CLASSICAL THEORY OF MAGNETO-OPTICAL PHENOMENA IN DENSE ISOTROPIC MEDIA

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A semi-macroscopic theory of magneto-optical effects in dense isotropic media and its microscopic interpretation on the basis of classical statistical methods is proposed. The non-linear variation of the optical permittivity tensor, as due to a strong DC magnetic field H, is shown to be given by the equation

$$\varepsilon_{\sigma\tau}-n^2\delta_{\sigma\tau} = F\varepsilon_{\sigma\tau\nu}H_\nu+AH^2\delta_{\sigma\tau}+C(3H_\sigma H_\tau-H^2\delta_{\sigma\tau}),$$

where F is Faraday's and C — the Cotton-Mouton constant, while A is a constant dependent *i.a.* on magnetostriction. Other processes, such as the magnetic anisotropy induced in an isotropic medium by an intense *e.g.* laser beam, the magneto-electrical or electro-magnetical cross effect, and similar magneto-optical effects are also discussed. By classical statistical methods, it is shown that for multi-component systems F, C, as well as other magneto-optical constants can be expanded in power series in the molar fractions, the first coefficient describing the additive properties of the perfect mixture, and the consecutive coefficients accounting for deviations from additivity due to the presence of molecular radial and angular correlations. Moreover, within the framework of molecular relaxational theory, the variations in complex refractive index in a strong oscillating magnetic field and variations in magnetic permeability in an intense oscillating electric field are calculated.

1. *Introduction*

Substances not naturally rotating the plane of polarization of light gain this property when in an external magnetic field. This is the well-known Faraday effect when light propagates within the medium parallel to the magnetic field lines. It is closely related with the Zeeman effect, which consists in a change in frequency of the light emitted by atoms in a magnetic field. The theoretical fundamentals (Lorentz's electron theory and the quantum-mechanical approach) have been established for either effect quite a number of years ago by various authors (*cf.* the paper by Serber and Groeneweg [1] and the earlier papers cited by them) and are still being developed in application to various substances [2—6]. The effect of a magnetic field on the optical or electric properties of substances is also apparent otherwise *e.g.* in

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the paramagnetoelectric effect [7], or inverse effects of optically induced magnetisation [2, 8] and inverse Faraday effect [9].

Another important magneto-optical effect consists in the birefringence induced in isotropic bodies by an intense magnetic field, thus in the Cotton-Mouton effect. In this case, too, the early theory of Voigt and Langevin has been developed by a number of authors on the basis of classical statistical mechanics [10—14]. At present, owing to the lasers at our disposal, it is possible to observe the inverse Cotton-Mouton effect consisting in the induction of magnetic anisotropy in isotropic bodies by means of a strong optical field [15]. The rapid development of laser techniques provides the experimental conditions for observing yet other magneto-optical processes, *e.g.* DC magnetic field-induced generation of the second harmonic, or the effect of a magnetic field on the optical activity, *etc.* [16].

Obviously, a theory of any magneto-optical process whatever has to be a quantum-mechanical theory. On the other hand, the formulation and elaboration of the latter for the case of dense systems involves considerable difficulties, which are conveniently avoided by first developing a classical theory. In many a case (to the exclusion of paramagnetic processes), this yields satisfactory agreement with the experimental results and permits to predict what microscopic factors should be taken into consideration. Such indeed is our intention in the present paper, which is aimed at proposing a classical statistical theory of magneto-optical effects in dense media based on earlier papers [15, 17] dealing with non-linear electrical, magnetic and optical phenomena in gases and liquids.

In order to ensure sufficient generality of the theory, we at first proceed by the semi-macroscopic method developed in the theory of dielectrics [17, 18, 19] and then go over to the microscopical picture, which brings forth the specific mechanisms of the magneto-optical effects under consideration. Previous to formulating the semi-macroscopic theory, we shall develop a formal molecular theory of magneto-optical effects in gases, as initiated by Born [10]. We shall start by applying molecular relaxational theory for calculating the effect of an intense oscillating electric field on the magnetic permeability and that of an intense oscillating magnetic field on the light refractive index.

2. *Molecular relaxational theory of nonlinear effects due to an oscillating electric or magnetic field*

Consider an isotropic medium of volume V containing N electrically and magnetically anisotropic molecules. We shall deal with the magnetic variations of its properties due to the effect of a strong electric field $\boldsymbol{E} = \boldsymbol{E}_0 \cos \omega t$ oscillating at frequency ω. If the density $\varrho = N/V$ is not excessive, the magnetic permeability of the diamagnetic medium is given by the fundamental formula

$$\mu_E - 1 = 4\pi\varrho \int \frac{\partial m_\sigma^m}{\partial H_\tau} h_\sigma h_\tau f(\Omega, \boldsymbol{E}) d\Omega, \tag{2.1}$$

where m_σ^m is the σ-component of the magnetic dipole moment induced in a molecule by the weak measuring magnetic field $\boldsymbol{H}$, whose direction is defined by the unit vector $\boldsymbol{h}$. In Eq. (2.1), $f(\Omega, \boldsymbol{E})$ is the statistical distribution function of molecules having the orientation Ω with respect to the strong oscillating field $\boldsymbol{E}$.

Assuming for simplicity that the diamagnetic molecules are linearly polarizable and are axially symmetrical with regard to the 3-axis defined by the unit vector $\boldsymbol{k}$, one can write

$$m_\sigma^m = a_{\sigma\tau}^{mm} H_\tau = a_m H_\sigma + (a_{33}^{mm} - a_{11}^{mm}) \left(k_\sigma k_\tau - \frac{1}{3} \delta_{\sigma\tau} \right) H_\tau, \tag{2.2}$$

$a_m = a_{\sigma\sigma}^{mm}/3$ being the mean diamagnetic polarizability of the molecule and $a_{11}^{mm} = a_{22}^{mm}$ as well as a_{33}^{mm} — the diamagnetic polarizability tensor components $a_{\sigma\tau}^{mm}$.

The statistical distribution function can be found by Debye's method as developed by Peterlin and Stuart [20] which, for axially-symmetrical molecules having the electric dipole moment μ_e and electric polarizability $a_{11}^{ee} = a_{22}^{ee}$ and a_{33}^{ee}, yields to within the square of the electric field [21]

$$f(\Omega, \boldsymbol{E}) = f(\Omega, 0) \left\{ 1 + \beta \frac{\mu_e k_\sigma E_{0\sigma} e^{i\omega t}}{1 + i\omega\tau_1} + \right.$$

$$\left. + \frac{\beta}{12} \left(a_{33}^{ee} - a_{11}^{ee} + \frac{\beta \mu_e^2}{1 + i\omega\tau_1} \right) \left(1 + \frac{e^{i2\omega t}}{1 + i2\omega\tau_2} \right) (3k_\sigma k_\tau - \delta_{\sigma\tau}) E_{0\sigma} E_{0\tau} + \ldots \right\}, \tag{2.3}$$

where $f(\Omega, 0) = 1/\Omega$ is the statistical distribution function of the molecules in the absence of an electric field, whereas $\tau_1 = \beta W/2$ and $\tau_2 = \beta W/6$ are the respective relaxation times; $\beta = 1/kT$, whereas W is a frictional torque.

On substituting (2.2) into Eq. (2.1), we obtain

$$\mu_E^{\cdot\cdot} - 1 = \frac{4\pi}{3} \varrho \int\int \{3a_m + (a_{33}^{mm} - a_{11}^{mm})(3k_\sigma k_\tau - \delta_{\sigma\tau}) h_\sigma h_\tau\} f(\Omega, \boldsymbol{E}) d\Omega, \tag{2.4}$$

whence with (2.3) and the following mean values computed from $f(\Omega, 0)$ at zero electric field:

$$\frac{1}{\Omega} \int k_\sigma k_\tau \, d\Omega = \frac{1}{3} \delta_{\sigma\tau},$$

$$\frac{1}{\Omega} \int k_\sigma k_\tau k_\nu k_\varrho d\Omega = \frac{1}{15} (\delta_{\sigma\tau}\delta_{\nu\varrho} + \delta_{\sigma\nu}\delta_{\tau\varrho} + \delta_{\sigma\varrho}\delta_{\tau\nu}), \tag{2.5}$$

we get finally

$$\mu_E - \mu_0 = \frac{2\pi\varrho}{45} \beta (a_{33}^{mm} - a_{11}^{mm}) \left\{ a_{33}^{ee} - a_{11}^{ee} + \frac{\beta \mu_e^2}{1 + i\omega\tau_1} \right\} \times$$

$$\times \left(1 + \frac{e^{i2\omega t}}{1 + i2\omega\tau_2} \right) \{3(\boldsymbol{h} \cdot \boldsymbol{e})^2 - 1\} E_0^2, \tag{2.6}$$

where μ_0 is the magnetic permeability at $\boldsymbol{E} = 0$, and $\boldsymbol{e}$ is the unit vector in the direction of the electric field $\boldsymbol{E}$.

The foregoing expression defines the change in magnetic permeability as due to the square of the strong oscillating electric field. If, in particular, the latter's oscillation frequency is zero ($\omega = 0$), Eq. (2.6) leads to the expression [15]

$$\mu_E - \mu_0 = \frac{4\pi\varrho}{45} \beta (a_{33}^{mm} - a_{11}^{mm})(a_{33}^{ee} - a_{11}^{ee} + \beta\mu_e^2) \{3(\boldsymbol{h} \cdot \boldsymbol{e})^2 - 1\} E_{DC}^2, \tag{2.7}$$

which defines the non-linear change in magnetic permeability produced by a strong DC electric field.

Conversely, if the oscillation frequency of the electric field is sufficiently high for us to write $\omega\tau_1 \to \infty$ and $\omega\tau_2 \to \infty$, Eq. (2.6) reduces to the simple form

$$\mu_E - \mu_0 = \frac{2\pi\varrho}{45}\beta(a_{33}^{mm} - a_{11}^{mm})(a_{33}^{ee} - a_{11}^{ee})\{3(\boldsymbol{h}\cdot\boldsymbol{e})^2 - 1\}E_0^2. \tag{2.8}$$

On computing herefrom the magnetic permeability values for the cases when $\boldsymbol{e}$ and $\boldsymbol{h}$ are parallel and mutually perpendicular, one obtains their difference in the form

$$\mu_{\parallel} - \mu_{\perp} = \frac{2\pi\varrho}{15}\beta(a_{33}^{mm} - a_{11}^{mm})(a_{33}^{ee} - a_{11}^{ee})E_0^2. \tag{2.9}$$

The expression thus derived defines the magnetic anisotropy induced in the medium by an intense optical field (electric field at optical frequencies).

We now proceed to discuss the change in light refractive index due to the effect of a strong oscillating magnetic field; this can be calculated from the fundamental equation

$$n_H^2 - 1 = 4\pi\varrho\int \frac{\partial m_\sigma^e}{\partial E_\tau} e_\sigma e_\tau f(\Omega, \boldsymbol{H})d\Omega, \tag{2.10}$$

where m_σ^e is a component of the electric dipole moment induced in a molecule by the electric field $\boldsymbol{E}$ of the incident light wave. In a linear approximation, Eq. (2.10) yields for axially-symmetrical molecules

$$n_H^2 - 1 = \frac{4\pi}{3}\varrho\int \{3a_e + (a_{33}^{ee} - a_{11}^{ee})(3k_\sigma k_\tau - \delta_{\sigma\tau})e_\sigma e_\tau\} f(\Omega, \boldsymbol{H})d\Omega, \tag{2.11}$$

where $a_e = a_{\sigma\sigma}^{ee}/3$ is the mean electric polarizability of the molecule, and $a_{11}^{ee} = a_{22}^{ee}$ as well as a_{33}^{ee} — its electric polarizabilities along the principal axes 1, 2 and 3.

In the case now under consideration, the statistical distribution function $f(\Omega, \boldsymbol{H})$ in the presence of the oscillating magnetic field $\boldsymbol{H}$ is again of the form (2.3) provided one replaces the electric dipole moment μ_e by the magnetic moment μ_m, the electric polarizabilities a_{11}^{ee} and a_{33}^{ee} by the respective magnetic quantities a_{11}^{mm} and a_{33}^{mm}, and $\boldsymbol{E}$ by $\boldsymbol{H}$. Thus, (2.11) yields the expression

$$n_H^2 - n_0^2 = \frac{2\pi\varrho}{45}\beta(a_{33}^{ee} - a_{11}^{ee})\left\{a_{33}^{mm} - a_{11}^{mm} + \frac{\beta\mu_m^2}{1 + i\omega\tau_1}\right\} \times$$

$$\times \left(1 + \frac{e^{i2\omega t}}{1 + i2\omega\tau_2}\right)\{3(\boldsymbol{e}\cdot\boldsymbol{h})^2 - 1\}H_0^2, \tag{2.12}$$

which defines the effect of a strong oscillating magnetic field on the refractive index of light; n_0 is the refractive index at $\boldsymbol{H} = 0$.

From Eq. (2.12), the magnetic birefringence is obtained in the form

$$n_{\parallel}^2 - n_{\perp}^2 = \frac{2\pi\varrho}{15}\beta(a_{33}^{ee} - a_{11}^{ee})\left\{a_{33}^{mm} - a_{11}^{mm} + \frac{\beta\mu_m^2}{1 + i\omega\tau_1}\right\}\left\{1 + \frac{e^{i2\omega t}}{1 + i2\omega\tau_2}\right\}H_0^2. \tag{2.13}$$

For the case of a DC magnetic field ($\omega = 0$), Eq. (2.13) goes over into the well-known Langevin-Born formula [10]

$$n_{\parallel}^2 - n_{\perp}^2 = \frac{4\pi\varrho}{15}\beta(a_{33}^{ee} - a_{11}^{ee})(a_{33}^{mm} - a_{11}^{mm} + \beta\mu_m^2)H_{DC}^2. \tag{2.14}$$

Eqs (2.12) and (2.13) show that in the case of an oscillating magnetic field the refractive index is a complex quantity and can be resolved by the well-known procedure into real and imaginary parts. For diamagnetic substances, by (2.12), these are respectively:

$$\mathrm{Re}\,(n_H^2 - n_0^2) = \frac{2\pi\varrho}{45}\beta(a_{33}^{ee} - a_{11}^{ee})(a_{33}^{mm} - a_{11}^{mm})\left\{1 + \right.$$

$$\left. + \frac{\cos 2\omega t + 2\omega\tau_2 \sin 2\omega t}{1 + 4\omega^2\tau_2^2}\right\}\{3(\boldsymbol{e}\cdot\boldsymbol{h})^2 - 1\}H_0^2, \tag{2.15}$$

$$\mathrm{Im}\,(n_H^2 - n_0^2) = \frac{2\pi\varrho}{45}\beta(a_{33}^{ee} - a_{11}^{ee})(a_{33}^{mm} - a_{11}^{mm})\times$$

$$\times \frac{2\omega\tau_2 \cos 2\omega t - \sin 2\omega t}{1 + 4\omega^2\tau_2^2}\{3(\boldsymbol{e}\cdot\boldsymbol{h})^2 - 1\}H_0^2. \tag{2.16}$$

Similarly, one can resolve the magnetic permeability (2.6) into a real and an imaginary part:

$$\mathrm{Re}(\mu_E - \mu_0) = \frac{2\pi\varrho}{45}\beta(a_{33}^{mm} - a_{11}^{mm})\left\{(a_{33}^{ee} - a_{11}^{ee})\left[1 + \frac{\cos 2\omega t + 2\omega\tau_2 \sin \omega t}{1 + 4\omega^2\tau_2^2}\right] + \right.$$

$$\left. + \frac{\beta\mu_e^2}{1 + \omega^2\tau_1^2}\left[1 + \frac{(1 - 2\omega^2\tau_1\tau_2)\cos 2\omega t + \omega(\tau_1 + 2\tau_2)\sin 2\omega t}{1 + 4\omega^2\tau_2^2}\right]\right\}\{3(\boldsymbol{h}\cdot\boldsymbol{e})^2 - 1\}E_0^2, \tag{2.17}$$

$$\mathrm{Im}\,(\mu_E - \mu_0) = \frac{2\pi\varrho}{45}\beta(a_{33}^{mm} - a_{11}^{mm})\left\{\frac{a_{33}^{ee} - a_{11}^{ee}}{1 + 4\omega^2\tau_2^2}(2\omega\tau_2 \cos 2\omega t - \sin 2\omega t) + \right.$$

$$\left. + \frac{\beta\mu_e^2}{1 + \omega^2\tau_1^2}\left[\omega\tau_1 + \frac{\omega(\tau_1 + 2\tau_2)\cos 2\omega t - (1 - 2\omega^2\tau_1\tau_2)\sin 2\omega t}{1 + 4\omega^2\tau_2^2}\right]\right\}\{3(\boldsymbol{h}\cdot\boldsymbol{e})^2 - 1\}E_0^2. \tag{2.18}$$

Eqs (2.15—2.18) define nonlinear dispersion and absorption of the refractive index and magnetic permeability.

3. Magneto-optical phenomena in gases

Let us first consider a gaseous medium presenting no interaction between microsystems (atoms or molecules) and let us assume that it is acted on simultaneously by an electric field $\boldsymbol{E}$ and a magnetic field $\boldsymbol{H}$. We moreover make the assumption that $\boldsymbol{E}$ and $\boldsymbol{H}$ are homogeneous; thus, we can restrict the problem to considering polarization of the dipolar type only. We assume, however, that the field strengths $\boldsymbol{E}$ and $\boldsymbol{H}$ are sufficiently great for producing not only linear but also non-linear polarization. On these assumptions, the potential

energy of a microsystem at configuration τ can be expanded as follows in a series in p owers of $\boldsymbol{E}$ and $\boldsymbol{H}$:

$$U(\tau, \boldsymbol{E}, \boldsymbol{H}) = U(\tau, 0) - \mu_\sigma^e E_\sigma - \mu_\sigma^m H_\sigma - \frac{1}{2}(a_{\sigma\tau}^{ee} E_\sigma E_\tau +$$

$$+ 2a_{\sigma\tau}^{em} E_\sigma H_\tau + a_{\sigma\tau}^{mm} H_\sigma H_\tau) - \frac{1}{6}(b_{\sigma\tau\nu}^{eee} E_\sigma E_\tau E_\nu + 3b_{\sigma\tau\nu}^{eem} E_\sigma E_\tau H_\nu +$$

$$+ 3b_{\sigma\tau\nu}^{emm} E_\sigma H_\tau H_\nu + b_{\sigma\tau\nu}^{mmm} H_\sigma H_\tau H_\nu) -$$

$$- \frac{1}{24}(c_{\sigma\tau\nu\varrho}^{eeee} E_\sigma E_\tau E_\nu E_\varrho + 4c_{\sigma\tau\nu\varrho}^{eeem} E_\sigma E_\tau E_\nu H_\varrho +$$

$$+ 6c_{\sigma\tau\nu\varrho}^{eemm} E_\sigma E_\tau H_\nu H_\varrho + 4c_{\sigma\tau\nu\varrho}^{emmm} E_\sigma H_\tau H_\nu H_\varrho + c_{\sigma\tau\nu\varrho}^{mmmm} H_\sigma H_\tau H_\nu H_\varrho) - \ldots, \tag{3.1}$$

where the physical meaning of the expansion coefficients will be given further on.

The expansion of Eq. (3.1) provides the basis for calculating the electric dipole moment components for a microsystem subjected to the fields $\boldsymbol{E}$ and $\boldsymbol{H}$:

$$m_\sigma^e = -\frac{\partial U}{\partial E_\sigma} = \mu_\sigma^e + a_{\sigma\tau}^{ee} E_\tau + \frac{1}{2} b_{\sigma\tau\nu}^{eee} E_\tau E_\nu + \frac{1}{6} c_{\sigma\tau\nu\varrho}^{eeee} E_\tau E_\nu E_\varrho + \ldots$$

$$+ a_{\sigma\tau}^{em} H_\tau + \frac{1}{2} b_{\sigma\tau\nu}^{emm} H_\tau H_\nu + \frac{1}{6} c_{\sigma\tau\nu\varrho}^{emmm} H_\tau H_\nu H_\varrho + \ldots$$

$$+ b_{\sigma\tau\nu}^{eem} E_\tau H_\nu + \frac{1}{2} c_{\sigma\tau\nu\varrho}^{eeem} E_\tau E_\nu H_\varrho + \frac{1}{2} c_{\sigma\tau\nu\varrho}^{eemm} E_\tau H_\nu H_\varrho + \ldots \tag{3.2}$$

Here, μ_σ^e is the component of the permanent electric dipole moment, whereas $a_{\sigma\tau}^{ee}$ — those of the electric linear polarizability tensor of the microsystem. The term $a_{\sigma\tau}^{em} H_\tau$ above defines the electric moment induced in a molecule by the magnetic field [22, 23].

Taking the derivative of the expansion (3.2) with respect to the electric field strength, one obtains the tensor of differential polarizability in the presence of the fields $\boldsymbol{E}$ and $\boldsymbol{H}$ as follows:

$$\frac{\partial m_\sigma^e}{\partial E_\tau} = a_{\sigma\tau}^{ee} + b_{\sigma\tau\nu}^{eee} E_\nu + \frac{1}{2} c_{\sigma\tau\nu\varrho}^{eeee} E_\nu E_\varrho + \ldots,$$

$$+ b_{\varrho\tau\nu}^{eem} H_\nu + c_{\sigma\tau\nu\varrho}^{eeem} E_\nu H_\varrho + \frac{1}{2} c_{\sigma\tau\nu\varrho}^{eemm} H_\nu H_\varrho + \ldots \tag{3.3}$$

The tensors $b_{\sigma\tau\nu}^{eee}$ and $c_{\sigma\tau\nu\varrho}^{eeee}$ are thus seen to define the non-linear variation of the electric differential polarizability tensor due to a strong electric field, whereas the other tensor of (3.3) — that due to a strong magnetic field.

Under the influence of a strong external electric and magnetic field, the gas becomes anisotropic, with electric permittivity tensor

$$\varepsilon_{\sigma\tau} - \delta_{\sigma\tau} = 4\pi \frac{\partial P_{e\sigma}}{\partial E_\tau}, \tag{3.4}$$

where $P_{e\sigma} = \varrho \langle m_\sigma^e \rangle_{E,H}$ is the electric polarization vector component.

Now, since we are interested here in the electric permittivity of the gas at optical frequencies, Eq. (3.4) can as well be rewritten as follows:

$$\varepsilon_{\sigma\tau}-\delta_{\sigma\tau} = 4\pi\varrho \left\langle \frac{\partial m_\sigma^e}{\partial E_\tau} \right\rangle_{E,H}, \tag{3.5}$$

wherein, for the case of classical statistical mechanics, the statistical average in the presence of the fields $\boldsymbol{E}$ and $\boldsymbol{H}$ is given by

$$\left\langle \frac{\partial m_\sigma^e}{\partial E_\tau} \right\rangle_{E,H} = \frac{\int \frac{\partial m_\sigma^e}{\partial E_\tau} \exp\{-\beta U(\tau, \boldsymbol{E}, \boldsymbol{H})\}\, d\tau}{\int \exp\{-\beta U(\tau, \boldsymbol{E}, \boldsymbol{H})\}\, d\tau}. \tag{3.6}$$

Eq. (3.5) together with (3.1), (3.3) and (3.6) provides the basis for a formal description of a variety of magneto-optical effects in gases. We shall now proceed to a discussion of these effects one by one.

A. The Faraday effect and Cotton-Mouton effect

Let us begin by considering the influence of a strong magnetic field on the optical permittivity tensor, which by (3.3) and (3.5) is defined by the expansion

$$\varepsilon_{\sigma\tau}-\delta_{\sigma\tau} = 4\pi\varrho \left\langle a_{\sigma\tau}^{ee} + b_{\sigma\tau\nu}^{eem} H_\nu + \frac{1}{2} c_{\sigma\tau\nu\varrho}^{eemm} H_\nu H_\varrho + \ldots \right\rangle_H. \tag{3.7}$$

Taking into consideration the expansion (3.1) and definition (3.6) at $\boldsymbol{E} = 0$, we obtain with accuracy up to the square of the magnetic field strength (see Appendix A)

$$\varepsilon_{\sigma\tau}-n_0^2\delta_{\sigma\tau} = F_{ee}^m \varepsilon_{\sigma\tau\nu} H_\nu + A_{ee}^{mm} H^2 \delta_{\sigma\tau} + B_{ee}^{mm}(3H_\sigma H_\tau - H^2\delta_{\sigma\tau}), \tag{3.8}$$

where n_0 is the refractive index in the absence of a magnetic field,

$$F_{ee}^m = \frac{2\pi}{3} \varrho \varepsilon_{\alpha\beta\gamma}(b_{\alpha\beta\gamma}^{eem} + \beta a_{\alpha\beta}^{ee} \mu_\gamma^m) \tag{3.9}$$

is the Faraday constant,

$$A_{ee}^{mm} = \frac{2\pi}{9} \varrho (c_{\alpha\alpha\beta\beta}^{eemm} + 2\beta b_{\alpha\alpha\beta}^{eem} \mu_\beta^m) \tag{3.10}$$

is a constant determining non-linear variations in optical permittivity of an isotropic kind, and

$$B_{ee}^{mm} = \frac{\pi\varrho}{45} \chi_{\alpha\beta\gamma\delta}(c_{\alpha\beta\gamma\delta}^{eemm} + \beta a_{\alpha\beta}^{ee} a_{\gamma\delta}^{mm} + 2\beta b_{\alpha\beta\gamma}^{eem} \mu_\delta^m + \beta^2 a_{\alpha\beta}^{ee} \mu_\gamma^m \mu_\delta^m) \tag{3.11}$$

— a constant accounting for the anisotropy induced in the gas by a strong magnetic field, also known as the Cotton-Mouton constant.

In Eqs (3.8) and (3.9), $\varepsilon_{\sigma\tau\nu}$ and $\varepsilon_{\alpha\beta\gamma}$ are Levi-Cività tensors, whereas the tensor $\chi_{\alpha\beta\gamma\delta}$ appearing in (3.11) is of the form

$$\chi_{\alpha\beta\gamma\delta} = 3\delta_{\alpha\gamma}\delta_{\beta\delta} + 3\delta_{\alpha\delta}\delta_{\beta\gamma} - 2\delta_{\alpha\beta}\delta_{\gamma\delta}. \tag{3.12}$$

In Eq. (3.9) of the Faraday constant, the first term, which does not depend directly on the temperature, defines the diamagnetic Faraday effect consisting in optical variations of the microsystems directly due to the linear magnetic field, whereas the second, temperature-dependent term describes the paramagnetic Faraday effect related with orientation of the magnetic dipoles in the strong magnetic field. For the case of diamagnetic substances, Eq. (3.9) leads to the well-known result of Born [10, 11]:

$$F_{ee}^{m} = \frac{2\pi}{3} \varrho \{b_{123}^{eem} - b_{213}^{eem} + b_{231}^{eem} - b_{321}^{eem} + b_{312}^{eem} - b_{132}^{eem}\}. \tag{3.13}$$

Similarly, Eq. (3.11) consists of a diamagnetic and a paramagnetic part. The former consists of an effect of non-linear deformation (Voigt effect as described by the first term of (3.11)) and an effect of molecular orientation (Langevin effect as described by the second term in (3.11)).

In the case of microsystems having the spherical symmetry,

$$\mu_{\alpha}^{m} = 0, \; a_{\alpha\beta}^{ee} = a_e \delta_{\alpha\beta}, \; a_{\alpha\beta}^{mm} = a_m \delta_{\alpha\beta},$$

$$c_{\alpha\beta\gamma\delta}^{eemm} = c_{1133}^{eemm} \delta_{\alpha\beta}\delta_{\gamma\delta} + \frac{1}{2}(c_{3333}^{eemm} - c_{1133}^{eemm})(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}), \tag{3.14}$$

and Eqs (3.10) and (3.11) reduce to the simple form

$$A_{ee}^{mm} = \frac{2\pi}{3} \varrho \, (c_{3333}^{eemm} + 2c_{1133}^{eemm}),$$

$$B_{ee}^{mm} = \frac{2\pi}{3} \varrho \, (c_{3333}^{eemm} - c_{1133}^{eemm}). \tag{3.15}$$

Hence, in substances consisting of spherical microsystems, magnetic birefringence appears due solely to the anisotropy induced in the microsystems by the square of the magnetic field (Voigt effect [10—15]). Similarly, Eqs (3.9—3.11) can be applied to microsystems of other types of symmetry.

Assuming the incident light to propagate along the Y-axis perpendicularly to the XZ-plane containing the strong magnetic field vector, Eq. (3.8) yields the following expression for the magnetic birefringence:

$$\varepsilon_{zz} - \varepsilon_{xx} = 3B_{ee}^{mm}(H_z^2 - H_x^2). \tag{3.16}$$

For light propagating parallel to the magnetic field *e.g.* along the Z-axis, Eq. (3.8) yields the tensor components of the optical permittivity characterizing the Faraday effect in the form

$$\varepsilon_{xy} = -\varepsilon_{yx} = F_{ee}^{m} H_z. \tag{3.17}$$

B. Electro-magnetic cross effect

On neglecting in (3.3) the terms in E^2 and H^2, we get on substitution into (3.5)

$$\varepsilon_{\sigma\tau}-\delta_{\sigma\tau}=4\pi\varrho\langle a^{ee}_{\sigma\tau}+b^{eee}_{\sigma\tau\nu}E_\nu+b^{eem}_{\sigma\tau\nu}H_\nu+c^{eeem}_{\sigma\tau\nu\varrho}E_\nu H_\varrho+\ldots\rangle_{E,H}, \tag{3.18}$$

whence on averageing, retaining the terms in EH,

$$\varepsilon_{\sigma\tau}-n_0^2\delta_{\sigma\tau}=2A^{em}_{ee}(\boldsymbol{E}\cdot\boldsymbol{H})\delta_{\sigma\tau}+B^{em}_{ee}[3E_\sigma H_\tau+3H_\sigma E_\tau-2(\boldsymbol{E}\cdot\boldsymbol{H})\delta_{\sigma\tau}] \tag{3.19}$$

Eq. (3.19) defines the cross effect consisting in a non-linear variation of the optical permittivity tensor due to simultaneous action on the gas of the electric field $\boldsymbol{E}$ and magnetic field $\boldsymbol{H}$.

The constants appearing in (3.19) are of the form

$$A^{em}_{ee}=\frac{2\pi}{9}\varrho\{c^{eeem}_{\alpha\alpha\beta\beta}+\beta(b^{eee}_{\alpha\alpha\beta}\mu^m_\beta+\mu^e_\alpha b^{eem}_{\alpha\beta\beta})\}, \tag{3.20}$$

$$B^{em}_{ee}=\frac{\pi\varrho}{45}\chi_{\alpha\beta\gamma\delta}\{c^{eeem}_{\alpha\beta\gamma\delta}+\beta a^{ee}_{\alpha\beta}a^{em}_{\gamma\delta}+\beta(b^{eee}_{\alpha\beta\gamma}\mu^m_\delta+\mu^e_\alpha b^{eem}_{\beta\gamma\delta})+\beta^2 a^{ee}_{\alpha\beta}\mu^e_\gamma\mu^m_\delta\}. \tag{3.21}$$

If both $\boldsymbol{E}$ and $\boldsymbol{H}$ are static fields and if they are mutually perpendicular ($\boldsymbol{E}\cdot\boldsymbol{H}=0$), Eq. (3.19) reduces to

$$\varepsilon_{\sigma\tau}-n^2\delta_{\sigma\tau}=3B^{em}_{ee}(E_\sigma H_\tau+H_\sigma E_\tau), \tag{3.22}$$

which means that in this case electro-magnetic anisotropy is alone induced in the medium.

Formally, Eq. (3.22) still holds as above when the fields $\boldsymbol{E}$ and $\boldsymbol{H}$ represent mutually perpendicular vectors of one and the same light wave; however, the field strengths $\boldsymbol{E}$ and $\boldsymbol{H}$ have now to be replaced by the amplitudes $E_0/\sqrt{2}$ and $H_0/\sqrt{2}$, and the constant (3.21) by

$$B^{em}_{ee}=\frac{\pi\varrho}{45}\chi_{\alpha\beta\gamma\delta}(c^{eeem}_{\alpha\beta\gamma\delta}+\beta a^{ee}_{\alpha\beta}a^{em}_{\gamma\delta}). \tag{3.23}$$

C. Optically induced magnetic anisotropy

By analogy to Eq. (3.4), the magnetic permeability tensor of a gas acted on by fields $\boldsymbol{E}$ and $\boldsymbol{H}$ is given as follows:

$$\mu_{\sigma\tau}-\delta_{\sigma\tau}=4\pi\frac{\partial P_{m\sigma}}{\partial H_\tau}. \tag{3.24}$$

Restricting our considerations to a diamagnetic gas in a strong electric field, we can rewrite Eq. (3.24) thus

$$\mu_{\sigma\tau}-\delta_{\sigma\tau}=4\pi\varrho\left\langle\frac{\partial m^m_\sigma}{\partial H_\tau}\right\rangle_E. \tag{3.25}$$

With regard to the fact that the tensor of differential magnetic polarizability is defined as

$$\frac{\partial m^m_\sigma}{\partial H_\tau}=-\frac{\partial^2 U(\tau,\boldsymbol{E},\boldsymbol{H})}{\partial H_\sigma\partial H_\tau} \tag{3.26}$$

we obtain from the expansion (3.1) retaining terms dependent on the electric field only

$$\frac{\partial m_\sigma^m}{\partial H_\tau} = a_{\sigma\tau}^{mm} + b_{\sigma\tau\nu}^{mme} E_\nu + \frac{1}{2} c_{\sigma\tau\nu\varrho}^{mmee} E_\nu E_\varrho + \ldots \tag{3.27}$$

Introducing (3.27) into Eq. (3.25) and taking account of (3.1) one gets on averageing

$$\mu_{\sigma\tau} - \mu_0 \delta_{\sigma\tau} = A_{mm}^{ee} E^2 \delta_{\sigma\tau} + B_{mm}^{ee} (3 E_\sigma E_\tau - E^2 \delta_{\sigma\tau}), \tag{3.28}$$

where μ_0 is the magnetic permittivity in the absence of a strong electric field. The constants A_{mm}^{ee} and B_{mm}^{ee} are given by (3.10) and (3.11) on interchanging the indices *ee* and *mm*.

A case of particular interest arises when the field $\boldsymbol{E}$ is the light vector of an intense beam incident on the gas. Once again, one obtains Eq. (3.28) wherein E has been replaced by $E_0/\sqrt{2}$ and the constants A_{mm}^{ee} and B_{mm}^{ee} are of the form [15]

$$A_{mm}^{ee} = \frac{2\pi}{9} \varrho c_{\alpha\alpha\beta\beta}^{mmee}, \tag{3.29}$$

$$B_{mm}^{ee} = \frac{\pi\varrho}{45} \chi_{\alpha\beta\gamma\delta} (c_{\alpha\beta\gamma\delta}^{mmee} + \beta a_{\alpha\beta}^{mm} a_{\gamma\delta}^{ee}). \tag{3.30}$$

In the case considered, by Eq. (3.28), one obtains the magnetic anisotropy induced in the gas by the intense light beam as follows:

$$\mu_{zz} - \mu_{xx} = \frac{3}{2} B_{mm}^{ee} (E_{0z}^2 - E_{0x}^2). \tag{3.31}$$

In this case, too, one can calculate a magneto-electric cross effect, given by an equation similar to (3.19) on replacing therein electric by magnetic quantities and vice versa.

4. Magneto-optical effects in dense media

The shape of magneto-optical phenomena in dense media depends not only on the optical and magnetic properties of the isolated microsystems, but moreover on their electric properties (permanent and induced dipolar, quadrupolar *etc.* moments) and, essentially, on their interaction and the presence of molecular fields. To take into account the influence of the various factors of a microscopic nature on magneto-optical phenomena in dense media, it is convenient to start by a semi-macroscopic approach to the theory and then to go over to its statistical-molecular interpretation. Such an approach provides for vast possibilities of deducing from the thus generally formulated theory various special cases, in which the role of the various statistical-molecular factors appear clearly. In this way, one can achieve an explanation of the microscopic mechanism of magneto-optical processes, whose occurrence is in fact dependent on a great variety of factors.

A. Semi-macroscopic theory

We consider a dense homogeneous medium, isotropic in the absence of external fields and having the shape of a spherical sample, of dielectric constant ε_e. At its centre we consider a smaller, albeit still macroscopic sphere of volume V and dielectric constant ε. When the

medium is acted on by an external electric field $\boldsymbol{E}$ of low field strength, the mean macroscopic electric field existing within the sphere of volume V is given by [24]

$$\boldsymbol{E}^M = \frac{3\varepsilon_e}{\varepsilon+2\varepsilon_e}\boldsymbol{E}. \tag{4.1}$$

We now assume the isotropic medium to be acted on, moreover, by a strong magnetic field $\boldsymbol{H}$ under whose influence it gains the properties of an anisotropic medium with electric permittivity tensor dependent on the field strength $\boldsymbol{H}$:

$$\varepsilon_{\sigma\tau}-\delta_{\sigma\tau} = 4\pi\left\{\left(\frac{\partial P_{e\sigma}}{\partial E_\nu}\right)_0 + \left(\frac{\partial^2 P_{e\sigma}}{\partial E_\nu \partial H_\varrho}\right)_0 H_\varrho + \right.$$

$$\left. + \frac{1}{2}\left(\frac{\partial^3 P_{e\sigma}}{\partial E_\nu \partial H_\varrho \partial H_\lambda}\right)_0 H_\varrho H_\lambda + \ldots\right\}\frac{\partial E_\nu}{\partial E_\tau^M}. \tag{4.2}$$

Assuming that the field $\boldsymbol{E}$ is that of the electric vector associated with a light wave incident on the medium, we can write

$$\frac{\partial P_{e\sigma}}{\partial E_\tau} = \left\langle \frac{1}{V}\frac{\partial M_{e\sigma}}{\partial E_\tau}\right\rangle_H \tag{4.3}$$

as now the dipole electric moment $\boldsymbol{M}_e$ induced in the sphere of volume V is a linear function of the field strength $\boldsymbol{E}$, and the volume V is not affected by the weak field $\boldsymbol{E}$. We shall moreover assume that the light wavelength λ is very large as compared with molecular dimensions and that the oscillation frequency of the field $\boldsymbol{E}$ lies outside the electronic absorption bands of the medium.

We now define, by classical statistical mechanics, the mean statistical value od (4.3) in the presence of the field $\boldsymbol{H}$:

$$\left\langle \frac{\partial M_{e\sigma}}{\partial E_\tau}\right\rangle_H = \frac{\int \frac{\partial M_{e\sigma}}{\partial E_\tau}\exp\{-\beta U(\tau, \boldsymbol{H})\}\,d\tau}{\int \exp\{-\beta U(\tau, \boldsymbol{H})\}\,d\tau}, \tag{4.4}$$

where $U(\tau, \boldsymbol{H})$ is the total potential energy of the medium when its microsystems are at configuration τ and the magnetic field $\boldsymbol{H}$ is acting on it.

By (4.3), the first external field-independent term is

$$\left(\frac{\partial P_{e\sigma}}{\partial E_\tau}\right)_0 = \frac{1}{V}\left\langle \frac{\partial M_{e\sigma}}{\partial E_\tau}\right\rangle, \tag{4.5}$$

where the symbol $\langle\ \rangle$ stands for statistical averageing in the absence of the external field as given by (4.4) at $\boldsymbol{H} = 0$.

When calculating higher coefficients of the expansion (4.2), it should be kept in mind that as a result of magnetostriction the volume V is in general a function of the field strength $\boldsymbol{H}$. For simplicity, let us assume that under the effect of the strong magnetic field the spherical

sample changes its total volume V isotropically, undergoing no change in shape, and that this variation is a quadratic function of $\boldsymbol{H}$ [14]:

$$V(H)-V=\frac{1}{2}\left(\frac{\partial^2 V}{\partial H^2}\right)_0 H^2=-\frac{1}{8\pi}\left\{\frac{\partial}{\partial p}\left[(\mu-1)V\right]\right\}_T H^2$$

$$=-\frac{V}{8\pi}\left\{\left(\frac{\partial\mu}{\partial p}\right)_T-(\mu-1)\,\beta_T\right\} H^2. \tag{4.6}$$

Above, μ is the magnetic permeability of the medium, β_T — its isothermal compressibility coefficient, and p the pressure. Hence, by (4.3), (4.4) and (4.6) we obtain

$$\left(\frac{\partial^2 P_{e\sigma}}{\partial E_\tau \partial H_\nu}\right)_0=\frac{1}{V}\left\langle\frac{\partial^2 M_{e\sigma}}{\partial E_\tau \partial H_\nu}-\beta\frac{\partial M_{e\sigma}}{\partial E_\tau}\frac{\partial U}{\partial H_\nu}\right\rangle, \tag{4.7}$$

$$\left(\frac{\partial^3 P_{e\sigma}}{\partial E_\tau \partial H_\nu \partial H_\varrho}\right)_0=\frac{1}{V}\left(\frac{\partial^2}{\partial H_\nu \partial H_\varrho}\left\langle\frac{\partial M_{e\sigma}}{\partial E_\tau}\right\rangle_H\right)_0-\frac{1}{V^2}\left\langle\frac{\partial M_{e\sigma}}{\partial E_\tau}\right\rangle\left(\frac{\partial^2 V}{\partial H^2}\right)_0\delta_{\nu\varrho}. \tag{4.8}$$

It is thus seen that the coefficient (4.8) is related with the change in volume of the sphere and in its electric polarizability as due to the square of the magnetic field:

$$\left(\frac{\partial^2}{\partial H_\nu \partial H_\varrho}\left\langle\frac{\partial M_{e\sigma}}{\partial E_\tau}\right\rangle_H\right)_0=\left\langle\frac{\partial^3 M_{e\sigma}}{\partial E_\tau \partial H_\nu \partial H_\varrho}-2\beta\frac{\partial^2 M_{e\sigma}}{\partial E_\tau \partial H_\nu}\frac{\partial U}{\partial H_\varrho}+\right.$$

$$-\frac{\partial M_{e\sigma}}{\partial E_\tau}\left(\frac{\partial^2 U}{\partial H_\nu \partial H_\varrho}-\beta\frac{\partial U}{\partial H_\nu}\frac{\partial U}{\partial H_\varrho}\right)\Bigg\rangle+$$

$$+\beta\left\langle\frac{\partial M_{e\sigma}}{\partial E_\tau}\right\rangle\left\langle\frac{\partial^2 U}{\partial H_\nu \partial H_\varrho}-\beta\frac{\partial U}{\partial H_\nu}\frac{\partial U}{\partial H_\varrho}\right\rangle. \tag{4.9}$$

On taking the mean values of (4.5) and (4.7—4.9) over all possible directions of the vectors $\boldsymbol{e}$ and $\boldsymbol{h}$ with respect to the axes of the laboratory coordinate system and on introducing the results into Eq. (4.2), one obtains the following, general equation:

$$\varepsilon_{\sigma\tau}-n_{0\sigma\tau}^2=F_{ee}^m\varepsilon_{\sigma\varrho\nu}\left(\frac{\partial E_\varrho}{\partial E_\tau^M}\right)_0 H_\nu+$$

$$+A_{ee}^{mm}\left(\frac{\partial E_\sigma}{\partial E_\tau^M}\right)_0 H^2+B_{ee}^{mm}\left\{3\left(\frac{\partial E_\nu}{\partial E_\tau^M}\right)_0 H_\sigma H_\nu-\left(\frac{\partial E_\sigma}{\partial E_\tau^M}\right)_0 H^2\right\}, \tag{4.10}$$

where

$$n_{0\sigma\tau}^2-\delta_{\sigma\tau}=\frac{4\pi}{3V}\left\langle\frac{\partial M_{e\alpha}}{\partial E_\alpha}\right\rangle\left(\frac{\partial E_\sigma}{\partial E_\tau^M}\right)_0 \tag{4.11}$$

is the optical permittivity tensor in the absence of the magnetic field,

$$F_{ee}^m=\frac{2\pi}{3V}\varepsilon_{\alpha\beta\gamma}\left\langle\frac{\partial^2 M_{e\alpha}}{\partial E_\beta \partial H_\gamma}-\beta\frac{\partial M_{e\alpha}}{\partial E_\beta}\frac{\partial U}{\partial H_\gamma}\right\rangle \tag{4.12}$$

is Faraday's constant, and

$$A_{ee}^{mm} = \frac{2\pi}{9V}\left\{\left\langle\frac{\partial^3 M_{e\alpha}}{\partial E_\alpha \partial H^2}\right\rangle - \frac{3}{V}\left\langle\frac{\partial M_{e\alpha}}{\partial E_\alpha}\right\rangle\left(\frac{\partial^2 V}{\partial H^2}\right)_0 - 2\beta\left\langle\frac{\partial^2 M_{e\alpha}}{\partial E_\alpha \partial H_\beta}\frac{\partial U}{\partial H_\beta}\right\rangle - \right.$$
$$-\beta\left[\left\langle\frac{\partial M_{e\alpha}}{\partial E_\alpha}\frac{\partial^2 U}{\partial H^2}\right\rangle - \left\langle\frac{\partial M_{e\alpha}}{\partial E_\alpha}\right\rangle\left\langle\frac{\partial^2 U}{\partial H^2}\right\rangle\right] +$$
$$\left. +\beta^2\left[\left\langle\frac{\partial M_{e\alpha}}{\partial E_\alpha}\frac{\partial U}{\partial H_\beta}\frac{\partial U}{\partial H_\beta}\right\rangle - \left\langle\frac{\partial M_{e\alpha}}{\partial E_\alpha}\right\rangle\left\langle\frac{\partial U}{\partial E_\beta}\frac{\partial U}{\partial H_\beta}\right\rangle\right]\right\}, \tag{4.13}$$

$$B_{ee}^{mm} = \frac{\pi}{45V}\chi_{\alpha\beta\gamma\delta}\left\langle\frac{\partial^3 M_{e\alpha}}{\partial E_\beta \partial H_\gamma \partial H_\delta} - 2\beta\frac{\partial^2 M_{e\alpha}}{\partial E_\beta \partial H_\gamma}\frac{\partial U}{\partial H_\delta} - \right.$$
$$\left. -\beta\frac{\partial M_{e\alpha}}{\partial E_\beta}\left(\frac{\partial^2 U}{\partial H_\gamma \partial H_\delta} - \beta\frac{\partial U}{\partial H_\gamma}\frac{\partial U}{\partial H_\delta}\right)\right\rangle \tag{4.14}$$

are constants which define non-linear variations of the isotropic and anisotropic kinds in the optical permittivity tensor.

Eq. (4.10) provides a general, semi-macroscopic description of the effect of a strong homogeneous magnetic field on the optical permittivity tensor of an arbitrary isotropic medium. The latter is seen to become optically anisotropic when in the field, as it is then characterized by different values of the refractive index for various directions of oscillation of the electric light vector $\boldsymbol{E}$ with respect to the applied magnetic field $\boldsymbol{H}$. In general, in the case considered, we have anisotropy both linear in the magnetic field strength (magnetic rotation) and quadratic (magnetic birefringence). The former is given by Faraday's constant (4.13), and the latter — by the Cotton-Mouton constant (4.14). These constants are dependent on the averaged optical and magnetic properties of the medium as well as on its thermodynamical state. The above effects are moreover accompanied by magnetostriction as implied by the constant (4.13) and defined by (4.6).

We further assume that both in the weak electric and strong magnetic field the linear and isotropic relationship (4.1) is fulfilled. Let the sphere of volume V now be in vacuum, $\varepsilon_e = 1$ (instead of in the medium of dielectric constant ε_e); in the optical case ($\varepsilon = n^2$) we now have

$$\frac{\partial E_\sigma}{\partial E_\tau^M} = \frac{n^2+2}{3}\delta_{\sigma\tau}. \tag{4.15}$$

On the foregoing assumptions, the definition

$$M_{m\gamma} = -\frac{\partial U}{\partial H_\gamma} \tag{4.16}$$

defines the total magnetic moment of the sphere of volume V acted on by a strong magnetic field.

By recurring to (4.15), the fundamental equation (4.10) together with (4.11) can be written in the form

$$\varepsilon_{\sigma\tau} - n_0^2\delta_{\sigma\tau} = \left(\frac{n_0^2+2}{3}\right)\{F_{ee}^m \varepsilon_{\sigma\tau\nu}H_\nu + A_{ee}^{mm}H^2\delta_{\sigma\tau} + B_{ee}^{mm}(3H_\sigma H_\tau - H^2\delta_{\sigma\tau})\}, \tag{4.17}$$

where

$$\frac{n_0^2-1}{n_0^2+2} = \frac{4\pi}{9V}\left\langle \frac{\partial M_{e\alpha}}{\partial E_\alpha}\right\rangle \tag{4.18}$$

is the refractive index of the isotropic medium in the absence of a strong field.

We now obtain from Eq. (4.17), in place of (3.15),

$$\varepsilon_{xy} = -\varepsilon_{yx} = \left(\frac{n_0^2+2}{3}\right) F_{ee}^m H_z, \tag{4.19}$$

where, by (4.12) and the definition of (4.16), the Faraday constant is of the form

$$F_{ee}^m = \frac{2\pi}{3V}\varepsilon_{\alpha\beta\gamma}\left\langle \frac{\partial^2 M_{e\alpha}}{\partial E_\beta \partial H_\gamma} + \beta \frac{\partial M_{e\alpha}}{\partial E_\beta} M_{m\gamma}\right\rangle. \tag{4.20}$$

Similarly, Eq. (4.17) yields for the magnetic birefringence

$$\varepsilon_{zz} - \varepsilon_{xx} = 3\left(\frac{n_0^2+2}{3}\right)^2 B_{ee}^{mm}(H_z^2 - H_x^2) \tag{4.21}$$

with the Cotton-Mouton constant in the form

$$B_{ee}^{mm} = \frac{\pi}{45V}\chi_{\alpha\beta\gamma\delta}\left\langle \frac{\partial^3 M_{e\alpha}}{\partial E_\beta \partial H_\gamma \partial H_\delta} + 2\beta \frac{\partial^2 M_{e\alpha}}{\partial E_\beta \partial H_\gamma} M_{m\delta} + \right.$$

$$\left. + \beta \frac{\partial M_{e\alpha}}{\partial E_\beta}\left(\frac{\partial M_{m\gamma}}{\partial H_\delta} + \beta M_{m\gamma} M_{m\delta}\right)\right\rangle. \tag{4.22}$$

In a similar way, the semi-macroscopic theory of other magneto-optical phenomena can be formulated. We shall restrict ourselves here to writing out the equations for the non-linear change in magnetic permittivity tensor induced by an intense optical field of amplitude E_0:

$$\mu_{\sigma\tau} - \mu_0\delta_{\sigma\tau} = \frac{1}{2} A_{mm}^{ee} E_0^2 \delta_{\sigma\tau} + \frac{1}{2} B_{mm}^{ee}(3E_{0\sigma}E_{0\tau} - E_0^2\delta_{\sigma\tau}). \tag{4.23}$$

Above,

$$A_{mm}^{ee} = \frac{2\pi}{9V}\left\{\left\langle \frac{\partial^3 M_{m\alpha}}{\partial H_\alpha \partial E^2}\right\rangle - \frac{3}{V}\left\langle \frac{\partial M_{m\alpha}}{\partial H_\alpha}\right\rangle\left(\frac{\partial^2 V}{\partial E^2}\right)_0 - \right.$$

$$\left. - \beta\left[\left\langle \frac{\partial M_{m\alpha}}{\partial H_\alpha}\frac{\partial M_{e\beta}}{\partial E_\beta}\right\rangle - \left\langle \frac{\partial M_{m\alpha}}{\partial H_\alpha}\right\rangle\left\langle \frac{\partial M_{e\beta}^{\pi}}{\partial E_\beta}\right\rangle\right]\right\}, \tag{4.24}$$

$$B_{mm}^{ee} = \frac{\pi}{45V}\chi_{\alpha\beta\gamma\delta}\left\langle \frac{\partial^3 M_{m\alpha}}{\partial H_\beta \partial E_\gamma \partial E_\delta} + \beta \frac{\partial M_{m\alpha}}{\partial H_\beta}\frac{\partial M_{e\gamma}}{\partial E_\delta}\right\rangle, \tag{4.25}$$

are constants determining respectively the isotropic and anisotropic non-linear changes in magnetic permeability tensor due to the effect of an intense light beam.

The term [21]

$$\frac{1}{2V}\left(\frac{\partial^2 V}{\partial E^2}\right)_0 E^2 = -\frac{1}{8\pi V}\left\{\frac{\partial}{\partial p}[n^2-1)V]\right\}_T E^2$$
$$= -\frac{1}{8\pi}\left\{\left(\frac{\partial n^2}{\partial p}\right)_T - (n^2-1)\beta_T\right\} E^2 \tag{4.26}$$

appearing in (4.24) determines the quadratic change in volume V produced by intense light *i.e.* opticostriction, which is the counterpart of electrostriction [24].

B. Molecular-statistical theory.

We now proceed from the foregoing general theory to a molecular-statistical theory aimed at gaining insight into the microscopic mechanism of the phenomena under consideration. To this aim, we assume for generality that the macroscopic sphere contains $N = \sum_i N_i$ microsystems of different species (N_i being the number of microsystems of species i), so that the macroscopical dipole moments $\boldsymbol{M}_e$ and $\boldsymbol{M}_m$ can now be expressed as follows:

$$\boldsymbol{M}_e = \sum_i \sum_{p=i}^{N_i} \boldsymbol{m}_e^{(p)}, \quad \boldsymbol{M}_m = \sum_j \sum_{q=1}^{N_j} \boldsymbol{m}_m^{(qj)}, \tag{4.27}$$

with $\boldsymbol{m}_e^{(pi)}$ and $\boldsymbol{m}_m^{(qj)}$ denoting the electric and magnetic dipole moment of the p-th and q-th microsystem of species i and j, respectively.

On substituting the moments (4.27) into the general expressions (4.20) and (4.22), we obtain the Faraday and Cotton-Mouton constants in molecular form:

$$F = \frac{2\pi}{3V}\varepsilon_{\alpha\beta\gamma}\left\{\sum_i \left\langle \sum_{p=1}^{N_i} \frac{\partial^2 m_{e\alpha}^{(pi)}}{\partial E_\beta \partial H_\gamma}\right\rangle + \right.$$
$$\left. + \beta \sum_{ij} \left\langle \sum_{p=1}^{N_i}\sum_{q=1}^{N_j} \frac{\partial m_{e\alpha}^{(pi)}}{\partial E_\beta} m_{m\gamma}^{(qj)}\right\rangle\right\}, \tag{4.28}$$

$$C = \frac{\pi}{45V}\chi_{\alpha\beta\gamma\delta}\left\{\sum_i \left\langle \sum_{p=1}^{N_i} \frac{\partial m_{e\alpha}^{(pi)}}{\partial E_\beta \partial H_\gamma \partial H_\delta}\right\rangle + \right.$$
$$+\beta \sum_{ij}\left\langle \sum_{p=1}^{N_i}\sum_{q=1}^{N_j}\left(2\frac{\partial^2 m_{e\alpha}^{(pi)}}{\partial E_\beta \partial H_\gamma} m_{m\delta}^{(qj)} + \frac{\partial m_{e\alpha}^{(pi)}}{\partial E_\beta}\frac{\partial m_{m\gamma}^{(qj)}}{\partial H_\delta}\right)\right\rangle +$$
$$\left. +\beta^2 \sum_{ijk}\left\langle \sum_{p=1}^{N_i}\sum_{q=1}^{N_j}\sum_{r=1}^{N_k} \frac{\partial m_{e\alpha}^{(pi)}}{\partial E_\beta} m_{m\gamma}^{(qj)} m_{m\delta}^{(rk)}\right\rangle\right\}, \tag{4.29}$$

which holds for an arbitrary multi-component system.

The expansions (3.2), (3.3) and (3.35) utilized previously are strictly valid only if the external fields $\boldsymbol{E}$ and $\boldsymbol{H}$ produce polarisation in an isolated molecule, as is the case in a rarefied gas. In a dense system, like a strongly compressed gas, a liquid, or a liquid mixture, molecular electric $\boldsymbol{F}_0$ and magnetic $\boldsymbol{G}_0$ fields exist even in the absence of an external field $\boldsymbol{E}$ or $\boldsymbol{H}$, due to the permanent or induced dipolar, quadrupolar *etc.* moments of the microsystems. In the presence of an external field $\boldsymbol{E}$ or $\boldsymbol{H}$, as a result of polarisation of the microsystems and of the system as a whole, the fields $\boldsymbol{F}_0$ and $\boldsymbol{G}_0$ undergo modification and have to be replaced by fields $\boldsymbol{F}$ and $\boldsymbol{G}$ which, in general, are functions of $\boldsymbol{E}$ and $\boldsymbol{H}$. Thus, a microsystem of the medium is acted on, in addition to the external fields $\boldsymbol{E}$ and $\boldsymbol{H}$, by the molecular fields $\boldsymbol{F}$ and $\boldsymbol{H}$, so that the moments $\boldsymbol{m}_e$ and $\boldsymbol{m}_m$ are now functions of the local fields $\boldsymbol{E}+\boldsymbol{F}$ and $\boldsymbol{H}+\boldsymbol{G}$. We thus have in place of (3.2) the following expansion (we write the relevant terms only [14]):

$$m_{e\alpha}^{(pi)} = \mu_{e\alpha}^{(pi)} + \{a_{\alpha\beta}^{ee(pi)} + b_{\alpha\beta\gamma}^{eee(pi)} F_{0\gamma}^{(pi)} + \ldots\}(E_\beta + F_\beta^{(pi)}) + \\ + b_{\alpha\beta\gamma}^{eem(pi)}(E_\beta + F_\beta^{(pi)})\,(H_\gamma + G_\gamma^{(pi)}) + \\ + \frac{1}{2} c_{\alpha\beta\gamma\delta}^{eemm(pi)}(E_\beta + F_\beta^{(pi)})\,(H_\gamma + G_\gamma^{(pi)})\,(H_\delta + G_\delta^{(pi)}) + \ldots, \tag{4.30}$$

where the polarizability tensors retain their former physical meaning, with the proviso that they now refer to the p-th microsystem of species i.

Similarly, one can write the expansion of the dipole magnetic moment of the q-th molecule of species j:

$$m_{m\alpha}^{(qj)} = \mu_{m\alpha}^{(qj)} + \{a_{\alpha\beta}^{mm(qj)} + b_{\alpha\beta\gamma}^{mme(qj)} F_{0\gamma}^{(qj)} + \ldots\}(H_\beta + G_\beta^{(qj)}). \tag{4.31}$$

In the case of not too dense media, in a first approximation one can neglect the direct effect of molecular fields, and with regard to (4.30) and (4.31), Eqs (4.28) and (4.29) yield

$$F_{ee}^{m} = \frac{2\pi}{3V}\varepsilon_{\alpha\beta\gamma}\left\{\sum_i \left\langle \sum_{p=1}^{N_i} b_{\alpha\beta\gamma}^{eem(pi)} \right\rangle + \beta \sum_{ij} \left\langle \sum_{p=1}^{N_i}\sum_{q=1}^{N_j} a_{\alpha\beta}^{ee(pi)} m_{m\gamma}^{(qj)} \right\rangle \right\}, \tag{4.32}$$

$$B_{ee}^{mm} = \frac{\pi}{45V}\chi_{\alpha\beta\gamma\delta}\left\{\sum_i \left\langle \sum_{p=1}^{N_i} c_{\alpha\beta\gamma\delta}^{eemm(pi)} \right\rangle + \beta \sum_{ij} \left\langle \sum_{p=1}^{N_i}\sum_{q=1}^{N_j} (2b_{\alpha\beta\gamma}^{eem(pi)} m_{m\delta}^{(qj)} + \right.\right. \\ \left.\left. + a_{\alpha\beta}^{ee(pi)} a_{\gamma\delta}^{mm(qj)}) \right\rangle + \beta^2 \sum_{ijk} \left\langle \sum_{p=1}^{N_i}\sum_{q=1}^{N_j}\sum_{r=1}^{N_k} a_{\alpha\beta}^{ee(pi)} m_{m\gamma}^{(qj)} m_{m\delta}^{(rk)} \right\rangle \right\}. \tag{4.33}$$

We shall first discuss in some detail the Faraday constant (4.32) now to be denoted by F. By statistical methods, it can be represented formally as the following expansion in powers of the mole fractions:

$$F = \sum_i x_i F_i + \sum_{ij}{}' x_i x_j F_{ij} + \ldots, \tag{4.34}$$

where the expansion coefficients F_i, F_{ij} are of the form

$$F_i = \frac{2\pi}{3} \varrho \varepsilon_{\alpha\beta\gamma} (b^{eem(i)}_{\alpha\beta\gamma} + \beta a^{ee(i)}_{\alpha\beta} \mu^{(i)}_{m\gamma}), \tag{4.35}$$

$$F_{ij} = \frac{2\pi}{3V} \varrho^2 \beta \int\int \varepsilon_{\alpha\beta\gamma} a^{ee(pi)}_{\alpha\beta} \mu^{(qj)}_{m\gamma} g^{(2)}_{ij}(\tau_p, \tau_q) d\tau_p d\tau_q, \tag{4.36}$$

with $x_i = N_i/N$ denoting the mole fraction of the i-th component of the mixture and $g^{(2)}_{ij}(\tau_p, \tau_q)$ — the binary correlation function of molecules p and q of species i and j at configurations τ_p and τ_q, respectively. The configurational variables τ_p involve the variables $\mathbf{r}_p$ and $\boldsymbol{\omega}_p$ defining, respectively, the position and orientation of the p-th molecule.

If, in particular, no intermolecular interactions occur within the system, all molecular configurations are equally probable in volume V and we have

$$g^{(2)}_{ij}(\tau_p, \tau_q) \to \frac{1}{\Omega^2}, \tag{4.37}$$

where the integral $\Omega = \int d\boldsymbol{\omega}_p$ extends over all possible orientations of the p-th molecule.

It is easily verified that, by (4.37), the binary correlation constant (4.36) vanishes and the expansion (4.34) goes over into the additivity principle for Faraday's constant:

$$F = \sum_i x_i F_i, \tag{4.38}$$

which is fulfilled only for the perfect mixture exhibiting no molecular correlations.

On applying the expressions (4.35) and (4.36) to diamagnetic molecules ($\mu_m = 0$), $F_{ij} = 0$ and the approximation adopted there is also seen to yield fulfillment of the addivity of the Faraday constant (4.38), albeit we now have

$$F_i = \frac{2\pi}{3} \varrho \, \varepsilon_{\alpha\beta\gamma} \, b^{eem(i)}_{\alpha\beta\gamma}. \tag{4.39}$$

If, however, one takes into account higher approximations of the theory under consideration, the Faraday constant ceases to be additive even in the case of diamagnetic molecules. In order to prove this statement, one has to go back to the general expression (4.28) and take into consideration in Eqs (4.30) and (4.31) the molecular fields neglected when proceeding to Eq. (4.32) (see Appendix B).

Analogously to the Faraday constant (4.34), one can derive from Eq. (4.33) the following expansion for the Cotton-Mouton constant (to be denoted by C):

$$C = \sum_i x_i C_i + \sum_{ij} x_i x_j C_{ij} + \sum_{ijk} x_i x_j x_k C_{ijk} + \ldots; \tag{4.40}$$

here, in the case of diamagnetic substances, the expansion coefficients are of the form

$$C_i = \frac{\pi\varrho}{45} \chi_{\alpha\beta\gamma\delta} (c^{eemm(i)}_{\alpha\beta\gamma\delta} + \beta a^{ee(i)}_{\alpha\beta} a^{mm(i)}_{\gamma\delta}), \tag{4.41}$$

$$C_{ij} = \frac{\pi\varrho^2\beta}{45V} \int\int \chi_{\alpha\beta\gamma\delta} a^{ee(pi)}_{\alpha\beta} a^{mm(qj)}_{\gamma\delta} g^{(2)}_{ij}(\tau_p, \tau_q) d\tau_p d\tau_q. \tag{4.42}$$

The first term in (4.40) defines additivity of the Cotton-Mouton constant, whereas the remaining ones provide a measure of its deviation from additivity as a result of molecular correlations. The constants (4.41) and (4.42) are already well-adapted for application to various special cases, when a given symmetry and type of interaction of the molecules is assumed [14].

A similar discussion could be made for the case of Eq. (4.25), which defines the magnetic anisotropy induced in a medium by an intense light beam.

5. Discussion and conclusions

By a semi-macroscopic approach to magneto-optical phenomena, we have derived the general equation (4.10) (or its special case (4.17)) determining the variations to which the optical permittivity tensor is subject under the influence of a strong homogeneous magnetic field. The term linear in the magnetic field is related with the effect of magneto-optical rotation as described by the Faraday constant in the general form (4.12) or (4.20). The quadratic terms are related with magnetic birefringence as defined by the Cotton-Mouton constant (4.14) or (4.22). From Eq. (4.17), the diagonal elements of the optical permittivity tensor are obtained as follows for an arbitrary direction of the magnetic field with respect to the axes X, Y, Z of the laboratory reference frame:

$$\varepsilon_{xx}-n_0^2=\left(\frac{n_0^2+2}{3}\right)\{AH^2+C(3H_x^2-H^2)\},$$

$$\varepsilon_{yy}-n_0^2=\left(\frac{n_0^2+2}{3}\right)\{AH^2+C(3H_y^2-H^2)\},$$

$$\varepsilon_{zz}-n_0^2=\left(\frac{n_0^2+2}{3}\right)\{AH^2+C(3H_z^2-H^2)\}, \tag{5.1a}$$

whereas the non-diagonal elements are

$$\varepsilon_{xy}=\left(\frac{n_0^2+2}{3}\right)\{FH_z+3CH_xH_y\},$$

$$\varepsilon_{yx}=\left(\frac{n_0^2+2}{3}\right)\{-FH_z+3CH_yH_x\},$$

$$\varepsilon_{yz}=\left(\frac{n_0^2+2}{3}\right)\{FH_x+3CH_yH_z\},$$

$$\varepsilon_{zy}=\left(\frac{n_0^2+2}{3}\right)\{-FH_x+3CH_zH_y\},$$

$$\varepsilon_{zx}=\left(\frac{n_0^2+2}{3}\right)\{FH_y+3CH_zH_x\},$$

$$\varepsilon_{xz}=\left(\frac{n_0^2+2}{3}\right)\{-FH_y+3CH_xH_z\}. \tag{5.1b}$$

From the expressions (5.1b), we obtain the difference of non-diagonal components:

$$\varepsilon_{xy}-\varepsilon_{yx} = 2\left(\frac{n_0^2+2}{3}\right) FH_z \tag{5.2}$$

which characterize magnetic rotation of the plane of polarization, a linear function of the magnetic field, independent of the Cotton-Mouton constant and of the constant A involving magnetostriction.

We have shown that in the case of a multi-component system the Faraday constant F and Cotton-Mouton constant C obey the additivity rule only for perfect mixtures wherein no molecular correlations exist. In dense mixtures (real gases, liquid solutions and so forth), as a result of correlations existing between microsystems, the constants F and C are no longer additive. In this way, investigation of the deviations of F and C from additivity can be a source of information on the nature and size of the intermolecular forces as well as on the structure of the systems considered. Such information is all the easier to obtain owing to the fact that similar data can be gained from the study of analogous phenomena, *e.g.* of molecular light scattering [25] and electric [26] or optical [27] birefringence where, too, the additivity rule fails to be fulfilled generally.

As an example, let us consider here the case of a two-component system, for which by (4.40) the Cotton-Mouton constant is obtained in the form

$$C = x_1C_1+x_2C_2+x_1^2C_{11}+x_1x_2(C_{12}+C_{21})+x_2^2C_{22}+\ldots \tag{5.3}$$

Particularly interesting is the case of a mixture wherein the molecules of componenent 1 are spherical and those of component 2 are anisotropic but present the axial symmetry and are linearly polarizable. By (4.41) and (4.42), this case results in

$$C_1 = \frac{2\pi}{3}\varrho(c_{3333}^{eemm(1)}-c_{1133}^{eemm(1)}), \tag{5.4}$$

$$C_2 = \frac{4\pi\varrho}{45}\beta(a_{33}^{ee(2)}-a_{11}^{ee(2)})(a_{33}^{mm(2)}-a_{11}^{mm(2)}), \tag{5.5}$$

$$C_{11} = 0,\ C_{12} = C_{21} = 0,\ C_{22} = C_2J_{22}, \tag{5.6}$$

where [14, 26]

$$J_{22} = \frac{\varrho}{2V}\int\int (3\cos^2\theta_{pq}-1)g_{22}^{(2)}(\tau_p, \tau_q)d\tau_p d\tau_q \tag{5.7}$$

is a integral parameter accounting for correlation between molecules p and q whose symmetry axes subtend the angle θ_{pq}. In general, the effect of non-linear deformation is negligibly small *i.e.* $C_1 = 0$, and by Eqs (5.4—5.6) the Cotton-Mouton constant (5.3) takes the form [28]:

$$C = x_2C_2+x_2^2C_{22} = x_2C_2(1+x_2J_{22}). \tag{5.8}$$

This theoretical dependence of the Cotton-Mouton constant on the concentration of the solution is found to be in good agreement with the experimental results obtained by Surma

[29] in a number of solutions of dipolar liquids in carbon tetrachloride. A similar discussion of Eq. (5.3) would also apply to solutions in which the molecules of the solvent as well as those of the solute are anisotropic, such as *e.g.* solutions of dipolar liquids in benzene, in which case also satisfactory agreement is obtained between the theory proposed here and the experimental results [28, 29].

Investigation of the Faraday and Cotton-Mouton effects and other magneto-optical and optico-magnetic effects in gases permits to gain data on the optical and magnetic properties of the isolated atoms and molecules, particularly their non-linear properties in strong optical and magnetic fields.

Defining the intensity tensor of incident light as

$$I_{\sigma\tau} = \frac{1}{2} E_{0\sigma} E_{0\tau} \tag{5.9}$$

we can write Eq. (4.23) as follows:

$$\mu_{\sigma\tau} - \mu_0 \delta_{\sigma\tau} = A^{ee}_{mm} I \delta_{\sigma\tau} + B^{ee}_{mm} (3I_{\sigma\tau} - I\delta_{\sigma\tau}), \tag{5.10}$$

where $I = I_{\sigma\sigma} = I_{xx} + I_{yy} + I_{zz}$ is the total incident light intensity.

If, in particular, the light incident on the medium propagates in the Y-direction, we have $I_{yy} = 0$ and by Eq. (5.10) the diagonal magnetic permeability tensor components result in the form

$$\begin{aligned} \mu_{xx} - \mu_0 &= A^{ee}_{mm}(I_{xx} + I_{zz}) + B^{ee}_{mm}(2I_{xx} - I_{zz}), \\ \mu_{yy} - \mu_0 &= (A^{ee}_{mm} - B^{ee}_{mm})(I_{xx} + I_{zz}), \\ \mu_{zz} - \mu_0 &= A^{ee}_{mm}(I_{xx} + I_{zz}) + B^{ee}_{mm}(2I_{zz} - I_{xx}), \end{aligned} \tag{5.11a}$$

whereas the non-diagonal components in the form

$$\begin{aligned} \mu_{xy} &= \mu_{yx} = \mu_{yz} = \mu_{zy} = 0, \\ \mu_{zx} &= 3B^{ee}_{mm} I_{zx}, \; \mu_{xz} = 3B^{ee}_{mm} I_{xz}. \end{aligned} \tag{5.11b}$$

Form the preceding expressions, the relative difference between diagonal magnetic permeability tensor components is

$$\mu_{zz} - \mu_{xx} = 3B^{ee}_{mm}(I_{zz} - I_{xx}) \tag{5.12}$$

defining the magnetic anisotropy induced by an intense light beam propagating along the Y-axis. This, as a matter of fact, is the inverse Cotton-Mouton effect for which in the case of a diamagnetic substance the constant B^{ee}_{mm} can be replaced by the usual Cotton-Mouton constant C and Eq. (5.12) yields

$$\mu_{zz} - \mu_{xx} = 3C(I_{zz} - I_{xx}). \tag{5.13}$$

This effect has become accessible to experimental investigation owing to the availability and steady progress of laser techniques which provide light beams of very high intensity of the order of 10^{10} e.s.u.

APPENDIX A

Classical statistical perturbation theory

Here, we shall derive Eq. (3.8), which results from the expansion of Eq. (3.7) and the definition of Eq. (3.6).

Consider an arbitrary function $\Phi(\tau, \boldsymbol{E}, \boldsymbol{H})$ describing the physical state of the system at configuration τ under the effect of the external fields $\boldsymbol{E}$ and $\boldsymbol{H}$. If the system is at thermodynamical equilibrium, the mean statistical value of the function Φ in the presence of the fields $\boldsymbol{E}$ and $\boldsymbol{H}$ is given in classical statistical mechanics as follows:

$$\langle \Phi \rangle_{E,H} = \frac{\int \Phi(\tau, \boldsymbol{E}, \boldsymbol{H}) \exp\{-\beta U(\tau, \boldsymbol{E}, \boldsymbol{H})\}\, d\tau}{\int \exp\{-\beta U(\tau, \boldsymbol{E}, \boldsymbol{H})\}\, d\tau}. \tag{A.1}$$

The total potential energy $U(\tau, \boldsymbol{E}, \boldsymbol{H})$ of the system can be resolved into a part $U(\tau, 0)$ independent of $\boldsymbol{E}$ and $\boldsymbol{H}$ and a part $W(\tau, \boldsymbol{E}, \boldsymbol{H})$ dependent on $\boldsymbol{E}$ and $\boldsymbol{H}$. In cases when the energy $W(\tau, \boldsymbol{E}, \boldsymbol{H})$ can be dealt with as a perturbation to the energy $U(\tau, 0)$, the Boltzmann factors in the definition of (A.1) can be expanded in series in powers of βW, and with accuracy up to β^2 we obtain

$$\langle \Phi \rangle_{E,H} = \langle \Phi \rangle - \beta(\langle \Phi W \rangle - \langle \Phi \rangle \langle W \rangle) +$$

$$+ \frac{1}{2}\beta^2[\langle \Phi W^2 \rangle - \langle \Phi \rangle \langle W^2 \rangle - 2(\langle \Phi W \rangle - \langle \Phi \rangle \langle W \rangle)\langle W \rangle] + \ldots, \tag{A.2}$$

where the symbols $\langle\ \rangle$ denote non-perturbated statistical averageing with the Boltzmann factor $\exp\{-\beta U(\tau, 0)\}$.

The expansion (A.2) is a result of classical statistical perturbation theory. We now proceed to apply it to the calculation of the statistical averages (3.7).

Since we are interested only in the terms dependent on the magnetic field, we obtain from the general expansion (3.1) with accuracy up to the square of the field

$$W(\tau, \boldsymbol{H}) = -\mu_\sigma^m H_\sigma - \frac{1}{2} a_{\sigma\tau}^{mm} H_\sigma H_\tau - \ldots \tag{A.3}$$

Consequently, in the same approximation we obtain by (A.2) for the consecutive terms of the expansion (3.7)

$$\langle a_{\sigma\tau}^{ee} \rangle_H = \langle a_{\sigma\tau}^{ee} \rangle + \beta(\langle a_{\sigma\tau}^{ee} \mu_\nu^m \rangle - \langle a_{\sigma\tau}^{ee} \rangle \langle \mu_\nu^m \rangle) H_\nu +$$

$$+ \frac{1}{2}\beta\{\langle a_{\sigma\tau}^{ee} a_{\nu\varrho}^{mm} \rangle - \langle a_{\sigma\tau}^{ee} \rangle \langle a_{\nu\varrho}^{mm} \rangle + \beta[\langle a_{\sigma\tau}^{ee} \mu_\nu^m \mu_\varrho^m \rangle -$$

$$- \langle a_{\sigma\tau}^{ee} \rangle \langle \mu_\nu^m \mu_\varrho^m \rangle - 2(\langle a_{\sigma\tau}^{ee} \mu_\nu^m \rangle - \langle a_{\sigma\tau}^{ee} \rangle \langle \mu_\nu^m \rangle)\langle \mu_\varrho^m \rangle]\} H_\nu H_\varrho, \tag{A.4}$$

$$\langle b_{\sigma\tau\nu}^{eem} \rangle_H H_\nu = \langle b_{\sigma\tau\nu}^{eem} \rangle H_\nu + \beta(\langle b_{\sigma\tau\nu}^{eem} \mu_\varrho^m \rangle - \langle b_{\sigma\tau\nu}^{eem} \rangle \langle \mu_\varrho^m \rangle) H_\nu H_\varrho,$$

$$\langle c_{\sigma\tau\nu\varrho}^{eemm} \rangle_H H_\nu H_\varrho = \langle c_{\sigma\tau\nu\varrho}^{eemm} \rangle H_\nu H_\varrho + \ldots$$

The tensors μ_σ^m, $a_{\sigma\tau}^{ee}$, ... appearing above, which are given in the laboratory reference frame X, Y, Z, are conveniently referred by means of the following transformation formulas to the molecular reference system 1, 2, 3 attached to the molecule:

$$\mu_\sigma = \omega_{\sigma\alpha}\mu_\alpha, \quad a_{\sigma\tau} = \omega_{\sigma\alpha}\omega_{\tau\beta}a_{\alpha\beta}, \ \ldots \tag{A.5}$$

Here, the transformation coefficients $\omega_{\sigma\alpha}$, ... in the case of rectangular reference frames have the meaning of cosines of the angles between the axes σ and α of the laboratory and molecular reference frames, respectively.

With the transformational formulas (A.5), the expressions (A.4) become

$$\begin{aligned}
\langle a_{\sigma\tau}^{ee}\rangle_H &= a_{\alpha\beta}^{ee}\langle\omega_{\sigma\alpha}\omega_{\tau\beta}\rangle + \beta a_{\alpha\beta}^{ee}\mu_\gamma^m(\langle\omega_{\sigma\alpha}\omega_{\tau\beta}\omega_{\nu\gamma}\rangle - \langle\omega_{\sigma\alpha}\omega_{\tau\beta}\rangle\langle\omega_{\nu\gamma}\rangle)H_\nu + \\
&+ \frac{1}{2}\beta\{a_{\alpha\beta}^{ee}a_{\gamma\delta}^{mm}(\langle\omega_{\sigma\alpha}\omega_{\tau\beta}\omega_{\nu\gamma}\omega_{\varrho\delta}\rangle - \langle\omega_{\sigma\alpha}\omega_{\tau\beta}\rangle\langle\omega_{\nu\gamma}\omega_{\varrho\delta}\rangle) + \\
&+ \beta a_{\alpha\beta}^{ee}\mu_\gamma^m\mu_\delta^m[\langle\omega_{\sigma\alpha}\omega_{\tau\beta}\omega_{\nu\gamma}\omega_{\varrho\delta}\rangle - \langle\omega_{\sigma\alpha}\omega_{\tau\beta}\rangle\langle\omega_{\nu\gamma}\omega_{\varrho\delta}\rangle - \\
&- 2(\langle\omega_{\sigma\alpha}\omega_{\tau\beta}\omega_{\nu\gamma}\rangle - \langle\omega_{\sigma\alpha}\omega_{\tau\beta}\rangle\langle\omega_{\nu\gamma}\rangle)\langle\omega_{\varrho\delta}\rangle]\}H_\nu H_\varrho, \qquad \text{(A.6)} \\
\langle b_{\varrho\tau\nu}^{eem}\rangle_H H_\nu &= b_{\alpha\beta\gamma}^{eem}\langle\omega_{\sigma\alpha}\omega_{\tau\beta}\omega_{\nu\gamma}\rangle H_\nu + \\
&+ \beta b_{\alpha\beta\gamma}^{eem}\mu_\delta^m(\langle\omega_{\sigma\alpha}\omega_{\tau\beta}\omega_{\nu\gamma}\omega_{\varrho\delta}\rangle - \langle\omega_{\sigma\alpha}\omega_{\tau\beta}\omega_{\nu\gamma}\rangle\langle\omega_{\varrho\delta}\rangle)H_\nu H_\varrho, \\
\langle c_{\sigma\tau\nu\varrho}^{eemm}\rangle_H H_\nu H_\varrho &= c_{\alpha\beta\gamma\delta}^{eemm}\langle\omega_{\sigma\alpha}\omega_{\tau\beta}\omega_{\nu\gamma}\omega_{\varrho\delta}\rangle H_\nu H_\varrho + \ldots
\end{aligned}$$

For a gas, calculation of the statistical averages in the absence of $\boldsymbol{H}$ reduces to averageing over all possible orientations of the molecule with respect to the axes of the laboratory reference frame, and we have [30]

$$\begin{aligned}
&\langle\omega_{\sigma\alpha}\rangle = 0, \quad \langle\omega_{\sigma\alpha}\omega_{\tau\beta}\rangle = \frac{1}{3}\delta_{\alpha\beta}\delta_{\sigma\tau}, \\
&\langle\omega_{\sigma\alpha}\omega_{\tau\beta}\omega_{\nu\gamma}\rangle = \frac{1}{6}\varepsilon_{\alpha\beta\gamma}\varepsilon_{\sigma\tau\nu}, \\
&\langle\omega_{\sigma\alpha}\omega_{\tau\beta}\omega_{\nu\gamma}\omega_{\varrho\delta}\rangle + \frac{1}{30}\{(4\delta_{\alpha\beta}\delta_{\gamma\delta} - \delta_{\alpha\gamma}\delta_{\beta\delta} - \delta_{\alpha\delta}\delta_{\beta\gamma})\delta_{\sigma\tau}\delta_{\nu\varrho} + \\
&+ (4\delta_{\alpha\gamma}\delta_{\beta\delta} - \delta_{\alpha\delta}\delta_{\beta\gamma} - \delta_{\alpha\beta}\delta_{\gamma\delta})\delta_{\sigma\nu}\delta_{\tau\varrho} + (4\delta_{\alpha\delta}\delta_{\beta\gamma} - \delta_{\alpha\beta}\delta_{\gamma\delta} - \delta_{\alpha\gamma}\delta_{\beta\delta})\delta_{\sigma\varrho}\delta_{\tau\nu}\}, \qquad \text{(A.7)}
\end{aligned}$$

where $\delta_{\alpha\beta}$ is the Kronecker unit tensor with components equal to unity for $\alpha = \beta$ and zero for $\alpha \neq \beta$, whereas $\varepsilon_{\alpha\beta\gamma}$ is the Levi-Cività extensor with components equalling ± 1 if all indices α, β, γ are different and their permutation even (sign +) or odd (sign −) and zero if at least two of the indices are the same.

With regard to the mean values (A.7), the coefficients of the expansion (A.6) finally assume the form

$$\langle a^{ee}_{\sigma\tau}\rangle_H = a_e\delta_{\sigma\tau} + \frac{1}{6}\beta\varepsilon_{\alpha\beta\gamma}a^{ee}_{\alpha\beta}\mu^m_\gamma\varepsilon_{\sigma\tau\nu}H_\nu +$$

$$+ \frac{\beta}{180}\chi_{\alpha\beta\gamma\delta}a^{ee}_{\alpha\beta}(a^{mm}_{\gamma\delta}+\beta\mu^m_\gamma\mu^m_\delta)(3H_\sigma H_\tau - H^2\delta_{\sigma\tau}),$$

$$\langle b^{eem}_{\sigma\tau\nu}\rangle_H H_\nu = \frac{1}{6}\varepsilon_{\alpha\beta\gamma}b^{eem}_{\alpha\beta\gamma}\varepsilon_{\sigma\tau\nu}H_\nu + \frac{\beta}{9}b^{eem}_{\alpha\alpha\beta}\mu^m_\beta H^2\delta_{\sigma\tau} + \frac{\beta}{90}\chi_{\alpha\beta\gamma\delta}b^{eem}_{\alpha\beta\gamma}\mu^m_\delta(3H_\sigma H_\tau - H^2\delta_{\sigma\tau}),$$

$$\frac{1}{2}\langle c^{eemm}_{\sigma\tau\nu\varrho}\rangle_H H_\nu H_\varrho = \frac{1}{18}c^{eemm}_{\alpha\alpha\beta\beta}H^2\delta_{\sigma\tau} + \frac{1}{180}\chi_{\alpha\beta\gamma\delta}c^{eemm}_{\alpha\beta\gamma\delta}(3H_\sigma H_\tau - H^2\delta_{\sigma\tau}), \tag{A.8}$$

where the tensor $\chi_{\alpha\beta\gamma\delta}$ is given by (3.12).

On substituting the expressions (A.8) into the expansion (3.7) and on ordering according to powers of the field H, we obtain Eq. (3.8).

APPENDIX B

Effect of molecular fields on the Faraday constant

On introducing the expansions (4.30) and (4.31) into the general equation (4.28) for the Faraday constant, we obtain, for diamagnetic substances, the expression

$$F = \frac{2\pi}{3V}\varepsilon_{\alpha\beta\gamma}\sum_i\left\langle\sum_{p=1}^{N_i} b^{eem(pi)}_{\alpha\varepsilon\eta}\left(\delta_{\varepsilon\beta}+\frac{\partial F^{(pi)}_\varepsilon}{\partial E_\beta}\right)\left(\delta_{\eta\gamma}+\frac{\partial G^{(pi)}_\eta}{\partial H_\gamma}\right)\right\rangle, \tag{B.1}$$

which contains the influence of the electric and magnetic molecular fields on the Faraday constant. In general, that of the magnetic molecular field is by far the smaller, and can be neglected in subsequent calculations, so that we can rewrite (B.1) in the form

$$F = \frac{2\pi}{3V}\varepsilon_{\alpha\beta\gamma}\sum_i\left\langle\sum_{p=1}^{N_i}\left(b^{eem(pi)}_{\alpha\beta\gamma}+b^{eem(pi)}_{\alpha\delta\gamma}\frac{\partial F^{(pi)}_\delta}{\partial E_\beta}\right)\right\rangle. \tag{B.2}$$

We shall restrict our further calculations to the electric molecular field related with interactions of the dipolar type defined by [14]:

$$F^{(pi)}_\alpha = -\sum_j\sum_{\substack{q=1\\ q\neq p}}^{N_j} T^{(pq)}_{\alpha\beta}m^{(qj)}_{e\beta}, \tag{B.3}$$

where the tensor

$$T^{(pq)}_{\alpha\beta} = -r^{-5}_{pq}(3r_{pq\alpha}r_{pq\beta}-r^2_{pq}\delta_{\alpha\beta}) \tag{B.4}$$

characterizes dipole type interaction between molecules p and q mutually distant by r_{pq}.

On substituting the expansion (4.30) into (B.3) and on retaining only terms linear in $\boldsymbol{E}$ we get

$$F_{\alpha}^{(pi)} = F_{0\alpha}^{(pi)} - \sum_{j} \sum_{\substack{q=1 \\ q \neq p}}^{N_j} T_{\alpha\beta}^{(pq)} a_{\beta\gamma}^{ee(qj)} E_{\gamma} + \\ + \sum_{jk} \sum_{\substack{q=1 \\ q \neq p}}^{N_j} \sum_{\substack{r=1 \\ r \neq q}}^{N_k} T_{\alpha\beta}^{(pq)} a_{\beta\gamma}^{ee(qj)} T_{\gamma\delta}^{(qr)} a_{\delta\varepsilon}^{(rk)} E_{\varepsilon} - \ldots, \tag{B.5}$$

where

$$F_{0\alpha}^{(pi)} = - \sum_{j} \sum_{\substack{q=1 \\ q \neq p}}^{N_j} T_{\alpha\beta}^{(pq)} \mu_{e\beta}^{(qj)} + \sum_{jk} \sum_{\substack{q=1 \\ q \neq p}}^{N_j} \sum_{\substack{r=1 \\ r \neq q}}^{N_k} T_{\alpha\beta}^{(pq)} a_{\beta\gamma}^{ee(qj)} T_{\gamma\delta}^{(qr)} \mu_{e\delta}^{(rk)} - \ldots \tag{B.6}$$

is the molecular electric field in the absence of external fields.

Taking into account the expansion (B.5), we can write out Eq. (B.2) as follows:

$$F = \frac{2\pi}{3V} \varepsilon_{\alpha\beta\gamma} \left\{ \sum_{i} \left\langle \sum_{p=1}^{N_i} b_{\alpha\beta\gamma}^{eem(pi)} \right\rangle - \sum_{ij} \left\langle \sum_{p=1}^{N_i} \sum_{\substack{q=1 \\ q \neq p}}^{N_j} b_{\alpha\delta\gamma}^{eem(pi)} T_{\delta\varepsilon}^{(pq)} a_{\varepsilon\beta}^{ee(qj)} \right\rangle + \right. \\ \left. + \sum_{ijk} \left\langle \sum_{p=1}^{N_i} \sum_{\substack{q=1 \\ q \neq p}}^{N_j} \sum_{\substack{r=1 \\ r \neq q}}^{N_k} b_{\alpha\delta\gamma}^{eem(pi)} T_{\delta\varepsilon}^{(pq)} a_{\varepsilon\eta}^{(qj)} T_{\eta\vartheta}^{(qr)} a_{\vartheta\beta}^{(rk)} \right\rangle - \ldots \right\}. \tag{B.7}$$

The above expression can formally be expanded in a series in powers of the molar fractions:

$$F = \sum_{i} x_i F_i + \sum_{ij} x_i x_j F_{ij} + \sum_{ijk} x_i x_j x_k F + \ldots \tag{B.8}$$

Here, the constant F_i is given by (4.39), and the other constants are of the form

$$F_{ij} = - \frac{2\pi}{3V} \varrho^2 \int\int \varepsilon_{\alpha\beta\gamma} \{ b_{\alpha\delta\gamma}^{eem(pi)} T_{\delta\varepsilon}^{(pq)} a_{\varepsilon\beta}^{ee(qj)} - \\ - b_{\alpha\delta\gamma}^{eem(pi)} T_{\delta\varepsilon}^{(pq)} a_{\varepsilon\eta}^{(qj)} T_{\eta\vartheta}^{(qp)} a_{\vartheta\beta}^{(pi)} + \ldots \} g_{ij}^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q, \tag{B.9}$$

$$F_{ijk} = \frac{2\pi}{3V} \varrho^3 \int\int\int \varepsilon_{\alpha\beta\gamma} b_{\alpha\beta\gamma}^{eem(pi)} T_{\delta\varepsilon}^{(pq)} a_{\varepsilon\eta}^{(qj)} T_{\eta\vartheta}^{(qr)} a_{\vartheta\beta}^{(rk)} g_{ijk}^{(3)}(\tau_p, \tau_q, \tau_r) d\tau_p d\tau_q d\tau_r, \tag{B.10}$$

where $g_{ijk}^{(3)}(\tau_p, \tau_q, \tau_r)$ is the ternary correlation function of molecules p, q and r of species i, j and k.

Thus indeed, in highly dense systems, as a result of interaction between the induced electric dipoles, the Faraday constant is not an additive quantity even in the case of diamagnetic substances.

Quite similarly, the Cotton-Mouton constant (4.29) with Eqs (4.30), (4.31) and (B.3) can be discussed for the various cases involving the effect of molecular fields [14].

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