[45] Systematic experiments are still completely missing. It seems however that the shift may extend over 100A or possibly over a still larger range. Kuhn (61) found in dispersed systems of cotton yellow a displacement of the absorption curve towards shorter waves as the size of the particles increased. Kuhn concluded from this observation that the dispersion is shifted with particle size, but the direction of the shift would be opposite to that indicated above. The direction in shift of the absorption band, as found by Kuhn, is very surprising, since it is opposite to the direction of shift found for numerous other dispersed systems, e.g., by Pihlblad (81). The theoretical approach of this problem, by Mie (82) also leads to the result that the absorption, whatever its nature, is shifted towards larger wave-lengths as the particle size increases.

variation of field strength or frequency may, therefore, lead to a reversal of sign. A morphic double refraction present at the same time would obviously predominate near the wave-length for which intrinsic double refraction changes sign, and it may, therefore, considerably enlarge the spectral region within which a change of sign can occur.[46] Since morphic double refraction itself may change sign in the region of anomalous optical dispersion, matters may become still more complicated.

If the experiments are carried out in the visible, these complications are obviously restricted to colloidal particles which have a complex refractive index in this region (e.g., metals, dyestuffs). Unless one is thoroughly informed beforehand on the optical and electrical properties of such particles, it is, therefore, not advisable to study the electric double refraction of their dispersed systems in the immediate neighborhood of an absorption band of the particles.

3. Direct Influence of the Electric Field Upon the Physical Constants

Excepting the hypothetical "electromorphic" double refraction, all effects of non-piezoelectric particles discussed so far are effects of orientation. They should, therefore, be covered by the Langevin (66) theory.[47] Beside orienting intrinsically or morphically anisotropic elements, the electric field may also create anisotropy in isotropic elements or alter a pre-existing intrinsic anisotropy. These effects are extremely small in gases and liquids. [The electric double refraction of CCl_4, for example, is 7×10^{-2} of the effect of nitrobenzene (5400A).] They can be explained as a Voigt effect (unequal influence of the electric field upon the optical polarizibility of substances parallel and perpendicular to the field). Only in the region of anomalous optical dispersion can these effects be expected to be well pronounced. It is in fact in this region that the existence of a Voigt effect has been proved beyond doubt, by Ladenburg and Kopfermann (68). (These authors did not investigate the influence of the electric field upon the optical dispersion parallel and perpendicular to the electric field, but the directly connected influence of the field upon the absorption. Sodium was used.)

The influence of the electric field upon the optical constants may be larger for crystals. In these cases, studied particularly by Pockels (69), the nature of the effect may be more complex. Part of it, found also in cubical crystals of tetartoedrical symmetry, such as $NaClO_3$, is due to electrical stress and it is quantitatively comparable to the double refraction produced, in the same specimen, by mechanical strain. Mostly stronger, e.g., 12 times stronger in $NaClO_3$, is another part of induced double refraction which is still of problematic nature, and which may, in turn, again consist (as in $NaClO_3$) of two distinct effects of possibly opposite sign.

These effects in crystals have been studied only on macroscopic specimens. But it is obvious that they should occur also in dispersed systems of such crystals. Dispersed systems of cubical $NaClO_3$ crystals, for example, should exhibit an electric double refraction though the crystals are optically isotropic in zero field. Since all these induced effects vary strongly with the orientation of the crystals towards the field, it can be expected that in dispersed systems of such crystals the induction of the effects would be accompanied by a torque attempting to orient the crystals.

It is certain that such additional complications will affect only the magnitude of the total effects, to a generally small extent, but not the sign, excepting possibly two cases: (*a*) if the particles are nearly or completely isotropic in zero field, (*b*) if the particles represent strongly piezoelectric crystals (e.g., quartz crystals or crystals of Seignette salt-Rochelle salt).[48] Particularly the crystals of Seignette salt may, according to Pockels (69) exhibit a considerable piezo-optical anisotropy (stress anisotropy), and, in addition,

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[46] Zocher and Jacoby (63) observed that in a benzopurpurine sol the inversion takes place at 4500A, whereas it occurs near 4800A in a dry preparation. This very large shift may possibly be due to such an interference of morphic double refraction, which should have a very unequal magnitude in the two cases. Morphic double refraction should also invalidate the rule of Cotton-Zocher.

[47] While this theory has been conclusively tested, by Pauthenier (71), for the Kerr effect of homogeneous systems, the test for dispersed systems remains still to be made. The only existing test for dispersed systems regards the magnetic field (72).

[48] Dispersed systems of Seignette salt have not been investigated as yet. The electrical dispersion of their effects would be most interesting.

a pronounced non-photoelastic effect of opposite sign (see also the very extensive re-examination of the electro-optical properties of these crystals by Müller (70).

IV. REMARKS ON THE ELECTRIC DICHROISM

Electric double refraction in dispersed systems will generally be accompanied by a dichroism. Four different types of dichroism are possible.[49] There may be a classical dichroism due to intrinsic anisotropy of consumptive absorption (absorption due to transformation of light energy into other forms of energy). This effect, correlated with intrinsic double refraction, may be termed "intrinsic consumptive" dichroism.

Anisotropy of shape of consumptively absorbing particles may lead to a "morphic consumptive" dichroism, correlated with morphic double refraction.

Both consumptive dichroisms will be strongest in the spectral region of strong consumptive absorption, and they will be practically negligible in spectral regions of high transparency. The so-called "white" colloidal particles, such as bentonite or proteins, will, therefore, hardly show either effect in the visible. Colloidal V_2O_5 crystals, on the other hand, exhibit at the highest frequencies of the visible spectrum a very strong consumptive dichroism. The rotation due to dichroism is there of the same order of magnitude as the phase difference due to double refraction both measured in radians. Morphic consumptive dichroism, like morphic double refraction, should strongly vary with the refractive index of the medium (experiments on this point are still completely missing).

A third and fourth type of dichroism will result from an anisotropy of "conservative" absorption[50] (weakening of the intensity of radiation in the direction of propagation, by diffraction or reflection, under maintenance of the total energy of radiation). This dichroism, the complement to anisotropic light diffraction (dityndallism)[51] or to "bireflection" may be termed "conservative" dichroism.[52] Like morphic consumptive dichroism, it requires a difference in the refractive index of particles and medium. Unlike the morphic consumptive dichroism and unlike the intrinsic consumptive dichroism, it does obviously not require a consumptive absorption. Anisotropy of light diffraction and, implicitly, conservative dichroism are caused in the first place by anisometry; both effects are stronger the higher the form factor (59). As long as the particles are smaller than the optical wavelength, the anisotropy effects increase also with the particle size (59). Intrinsic anisotropy should also lead to anisotropic light diffraction and to conservative dichroism, since the differences between the refractive indices $n_e - n_m$ and $n_0 - n_m$ are unequal. (If the maximum refractive index of the particles, n_γ, is perpendicular to their longest dimension, the intrinsic part of conservative dichroism—"intrinsic conservative" dichroism—and the morphic part of conservative dichroism—"morphic conservative" dichroism—will have opposite sign.) It can be anticipated, however, that the intrinsic part of conservative dichroism will play a significant role beside the morphic part only in two instances:[53] (*a*) if $(n_m - n_e)/(n_m - n_o)$ deviates strongly from 1.0, either because n_m is almost equal to either n_γ

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[49] For a more detailed discussion see (59).

[50] The terms "consumptive" and "conservative" damping have been introduced by Planck (73).

[51] While the anisotropy of light diffraction by individual anisometric particles has been known since the early days of ultramicroscopy (39)—it has been studied extensively by Siedentopf (74) and Szegvari (75)—the macroscopic effect in dispersed systems of oriented particles was discovered only 25 years later, by Diesselhorst and Freundlich (76). (In some recent papers on anisotropic light scattering of colloids, the discovery of this effect is erroneously attributed to a far more recent author.) Zocher (77) was the first to point out that this anisotropy of light diffraction should lead to a dichroism-like effect in the direction of the primary beam. Only fairly recently (59), an attempt has been made (incomplete because of external circumstances) to investigate this effect systematically.

[52] In the terminology of Zocher and Freundlich, both anisotropic light diffraction and its effect upon the transmitted light are called dityndallism (or "double diffraction"). The distinction between these two effects, as proposed here, seems to be preferable.

[53] Conservative dichroism (and dityndallism) are, therefore, most promising effects for determining form and form factor of ultramicroscopic particles whenever their orientation is possible. By contrast, depolarization measurements, the value of which has been somewhat exaggerated of late (as far as colloidal particles are concerned), cannot furnish any conclusive proof of shape anisotropy, unless the experiments are carried out in a region of anomalous optical dispersion. Otherwise, the depolarization, as far as it is not due to particle size or to multiple diffraction, is predominantly determined by the intrinsic anisotropy. (Krishnan's method (78) permits an indirect separation of the size effect from the rest of the effect.)

or n_α, or because $n_e - n_o$ is exceptionally large; (*b*) if the particles are microscopic.[54]

Dispersed systems of anisometric particles which are consumptively absorbing and intrinsically anisotropic will show a complex dichroism consisting of all four effects. From a practical point of view, such a complex dichroism will help little for interpreting a complex electric double refraction, and it may only complicate accurate measurements of double refraction.[55]

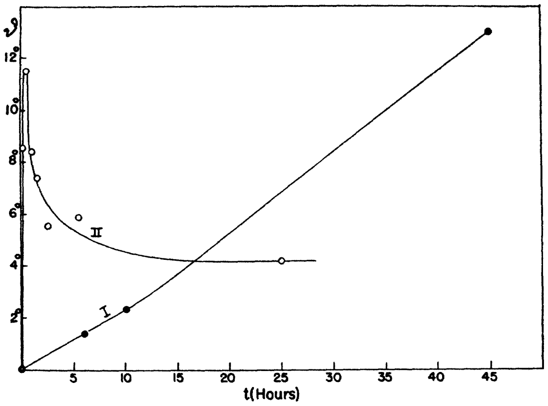

FIG. 8. Conservative dichroism in coagulating dispersed systems of ultramicroscopic FeOOH crystals. ϑ: rotation due to dichroism; 8700 gauss; 6200A; 1 cm layer; 1 g Fe per liter sol. *t*: time elapsed since start of coagulation; I: mechanical coagulation by stirring (1000 rot./min.); the sol, 3 months old, was obtained from $Fe(CO)_5$; 0.523 g Fe per liter sol; II: $(10\times\vartheta)$; coagulation by electrolyte; 500 millimoles NaCl per liter sol; the sol, 3 months old, was obtained from iron acetate; 0.550 g Fe per liter sol.

The situation will be entirely different if the particles do not absorb selectively in the spectral region considered. A dichroism can then only be conservative. If pronounced, it will indicate an anisometric shape. Its sign will then be an infallible indicator of the direction of orientation of the anisometric particles (as long as they have ultramicroscopic size): positive dichroism will indicate an orientation parallel to the field, a negative dichroism will signify perpendicular orientation. An inversion of the sign with rising field strength or frequency would at once indicate a change in the direction of orientation, and it could, therefore, become a decisive criterion regarding the cause of a change in sign of double refraction with *E* or ν. The magnitude of the dichroism will permit an estimation of the form-factor. Variations in the magnitude of the effect will permit definite conclusions as regards variations of form-factor and size. This is illustrated in Fig. 8 [see also (59)]. It shows the conservative magnetic dichroism in α-FeOOH sols (plate-like particles) at 6200A, where consumptive absorption is negligibly small. Curve *I* shows the variation of the effect during "mechanical"

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[54] If all faces of the particles have a microscopic area, the dichroism will be due to an anisotropy in reflection ("bireflection"), and it will consequently be governed by the intrinsic anisotropy of the particles. (This type of dichroism has been studied very extensively by Meslin (79), but its nature was first recognized by Cotton and Mouton (80).) It is therefore conceivable that the conservative dichroism changes sign with an increase of the particle size beyond the microscopic limit provided n_γ is perpendicular to the longest dimension of the particle.

[55] It is imperative to take a dichroism properly into account lest double refraction measurements lose their quantitative significance. A few remarks seem to be advisable since an impressive number of recent publications on electric and, particularly, on hydrodynamic double refraction in dispersed systems are deficient in this respect. Considering first the few cases where the existence of a rotation had been recognized and the analyzer had been adjusted before measuring double refraction: If double refraction is in such a case measured by using a quarter wave compensator, it must be kept in mind that the compensator will now no longer act as a quarter wave compensator, i.e., it will no longer be possible to calculate double refraction on the basis of the simple relation usually (directly or implicitly) given (54, 10)

$$\delta = 2\beta, \tag{11}$$

where β is the rotation resulting from re-establishment of linearly polarized light. If δ is 20°, for example, the error introduced on applying formula (11) will be 1.7, 5.7, 11.8, and 27 percent in case of a dichroitic rotation of 1°, 5°, 10°, and 20°, respectively. Since the conservative dichroism is most pronounced for the largest particles, the error may vary with *E* and ν. Far more serious is the complete disregard of dichroism, particularly if the light intensity transmitted through crossed nicols is taken as a measure for double refraction (by six recent authors investigating hydrodynamic double refraction in colloidal solutions). While this in an excellent method for measuring double refraction in non-absorbing gases, liquids, and crystals, it is inadmissible for dispersed systems. If there be no double refraction, a rotation of *n* radian due to dichroism will lead to a "pseudo-phase difference" of $2n$ radian. If this method were used for measuring the double refraction of a Polaroid sheet, for example, a pseudo-phase difference of $\pi/2$ would be obtained. Suppose there is no detectable dichroism. The transmission method will still be inapplicable unless the colloidal particles are very small as compared to the wave-length. For, a pseudo-double refraction will be introduced also by the transmission of the completely depolarized longitudinally diffracted light. Longitudinal diffraction, present of course also in zero field, varies strongly (increases or decreases) upon orientation of anisometric particles (quantitative experiments are still completely missing). Its intensity increases rapidly with particle size once the particles are larger than ~1000A (owing to the Mie effect). How strong longitudinal light diffraction may be in case of large ultramicroscopic particles can easily be seen from the fact that half shades (of biquartz, for example) may become very insensitive as compared to their sensitivity in measurements on non-diffracting systems.

coagulation (coagulation by stirring), curve *II* shows the variation during a very slow coagulation brought about by adding a coagulating electrolyte.[56] In both cases, aggregates are formed and they grow in size with time. The dichroism and its change with time show that the aggregates formed by mechanical coagulation are strongly anisometric from the beginning and remain strongly anisometric during their growth; aggregates formed by electrolyte action, on the other hand, are less anisometric and stay fairly anisometric only as long as they are small. Their anisometry decreases as they grow. Both curves show, implicitly, that both primary particles and aggregates are oriented parallel to the magnetic field. A more thorough knowledge of conservative dichroism would probably allow one to obtain also quantitative information on form factor and size of ultramicroscopic particles.

V. REMARKS ON THE ORIGIN AND ON THE COMPLICATIONS OF MAGNETIC DOUBLE REFRACTION AND MAGNETIC DICHROISM OF DISPERSED SYSTEMS OBSERVED IN THE TRANSVERSE MAGNETIC FIELD

The results of the preceding critical discussion will evidently, in many instances, be directly applicable also to the Majorana phenomenon, which, under a different angle, has been discussed before (59). This holds particularly for those sections, in which we dealt with the orientation due to an induced moment, to a permanent moment, and to anisometry, and with the possible competition of intrinsic and morphic optical effects. On the whole, however, magnetic double refraction is less involved. There is no complement in the magnetic field for electrophoretic (electro-osmotic) double refraction nor for a double refraction due to a deformation of the electrostatic double layer. The greater part of the other, minor, optical and non-optical complications, are also practically absent in the magnetic field. Though, therefore, the magneto-optical method has in principle, and for studies on dispersed systems, definite practical advantages over the electro-optical method, this advantage will often be more than upset by the fact that, generally and under comparable experimental conditions, electro-optical effects are far larger.

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[56] The measurements were made after a re-suspension, by gentle shaking, of the settled coagulum. At the time of the latest measurements recorded in Fig. 8, 86.2 percent (curve I) and 100 percent (curve II), respectively, of the dispersed phase were represented by settling aggregates.

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