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Conservative dichroism of polydisperse colloids and suspensions subjected to electric field

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An electro-optical technique for studying colloids and suspensions with particles of a wide range of sizes is considered. This technique can be used to study the formation of aggregates in liquid disperse systems, as well as the electrical polarizability of particles, which depends on the electrical and adsorption characteristics of their surface. Relationships were obtained that allow to distinguish two electro-optical effects from the observed change in the dependences of light intensity caused by the external electric field. One effect is determined by the polarization of incident light dichroism. The other effect is not related to the polarization of light. Experimental studies of aqueous colloids of diamond and graphite confirmed the applicability of the obtained relationships used to determine the electric field-induced dichroism of colloids and the electro-optical effect independently of light polarization. It is shown that the polarization-independent effect is not observed in systems with small particles, but as the particle size increases, this second effect becomes comparable to dichroism.

Keywords: colloids, suspensions, electrooptical effect, dichroism, extinction coefficient, polarized light.

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Introduction

Colloids and suspensions belong to heterogeneous systems, and their optical properties should largely be associated with light scattering by particles of the dispersed phase, the intensity of which exceeds by several orders of magnitude the intensity of molecular scattering of the dispersion medium. The main concept of the orientation theory by P. Langevin [1] and M. Born [2], explaining the Kerr effect in single-phase systems, is applicable to colloids as well, but the nature of this effect differs [3]. According to W. Heller's classification, optical effects caused by anisotropy of light scattering in colloids during orientation ordering of particles include double refraction, conservative dichroism, and the Tyndall effect [4]. All these effects are experimentally observed during particle orientation by an electric field and used in colloid studies [3,5–8]. Theory of these effects began to develop in the second half of the 20th century and is still being refined. Major achievements [9–11] relate to advances in light scattering theory by non-spherical particles. In dispersed systems including colloids and suspensions containing particles sized tens of nanometers or more, particle orientation order can be controlled by applying short electric field pulses up to 10 kV/cm without altering the system itself. This allows wide possibilities for electro-optical methods.

Electric birefringence (EB), dichroism (ED), and light scattering (ELS) of colloids and suspensions are widely used to study adsorption of ionogenic and nonionogenic surfactants on nano- and submicron particles; investigate their double electric layer; determine particle size, shape, and distribution; study stability of liquid nanodispersed systems and aggregation processes. EB has been used to study the influence of gold nanoparticle coatings on particle orientation in an electric field [12] and orientation order dispersion in aqueous silver nanowire dispersions [13]. Using log-normal law approximation, influence of particle size distribution on transient EB processes was studied [14]. A new mathematical method analyzing polydispersity via integral equations in relaxation studies of EB, ED, and ELS was proposed [15]. ED [16] and EB [17] studied particle polarizability linked to polarization of their double electric layer in monovalent electrolytes. ED study of diamond sols analyzed dielectric particle polarizability theory in electrolytes [18]. Influence of electrolytes on Kerr constant in aqueous graphene oxide colloidal solutions was investigated [19]. Electro-optical methods demonstrated possibilities in kinetic studies of coagulation and paired aggregate formation of graphite particles in water [20]. ED and EB studied effect of near-electrode charge on electrophoretic mobility [21]. ELS studied electric dipole moments of Escherichia coli HB 101 bacteria in aqueous electrolytes [22].

Analysis [11] of particle size impact on EB and ED in dispersed systems with colloids established criteria to separate these effects in experimental polarization analysis of light transmitted through the system. Electro-optical effects observed in dispersed systems linked to electric field-induced changes in transmitted light intensity have one part dependent on incident light polarization direction (ED), another independent part caused by another electro-optical effect designated as effect A). A effect is not observed in small-particle systems with pronounced EB and increases with particle size.

This study aims to consider electro-optical effects observed in light passing through dispersed systems based on light scattering theory by particles and develop criteria distinguishing ED and A effect. Experimental results show influence of particle size, shape, and composition on ratio between ED and effect A in several dispersed systems.

Theoretical section

Light attenuation in dispersed systems under electric field

Orientation of nonspherical particles along electric field in dispersed systems like colloids and suspensions causes extinction coefficient to depend on angle between field intensity and polarization plane of incident linearly polarized light. This reflects system anisotropy and changes light scattering characteristics. Complex amplitude of electric field of light wave accounts for magnitude and initial phase of field oscillations. Orientation of particles in the electric field causes complex amplitude of transmitted light to depend on incident light polarization: The dependence of the real part of the complex amplitude of transmitted light characterizes the ED, and the imaginary part characterizes the EB. ED and EB processes in colloids differ fundamentally from those in gases, liquids, and crystals; in colloids and suspensions, they are conservative phenomena governed by anisotropy of light scattering due to particle orientation changes rather than molecular absorption/refraction anisotropy. The terms „conservative absorption“ and „conservative dichroism“ introduced by M. Planck and V. Heller used in discussing light attenuation and dichroism in solutions and liquid dispersed systems caused by scattering on high valency ions and particles [23].

We will denote by subscripts $(\perp)$ and $(\|)$ the quantities related to polarization directions perpendicular (ordinary ray) and parallel (extraordinary ray) to the external electric field. Let light propagate perpendicular to the external field, and let vectors $\mathbf{E^0}$ and $\mathbf{E}$ represent the incident and transmitted light waves through the dispersed system. The projections of $\mathbf{E^0}$ and $\mathbf{E}$ onto these directions can be related by the matrix relation [24,25].

$$\begin{bmatrix} E_{\|} \\ E_{\perp} \end{bmatrix} = \begin{bmatrix} 1 - qS_2 & qS_3 \\ qS_4 & 1 - qS_1 \end{bmatrix} \begin{bmatrix} E^0_{\|} \\ E^0_{\perp} \end{bmatrix},$$

where $q = 2\pi n_p l/\lambda$, l -are the path length of the light beam in the colloidal system, λ is the wavelength of light in it, n_p — is the number of particles per unit volume, and S_1, S_2, S_3 and S_4 are complex elements of the forward light scattering matrix by the particles. Here it is assumed that the particle concentration is low and scattering is single. In systems containing particles of different sizes, shapes, and varying orientations relative to the directions of propagation and polarization of incident light, elements S_1, S_2, S_3 and S_4 are averaged scattering matrix elements of individual particles over sizes, shapes, and orientation angles defining particle orientation. The size of a rigid particle is usually taken as the radius of a sphere r, whose volume equals the particle volume. The shape parameter p is taken as the ratio of the semi-axes of the ellipsoid of revolution most closely resembling the particle shape [26]. In some cases, approximation of particles by truncated cylinders or Chebyshev polynomials (Chebyshev particles) is used [27].

If a complex refractive index is used to describe dispersed systems, then for the ordinary and extraordinary rays defining birefringence and dichroism, the following relation is valid [28]:

$$n_{\perp,\|} - \mathrm{i}n'_{\perp,\|} = n_0\Big(1 - i2\pi \frac{n_p}{k^3} S_{1,2}\Big), \tag{1}$$

where $n_{\perp,\|}$ and $n'_{\perp,\|}$ are the real and imaginary parts of the refractive index of the dispersed system scattering light, n_0 is the refractive index of the transparent medium in which particles are suspended, $k = 2\pi n_0/\lambda$, $S_{1,2}(0)$ are averaged forward scattering matrix elements [29]. In the case of chaotic orientation of particles: $S_1 = S_2$.

Replacing particles by spheres and defining S within the Mie theory framework allows estimating the influence of particle sizes on the refractive index of the dispersed system. Calculations show [30] that for an aqueous diamond colloid scattering light once, an increase in r/λ from 0.1 to 0.2 causes a decrease in $n - n_0$ by 2.1 times and an increase in n' by 7.5 times in the visible spectral region. Further increase of r/λ leads to a non-monotonic decrease of $n - n_0$ to zero and passage of n' through regions of local maxima at $0.15 < r/\lambda < 0.4$ (regions of diffraction resonance) followed by its further decrease. For dispersed systems with light-absorbing particles, dependencies of $n - n_0$ and n' on r/λ — show decreasing trends, with $n - n_0$ values decreasing faster with increasing r/λ than in cases of non-light-absorbing particles.

Formula (1) accounts only for the electric component of the light wave in determining the refractive index of the dispersed system. Using theory that accounts for the magnetic component of light waves when determining the refractive index of a system with particles comparable in size to the light wavelength leads to similar results [31,32]. It can be concluded that increasing particle sizes leads to a decrease in electric birefringence (EB) and an increase in electric dichroism (ED) caused by light scattering of dispersed systems. Such a conclusion was previously made based on experimental studies of electro-optical properties of colloids [33–35]. As follows from relation (1), intensities $J_{\|}$ and $J_{\perp}$ of light passing through the dispersed system can be represented by formulas:

$$J_{\|}/J^0_{\|} = (1 - 2q\mathrm{Re}\,(S_2)) \text{ and } J_{\perp}/J^0_{\perp} = (1 - 2q\mathrm{Re}\,(S_1)), \tag{2}$$

where $J^0_{\|}$ and $J^0_{\perp}$ are intensities of incident light polarized parallel and perpendicular, respectively, to the field applied to the dispersed system. Here we neglect values $q^2S^2_{1,2}$

because of their smallness [24]. Use of non-monochromatic light also leads to averaging S_1 and S_2 over sizes, shape parameters, and wavelengths.

Dichroism N accounting for both absorption and light scattering, is defined as the difference $J_\perp/J_\perp^0$ minus $J_\parallel/J_\parallel^0$ and, taking into account (2), can be represented as:

$$N = J_\perp/J_\perp^0 - J_\parallel/J_\parallel^0 = 2q\mathrm{Re}\,(S_1 - S_2)\,. \tag{3}$$

To determine values S_1 and S_2, one must construct scattering matrices $\mathbf{S_p}$ of individual particles in coordinate systems linked with them, determine matrix elements $\mathbf{S_p}$ in the laboratory coordinate system, and average them over particle orientation angles, sizes, and shape parameters. In calculations of matrix elements $\mathbf{S_p}$ corresponding to different angles of light incidence on particles and scattering angles, algorithms applicable to dispersed systems and based on several methods of light scattering research by nonspherical particles are used, including discrete dipole approximation, separation of variables method, null-field method, and others [36–39]. The choice of method depends on particle sizes, shape parameters, and substance. The most general and widely used method is the T-matrix method [40–42]. All these methods are effective and applicable to calculating light scattering by systems with particles oriented in electric and magnetic fields but require large computational resources [26], which are not always available in laboratory conditions. For simpler algorithms enabling the use of ED in laboratory studies of colloids and suspensions, additional theoretical assumptions are necessary.

Phenomenological theory

Let us assume particles have an axis of rotation. Introduce a coordinate system linked to the particle such that axis 1 is the symmetry axis of the particle, and axes 2 and 3 lie in the plane perpendicular to it. Let κ_1 and κ_2 be the extinction cross sections of the particle for light propagating perpendicular to axis 1 and polarized along axes 1 and 2, respectively, and let extinction cross section κ_3 correspond to light propagating along axis 1. Cross section κ_3 does not depend on the polarization direction of incident light. Consider small particles for which extinction cross sections change proportionally to the imaginary parts of their polarizabilities [24,28]. For such particles, the relations $\kappa_1 = 4\pi k\alpha_1'$, $\kappa_2 = 4\pi k\alpha_2'$ and $\kappa_3 = 4\pi k\alpha_3'$, where α_1', α_2' and α_3' are imaginary parts of the principal elements of the optical polarizability tensor of the particles.

Let in the laboratory coordinate system XYZ light propagate along axis X, the electric field orienting the particles be directed along axis Z, and the orientation direction of the particle's axis of rotation be set by polar angle θ and azimuthal angle φ as shown in Fig. 1. With chaotic orientation of small particles, mean values of light attenuation cross section $\langle\kappa\rangle$ and polarizability $\langle\alpha'\rangle$ of particles are connected by the similar relation $\langle\kappa\rangle = 4\pi k\langle\alpha'\rangle$. As follows from the theory of ED and EB in dispersed systems with small particles [1,43], in an electric field the mean values of cross sections $\kappa_\parallel$, $\kappa_\perp$ for light polarized along axes Z and Y respectively, can be represented by the relations:

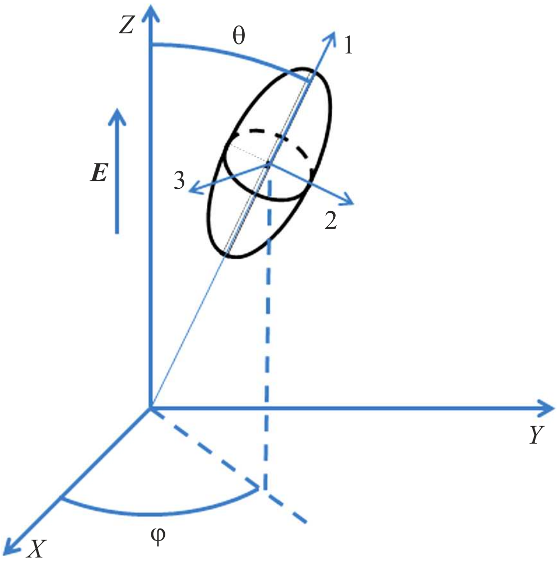

Figure 1. Particle orientation in the laboratory coordinate system.

$$\kappa_\parallel = \int_\omega \sum_{i=1}^{3} \kappa_i \cos^2(Z, i) W d\omega,$$

$$\kappa_\perp = \int_\omega \sum_{i=1}^{3} \kappa_i \cos^2(Y, i) W d\omega, \quad i = 1, 2, 3. \tag{4}$$

Here, (Z,i), and (Y,i) are angles between axes Z and Y of the laboratory coordinate system and axes 1, 2, and 3 of the coordinate systems linked to the particles, W is the distribution function of axis 1 of particles over angles θ and φ, $d\omega$ is an element of solid angle. With chaotic particle orientation, $\langle\kappa\rangle = \kappa_\parallel = \kappa_\perp$ and

$$\int_\omega \cos^2(Z, i) W d\omega = \int_\omega \cos^2(Y, i) W d\omega = \frac{1}{3}.$$

Taking this into account, one can write:

$$\langle\kappa\rangle = \frac{\kappa_1 + \kappa_2 + \kappa_3}{3}\,. \tag{5}$$

Particle orientational ordering does not depend on angle φ in this case $\theta = (Z, 1)$ and $W = W(\theta)$. After averaging $\kappa_\parallel$ and $\kappa_\perp$over azimuthal angle φsimilarly to EB [43] we obtain:

$$\left(\kappa_\parallel - \langle\kappa\rangle\right) / \left(\kappa_\perp - \langle\kappa\rangle\right) = -2, \tag{6}$$

$$\kappa_\parallel - \kappa_\perp = (\kappa_1 - \kappa_2) \int_0^\pi P_2(\cos\theta) W(\theta) \sin\theta d\theta,$$

where $P_2(\cos\theta) = \left(3\cos^2\theta - 1\right)/2$.

At steady-state particle orientation in the field, the function $W(\theta)$ can be obtained by solving the diffusion equation in a force field; it is given by the Boltzmann formula:

$$W(\theta, E) = C\exp\left(u(\theta)/k_B T\right).$$

Here $u(\theta)$ is the potential energy of particles, C is the normalization coefficient, k_B is the Boltzmann constant, and T is the temperature. The potential energy of particles $u(\theta)$ depends on the anisotropy of the polarizability $\Delta\gamma$ of particles at the field frequency, the permanent dipole moment of the particles μ and the intensity of the applied field E. It can be expressed as:

$$u(\theta) = \Delta\gamma E^2\cos^2\theta + \mu E\cos\theta.$$

As a result, at steady-state particle orientation, one can write:

$$\kappa_{\parallel} - \kappa_{\perp} = (\kappa_1 - \kappa_2)\,\Phi_{\mathrm{st}}(\Delta\gamma, \mu, E), \tag{7}$$

where

$$\Phi_{\mathrm{st}}(\Delta\gamma, \mu, E) = \int\limits_{-1}^{1} x^2\exp\left(\frac{\Delta\gamma}{k_B T}x^2 + \frac{\mu}{k_B T}x\right)dx \Bigg/ \int\limits_{-1}^{1}\exp\left(\frac{\Delta\gamma}{k_B T}x^2 + \frac{\mu}{k_B T}x\right)dx. \tag{8}$$

For the relaxation of the orientational ordering of particles [44]

$$W(\theta, t) = \sum_{j=1}^{\infty} c_j P_j(\cos\theta)\exp\left(-j(j+1)D_r t\right).$$

Here $P_j(\cos\theta)$ are associated Legendre polynomials, t is time, D_r is the rotational diffusion constant of particles. When determining coefficients c_j the dependence of $W(\theta)$ at the initial relaxation moment is used. During relaxation, the following relation holds:

$$\kappa_{\parallel} - \kappa_{\perp} = (\kappa_1 - \kappa_2)\,\Phi_{\mathrm{rel}}(D_r, t), \tag{9}$$

in which

$$\Phi_{\mathrm{rel}} = \Phi_{\mathrm{st}}\exp(-6D_r t). \tag{10}$$

For light transmitted through the dispersed system, the relations hold:

$$J_{\parallel} = J_0\left(1 - n_p l\kappa_{\parallel}\right), \quad J_{\perp} = J_0\left(1 - n_p l\kappa_{\perp}\right),$$
$$J = J_0\left(1 - n_p l\langle\kappa\rangle\right), \tag{11}$$

where J_0 is the intensity of light incident on the dispersed system, J is the transmitted light intensity at chaotic particle concentration, $J_{\parallel}$ and $J_{\perp}$ are intensities of light transmitted polarized parallel and perpendicular to the orienting field, respectively. Here, it is assumed that the intensity J_0 is the same for both polarizations of light. As before, l is the path length of the light beam in the dispersed system, and n_p is the number of particles per unit volume. Dichroism, defined by relation (3), is connected with $\kappa_{\parallel}$ and $\kappa_{\perp}$ by the equality:

$$N = n_p l\left(\kappa_{\parallel} - \kappa_{\perp}\right).$$

The values of $\kappa_{\parallel}$, $\kappa_{\perp}$ and $\langle\kappa\rangle$ depend on particle sizes, and in polydisperse systems, when determining $J_{\parallel}$, $J_{\perp}$ and J the size distribution function $\phi(r)$ of particles by size $r$should be taken into account. For such systems, in relations (11), the substitutions should be made:

$$n_p l\kappa_{\parallel} \to n_p l\int\kappa_{\parallel}(r)\phi(r)dr,$$

$$n_p l\kappa_{\perp} \to n_p l\int\kappa_{\perp}(r)\phi(r)dr,$$

$$n_p l\kappa \to n_p l\int\kappa(r)\phi(r)dr.$$

Taking into account (11), instead of equality (6), valid for small particles, one can write:

$$\left(J_{\parallel} - J\right)/\left(J_{\perp} - J\right) = -2. \tag{12}$$

This equality does not depend on particle orientation degree and applies to both monodisperse and polydisperse systems.

Considering (7) and (9), the stationary dichroism and its relaxation for polydisperse systems can be expressed by the relations:

$$N(E) = \int\limits_{r0}^{r1}\Delta K(r)\Phi_{\mathrm{st}}\left(\Delta\gamma(r), \mu(r), E\right)\phi(r)dr, \tag{13}$$

$$N(t) = \int\limits_{r0}^{r1}\Delta K(r)\Phi_{\mathrm{rel}}\left(D_r(r), t\right)\phi(r)dr. \tag{14}$$

Here $\Delta K(r) = \left(\kappa_1(r) - \kappa_2(r)\right)n_p l$ is the dichroic weight.

If particles are comparable in size to or larger than the wavelength of incident light, relations (4)–(6) and (12) do not hold. For systems with such particles, $\kappa_{\parallel}$, $\kappa_{\perp}$ and κ are represented as:

$$\kappa_{\parallel} = \int\limits_{\omega}\sum_{i=1}^{3}\kappa_i\cos^2(Z, i)\,W d\omega + s_{\parallel}, \tag{15}$$

$$\kappa_{\perp} = \int\limits_{\omega}\sum_{i=1}^{3}\kappa_i\cos^2(Y, i)\,W d\omega + s_{\perp}, \tag{16}$$

$$\langle\kappa\rangle = \frac{\kappa_1 + \kappa_2 + \kappa_3}{3} + s. \tag{17}$$

Here,

$$s_{\parallel} = \int\limits_{0}^{\pi}\int\limits_{0}^{2\pi} s_{\parallel}(\theta, \varphi)\,d\varphi W(\theta)\sin\theta d\theta,$$

$$s_\perp = \int_0^\pi \int_0^{2\pi} s_\perp(\theta, \varphi)\, d\varphi W(\theta) \sin\theta d\theta,$$

$$\langle s \rangle = \int_0^\pi \int_0^{2\pi} s(\theta, \varphi)\, d\varphi W(\theta) \sin\theta d\theta.$$

Angular dependencies $s_\parallel(\theta, \varphi)$, $s_\perp(\theta, \varphi)$ and $s(\theta, \varphi)$ are determined by elements of the particle light scattering matrix. They depend on particle size, shape, and size-to-wavelength ratio. For systems with particles of various sizes and shapes, averaging of dependencies $s_\parallel(\theta, \varphi)$, $s_\perp(\theta, \varphi)$ and $s(\theta, \varphi)$ characteristic of individual particles over r, p and r/λ substantially smooths them. Using broadband light sources, r/λ varies widely even for monodisperse systems. From relations $(15)-(17)$ it follows that for chaotic particle orientation, values $s_\parallel$, $s_\perp$ and $\langle s \rangle$ coincide. For particles fully oriented along the field, the values for light polarized along the field are $\kappa_\parallel = \kappa_1$ and $\sum_{i=1}^{3} \kappa_i \cos^2(Z, i)\, W d\omega = \kappa_1$. Substituting these values into (15) gives $s_\parallel = 0$. Analogously, for light polarized perpendicular to the field, we have $s_\perp = 0$. As a result, the equality $s_\parallel = s_\perp$ holds both for full and chaotic particle orientations. We suppose that the equality

$$s_\parallel = s_\perp \tag{18}$$

holds for arbitrary degrees of particle orientation. However, the applicability of this assumption requires experimental confirmation, which was carried out.

Additional intensity caused by values $s_\parallel$, $s_\perp$ and$\langle s \rangle$, which should be taken into account when determining $J_\parallel$, $J_\perp$ and J by formulas (11), can be defined by the relations:

$$\Delta J_\parallel = J_0\, n_p\, l\, s_\parallel, \quad \Delta J_\perp = J_0\, n_p\, l\, s_\perp, \quad \Delta J = J_0\, n_p\, l \langle s \rangle.$$

Since the dichroism N value depends on the difference $J_\perp - J_\parallel$, under fulfillment of equality $\Delta J_\perp = \Delta J_\parallel$, resulting from relation (18), the magnitude N does not depend on $\Delta J_\parallel$, $\Delta J_\perp$, ΔJ and formulas (13) and (14) remain applicable to dispersed systems containing both small and large particles.

Relation (18) corresponds to the results of studies associated with the determination of dichroism N. Use of formula (13) for particle polarizability studies leads to results consistent with polarizability theory [16,18]. Distribution functions $\phi(r)$ determined by formula (14) correspond to particle size distribution histograms obtained by scanning electron microscopy [20]. This matches relation (18) in such experiments, as equations (13) and (14) hold only when it is satisfied. Functions $f(r) = \Delta K(r)\phi(r)$ defined by solving equation (14) were used in studying kinetic coagulation of graphite sols [20]. The results correspond to Smoluchowski's rapid coagulation theory, which also agrees with (18).

In systems where $s_\parallel$, $s_\perp$ and $\langle s \rangle$, must be considered, relation (12) ceases to hold and $\left(J_\parallel - J\right) / \left(J_\perp - J\right) \neq -2$. However,

$$\left(J_\parallel - J - J_A\right) / \left(J_\perp - J - J_A\right) = -2,$$

if:

$$J_A = \left(J_\parallel - J\right)/3 + 2\left(J_\perp - J\right)/3. \tag{19}$$

The intensity J_A like intensities $J_\parallel$ and $J_\perp$ depends on the particle orientation in the field. At $E = 0$ particle orientation is chaotic, and $J_A = 0$, and at $E \to \infty$ particle orientation approaches full, and $J_A \to \Delta J$. The quantity $A = J_A/J_0$ determines the electro-optical effect caused by parameters $s_\parallel$, $s_\perp$, $\langle s \rangle$ independent of light polarization. In systems with small particles, $s_\parallel = s_\perp = \langle s \rangle = 0$ this effect is not observed.

Experimental Technique and Materials

Determination of $J_\parallel$ and $J_\perp$dependencies on field and time

The experimental setup used to determine the dependence of $J_\parallel$ and $J_\perp$ on the orienting field at steady particle orientation and the time dependence during the establishment and relaxation of orientational ordering is shown in Fig. 2. A narrow beam of unpolarized light is created by a broadband source (S), passes through a diaphragm (D), traverses the plane-parallel electrodes of a cuvette (C) filled with colloid or suspension, and is split by a beam splitter prism (DP) into two beams of equal intensity J, which after passing through polarizers P_1 and P_2 become linearly polarized parallel and perpendicular to the field in the cuvette and fall onto photodetectors (PD1) and (PD2).

Intensities $J_\parallel$ and $J_\perp$ of both beams are simultaneously recorded by a data acquisition board (L-Card E-502) connected to the photodetectors (PD1) and (PD2) and a computer (PC). Before each measurement, when particle orientation is chaotic, a microprocessor (MPU) located in the photoreceiver device additionally balances intensities $J_\parallel$ and $J_\perp$improving accuracy of their determination upon particle orientation.

To determine $J_\parallel^0$ and $J_\perp^0$ necessary for calculating electro-optical effects N and A, the light attenuation coefficient of the studied system in the cuvette at chaotic particle orientation is measured.

To create the field in the cuvette, a voltage generator (GEN) of specified form and variable value is used, which is connected to a power amplifier (AMP) coupled with the cuvette electrodes C. The magnitude, duration, and duty cycle of field pulses in the cuvette are set using a data acquisition card connected via digital-to-analog converter to the voltage generator.

Computer data processing software ensures measuring intensities $J_\parallel$ and $J_\perp$ at set fields at chosen measurement times and builds field dependencies $J_\parallel(E)$, $J_\perp(E)$ and time dependencies $J_\parallel(t)$, $J_\perp(t)$.

Light beams converted by photodetectors PD1 and PD2 into electrical signals are recorded by the data acquisition board's analog-to-digital converter L-Card E-502 (16-bit). The ADC resolution allows recording signals with accuracy

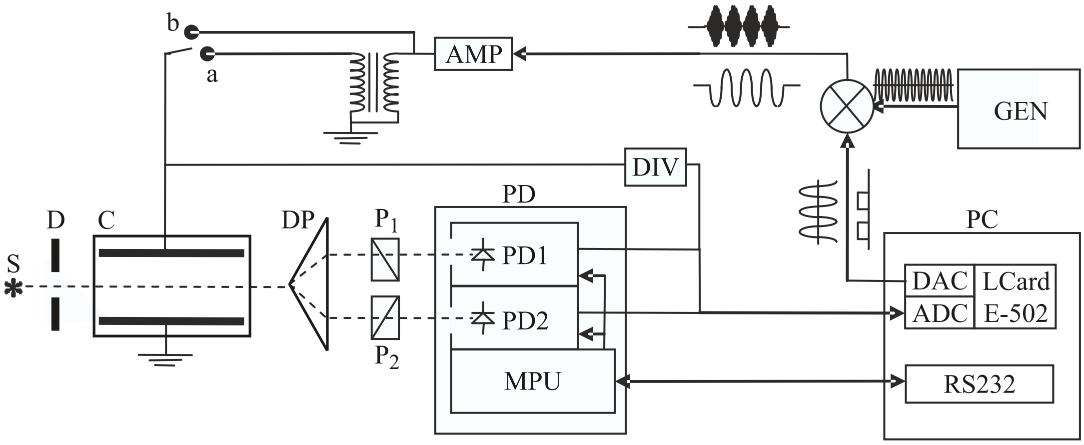

Figure 2. Block diagram of the electro-optical setup.

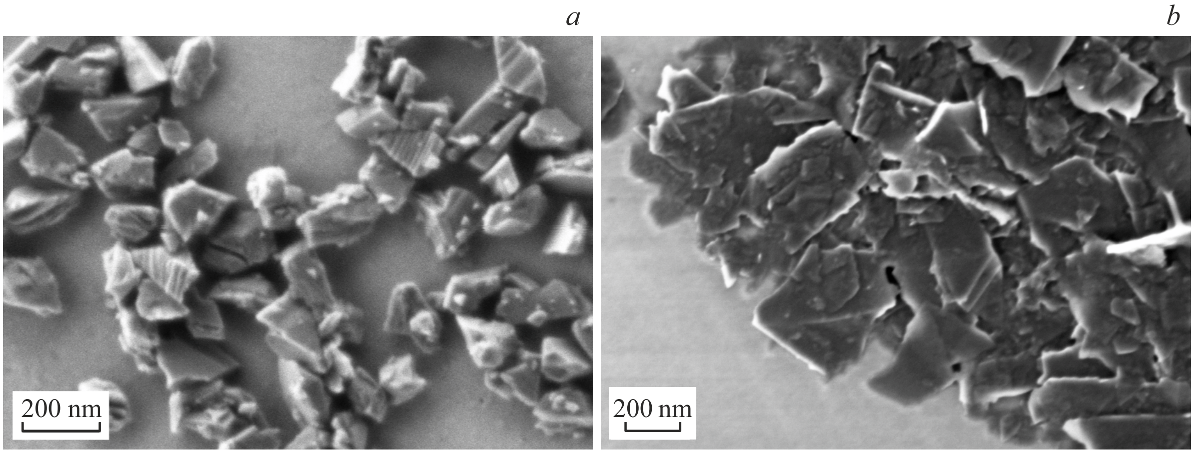

Figure 3. Electron microscopy images of diamond particles (sample No. 2) left and graphite particles (sample No. 3) right.

better than 0.01%, enabling observation of noise from various sources. Recorded signals can be averaged to reduce noise influence.

Investigated systems

Four samples were prepared for the study, consisting of polydisperse systems containing both light-absorbing and non-absorbing particles. The volume fraction of particles in the samples was less than a thousandth of a percent. Light scattering by the samples in the cuvette was single, and its intensity, as well as the observed electro-optical effects, were proportional to the particle concentration.

Sample No. 1 was an aqueous colloid with diamond particles synthesized at high temperature and pressure. The sizes of the particles, determined as the radii of spheres equal in volume to them, ranged between 200–400 nm. Sample № 2 was obtained by centrifuging sample № 1 and contained smaller diamond particles, with radii ranging from 50 to 100 nm. Particles of samples № 1 and № 2 did not absorb light. As samples whose particles both absorb and scatter light, aqueous suspensions of graphite were chosen. Sample № 3 contained particles obtained by the electric arc method during dispersion of a graphite rod in oil and underwent surface cleaning with solvents. The graphite particles had the shape of thin plates. Their sizes, determined as the radii of circles equal in area to the flat surfaces of the graphite particles, ranged from 100 to 300 nm. Sample № 4 was obtained by ultrasonic treatment of sample № 3. To further remove the largest and smallest particles from the samples, centrifugation, settling, and ultrasonic treatment of their aqueous suspensions were used.

Particles of samples No. 1 and No. 2 did not have a well-defined shape, but if approximated by ellipsoids of revolution with symmetry axes oriented along the largest particle dimensions, the ratio of the semi-axes of most of such ellipsoids varied between 1.2–1.6. The thickness of the graphite particles practically did not depend on their planar sizes. The thickness-to-planar size ratio for most graphite particles in sample No. 3 ranged between 10–20 and for smaller particles of sample No. 4 between 5–10. Scanning

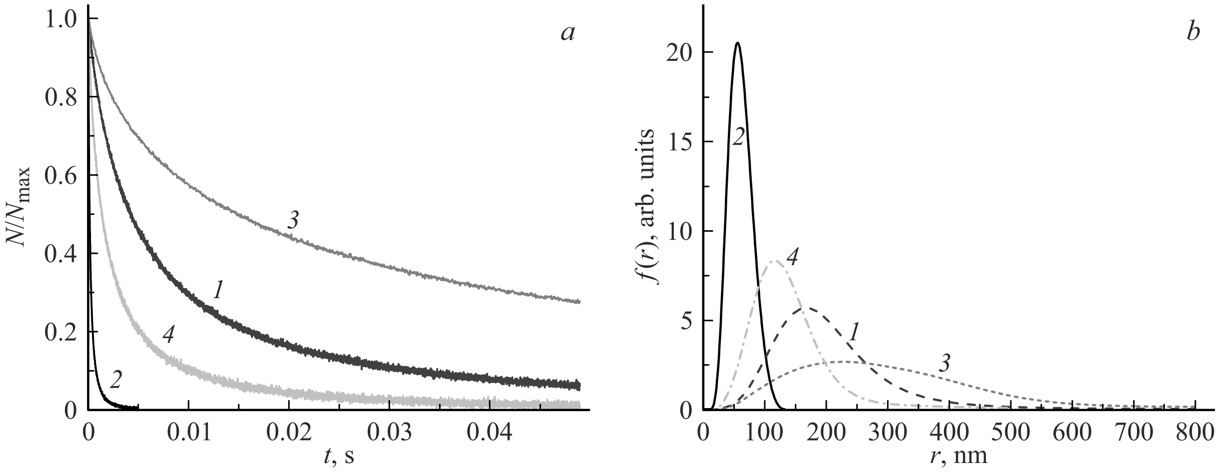

Figure 4. Normalized to the maximum value $N_{\max}$ relaxation curves of the electro-optical effect $N(t)$ (without averaging) and the distribution function $f(r)$ for samples № 1 (*1*), № 2 (*2*), № 3 (*3*), № 4 (*4*).

electron microscope images of particles of samples No. 2 and No. 3 are presented in Fig. 3.

One can assume that the particles freely rotate relative to the axis they align along in the orienting field. In this case, the particle can be considered axisymmetric, and extinction cross sections κ_1, κ_2, κ_3 should be regarded as averaged over the rotation angle. The influence of particle shape on light scattering features is considered in work [25].

The prepared samples were polydisperse. To determine the contribution of particles of different sizes to the observed electro-optical effects, relaxation dependencies of dichroism $N(t)$ were determined. If relaxation starts from the state of full particle orientation created by the electric field, then, as follows from relation (8), $\Phi_{\mathrm{st}}(\Delta\gamma, \mu, E) = 1$ for all particles in the sample. Taking this and (10) into account, instead of relation (16) one can write

$$N(t) = \int\limits_{r0}^{r1} \exp(-6D, t)\, f(r) dr. \qquad (20)$$

The distribution function of particles by size with dichroic weight $f(r) = \Delta K(r)\phi(r)$ entering relation (20) characterizes the maximum contribution made by particles of size r to the electro-optical effect N. It can be determined as a numerical solution of equation (20) if the experimental dependence $N(t)$ for the studied system is known. The rotational diffusion constant of particles entering this equation can be represented by relation $D_r = k_B T \left(8\pi\eta r^3\right)^{-1}$, in which η is the viscosity of the dispersion medium. Here, r is the hydrodynamic radius of the particle. It is close to the radius determined by the particle volume for diamond particles and to the radius determined by the area of the flat surface for graphite particles. If the distribution function $f(r)$ is assumed to be continuous in the domain $[r0, r1]$, it can be determined by the regularization method proposed by A. N. Tikhonov [45] or the penalty function method proposed by L. K. Babadzhanyants [15]. For the studied samples, the distribution functions $f(r)$ calculated from relaxation curves $N(t)$, are presented in Fig. 4.

Experimental results and discussion thereof

In an alternating electric field of sufficiently high frequency, particles orient along the axis of their greatest polarizability aligned with the field. If the principal axes of the particle's polarizability tensor at the optical frequency and the frequency of the applied field coincide, then, as follows from relations (4) and (12), for systems with small Rayleigh particles the greatest attenuation in the cuvette is observed for light polarized along the applied field. For such systems, the inequalities $\left(J_{\parallel} - J\right)/J < 0$, $(J_{\perp} - J)/J > 0$ must hold. For small particles, the values $\langle s \rangle$, $s_{\parallel}$, $s_{\perp}$ appearing in relations (15)–(17), are negligibly small, and the equalities $L = -2$, $A = 0$ hold for systems with such particles. Here, $L = \left(J_{\parallel} - J\right)/(J_{\perp} - J)$. These equalities cease to hold for particles of larger sizes.

Electro-optical studies were conducted on samples № 1– № 4 by orienting particles with pulses of a sinusoidal field of variable strength and duration. The field frequency was 10 kHz, which allowed exclusion of the influence of permanent dipole moments of particles on their orientation, and particles oriented along the field with their axis of greatest polarizability. Experimental studies showed that for all prepared samples the inequalities $\left(J_{\parallel} - J\right)/J < 0$ and $(J_{\perp} - J)/J > 0$ hold at different field values defining the orientational order of the particles.

For the studied systems, the error in determining values $J_{\parallel}$, $J_{\perp}$, J and J_0 did not exceed 0.1 %. The error in determining ratios $\left(J_{\parallel} - J\right)/J$, $(J_{\perp} - J)/J$ in a strong field did not exceed 1%, and in a weak field 5%, which ensured the error in determining ratios L and A/N not

Table 1. Values $\left(J_{\parallel}-J\right)/J$, $\left(J_{\perp}-J\right)/J$, L, N, A, A/N for samples № 1– № 4

Sample, №	$\left(J_{\parallel}-J\right)/J$	$\left(J_{\perp}-J\right)/J$	L	N	A	A/N
1	−0.046	0.041	−1.1	0.085	0.012	0.14
2	−0.141	0.071	−1.95	0.212	0.00033	0.0016
3	−0.092	0.029	−3.1	0.121	−0.0113	−0.094
4	−0.021	0.011	−1.94	0.033	0.00033	0.01

Table 2. The influence of the spectral composition of light on the value of L

λ, nm	Sample № 1	Sample № 2	Sample № 3	Sample № 4
400–460	−1.30	−2.05	−3.77	−2.15
520–560	−1.15	−2.2	−3.23	−2.06
600–650	−0.88	−2.28	−2.82	−1.88

more than 2% in a strong field and 10% in a weak field. The dependencies of $\left(J_{\parallel}-J\right)/J$, $\left(J_{\perp}-J\right)/J$ on the field strength E for sample № 1, containing both large and small diamond particles, are shown in Fig. 5.

Similar dependencies are observed for samples № 2– № 4. Values of L are close to -2 only for samples № 2 and № 4, which do not contain large particles. For these samples, inequality $N \gg A$ also holds. The dependencies of N, A and L on the field strength E only for samples № 2, which do not contain large particles.

Similar dependencies are observed for sample № 4, containing small particles of graphite. For sample No. 1, the values of L are close to -1, and for sample № 3 they are close to -3. For these samples, the values of A were within the range of 9–14% from N. For sample № 1, containing large diamond particles, $A > 0$, and for sample № 3, containing large graphite particles, they were $A < 0$. The sign of the effect A depends on the size, shape, and composition of the particles. Dimensionless quantities $\left(J_{\parallel}-J\right)/J$, $\left(J_{\perp}-J\right)/J$, L, N, A, A/N determined at saturated particle orientation for samples № 1– № 4, are presented in Table 1.

Studies showed that values L and A/N weakly depend on the degree of particle orientation but significantly depend on particle size and composition. However, in a weak field, where only the largest particles orient, while smaller ones remain practically randomly oriented, L has different values. Thus at $E \to 0$ for sample № 1 $L \to -5$, for sample № 2 $L \approx -2$, for samples № 3 and № 4 $L \to -4$. This indicates that the value of L changes significantly even with a small amount of large particles in the system. In the studied systems, large particles practically did not affect the value of A which allows concluding their proportion is small. Studies showed that for samples № 1 and № 3, containing larger particles, after turning off the field, the relaxation dependencies $A(t)$ decay slower than the dependencies $N(t)$. This confirms that the effect A is determined by larger particles than the effect N. Studies, the results of which are presented in Table 1, were carried out using light from a continuous spectrum source with wavelengths from 400 to 750 nm. In this case r/λ varies widely. To assess the influence of the spectral composition of light on the magnitude of L studies were conducted in the red, green and blue regions of the incident light spectrum. For samples № 1– № 4 values of L, corresponding to these spectral regions are presented in Table 2. As can be seen from the table, the influence of the spectral region of the incident light on the magnitude is small. Observed changes in L for samples № 1 and № 3, containing large particles, are greater than for samples № 2 and № 4, containing smaller particles.

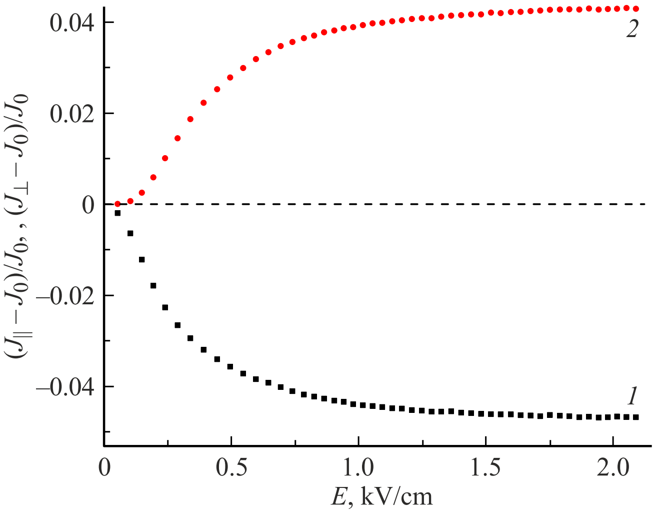

Figure 5. Dependencies of $\left(J_{\parallel}-J\right)/J$ (*1*), $\left(J_{\perp}-J\right)/J$ (*2*) on the field strength E for sample № 1.

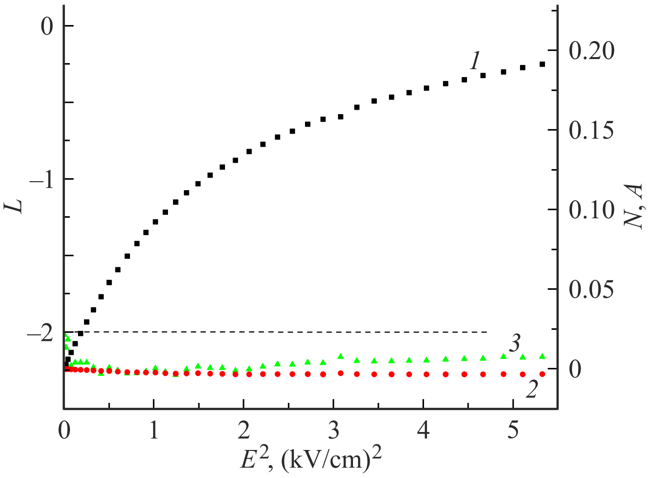

Figure 6. Dependences of $N(E)$ (1), $A(E)$ (2), $L(E)$ (3) on the square of the field strength E^2 for sample No. 2.

Conclusions

1. The conducted studies showed that the influence of the electric field on the intensity of light passing through colloids and suspensions is determined by two electro-optical effects N and A related to light scattering by particles during their orientational ordering. The first, conservative dichroism, is determined by the difference in extinction coefficients of colloids and suspensions corresponding to linear polarization of light parallel and perpendicular to the direction of particle orientation. The dependence of the effect N on particle orientation is described similarly to dichroism or double refraction in pure molecular media and solutions. This effect is observed in dispersed systems both with small particles that scatter light like dipoles and with large particles whose scattering is complex and significantly depends on the optical and geometric characteristics of the particles. The magnitude of the effect N is large when the particle sizes are comparable to the wavelengths of the light scattered by them and decreases with further increasing particle size. The effect A is not observed in dispersed systems with small particles, is comparable to the effect N in systems where particle sizes are comparable to the wavelengths of light passing through the dispersed system, and becomes the main electro-optical effect in systems with large particles. A criterion has been developed to distinguish between the effects N and A.

2. In electro-optical studies of polydisperse systems with a wide distribution of particle sizes, it is advisable to separate both effects and study them individually. This approach allows determining even small additions of large particles in systems with small particles.

3. Studies have shown that in different colloids and suspensions the values of $L = \left(J_{\|} - J\right) / \left(J_{\perp} - J\right)$ and $A/N = \left(J_{\|} + J_{\perp} + 3 \cdot J\right) / \left(3 \cdot J_{\perp} - 3 \cdot J_{\|}\right)$ can differ significantly. A decrease in particle sizes in colloids and suspensions leads to the ratio A/N approaching zero and L approaching -2. Conversely, the formation of aggregates from particles should lead to an increase in the ratio A/N and significant changes in L. These features of electro-optical studies can be used in investigating aggregation processes.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] P. Langevin. Le Radium. 7, 249 (1910). DOI: 10.1051/radium:0191000709024900
[2] M. Born. *Optik* (Springer, Berlin, 1933). DOI: 10.1007/978-3-642-99599-6
[3] H. Disselhorst, H. Freundlich, W. Leonhardt. Phisik Zeits, **17**, 117 (1916).
[4] W. Heller. Rev. Mod. Phys., **31** (4), 1072 (1959). DOI: 10.1103/RevModPhys.31.1072
[5] N.A. Tolstoj, A.A. Spartakov, G.I. Hil'ko. Kolloid. zhurn., **22** (6), 705 (1960). (in Russian).
[6] P.J. Rudd, V.J. Morris, B.R. Jennings. Appl. Phys., **8** (2), 170 (1975). DOI: 10.1088/0022-3727/8/2/011
[7] S. Stoylov, A. Sheludko, R. Chernev. Godishnik Sofiskiya Univ., Khim Fak., **58**, 113 (1963/64).
[8] M.P. Petrov, V.V. Vojtylov, S.A. Klemeshev, A.A. Trusov. Opt. i spektr., **111** (5), 871 (2011) (in Russian). DOI: 10.21883/OS.2020.06.49401.22-20
[9] N.G. Khlebtsov, A.G. Melnikov. Coll. J., **52** (5), 928 (1990).
[10] S.J. Kielich. Coll. Interf. Sci., **28** (2), 214 (1968). DOI: 10.1016/0021-9797(68)90122-7
[11] V.V. Vojtylov, M.P. Petrov, A.A. Spartakov, A.A. Trusov. Opt. i spektr., **114** (4), 687 (2013).
[12] P. Arenas-Guerrero, S. Ahualli, A.V. Delgado, M.L. Jiménez. J. Phys. Chem. C, **123** (43), 26623 (2019). DOI: 10.1021/acs.jpcc.9b06703
[13] P. Arenas-Guerrero, A.V. Delgado, A. Ramos, M.L. Jiménez. Langmuir, **35** (3), 687 (2018). DOI: 10.1021/acs.langmuir.8b03122
[14] P. Arenas-Guerrero, Á.V. Delgado, K.J. Donovan, K. Scott, T. Bellini, F. Mantegazza, M.L. Jiménez. Sci. rep., **8** (1), 9502 (2018). DOI: 10.1038/s41598-018-27840-0
[15] L.K. Babadzhanyanc, A.V. Vojtylov, V.V. Vojtylov, A.A. Trusov. Vysokomolekulyarnye soedineniya, **52** (7), 1329 (2010) (in Russian). DOI: 10.1134/S181123821001011X
[16] S.A. Klemeshev, M.P. Petrov, A.A. Trusov, V.N. Shilov. Opt. i spektr., **122** (3), 451 (2017) (in Russian). DOI: 10.7868/S0030403417030230
[17] M.L. Jiménez, L. Fornasari, F. Mantegazza, M.C. Mourad, T. Bellini. Langmuir, **28**, 251 (2012). DOI: 10.1021/la2036949

[18] M.P. Petrov, V.N. Shilov, A.A. Trusov, A.V. Voitylov, V.V. Vojtylov. Coll. Surf. A, **506**, 40 (2016). DOI: 10.1016/j.colsurfa.2016.05.087

[19] S.H. Hong S.H., T.Z. Shen, J.K. Song. J. Phys. Chem. C, **118** (45), 26304 (2014). DOI: 10.1021/jp504892s

[20] O.S. Vezo, A.V. Vojtylov, V.V. Vojtylov, M.P. Petrov, A.A. Trusov. Opt. i spektr., **128** (6), 713 (2020) (in Russian). DOI: 10.21883/OS.2020.06.49401.22-20

[21] K.V. Erin. Kolloidn. zhurn., **77** (1), 24 (2015). DOI: 10.7868/S0023291215010073

[22] S.P. Stoylov, A.Y. Gyurova, V. Bunin, A. Angersbach, R.N. Georgieva, S.T. Danova. Bioelectrochemistry, **75** (1), 50 (2009). DOI: 10.1016/j.bioelechem.2009.02.001

[23] W. Heller. Rev. Mod. Phys., **14** (4), 390 (1942). DOI: 10.1103/RevModPhys.14.390

[24] G. Van de Hyulst. *Rasseyanie sveta malymi chasticami* (In. lit., M., 1961).

[25] M.I. Mishchenko, J.W. Hovenier, L.D. Travis. *Light scattering by nonspherical particles. Theory, measurements, and applications* (Academic Press, N.Y., 2000).

[26] B. Vandenbroucke, M. Baes. Camps P. Astronom. J., **160** (1), 55 (2020). https//doi.org//10.3847/1538-3881/ab9cbd

[27] T. Rother, K. Schmidt, J. Wauer, V. Shcherbakov, J.F. Gayet. Appl. Opt., **45** (23), 6030 (2006). DOI: 10.1364/AO.45.006030

[28] K.S. Shifrin. *Rasseyanie sveta v mutnoj srede* (GITTL, M.–L., 1951). (in Russian)

[29] M.I. Mishchenko. JOSA A, **8** (6), 871 (1991). DOI: 10.1364/JOSAA.8.000871

[30] A.V. Voitylov, O.S. Veso, M.P. Petrov, V.I. Rolich, A.A. Trusov, V.V. Vojtylov. Coll. Surf. A, **538**, 417–422 (2017). DOI: 10.1016/j.colsurfa.2017.10.072

[31] A. Reyes Coronado, A. Garsia-Vlenzuela, C. Sanchez-Perez, R.G. Barrera. J. Phys., **7** (1), 89 (2005). DOI: 10.1088/1367-2630/7/1/089

[32] A. Garcia-Valenzuela, R.G. Barrera, E. Gutierrez Reyes. Opt. Expr., 16, 19743 (2008). DOI: 10.1364/OE.16.019741

[33] N.A. Tolstoj, P.P. Feofilov. DAN SSSR, **66**, 617 (1949). (in Russian).

[34] H. Muller. JOSA, **31**, 286 (1941). DOI: 10.1364/JOSA.31.000286

[35] E.V. Shpol'skij. UFN., **27** (1), 96 (1945). (in Russian).

[36] B.T. Draine, P.J. Flatau. JOSA A, **11** (4), 1491 (1994). DOI: 10.1364/JOSAA.110111491

[37] N.V. Voshchinnikov, V.G. Farafonov. Astrophys. Space Sci., **204**, 19 (1993). DOI: 10.1007/BF00658095

[38] A. Doicu, Y. Eremin, D.S. Efremenko, T. Trautmann. *The Generalized Multipole Technique for Light Scattering: Recent Developments* (Springer, Switzerland, 2018), 99, ch.3. DOI: 10.1007/978-3-319-74890-0

[39] J.W. Hovenier, K. Lumme, M.I. Mishchenko, N.V. Voshchinnikov, D.W. Mackowski, J. Rahola. JQSRT, **55** (6), 695 (1996). DOI: 10.1016/0022-4073(96)00067-2

[40] M.I. Mishchenko. Applied optics, **39** (6), 1026 (2000). DOI: 10.1364/AO.39.001026

[41] M.I. Mishchenko. Astrophys. J., Part 1, **367** (1), 561 (1991). DOI: 10.1086/169652

[42] N.G. Khlebtsov. Appl. Opt., **31** (25), 5359 (1992). DOI: 10.1364/AO.31.005359

[43] E. Fredericq, C. Houssier. *Electric Dichroism and Electric Birefringence* (Clarendon Press, Oxford, 1973).

[44] M.A. Leontovich. *Vvedenie v termodinamiku. Statisticheskaya fizika* (Nauka, M., 1983) (in Russian)

[45] A.N. Tihonov, S.Ya. Arsenin. Metody resheniya nekorrektnyh zadach (Nauka, M., 1979). (in Russian)

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