LIGHT SCATTERING IN SOLUTIONS OF RIGID ASYMMETRIC BIOMACROMOLECULES ALIGNED IN AN ELECTRIC OR MAGNETIC FIELD

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A classical-statistical theory of Rayleigh light scattering by solutions of rigid assymmetric biomacromolecules (proteins, polypeptides, viruses, *etc.*) in an electric or magnetic field is proposed. The variations of scattered light intensity components are calculated for two cases: (*i*) weak orientation of macromolecules due to an AC electric or magnetic field; (*ii*) complete ordering of all macromolecules in an intense DC electric or magnetic field. In case (*i*), the variations are shown to be quadratic in the applied field strength, and their knowledge permits determinations of the dipole moment and electric or magnetic anisotropy of the macromolecule, as well as its relaxation times. In case (*ii*), which is that of electric or magnetic saturation, we obtain the possibility to determine directly the value and sign of the optical anisotropy of "cigar" and "disc" shaped macromolecules. Numerical evaluations are made, and point to large variations in intensity of light scattered by solutions of biomacromolecules or colloids. These variations exceed by several orders of magnitude those resulting in molecular liquids.

1. Introduction

The process of Rayleigh light scattering by a solution of macromolecules placed in a DC electric field is subject to well-defined variations, which are accessible to experimental detection. Thus, variations of the scattered light intensity which result by applying a DC electric field have been observed in solutions of Tobacco Mosaic Virus [1–3], poly-γ-benzyl-L-glutamate [1, 4], as well as DNA [5]. Among other problems, these observations permitted to decide whether the macromolecule possessed only an induced or permanent dipole moment, or both. Much more complete information concerning structure is provided by studies of light scattering by solutions in an AC electric field [1, 2] when, in addition to the steady (nonalternating) component of intensity, an alternating component varying at twice the frequency of the applied field [2] appears. Such studies permit determinations not only

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of the Debye dipole relaxation time [6] but moreover of the anisotropy relaxation time of the molecule [7, 8]. Also, attempts have been made to detect similar variations under the influence of a magnetic field, in light scattering by suspensions of graphite [9].

In gases and molecular liquids, the scattered intensity variations caused by orientation of molecules in a DC electric or magnetic field are very small [10] and, as yet, experiments aimed at rendering them apparent have not been successful.

Hitherto [1–3], the variations induced by an external DC electric field in the intensity of scattered light have been considered as occurring by way of the particle scattering factor $P(\theta)$ alone and as related essentially with the size of the particles. This assumption is correct for very large particles, of size comparable to the light wavelength, provided they are optically isotropic or but very slightly anisotropic. But if the particles have perceptibly anisotropic optical properties, there occur direct changes in the anisotropic components of scattered light intensity [11], entailing changes in depolarization of the observed scattering. Obviously, in the case of not very large particles, the effect of size is quite subordinate, and optical anisotropy is the chief cause of the variations in intensity of scattered light. To this circumstance is due possibility of determining directly the amount and sign of the anisotropy of optical polarizability in macromolecules and colloid particles [11].

In the present paper, we shall give a complete and consistent theory of light scattering by solutions of rigid macromolecules in a DC or AC electric field. Particular attention will be given to variations in intensity of the anisotropic components in weak fields as well as in very strong electric fields, when total ordering (field-alignment) of all the particles can be achieved [3]. The effect of pure orientation in the electric field will be assumed as essentially decisive, thus justifying us in omitting the effect of nonlinear deformation [12] which, in the case of rigid macromolecules, is quite unimportant. This assumption enables us to express the relative variations of the scattered light intensity components by three reorientation functions, which we calculate and present diagrammatically for arbitrary values of electric and magnetic field strengths.

The results are particularized to various, specific substances, and numerical evaluations of some effects predictably accessible to experimental detection are included.

2. Light scattering by free macromolecules

We consider the process consisting in the scattering of light by a dilute solution of macromolecules. The latter are assumed as not interacting with one another, or with the molecules of the solvent, the latter being dealt with as an optically isotropic medium. Considering the macromolecules as rigid, of linear dimensions small in comparison with the light wavelength (thus not exceeding $\lambda/20$), we can for simplicity restrict the problem to scattering of the electric dipolar kind neglecting higher multipole scattering as well as scattering due to intramolecular interference. Consequently, we can define the intensity tensor I_{ij}^S of light scattered by the solution of number density ϱ of macromolecules, in laboratory coordinates X, Y, Z, as follows [12]:

$$I_{ij}^S = \frac{\varrho}{c^4} \left\langle \frac{d^2 m_i(t)}{dt^2} \frac{d^2 m_j(t)}{dt^2} \right\rangle_{\varrho,t},$$

(1)

where the symbol $\langle \ \rangle_{\Omega,t}$ stands for averageing over all possible orientations Ω of macromolecules and over the period of oscillations of the electric field $\boldsymbol{E}(t) = \boldsymbol{E_0} \cos \omega t$ of the light wave, oscillating at frequency ω.

Let us assume the electric field strength $E(t)$ of the wave so small as to cause only a linear polarization of the macromolecule. The i-component of the induced dipole moment resulting by this polarization is given by the relation:

$$m_i(t) = a_{ik}E_k(t), \tag{2}$$

where the a_{ik}'s are components of the optical polarizability tensor of the isolated macromolecule. Summation over the recurring index k in Eq. (2) is implicite.

On inserting (2) into Eq. (1), we obtain the scattering tensor I_{ij}^S in the form:

$$I_{ij}^S = \varrho \left(\frac{\omega}{c} \right)^4 \langle a_{ik}a_{jl} \rangle_\Omega \langle E_k E_l \rangle_t . \tag{3}$$

With the aim of further calculations, we assume the solute (and solvent) as naturally inactive optically, and the system as revealing no energy absorption (absence of electronic dispersion and absorption). The polarizability tensor a_{ik} is now symmetric in both indices i and k, and transforms from laboratory coordinates X, Y, Z to the reference system of principal axes 1, 2, 3 of the macromolecule by the transformation equations:

$$a_{ik} = \sum_{s=1}^{3} a_s c_{is} c_{ks}, \tag{4}$$

c_{is} being the cosine of the angle between the laboratory i-axis and the principal s-axis.

The principal values of the macromolecular polarizability tensor are defined by Maxwell's expression [7, 12]:

$$a_s = \frac{V(n_s^2 - n_0^2)n_0^2}{4\pi[n_0^2 + (n_s^2 - n_0^2) L_s]}, \tag{5}$$

where n_s $(s = 1, 2, 3)$ are the principal refractive indices of the macromolecule; its geometrical shape is described by the parameters L_s, with $L_1 + L_2 + L_3 = 1$; the quantity n_0 is the refractive index of the optically isotropic solvent.

We furthermore attribute to the macromolecules the symmetry of rotational ellipsoids. The optical axis of the macromolecule is assumed as coinciding with its geometrical axis (the 3-axis). Let a_3 be the polarizability parallel to the symmetry 3-axis, and $a_1 = a_2$ the polarizabilities perpendicular thereto. Eq. (4) now simplifies to the form:

$$a_{ik} = a\delta_{ik} + a\varkappa(3c_{i3}c_{k3} - \delta_{ik}), \tag{6}$$

where

$$a = \frac{a_3 + 2a_1}{3} \qquad \varkappa = \frac{a_3 - a_1}{a_3 + 2a_1}, \tag{7}$$

a being the mean optical polarizability and $\varkappa$ the anisotropy of optical polarizability of the macromolecule; δ_{ik} is Kronecker's unit tensor with elements equalling unity for $i = k$ and vanishing if $i \neq k$.

Let the macromolecule's symmetry 3-axis subtend the angle ϑ with the laboratory Z-axis. The directional cosines are:

$$c_{x3} = \sin \vartheta \cos \varphi,$$

$$c_{y3} = \sin \vartheta \sin \varphi,$$

$$c_{z3} = \cos \vartheta, \tag{8}$$

φ being the azimuth of the symmetry axis.

On inserting (6) into Eq. (3) we obtain for axially symmetric macromolecules:

$$I_{ij}^s = \{\delta_{ik}\delta_{jl} + \varkappa\langle 3c_{i3}c_{k3}\delta_{jl} + 3\delta_{ik}c_{j3}c_{l3} - 2\delta_{ik}\delta_{jl}\rangle_\Omega +$$

$$+ \varkappa^2\langle 9c_{i3}c_{j3}c_{k3}c_{l3} - 3c_{i3}c_{k3}\delta_{jl} - 3\delta_{ik}c_{j3}c_{l3} + \delta_{ik}\delta_{jl}\rangle_\Omega\} I_{kl}^{is}, \tag{9}$$

where

$$I_{kl}^{is} = \varrho \left(\frac{\omega}{c}\right)^4 a^2\langle E_k E_l\rangle_t \tag{10}$$

is the intensity tensor of isotropically scattered light.

Let the incident light beam propagate along the y-axis, and let observation of the scattered light take place parallel to x. We shall moreover need the following notations: $V = I_{zz}^s$ is the scattered intensity component with electric vector oscillating along z vertically to the plane of observation; $H = I_{yy}^s$ is the component with horizontal electric oscillations along y); the symbols v and h used in this context will indicate the state of polarization of ncident light, thus respectively vertical (z-directed) and horizontal (x-directed) oscillations of the electric light vector $\boldsymbol{E}$. In this way, we obtain with regard to Eqs (8)–(10):

$$V_v = \{1 + 2\varkappa \langle 3\cos^2 \vartheta - 1\rangle_\Omega + \varkappa^2 \langle 9\cos^4 \vartheta - 6\cos^2 \vartheta + 1\rangle_\Omega\} I_{zz}^{is},$$

$$H_v = 9\varkappa^2 \langle\cos^2 \vartheta \sin^2 \vartheta \sin^2 \vartheta\rangle_\Omega I_{zz}^{is},$$

$$V_h = 9\varkappa^2 \langle\cos^2 \vartheta \sin^2 \vartheta \cos^2 \varphi\rangle_\Omega I_{xx}^{is},$$

$$H_h = 9\varkappa^2 \langle\sin^4 \vartheta \cos^2 \varphi \sin^2 \varphi\rangle_\Omega I_{xx}^{is}, \tag{11}$$

where the intensity components of isotropically scattered light are:

$$I_{zz}^{is} = \varrho \left(\frac{\omega}{c}\right)^4 a^2\langle E_z^2\rangle_t, \qquad I_{xx}^{is} = \varrho \left(\frac{\omega}{c}\right)^4 a^2\langle E_x^2\rangle_t. \tag{12}$$

In the absence of external fields, the spatial distribution and orientation of the macro-molecules in solution are quite random with respect to the plane of observation of the scattered light. In consequence, on calculating mean values with equal probability, we ob-tain the following non-vanishing angular functions:

$$\langle\cos^{2n} \vartheta\rangle_\Omega = \frac{1}{2n+1},$$

$$\langle\cos^{2n} \varphi\rangle_\Omega = \frac{(2n-1)!!}{2^n \cdot n!}, \tag{13}$$

which, with Eq. (11), lead to the well-known results for the components of usual Rayleigh scattering [13]:

$$V_v = \left(1 + \frac{4}{5} \varkappa^2\right) I_{zz}^{is},$$ (14)

$$\frac{H_v}{I_{zz}^{is}} = \frac{V_h}{I_{xx}^{is}} = \frac{H_h}{I_{xx}^{is}} = \frac{3}{5} \varkappa^2,$$ (15)

the last expression defining the Rayleigh-Krishnan reciprocity relation [14].

3. Light scattering by macromolecules reoriented by an AC electric field

We shall now deal with the case when the scattering solution is acted on by an externally applied electric field of strength F. Its action causes a reorientation of the macromolecules. Once we assume a macromolecule as possessing the permanent electric dipole moment μ, its potential energy in the field F is [15]:

$$u(\Omega, F) = -\mu_i F_i - \frac{1}{2} \alpha_{ij} F_i F_j,$$ (16)

α_{ij} being the tensor of its electric polarizability.

Restricting our considerations, as previously, to macromolecules (particles) having the symmetry of a rotation ellipsoid whose symmetry 3-axis is at an angle ϑ_F to the field direction F, we can rewrite Eq. (16) as follows:

$$u(\Omega, F) = -\mu F \cos \vartheta_F - \frac{1}{2} \left\{ \alpha + (\alpha_3 - \alpha_1) \left(\cos^2 \vartheta_F - \frac{1}{3} \right) F^2 \right\}.$$ (17)

The electric field F applied to the solution reorients the particles; when thermodynamical equilibrium sets in (at temperature T), their distribution is described in accordance with classical Maxwell-Boltzmann statistics by the function [6]:

$$f(\Omega, F) = \frac{\exp\left[-\beta u(\Omega, F)\right]}{\int \exp\left[-\beta u(\Omega, F)\right] d\Omega}$$ (18)

in which the integral extends over all orientations Ω of particles, and $\beta = 1/kT$.

At not very large field strengths F we have $\beta u < 1$, so that the distribution function (18) can be expanded in the power series:

$$f(\Omega, F) = f_0 + f_1 + f_2 + \cdots,$$ (19)

$f_0 = 1/\Omega$ denoting the distribution function in the absence of the external field F i. e. at random orientation. The contributions of the first and second approximations, with regard to Eq. (17), are of the form:

$$f_1 = f_0 \left\{ p \cos \vartheta_F + q \left(\cos^2 \vartheta_F - \frac{1}{3} \right) \right\},$$

$$f_2 = \frac{1}{2} f_0 p^2 \left(\cos^2 \vartheta_F - \frac{1}{3} \right),$$ (20)

where we have introduced the dimensionless parameters [8]:

$$p = \frac{\mu F}{kT}, \tag{21}$$

$$q = \frac{\alpha_3 - \alpha_1}{2\,kT}\,F^2, \tag{22}$$

describing the reorientation undergone by the electric dipole and polarizability ellipsoid of the macromolecule in the electric field F.

In the case when the macromolecules are subject to reorientation in an AC electric field $F(t)$, the distribution functions (18)–(20) are no longer applicable; appropriate functions can be found within the framework of the theory of dielectric relaxation formulated by Debye [6] for dipolar molecules, and subsequently extended to the case of anisotropic molecules in a strong electric field [7, 8]. Putting the AC field in the general form:

$$F(t) = \sum_n F_n^0 e^{i\omega_n t}, \tag{23}$$

where summation is over all (positive and negative) frequencies ω_n and F_n^0 is the field amplitude, we derive in place of Eq. (20) the following formula:

$$f(t) = f_0 \{1 + p(t)\cos\vartheta_F + g(t)(\cos^2\vartheta_F - 1/3) + ...\}, \tag{24}$$

wherein we have introduced the time-dependent reorientation parameters:

$$p(t) = \frac{\mu}{kT} \sum_n F_n^0 \frac{e^{i\omega_n t}}{1 + i\omega_n \tau_D}, \tag{25}$$

$$g(t) = \frac{1}{2\,kT} \sum_{nm} F_n^0 F_m^0 \frac{e^{i(\omega_n + \omega_m)t}}{1 + i(\omega_n + \omega_m)\tau_B} \left\{ \alpha_3 - \alpha_1 + \frac{\mu^2}{2kT} \left(\frac{1}{1 + i\omega_n \tau_D} + \frac{1}{1 + i\omega_m \tau_D} \right) \right\}, \tag{26}$$

τ_D denoting the Debye relaxation time [6], and $\tau_B = \tau_{D/3}$ the relaxation time of induced birefringence [7, 15].

In the case now under consideration the unweighted mean values $\langle\ \rangle_\Omega$ of Eqs (11) have to be replaced by quantities obtained as a result of statistical averageing in the presence of the external field F and defined as follows:

$$\langle G \rangle_{\Omega, F} = \int G(\Omega) f(\Omega, F)\, d\Omega. \tag{27}$$

Now, since in the case of axially symmetric particles the distribution function $f(\Omega, F)$ is a function of the angle ϑ alone, we can first perform an unweighted averageing over the azimuth φ in the right hand terms of Eqs (11), thus obtaining the following relative variations of the intensity components of scattered light (applying F along the z-axis):

$$\delta V_v^F \equiv \frac{V_v^F - V_v}{V_v} = \frac{20\varkappa\Phi(F) + 8\varkappa^2[Q(F) + T(F)]}{5 + 4\varkappa^2}, \tag{28}$$

$$\delta H_v^F \equiv \frac{H_v^F - H_v}{H_v} = \frac{V_h^F - V_h}{V_h} \equiv \delta V_h^F = -Q(F), \tag{29}$$

$$\delta H_h^F \equiv \frac{H_h^F - H_h}{H_h} = -T(F), \tag{30}$$

where we have introduced the functions of reorientation in the external electric field $\boldsymbol{F}$:

$$\Phi(F) = \frac{1}{2} \langle 3 \cos^2 \vartheta - 1 \rangle_{\Omega,F}, \tag{31}$$

$$Q(F) = \frac{1}{2} \langle 15 \cos^4 \vartheta - 15 \cos^2 \vartheta + 2 \rangle_{\Omega,F}, \tag{32}$$

$$T(F) = \frac{1}{8} \langle 30 \cos^2 \vartheta - 15 \cos^4 \vartheta - 7 \rangle_{\Omega,F}. \tag{33}$$

These reorientation functions are defined in a manner to vanish in the absence of an external field (at $F = 0$), when the unweighted averageing procedure (13) is the correct one.

At complete parallel orientation (alignment) of all the particles in the direction of the field vector $\boldsymbol{F}$, in other words at $\cos \vartheta = 1$, the functions (31)–(33) tend to the limiting value

$$\Phi(F) = Q(F) = T(F) = 1. \tag{34}$$

In the presence of a not very strong AC electric field when, in accordance with the definition (27), averageing has to be carried out with the distribution function (24), we get with regard to (31)–(33):

$$\Phi(F) = \frac{2}{15} g(t). \tag{35}$$

$$T(F) = -2Q(F) = \frac{4}{21} g(t), \tag{36}$$

In the case when the AC electric field $\boldsymbol{F}$ oscillates at a single frequency ω_F different from the frequency ω of the incident light wave ($\omega_F \neq \omega$), the complex reorientation parameter (26) can be resolved in the well-known way into a real and an imaginary part:

$$\text{Re } g(t) = \frac{F^2}{4kT} \left\{ (\alpha_3 - \alpha_1) \left(1 + \frac{\cos 2\omega_F t + 2\omega_F \tau_B \sin 2\omega_F t}{1 + 4\omega_F^2 \tau_B^2} \right) + \right.$$
$$\left. + \frac{\mu^2}{1 + \omega_F^2 \tau_D^2} \left[1 + \frac{(1 - 2\omega_F^2 \tau_D \tau_B) \cos 2\omega_F t + \omega_F (\tau_D + 2\tau_B) \sin 2\omega_F t}{1 + 4\omega_F^2 \tau_B^2} \right] \right\}, \tag{37}$$

$$\text{Im } g(t) = \frac{F^2}{4kT} \left\{ \frac{\alpha_3 - \alpha_1}{1 + 4\omega_F^2 \tau_B^2} (2\omega_F \tau_B \cos 2\omega_F t - \sin 2\omega_F t) + \right.$$
$$\left. + \frac{\mu^2}{1 + \omega_F^2 \tau_D^2} \left[\omega_F \tau_D + \frac{\omega_F (\tau_D + 2\tau_B) \cos 2\omega_F t - (1 - 2\omega_F^2 \tau_D \tau_B) \sin 2\omega_F t}{1 + 4\omega_F^2 \tau_B^2} \right] \right\}. \tag{38}$$

In particular, for the case of a DC electric field $\boldsymbol{F}$, that is for $\omega_F = 0$, we obtain:

$$g(0) = \frac{F^2}{2kT} \left(\alpha_3 - \alpha_1 + \frac{\mu^2}{kT} \right), \tag{39}$$

whereas in the other limiting case — that of optical frequencies — when $\omega_F \tau_D \to \infty$ and $\omega_F \tau_B \to \infty$ simultaneously, we get:

$$g(\infty) = \frac{\alpha_3 - \alpha_1}{2kT} \langle F^2 \rangle_t. \tag{40}$$

The last-named case is that of light scattering in the presence of another, intense light beam, thus emitted by a ruby laser [11, 12].

4. Scattering by macromolecules completely aligned in a DC electric field

Let us now proceed to the case when the DC electric field applied to the scattering solution is sufficiently strong to cause complete orientation of the macromolecules. The appropriate distribution function is now that of Eq. (18) which, with regard to (17), takes the following form when the macromolecules are axially-symmetric:

$$f(\vartheta_F, F) = \frac{\exp\left(p \cos \vartheta_F + q \cos^2 \vartheta_F\right)}{2\pi \int\limits_0^\pi \exp\left(p \cos \vartheta_F + q \cos^2 \vartheta_F\right) \sin \vartheta_F d\vartheta_F}. \tag{41}$$

The orientation parameters p and q are defined by Eqs (21) and (22).

a) Dipolar non-polarizing macromolecules

We shall begin by the case when the macromolecules are strongly dipolar, with permanent electric moment parallel to the symmetry axis, the latter subtending the angle ϑ_F with the field $\boldsymbol{F}$. Assuming for the sake of simplicity that the macromolecules do not polarize anisotropically ($q = 0$) and supposing the field $\boldsymbol{F}$ to be applied along z (thus $\vartheta = \vartheta_F$) the distribution function (41) reduces to the form:

$$f(\vartheta, F) = \frac{\exp\left(p \cos \vartheta\right)}{2\pi \int\limits_0^\pi \exp\left(p \cos \vartheta\right) \sin \vartheta d\vartheta} \tag{42}$$

and in accordance with the definition (27) of the averageing procedure we introduce the following generalized Langevin functions [16] of the n-th order [17]:

$$L_n(p) = \langle \cos^n \vartheta \rangle_F = \frac{\int\limits_0^\pi \cos^n \vartheta \exp\left(p \cos \vartheta\right) \sin \vartheta d\vartheta}{\int\limits_0^\pi \exp\left(p \cos \vartheta\right) \sin \vartheta d\vartheta}. \tag{43}$$

On substituting the variable $t = p \cos \vartheta$ and integrating the numerator per partes:

$$\int t^n e^t dt = e^t \sum_{k=0}^n (-1)^k \frac{n!}{(n-k)!} t^{n-k},$$

we have quite generally [18]:

$$L_n(p) = \sum_{k=0}^{n} \frac{n!}{(n-k)!} \frac{(-1)^k e^p - (-1)^n e^{-p}}{p^k (e^p - e^{-p})}.$$ (44)

In particular, for $n = 0, 1, 2, 3, 4, \ldots$

$$L_0 = 1, \qquad\qquad L_1(p) = L(p) = \coth p - \frac{1}{p},$$

$$L_2(p) = 1 - 2\frac{L(p)}{p}, \qquad L_3(p) = L(p) - \frac{2}{p}\left[1 - 3\frac{L(p)}{p}\right],$$

$$L_4(p) = 1 - 4\frac{L(p)}{p} + \frac{8}{p^2}\left[1 - 3\frac{L(p)}{p}\right], \ldots$$ (45)

where $L(p)$ is the usual Langevin function [16].

By means of the generalized Langevin functions (43), we re-write the reorientation functions (31)–(33) in a form adapted to numerical calculations:

$$\Phi(p) = \frac{1}{2}\{3L_2(p) - 1\},$$

$$Q(p) = \frac{1}{2}\{15 L_4(p) - 15 L_2(p) + 2\},$$

$$T(p) = \frac{1}{8}\{30 L_2(p) - 15 L_4(p) - 7\}.$$ (46)

The functions (46) are plotted in Fig. 1.

In the case of very incomplete, or indeed weak orientation of the macromolecules (at $p < 1$), we are justified in expanding the Langevin functions (43) in power series. For even and odd functions, we obtain respectively:

$$L_{2n}(p) = \sum_{k=0}^{\infty} A_k^n p^{2k}$$ (47)

$$L_{2n-1}(p) = \sum_{k=0}^{\infty} B_k^n p^{2k+1},$$ (48)

the expansion coefficients A_k^n and B_k^n being of the form:

$$A_k^n = \frac{1}{(2n+2k+1)(2k)!} - \sum_{l=1}^{k} \frac{A_{k-l}^n}{(2l+1)(2l)!},$$ (49)

$$B_k^n = \frac{1}{(2n+2k+1)(2k+1)!} - \sum_{l=1}^{k} \frac{B_{k-l}^n}{(2l+1)(2l)!}.$$ (50)

By Eqs (47)–(50), we obtain in a satisfactory approximation:

$$L_1(p) = \frac{p}{3} - \frac{p^3}{45} + \frac{2p^5}{945} - \frac{p^7}{4725} + \dots,$$

$$L_2(p) = \frac{1}{3} + \frac{2p^2}{45} - \frac{4p^4}{945} + \dots,$$

$$L_3(p) = \frac{p}{5} - \frac{p^3}{105} + \frac{4p^5}{4725} - \dots,$$

$$L_4(p) = \frac{1}{5} + \frac{4p^2}{105} - \frac{16p^4}{4725} + \dots \tag{51}$$

and the reorientation functions (46) become:

$$\Phi(p) = \frac{p^2}{15} - \frac{2p^4}{315} + \dots$$

$$Q(p) = -\frac{p^2}{21} + \frac{2p^4}{315} -$$

$$T(p) = \frac{2p^2}{21} - \frac{p^4}{105}. \tag{52}$$

For large values of the parameter p, one can express the Langevin functions (44) with sufficient approximation as follows:

$$L_n(p) = 1 + \sum_{k=1}^{n} \frac{n!}{(n-k)!} \left(-\frac{1}{p}\right)^k \tag{53}$$

whence, at $n = 1, 2, 3, 4$, we have:

$$L_1(p) = 1 - \frac{1}{p}, \qquad\qquad L_2(p) = 1 - \frac{2}{p} + \frac{2}{p^2},$$

$$L_3(p) = 1 - \frac{3}{p} + \frac{6}{p^2} - \frac{6}{p^3}, \quad L_4(p) = 1 - \frac{4}{p} + \frac{12}{p^2} - \frac{24}{p^3} + \frac{24}{p^4}, \tag{54}$$

permitting one to compute the reorientation function (46) according to the following limiting formulas $(p \geqslant 10)$:

$$\Phi(p) = 1 - \frac{3}{p} + \frac{3}{p^2},$$

$$Q(p) = 1 - \frac{15}{p} + \frac{75}{p^2} - \frac{180}{p^3} + \frac{180}{p^4},$$

$$T(p) = 1 - \frac{60}{p^2} + \frac{180}{p^3} - \frac{180}{p^4}, \tag{55}$$

In the case of electric saturation *i. e.* when all the electric dipoles are aligned in the direction of the applied electric field, the Langevin functions (53) tend to unity at p tending to infinity. In this case, the reorientation functions (55), too, tend to unity:

$$\Phi(\infty) = Q(\infty) = T(\infty) = 1. \tag{56}$$

b) Dipolar polarizing macromolecules

We now extend our considerations to dipolar macromolecules which are anisotropically polarizable. Here, two kinds of macromolecules have to be distinguished: (*i*) "cigar-shaped" ones, where both the permanent electric dipole moment and the largest principal polarizability are directed along the symmetry axis, and (*ii*) "disc-shaped" macromolecules having their dipole moment in the direction of the symmetry axis but their largest polarizability lying in the plane perpendicular thereto. Case (*i*) is that of positive optical anisotropy, $\alpha_3 > \alpha_1$; case (*ii*) corresponds to negative optical anisotropy, $\alpha_3 < \alpha_1$.

Accordingly, the distribution function (41) becomes (with $\vartheta = \vartheta_F$):

$$f(\vartheta, F) = \frac{\exp\left(p\cos\vartheta \pm q\cos^2\vartheta\right)}{2\pi \int\limits_0^\pi \exp\left(p\cos\vartheta \pm q\cos^2\vartheta\right)\sin\vartheta d\vartheta} \tag{57}$$

the sign "$+$" referring to positive optical anisotropy, and "$-$" to negative optical anisotropy of the macromolecule.

Resorting to the distribution function (57), we now define the ensuing, generalized Langevin functions:

$$L_n(p, \pm q) = \frac{\int\limits_0^\pi \cos^n\vartheta \exp\left(p\cos\vartheta \pm q\cos^2\vartheta\right)\sin\vartheta d\vartheta}{\int\limits_0^\pi \exp\left(p\cos\vartheta \pm q\cos^2\vartheta\right)\sin\vartheta d\vartheta}. \tag{58}$$

With the substitution [19]:

$$t = \sqrt{q}\cos\vartheta \mp \frac{p}{2\sqrt{q}}, \quad q \neq 0 \tag{59}$$

they take the form:

$$L_n(p, \pm q) = \frac{e^{\mp\left(\frac{p^2}{4q} + q\right)}}{2q^{n/2}\, I(p, \pm q)} \int\limits_{z_1}^{z_2} \left(t \mp \frac{p}{2\sqrt{q}}\right)^n e^{\pm t^2}\, dt, \tag{60}$$

where we have introduced the integrals:

$$I(p, \pm q) = \frac{1}{2}\, e^{\mp\left(\frac{p^2}{4q} + q\right)} \int\limits_{z_1}^{z_2} e^{\pm t^2}\, dt \tag{61}$$

with the integration limits:

$$z_1 = -\sqrt{q} \pm \frac{p}{2\sqrt{q}}, \quad z_2 = \sqrt{q} \pm \frac{p}{2\sqrt{q}}. \tag{62}$$

Using the recurrential formula:

$$\int t^n e^{\pm t^2} dt = \pm \frac{1}{2} t^{n-1} e^{\pm t^2} \mp \frac{n-1}{2} \int t^{n-2} e^{\pm t^2} dt \qquad (63)$$

we particularize the functions $L_n(p, \pm q)$ of Eq. (60) in turn for $n = 1, 2, 3, 4$ as follows:

$$L_1(p, \pm q) = \mp \frac{p}{2q} \pm \frac{e^p - e^{-p}}{4q^{1/2} I(p, \pm q)},$$

$$L_2(p, \pm q) = \frac{p^2 \mp 2q}{4q^2} \pm \frac{e^p + e^{-p}}{4q^{1/2} I(p, \pm q)} - \frac{p(e^p - e^{-p})}{8q^{3/2} I(p, \pm q)},$$

$$L_3(p, \pm q) = \mp \frac{p(p^2 \mp 6q)}{8q^3} - \frac{p(e^p + e^{-p})}{8q^{3/2} I(p, \pm q)} \pm \frac{(p^2 \mp 4q + 4q^2)(e^p - e^{-p})}{16q^{5/2} I(p, \pm q)},$$

$$L_4(p, \pm q) = \frac{p^4 + 12q(q \mp p^2)}{16q^4} \pm \frac{(p^2 \mp 6q + 4q^2)(e^p + e^{-p})}{16q^{5/2} I(p, \pm q)} -$$

$$- \frac{p(p^2 + 4q^2 \mp 10q)(e^p - e^{-p})}{32q^{7/2} I(p, \pm q)}, \qquad (64)$$

In the case now under consideration, the reorientation functions (31)–(33) take the form:

$$\Phi(p, \pm q) = \frac{1}{2} \{3L_2(p, \pm q) - 1\},$$

$$Q(p, \pm q) = \frac{1}{2} \{15L_4(p, \pm q) - 15L_2(p, \pm q) + 2\},$$

$$T(p, \pm q) = \frac{1}{8} \{30L_2(p, \pm q) - 15L_4(p, \pm q) - 7\}, \qquad (65)$$

where the Langevin functions L_2 and L_4 are defined by Eqs (64). The functions (65) are plotted in Figs 2–7.

Strikingly, in the case of macromolecules of low optical anisotropy ($\varkappa \leqslant 0,1$), the change in vertical component (28) results in the form:

$$\delta V_v^F = 4\varkappa \, \Phi(p, \pm q). \qquad (66)$$

In other words, the variation of the vertical component of Eq. (28) is simply four times the product of the optical anisotropy $\varkappa$ of the macromolecule and the reorientation function $\Phi(p, \pm q)$, which intervenes directly in Kerr's effect [19, 20] and is thus accessible to measurement.

c) Non-dipolar anisotropically polarizing macromolecules

In the case of non-dipolar macromolecules the dipole parameter p vanishes and, if they are polarizable anisotropically ($q \neq 0$), the Langevin functions (45) of odd order
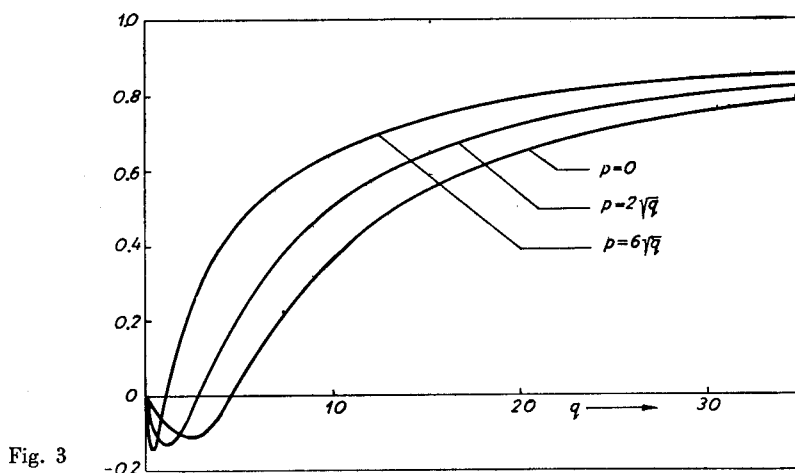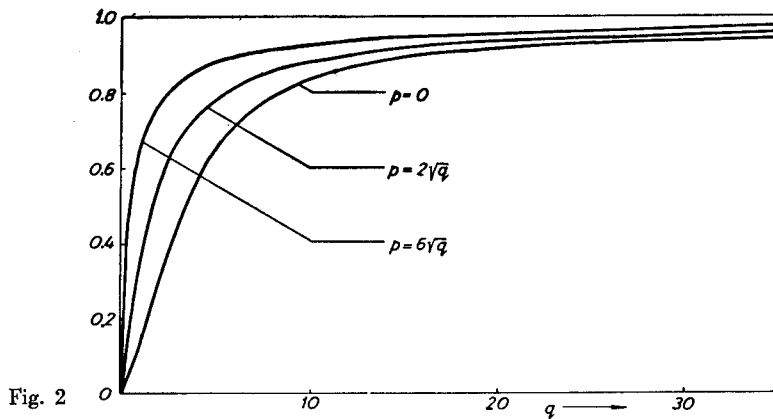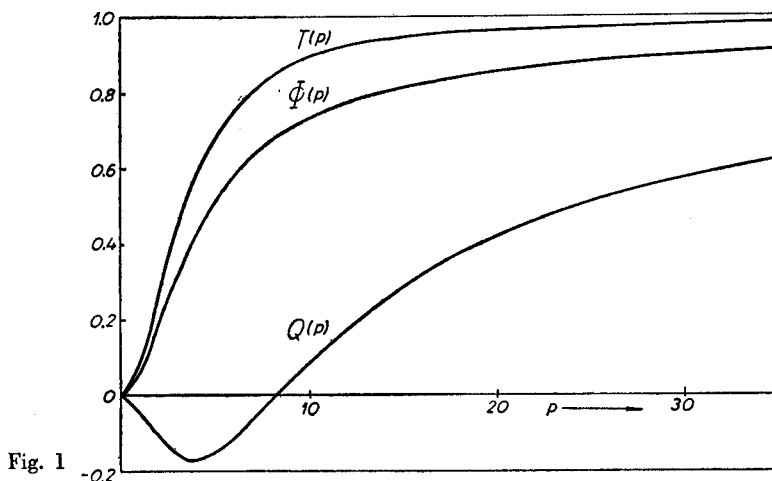
Fig. 1

Fig. 2

Fig. 3

Fig. 1. Reorientation functions, Eqs (46), for dipolar nonpolarizing macromolecules

Fig. 2. Reorientation function $\Phi(p, +q)$ for dipolar polarizable macromolecules with positive anisotropy

Fig. 3. Reorientation function $Q(p, +q)$ for dipolar polarizable macromolecules with positive anisotropy
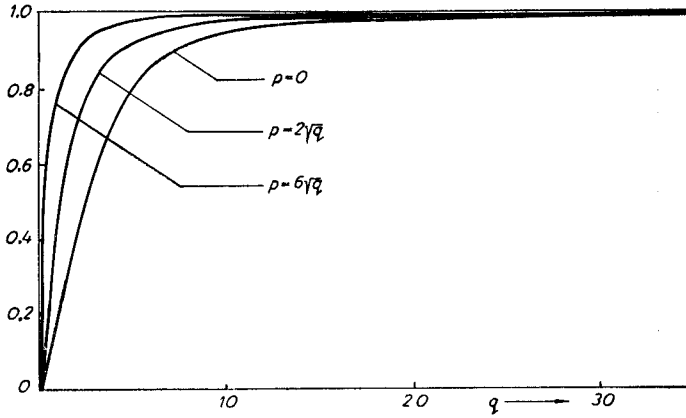
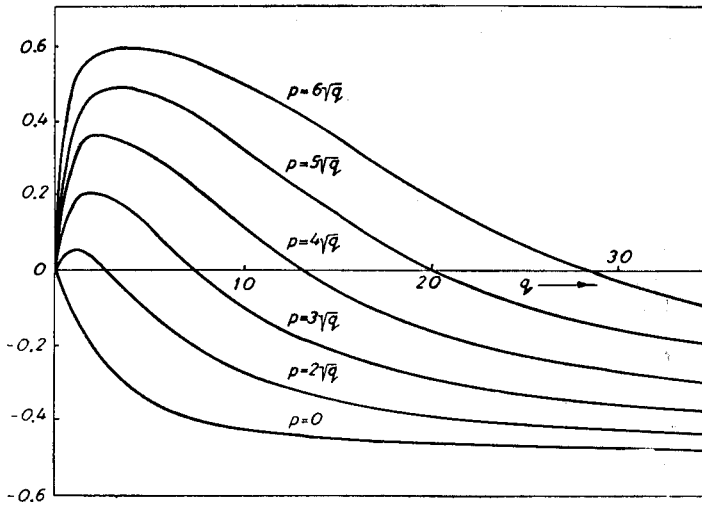Fig. 4. Reorientation function $T(p, +q)$ for dipolar polarizable macromolecules with positive anisotropy

Fig. 5. Reorientation function $\Phi(p, -q)$ for dipolar polarizable macromolecules with negative anisotropy

$L_1(0, \pm q)$, $L_3(0, \pm q)$, ... vanish whereas those of even order reduce to those derived formerly [11]:

$$L_2(0, \pm q) = \mp \frac{1}{2q} \pm \frac{1}{2q^{1/2}I(0, \pm q)},$$

$$L_4(0, \pm q) = \frac{3}{4q^2} \pm \frac{2q \mp 3}{4q^{3/2}I(0, \pm q)}. \tag{67}$$

The integrals of Eq. (61) now take the simple form:

$$I(0, \pm q) = e^{\mp q} \int_0^{\sqrt{q}} e^{\pm t^2} dt. \tag{68}$$
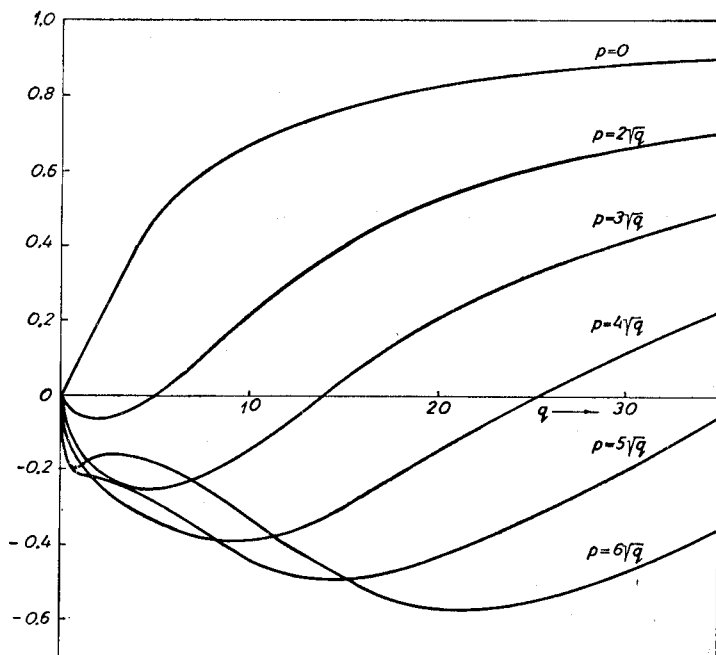
Fig. 6. Reorientation function $Q(p, -q)$ for dipolar polarizable macromolecules with negative anisotropy
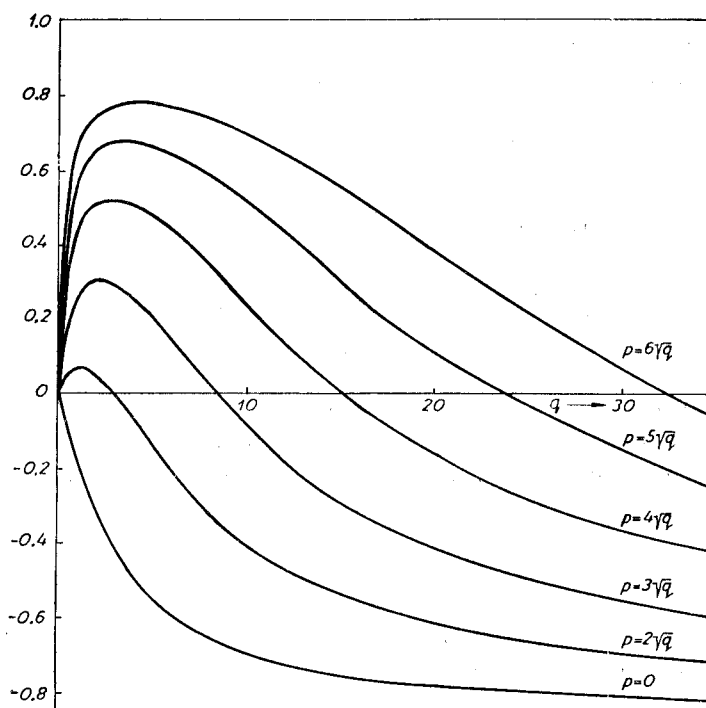

Fig. 7. Reorientation function $T(p, -q)$ for dipolar polarizable macromolecules with negative anisotropy

For small values of q, we can expand the functions (67) as follows:

$$L_2(0, \pm q) = \frac{1}{3} \pm \frac{4q}{45} + \frac{8q^2}{945} \mp \frac{16q^3}{14175} + \ldots,$$

$$L_4(0, \pm q) = \frac{1}{5} \pm \frac{8q}{105} + \frac{16q^2}{1575} \mp \frac{32q^3}{51975} + \ldots \qquad (69)$$

and the reorientation functions (65) become:

$$\Phi(0, \pm q) = \pm \frac{2q}{15} + \frac{4q^2}{315} \mp \frac{8q^3}{4725} + \ldots,$$

$$Q(0, \pm q) = \mp \frac{2q}{21} + \frac{4q^2}{315} \pm \frac{8q^3}{2079} + \ldots,$$

$$T(0, \pm q) = \pm \frac{4q}{21} + \frac{4q^2}{315} \mp \frac{32q^3}{10395} + \ldots. \qquad (70)$$

In the case of electric saturation, at $q \to \infty$, we now have for "cigar-shaped" macromolecules of positive anisotropy $L_2(0, +\infty) = L_4(0, +\infty) = 1$ and the reorientation functions tend to unity:

$$\Phi(0, \infty) + = Q(0, +\infty) = T(0, +\infty) = 1, \qquad (71)$$

whereas for "disc-shaped" macromolecules of negative anisotropy $L_2(0, -\infty) = L_4(0, -\infty) = 0$ and the reorientation functions (65) take the limiting values:

$$\Phi(0, -\infty) = -\frac{1}{2}, \quad Q(0, -\infty) = 1, \quad T(0, -\infty) = -\frac{7}{8}. \qquad (72)$$

In the two cases (71) and (72) respectively, the change in vertical component (66) assumes the form:

$$\delta V_v^F \equiv \frac{V_v^F - V_v}{V_v} = \begin{cases} 4\varkappa \text{ for cigar-shaped macromolecules,} \\ -2\varkappa \text{ for disc-shaped macromolecules.} \end{cases} \qquad (73)$$

One sees that measurements of light scattering at electric saturation enable one to determine the anisotropy $\varkappa$ not only as to its value but also as to its sign. It is abvious from Eqs (14) and (15) that usual Rayleigh scattering yields only the square of the optical anisotropy, $\varkappa^2$.

5. Nonlinear changes in depolarization ratio

In the case of light incident with electric vector oscillating vertically, the depolarization ratio of scattered light is defined [13] as:

$$D_v = \frac{H_v}{V_v} \qquad (74)$$

and with regard to (14) and (15) one obtains for usual Rayleigh scattering the well-known formula [13]:

$$D_v = \frac{3\varkappa^2}{5+4\varkappa^2}.$$ (75)

In the presence of an external electric or magnetic field, one has the components (28) and (29) and finds in accordance with the definition (74):

$$D_v^F = \frac{3\varkappa^2[1-Q(F)]}{5+4\varkappa^2+20\varkappa\Phi(F)+8\varkappa^2[Q(F)+T(F)]}.$$ (76)

In the case of electric saturation this depolarization decreases to zero both for "cigar-shaped" and "disc-shaped" macromolecules.

In the case of light incident with horizontal oscillations of the electric vector, the ratio is defined as [13]:

$$D_h = \frac{V_h}{H_h},$$ (77)

whence with regard to Eqs (29) and (30) we get:

$$D_h^F = \frac{1-Q(F)}{1-T(F)} = 1 + \frac{T(F)-Q(F)}{1-T(F)}.$$ (78)

In the absence of external fields this yields a value of 1 which, at electric saturation, decreases to zero in the case of "disc-shaped" macromolecules. For "cigar-shaped" ones, Eq. (78) at saturation is indeterminate.

Eq. (78) is of especial interest in the case of weak orientation of macromolecules in an AC electric field, when with regard to (36) the change in depolarization ratio results in the form [15]:

$$D_h^F - 1 = -\frac{2}{7} g(t)$$ (79)

permitting direct determinations of the reorientation parameter $g(t)$ defined in general by Eq. (26) and in particular cases by Eqs (37)–(40). Quite obviously, formula (79) provides the experimental possibility of determining the sign and value of the electric anisotropy of the macromolecule or the birefringence relaxation time τ_B.

In the case or unpolarized incident light, the depolarization ratio is [13]:

$$D_u = \frac{H_v+H_h}{V_v+V_h},$$ (80)

or, with regard to Eqs (28)–(30), in explicit form:

$$D_u^F = \frac{3\varkappa^2[2-Q(F)-T(F)]}{5+7\varkappa^2+20\varkappa\Phi(F)+\varkappa^2[5Q(F)+8T(F)]}.$$ (81)

In the absence of external fields, this yields the well-known formula [13]:

$$D_u = \frac{6\varkappa^2}{5+7\varkappa^2}.$$ (82)

At saturation, the depolarization of formula (81) tends to zero for "cigar-shaped" macromolecules, and to:

$$D_u^- = \frac{9\varkappa^2}{8(1-2\varkappa+\varkappa^2)}$$ (83)

for "disc-shaped" ones.

6. Discussion and conclusions

The theory developed by us here is applicable strictly to solutions of molecules or macromolecules the linear dimensions of which are smaller than the light wavelength. However, as is apparent from Table I, in the case of ordinary molecules the reorientation parameters (21) and (22) are very small even if a local field, thus of the Lorentz type $F = (\varepsilon+2) E/3$, is taken into account. Specifically, in nitrobenzene we have $p = 1.2 \times 10^{-3}E$ and $q = -1.4 \times 10^{-8} E^2$. Even when working with most carefully purified nitrobenzene, it is hardly possible to apply fields upward of 10^3 e. s. u. if electric breakdown is to be avoided. Fields of this order yield, at the best, reorientation parameters $p \simeq 1$ and $q \simeq 10^{-2}$. Consequently, complete electric saturation cannot be achieved in a molecular liquid, although the degree of ordering (alignment) of the molecular dipoles can be sufficient for causing variations of the order of thousandths in the scattered light intensity — variations well within the range of recording by sensitive measuring procedures.

The assumptions of the present theory are fulfilled by solutions of certain biopolymers, such as proteins, nucleic acids, and viruses, as well as colloid suspensions (thus, V_2O_5, etc.), where the macromolecules (particles) can be regarded as rigid, continuous rotational ellipsoids (rods or discs). The reorientation functions (31)–(34), as is seen from Eqs (28)–(30), directly define the relative variations of the intensity components of scattered light, and consequently depend but weakly on macromolecular size. These reorientation functions (31)–(34) remain fully valid for non-deformable microsystems with linear dimensions less than 1000 Å. For bigger microsystems (upward of 1000 Å) the values of these functions decrease by several hundredths; upward of 3000 Å, the decrease exceeds 50 per cent.

We hence conclude that the above-derived formulas permit to make numerical evaluations of the order of magnitude of the variations to be expected from almost all the microsystems listed in Table I. For example, our theory is applicable quite strictly to Fibrinogen and Edestine, for which it leads to reorientation parameters $p = 0.03\ E$ and $q = 10^{-4}\ E^2$ permitting to predict a beginning of electric saturation in a field of 100 e. s. u. Complete electric saturation should be achievable in solutions of rigid polypeptides (e. g. poly-γ-benzyl-L-glutamate, Collagen, etc.) and rigid polyelectrolytes like Tobacco Mosaic Virus, where the reorientation parameters (21) and (22) assume the enormously large values $p = E$ and $q = 0.4\ E^2$. In the latter case, a field of 10 e. s. u. should be quite sufficient for obtaining

TABLE I

Geometrical and electrical parameters of some molecules and macromolecules

	Average molecular weight $Mw \times 10^{-3}$	Length [Å]	Diameter [Å]	Relaxation time τ_D [10^{-8} sec]	Electric dipole moment μ [10^{-18} e.s.u. cm]	Electric anisotropy $\alpha_3 - \alpha_1$ [10^{-24} cm^3]	References
Carbon disulphide	76×10^{-3}	5.2	2.7	8.3×10^{-5}	0	9.60	a, b
Water	18×10^{-3}	3.8	3.2	4.5×10^{-4}	1.85	0.60	a, b, c
Nitrobenzene	123×10^{-3}	8.5	4.9	7.3×10^{-4}	4.24	−7.64	a, b, c
Ovalbumin	45	109	28	9	250		d, e
Insulin	40		46	1.6	360		d, e
Hemoglobin	67	47	60	10	met- 70 oxy-120		d, f
Zein	40	320	40	11	380		d
γ-Globulin	150	235	44	72	1100		d, e
Beta-Lactoglobulin	40	122	28	4.3	730		d, e
Fibrinogen	400	700	38		1200	1.2×10^7	d
Edestin	310	860	96	98	1400		d
Poly-γ-benzyl-L--glutamate	175	1250		5×10^3	2800		g
	195	1335	30	5×10^3	2700	8×10^5	h
	250	1550		1.5×10^4	3920	1.2×10^6	i
Collagen	280	2800	14	4.5×10^4	15000	3×10^9	j
Tobacco Mosaic Virus (TMV)	49.5×10^3	3200	150	1.3×10^5	41000	3.3×10^{10}	k
Deoxyribonucleic acid (DNA)	400	5000	40	1.5×10^6	20000	1.4×10^9	l
Bentonite		2500	thin disc		10^5	3.1×10^{11}	m

a C. G. Le Fevre and R. J. W. Le Fevre, *Rev. Pure and Appl. Chem.*, **5**, 261 (1955); J. F. Harrison, *J. Chem. Phys.*, **49**, 3321 (1968).

b C. P. Smyth, *Ann. Rev. Phys. Chem.*, **17**, 433 (1966); S. K. Garg, J. E. Bertie, H. Kilp and C. P. Smyth, *J. Chem. Phys.*, **49**, 2551 (1968); M. Davies, *Sci. Prog.*, **56**, 337 (1968).

c R. D. Nelson, Jr., D. R. Lide, Jr. and A. A. Maryott, *Selected values of electric dipole moments for molecules in the gas phase* U. S. Department of Commerce, National Bureau of Standards, Washington 1967.

d *Die Physik der Hochpolymeren, Band II, Das Makromolekul in Lösungen*, Edited by H. A. Stuart (Springer-Verlag, Berlin 1953) and Ref. [20].

e S. Krause and C. T. O'Konski, *Biopolymers*, **1**, 503 (1963).

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g G. Boeckel, J. C. Genzeling, G. Weill, H. Benoit, *J. Chim. Phys.*, 999 (1962).

h Reference [19].

i Reference [4].

j K. Yoshioka and O'Konski, *Biopolymers*, **4**, 499 (1966).

k References [2], [19] and Stoylov, Y. Mauss, C. Hornick and G. Weill, *Bulgarian Acad. Sci. Commun. Chem.*, **1**, 99 (1968).

l G. Weill, C. Hornik and S. Stoylov, *J. Chim. Phys.*, **65**, 182 (1968).

m Reference [20] and S. Stoylov, S. Sokerov, I. Pethanchin, N. Ibroshev, *Dokl. Akad. Nauk SSSR*, **180**, 1165 (1968).

complete electric dipole saturation, whereas saturation by orientation of the polarizability ellipsoids should occur in even weaker fields.

The theory moreover applies automatically to the case when the microsystems undergo orientation through the agency of a DC magnetic field $\boldsymbol{H}$, since one need but replace the reorientation parameters (21) and (22) by:

$$p_m = \frac{\mu_m H}{kT}, \quad q_m = \frac{\chi_3 - \chi_1}{2\,kT}\,H^2 \tag{84}$$

μ_m denoting the magnetic dipole moment, and χ_3, χ_1 the magnetic polarizabilities respectively parallel and perpendicular to the symmetry axis of the microsystem.

In molecular liquids (like C_6H_6) the diamagnetic anisotropy is at the most of order 10^{-28} cm^3 [21]; accordingly, the reorientation parameter (84) is of order $10^{-15}\,H^2$, so that magnetic saturation cannot be hoped for, even were one to use the strongest magnetic fields of 10^6 Oe now available [22]. The prospects seem brighter in colloid solutions, e. g. in anisaldazine, where magnetic anisotropy is about 10^{-20} cm^3 [23] and $q \approx 10^{-7}\,H^2$ pointing to magnetic saturation in a field of 10^4 Oe. In other colloid suspensions [24] also, and particularly in colloids of ferromagnetic particles (where the permanent magnetic moments are very large, thus amounting [25] to 8×10^{-16} e. m. u. in Fe_3O_4 for particle radius 74 Å), strong orientation of the moments takes place. Likewise encourageing are solutions of DNA and RNA, since they exhibit considerable magneto-optical birefringence [26].

Hence, the study of light scattering by a solution of macromolecules or particles when the microsystems are completely aligned in the direction of an external electric or magnetic field provides a method of determining the optical anisotropy as well as the geometrical shape of the microsystems.

In concluding, it may be appropriate to stress the significance of the variations in purely anisotropic components (29) and (30), which do not depend directly on optical anisotropy like the variation (28), but depend only on the reorientation functions (32) and (33). Such studies are promising, as recently a rapid method of measuring the horizontal component by laser technique has been made available [27] permitting in accordance with Eq. (15) to determine the square of the optical anisotropy [27]. Although as yet attempts to use this method in order to make apparent nonlinear variations in horizontal component due to intense ruby laser light have remained undecisive with regard to molecular liquids [29], it is to be hoped that the effect can be observed in solutions of strongly optically anisotropic macromolecules [30].

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