A MOLECULAR THEORY OF MAGNETIC BIREFRINGENCE IN DIAMAGNETIC MEDIA

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From classical electrodynamics and statistical mechanics, an equation for the molecular Cotton-Mouton constant C_m is derived, of such generality as to contain factors of a microscopic nature not taken into account hitherto in theories of the magnetic birefringence of diamagnetic fluids. This general equation is discussed in detail for gases, non-dipolar liquids and dipolar liquids. Moreover, the fundamentals of a theory of the magnetic birefringence of multi-component systems, with application to gas mixtures and liquids in solution, are proposed. The radial and angular correlations of the molecules of the liquids and their solutions are accounted for by means of molecular functions of the configurational distribution.

I. Introduction

An optically isotropic medium, if placed in a strong homogeneous electric or magnetic field, becomes birefringent with the properties of a uniaxial crystal whose optical axis is directed along the lines of force of the field applied. Electrical birefringence was discovered by Kerr (1875), and magnetic birefringence — by Cotton and Mouton (1907). Notwithstanding the fact that they have been so long known, both these effects still present considerable scientific interest, as they not only provide valuable information on the structure and the electric, magnetic and optical properties of the isolated molecule, but moreover are a source of data relating to the nature of the intermolecular forces and to the structure of fluids. The present paper deals with the theory of magnetic birefringence *i. e.* of the Cotton-Mouton effect.

Voigt (1908) explained magnetic birefringence (and electric birefringence, too) by direct action of the magnetic field on the electrons in the atoms or molecules of the medium. This constitutes the non-linear deformational effect referred to as Voigt's effect. The birefringence thus produced in the medium is extremely small, and is not easily accessible to measurement; it reveals itself clearly in atomic gases or vapours only, as anomalous magnetic birefringence at frequencies of the light wave near the absorption line.

In a great number of other liquids, and notably in organic compounds, the numerical value of the experimentally measured magnetic birefringence considerably exceeds the

one predicted by Voigt's theory. This is adequately explained by Langevin's theory (1910), notwithstanding the fact that the latter was developed for the case of gases. According to Langevin, the molecules of the medium present a degree of anisotropy of their electric, magnetic and optical properties even when not acted on by an external field, *i. e.* they undergo polarization to a different degree parallel and perpendicular to their symmetry axes. If no perturbating factors, such as thermal motion, were present, the molecules when acted on by an external magnetic field would align with their axes of maximum polarizability parallel to the field vector, and the medium would become maximum birefringent. In reality, however, the perturbating factors counteract total alignment of the molecules; as a result, the observed birefringence is generally insignificant even in liquids, increasing with the magnetic field strength and decreasing towards higher temperatures.

In general, the molecular orientational Langevin effect is always accompanied by the second-order deformational effect of Voigt, which does not depend directly on the temperature. A theory of the Cotton-Mouton effect in gases consisting of molecules presenting arbitrary symmetry, and accounting for both effects jointly, was proposed by Born (1933) and, subsequently, by Volkenshteyn (1951) and Buckingham and Pople (1956).

The first to attempt an extension of Langevin's orientational theory to liquids were Raman and Krishnan (1927); according to their theory, the molecules of the liquid possess an effective electric and magnetic polarizability depending on the parameters of the anisotropy of the electric or magnetic local field acting on the molecule. However, Piekara (1939) proved that direct dipole coupling of the molecules is more essential in determining the dependence of the magnetic birefringence of dipolar liquids and their solutions in non-dipolar solvents on the temperature or concentration.

The theory of molecular orientational effects in liquids, as proposed by Piekara (1939, 1950), is based on the assumption of three kinds of coupling to which the molecules in the liquid are subject. Coupling of the first kind is the rotational coupling introduced by Fowler (1935) in his theory of the dielectric permittivity of material containing librating-rotating dipoles and Debye (1935) in the theory of the dielectric permittivity of liquids. According to the Fowler-Debye model, rotation of a dipolar molecule in a liquid is impeded by the electric field produced by the very numerous molecules surrounding it in almost regular array, as in a crystal lattice. Coupling of the second kind acts in a manner to bind the dipolar molecule under consideration and its nearest neighbour so that they shall form a momentary non rigid assembly of two. Finally, the third kind of coupling is when pairwise dipole assemblies, if sufficiently strong, couple pairwise to produce double pairs. It is coupling of the second kind that plays the predominant part in solutions of dipolar liquids in non-dipolar solvents; at very high concentrations, coupling of the third kind comes to play a part too.

Peterlin and Stuart (1939) also proposed a theory of magnetic birefringence in non-dipolar and dipolar liquids. Herein, in addition to anisotropy of the local fields, account is taken of intermolecular coupling as computed in accordance with the Fowler-Debye model. A similar theory for non-dipolar liquids, basing on Mueller's (1936) model, is due to Snellman (1949).

The theories of molecular orientation phenomena utilizing Debye's and Mueller's model were critically reviewed by Frenkel (1946) and Anselm (1947). The latter proposed

to describe orientational interaction of non-dipolar molecules by means of the correlation function $g(r, \omega)$ having the properties of Zernike's and Prins' (1927) radial distribution function $g(r)$ generalized for the case of variable orientation ω of the molecules.

The foregoing theories have this in common that they assume a special mechanism of coupling between the dipolar or non-dipolar molecules; owing to this, they cannot aspire to generality. Theories of the Cotton-Mouton effect in liquids, requiring no special models of intermolecular coupling, were proposed by Buckingham and Pople (1956), and by Piekara and the present author (1957, 1958). Albeit, these present a degree of generality still insufficient for their providing the possibility of taking into account molecular factors other than those already mentioned and likely to affect the magnetic birefringence of diamagnetic fluids, such as i. a. the electric fields of the molecular dipoles or quadrupoles, and the hyperpolarizability induced in the molecules by these fields.

In order that the influence of various factors of a microscopic nature on magnetic birefringence may be taken into account, the present author proposes a general statistic-molecular theory of the effect for an arbitrary isotropic diamagnetic medium. The theory is then applied to non-dipolar liquids consisting in particular of spherical molecules, and to dipolar and quadrupolar liquids; in addition to angular correlations, the immediate effect of the permanent dipolar or quadrupolar moment of the molecule on Langevin's orientational effect is considered. The theory of the magnetic birefringence of multi-component systems with applications to gas mixtures and to solutions of dipolar liquids is also given.

2. General Theory

We shall consider an isotropic medium in the form of a macroscopic spherical specimen of volume V_S, at the centre of which we place the origin O of the Cartesian reference system X_1, X_2, X_3, to be termed the macroscopic or laboratory reference system. We assume a homogeneous magnetic field of strength H directed along the X_3-axis. Along X_2 and perpendicularly to the vector $\boldsymbol{H}$, a plane polarized light beam is incident. The electric vector $\boldsymbol{E}$ of the light wave oscillates in the X_1OX_3-plane and subtends the constant angle Ω with $\boldsymbol{H}$.

In the case under consideration, we have the fundamental equation

$$\frac{n_\Omega^2 - 1}{n_\Omega^2 + 2} \, E = \frac{4\pi}{3V_S} \, \langle \boldsymbol{M}^{ind} \cdot \boldsymbol{e} \rangle_{E,H}, \tag{2.1}$$

wherein n_Ω is the light refractive index when the medium is acted on by external fields whose vectors $\boldsymbol{E}$ and $\boldsymbol{H}$ form the angle Ω. Moreover, $\boldsymbol{M}^{ind}$ is the dipole moment induced in the spherical specimen of volume V_S by the electric field $\boldsymbol{E}$ of the light wave in the presence of the magnetic field $\boldsymbol{H}$, and $\boldsymbol{e}$ is a unit vector in the direction of $\boldsymbol{E}$. The moment $\boldsymbol{M}^{ind}$ is a function of the fields $\boldsymbol{E}$ and $\boldsymbol{H}$ and of the variables Γ determining the configuration of the system.

$\langle \Phi \rangle_{E,H}$ in Eq. (2.1) denotes the statistical mean value of an arbitrary function of state $\Phi = \Phi(\Gamma, \boldsymbol{E}, \boldsymbol{H})$ of the system at configuration Γ in the presence of an external

electric and magnetic field. Classically, the configurational variables Γ are continuous, and classical statistical mechanics yields, at thermodynamical equilibrium,

$$\langle \Phi \rangle_{E,H} = \frac{\int \Phi(\Gamma, E, H) \, e^{-\frac{U(\Gamma, E, H)}{kT}} \, d\Gamma}{\int e^{-\frac{U(\Gamma, E, H)}{kT}} \, d\Gamma} , \tag{2.2}$$

wherein $U(\Gamma, E, H)$ is the total potential energy of the system in the configuration Γ with the fields E and H, k — Boltzmann's constant, and T — the Kelvin temperature. Integration in (2.2) extends over all values of the variables Γ of the configurational space.

Let $M^e = M^e(\Gamma, E, H)$ denote the total electric dipole moment of the macroscopic sphere at configuration Γ acted on by the fields E and H. As the total moment M^e consists of the electric moment $M_0^e = M^e(\Gamma, 0)$ of the sphere at zero external field strengths and the induced moment M^{ind}, Eq. (2.1) can be put in the form of

$$\frac{n_\Omega^2 - 1}{n_\Omega^2 + 2} \, E = \frac{4\pi}{3V_S} \langle (M^e - M_0^e) \cdot e \rangle_{E,H} . \tag{2.3}$$

On expanding the right hand side of this equation in a power series in E and H, we obtain, to within the second power of the magnetic field strength (see, appendix A),

$$\frac{n_\Omega^2 - 1}{n_\Omega^2 + 2} = \frac{4\pi}{3V_S} \left\{ \left\langle \frac{\partial M_\sigma^e}{\partial E_\tau} e_\sigma e_\tau \right\rangle \left[1 - \frac{1}{2V_S} \left(\frac{\partial^2 V_S}{\partial H^2} \right)_0 H^2 + \right. \right.$$

$$+ \frac{1}{2kT} \left\langle \left(\frac{\partial^2 U}{\partial H_\nu \partial H_\varrho} - \frac{1}{kT} \frac{\partial U}{\partial H_\nu} \frac{\partial U}{\partial H_\varrho} \right) h_\nu h_\varrho \right\rangle H^2 \right] + \frac{1}{2} \left\langle \left(\frac{\partial^3 M_\sigma^e}{\partial E_\tau \partial H_\nu \partial H_\varrho} - \right. \right.$$

$$- \frac{2}{kT} \frac{\partial^2 M_\sigma^e}{\partial E_\tau \partial H_\nu} \frac{\partial U}{\partial H_\varrho} - \frac{1}{kT} \frac{\partial M_\sigma^e}{\partial E_\tau} \frac{\partial^2 U}{\partial H_\nu \partial H_\varrho} + \frac{1}{k^2 T^2} \frac{\partial M_\sigma^e}{\partial E_\tau} \frac{\partial U}{\partial H_\nu} \frac{\partial U}{\partial H_\varrho} \right) e_\sigma e_\tau h_\nu h_\varrho \right\rangle H^2 + ... \bigg\} , \tag{2.4}$$

where

$$\langle \Phi \rangle = \frac{\int \Phi(\Gamma, 0) \, e^{-\frac{U(\Gamma, 0)}{kT}} \, d\Gamma}{\int e^{-\frac{U(\Gamma, 0)}{kT}} \, d\Gamma} \tag{2.5}$$

is the statistical mean value of Φ at zero external fields, and $U(\Gamma, 0)$ — the potential energy of the sphere at configuration Γ and $E = H = 0$. The quantity

$$\frac{H^2}{2} \left(\frac{\partial^2 V_S}{\partial H^2} \right)_{H=0} = - \frac{1}{8\pi} \left\{ \frac{\partial}{\partial p} \left[(\mu' - 1) V_S \right] \right\}_T H^2 =$$

$$= - \frac{V_S}{8\pi} \left\{ \left(\frac{\partial \mu'}{\partial p} \right)_T - (\mu' - 1) \beta_T \right\} H^2 \tag{2.6}$$

determines the change in volume of the isotropic sample due to magnetostriction. Herein,

μ' is the magnetic permittivity of the sample, p — the pressure, and $\beta_T = -\dfrac{1}{V_S}\left(\dfrac{\partial V_S}{\partial p}\right)_T$ — the isothermal compressibility of the medium.

The summation indices σ, τ, ν and ϱ in (2.4) assume the values 1, 2, 3 corresponding to the vector or tensor components along the axes X_1, X_2, X_3 of the laboratory system of reference. The quantities e_σ and h_ν are the coordinates of the unit vectors $\boldsymbol{e}$ and $\boldsymbol{h}$ in the directions of the fields $\boldsymbol{E}$ and $\boldsymbol{H}$, respectively; in the laboratory system, these coordinates, being directional cosines, fulfill the relations

$$e_\sigma e_\sigma = h_\sigma h_\sigma = 1 \quad \text{and} \quad e_\sigma h_\sigma = \cos \Omega.$$

At zero electric and magnetic fields, all directions of the unit vectors $\boldsymbol{e}$ and $\boldsymbol{h}$ with respect to $X_1 X_2 X_3$ have the same probability, so that the products of the coordinates e_σ and h_ν appearing in the expansion (2.4) can be averaged isotropically $i.~e.$ averaged with equal probability for all possible directions of the vectors $\boldsymbol{e}$ and $\boldsymbol{h}$, yielding

$$\overline{e_\sigma e_\tau} = \overline{h_\sigma h_\tau} = \tfrac{1}{3}\delta_{\sigma\tau},$$

$$\overline{e_\sigma e_\tau h_\nu h_\varrho} = \tfrac{1}{90}\{10\delta_{\sigma\tau}\delta_{\nu\varrho} + (3\cos^2\Omega - 1)\,\varepsilon_{\sigma\tau:\,\nu\varrho}\}, \tag{2.6a}$$

where

$$\varepsilon_{\sigma\tau:\,\nu\varrho} = -2\delta_{\sigma\tau}\delta_{\nu\varrho} + 3\delta_{\sigma\nu}\delta_{\tau\varrho} + 3\delta_{\sigma\varrho}\delta_{\tau\nu}, \tag{2.6b}$$

and $\delta_{\sigma\tau}$ is the unit tensor with components equalling unity for $\sigma = \tau$ and vanishing for $\sigma \neq \tau$.

With respect to the foregoing result, the expansion (2.4) yields the following general equation:

$$\frac{n_\Omega^2 - 1}{n_\Omega^2 + 2} = \frac{n^2 - 1}{n^2 + 2}\left\{1 - \frac{H^2}{8\pi V_S}\left[\left(\frac{\partial\mu'}{\partial p}\right)_T - (\mu' - 1)\beta_T\right] + \frac{H^2}{6kT}\left\langle\frac{\partial^2 U}{\partial H_\sigma \partial H_\sigma} - \frac{1}{kT}\frac{\partial U}{\partial H_\sigma}\frac{\partial U}{\partial H_\sigma}\right\rangle\right\} +$$

$$+ \frac{\pi}{135 V_S}\{10\,\delta_{\sigma\tau}\delta_{\nu\varrho} + (3\cos^2\Omega - 1)\,\varepsilon_{\sigma\tau:\,\nu\varrho}\}\left\langle\frac{\partial^3 M_\sigma^e}{\partial E_\tau \partial H_\nu \partial H_\varrho} - \right.$$

$$\left. - \frac{1}{kT}\left(2\frac{\partial^2 M_\sigma^e}{\partial E_\tau \partial H_\nu}\frac{\partial U}{\partial H_\varrho} + \frac{\partial M_\sigma^e}{\partial E_\tau}\frac{\partial^2 U}{\partial H_\nu \partial H_\varrho}\right) + \frac{1}{k^2 T^2}\frac{\partial M_\sigma^e}{\partial E_\tau}\frac{\partial U}{\partial H_\nu}\frac{\partial U}{\partial H_\varrho}\right\rangle H^2, \tag{2.7}$$

with the equation

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{9 V_S}\left\langle\frac{\partial M_\sigma^e}{\partial E_\sigma}\right\rangle \tag{2.8}$$

defining the refractive index of light at zero magnetic field strength.

Eq. (2.7) determines the effect of a strong homogeneous magnetic field on the refractive index of an arbitrary isotropic medium. From (2.7), in a first approximation n_Ω is seen to be equal to the refractive index n as given by Eq. (2.8). In the second approximation, n_Ω depends on the second power of the magnetic field strength and also on the averaged properties of the medium and the thermodynamical state of the latter. The fact that n depends on the angle Ω means that the medium has become optically anisotropic in the magnetic

field and is now characterized by different values of its refractive index for different directions of oscillation of the vector E with respect to H.

It is customary to define the optical anisotropy induced in the medium as the difference $n_{||} - n_\perp$ between its refractive indices for light oscillations parallel and perpendicular to the direction of the magnetic vector H, respectively. The quantity $n_{||} - n_\perp$ provides a measure of the magneto-optical anisotropy of the medium. The values of the indices $n_{||}$ and $n_\perp$ can be computed directly from the fundamental equation (2.7) by substituting $\Omega = 0°$ and $\Omega = 90°$, respectively. This yields the difference between the optical refractions, as resulting in an isotropic medium from a strong magnetic field, in the form

$$\frac{n_{||}^2 - 1}{n_{||}^2 + 2} - \frac{n_\perp^2 - 1}{n_\perp^2 + 2} = \frac{\pi}{45 V_S}\, \varepsilon_{\sigma\tau:\nu\varrho} \left\langle \frac{\partial^3 M_\sigma^e}{\partial E_\tau\, \partial H_\nu\, \partial H_\varrho} - \right.$$

$$\left. - \frac{1}{kT} \left(2\frac{\partial^2 M_\sigma^e}{\partial E_\tau\, \partial H_\nu}\frac{\partial U}{\partial H_\varrho} + \frac{\partial M_\sigma^e}{\partial E_\tau}\frac{\partial^2 U}{\partial H_\nu\, \partial H_\varrho} \right) + \frac{1}{k^2 T^2}\frac{\partial M_\sigma^e}{\partial E_\tau}\frac{\partial U}{\partial H_\nu}\frac{\partial U}{\partial H_\varrho} \right\rangle H^2. \tag{2.9}$$

Hence, the birefringence of an isotropic medium is independent of the magnetostriction as given by Eq. (2.6).

The constant of magneto-optical birefringence C, known as the Cotton-Mouton constant, is given as follows:

$$C = \frac{n_{||} - n_\perp}{n}\frac{1}{H_S^2}, \tag{2.10}$$

where H_S is the mean macroscopic magnetic field strength existing within the spherical sample. For a diamagnetic medium, H_S is practically identical with the magnetic field strength *in vacuo*, $H_S = H$. As $n_{||}$ and $n_\perp$ differ but little from n, the definition (2.10) can be rewritten as follows:

$$C = \frac{(n^2 + 2)^2}{6n^2}\left\{\frac{n_{||}^2 - 1}{n_{||}^2 + 2} - \frac{n_\perp^2 - 1}{n_\perp^2 + 2}\right\}\frac{1}{H_S^2}, \tag{2.11}$$

whence, by (2.9), we have

$$C = \frac{\pi(n^2 + 2)^2}{270n^2 V_S}\left(\frac{H}{H_S}\right)^2 \varepsilon_{\sigma\tau:\nu\varrho} \left\langle \frac{\partial^3 M_\sigma^e}{\partial E_\tau\, \partial H_\nu\, \partial H_\varrho} + \right.$$

$$\left. + \frac{1}{kT} \left(2\frac{\partial^2 M_\sigma^e}{\partial E_\tau\, \partial H_\nu} M_\varrho^m + \frac{\partial M_\sigma^e}{\partial E_\tau}\frac{\partial M_\nu^m}{\partial H_\varrho} \right) + \frac{1}{k^2 T^2}\frac{\partial M_\sigma^e}{\partial E_\tau} M_\nu^m M_\varrho^m \right\rangle, \tag{2.12}$$

with

$$M_\nu^m(\Gamma, E, H) = -\frac{\partial}{\partial E_\nu}\, U(\Gamma, E, H) \tag{2.13}$$

denoting the component of the magnetic dipole moment of the spherical sample presenting the configuration Γ in the presence of the fields E and H.

Eq. (2.12) presents the general form of the Cotton-Mouton constant for an arbitrary isotropic medium. If the latter is diamagnetic, *i. e.* if the magnetic dipole moment of the

sphere vanishes in the absence of an external magnetic field, $M^m(\Gamma, 0) = 0$, the general equation (2.12) goes over into

$$[C = \frac{\pi(n^2 + 2)^2}{270n^2 V_S} \left(\frac{H}{H_S}\right)^2 \varepsilon_{\sigma\tau:\nu\varrho} \left\langle \frac{\partial^3 M_\sigma^e}{\partial E_\tau \partial H_\nu \partial H_\varrho} + \frac{1}{kT} \frac{\partial M_\sigma^e}{\partial E_\tau} \frac{\partial M_\nu^m}{\partial H_\varrho} \right\rangle. \tag{2.14}$$

3. Molecular Cotton-Mouton Constant

According to König (1938), we define the molecular Cotton-Mouton constant C_m as follows:

$$C_m = \left\{ \frac{n_{\|}^2 - 1}{n_{\|}^2 + 2} - \frac{n_{\perp}^2 - 1}{n_{\perp}^2 + 2} \right\} \frac{V}{H^2}, \tag{3.1}$$

with V denoting the molar volume of the spherical sample.

The definitions of (2.11) and (3.1) yield jointly the relation

$$C_m^{\iota} = \frac{6n^2}{(n^2 + 2)^2} \left(\frac{H_S}{H}\right)^2 VC, \tag{3.2}$$

making possible the computation of the molar constant C_m from the experimentally measured Cotton-Mouton constant C.

On substitution of (2.9) in the definition (3.1), and by (2.13), the following equation is obtained for a diamagnetic medium:

$$C_m = \frac{\pi}{45} \varepsilon_{\sigma\tau:\nu\varrho} \left\langle \frac{\partial^3 M_\sigma^e}{\partial E_\tau \partial H_\nu \partial H_\varrho} + \frac{1}{kT} \frac{\partial M_\sigma^e}{\partial E_\tau} \frac{\partial M_\nu^m}{\partial H_\varrho} \right\rangle; \tag{3.3}$$

herein, the moments M_σ^e and M_ν^m now refer to the molar volume V. Obviously, (3.3) could also be derived from the relation (3.2) and Eq. (2.14).

The mechanism of magnetic birefringence can be explained within the framework of the atomic-molecular theory of the structure of the medium. To this effect, the moments M^e and M^m of the macroscopic sphere, as appearing in the general equation (3.3), have to be expressed by means of the respective moments relating to the microscopic properties of the individual atoms or molecules. Thus, let the macroscopic sphere of volume V contain N (Avogadro's number) molecules of one species. The dipole moments M_σ^e and M_ν^m of the volume V can now be expressed as the sums of the dipole moments present therein:

$$M_\sigma^e = \sum_{p=1}^{N} m_\sigma^{e(p)}, \qquad M_\nu^m = \sum_{q=1}^{N} m_\nu^{m(q)}, \tag{3.4}$$

where $m_\sigma^{e(p)}$ and $m_\nu^{m(q)}$ are the components, respectively, of the electric and magnetic moment of the p-th and q-th molecule of the specimen subjected to the external fields E and H.

Substitution of (3.4) in (3.3) yields the molecular Cotton-Mouton constant of a diamagnetic medium as follows:

$$C_m = \frac{\pi}{45} \varepsilon_{\sigma\tau:\nu\varrho} \left\langle \sum_{p=1}^{N} \frac{\partial^3 m_\sigma^{e(p)}}{\partial E_\tau \partial H_\nu \partial H_\varrho} + \frac{1}{kT} \sum_{p=1}^{N} \sum_{q=1}^{N} \frac{\partial m_\sigma^{e(p)}}{\partial E_\tau} \frac{\partial m_\nu^{m(q)}}{\partial H_\varrho} \right\rangle. \tag{3.5}$$

The p-th molecule immersed in the sphere is acted on by the effective electric field $\boldsymbol{E}+\boldsymbol{F}^{(p)}$ and effective magnetic field $\boldsymbol{H}+\boldsymbol{G}^{(p)}$. The additional electric field $\boldsymbol{F}^{(p)}$ and magnetic field $\boldsymbol{G}^{(p)}$ existing at the centre of the p-th molecule are given rise to by the remaining molecules in the sphere, and should be dealt with microscopically. Moreover, we assume the light wavelength to be considerably larger than the linear dimensions of the molecules, and its oscillation frequency to lie below the electronic absorption band of the medium. On expanding the electric moment $\boldsymbol{m}^{e(p)}$ in powers of the effective field strengths $\boldsymbol{E}+\boldsymbol{F}^{(p)}$ and $\boldsymbol{H}+\boldsymbol{G}^{(p)}$, we obtain in the case of diamagnetic molecules

$$m_\sigma^{e(p)} = \mu_\sigma^{(p)} + (\alpha_{\sigma\tau}^{(p)} + \beta_{\sigma\tau:\,\nu}^{(p)} F_\nu^{(p)} + \tfrac{1}{2}\,\gamma_{\sigma\tau:\,\nu\varrho}^{(p)} F_\nu^{(p)} F_\varrho^{(p)} + \ldots)\,(E_\tau + F_\tau^{(p)}) +$$

$$+\,\tfrac{1}{2}\,\xi_{\sigma:\,\tau\nu}^{(p)}(H_\tau + G_\tau^{(p)})\,(H_\nu + G_\nu^{(p)}) + \tfrac{1}{2}\,\eta_{\sigma\tau:\,\nu\varrho}^{(p)}(E_\tau + F_\tau^{(p)})\,(H_\nu + G_\nu^{(p)})\,(H_\varrho + G_\varrho^{(p)}) + \ldots, \quad (3.6)$$

wherein $\mu_\sigma^{(p)}$ is the σ-component of the dipole moment of the p-th isolated molecule, and $\alpha_{\sigma\tau}^{(p)}$ — the tensor of its electric polarizability. The tensors $\beta_{\sigma\tau:\nu}^{(p)}$, $\gamma_{\sigma\tau:\nu\varrho}^{(p)}$, $\xi_{\sigma:\tau\nu}^{(p)}$ and $\eta_{\sigma\tau:\nu\varrho}^{(p)}$ define the non-linear deformation of the p-th molecule due to the electric or magnetic field, and were originally introduced by Born (1933) in molecular optics of gases, and subsequently by Volkenshteyn (1951) and Buckingham and Pople (1955, 1956) under the designation of hyperpolarizability tensors[1].

The molecular electric field $\boldsymbol{F}^{(p)}$ is defined to within dipole interaction by the following equation (see, Kirkwood 1936):

$$F_\sigma^{(p)} = -\sum_{\substack{q=1 \\ q\neq p}}^{N} T_{\sigma\tau}^{(pq)}\, m_\tau^{(q)}; \quad (3.7)$$

herein, the tensor

$$T_{\sigma\tau}^{(pq)} = -\,r_{pq}^{-5}\,(3r_{pq\sigma}r_{pq\tau} - r_{pq}^2\,\delta_{\sigma\tau}) \quad (3.8)$$

accounts for interactions of the dipolar type, and $\boldsymbol{r}_{pq}$ is the vector connecting the centres of molecules p and q.

The molecular magnetic field is defined in analogy to (3.7) (see, Stephen 1958):

$$G_\sigma^{(p)} = -\sum_{\substack{q=1 \\ q\neq p}}^{N} T_{\sigma\tau}^{(pq)}\, m_\tau^{m(q)}, \quad (3.9)$$

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[1] By (3.6), the tensor of the differential polarizability of the molecule immersed in the medium at zero external fields is

$$\left(\frac{\partial m_\sigma^{e(p)}}{\partial E_\chi}\right)_0 = \left\{\alpha_{\sigma\tau}^{(p)} + \beta_{\sigma\tau:\nu}^{(p)} F_{o\nu}^{(p)} + \frac{1}{2}\,\gamma_{\sigma\tau:\nu\varrho}^{(p)} F_{o\nu}^{(p)} F_{o\varrho}^{(p)} + \ldots\right\}\left\{\delta_{\tau\chi} + \frac{\partial F_\tau^{(p)}}{\partial E_\chi}\Big|_0\right\}. \quad (3.6a)$$

Thus, in spite of the fact that the electric field strength E of the light wave is small and insufficient for producing non-linear polarization of the molecule, the existence of a (generally) very strong molecular electric field F in the condensed medium leads to non-linear deformation of the molecule as described by the tensors $\beta_{\sigma\tau:\nu}$ and $\gamma_{\sigma\tau:\nu\varrho}$. For this reason, we have introduced into Eq. (3.6) the terms $\beta_{\sigma\tau:\nu}^{(p)} F_\nu^{(p)}$ and $\frac{1}{2}\gamma_{\sigma\tau:\nu\varrho}^{(p)} F_\nu^{(p)} F_\varrho^{(p)}$, which do not appear in the case of a gaseous medium.

wherein, for diamagnetic molecules, the magnetic moment components are given as follows:

$$m_\sigma^{m(p)} = (\chi_{\sigma\tau}^{(p)} + \xi_{\nu:\sigma\tau}^{(p)} F_\nu^{(p)} + \tfrac{1}{2}\, \eta_{\nu\varrho:\sigma\tau}^{(p)} F_\nu^{(p)} F_\varrho^{(p)} + ...) (H_\tau + G_\tau^{(p)}) + ..., \qquad (3.10)$$

where $\chi_{\sigma\tau}^{(p)}$ is the magnetic polarizability tensor of molecule p.

From Eqs. (3.6), (3.7), (3.9) and (3.10), we have approximately

$$F_\sigma^{(p)} = F_{0\sigma}^{(p)} - \sum_{\substack{q=1 \\ q \neq p}}^{N} T_{\sigma\tau}^{(pq)} \alpha_{\tau\nu}^{(q)} E_\nu + \sum_{\substack{q=1 \\ q \neq p}}^{N} \sum_{\substack{r=1 \\ r \neq q}}^{N} T_{\sigma\tau}^{(pq)} \alpha_{\tau\nu}^{(q)} T_{\nu\varrho}^{(qr)} \alpha_{\varrho\lambda}^{(r)} E_\lambda - ... \qquad (3.11)$$

$$G_\sigma^{(p)} = - \sum_{\substack{q=1 \\ q \neq p}}^{N} T_{\sigma\tau}^{(pq)} \chi_{\tau\nu}^{(q)} H_\nu + \sum_{\substack{q=1 \\ q \neq p}}^{N} \sum_{\substack{r=1 \\ r \neq q}}^{N} T_{\sigma\tau}^{(pq)} \chi_{\tau\nu}^{(q)} T_{\nu\varrho}^{(qr)} \chi_{\varrho\lambda}^{(r)} H_\lambda - ... \qquad (3.12)$$

wherein

$$F_{0\sigma}^{(p)} = - \sum_{\substack{q=1 \\ q \neq p}}^{N} T_{\sigma\tau}^{(pq)} \mu_\tau^{(q)} + \sum_{\substack{q=1 \\ q \neq p}}^{N} \sum_{\substack{r=1 \\ r \neq q}}^{N} T_{\sigma\tau}^{(pq)} \alpha_{\tau\nu}^{(q)} T_{\nu\varrho}^{(qr)} \mu_\varrho^{(r)} - ... \qquad (3.13)$$

is the electric field strength at the centre of the p-th molecule of the medium, at vanishing external fields ($E = H = 0$).

In the case now under consideration, the configurational variables Γ of the system form a set of variables $\tau^N \equiv (r^N, \omega^N)$ describing the configuration of all N molecules present therein. This set of variables τ^N consists of the variables $r^N = (r_1, r_2 \dots r_N)$ describing the positions of the molecules, and of the variables $\omega^N \equiv (\omega_1, \omega_2, \dots \omega_N)$ determining their orientations. The statistical averaging operation denoted by brackets $\langle \quad \rangle$ in Eq. (3.5) can now be defined thus

$$\langle \Phi \rangle = \int \dots \int_{(n)} \Phi(\tau^N) P^{(n)}(\tau^n)\, d\tau^n, \qquad (3.14)$$

wherein

$$P^{(n)}(\tau^n) = \frac{\displaystyle\int \dots \int_{(N-n)} e^{-\frac{U(\tau^N)}{kT}}\, d\tau^{N-n}}{\displaystyle\int \dots \int_{(N)} e^{-\frac{U(\tau^N)}{kT}}\, d\tau^N} \qquad (3.15)$$

is the probability for a selected group of n molecules to present the configuration $\tau^n \equiv (\tau_1, \dots \tau_n) \equiv (r_1, \dots r_n; \omega_1, \dots \omega_n)$ independently of the configuration of the remaining N-n molecules of the system. The probability (3.15) fulfills the normalisation condition

$$\int \dots \int_{(n)} P^{(n)}(\tau^n) d\tau^n = 1. \qquad (3.16)$$

In the case of random molecular distribution, as for $r \to \infty$ or $T \to \infty$ (perfect gas), the probability (3.15) yields

$$\lim_{r \to \infty} P^{(n)}(\tau^n) = \lim_{T \to \infty} P^{(n)}(\tau^n) = \frac{1}{(\Omega V)^n}, \qquad (3.17)$$

wherein

$$V = \int d\boldsymbol{r}_1 = \ldots = \int d\boldsymbol{r}_{n}, \varOmega = \int d\omega_1 = \ldots = \int d\omega_{n'}$$

Henceforth, we shall utilize the statistical mean values of the respective sums of func-tions $\varPhi(\tau^n)$ as given by the expressions

$$\left\langle \sum_{p=1}^{N} \varPhi(\tau_p) \right\rangle = \varrho \int \varPhi(\tau_p)\, g^{(1)}(\tau_p)\, d\tau_p,$$

$$\left\langle \sum_{p=1}^{N} \sum_{\substack{q=1 \\ q\neq p}}^{N} \varPhi(\tau_p,\tau_q) \right\rangle = \varrho^2 \int \int \varPhi(\tau_p,\tau_q)\, g^{(2)}(\tau_p,\tau_q)\, d\tau_p\, d\tau_q,$$

$$\left\langle \sum_{p=1}^{N} \sum_{\substack{q=1 \\ q\neq p}}^{N} \sum_{\substack{q=1 \\ r\neq p \\ r\neq q}}^{N} \varPhi(\tau_p,\tau_q,\tau_r) \right\rangle = \varrho^3 \int \int \int \varPhi(\tau_p,\tau_q,\tau_r)\, g^{(3)}(\tau_p,\tau_q,\tau_r)\, d\tau_p\, d\tau_q\, d\tau_r, \ldots, \quad (3.18)$$

where $g^{(n)}(\tau^n) = g^{(n)}(r^n, \omega^n)$ are correlation functions of the configurational distribution, related to the probability $P^{(n)}(\tau^n)$ of (3.15) as follows:

$$g^{(n)}(\tau^n) = \frac{N!}{\varrho^n (N-n)!}\, P^{(n)}(\tau^n); \qquad (3.19)$$

herein, $\varrho = N/V$ is the number density of molecules of the medium.

For a distribution of the molecules independent of their mutual orientation, integra-tion of both sides of Eq. (3.19) extending over all orientations of the molecules yields the correlation functions

$$g^{(n)}(\boldsymbol{r}_{\blacksquare}^{n}) = \int \ldots \int_{(n)} g^{(n)}(r^n, \omega^n)\, d\omega^n = \frac{N!}{\varrho^n (N-n)!}\, P^{(n)}(\boldsymbol{r}^n), \qquad (3.20)$$

as employed and discussed by Kirkwood (see, Hill 1956) and De Boer (1949).

4. Non-dipolar Diamagnetic Fluids

We now proceed to a discussion of the general equation (3.5) for non-dipolar diamagnetic fluids. In a first approximation, the contributions from the molecular fields $\boldsymbol{F}$ and $\boldsymbol{G}$ to the expansions (3.6) and (3.10) can be neglected, whence

$$C_m = \frac{\pi}{45}\, \varepsilon_{\sigma\tau:\nu\varrho} \left\langle \sum_{p=1}^{N} \eta_{|\sigma\tau:\nu\varrho}^{(p)} + \frac{1}{kT} \sum_{p=1}^{N} \sum_{q=1}^{N} \alpha_{\sigma\tau}^{(p)} \chi_{\nu\varrho}^{(q)} \right\rangle. \qquad (4.1)$$

Assume a Cartesian coordinate system $X_1^{(p)} X_2^{(p)} X_3^{(p)} = (X_\alpha^{(p)})$, $\alpha = 1, 2, 3$, to be termed the molecular system, with origin at the centre of the p-th molecule. Similarly, the molecular system $(X_\gamma^{(q)})$, $\gamma = 1, 2, 3$ is attached to the centre of molecule q. We shall now carry out the transformation of the tensors $\alpha_{\sigma\tau}^{(p)}$, $\eta_{|\sigma\tau:\nu\varrho}^{(p)}$ and $\chi_{\nu\varrho}^{(q)}$ from the macroscopic coordinate

system (X_σ) to the molecular systems $(X_\alpha^{(p)})$ and $(X_\gamma^{(q)})$ by the formulas

$$\alpha_{\sigma\tau}^{(p)} = \omega_{\sigma\alpha}^{(p)} \omega_{\tau\beta}^{(p)} \alpha_{\alpha\beta}^{(p)}, \quad \chi_{\nu\varrho}^{(q)} = \omega_{\nu\gamma_i}^{(q)} \omega_{\varrho\delta}^{(q)} \chi_{\gamma\delta}^{(q)}, \quad \eta_{\sigma\tau:\nu\varrho}^{(p)} = \omega_{\sigma\alpha}^{(p)} \omega_{\tau\beta}^{(p)} \omega_{\nu\gamma}^{(p)} \omega_{\varrho\delta}^{(p)} \eta_{\alpha\beta:\gamma\delta}^{(p)}. \tag{4.2}$$

Here, the coefficients $\omega_{\sigma\alpha}^{(p)}, \ldots \omega_{\varrho\delta}^{(p)}$ of the transformation are the cosines of the angles subtended by the axes $X_\sigma, \ldots X_\varrho$ of the laboratory system and the axes $X_\alpha^{(b)}, \ldots X_\delta^{(p)}$ and $X_\alpha^{(q)}, \ldots X_\delta^{(q)}$ of the respective molecular systems. The directional cosines $\omega_{\sigma\alpha}^{(p)}, \ldots \omega_{\varrho\delta}^{(p)}$ fulfill the conditions of orthonormality

$$\delta_{\sigma\nu} \omega_{\sigma\alpha}^{(p)} \omega_{\nu\gamma}^{(p)} = \delta_{\alpha\gamma}, \quad \delta_{\tau\varrho} \omega_{\tau\beta}^{(p)} \omega_{\varrho\delta}^{(p)} = \delta_{\beta\delta}, \tag{4.3}$$

whereas, for the directional cosines $\omega_{\sigma\alpha}^{(p)}, \ldots \omega_{\varrho\delta}^{(p)}$ and $\omega_{\sigma\alpha}^{(q)}, \ldots \omega_{\varrho\delta}^{(q)}$, we have the conditions

$$\delta_{\sigma\nu} \omega_{\sigma\alpha}^{(p)} \omega_{\nu\gamma}^{(q)} = \omega_{\alpha\gamma}^{(pq)}, \quad \delta_{\tau\varrho} \omega_{\tau\beta}^{(p)} \omega_{\varrho\delta}^{(q)} = \omega_{\beta\delta}^{(pq)}, \ldots, \tag{4.4}$$

wherein $\omega_{\alpha\gamma}^{(pq)}$ is the cosine of the angle between the axes $X_\alpha^{(p)}$ and $X_\gamma^{(q)}$ of the molecular system attached to the p-th and q-th molecule, *etc.*

By Eqs. (4.2), (4.3) and (4.4), the following equation is obtained from (4.1) for the molecular constant of magnetic birefringence (see, Piekara and Kielich 1958, 1959):

$$C_m = \frac{\pi}{45} \left\langle \sum_{p=1}^{N} (3\eta_{\alpha\beta:\alpha\beta}^{(p)} + 3\eta_{\alpha\beta:\beta\alpha}^{(p)} - 2\eta_{\alpha\alpha:\beta\beta}^{(p)}) + \right.$$

$$\left. + \frac{1}{kT} \sum_{p=1}^{N} \sum_{q=1}^{N} \alpha_{\alpha\beta}^{(p)} \chi_{\gamma\delta}^{(q)} (3\omega_{\alpha\beta}^{(pq)} \omega_{\beta\delta}^{(pq)} + 3\omega_{\alpha\delta}^{(pq)} \omega_{\beta\gamma}^{(pq)} - 2\delta_{\alpha\beta} \delta_{\gamma\delta}) \right\rangle. \tag{4.5}$$

Taking into account the definitions of Eq. (3.18), the foregoing equations go over into

$$C_m = \frac{\pi\varrho}{45} \left\{ \varepsilon_{\alpha\beta:\gamma\delta} \int (\eta_{\alpha\beta:\gamma\delta}^{(p)} + \frac{1}{kT} \alpha_{\alpha\beta}^{(p)} \chi_{\gamma\delta}^{(p)}) g^{(1)} (\tau_p) \, d\tau_p + \right.$$

$$\left. + \frac{1}{kT} \varrho \iint \alpha_{\alpha\beta}^{(p)} \chi_{\gamma\delta}^{(q)} (3\omega_{\alpha\gamma}^{(pq)} \omega_{\beta\delta}^{(pq)} + 3\omega_{\alpha\delta}^{(pq)} \omega_{\beta\gamma}^{(pq)} - 2\delta_{\alpha\beta} \delta_{\gamma\delta}) g^{(2)} (\tau_p, \tau_q) \, d\tau_p \, d\tau_q \right\} \tag{4.6}$$

yielding finally

$$C_m = \frac{\pi N}{45} \left\{ 3\eta_{\alpha\beta:\alpha\beta} + 3\eta_{\alpha\beta:\beta\alpha} - 2\eta_{\alpha\alpha:\beta\beta} + \frac{1}{kT} (3\alpha_{\alpha\beta} \chi_{\alpha\beta} + 3\alpha_{\alpha\beta} \chi_{\beta\alpha} - 2\alpha_{\alpha\alpha} \chi_{\beta\beta}) + \right.$$

$$\left. + \frac{\varrho}{kT} \alpha_{\alpha\beta} \chi_{\gamma\delta} \int (3\omega_{\alpha\gamma}^{(pq)} \omega_{\beta\delta}^{(pq)} + 3\omega_{\alpha\delta}^{(pq)} \omega_{\beta\gamma}^{(pq)} - 2\delta_{\alpha\beta} \delta_{\gamma\delta}) g(\tau_{pq}) \, d\tau_{pq} \right\}, \tag{4.7}$$

with the notation $d\tau_{pq} = d\boldsymbol{r}_{pq} \, d\omega_p \, d\omega_q$.

In the case of a perfect gas, by (3.17) and (3.19), we have $g(\tau_{pq}) = \frac{1}{\Omega^2}$, whence

$$\alpha_{\alpha\beta} \chi_{\gamma\delta} \iint (3\omega_{\alpha\gamma}^{(pq)} \omega_{\beta\delta}^{(pq)} + 3\omega_{\alpha\delta}^{(pq)} \omega_{\beta\gamma}^{(pq)} - 2\delta_{\alpha\beta} \delta_{\gamma\delta}) \frac{d\omega_p \, d\omega_q}{\Omega^2} = 0. \tag{4.8}$$

If, moreover, the tensors $\alpha_{\alpha\beta}$ and $\chi_{\alpha\beta}$ are entirely symmetrical, and if the tensor $\eta_{\alpha\beta:\gamma\delta}$ is symmetrical in the pairs of indices $\alpha\beta$ and $\gamma\delta$, Eq. (4.7) with respect to (4.8) reduces to

$$C_m^{\text{gas}} = \frac{2\pi N}{45} \left\{ 3\eta_{\alpha\beta:\alpha\beta} - \eta_{\alpha\alpha:\beta\beta} + \frac{1}{kT} \left(3\alpha_{\alpha\beta}\,\chi_{\alpha\beta} - \alpha_{\alpha\alpha}\,\chi_{\beta\beta} \right) \right\}. \tag{4.9}$$

The constant C_m was derived in similar form by Born (1933), Volkenshteyn (1951), and Buckingham and Pople (1956)[2]. The first term herein, $(3\eta_{\alpha\beta:\alpha\beta} - \eta_{\alpha\alpha:\beta\beta})$, accounts for the temperature-independent effect of molecular deformation, whereas the second term, $(3\alpha_{\beta\alpha}\,\chi_{\alpha\beta} - \alpha_{\alpha\alpha}\,\chi_{\beta\beta})\,(kT)^{-1}$, — for Langevin's (1910) effect of molecular orientation, which decreases towards higher temperatures. Outside the range of absorption of the substance, the effect of molecular deformation is extremely small and can be neglected with respect to that of molecular orientation, which predominates in the case of anisotropic molecules.

For a gas whose molecules possess the spherical symmetry, we have

$$\alpha_{\alpha\beta} = \alpha\delta_{\alpha\beta}, \; \chi_{\alpha\beta} = \chi\delta_{\alpha\beta}, \; \eta_{\alpha\beta:\gamma\delta} = \eta_\perp\,\delta_{\alpha\beta}\,\delta_{\gamma\delta} + \tfrac{1}{2}\,(\eta_\| - \eta_\perp)\,(\delta_{\alpha\gamma}\,\delta_{\beta\delta} + \delta_{\alpha\delta}\,\delta_{\beta\gamma}), \tag{4.10}$$

and Eq. (4.9) reduces to the Buckingham-Pople formula (1956)

$$C_m^{\text{gas}} = \frac{2\pi}{3}\,N\,(\eta_\| - \eta_\perp), \tag{4.11}$$

wherein the coefficients $\eta_\|$ and $\eta_\perp$ account for the change in polarizability produced in the spherical molecule by the strong magnetic field, in the direction parallel and perpendicular to H, respectively. Eq. (4.11) is the molecular counterpart of Voigt's (1908) deformational theory: a gas consisting of spherical molecules becomes optically birefringent owing to the anisotropy induced in its molecules by the deformational effect of the external magnetic field. In gases consisting of atoms or of spherical molecules, Voigt's deformational effect is the only factor producing optical birefringence. Thus, Eq. (4.11) provides direct information on the changes undergone by an atom or spherical molecule when in a strong magnetic field.

If the axes of the molecular systems coincide with the principle axes of the molecules, Eq. (4.7) assumes the form

$$C_m = \frac{2\pi N}{45} \left\{ 3\eta_{\alpha\beta:\alpha\beta} - \eta_{\alpha\alpha:\beta\beta} + \frac{1}{kT} \sum_{s,t=1}^{3} \alpha_s\,\chi_t \left[3\delta_{st} - 1 + \right. \right.$$
$$\left. \left. + \varrho \int (3\cos^2 \theta_{st}^{(pq)} - 1)\,g(\tau_{pq})\,d\tau_{pq} \right] \right\}, \tag{4.12}$$

wherein $\theta_{st}^{(pq)}$ is the angle between the principal axes $X_s^{(p)}$ and $X_t^{(q)}$ of molecules p and q, respectively, α_s and χ_t being their polarizabilities in the direction of these axes.

For molecules of the diamagnetic liquid presenting the axial symmetry, Eq. (4.12)

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[2] The constant C_m in the paper by Buckingham and Pople (1956) differs by the factor 1/9, and the tensor $\eta_{\alpha\beta;\gamma\delta}$ — by a factor of 2.

yields the expression

$$C_m = \frac{2\pi N}{45} \left\{ 3\eta_{\alpha\beta:\alpha\beta} - \eta_{\alpha\alpha:\beta\beta} + \frac{18}{kT} \alpha\delta_\alpha \chi\delta_\chi (1 + J_A) \right\}, \tag{4.13}$$

where

$$J_A = \tfrac{1}{2}\varrho \int (3\cos^2 \theta^{(pq)} - 1)\, g(\tau_{pq})\, d\tau_{pq} \tag{4.14}$$

is an integral parameter accounting for the angular correlations of the axially symmetric molecules; $\theta^{(pq)}$ denotes the angle between the axis of symmetry of molecule p and that of molecule q. The dimensionless quantities introduced by Langevin

$$\delta_\alpha = \frac{\alpha_3 - \alpha_1}{3\alpha}, \qquad \delta_\chi = \frac{\chi_3 - \chi_1}{3\chi} \tag{4.15}$$

are a measure of the anisotropy of the optical and magnetic polarizability of the isolated molecule, wherein the polarizabilities in the direction of the symmetry axis of the molecule are denoted by α_3 and χ_3, and those in the direction perpendicular thereto — by α_1 and χ_1. The quantities

$$\alpha = \tfrac{1}{3}(\alpha_3 + 2\alpha_1), \qquad \chi = \tfrac{1}{3}(\chi_3 + 2\chi_1) \tag{4.16}$$

denote the mean optical and magnetic polarizability of the isolated molecule, respectively.

Eq. (4.13) with the parameter J_A given by Eq. (4.14) is analogical with results of Buckingham and Pople (1956).

We shall take account of the effect of the molecular fields $\boldsymbol{F}$ and $\boldsymbol{G}$ on the magnetic birefringence of the liquid. At first we shall restrict the problem to the case of isotropically polarizable molecules. On substituting the expansions (3.6) and (3.10) in the general equation (3.5), and by (4.10), we have

$$C_m = \frac{2\pi}{45} \left\{ 5(\eta_{||} - \eta_{\perp}) \left\langle \sum_{p=1}^{N} \left(3 + \frac{\partial F_\alpha^{(p)}}{\partial E_\alpha} + ... \right) \right\rangle + \right.$$

$$\left. + \frac{\alpha\chi}{kT} \left\langle \sum_{p=1}^{N} \sum_{q=1}^{N} \left(3 \frac{\partial F_\alpha^{(p)}}{\partial E_\beta} \frac{\partial G_\alpha^{(q)}}{\partial H_\beta} - \frac{\partial F_\alpha^{(p)}}{\partial E_\alpha} \frac{\partial G_\beta^{(q)}}{\partial H_\beta} \right) + ... \right\rangle \right\}. \tag{4.17}$$

In the case of spherical molecules, Eqs. (3.11) and (3.12) yield

$$\frac{\partial F_\alpha^{(p)}}{\partial E_\chi} = -\alpha \sum_{\substack{r=1 \\ r \neq p}}^{N} T_{\alpha\chi}^{(pr)} + \alpha^2 \sum_{\substack{r=1 \\ r \neq p}}^{N} \sum_{\substack{s=1 \\ s \neq r}}^{N} T_{\alpha\beta}^{(pr)} T_{\beta\chi}^{(rs)} - ...,$$

$$\frac{\partial G_\alpha^{(q)}}{\partial H_\chi} = -\chi \sum_{\substack{r=1 \\ r \neq q}}^{N} T_{\alpha\chi}^{(qr)} + \chi^2 \sum_{\substack{r=1 \\ r \neq q}}^{N} \sum_{\substack{s=1 \\ s \neq q}}^{N} T_{\alpha\beta}^{(qr)} T_{\beta\chi}^{(rs)} - ..., \tag{4.18}$$

whence Eq. (4.17) goes over into

$$C_m = \frac{2\pi}{15} \left\{ 5 \left(\eta_{||} - \eta_\perp\right) \left\langle \sum_{p=1}^{N} \left(1 + \frac{\alpha^2}{3} \sum_{\substack{r=1 \\ r \neq p}}^{N} \sum_{\substack{s=1 \\ s \neq r}}^{N} T_{\alpha\beta}^{(pr)} T_{\alpha\beta}^{(rs)} + \dots \right) \right\rangle + \right.$$

$$\left. + \frac{\alpha^2 \chi^2}{kT} \left\langle \sum_{p=1}^{N} \sum_{q=1}^{N} \sum_{\substack{r=1 \\ r \neq p}}^{N} \sum_{\substack{s=1 \\ s \neq q}}^{N} T_{\alpha\beta}^{(pr)} T_{\alpha\beta}^{(qs)} + \dots \right\rangle \right\}. \tag{4.19}$$

Eq. (4.19) is rewritten as follows:

$$C_m = \frac{2\pi N}{15} \left\{ 5(\eta_{||} - \eta_\perp)\,(1 + \alpha^2 J_R) + 6\,\frac{\alpha^2 \chi^2}{kT}\,J_R' \right\}, \tag{4.20}$$

wherein, by (3.18), we have

$$J_R = \frac{1}{3N} \left\langle \sum_{p=1}^{N} \sum_{\substack{r=1 \\ r \neq p}}^{N} \sum_{\substack{s=1 \\ s \neq r}}^{N} T_{\alpha\beta}^{(pr)} T_{\alpha\beta}^{(rs)} + \dots \right\rangle =$$

$$= \frac{\varrho}{3V} \left\{ \iint T_{\alpha\beta}^{(pq)} T_{\alpha\beta}^{(pq)} g^{(2)}(\tau_p,\,\tau_q)\,d\tau_p d\tau_q + \right.$$

$$\left. + \varrho \iiint T_{\alpha\beta}^{(pq)} T_{\alpha\beta}^{(qr)} g^{(3)}(\tau_p,\,\tau_q,\,\tau_r)\,d\tau_p d\tau_q d\tau_r + \dots \right\},$$

$$J_R' = \frac{1}{6N} \left\langle \sum_{p=1}^{N} \sum_{q=1}^{N} \sum_{\substack{r=1 \\ r \neq p}}^{N} \sum_{\substack{s=1 \\ s \neq q}}^{N} T_{\alpha\beta}^{(pr)} T_{\alpha\beta}^{(qs)} + \dots \right\rangle =$$

$$= \frac{\varrho}{3V} \left\{ \iint T_{\alpha\beta}^{(pq)} T_{\alpha\beta}^{(pq)} g^{(2)}(\tau_p,\,\tau_q)\,d\tau_p d\tau_q + \right.$$

$$\left. + 2\varrho \iiint T_{\alpha\beta}^{(pq)} T_{\alpha\beta}^{(qr)} g^{(3)}(\tau_p,\,\tau_q,\,\tau_r)\,d\tau_p d\tau_q d\tau_r + \dots \right\}. \tag{4.21}$$

Restricting ourselves to pairwise correlations, we have by Eq. (4.21):

$$J_R = J_R' = 2\varrho \int r_{pq}^{-6}\, g(r_{pq})\, dr_{pq} = 8\pi\varrho \int_0^\infty r^{-4}\, g(r)\, dr. \tag{4.22}$$

The integral parameter J_R describes the radial correlations of the spherical molecules; $g(r)$ is the radial correlation function introduced by Zernike and Prins (1927) into the theory of X-ray scattering in liquids.

For molecules not presenting hyperpolarizability, $\eta_{||} - \eta_\perp = 0$, and by Eq. (4.20) we have

$$C_m = \frac{4\pi}{5kT}\,\alpha^2 \chi^2\, N J_R. \tag{4.23}$$

The foregoing result is equivalent to the statement that, in fluids of spherical molecules, radial correlations of the molecules can lead to magnetic birefringence even in the absence of molecular hyperpolarizability[3].

Non-linear variations of the molecular polarizability can be given rise to not only by an external field, as is the case in gases, but also by the molecular fields F or G, provided the medium is sufficiently condensed. Applying the expansions of Eqs. (3.6) and (3.10), we have from the general equation (3.5), for non-dipolar liquids whose molecules present a centre of inversion,

$$C_m = \frac{\pi}{45}\, \varepsilon_{\sigma\tau:\,\nu\varrho} \left\langle \sum_{p=1}^{N} (\eta_{\sigma\tau:\,\nu\varrho}^{(p)} + \ldots) + \frac{1}{kT} \sum_{p=1}^{N} \sum_{q=1}^{N} \left(\alpha_{\sigma\tau}^{(p)} \chi_{\nu\varrho}^{(q)} + \right.\right.$$

$$\left.\left. + \frac{1}{2}\, \alpha_{\sigma\tau}^{(p)} \eta_{\lambda\mu:\,\nu\varrho}^{(q)} F_{0\lambda}^{(q)} F_{0\mu}^{(q)} + \frac{1}{2}\, \chi_{\nu\varrho}^{(q)} \gamma_{\sigma\tau:\,\lambda\mu}^{(p)} F_{0\lambda}^{(p)} F_{0\mu}^{(p)} + \ldots \right) \right\rangle. \tag{4.24}$$

In the case of non-dipolar molecules possessing a permanent quadrupole moment, the molecular electric field $F_0^{(p)}$ in Eq. (4.24) assumes the form

$$F_{0\gamma}^{(p)} = \tfrac{1}{3} \sum_{\substack{q=1 \\ q \neq p}}^{N} T_{\lambda\varepsilon\eta}^{(pq)}\, \Theta_{\varepsilon\eta}^{(q)}. \tag{4.25}$$

The permanent quadrupole moment of the q-th molecule is given by the tensor

$$\Theta_{\varepsilon\eta}^{(q)} = \tfrac{1}{2} \sum_{n} e_n^{(q)} (3 r_{n\varepsilon}^{(q)} r_{n\eta}^{(q)} - r_{nq}^2\, \delta_{\varepsilon\eta}), \tag{4.26}$$

wherein $e_n^{(q)}$ is the n-th electric charge of the q-th molecule, and $\boldsymbol{r}_n^{(q)}$ — its radius vector. The tensor

$$T_{\lambda\varepsilon\eta}^{(pq)} = 3 r_{pq}^{-7} \{ 5 r_{pq\lambda} r_{pq\varepsilon} r_{pq\eta} - r_{pq}^2 (r_{pq\lambda}\delta_{\varepsilon\eta} + r_{pq\varepsilon}\,\delta_{\eta\lambda} + r_{pq\eta}\delta_{\lambda\varepsilon}) \} \tag{4.27}$$

accounts for interaction of the quadrupole-quadrupole type.

A more advanced discussion of Eq. (4.24) leads to highly involved expressions, even if the quadrupolar molecules have the axial symmetry. Thus, we shall refrain from pushing forward with it at present. Our sole aim was to stress that, in general, the orientational part of C_m can be dependent on the molecular electric field given rise to by the quadrupole moments of the molecules of nondipolar liquids.[4]

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[3]) Similarly, the effect of the terms $\partial F_\alpha/\partial E_\beta$ and $\partial G_\alpha/\partial H_\beta$ on the constant C_m can be computed for the case of anisotropic molecules of non-dipolar liquids. Expressions are obtained which, on replacing therein the magnetic by the electric polarizability, are analogons of the formulas derived by Mazur and Postma (1959) for Kerr's constant in non-dipolar liquids.

[4]) By writing the mean square of the reaction field gradient resulting from Onsager's model in place of F^2, Eq. (4.24) can be brought to a form adapted to numerical evaluations, by a procedure quite similar to that used in a paper by the present author on light scattering in quadrupolar liquids (Kielich 1960).

5. Dipolar Diamagnetic Fluids

Since magnetic birefringence does not involve orientation of the electric dipoles in the external magnetic field as is the case for electric birefringence, Eq. (4.9) extends to dipolar gases also. In certain cases, Eqs. (4.7), (4.12) or (4.13) also can be applied to dipolar liquids, as done in the existing theories of the Cotton-Mouton effect. However, in dipolar fluids whose molecules possess large dipolar moments, a strong molecular electric field F generally exists, which can affect the shape of the magnetic birefringence noticeably. The following equation now holds:

$$C_m^{\cdot} = \frac{\pi}{45}\, \varepsilon_{\sigma\tau:\nu\varrho} \left\langle \sum_{p=1}^{N} (\eta_{\sigma\tau:\nu\varrho}^{(p)} + \ldots) + \frac{1}{kT} \sum_{p=1}^{N} \sum_{q=1}^{N} (\alpha_{\sigma\tau}^{(p)}\, \chi_{\nu\varrho}^{(q)} + \right.$$

$$\left. + \alpha_{\sigma\tau}^{(p)}\, \xi_{\lambda:\nu\varrho}^{(q)}\, F_{0\lambda}^{(q)} + \chi_{\nu\varrho}^{(q)}\, \beta_{\sigma\tau:\lambda}^{(p)}\, F_{0\lambda}^{(p)} + \beta_{\sigma\tau:\lambda}^{(p)}\, \xi_{\mu:\nu\varrho}^{(q)}\, F_{0\lambda}^{(p)} F_{0\mu}^{(q)} + \ldots) \right\rangle \tag{5.1}$$

as derived from the general equation (3.5) and Eqs. (3.6) and (3.10); the molecular field F_0 is given by (3.13).

We shall now proceed to a discussion of the foregoing equation for the case of dipolar molecules having the axial symmetry. On taking the axis of symmetry of the molecule as axis 3 of the molecular system, we have, by the transformational formulas (4.2),

$$\alpha_{\sigma\tau}^{(p)} = \alpha\delta_{\sigma\tau} + \alpha\delta_{\alpha}(3\omega_{3\sigma}^{(p)}\omega_{3\tau}^{(p)} - \delta_{\sigma\tau}), \qquad \chi_{\nu\varrho}^{(q)} = \chi\delta_{\nu\varrho} + \chi\delta_{\chi}(3\omega_{3\nu}^{(q)}\omega_{3\varrho}^{(q)} - \delta_{\nu\varrho}),$$

$$\beta_{\sigma\tau:\varepsilon}^{(p)} = \beta\delta_{\sigma\tau}\omega_{3\varepsilon}^{(p)} + \beta\delta_{\beta}(3\omega_{3\sigma}^{(p)}\omega_{3\tau}^{(p)} - \delta_{\sigma\tau})\omega_{3\varepsilon}^{(p)}, \qquad \xi_{\varepsilon:\nu\varrho}^{(q)} = \xi\delta_{\nu\varrho}\omega_{3\varepsilon}^{(q)} + \xi\delta_{\xi}(3\omega_{3\nu}^{(q)}\omega_{3\varrho}^{(q)} - \delta_{\nu\varrho})\omega_{3\varepsilon}^{(q)},$$

$$\tag{5.2}$$

wherein the quantities

$$\delta_{\beta} = \frac{\beta_3 - \beta_1}{3\beta}, \qquad \delta_{\xi} = \frac{\xi_3 - \xi_1}{3\xi}, \tag{5.3}$$

$$\beta = \tfrac{1}{3}(\beta_3 + 2\beta_1), \qquad \xi = \tfrac{1}{3}(\xi_3 + 2\xi_1) \tag{5.4}$$

provide a measure of the anisotropy of the respective hyperpolarizabilities of the molecules, together with their mean hyperpolarizabilities; herein, we have used the following notation:

$$\beta_{11:3} = \beta_{22:3} = \beta_1, \qquad \xi_{3:11} = \xi_{3:22} = \xi_1,$$

$$\beta_{33:3} = \beta_3, \qquad \xi_{3:33} = \xi_3.$$

Restricting ourselves to the first term in the expansion of Eq. (3.13), we have

$$F_{0\varepsilon}^{(p)} = -\sum_{\substack{r=1 \\ r\neq p}}^{N} T_{\varepsilon\eta}^{(pr)}\mu_{\eta}^{(r)} = -\mu\sum_{\substack{r=1 \\ r\neq p}}^{N} T_{\varepsilon\eta}^{(pr)}\omega_{3\eta}^{(r)}, \tag{5.5}$$

and Eq. (5.1) yields, by (5.2) and (5.5)

$$
C_m = \frac{2\pi}{45} \left\langle \sum_{p=1}^{N} (3\eta_{\alpha\beta:\alpha\beta}^{(p)} - \eta_{\alpha\alpha:\beta\beta}^{(p)}) + \frac{9}{kT}\, \alpha\delta_\alpha\, \chi\delta_\chi \sum_{p=1}^{N} \sum_{q=1}^{N} (3\cos^2\theta^{(pq)} - 1) \left\{ 1 + \right.\right.
$$

$$
+ \frac{\beta\delta_\beta}{\alpha\delta_\alpha}\, \mu \sum_{\substack{r=1 \\ r \neq p}}^{N} (3\cos\theta^{(p)}\cos\theta^{(r)} - \cos\theta^{(pr)})\, r_{pr}^{-3} +
$$

$$
+ \frac{\xi\delta_\xi}{\chi\delta_\chi}\, \mu \sum_{\substack{r=1 \\ r \neq q}}^{N} (3\cos\theta^{(q)}\cos\theta^{(r)} - \cos\theta^{(qr)})\, r_{qr}^{-3} + \dots \left.\left.\right\} \right\rangle. \tag{5.6}
$$

Herein, $\cos\theta^{(pq)} = \cos\theta^{(p)}\cos\theta^{(q)} + \sin\theta^{(p)}\sin\theta^{(q)}\cos(\varphi_q - \varphi_p)$, with $\theta^{(p)}$ and $\theta^{(q)}$ denoting the angles between the axis of symmetry of the p-th or q-th molecule, respectively, and the vector $\boldsymbol{r}_{pq}$ connecting their centres, whereas φ_p and φ_q are the azimuths of their axes of symmetry.

On introducing into (5.6) the correlation functions as given by Eqs. (3.18) and (3.19), we have

$$
C_m = \frac{2\pi\varrho}{45} \left\{ (3\eta_{\alpha\beta:\alpha\beta} - \eta_{\alpha\alpha:\beta\beta})\, V + \frac{18}{kT}\, \alpha\delta_\alpha\, \chi\delta_\chi \left[V + \right.\right.
$$

$$
+ \frac{1}{2}\, \varrho \iint (3\cos^2\theta^{(pq)} - 1)\, g^{(2)}(\tau_p, \tau_q)\, d\tau_p\, d\tau_q \left.\right] +
$$

$$
+ \frac{9\mu}{kT}\, (\alpha\delta_\alpha\, \xi\delta_\xi + \chi\delta_\chi\, \beta\delta_\beta)\, \varrho \left[\iint (3\cos^2\theta^{(pq)} + 1) \times \right.
$$

$$
\times\, (3\cos\theta^{(p)}\cos\theta^{(q)} - \cos\theta^{(pq)})\, r_{pq}^{-3}\, g^{(2)}(\tau_p, \tau_q)\, d\tau_p\, d\tau_q + \varrho \iiint (3\cos^2\theta^{(pq)} - 1) \times
$$

$$
\times\, (3\cos\theta^{(p)}\cos\theta^{(q)} - \cos\theta^{(pr)})\, r_{pr}^{-3}\, g^{(3)}(\tau_p, \tau_q, \tau_r)\, d\tau_p\, d\tau_q\, d\tau_r \left.\left.\right] \right\}. \tag{5.7}
$$

On neglecting three-fold and higher correlations herein, we have, finally,

$$
C_m = \frac{2\pi N}{45} \left\{ (3\eta_{\alpha\beta:\alpha\beta} - \eta_{\alpha\alpha:\beta\beta}) + \frac{18}{kT}\, \alpha\delta_\alpha\, \chi\delta_\chi \left[1 + J_A + \right.\right.
$$

$$
+ \frac{1}{2}\, \mu\varrho \left(\frac{\beta\delta_\beta}{\alpha\delta_\alpha} + \frac{\xi\delta_\xi}{\chi\delta_\chi} \right) \int (3\cos^2\theta^{(pq)} + 1)(3\cos\theta^{(p)}\cos\theta^{(q)} -
$$

$$
- \cos\theta^{(pq)})\, r_{pq}^{-3}\, g(\tau_{pq})\, d\tau_{pq} \left.\left.\right] \right\}. \tag{5.8}
$$

Thus, we have computed the contributions to the orientational part of the constant C_m due to the permanent dipoles and hyperpolarizability of the molecules.

Eq. (5.8) as given above is not adapted to numerical evaluations, as not all molecular parameters appearing therein are known. This obstacle is circumvented by means of the Onsager model (1936) replacing the molecular field $\boldsymbol{F_0}$ by the mean reaction field $\boldsymbol{\overline{R}}$; for anisotropic molecules, the latter is given as follows (Kielich 1960):

$$F_{0s}^{(p)} = \overline{R}_s = \frac{[2(\varepsilon - 1)\,(n^2 - 1)]}{(2\varepsilon + 1)\,(n^2 + 2) - 2(\varepsilon - 1)\,(n^2 - 1)\,\lambda_s} \cdot \frac{\mu_s}{\alpha}\,, \qquad (5.9)$$

where $\lambda_s = \alpha_s/\alpha$ is the parameter of anisotropy of the polarizability per isolated molecule, and ε — the electric permittivity of the dipolar liquid.

On substituting in Eq. (5.1) the mean molecular field of Eq. (5.9), and by utilizing the expressions (5.2), we obtain, on neglecting angular correlations (the temperature-independent term, which is small in this case, is omitted):

$$C_m = \frac{4\pi N}{5kT}\,\alpha\delta_\alpha\chi\delta_\chi \left\{1 + \left(\frac{\beta\delta_\beta}{\alpha\delta_\alpha} + \frac{\xi\delta_\xi}{\chi\delta_\chi}\right)\frac{\mu^*}{\alpha}\right\}, \qquad (5.10)$$

with the notation

$$\frac{\mu^*}{\mu} = \frac{2(\varepsilon - 1)\,(n^2 - 1)}{(2\varepsilon + 1)\,(n^2 + 2) - 2(\varepsilon - 1)\,(n^2 - 1)\,\lambda_3}\,. \qquad (5.11)$$

6. Magnetic Birefringence of Multi-component Systems

We shall now consider the case of the macroscopic sphere of volume V containing molecules of different species, namely, $N_1 = x_1 N$ molecules of the first species, $N_2 = x_2 N$ ones of the second, ... and $N_i = x_i N$ molecules of the i-th species, with

$$x_i = \frac{N_i}{N} = \frac{N_i}{\sum\limits_i N_i},$$

denoting the mole fraction of the i-th component of the system. Summation over the mole fraction of all components of the system yields unity, $\sum\limits_i x_i = 1$.

For the multi-component system as defined above, Eq. (3.4) has to be replaced by the following set of equations:

$$M_\sigma^e = \sum_i \sum_{p=1}^{Ni} m_\sigma^{e(p,i)}, \quad M_\nu^m = \sum_j \sum_{q=1}^{Nj} m_\nu^{m(q,j)}. \qquad (6.1)$$

Herein, $m_\sigma^{e(p,i)}$ and $m_\nu^{m(q,j)}$ are the components of the electric and magnetic dipole moments, respectively, of the p-th molecule belonging to species i and of the q-th one of species j. In the present case, the expressions (3.6)—(3.13) remain valid, provided the index i or j is added everywhere beside p or q. The general equation (3.3) holds for an arbitrary

diamagnetic medium and, hence, it is valid for multi-component systems, so that with (6.1) we now have

$$C_m = \frac{\pi}{45} \, \varepsilon_{\sigma\tau:\nu\varrho} \left\langle \sum_i \sum_{p=1}^{Ni} \frac{\partial^3 m_\sigma^{e(p,i)}}{\partial E_\tau \, \partial H_\nu \, \partial H_\varrho} + \right.$$

$$\left. + \frac{1}{kT} \sum_i \sum_j \sum_{p=1}^{Ni} \sum_{q=1}^{Nj} \frac{\partial m_\sigma^{e(p,i)}}{\partial E_\tau} \frac{\partial m_\nu^{m(q,j)}}{\partial H_\varrho} \right\rangle, \qquad (6.2)$$

being the general equation for the molecular constant of magnetic birefringence in a multi-component system.

By a procedure analogous to that of Section 4, Eq. (6.2) yields in a first approximation

$$C_m = \frac{\pi}{45} \left\langle \sum_i \sum_{p=1}^{Ni} (3\eta_{\alpha\beta:\alpha\beta}^{(p,i)} + 3\eta_{\alpha\beta:\beta\alpha}^{(p,i)} - 2\eta_{\alpha\alpha:\beta\beta}^{(p,i)}) + \right.$$

$$\left. + \frac{1}{kT} \sum_i \sum_j \sum_{p=1}^{Ni} \sum_{q=1}^{Nj} \alpha_{\alpha\beta}^{(p,i)} \chi_{\gamma\delta}^{(q,j)} (3\omega_{\alpha\gamma}^{(pq,ij)} \omega_{\beta\delta}^{(pq,ij)} + 3\omega_{\alpha\delta}^{(pq,ij)} \omega_{\beta\gamma}^{(pq,ij)} - 2\delta_{\alpha\beta}\delta_{\beta\gamma}) \right\rangle, \qquad (6.3)$$

with $\omega_{\alpha\gamma}^{(pq,ij)}$ denoting the cosine of the angle between the axes $X_\alpha^{(p)}$ and $X_\gamma^{(q)}$ of the molecular systems attached to the p-th molecule of the i-th species and to the q-th one of the j-th species. The tensors $\alpha_{\alpha\beta}^{(p,i)}$, $\eta_{\alpha\beta:\gamma\delta}^{(p,i)}$ and $\chi_{\gamma\delta}^{(q,j)}$ retain their physical meaning, albeit with respect to molecule p of species i or to molecule q of species j.

By analogy to the expressions (3.18), we now have

$$\left\langle \sum_{p=1}^{Ni} \Phi_i(\tau_p) \right\rangle = x_i \varrho \int \Phi_i(\tau_p) \, g_i^{(1)}(\tau_p) \, d\tau_p,$$

$$\left\langle \sum_{\substack{p=1 \\ q \neq p}}^{Ni} \sum_{q=1}^{Nj} \Phi_{ij}(\tau_p, \tau_q) \right\rangle = x_i x_j \varrho^2 \int\int \Phi_{ij}(\tau_p, \tau_q) \, g_{ij}^{(2)}(\tau_p, \tau_q) \, d\tau_p d\tau_q,$$

$$\left\langle \sum_{\substack{p=1 \\ q \neq p \\ r \neq q}}^{Ni} \sum_{\substack{q=1 \\ r \neq p}}^{Nj} \sum_{r=1}^{Nk} \Phi_{ijk}(\tau_p, \tau_q, \tau_r) \right\rangle$$

$$= x_i x_j x_k \varrho^3 \int\int\int \Phi_{ijk}(\tau_p, \tau_q, \tau_r) \, g_{ijk}^{(3)}(\tau_p, \tau_q, \tau_r) \, d\tau_p d\tau_q d\tau_r, \dots, \qquad (6.4)$$

wherein $g_i^{(1)}$ is the ordinary correlation function for the molecules of species i, $g_{ij}^{(2)}$ — the binary correlation function for molecules of species i and j, $g_{ijk}^{(3)}$ — the ternary correlation function for those of species i, j and k, and so on.

With respect to the expressions of (6.4), Eq. (6.3) now assumes the form

$$C_m = \frac{\pi N}{45} \left\{ \sum_i x_i (3\eta_{\alpha\beta:\alpha\beta}^{(i)} + 3\eta_{\alpha\beta:\beta\alpha}^{(i)} - 2\eta_{\alpha\alpha:\beta\beta}^{(i)}) + \frac{1}{kT} \sum_i \sum_j \alpha_{\alpha\beta}^{(i)} \chi_{\gamma\delta}^{(j)} [x_i \delta_{ij} \varepsilon_{\alpha\beta:\gamma\delta} + \right.$$

$$\left. + x_i x_j \varrho \int (3\omega_{\alpha\gamma}^{(pq,ij)} \omega_{\beta\delta}^{(pq,ij)} + 3\omega_{\alpha\delta}^{(pq,ij)} \omega_{\beta\gamma}^{(pq,ij)} - 2\delta_{\alpha\beta}\delta_{\gamma\delta}) \, g_{ij}(\tau_{pq}) \, d\tau_{pq}] \right\}. \qquad (6.5)$$

If the molecules of all components of the system present the axial symmetry, Eq. (6.5) reduces to

$$C_m = \frac{2\pi N}{45} \left\{ \sum_i x_i (3\eta^{(i)}_{\alpha\beta:\,\alpha\beta} - \eta^{(i)}_{\alpha\alpha:\,\beta\beta}) + \frac{18}{kT} \sum_i \sum_j \alpha_i \delta_{\alpha,\,i}\, \chi_j \delta_{\chi,\,j}\, (x_i\delta_{ij} + x_i x_j J^{(ij)}_A) \right\}, \quad (6.6)$$

wherein

$$J^{(ij)}_A = \tfrac{1}{2}\varrho \int (3\cos^2\theta^{(ij)}_{pq} - 1)\, g_{ij}(\tau_{pq})\, d\tau_{pq}, \quad (6.7)$$

is the parameter of angular correlation of the axially symmetric molecules of species i and j.

The angular correlation factor $(x_i\,\delta_{ij} + x_i x_j J^{(ij)}_A)$ appearing in Eq. (6.6) was derived by the present author in an earlier paper on the theory of molecular scattering of light in multi-component systems (see, Kielich 1960, 1961).

Eq. (6.5) can be put in the form

$$C_m = \sum_i x_i\, C^{(i)}_m + \sum_i \sum_j x_i x_j\, C^{(ij)}_m + \dots, \quad (6.8)$$

with

$$C^{(i)}_m = \frac{2\pi}{45}\, N \left\{ 3\eta^{(i)}_{\alpha\beta:\,\alpha\beta} - \eta^{(i)}_{\alpha\alpha:\,\beta\beta} + \frac{1}{kT}\, (3\alpha^{(i)}_{\alpha\beta}\,\chi^{(i)}_{\alpha\beta} - \alpha^{(i)}_{\alpha\alpha}\,\chi^{(i)}_{\beta\beta}) \right\}, \quad (6.9)$$

$$C^{(ij)}_m = \frac{\pi N}{45 kT}\, \alpha^{(i)}_{\alpha\beta}\,\chi^{(j)}_{\gamma\delta}\,\varrho \int (3\omega^{(pq,\,ij)}_{\alpha\gamma}\omega^{(pq,\,ij)}_{\beta\delta} + 3\omega^{(pq,\,ij)}_{\alpha\delta}\omega^{(pq,\,ij)}_{\beta\gamma} - 2\delta_{\alpha\beta}\delta_{\gamma\delta})\, g_{ij}(\tau_{pq})\, d\tau_{pq}. \quad (6.10)$$

From the shape of Eq. (6.8), the molecular Cotton-Mouton constant of a multi-component system is independent of the density and intermolecular correlations in the first approximation only. If the system presents no molecular interaction, we have $C^{(ij)}_m = 0$, and Eq. (6.8) becomes

$$C_m = \sum_i x_i\, C^{(i)}_m, \quad (6.11)$$

expressing additivity of the molecular constants $C^{(i)}_m$ of the components.

Obviously, Eq. (6.11) obtains for a mixture of diamagnetic gases wherein intermolecular correlation is zero or so small as to be negligible. In the general case, by Eq. (6.8), the constant C_m of a multi-component system does not fulfill the law of additivity as a result of interaction both between molecules of the same species and between those of the various components in condensed systems.

For axially symmetric molecules, the term in C_m of Eq. (6.8) accounting for angular correlation of molecules i and j is of the form

$$C^{(ij)}_m = \frac{4\pi N}{5 kT}\, \alpha_i \delta_{\alpha,\,i}\, \chi_j \delta_{\chi,\,j} J^{(ij)}_A. \quad (6.12)$$

If, in particular, a two-component system is considered, Eq. (6.8) yields:

$$C_m = x_1\, C^{(1)}_m + x_2\, C^{(2)}_m + x_1^2\, C^{(11)}_m + x_1 x_2\, (C^{(12)}_m + C^{(21)}_m) + x_2^2\, C^{(22)}_m + \dots, \quad (6.13)$$

with $x_1 + x_2 = 1$.

In the case when all molecules possess the axial symmetry, we have on the basis of (6.9) and (6.12) (the small hyperpolarizability effect will be neglected):

$$C_m^{(11)} = C_m^{(1)} J_A^{(11)}, \quad C_m^{(22)} = C_m^{(2)} J_A^{(22)} \tag{6.14}$$

$$C_m^{(1)} = \frac{4\pi N}{5kT} \alpha_1 \delta_{\alpha,1} \chi_1 \delta_{\chi,1}, \quad C_m^{(2)} = \frac{4\pi N}{5kT} \alpha_2 \delta_{\alpha,2} \chi_2 \delta_{\chi,2}, \tag{[(6.15)}$$

$$C_m^{(12)} = \frac{4\pi N}{5kT} \alpha_1 \delta_{\alpha,1} \chi_2 \delta_{\chi,2} J_A^{(12)}, \quad C_m^{(21)} = \frac{4\pi N}{5kT} \alpha_2 \delta_{\alpha,2} \chi_1 \delta_{\chi,1} J_A^{(21)}. \tag{6.16}$$

7. Discussion

We shall now proceed to numerical evaluations which will bring to the fore the contributions of the various molecular factors to the magnetic birefringence of the liquid.

In the first place, we shall consider a liquid of spherical molecules. In this case, from Eqs. (4.11) and (4.20), evaluation of C_m requires knowledge of the values of the magnetic hyperpolarizability $\eta_{||}$ and $\eta_{\perp}$ of the atoms or molecules, which as yet we do not possess. The sole exception is that of atomic hydrogen, for which, according to a computation by Buckingham and Pople (1956),

$$\eta_{||}^H = -\frac{159}{8} \frac{a_0^6}{mc^2} = -53 \times 10^{-44} \text{ e. m. u.}$$

$$\eta_{\perp}^H = -\frac{797}{24} \frac{a_0^6}{mc^2} = -89 \times 10^{-44} \text{ e. m. u.,} \tag{7.1}$$

where a_0 is the Bohr radius in the ground state, m—the electron mass, and c—the velocity of light. Identical values of $\eta_{||}$ and $\eta_{\perp}$ can be assumed for the argon atom, as the atoms of hydrogen and argon present almost identical electric hyperpolarizability (see, Buckingham and Pople 1955) amounting to

$$\gamma^H = 0.67 \times 10^{-36} \text{ e. s. u. }, \quad \gamma^{Ar} = 0.7 \times 10^{-36} \text{ e. s. u.}$$

On substituting the figures of (7.1) in Eq. (4.11), we have, for both hydrogen and argon in the gaseous state,

$$C_m^{gas} = 45.4 \times 10^{-20} \text{ e. m. u.}$$

Let us now turn to liquid argon and compute the effect of the molecular fields therein on the constant C_m according to Eq. (4.20), which we now write as follows:

$$C_m = C_m^{gas} \left\{ 1 + \left[1 + \frac{6\chi^2}{5(\eta_{||} - \eta_{\perp})kT} \right] \alpha^2 J_R \right\}, \tag{7.2}$$

with the constant C_m^{gas} given by (4.11), and J_R — by (4.22).

The parameter of radial correlations, J_R, can be determined from the results on X-ray scattering due to Eisenstein and Gringrich (1942). In particular, for liquid argon under a pressure of 0.8 atm and at $T = 84.4°K$, we have (see, Buckingham and Stephen 1957)

$J_R = 8.4 \times 10^{45}$ cm^{-6}. Introducing moreover $\alpha = 1.63 \times 10^{-24}$ cm^3 and $\chi = -3.2 \times 10^{-29}$cm^3 we have, by (7.2),

$$C_m = C_m^{\text{gas}}(1 + 0.03) = 0.47 \times 10^{-18} \text{ e. m. u.}$$

Hence, the contribution to C_m due to the existence of an electric and magnetic molecular field in liquid argon amounts to no more than 3%.

The parameter J_R can also be determined numerically from formulas yielding the degree of depolarization D of scattered light and the coefficient of Rayleigh scattering S which, in the approximation of the present theory, are of the form (Buckingham and Stephen 1957, Kielich 1960)

$$D = \frac{6\alpha^2 J_R}{5\varrho kT\beta_T (1 + \ldots) + 7\alpha^2 J_R}, \qquad (7.3)$$

$$S = \frac{\pi^2(n^2 - 1)^2}{10\,\lambda^4\varrho}\{5\varrho kT\beta_T(1 + \ldots) + 13\alpha^2 J_R\}; \qquad (7.4)$$

herein, β_T is the isothermal compressibility coefficient of the medium.

Let us consider e. g. the case of carbon tetrachloride with $\alpha = 10.5 \times 10^{-24}$ cm^3, $\varrho = 6.23 \times 10^{21}$ cm^{-3}, $\beta_T = 105 \times 10^{-12}$ cgs, and $D = 0.06$ at 20°C (Bhagavantam 1942) whence, by (7.3), we have

$$J_R = \frac{5\varrho kT\beta_T D}{\alpha^2(6 - 7D)} = 1.3 \times 10^{43} \text{ cm}^{-6}.$$

We shall now utilize the foregoing value of J_R for computing the electric hyperpolar izability of the CCl$_4$ molecule from the equation for the molecular Kerr constant of liquid consisting of spherical molecules (Kielich 1960):

$$K_m = \frac{2\pi N}{15}\left\{5(\gamma_{\parallel} - \gamma_{\perp})(1 + \ldots) + 6\,\frac{\alpha^2 a^2}{kT}\,J_R\right\}, \qquad (7.5)$$

with a denoting the mean static polarizability of the spherical molecules.

The molecular constant K_m of CCl$_4$ will be computed from the following experimental data at 20°C: $V = 96.5$ cm^3, $n = 1.461$, $\varepsilon = 2.24$ and $K = 31.4 \times 10^{-14}$ e. s. u. (see, Stuart and Volkman 1933), whence

$$K_m = \frac{54n^2 V}{(n^2 + 2)^2 (\varepsilon + 2)^2}\,K = 11.37 \times 10^{-12} \text{ e. s. u.}$$

On substituting the foregoing values of K_m and J_R in Eq. (7.5), the change in electric polarization of the CCl$_4$ molecule, as due to a strong electric field, results as

$$\gamma_{\parallel} - \gamma_{\perp} = \tfrac{2}{3}\gamma = 4.34 \times 10^{-36} \text{ e. s. u.}$$

There is one point to be made here. In the case of the electric birefringence of liquid CCl$_4$, the contribution to K_m from radial correlations and the molecular electric field,

$$K_m^R = \frac{4\pi N}{5kT}\,\alpha^2 a^2 J_R = 5.9 \times 10^{-12} \text{ e. s. u.,}$$

is somewhat larger than the amount

$$K_m^{\text{def}} = \frac{2\pi}{3} N (\gamma_{||} - \gamma_{\perp}) (1 + \ldots) = 5.47 \times 10^{-12} \text{ e. s. u.}$$

resulting from the effect of molecular deformation (Voigt's effect).

We thus see that the mean electric hyperpolarizability of the CCl_4 molecule as computed above, $\gamma = 6.51 \times 10^{-36}$ e. s. u., is 9.7 times larger than the electric hyperpolarizability of the hydrogen atom, $\gamma = 0.67 \times 10^{-36}$ e. s. u. If we now assume that their magnetic hyperpolarizabilities present much the same ratio (this is justified with respect to the accuracy of our evaluation), we can write for the CCl_4 molecule, by (7.1),

$$\eta_{||}^{CCl_4} = 9.7 \eta_{||}^H = -514 \times 10^{-44} \text{ e. m. u.}, \qquad \eta_{\perp}^{CCl_4} = 9.7 \eta_{\perp}^H = -863 \times 10^{-44} \text{ e. m. u.}$$

Introducing these values in Eq. (4.11) yields

$$C_m^{\text{gas}} = 4.4 \times 10^{-18} \text{ e. m. u.}$$

We shall also evaluate the effect of the molecular fields on C_m in liquid carbon tetrachloride. On substituting in (7.2), in addition to the above data, $\chi = -10.9 \times 10^{-29}$ cm^3, we have

$$C_m = C_m^{\text{gas}} (1 + 0.002) = 4.4 \times 10^{-18}.$$

These evaluations of K_m and C_m for liquid CCl_4 make it clear that, inasmuch as the contribution to its electric birefringence from the effect related to the molecular field and radial correlations of the molecules is very high (51%), it plays no part at all in the magnetic birefringence (0.2%) where Voigt's effect predominates decisively.

As yet, no measurements of the magnetic birefringence of carbon tetrachloride are available. The evaluation of a constant amounting to $C_m = 4.4 \times 10^{-18}$ shows that there is some hope for the experimental detection of magnetic birefringence in CCl_4 by applying a strong magnetic field and a measuring device of sufficient sensitivity.

For liquids whose molecules are strongly anisotropic, the numerically small term $(3\eta_{\alpha\beta:\alpha\beta} - \eta_{\alpha\alpha:\beta\beta})$ in Eq. (4.13) can be dropped, yielding

$$C_m = C_m^{\text{gas}} (1 + J_A) \qquad (7.6)$$

wherein

$$C_m^{\text{gas}} = \frac{4\pi N}{5kT} \alpha \delta_\alpha \chi \delta_\lambda \qquad (7.7)$$

is the molecular Cotton-Mouton constant of the diamagnetic fluid in the state of gas, and J_A — the angular correlation parameter defined by Eq. (4.14).

The numerical computation of J_A for a liquid is a highly involved matter. We are, however, able to determine J_A numerically from Eq. (7.6), provided the constants C_m and C_m^{gas} are experimentally known. Thus, e. g. for benzene at 20°C we have $C_m = 171 \times 10^{-17}$ (Burge and Snellman 1949) and $C_m^{\text{gas}} = 335 \times 10^{-17}$ (König 1938), for which Eq. (7.6) yields

$$J_A = \frac{C_m}{C_m^{\text{gas}}} - 1 = -0.49. \qquad (7.8)$$

For comparison, we shall now determine J_A from the degree of depolarization of scattered light (Anselm 1947, Kielich 1960):

$$D = \frac{6\delta_\alpha^2 (1 + J_A)}{5\varrho kT \beta_T + 7 \delta_\alpha^2 (1 + J_A)} \, . \tag{7.9}$$

For benzene, $\delta_\alpha^2 = 3.69 \times 10^{-2}$, $\beta_T = 94 \times 10^{-6}$ atm^{-1}, $\varrho = 6.78 \times 10^{21}$ cm^{-6}, and $D = 43.5 \times 10^{-2}$ (De Vaucouleurs 1951), so that Eq. (7.9) now yields a value of

$$J_A' = \frac{5\varrho kT \beta_T^* D}{\delta_\alpha^2 (6 - 7D)} - 1 = - 0.48. \tag{7.10}$$

Consequently, for benzene the formulas (7.8) and (7.10) yield coinciding values of the parameter J_A.

From Eqs. (7.6) and (7.9) we have the relation

$$C_m = C_m^{\text{gas}} \frac{5\varrho kT \beta_T D}{\delta_\alpha^2 (6 - 7D)} \tag{7.11}$$

making possible to compute the constant C_m of a liquid if the degree of depolarization of scattered light D for it is known experimentally.

Let us now go over to the discussion of Eq. (5.10), which holds in the case of dipolar liquids. As get, we have no knowledge of the numerical values of the hyperpolarizabilities β and ξ of dipolar molecules. One of these, β, can be derived with comparative ease from the light scattering constant (Rayleigh ratio) and the degree of depolarization of scattered light (see, Kielich 1960):

$$S = \frac{\pi^2 (n^2 - 1)^2}{2\lambda^4 \varrho} \left\{ \left(1 + 2 \frac{\mu^* \beta}{\alpha^2}\right) \varrho kT \beta_T + \frac{13}{5} \left(1 + 2 \frac{\mu^* \beta \delta_\beta}{\alpha^2 \delta_\alpha}\right) \delta_\alpha^2 \right\}, \tag{7.12}$$

$$D = \frac{6 \left(1 + 2 \frac{\mu^* \beta \delta_\beta}{\alpha^2 \delta_\alpha}\right) \delta_\alpha^2}{5 \left(1 + 2 \frac{\mu^* \beta}{\alpha^2}\right) \varrho kT \beta_T + 7 \left(1 + 2 \frac{\mu^* \beta \delta_\beta}{\alpha^2 \delta_\alpha}\right) \delta_\alpha^2}, \tag{7.13}$$

wherein the dipolar moment μ^* of the axially symmetric molecule is given by Eq. (5.11). If we assume the approximation of $\lambda_3 = 1$, which is exact for an isotropically polarizable molecule, Eq. (5.11) reduces to

$$\frac{\mu^*}{\mu} = \frac{2(\varepsilon - 1)(n^2 - 1)}{3(2\varepsilon + n^2)} \tag{7.14}$$

and Eq. (7.13) becomes identical with the one derived by Buckingham and Stephen (1957).

In the case of chloroform, at 20°C, we have $\varepsilon = 4.81$, $n = 1.458$, $\mu = 1.05 \times 10^{-18}$ e. s. u., $\alpha_3 = 6.68 \times 10^{-24}$ cm^3, $\alpha_1 = 9.01 \times 10^{-24}$ cm^3, $\varrho = 7.5 \times 10^{21}$ cm^{-3}, $\beta_T = 94 \times \times 10^{-6}$ atm^{-1}, $D = 0.242$ and $S = 18.7 \times 10^{-6}$ cm^{-1}. Here, the light scattering constant was computed from the relation $S = 0.4 S_{\text{C}_6\text{H}_6}$ (see, Bhagavantam, 1942), wherein the scattering constant for benzene was assumed as $S_{\text{C}_6\text{H}_6} = 46.8 \times 10^{-6}$ cm^{-1} from measurements

by Carr and Zimm (1950) at $\lambda = 4358$ Å reduced to $t = 20°C$. Substitution of these data in Eqs. (7.12) and (7.13) yields

$$\beta_3 = 9.6 \times 10^{-29} \text{ e. s. u.}, \qquad \beta_1 = 12.1 \times 10^{-29} \text{ e. s. u.},$$

whence the electric hyperpolarizability anisotropy of the $CHCl_3$ molecule amounts to

$$3\beta\delta_\beta = \beta_3 - \beta_1 = -2.5 \times 10^{-29} \text{ e. u. s.}$$

With this evaluation of the hyperpolarizabilities, we have

$$\frac{\beta\delta_\beta}{\alpha\delta_\alpha} \frac{\mu^*}{\alpha} = 0.32,$$

which means that the contribution to the constant C_m as given by Eq. (5.10) from the molecule's electric hyperpolarizability alone is considerable, amounting to 32%.

If the magnetic polarizability anisotropy $3\chi\delta_\varkappa = \chi_3 - \chi_1$ of the isolated molecule were also known (e. g. from measurements of the magnetic birefringence in the gaseous state), it would be quite easy to compute the change in anisotropy of the magnetic polarizability, $3\xi\delta_\xi = \xi_3 - \xi_1$, due to the molecular electric field existing in the liquid, from Eq. (5.10).

Obviously, in dealing with liquids whose molecules present a large dipole moment (e. g. one exceeding 1.5 Debye), it is to be expected that the part played in the magnetic birefringence by the molecular electric field and the effect of hyperpolarizability of the dipolar molecules related thereto will be much greater.

From the expansion of Eq. (3.6a) we derive approximate formulas for the components of the effective polarizability parallel and perpendicular to the axis of symmetry of the molecule:

$$\pi_3 = \alpha_3 + \beta_3 \overline{F}_3 + \ldots,$$

$$\pi_1 = \alpha_1 + \beta_1 \overline{F}_3 + \ldots \qquad (7.15)$$

For the Onsager model, with respect to Eq. (5.9), the mean molecular field $\overline{F}_3$ is given by

$$\overline{F}_3 = \frac{\mu^*}{\alpha}, \qquad (7.16)$$

where μ^* is the dipole moment (5.11).

In the case of chloroform, $\alpha = 8.233 \times 10^{-24} \text{ cm}^3$, $\mu^* = 24.5 \times 10^{-20}$ e. s. u., $\beta_1 = 12.1 \times 10^{-29}$ e. s. u. and $\beta_3 = 9.6 \times 10^{-29}$ e. s. u., and Eq. (7.15) yields

$$\pi_3 = \alpha_3 \left(1 + \frac{\beta_3}{\alpha_3} \overline{F}_3 + \ldots \right) = \alpha_3 (1 + 0.43) = 9.55 \times 10^{-24} \text{cm}^3,$$

$$\pi_1 = \alpha_1 \left(1 + \frac{\beta_1}{\alpha_1} \overline{F}_3 + \ldots \right) = \alpha_1 (1 + 0.40) = 12.61 \times 10^{-24} \text{ cm}^3.$$

Thus, owing to non-linear deformation produced by the strong electric molecular field, the $CHCl_3$ molecule on passing from a gaseous into a condensed medium raises its polarizability by as much as 40%.

The foregoing considerations thus lead to the conclusion that the effect of non-linear molecular deformation due to the strong electric molecular field in the liquid plays a much greater part in the magnetic birefringence than the analogical effect brought about by an external magnetic field, *i. e.* than Voigt's effect.

8. *Conclusions*

From the foregoing molecular theory of magnetic birefringence and its discussion it is clear that the molecular Cotton-Mouton constant, C_m, of diamagnetic fluids can depend quite generally on a considerable number of factors of a microscopic nature. The part played by each of these factors can be generally said to be different, and is dependent in principle on the species and structure of the atoms or molecules and on the interaction between them.

Investigation of the magnetic birefringence in the gaseous state is a source of data on the optical and magnetic properties of the isolated molecules. In liquids, the molecular constant C_m depends not only on the optical and magnetic properties of the isolated molecule, but is moreover dependent on their electric properties (*e. g.* on their dipole or quadrupole moments). The electric properties of the molecules influence the magnetic birefringence of the liquid indirectly, both through the potential energy of molecular interaction or the molecular correlation function, and through the molecular electric field producing hyperpolarizability of the dipolar or quadrupolar molecules.

In the case of an atomic gas or of one consisting of spherical molecules, magnetic birefringence is due to the temperature-independent non-linear deformational effect alone. In the liquid state, however, this effect appears together with a temperature-dependent effect resulting from radial correlations of the spherical atoms or molecules. This latter effect is determined by the parameter J_R. The magnetic birefringence of a liquid whose molecules are anisotropic depends almost entirely on the effect of molecular orientation intimately related to angular correlations of the molecules. In the special case of axially symmetric molecules and in the first approximation of the theory, the angular correlations are described by the single integral parameter J_R. Identical parameters J_R and J_A appear in the theory of light scattering also. It should be possible to apply the parameters J_R and J_A as determined from both these effects for obtaining fuller understanding of other molecular orientational effects, such as *e. g.* the Kerr effect or that of dielectric saturation involving, in addition to J_R and J_A, other more highly complicated parameters of the angular correlations. In the case of dipolar liquids, the formulas for the molecular Cotton-Mouton constant C_m, the degree of depolarization of scattered light D, and the scattering constant S make possible to assess numerically the anisotropy of hyperpolarizability of the dipolar molecules. In particular, the anisotropy of the electric hyperpolarizability of the chloroform molecule was determined.

The theory of the magnetic birefringence of multi-component systems presents a high degree of complication, as involving not only correlations between molecules belonging to the same species but also correlations between molecules of the different components of the system. The molecular constant C_m behaves additively in the case of a mixture of perfect gases only. In solutions. owing to intermolecular correlations, the orientational part

of C_m fails to fulfill the condition of additivity. Light scattering in multi-component systems is similarly dependent on the intermolecular correlations.

Thus, research work on magnetic birefringence and light scattering is a source of valuable information concerning the electric, magnetic and optical properties of the isolated molecule and various molecular correlations. Data thus obtained on the molecular functions of the configurational distribution may well be of decisive importance in the statistical theory of liquids with spherical or anisotropic molecules.

APPENDIX A

Expansion of $\langle \Phi \rangle_{E,H}$ in powers of the field strengths E and H

Let us consider an arbitrary function $\Phi = \Phi(\Gamma, \boldsymbol{E}, \boldsymbol{H})$ describing the state of the system at configuration Γ and subjected to the effect of the external fields $\boldsymbol{E}$ and $\boldsymbol{H}$. We denote the mean statistical value of Φ in the presence of the fields $\boldsymbol{E}$ and $\boldsymbol{H}$ by $\langle \Phi \rangle_{E,H}$. By classical statistical mechanics, $\langle \Phi \rangle_{E,H}$ is given by the formula

$$\langle \Phi \rangle_{E,H} = \frac{\int \Phi(\Gamma, \boldsymbol{E}, \boldsymbol{H}) e^{-\frac{U(\Gamma, \boldsymbol{E}, \boldsymbol{H})}{kT}} d\Gamma}{\int e^{-\frac{U(\Gamma, \boldsymbol{E}, \boldsymbol{H})}{kT}} d\Gamma}. \tag{A.1}$$

In the case under consideration, the electric field strength of the light wave is generally small, and we can restrict ourselves to the linear approximation in E when expanding $\langle \Phi \rangle_{E,H}$ in powers of E and H, thus

$$\langle \Phi \rangle_{E,H} = \langle \Phi \rangle + \left\{ \frac{\partial}{\partial E} \langle \Phi \rangle_{E,H} \right\}_0 E +$$

$$+ \left\{ \frac{\partial^2}{\partial E \partial H} \langle \Phi \rangle_{E,H} \right\}_0 EH + \frac{1}{2} \left\{ \frac{\partial^3}{\partial E \partial H^2} \langle \Phi \rangle_{E,H} \right\}_0 EH^2 + ..., \tag{A.2}$$

wherein $\langle \Phi \rangle$ without indices denotes the mean statistical value of the function Φ in the absence of external fields as given by Eq. (2.5). It should be held in mind that, by the definition of (A.1), $\langle \Phi \rangle_{E,H}$ depends on E and H both directly, through the function $\Phi(\Gamma, \boldsymbol{E}, \boldsymbol{H})$ and indirectly, through the potential energy $U(\Gamma, \boldsymbol{E}, \boldsymbol{H})$. The respective coefficients of the expansion (A.2) are now obtained as follows:

$$\left\{ \frac{\partial}{\partial E} \langle \Phi \rangle_{E,H} \right\}_0 = \left\langle \frac{\partial \Phi}{\partial E} - \frac{\Phi}{kT} \frac{\partial U}{\partial E} \right\rangle + \frac{1}{kT} \langle \Phi \rangle \left\langle \frac{\partial U}{\partial E} \right\rangle,$$

$$\left\{ \frac{\partial^2}{\partial E \partial E} \langle \Phi \rangle_{E,H} \right\}_0 = \left\langle \frac{\partial^2 \Phi}{\partial E \partial H} - \frac{1}{kT} \left(\frac{\partial \Phi}{\partial E} \frac{\partial U}{\partial H} + \frac{\partial \Phi}{\partial H} \frac{\partial U}{\partial E} + \Phi \frac{\partial^2 U}{\partial E \partial H} \right) + \right.$$

$$+ \frac{\Phi}{k^2 T^2} \frac{\partial U}{\partial E} \frac{\partial U}{\partial H} \right\rangle + \frac{1}{kT} \left\langle \frac{\partial \Phi}{\partial E} - \frac{\Phi}{kT} \frac{\partial U}{\partial E} \right\rangle \left\langle \frac{\partial U}{\partial H} \right\rangle +$$

$$+ \frac{1}{kT} \left\langle \frac{\partial \Phi}{\partial H} - \frac{\Phi}{kT} \frac{\partial U}{\partial H} \right\rangle \left\langle \frac{\partial U}{\partial E} \right\rangle + \frac{\langle \Phi \rangle}{kT} \left\langle \frac{\partial^2 U}{\partial E \partial H} + \frac{1}{kT} \left(2 \left\langle \frac{\partial U}{\partial E} \right\rangle - \frac{\partial U}{\partial E} \right) \frac{\partial U}{\partial H} \right\rangle ,$$

$$\left\{ \frac{\partial^3}{\partial E \partial H^2} \langle \Phi \rangle_{E,H} \right\}_0 = \left\langle \frac{\partial^3 \Phi}{\partial E \partial H^2} - \frac{1}{kT} \left(2 \frac{\partial^2 \Phi}{\partial E \partial H} \frac{\partial U}{\partial H} + \frac{\partial^2 \Phi}{\partial H^2} \frac{\partial U}{\partial E} + \Phi \frac{\partial^3 U}{\partial E \partial H^2} + \right. \right.$$

$$\left. + 2 \frac{\partial \Phi}{\partial H} \frac{\partial^2 U}{\partial E \partial H} + \frac{\partial \Phi}{\partial E} \frac{\partial^2 U}{\partial H^2} \right) + \frac{\Phi}{k^2 T^2} \left(\frac{\partial U}{\partial E} \frac{\partial^2 U}{\partial H^2} + 2 \frac{\partial^2 U}{\partial E \partial H} \frac{\partial U}{\partial H} \right) +$$

$$\left. + \frac{1}{k^2 T^2} \left(\frac{\partial \Phi}{\partial E} \frac{\partial U}{\partial H} + 2 \frac{\partial \Phi}{\partial H} \frac{\partial U}{\partial E} \right) \frac{\partial U}{\partial H} - \frac{\Phi}{k^3 T^3} \frac{\partial U}{\partial E} \left(\frac{\partial U}{\partial H} \right)^2 \right\rangle +$$

$$+ \frac{\langle \Phi \rangle}{kT} \left\langle \frac{\partial^3 U}{\partial E \partial H^2} - \frac{1}{kT} \left(\frac{\partial U}{\partial E} \frac{\partial^2 U}{\partial H^2} + 2 \frac{\partial^2 U}{\partial E \partial H} \frac{\partial U}{\partial H} \right) + \frac{1}{k^2 T^2} \frac{\partial U}{\partial E} \left(\frac{\partial U}{\partial H} \right)^2 \right\rangle +$$

$$+ \frac{2}{kT} \left\langle \frac{\partial^2 \Phi}{\partial E \partial H} - \frac{1}{kT} \left(\Phi \frac{\partial^2 U}{\partial E \partial H} + \frac{\partial \Phi}{\partial E} \frac{\partial U}{\partial H} + \frac{\partial \Phi}{\partial H} \frac{\partial U}{\partial E} \right) + \frac{\Phi}{k^2 T^2} \frac{\partial U}{\partial E} \frac{\partial U}{\partial H} \right\rangle \left\langle \frac{\partial U}{\partial H} \right\rangle +$$

$$+ \frac{1}{kT} \left\langle \frac{\partial^2 \Phi}{\partial H^2} - \frac{1}{kT} \left(\Phi \frac{\partial^2 U}{\partial H^2} + 2 \frac{\partial \Phi}{\partial H} \frac{\partial U}{\partial H} \right) + \frac{\Phi}{k^2 T^2} \left(\frac{\partial U}{\partial H} \right)^2 \right\rangle \left\langle \frac{\partial U}{\partial E} \right\rangle +$$

$$+ \frac{1}{kT} \left\langle \frac{\partial \Phi}{\partial E} + \frac{1}{kT} (2 \langle \Phi \rangle - \Phi) \frac{\partial U}{\partial E} \right\rangle \left\langle \frac{\partial^2 U}{\partial H^2} + \frac{1}{kT} \left(2 \left\langle \frac{\partial U}{\partial H} \right\rangle - \frac{\partial U}{\partial H} \right) \frac{\partial U}{\partial H} \right\rangle +$$

$$+ \frac{2}{kT} \left\langle \frac{\partial \Phi}{\partial H} + \frac{1}{kT} (2 \langle \Phi \rangle - \Phi) \frac{\partial U}{\partial H} \right\rangle \left\langle \frac{\partial^2 U}{\partial E \partial H} + \frac{1}{kT} \left(2 \left\langle \frac{\partial U}{\partial E} \right\rangle - \frac{\partial U}{\partial E} \right) \frac{\partial U}{\partial H} \right\rangle +$$

$$+ \frac{6}{k^3 T^3} \langle \Phi \rangle \left\langle \frac{\partial U}{\partial E} \right\rangle \left\langle \frac{\partial U}{\partial H} \right\rangle^2 , \dots \tag{A.3}$$

By Eq. (2.3), the function of state is now of the form

$$\Phi = \frac{1}{V_S} (\boldsymbol{M}^e - \boldsymbol{M}_0^e) \cdot \boldsymbol{e} = \frac{1}{V_S} (M_\sigma^e - M_{0\sigma}^e) e_\sigma. \tag{A.4}$$

We assume that the sample of the isotropic medium when acted on by a strong magnetic field changes its total volume V_S only, without undergoing a change in shape, and that this change is a quadratic function of the field strength H. The moment $\boldsymbol{M}^e$ being a function of the fields $\boldsymbol{E}$ and $\boldsymbol{H}$, we have, on taking magnetostriction into account,

$$\left\langle \frac{\partial \Phi}{\partial E} \right\rangle = \frac{1}{V_S} \left\langle \frac{\partial M_\sigma^e}{\partial E_\tau} e_\sigma e_\tau \right\rangle ,$$

$$\left\langle \frac{\partial^2 \Phi}{\partial E \partial H} \right\rangle = \frac{1}{V_S} \left\langle \frac{\partial^2 M_\sigma^e}{\partial E_\tau \partial H_\nu} e_\sigma e_\tau h_\nu \right\rangle ,$$

$$\left\langle \frac{\partial^3 \Phi}{\partial E \partial H^2} \right\rangle = \frac{1}{V_S} \left\{ \left\langle \frac{\partial^3 M_\sigma^e}{\partial E_\tau \partial H_\nu \partial H_\varrho} e_\sigma e_\tau h_\nu h_\varrho \right\rangle - \frac{1}{V_S} \left\langle \frac{\partial M_\sigma^e}{\partial E_\tau} e_\sigma e_\tau \right\rangle \left(\frac{\partial^2 V_S}{\partial H^2} \right)_0 \right\} . \tag{A.5}$$

On substitution of (A.4) and (A.5) in the expansion (A.2) and (A.3), and on taking into account that isotropic averageing involves the vanishing of all terms containing odd powers of the coordinates of the unit vectors $\boldsymbol{e}$ and $\boldsymbol{h}$, Eq. (2.3) yields the expansion (2.4).

REFERENCES

Anselm, A. J., *Zh. exper. teor. Fiz.*, **17,** 489 (1947).

Bhagavantam, S., *Scattering of Light and the Raman Effect* (Chemical Publishing Co., New York, 1942).

De Boer, J., *Rep. Progr. Phys.*, **12,** 305 (1949).

Born, M., *Optik* (J. Springer, Berlin, 1933).

Buckingham, A. D., and Pople, J. A., *Proc. Phys. Soc.* (London), **A 68,** 905 (1955); *B* **69,** 1133 (1956).

Buckingham, A. D. and Stephen, M. J., *Trans. Faraday Soc.*, **53,** 884 (1957).

Burge, F. J. and Snellman, O., *Phil. Mag.*, **40,** 994 (1949).

Carr, C. I. and Zimm, B. H., *J. Chem. Phys.*, **18,** 1616 (1950).

Cotton, A., and Mouton, H., *C. R. Acad. Sci.* (Paris), **145,** 229 (1907).

Debye, P., *Phys. Z.*, **36,** 100, 193 (1935).

Eisenstein, A., and Gingrich, N. S., *Phys. Rev.*, **58,** 307 (1940); **62,** 261 (1942).

Fowler, R. H., *Proc. Roy. Soc.*, **A 149,** 1 (1935).

Frenkel, J., *Kinetic Theory of Liquids* (Oxford University Pres, 1946).

Hill, T. L., *Statistical Mechanics* (Mc Graw-Hill Book Company, Inc., New York, 1956).

Kerr, J., *Phil. Mag.*, 4, **50,** 337, 446 (1875).

Kielich, S., *Acta phys. Polon.*, **17,** 239 (1958); **19,** 149, 573 (1960); **20,** 83 (1961).

Kielich, S., and Piekara, A., *Acta phys. Polon.*, **18,** 439 (1959).

Kirkwood, J. G., *J. Chem. Phys.*, **4,** 592 (1936).

Konig, H., *Ann. Phys.*, Leipzig, **31,** 289 (1938).

Langevin, P., *Le Radium*, **7,** 249 (1910).

Mazur, P., and Postma, B. J., *Physica*, **25,** 251 (1959).

Mueller, H., *Phys. Rev.*, **50,** 547 (1936).

Onsager, L., *J. Amer. Chem. Soc.*, **58,** 1486 (1936).

Peterlin, A., and Stuart, H. A., *Z. Phys.*, **113,** 663 (1939).

Piekara, A., *C. R. Acad.*, Paris, **208,** 990 (1939); *Proc. Roy. Soc.*, **A 172,** 360 (1939); *Acta phys. Polon.*, **10,** 37, 107 (1950).

Piekara, A., and Kielich, S., *J. Phys. Radium*, **18,** 490 (1957); *J. Chem. Phys.*, **29,** 1292 (1958); *Acta phys. Polon.*, **17,** 209 (1958).

Raman, C. V., and Krishnan, K. S., *Proc. Roy. Soc.*, London, **A 117,** 1 (1927).

Snellman, O., *Phil. Mag.*, **40,** 983 (1949).

Stephen, M. J., *Mol. Phys.*, **1,** 223 (1958).

Stuart, H. A., and Volkman, H., *ZS. f. Physik*, **83,** 444 (1933).

De Vaucouleurs, G., *Ann. de Phys.*, **6,** 213 (1951).

Voigt, W., *Lehrb. der Magneto- und Elektro-optik* (Teubner, Leipzig, 1908).

Volkensteyn, M. V., *Molekularnaya Optika* (Moskva, 1951).

Zernike, F., and Prins, J. A., *Z. f. Phys.*, **41,** 184 (1927).