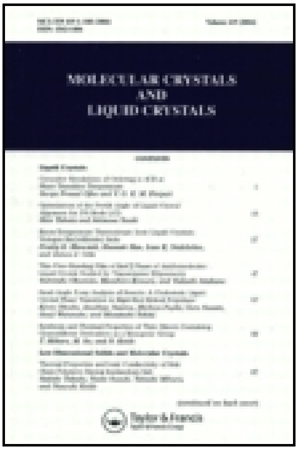

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Cotton-Mouton Effect in Monodisperse Suspensions of Liquid Crystals

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The collective Cotton-Mouton (C-M) effect in the system of micron-size liquid-crystal droplets freely suspended in the isotropic liquid is studied experimentally and theoretically. The collective C-M constant in liquid-crystal suspensions is found to be from 10^4 to 10^8 times higher than the respective "molecular" C-M constant in the isotropic phase of the same substance. These large values cause the saturation in the C-M effect at relatively low magnetic fields. Using the generalized *n*th order Langevin's functions L_n, the statistical therory is presented for the collective C-M effect in the monodisperse liquid-crystal suspensions. As a result, the induced birefringence is obtained in the form $\Delta n = 1/2(\Delta n)_\infty (3L_2 - 1)$, where $(\Delta n)_\infty$ is the induced birefringence at saturation. The collective C-M constant is $C_c = CN_gS_g$ where N_g is the number of molecules in the droplet, S_g is the orientational order parameter of the long molecular axes in the droplet, and C is the "molecular" C-M constant. The resultant (measured) C-M constant is $C_s = C(1 + N_gS_g)$. The relaxation time τ depends on the rotational (Brownian) diffusion constant D and after removing the field B the orientational order parameter of the optical axes of droplets in the suspension $S_s = 1/2(3L_2 - 1)$ vanishes exponentially as $S_s = \exp(-6Dt)$. Hence, the relaxation time $\tau = (6D)^{-1}$.

The collective C-M effect and its saturation can be used as methods for the analysis of the presence and change of the orientational order within colloidal grains and the derivation of several parameters characterizing the aggregation, self-organization, and morphogenesis processes in multicomponent complex systems.

Keywords: Cotton-Mouton effect, magnetic birefringents, liquid crystal suspensions

1. INTRODUCTION

Nonlinear magnetooptical effect, called the Cotton-Mouton (C-M) effect, is observed as birefringence Δn induced in isotropic medium by magnetic field B. Induced optical axis is parallel to B. For the light beam perpendicular to B the value of Δn is given by

$$\Delta n = CB^2\lambda \tag{1}$$

where λ is wavelength of the light and C is the C-M constant.

As a rule, the C-M constants for the isotropic phases of the liquid crystal substances (mesogens) are a hundred times higher than for non-mesogenic liquids, especially in the vicinity of the transition to the mesomorphic state.[1,2] This large value of the constant C is the result of fluctuations in the isotropic phase of the mesogens which generate the swarms having short-range liquid-crystal structure. The sizes of these swarms are of the order of the coherence length $\xi(T)$

$$\xi(T) = \xi_o\left(\frac{T^*}{T - T^*}\right)^{1/2} \tag{2}$$

where ξ_o is a molecular length and T^* is a temperature of the virtual second-order transition. The Landau-type continuum theory, based on the assumption that the correlation between the swarms is of the Ornstein-Zernicke type, $1/R \exp(-R/\xi)$, where R is the distance between the centers of the swarms, leads to the quadratic proportionality between C-M constant and the coherence length[3-5]

$$C \propto \xi^2 \tag{3}$$

Because the magnetic field intersects with the swarms as a whole, the induced orientation can be considered as the collective C-M effect. Probably, the earliest experimental investigations of the C-M effect in the isotropic phase of the nematogen have been performed by Zadoc-Kahn for the PAA.[6] Explicit formula for the magnetic birefringence in the isotropic phase of mesogens was obtained by K. Muta and co-workers on the basis of the phenomenological Landau approximation of the free energy density.[7] Using the Vuks approximation[8] of the Lorentz-Lorenz equation, these authors have obtained the magnetic birefringence in the form

$$\Delta n = \frac{(n^2 + 2)^2}{6n}\frac{N_A\,\Delta\alpha^e\,\bar{S}(B)}{\varepsilon_0 V} \tag{4}$$

where the mean orientational order parameter of the long molecular axes $\bar{S}(B)$ is

$$\bar{S}(B) = \frac{2N_A\,\Delta\alpha^m}{9V}\frac{1}{a(T - T^*)}\frac{B^2}{\mu_o} \tag{5}$$

In the above, V is the molar volume, N_A is the Avogadro number, n is the refraction index of the liquid (in the absence of the magnetic field), $\Delta\alpha^e$ and $\Delta\alpha^m$ are the anisotropies of the electric (in the optical region) and diamagnetic polarizabilities, respectively, and a is a phenomenological parameter.

The second-type medium in which the collective C-M effect can be observed is the isotropic phase of the lyotropic liquid crystal, i.e., the isotropic solution of the stiff and highly anisometric (rod- or disc-like) molecules or micelles. The C-M effect in the isotropic solutions of the cesium perfluorooctanoate in water has been investigated experimentally by Ch. Rosenblatt and co-workers.[9] The result of their experiment shows that the induced birefringence Δn is nonlinear in B^2. The dependence of the constant C on the concentration of the solution is complicated by the connection between the concentration and the structure of the micelles. The C-M constant in the isotropic solutions has been interpreted generally by P. Photinos and A. Saupe[10] in terms of interparticle potentials.

The third type of the isotropic liquid media in which the collective C-M effect appears are colloidal suspensions of the crystal or liquid-crystal substances. The peculiar feature of these colloids is presence of the long-range orientational and translational (in the case of crystals and some smectics) order inside the grains. These colloids can be prepared by the dispersion of the crystal or liquid-crystal substance in isotropic liquids which are not a solvent for this substance.

We present here a detailed study of the C-M effect in the liquid-crystal colloids. The experimental results reported here are obtained for the simplest case of the nematic ordering within the grains. The first announcement about the presence of very large C-M effect in the suspensions of the diamagnetic liquid crystals and the preliminary experimental results have been presented by the author on the Fifth International Liquid Crystal Conference of the Socialist Countries in Odessa (1983).[11] Here, complete typical experimental results and the statistical description of the collective C-M effect in monodisperse liquid-crystal suspensions were presented.

The collective C-M constant in the liquid-crystal suspensions is found to be from 10^4 to 10^8 times larger than the "molecular" C-M constant for the same substance. Similar very large C-M effect, but of quite different physical nature, has recently been developed by S. Taketomi in the ferromagnetic fluids.[12] In this case, the rodlike chains formed by spherical ferrite grains having the net spontaneous magnetic dipole moment are oriented in the magnetic field. The collective C-M constant in these ferromagnetic suspensions is of the order from 10^6 to 10^7 higher than the "molecular" C-M constant in nitrobenzene.

2. LIQUID-CRYSTAL SUSPENSIONS

In this work, the collective C-M effect has been investigated experimentally mainly in the suspensions of the nematic liquid crystal in the isotropic liquids. In addition, the initial investigations of the suspensions of the chiral nematics, smectics, and chiral smectics have been carried out. As the basic isotropic liquid, the deionized or re-distilled water was used. In both the cases the results were quite similar. In order to investigate the relaxation time, glycerol/water mixtures of weight concentrations ranging from 10% to 90% were used as the isotropic liquid. For typical measurements, the colloidal liquid-crystal droplets were not coated with any surfactants.

A. Preparations of the suspensions

The suspensions of the thermotropic nematics or smectics in isotropic liquids were obtained using the condensation technique in one of two ways. In the first one, the solutions of liquid-crystal substance in the water-soluble solvents, e.g., methanol, ethanol, acetone, etc., were mixed with water. Solutions of weight concentrations from 10 to 50 mg of liquid-crystal substance in 10 g of the organic solvent were used. In order to obtain the suspension, the amount of solution of about 0.1 ÷ 0.5 ml was mixed with 10 ml of water. The volume fraction occupied by the dispersed liquid crystal is quite small and varies typically from 10^{-5} to 2.5×10^{-4} in the dispersion. The fresh suspension is polydisperse with droplets ranging from about 1 to 5 microns in diameter. After the aging in the course of about 50 hours the suspensions become almost monodisperse with droplets from about 1 to 1.5 micron in diameter. In order to modify the density, viscosity, and refractive indices of the isotropic liquid, the glycerol/water mixtures can be used instead water. These properties of the glycerol/water mixtures have been measured with high accuracy.[13,14]

In the second condensation method, the liquid crystal is dissolved in a weak solvent at high temperature and the solution is then cooled to the room temperature. The cooling results in the supersaturation of the solution and then condensation of the liquid-crystal material.

B. Stability of the suspensions

The sedimentation and coagulation phenomena play an important role in the aging processes of the fresh suspension. As the probabilities of the coagulation and sedimentation are proportional to the diameter of the droplets, the aging results in increase of both the monodispersity of the suspension and relative content of low-diameter droplets in it. The diameters of the droplets and volume fraction of the liquid-crystal phase in the suspension were estimated with the polarizing microscope. After aging during about 50 hours, the suspension becomes almost stable and only small changes are observed over several weeks. Further sedimentation can be slowed down by adjusting the densities of both the isotropic liquid and suspended liquid crystal, e.g., using the glycerol/water mixture of proper density. The stability of the liquid-crystal suspension with respect to the coagulation increases considerably when a small amount of gelatine or polyvinyl alcohol is added to water.

C. Optical properties

The suspensions of the nematics and smectics are isotropic and optically not active. However, the spontaneous optical anisotropy of individual droplets and the depolarization of the scattered light cause some small brightening of the visual field when the layer of the liquid-crystal suspension is placed between crossed polarizers. The suspensions of both chiral nematics and chiral smectics are isotropic and optically active. Typical rotatory power of liquid-crystal suspensions used in C-M investigations is of the order of 10^3 deg·m^{-1} and can be easily measured with the differential polarimeter. The temperature dependence of the rotatory power of the chiral suspensions is related to the thermal change of the pitch of chiral structure of the liquid crystal. The scattering-produced depolarization of light, giving the background for useful optical C-M signal, can be minimized by reduction of the difference between the average refractive index of the liquid crystal $1/3(n_e + 2n_o)$ and the refractive index of the isotropic liquid. This reduction can be achieved through the use of the glycerol/water mixtures covering the range of the refractive indices typical for most of the liquid crystal substances.[14] The liquid-crystal suspension, when the refractive indices are carefully compensated, becomes almost transparent above the clearing point T_c.

3. EXPERIMENTAL ARRANGEMENT

The experimental apparatus used to measure the magnetic birefringence in liquid-crystal suspensions is schematically shown in Figure 1. The non-polarized He–Ne laser beam L ($\lambda = 632.8$ nm, power 5 mW, diameter of the beam 2 mm) propagates horizontally through the system containing polarizer P, cuvette C filled with the suspension and placed in a perpendicular magnetic field B, quarter-wave plate QP, analyzer A, and photomultiplier tube PM. Polarizer and analyzer are crossed and at 45° with respect to B. The "fast" axis of the quarter-wave plate is parallel to the axis of the polarizer. Photomultiplier is shielded magnetically and electrically and is placed about 1.5 m from the axis of the magnet M. The cuvette is located in the thermostatized chamber, mounted between the pole shoes of the magnet, whose temperature is controlled to within 0.1 K. For temperature measurement, a calibrated thermistor is placed on the clamp adjacent to the cuvette. Path length

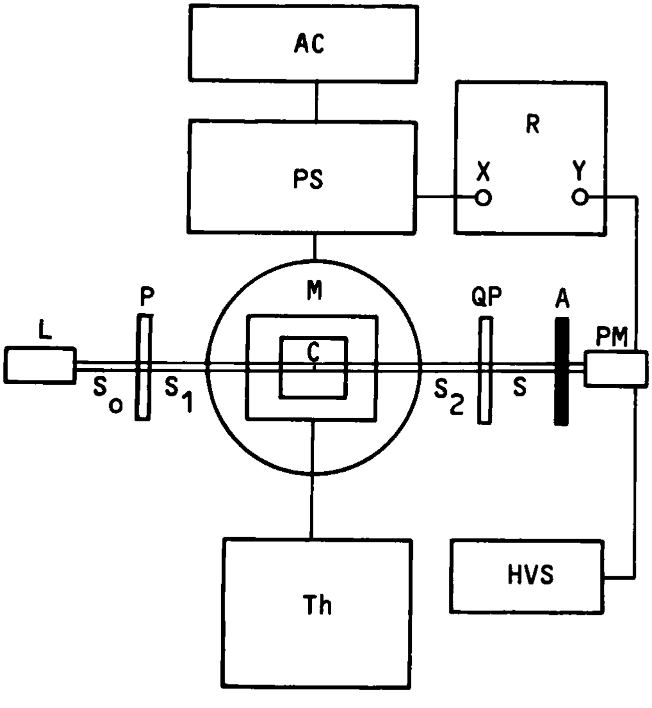

FIGURE 1 Schematic arrangement of the elements of the experimental setup. L, He–Ne laser; P, polarizer; M, magnet; C, cuvette; QP, quarter-wave plate; A, analyzer; PM, photomultiplier; AC, automatic controller; PS, power supplier; R, recorder; HVS, high-voltage supplier; Th, thermostat. Symbols S denote appropriate Stokes vectors.

of the laser beam in the suspension is 1 cm. The diameter of the pole shoes is 250 mm and the homogeneity of the magnetic field is better than 5% in the region occupied by the sample. With the automatic controller AC of the power supplier PS the magnetic field B can be scanned in a linear fashion from 0 to 1.25 T during the time from 1 to 30 minutes or can be maintained on arbitrary level. The rise time is equal to decay time. The signals proportional to the field B and to the light intensity are applied to the *x* and *y* inputs of the *X*-*Y* recorder, respectively.

When the applied magnetic field B induces the birefringence Δn in the sample of thickness h, the resulting phase shift ϕ in a beam of light of wavelength λ is

$$\phi = 2\pi \frac{\Delta nh}{\lambda} \tag{6}$$

One may show (see the Appendix) that the light beam passed through the sample and the quarter-wave plate is linearly polarized and its polarization plane at the analyzer is rotated of the angle Φ from the initial direction. The angle Φ is simply related to the phase shift ϕ and is

$$\Phi = \frac{\phi}{2} \tag{7}$$

As the polarizer and analyzer are crossed, the intensity of the light I detected by photomultiplier is according to the Malus rule

$$\mathrm{I} = \mathrm{I}_A \sin^2 \Phi = \mathrm{I}_A \sin^2 \pi \frac{\Delta nh}{\lambda} \tag{8}$$

where I_A is the intensity of light incident on analyzer.

In order to calibrate the measurement system, the birefringent plate having known optical-path difference $\delta_s = \Delta nh$ can be introduced instead the sample. In order to account the scattering loss of the light intensity, the sample must be located between the laser and polarizer during the calibration. In this work, the birefringent plate of optical-path difference $\delta_s = 125$ nm (for $\lambda = 633$ nm) was used.

5. EXPERIMENTAL RESULTS

We give typical results of the collective C-M effect measurements in water and water/glycerol suspensions of thermotropic nematic 4-cyano-4′-(*n*-pentyl) biphenyl (5CB). 5CB was chosen for its relative chemical simplicity and stability. 5CB has the nematic phase between 22.5°C (phase transition from the crystal to nematic phase) and 35°C (transition to the isotropic liquid).

The intensity of the light incident on the photomultiplier in the measurement system used is a direct measure of the magnetically induced birefringence Δn. These light intensities measured as a function of the magnetic field B at 24°C are shown in Figures 2 and 3 for low and high viscosities of the isotropic liquid, respectively.

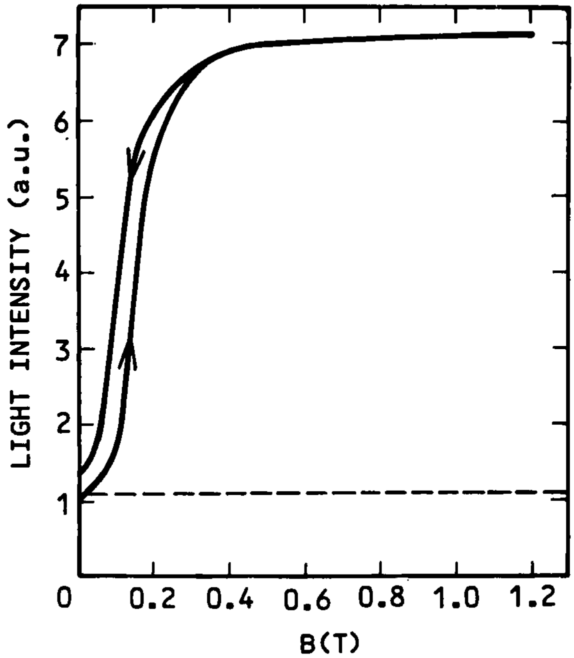

FIGURE 2 Light intensity, in arbitrary units, as a measure of the magnetically induced birefringence Δn, Equation (10), plotted against the magnetic field B for the suspension of 5CB in water. The hysteresis behavior is relatively weak. The rise and decay times for the magnetic field are the same and equal 1 min.

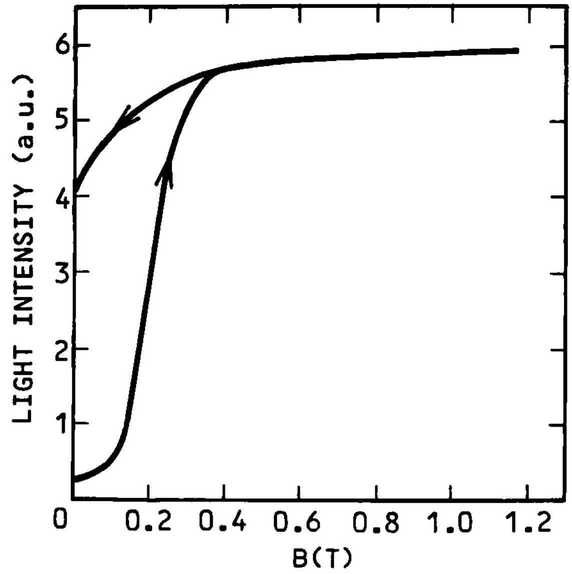

FIGURE 3 Light intensity, in arbitrary units, plotted against the magnetic field B for the suspension of 5CB in 80% wt. glycerol/water mixture. The hysteresis behavior is very distinct. The rise and decay times for the magnetic field are 1 min.

The temperature dependence of the magnetically induced birefringence Δn is shown in Figure 4. Immediate relation between Δn and B is shown in Figure 5. The diameter of nematic droplets was about 1.5 micron in all the measurements reported here. To reveal the hysteresis effects, the magnetic field was scanned with the rise and decay times of 1 minute which is the minimum range for the automatic controller used.

The intensity of the transmitted light as a function of increasing and then decreasing field B for the suspension of pure 5CB in redistilled water is shown in Figure 2. The non-zero initial level of the light intensity, depicted by dashed line in Figure 2, is mainly caused by the depolarization of light in the suspension. The main characteristic behavior of Δn is the appearance of the saturation of the C-M effect at very low field $B < 0.5$ T.

The size of the magnetooptical hysteresis, as registered during the increasing-decreasing cycle of the field B, depends on the value of the rotational diffusion coefficient D in the rotational Brownian motion of the droplets. Since the coefficient D is linear with the viscosity, the size of the magnetooptical hysteresis increases remarkably when the viscosity of the isotropic medium increases. This effect is shown in Figure 3 representing the result obtained for suspension of 5CB in 80% wt. glycerol mixture with water. This mixture has the viscosity about 60 times larger than the viscosity of water.[13] For the scanning time used, the bright features observed in Figure 3 are delay of the optical response to increasing field B and relatively large orientational remanence when the field B becomes zero. This residual orientation disappears spontaneously with relaxation time of about 15 min. As a result of the immersion reduction of the difference between the refractive indices, the intensity of the scattering-depolarized light (the initial level of the light

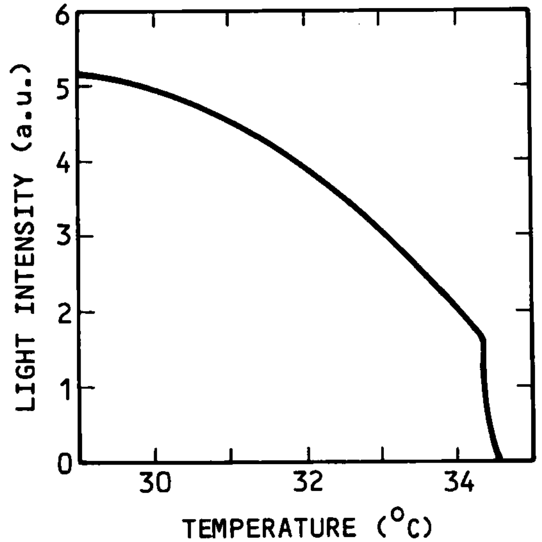

FIGURE 4 Light intensity, in arbitrary units, plotted against the temperature at constant magnetic field B = 1 T. Nematic–isotropic phase transition is observed at about 35°C.

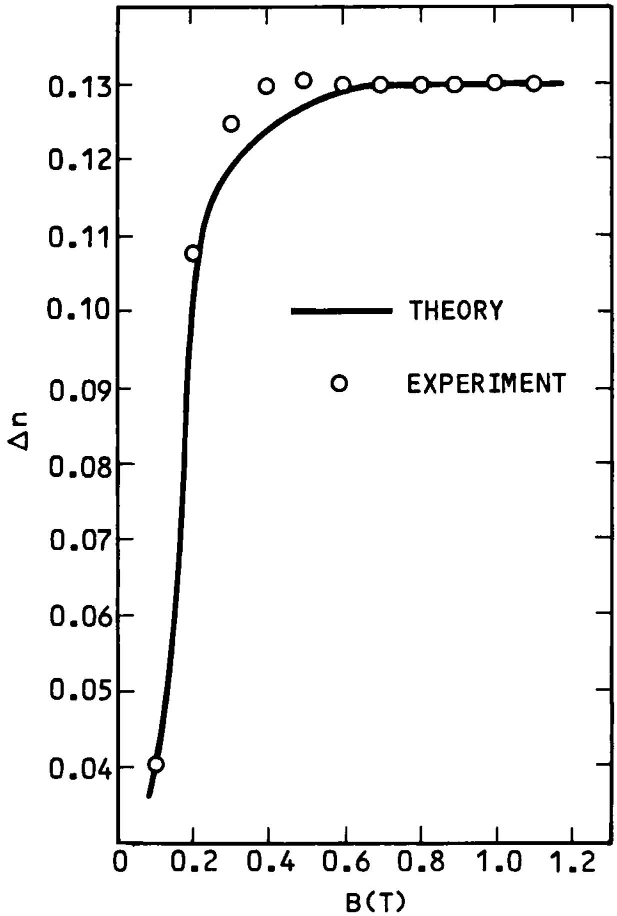

FIGURE 5 Comparison for 5CB suspension in water between experimental values (dots) of the magnetically induced birefringence Δn and the theoretical curve (solid line) as calculated from Equation (25).

intensity at B = 0) is several times smaller for the suspensions of 5CB in glycerol/water mixtures (Figure 3) than for the suspensions of 5CB in pure water (Figure 2).

In order to confirm the connection between the collective character of the C-M effect in liquid crystal suspensions and the presence of the liquid crystalline internal structure of droplets, the C-M effect has been measured as a function of temperature at constant field B = 1 T (well above the saturation). We have found that the C-M effect in the nematic suspensions decreases monotonically with increasing temperature and rapidly disappears at the temperature of the nematic–isotropic phase transition, Figure 4. As the orientational order parameter becomes zero above the clearing point T_c, the C-M effect diminishes to the "molecular" level in the isotropic phase and cannot be detected here because of very small amount of the nematic substance contained in the sample.

Numerical values of the magnetic birefringence Δn are calculated with the use of two experimental light intensities I and I_s as registered in arbitrary units for the sample and the standard plate, respectively

$$I = I_A \sin^2 \pi \frac{\Delta n h}{\lambda}; \qquad I_s = I_A \sin^2 \pi \frac{\delta_s}{\lambda} \tag{9}$$

Therefore, the magnetic birefringence is

$$\Delta n = \frac{\lambda}{\pi h} \arcsin \left[\left(\frac{I}{I_s} \right)^{1/2} \sin \pi \frac{\delta_s}{\lambda} \right] \tag{10}$$

The effective thickness h of the equivalent liquid-crystal "layer" in the sample is

$$h = L \frac{V_m}{V_o} \tag{11}$$

where L is the thickness of the cuvette, V_m is the volume of pure mesomorphic substance in the suspension, and V_o is the total volume of the suspension. Experimental values of Δn, as obtained with Equation (10), are presented in Figure 5. From this figure it can also be seen that optical axes of droplets in the suspension are almost completely oriented in relatively low magnetic fields. Moreover, we see in Figure 5 that the magnetic birefringence at saturation, $(\Delta n)_\infty = 0.13$, distinctly differs from the birefringence of 5CB, $n_e - n_o = 0.18$, as measured for homogeneous uniformly oriented layer. This is because the molecular orientation within the droplet is disturbed by the point defects of various topology (see Section 6). The shape of the theoretical curve in Figure 5 will be discussed in Section 6.

From Equations (10) and (1) we obtain the collective C-M constant C_c which for the aged water suspensions of 5CB at the field B = 0.15 T (well below the saturation) and for $\lambda = 633$ nm has the value $C_c = 4.3 \times 10^6 \text{ m}^{-1} \text{T}^{-2}$. This value is about 10^4 times larger than the molecular C-M constants for nitrobenzene and biphenyl which are approximately 250 and 140 $\text{m}^{-1} \text{T}^{-2}$, respectively.

5. THEORY

The induced birefringence Δn in a sample of macroscopically isotropic liquid-crystal suspension is a result of the orientation of the optical axes of individual optically anisotropic droplets in an external magnetic field B. The degree of this orientation can be described by the order parameter of the suspension S_s expressed by the angle β between the optical axis of individual droplet and the magnetic field B (Figure 6) in the form

$$S_s = \frac{3}{2} \langle \cos^2 \beta \rangle - \frac{1}{2} \tag{12}$$

Averaging is performed over all the volume of the suspension. Since the order

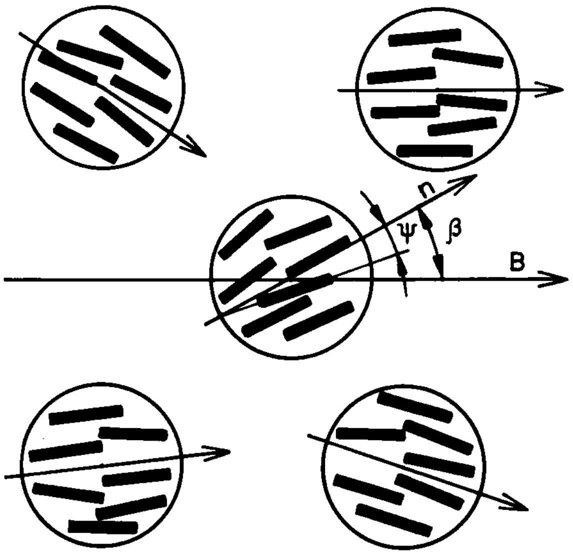

FIGURE 6 Simplified diagram showing the orientation of liquid-crystal droplets in a magnetic field. Here, β is the angle between the magnetic field vector B and the director *n*, and ψ is the angle between the director *n* and the long axis of an individual molecule.

parameter S_s varies between 0 and 1, the actual birefringence Δn of the suspension can be expressed by the maximum birefringence at saturation, $(\Delta n)_\infty$, in the form

$$\Delta n = (\Delta n)_\infty S_s \tag{13}$$

In order to obtain the relation between the angle β and the field B, we will consider the droplets as the magnetic-polarizability ellipsoids and then use the distribution function of the form

$$f(\beta) = \frac{\exp(-U/kT)}{4\pi^2 \int_0^\pi \exp(-U/kT)\sin\beta \, d\beta} \tag{14}$$

Hence, the mean value of $\cos^2\beta$ is given by

$$\langle\cos^2\beta\rangle = \frac{\int_0^\pi \cos^2\beta \exp(-U/kT)\sin\beta \, d\beta}{\int_0^\pi \exp(-U/kT)\sin\beta \, d\beta} \tag{15}$$

The potential energy *U* depends on the magnetization M of unit volume of a diamagnetic liquid crystalline substance. In the case of liquid crystals with positive diamagnetic anisotropy, e.g., 5CB and other aromatic compounds, the magnetization can be expressed as

$$\mathrm{M} = \frac{\chi_\perp}{\mu_o}\mathrm{B} + \frac{\Delta\chi}{\mu_o} n\mathrm{B}\cos\beta \tag{16}$$

where n is the director, $\Delta\chi = \chi_\| - \chi_\perp$, $\chi_\|$ and $\chi_\perp$ are the diamagnetic susceptibilities of the unit volume as measured in parallel and perpendicularly to the director, respectively. The free energy of the unit volume of the nematic in a magnetic field is given by

$$F = -\int \mathrm{B}\, d\mathrm{M} \tag{17}$$

Orientational potential energy U of the droplet of volume V_g is the angle-dependent part of the free energy F, i.e.,

$$U = -\frac{\Delta\chi \mathrm{V}_g}{2\mu_o}\mathrm{B}^2\cos^2\beta \tag{18}$$

Substituting Equation (18) into Equation (15) we obtain

$$\langle\cos^2\beta\rangle = \frac{\int_0^\pi \cos^2\beta \exp(q\cos^2\beta)\sin\beta\, d\beta}{\int_0^\pi \exp(q\cos^2\beta)\sin\beta\, d\beta} \tag{19}$$

where

$$q = \frac{\Delta\chi \mathrm{V}_g\mathrm{B}^2}{2\mu_o kT} \tag{20}$$

The right-hand side of Equation (19) is a representation of the generalized nth order Langevin function

$$L_n(p,\pm q) = \frac{\int_0^\pi \cos^n\beta \exp(p\cos\beta \pm q\cos^2\beta)\sin\beta\, \mathrm{d}\beta}{\int_0^\pi \exp(p\cos\beta \pm q\cos^2\beta)\sin\beta\, d\beta} \tag{21}$$

In the case of positive diamagnetic anisotropy, $p = 0$ and q is positive. Therefore, for liquid crystal substances investigated here, the function $L_2(p, \pm q) = L_2(q) = \langle \cos^2\beta \rangle$ can be simplified to the form[15]

$$L_2(q) = \frac{1}{2}\left[\frac{1}{a\,\mathrm{I}(q)} - \frac{1}{q}\right] \tag{22}$$

where

$$\mathrm{I}(q) = \exp(-q)\int_0^a \exp(t^2)\,dt; \qquad a = q^{1/2} \tag{23}$$

In order to obtain the general expressions for S_s and Δn, we rewrite Equations (12) and (13) in terms of $L_2(q)$ given by Equations (22) and (23)

$$S_s = \frac{1}{2}\,[3L_2(q) - 1] \tag{24}$$

$$\Delta n = \frac{(\Delta n)_\infty}{2}\,[3L_2(q) - 1] \tag{25}$$

Equations (24) and (25) are valid for any value of the field B including the saturation region.

A. The collective C-M constant

We consider the dependence of Δn on B for $q < 1$ (below enough the saturation). In this case, the proper Boltzmann factors in Equation (21) can be expanded into a power series giving $L_2(q)$ in the form

$$L_2(q) = \frac{\sum_{n=0}^{\infty} \frac{1}{n!}\langle \cos^{2n+2}\beta \rangle\, q^n}{\sum_{n=0}^{\infty} \frac{1}{n!}\langle \cos^{2n}\beta \rangle\, q^n} \tag{26}$$

with the main values $\langle \cos^k \beta \rangle = 1/(k+1)$.
Four initial terms of the series (26) represent $L_2(q)$ with sufficient exactness

$$L_2(q) = \frac{1}{3} + \frac{4q}{45} + \frac{8q^2}{945} - \frac{16q^3}{14175} - \ldots \tag{27}$$

Restricting ourselves to two initial terms of the series (27) and making use of Equations (12) and (13), we obtain sufficiently exact expression for the magnetically induced birefringence in the monodisperse approximation

$$\Delta n = (\Delta n)_\infty \frac{\Delta\chi V_g}{15\mu_o kT}\,\mathrm{B}^2 \tag{28}$$

Comparing Equation (28) with the phenomenological expression (1), we obtain the collective C-M constant in the form

$$C_c = (\Delta n)_\infty \frac{V_g}{15\mu_o \lambda k T} \tag{29}$$

In order to calculate the extremum value $(\Delta n)_\infty$, we use the Clausius-Mossotti equation with Lorentz local field. Taking in the summation the approximation $n_{\parallel\infty} \approx n_{\perp\infty} \approx n$, we obtain

$$\frac{6n\,(\Delta n)_\infty}{(n^2 + 2)^2} = \frac{N\Delta\alpha^e}{3\varepsilon_o} \tag{30}$$

where N is the number of molecules in the unit volume of a droplet. The anisotropy of the diamagnetic susceptibility of the liquid-crystal substance in a droplet can be given by

$$\Delta\chi = (\Delta\chi)_\infty S_g \tag{31}$$

where

$$(\Delta\chi)_\infty = \mu_o N \Delta\alpha^m \tag{32}$$

is the anisotropy of the diamagnetic susceptibility at perfect uniform order within a droplet. The orientational order parameter for long molecular axes within a droplet S_g we define as

$$S_g = \frac{1}{2}\langle 3\cos^2\psi - 1\rangle \tag{33}$$

In the above, $\Delta\alpha^m$ is the anisotropy of the diamagnetic polarizability of a molecule and ψ is the angle between the long axis of the individual molecule and the optical axis of a droplet (Figure 6). Averaging is performed over all the volume of a droplet. Substituting $(\Delta_n)_\infty$ from Equation (30) into Equation (29) and using Equations (31) and (32) we obtain the collective C-M constant C_c in the form

$$C_c = \frac{(n^2 + 2)^2}{6n}\,\frac{N}{\lambda\varepsilon_o}\,\frac{\Delta\alpha^e\Delta\alpha^m}{45\,kT}\,S_g N_g \tag{34}$$

where $N_g = NV_g$ is the number of molecules in a droplet. This formula is identical with the well known Langevin equation[16] in which $\Delta\alpha^m$ is substituted by $\Delta\alpha^m N_g S_g$. Thus, the collective C-M constant C_c is simply expressed by the "molecular" C-M constant C as

$$C_c = C\,N_g S_g \tag{35}$$

Since the dimensions of the polarizabilities α^e and α^m are $\varepsilon_o \cdot m^3$ and $\mu_o^{-1} \cdot m^3$, respectively, the constants C and C_c have the dimension $m^{-1}\ T^{-2} = mA^2N^{-2}$ in SI units.

Finally, it should be noted that the C-M constant as measured in liquid crystal suspensions is the sum of the collective C-M constant C_c, dependent on the orientation of the droplets as a whole, and the "molecular" C-M constant C, dependent on the orientation of the long molecular axes within a droplet induced by an external magnetic field. Denoting the resultant C-M constant as C_s, we can write

$$C_s = C_c + C = C(1 + N_g S_g) \tag{36}$$

Since $N_g S_g >> 1$ in liquid-crystal suspension below the clearing point T_c, the resultant C-M constant C_s is measured as practically equal to C_c in this case. Above the clearing point T_c, the liquid crystalline order within the droplets disappears and the resultant C-M constant becomes equal to the "molecular" constant C.

B. Relaxation time

When the orienting magnetic field is switched off, the initial disordered state of the suspension is restored by the rotational Brownian motion. If the rate of decay of the magnetic field is sufficiently high, the disorientation process does not follow the field and the residual orientation remains in the sample when the field becomes zero. This residual orientation vanishes spontaneously with relaxation time of the order from 10^1 to 10^3 s. This effect is the cause of the hysteresis shape of the C-M curve as obtained in the full increase–decrease cycle of applied magnetic field. To estimate the relaxation time we can consider the Einstein theory of the Brownian motion[17] adapted to the rotational motion. Taking the state of full orientation of the long molecular axes along the field B as the initial state, $\langle \sin^2\beta \rangle = 0$, for the rate of decay of the orientation we obtain

$$\langle \sin^2\beta \rangle = \frac{2}{3}(1 - e^{-6Dt}) \tag{37}$$

where t is the time and D is the rotational diffusion coefficient. The spontaneous decrease of the orientation is equivalent to decay of the order parameter S_s of the optical axes of droplets [Equation (12)]

$$S_s = e^{-6Dt} \tag{38}$$

Rotational diffusion coefficient D for spherical droplets of radius a immersed in an isotropic liquid of viscosity η is

$$D = \frac{kT}{8\ \pi\eta a^3} \tag{39}$$

Hence, in view of Equations (38) and (39), the relaxation time for the decay of the orientation can be written as

$$\tau = \frac{1}{6D} = \frac{48\,\pi\eta a^3}{kT} \tag{40}$$

6. DISCUSSION

The expression for the potential energy U of the droplet in an external magnetic field, Equation (18), was obtained with the assumption that the interaction between droplets is negligibly small and has no influence upon orientation. The interaction between colloidal particles in solution is determined by van der Waals forces of attraction and the electrostatic repulsion caused by the electric double layers. The van der Waals part of interactions is usually estimated by empirical Hamaker constant A.[18] Exact expression of this part of interactions is complicated and can be obtained as a consequence of Lifshitz macroscopic theory of van der Waals forces.[19] In complex, three-component at least, colloidal systems the occurrence of van der Waals forces of the repulsion type has also been demonstrated.[20] The assumption on negligibility of the interactions between droplets is quite substantiated for the suspensions investigated. Microscopic measurements show that the distance between droplets R is on the average larger than 10 d, where d is the diameter of the droplet. In this case, the effective van der Waals interaction between droplets turns out to be[21]

$$\Phi(R) = -\frac{A}{12}\left[\frac{d^2}{R^2 - d^2} + \frac{d^2}{R^2} + 2\ln\left(1 - \frac{d^2}{R^2}\right)\right] \tag{41}$$

where A is Hamaker constant. For $R = 10d$, the potential $\Phi(R)$ has very small value $-A/600$.

The second simplification assumed is that the parameter S_g, describing the average orientation within a droplet, is independent of the field B. This assumption should only be fulfilled in some idealized situation when the director field is uniform within every droplet. In achiral phases, the uniformity of the director field is disturbed by point defects in a droplet, disclination lines, and anisotropic surface stress. In this case, the field B magnifies the diamagnetic anisotropy of the droplet as a whole. The influence of the field B on the order parameter S_g is especially strong in the suspensions of the chiral liquid crystals. This is because the magnetically induced phase transition occurs when the field B exceeds some critical value. The chirality of the liquid-crystal structure decreases at every magnetic field.

In nematic droplets, we meet the director field of various configurations ranged between two extreme topologies: "hedgehog" with the centrosymmetric director field and "dressed hedgehog" with one at least singular point, called the "boojum"[22,23] in analogy to the topology of the vortices in A-phase of the superfluid ^{3}He. In suspensions of a typical liquid crystal with diamagnetic anisotropy of the order of 10^{-5} SI units, the orienting energy of an idealized uniformly ordered droplet in

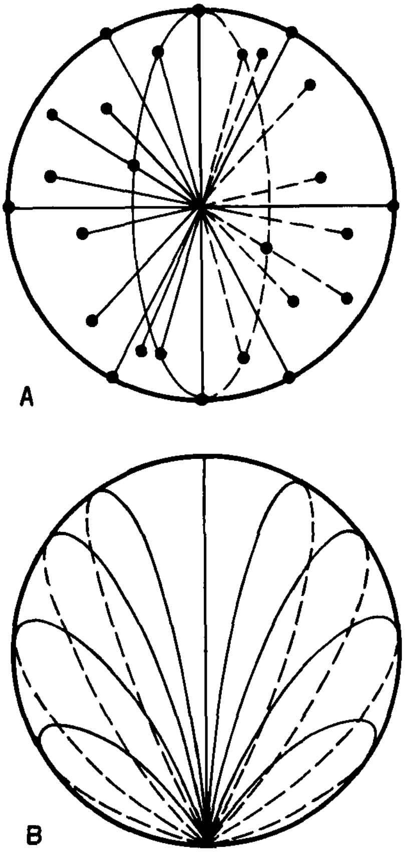

FIGURE 7 A. Hedgehog-type droplet at normal boundary conditions. B. Boojum-type droplet at tangential boundary conditions.

field B = 1.25 T should be comparable with kT at T = 300 K for droplets of diameter d = 100 nm. In reality, this diameter will be larger than estimated above because of the nonuniformity of the director field. Magnetic deformation of the initial director field inside a droplet results in saturation of C-M effect faster than it is anticipated by Equation (25). This effect is shown in Figure 5 by comparing the experimental values of Δn to the theoretical curve which is a plot of Equation (25) with one only value of the quotient $\Delta\chi V_g(2\mu_o kT)^{-1} = 200$, Equation (20), for which the theoretical value of Δn is forced to be equal to that experimental at B = 0.15 T (far below the saturation).

The saturation in the C-M effect observed here is analogous to the saturation registered in Kerr effect in systems where this effect can be interpreted as collective. Full saturation in Kerr effect has been found in solutions of PBLG in dichloroethane and tobacco mosaic virus in water,[24] and also in suspensions of bentonite.[25] Nonlinear light scattering proves that complete orientation of anisotropic particles is possible also under action of intense linearly polarized light beam on solutions of macromolecules and colloids.[26]

The saturation in the C-M effect, although in much higher magnetic fields, has been found by other authors in biological structures which can be regarded as the isotropic phases of lyotropic liquid crystals. Investigations have been performed on chloroplasts,[27,28] retinal rods,[29,30] muscle fibers,[31] and solutions of biopolymers and membranes.[32]

6. CONCLUSIONS

It has been shown that C-M effect in liquid-crystal suspensions is collective in nature with the saturation at relatively low magnetic fields. The "collective" and "molecular" C-M constants are in ratios from 10^4 to 10^8 in these suspensions. The collective C-M effect was shown to be completely determined by the orientational molecular order within the grains or droplets. From the measured birefringence we find that the collective C-M effect has hysteresis-type behavior with relaxation time of the orders from 10^1 to 10^3 s for the residual orientation. Our use of the generalized *n*th order Langevin functions, Equation (21), has allowed the birefringence in C-M effect to be written in one form, Equation (25), for every value of the magnetic field including the saturation region. This theoretical description is applicable to any system containing freely suspended optically anisotropic grains or droplets.

The magnetooptics of colloids can be regarded as an analogue of well developed electrooptics of colloids.[33,34] The real advantage of the magnetooptical methods with respect to the electrooptical ones is the possibility to perform the measurements in dielectric liquids as well as in liquids with high electric conductivity, e.g., in liquids which are typical for biological systems. Magnetooptical phenomena in liquid-crystal colloids and suspensions offer a new and potentially powerful technique for studying various physical phenomena in the dispersed systems, e.g., development of the presence of the ordered structure within colloidal grains, investigations of the phase transitions within these grains, and investigations of the rotational Brownian motion.

APPENDIX

Relation (7) can simply be obtained using the matrix-optics methods. We suppose that the light propagates along the axis of the optical system parallel to z axis of the orthogonal coordinate system x,y,z. We neglect the absorption and scattering of light. Initial intensity in the beam is I. At any point of the optical path the light beam is described by Stokes vector S

$$S = \begin{bmatrix} \mathrm{I} \\ \mathrm{Q} \\ \mathrm{U} \\ \mathrm{V} \end{bmatrix} = \mathrm{I} \begin{bmatrix} 1 \\ \cos 2\Phi \\ \sin 2\Phi \cos\Delta \\ \sin 2\Phi \sin\Delta \end{bmatrix} \tag{A1}$$

where Φ is the azimuthal angle (the angle measured from the positive ray of the x axis) of the vector E of light wave, and Δ is the phase shift between the components E_x and E_y of E. The problem is then reduced to finding of the Stokes vector S_A which describes the light beam incident on the analyzer. This beam results from the unpolarized light beam passed in sequence through the polarizer, the sample, and the quarter-wave plate. Multiplying the Stokes vector of the unpolarized laser beam S_o ($I = I$, $Q = U = V = 0$) by the Mueller matrices[35] of the polarizer M_p with the azimuth of the axis $\alpha = 0$, investigated birefringent sample $M\phi$ with the azimuth of optical axis $\gamma = \pi/4$ and unknown phase shift ϕ, and quarter-wave plate M_q with the azimuth of the fast axis $\theta = 0$ leads to the vector S_A

$$S_A = M_q \cdot M\phi \cdot M_p \cdot S_o \tag{A2}$$

From this product we obtain

$$S_A = \frac{I}{2}\begin{bmatrix} 1 \\ \cos\phi \\ \sin\phi \\ 0 \end{bmatrix} \tag{A3}$$

Upon comparing (A3) with (A1) we see that $\Delta = 2k\pi$, $k = 0, \pm 1, \pm 2, \ldots$ and

$$\Phi = \frac{\phi}{2} \tag{A4}$$

References

1. P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1975), 2nd ed., p. 50.
2. S. Chandrasekhar, *Liquid Crystals* (Cambridge University, Cambridge, England, 1977), p. 66.
3. P. G. de Gennes, *Phys. Lett.*, **30A**, 454 (1969).
4. M. J. Stephen and C. P. Fan, *Phys. Rev. Lett.*, **25**, 500 (1970).
5. P. G. de Gennes, *Mol. Cryst. Liq. Cryst.*, **12**, 193 (1971).
6. J. Zadoc-Kahn, *Ann. Physique*, (series 2) **6**, 455 (1936).
7. K. Muta, H. Takezoe, A. Fukuda, and E. Kuze, *Jpn. J. Appl. Phys*, **20**, 503 (1981).
8. M. F. Vuks, *Opt. Spectrosc.*, **20**, 361 (1966).
9. Ch. Rosenblatt, S. Kumar, and J. D. Litster, *Phys. Rev.*, **A29**, 1010 (1984); Ch. Rosenblatt, *Phys. Rev.*, **A32**, 1924 (1985).
10. P. Photinos and A. Saupe, *Mol. Cryst. Liq. Cryst.*, **123**, 217 (1985).
11. A. Adamczyk, *Vth Liq. Cryst. Conf. Socialist Countries*, Odessa, 10–15 Oct. 1983, Abstracts, vol. 2, part 1, p. 107.
12. S. Taketomi, *Jpn. J. Appl. Phys.*, **22**, 1137 (1983).
13. J. D'Ans and E. Lax, Taschenbuch für Chemiker und Physiker (Springer, Berlin, 1943), p. 1103.
14. L. P. Hoyt, *Ind. Eng. Chem.*, **26**, 329 (1934).
15. S. Kielich, *Opto-Electronics*, **2**, 5 (1970).
16. P. Langevin, *Le Radium*, **7**, 249 (1910).
17. A. Einstein, *Ann. Phys.*, **17**, 549 (1905).
18. H. C. Hamaker, *Physica*, **4**, 1058 (1937).
19. I. E. Dzyaloshinskii, E. M. Lifshitz, and L. P. Pitaevskii, *Adv. Phys.*, **10**, 165 (1961).
20. J. Visser, *Adv. Colloid Interface Sci.*, **15**, 157 (1981).
21. M. J. Grimson and P. Richmond, *J. Physique*, **46**, 447 (1985).

22. N. D. Mermin, *Quantum Fluids and Solids*, Ed. S. B. Trickey, E. Adams, and J. Duffy (Plenum, New York, 1977).
23. D. L. Stein, R. D. Pisarski, and P. W. Anderson, *Phys. Rev. Lett.*, **40**, 1269 (1978).
24. C. T. O'Konski, K. Yoshicka, and W. H. Orttung, *J. Phys. Chem.*, **63**, 1558 (1959).
25. M. J. Shah, *J. Phys. Chem.*, **67**, 2215 (1963).
26. S. Kielich, *J. Colloid Interface Sci.*, **27**, 432 (1968); **28**, 214 (1968); **33**, 142 (1970); **34**, 228 (1970).
27. N. E. Geacintov, P. V. Nostrand, J. F. Becker, and J. B. Tinkel, *Biochim. Biophys. Acta*, **267**, 65 (1972).
28. J. Brenton, E. Roux, and J. Whitmarsh, *Biochim. Biophys. Res. Commun.*, **64**, 1274 (1975).
29. N. Chalazonitis, R. Chagneux, and A. Arvanitaki, *C. R. Acad. Sci.* Paris **271D**, 130 (1970).
30. M. Chabre, *Biochim. Biophys. Acta*, **382**, 322 (1975).
31. W. Arnold, R. Steele, and H. Mueller, *Proc. Nat. Acad. Sci.*, **44**, 1 (1958).
32. G. Maret and K. Dransfeld, *Physica*, **86-88 B**, 1077 (1977); *Strong and Ultrastrong Magnetic Fields*, Ed. F. Herlach (Springer, Berlin, 1985), pp. 143–204.
33. Electrooptics of Colloids (in Russian), Ed. S. S. Dukhin (Naukova Dumka, Kiev, 1977).
34. Electro-Optics and Dielectrics of Macromolecules and Colloids, Ed. B. R. Jennings (Plenum, New York, 1979).
35. A. Gerrard and J. M. Burch, *Introduction to Matrix Methods in Optics* (Wiley, London, 1975).