Light Scattering from Fluctuations in an Optically Active Fluid *

Kin-Wah Li
Department of Physics, University of Minnesota, Minneapolis, Minnesota
and John S. Dahler
Departments of Chemistry and Chemical Engineering, University of Minnesota, Minneapolis, Minnesota

(Z. Naturforsch. **28 a**, 805 – 814 [1973] ; received 27th December 1972)

This paper is dedicated to Ludwig Waldmann in celebration of his 60th birthday

The theory of light scattering by fluctuations has been extended to optically active fluids. The new feature is the "gyration parameter", a second rank asymmetric tensor, the fluctuations of which must be counted along with the familiar isotropic (scalar) and anisotropic (traceless and symmetric) fluctuations of the electric permeability tensor. Scattering equations are derived and solved in order to obtain the spectrum of scattered light. It is found that the angular dependence of scattering caused by fluctuations of permeability alone does not involve the propagation vectors of the incident or scattered fields whereas that which involves fluctuations of the gyration parameter depends explicitly upon these two vectors. This gyration tensor also has distinguishable effects upon the depolarization, ellipticity, and rotation or tilt of the scattered quasi-monochromatic light. The total intensity is resolved into a sum of five distinct contributions, each associated with different irreducible components of the gyration and permeability tensors and each with a different dependence upon the scattering angle and polarizations of the incident and scattered light. Experiments are suggested which emphasize effects originating from the optical activity of the scattering medium.

It long has been known that the familiar Rayleigh scattering[1] is due to microscopic variations of electric permeability (or index of refraction) associated with local fluctuations of density and temperature. The polarization of the light scattered by these scalar or isotropic fluctuations is the same as that of the incident field. More recently[2–5] it has been recognized that the experimentally observed depolarization of scattered light originates from anisotropic, tensor valued fluctuations of permeability. Theory predicts[5] that the intensities of scattering due to these scalar and tensor (symmetric and traceless) valued fluctuations of permeability should be proportional to $(\hat{e} \cdot \hat{e}')^2$ and $\frac{1}{2}[3 + (\hat{e} \cdot \hat{e}')^2]$, respectively, with $\hat{e}$ and $\hat{e}'$ denoting the polarizations of the incident and scattered beams.

The purpose of the present investigation is to determine how these conclusions are modified for scattering from an optically active fluid. Specific items of interest include the systematic rotation of the plane of polarization of transmitted light and the characteristics of the scattering caused by fluctuations of the second rank (asymmetric) pseudotensor, gyration parameter, $\mathbf{g}$. In part I we construct the inhomogeneous differential equation which governs the electric induction of the field scattered from an optically active fluid. The differences between this equation and the corresponding equation for an inactive fluid arise from additional terms that occur in the "constitutive relationships", that is, in the connections among the $\boldsymbol{D}$, $\boldsymbol{B}$, $\boldsymbol{E}$, and $\boldsymbol{H}$ fields. There are contributions to the inhomogeneous portion of this wave equation due to fluctuations of $\mathbf{g}$ and contributions to the differential operator (or propagator) which account for the rotation of the polarization of the scattered light. From the solution of this equation we compute the electric field at a point far from that at which scattering occurs and then derive a formula for the spectral intensity of the scattered light.

In part II we resolve this intensity into contributions due to fluctuations of electric permeability and gyration parameter and derive explicit formulas for the dependence of each of these contributions upon the polarization and propagation vectors of the incident and scattered fields. It is found that the intensity of a scattering component which involves a fluctuation of $\mathbf{g}$ is dependent upon all four of these quantities whereas terms arising from fluctuations of permeability alone depend only upon $\hat{e}$ and $\hat{e}'$. The intensities of the various terms are related to correlation functions specific to the different fluctuations. Finally, we introduce the coherence matrix of Born and Wolf[6] in order to de-

Reprint requests to Prof. Dr. J. S. Dahler, Departments of Chemistry and Chemical Engineering, University of Minnesota, *Minneapolis, Minn.*, U.S.A.

Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung") beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition "no derivative works"). This is to allow reuse in the area of future scientific usage.

scribe the polarization state of the scattered quasi-monochromatic light. It is found that for several commonly used experimental arrangements the autocorrelation of $\Delta\mathbf{g}$ (the fluctuation of $\mathbf{g}$) has distinguishable effects upon the depolarization and that the cross correlation of this tensor with $\Delta\boldsymbol{\epsilon}$ (the fluctuation of $\boldsymbol{\epsilon}$) contributes to the ellipticity and tilt of the polarized component of scattered light.

Throughout this presentation we adhere closely to the notation and mathematical format of the excellent paper by Hess[5]. To avoid repetition we have omitted many conceptual and mathematical details which can be found in Hess[5] or in one of the standard references[1–3].

I. Construction and Solution of the Wave Equation for Scattered Light

Our treatment of light scattering by an optically active fluid is a modest and straightforward generalization of a theory which has evolved over a period of more than half a century[1–5]. The essence of this theory is contained in the description or model which it adopts of the scattering medium. Once this model is accepted the mathematical structure of the theory then follows as a natural consequence of Maxwell's equations and of the application of statistical mechanics techniques for handling the fluctuations and correlations of dynamical variables. Therefore, we shall begin with a brief summary of the conceptual basis of the theory and then proceed directly to a compact formulation of its mathematical aspects.

We consider a fluid which is in a state of thermodynamic and mechanical equilibrium. This does not, of course, preclude the occurence of fluctuations which can be characterized in terms of the arrangement and motions of the centers of mass and orientations of groups of molecules which number much less than the total population of the fluid. Except in the vicinity of a phase transition, these fluctuations will be highly localized events which involve correlations of molecular arrangement and motion over distances no more than an order of magnitude greater than the mean spacing between neighboring molecules. Therefore, the fluid can be treated as if it were divided into a large number of quasi-independent subsystems each of which is of infinitesimal volume from a macroscopic point of view but which nevertheless contains very many molecules. Light scattered from these different subsystems or "cells" will be incoherent.

To compute the electromagnetic field caused by scattering from the fluid one takes advantage of the vast difference between the time scale ($> 10^{-12}$ sec) associated with changes of molecular arrangement and the characteristic response time ($< 10^{-16}$ sec) of the electronic state of the system to the incident field. The scattering then can be described in terms of the instantaneous arrangement of the molecules and properties of the associated adiabatic (in the sense of the Born-Oppenheimer separation) electronic state such as the local, arrangement-dependent values of magnetization and electric polarization. Although the macroscopic state of the system may be isotropic (as it is when there is thermodynamic and mechanical equilibrium and no external fields), the localized regions in which scattering occurs are not subject to this symmetry constraint. Thus, for example, while the local value of the electric permeability tensor must be symmetric, it need not be isotropic.

In an isotropic medium the arrangement average of the scattered field is zero. However, the intensity of scattered radiation is porportional to the square of the field strength and the average of this generally does not vanish.

Let us denote by $\boldsymbol{D}$, $\boldsymbol{B}$, $\boldsymbol{E}$, $\boldsymbol{H}$, and $\boldsymbol{k}$, respectively, the electric induction, magnetic-induction, electric field, magnetic field, and wave vector, which are specific to the incident radiation. The corresponding quantities associated with the scattered light will be labelled with the corresponding primed variables. (This convention is the same as that used by Landau and Lifshitz[2] but opposite to that adopted by Hess[5].) The constitutive relations appropriate to an isotropic optically active fluid are[7] (also see Appendix A)

$$\boldsymbol{D} = \varepsilon \boldsymbol{E} - g\,\partial_t \boldsymbol{H}, \quad \boldsymbol{B} = \mu \boldsymbol{H} + g\,\partial_t \boldsymbol{E} \qquad (1)$$

where ε, g, and μ (which we henceforth equate to unity) are the volume averaged isotropic values of the electric permability, gyration parameter, and magnetic permeability. Because of the fluctuations of molecular arrangement which previously have been discussed the constitutive relations appropriate to one of the elementary scattering regions will be of the form

$$\begin{aligned} \boldsymbol{D} + \boldsymbol{D}' &= (\varepsilon \boldsymbol{\delta} + \Delta\boldsymbol{\epsilon}) \cdot (\boldsymbol{E} + \boldsymbol{E}') \\ &\quad - (g\boldsymbol{\delta} + \Delta\mathbf{g}) \cdot \partial_t(\boldsymbol{H} + \boldsymbol{H}'), \qquad (2) \\ \boldsymbol{B} + \boldsymbol{B}' &= (\boldsymbol{H} + \boldsymbol{H}') + (g\boldsymbol{\delta} + \Delta\mathbf{g}^{\mathrm{T}}) \cdot \partial_t(\boldsymbol{E} + \boldsymbol{E}') \end{aligned}$$

where the two second rank tensors $\mathbf{\Delta\epsilon} = \mathbf{\Delta\epsilon}(t\boldsymbol{x})$ and $\mathbf{\Delta g} = \mathbf{\Delta g}(t\boldsymbol{x})$ denote the local instantaneous values of the fluctuating contributions to the electric permeability and gyration parameter and where $\mathbf{\Delta g}^{\mathrm{T}}$ is the tensor transpose of $\mathbf{\Delta g}$. We now assume the intensity of the scattered field to be much less than that of the incident light and then use Eq. (1) to eliminate $\boldsymbol{D}$ and $\boldsymbol{B}$ from Equation (2). This results in the pair of relationships

$$\boldsymbol{D}' \approx \varepsilon \boldsymbol{E}' - g\,\partial_t \boldsymbol{H}' + \boldsymbol{d}, \quad \boldsymbol{B}' \approx \boldsymbol{H}' + g\,\partial_t \boldsymbol{E}' + \boldsymbol{b} \tag{3}$$

where

$$\boldsymbol{d} = \mathbf{\Delta\epsilon}\cdot\boldsymbol{E} - \mathbf{\Delta g}\cdot\partial_t\boldsymbol{H} \quad \text{and} \quad \boldsymbol{b} = \mathbf{\Delta g}^{\mathrm{T}}\cdot\partial_t\boldsymbol{E} \tag{4}$$

give the explicit dependence of the scattered fields upon the local fluctuations of the fluid and upon the characteristics of the incident beam. By substituting the connections Eq. (3) into the Maxwell equations one obtains for the electric induction of the scattered field the inhomogeneous differential equation

$$[\Delta - (\varepsilon/c^2)\,\partial_t^2]\,\boldsymbol{D}' - 2\,(g/c)\,\mathrm{curl}\,\partial_t^2\boldsymbol{D}' - (g^2/c^2)\,\partial_t^4\boldsymbol{D}' = \boldsymbol{F} \tag{5}$$

where Δ denotes the Laplacian operator. The magnetic induction satisfies a similar equation.

Because the incident light must pass through the optically active fluid to the point where scattering occurs, the polarizations of the $\boldsymbol{E}$ and $\boldsymbol{H}$ fields which appear in $\boldsymbol{d}$ and $\boldsymbol{b}$ of

$$\boldsymbol{F} = -\,\mathrm{curl}\,\mathrm{curl}\,\boldsymbol{d} - (g/c)\,\mathrm{curl}\,\partial_t^2\,\boldsymbol{d} + (\varepsilon/c)\,\mathrm{curl}\,\partial_t\,\boldsymbol{b} \tag{6}$$

are rotated by amounts proportional to the distance from the boundary of the fluid to the location of the fluctuations $\mathbf{\Delta\epsilon}$ and $\mathbf{\Delta g}$. In Appendix B it is shown that the rotation of the polarization of the scattered light is accounted for by the last two terms on the left hand side of Equation (5). For fluid samples which are sufficiently thin these rotatory effects are of negligible importance. The condition for this is $g\,\omega^2 L/c \ll 1$ where ω denotes the frequency of the incident light and where L is the thickness of the sample. However, even if this criterion is not met the effects of optical rotation can be compensated by suitable adjustments of the polarizers and analyzers. We henceforth ignore such complications and confine our attention to the simplified wave equation

$$[\Delta - (\varepsilon/c^2)\,\partial_t^2]\,\boldsymbol{D}' = \boldsymbol{F}. \tag{7}$$

Let us denote by $\boldsymbol{D}'(\omega', \boldsymbol{x})$ and $\boldsymbol{F}(\omega', \boldsymbol{x})$ the time Fourier transform of $\boldsymbol{D}'(t, \boldsymbol{x})$ and of $\boldsymbol{F}(t, \boldsymbol{x})$, respectively. Then, the electric induction at a point $\boldsymbol{x}$ which is far from an elementary scattering region of volume Ω is given by

$$\boldsymbol{D}'(\omega', \boldsymbol{x}) \approx (-\,e^{ik'x}/4\pi x)\int_{\Omega} \mathrm{d}^3y\, e^{-i\boldsymbol{k}'\cdot\boldsymbol{y}}\,\boldsymbol{F}(\omega', \boldsymbol{y}) \tag{8}$$

where $\boldsymbol{k}' = k'\hat{x}$ with $\hat{x} = \boldsymbol{x}/x$ and $k'^2 = \varepsilon\,\omega'^2/c^2$.

We now select for the incident light the plane polarized pulse

$$\boldsymbol{E} = \hat{e}\,E\exp i(\boldsymbol{k}\cdot\boldsymbol{x} - \omega t)\begin{Bmatrix} 1; & 0 < t < \mathscr{T} \\ 0; & \text{otherwise} \end{Bmatrix}. \tag{9}$$

The spectral intensity J,[5] defined as the intensity per frequency interval with polarization $\hat{e}'$ which is scattered into the direction $\hat{x}$, then can be written in the form

$$J = (c/4\pi)\,(1/2\pi\mathscr{T})\langle|\hat{e}'\cdot\boldsymbol{E}'(\omega', \boldsymbol{x})|^2\rangle\,x^2 \tag{10}$$

where the bracket $\langle\ \rangle$ denotes an ensemble average of the fluctuations. More generally one defines the spectral intensity matrix with components

$$J_{mn} = (c/4\pi)\,(1/2\pi\mathscr{T})\langle E_m'(\omega', \boldsymbol{x})\,E_n'^{*}(\omega', \boldsymbol{x})\rangle\,x^2 \tag{11}$$

referred to the two orthogonal unit vector[5] $\hat{e}_1' \equiv \hat{e}'$ and $\hat{e}_2' \equiv \hat{f}' \equiv \hat{k}' \wedge \hat{e}'$ which lie in the plane perpendicular to the direction of propagation $\hat{k}'$. It follows from (8) and (11) that this intensity is related to the scattering matrix

$$I_{mn} = (1/2\pi\mathscr{T})\,(1/4\pi)^2\int_0^{\mathscr{T}}\mathrm{d}t\int_0^{\mathscr{T}}\mathrm{d}t'\,e^{i(\omega'-\omega)(t-t')}\langle h_m(t)\,h_{\boldsymbol{n}}^{*}(t')\rangle \tag{12}$$

by the formula

$$J_{mn} = (c/4\pi)\,(\omega'/c)^4\,E^2\,I_{mn}(\omega' - \omega, q; \hat{e}, \hat{f}, \hat{e}', \hat{f}'). \tag{13}$$

Here $\boldsymbol{q} = \boldsymbol{k}' - \boldsymbol{k}$ is the momentum transfer and

$$h_n(t) = \hat{e}\cdot\mathbf{\Delta\epsilon}(t, \boldsymbol{q})\cdot\hat{e}_n' + i\,\omega\sqrt{\varepsilon}\,\{\hat{e}_n'\cdot\mathbf{\Delta g}(t, \boldsymbol{q})\cdot\hat{f} - \hat{f}_n'\cdot\mathbf{\Delta g}^{\mathrm{T}}(t, \boldsymbol{q})\cdot\hat{e}\} \equiv \boldsymbol{\alpha}^{(n)} : \mathbf{\Delta\epsilon} + i\,\omega\sqrt{\varepsilon}\,\boldsymbol{\beta}^{(n)} : \mathbf{\Delta g} \tag{14}$$

with

$$\boldsymbol{\Delta\epsilon}(t, \boldsymbol{q}) = \int \mathrm{d}^3y\, e^{-i\boldsymbol{q}\cdot\boldsymbol{y}} \boldsymbol{\Delta\epsilon}(t, \boldsymbol{y}), \quad \boldsymbol{\Delta}\mathbf{g}(t, \boldsymbol{q}) = \int \mathrm{d}^3y\, e^{-i\boldsymbol{q}\cdot\boldsymbol{y}} \boldsymbol{\Delta}\mathbf{g}(t, \boldsymbol{y}). \tag{15}$$

Finally, $\hat{f} = \hat{k} \wedge \hat{e}$, $\hat{f}_n{}' = \hat{k}' \wedge \hat{e}_n{}' = \hat{x} \wedge \hat{e}_n{}'$, $\boldsymbol{\alpha}^{(n)} = \hat{e}\,\hat{e}_n{}'$, and $\boldsymbol{\beta}^{(n)} = \hat{f}\hat{e}_n{}' - \hat{f}_n{}'\hat{e}$. From these definitions it follows that $\hat{f}_1{}' = \hat{e}_2{}' \equiv \hat{f}'$, $\hat{f}_2{}' = \hat{k}' \wedge \hat{f}' = -\hat{e}'$, $\boldsymbol{\alpha}^{(1)} = \hat{e}\,\hat{e}'$, $\boldsymbol{\alpha}^{(2)} = \hat{e}\hat{f}'$, $\boldsymbol{\beta}^{(1)} = \hat{f}\hat{e}' - \hat{f}'\hat{e}$, and $\boldsymbol{\beta}^{(2)} = \hat{f}\hat{f}' + \hat{e}'\hat{e}$.

In the case of a stationary ensemble $\langle h_m(t) h_n{}^*(t')\rangle = \langle h_m(t - t') h_n{}^*(0)\rangle$. Equation (12) for the scattering matrix then reduces to the simpler and more explicit form

$$\begin{aligned}(4\pi)^2 I_{mn} = \int_0^{\mathscr{T}} \mathrm{d}t (1 - t/\mathscr{T}) [&\boldsymbol{\alpha}^{(m)} : \mathbf{R}^{(\varepsilon\varepsilon)} : \boldsymbol{\alpha}^{(n)} + \omega^2 \varepsilon\, \boldsymbol{\beta}^{(m)} : \mathbf{R}^{(gg)} : \boldsymbol{\beta}^{(n)} \\ &- i\omega\sqrt{\varepsilon}\{\boldsymbol{\alpha}^{(m)} : \mathbf{R}^{(\varepsilon g)} : \boldsymbol{\beta}^{(n)} - \boldsymbol{\alpha}^{(n)} : \mathbf{R}^{(\varepsilon g)} : \boldsymbol{\beta}^{(m)}\}]\end{aligned} \tag{16}$$

with

$$\mathbf{R}^{(\mu\nu)}(\omega' - \omega, t, \boldsymbol{q}) = \mathrm{Re}\{(1/\pi) e^{i(\omega' - \omega)t} \langle \boldsymbol{\Delta\mu}(t, \boldsymbol{q}) \boldsymbol{\Delta\nu}^*(0, \boldsymbol{q})\rangle\}.$$

Henceforth we assume the limit $\mathscr{T} \to \infty$ and replace the integrand factor $(1 - t/\mathscr{T})$ with unity.

To obtain the formula (16) we have invoked the "reciprocal relations"

$$\langle \mathbf{a}(t, \boldsymbol{x}) \mathbf{b}(0, \boldsymbol{x})\rangle = \langle \mathbf{a}(0, \boldsymbol{x}) \mathbf{b}(t, \boldsymbol{x})\rangle \quad \text{or} \quad \langle \mathbf{a}(t, \boldsymbol{q}) \mathbf{b}^*(0, \boldsymbol{q})\rangle = \langle \mathbf{a}^*(0, \boldsymbol{q}) \mathbf{b}(t, \boldsymbol{q})\rangle$$

with $\mathbf{a}$ and $\mathbf{b}$ equal to $\boldsymbol{\Delta\epsilon}$ or $\boldsymbol{\Delta}\mathbf{g}$. These are so because the time dependence of the tensors $\boldsymbol{\Delta\epsilon}(t, \boldsymbol{x})$ and $\boldsymbol{\Delta}\mathbf{g}(t, \boldsymbol{x})$ is due exclusively to the translational and rotational motions of the molecules and involves the electrons only to the extent that the adiabatic electronic state determines the interactions among the molecules.

II. Characteristics of the Scattering from Different Kinds of Fluctuations

The second rank tensors $\boldsymbol{\Delta\epsilon}$ and $\boldsymbol{\Delta}\mathbf{g}$ can be resolved into the sums

$$\boldsymbol{\Delta\epsilon} = \varepsilon'\boldsymbol{\delta} + \overline{\boldsymbol{\Delta\epsilon}} + \overset{\sqcup}{\boldsymbol{\Delta\epsilon}}, \quad \boldsymbol{\Delta}\mathbf{g} = g'\boldsymbol{\delta} + \overline{\boldsymbol{\Delta}\mathbf{g}} + \overset{\sqcup}{\boldsymbol{\Delta}\mathbf{g}} \tag{17}$$

of isotropic ($\varepsilon'\boldsymbol{\delta}$ and $g'\boldsymbol{\delta}$), traceless symmetric ($\overline{\boldsymbol{\Delta\epsilon}}$ and $\overline{\boldsymbol{\Delta}\mathbf{g}}$), and anti-symmetric ($\overset{\sqcup}{\boldsymbol{\Delta\epsilon}}$ and $\overset{\sqcup}{\boldsymbol{\Delta}\mathbf{g}}$) contributions. However, since the electric permeability tensor is symmetric[2], (also see Appendix A) $\overset{\sqcup}{\boldsymbol{\Delta\epsilon}}$ must vanish. The integrand of Eq. (16) contains quantities $\langle \mathbf{a}(t, \boldsymbol{q}) \mathbf{b}(\boldsymbol{q})\rangle$ with $\mathbf{a}$ and $\mathbf{b}$ equal either to $\boldsymbol{\Delta\epsilon}$ or $\boldsymbol{\Delta}\mathbf{g}$. Therefore, with fourth rank tensors $\mathrm{A}(t|\boldsymbol{q})$ and $\mathbf{B}(t|\boldsymbol{q})$ defined by

$$\boldsymbol{\Delta\epsilon}(t, \boldsymbol{q}) = \mathbf{A}(t|\boldsymbol{q}) : \boldsymbol{\Delta\epsilon}(\boldsymbol{q}), \quad \boldsymbol{\Delta}\mathbf{g}(t, \boldsymbol{q}) = \mathbf{B}(t|\boldsymbol{q}) : \boldsymbol{\Delta}\mathbf{g}(\boldsymbol{q}) \tag{18}$$

it follows that $\langle \mathbf{a}(t, \boldsymbol{q}) \mathbf{b}(\boldsymbol{q})\rangle = \mathbf{C}(t|\boldsymbol{q}) : \langle \mathbf{a}(\boldsymbol{q}) \mathbf{b}(\boldsymbol{q})\rangle$ where $\mathbf{C}$ is either $\mathbf{A}$ or $\mathbf{B}$. In the case of an isotropic fluid the fourth rank tensors $\mathbf{C}(t|\boldsymbol{q})$ and $\langle \mathbf{a}(\boldsymbol{q}) \mathbf{b}(\boldsymbol{q})\rangle$ can be written as sums

$$\mathbf{C}(t|\boldsymbol{q}) = \Sigma_k C_k(t|\boldsymbol{q}) \mathbf{T}_k{}^{(4,0)}, \quad \langle \mathbf{a}(\boldsymbol{q}) \mathbf{b}(\boldsymbol{q})\rangle = \Sigma_k \langle \mathbf{a}(\boldsymbol{q}) \mathbf{b}(\boldsymbol{q})\rangle_k \mathbf{T}_k{}^{(4,0)} \tag{19}$$

with isotropic basis tensors $\mathbf{T}_k{}^{(4,0)}$ (the notation is that of Coope and Snider[8]) which are so defined that

$$\mathbf{T}_k{}^{(4,0)} : \mathbf{T}_n{}^{(4,0)} = \delta_{kn} \mathbf{T}_k{}^{(4,0)}, \quad \Sigma_k \mathbf{T}_k{}^{(4,0)} = \mathbf{1}^{(4)} \tag{20}$$

and where $\mathbf{1}^{(4)}$ is the fourth rank identity tensor.

The components of these projection operators are given by

$$T^{(4,0)}_{1,ijkl} = \tfrac{1}{2}\delta_{ik}\delta_{jl} + \tfrac{1}{2}\delta_{il}\delta_{jk} - \tfrac{1}{3}\delta_{ij}\delta_{kl}, \quad T^{(4,0)}_{2,ijkl} = \tfrac{1}{2}\delta_{ik}\delta_{jl} - \tfrac{1}{2}\delta_{il}\delta_{jk}, \quad \text{and} \quad T^{(4,0)}_{3,ijkl} = \tfrac{1}{3}\delta_{ij}\delta_{kl}.$$

The scalar valued coefficients $\langle \mathbf{a}(\boldsymbol{q}) \mathbf{b}(\boldsymbol{q})\rangle_k$ are related to components of $\langle \mathbf{a}(\boldsymbol{q}) \mathbf{b}(\boldsymbol{q})\rangle$ by the formulas

$$\langle \mathbf{a}\,\mathbf{b}\rangle_1 = \tfrac{1}{5}\langle \overline{\mathbf{a}} : \overline{\mathbf{b}}\rangle, \quad \langle \mathbf{a}\,\mathbf{b}\rangle_2 = -\tfrac{1}{3}\langle \overset{\sqcup}{\mathbf{a}} : \overset{\sqcup}{\mathbf{b}}\rangle, \quad \text{and} \quad \langle \mathbf{a}\,\mathbf{b}\rangle_3 = \tfrac{1}{3}\langle \boldsymbol{\delta} : \mathbf{a}\,\boldsymbol{\delta} : \mathbf{b}\rangle. \tag{21}$$

By substituting these results into Eq. (16) we are able to express the elements of the scattering matrix in the form

$$I_{mn} = (4\pi)^{-2} \sum_k \left[U_k^{(\varepsilon\varepsilon)} (\boldsymbol{\alpha}_k^{(m)} : \boldsymbol{\alpha}_k^{(n)}) + U_k^{(gg)} (\boldsymbol{\beta}_k^{(m)} : \boldsymbol{\beta}_k^{(n)}) + U_k^{(\varepsilon g)} (\boldsymbol{\alpha}_k^{(m)} : \boldsymbol{\beta}_k^{(n)} - \boldsymbol{\alpha}_k^{(n)} \boldsymbol{\beta}_k^{(m)})\right] \tag{22}$$

with

$$\begin{aligned} \boldsymbol{\alpha}_k^{(m)} &= T_k^{(4,0)} : \boldsymbol{\alpha}^{(m)}, \quad \boldsymbol{\beta}_k^{(m)} = T_k^{(4,0)} : \boldsymbol{\beta}^{(m)}, \quad \text{and} \\ U_k^{(\varepsilon\varepsilon)} &= S_{\mathrm{A}k}(\omega' - \omega \,|\, \boldsymbol{q}) \langle \boldsymbol{\Delta\epsilon}(\boldsymbol{q})\, \boldsymbol{\Delta\epsilon}^*(\boldsymbol{q})\rangle_k, \\ U_k^{(gg)} &= \omega^2 \varepsilon\, S_{\mathrm{B}k}(\omega' - \omega \,|\, \boldsymbol{q}) \langle \boldsymbol{\Delta}\mathbf{g}(\boldsymbol{q})\, \boldsymbol{\Delta}\mathbf{g}^*(\boldsymbol{q})\rangle_k \\ U_k^{(\varepsilon g)} &= - i\,\omega \sqrt{\varepsilon}\, \mathrm{Re}\{\mathcal{S}_{\mathrm{A}k}(\omega' - \omega \,|\, \boldsymbol{q}) \langle \boldsymbol{\Delta\epsilon}(\boldsymbol{q})\, \boldsymbol{\Delta}\mathbf{g}^*(\boldsymbol{q})\rangle_k\} \\ &= - i\,\omega \sqrt{\varepsilon}\, \mathrm{Re}\{\mathcal{S}_{\mathrm{B}k}(\omega' - \omega \,|\, \boldsymbol{q}) \langle \boldsymbol{\Delta\epsilon}(\boldsymbol{q})\, \boldsymbol{\Delta}\mathbf{g}^*(\boldsymbol{q})\rangle_k^*\} \end{aligned} \tag{23}$$

and where $S_{\mathrm{C}k}$ (with C = A or B) is the real part of

$$\mathcal{S}_{\mathrm{C}k}(\omega' - \omega \,|\, \boldsymbol{q}) = (1/\pi) \int_0^\infty \mathrm{d}t\, e^{i(\omega' - \omega)t}\, C_k(t \,|\, \boldsymbol{q}). \tag{24}$$

Because $\mathbf{C}(0 \,|\, \boldsymbol{q}) = \mathbf{1}^{(4)}$ we see that $C_k(0 \,|\, \boldsymbol{q})$ and $\int_{-\infty}^{+\infty} \mathrm{d}\omega' \mathcal{S}_{\mathrm{C}k}(\omega' - \omega \,|\, \boldsymbol{q})$ are both equal to unity. Furthermore, since the diagonal elements of I_{mn} are positive definite and the irreducible parts of $\boldsymbol{\alpha}^{(m)}$ and $\boldsymbol{\beta}^{(m)}$ linearly independent, it follows that $U_k^{(\varepsilon\varepsilon)} \geqq 0$ and $U_k^{(gg)} \geqq 0$.

Each term in the sum Eq. (22) has a unique dependence upon the polarization and propagation vectors of the incident and scattered light. The explicit forms of these terms are collected in Table 1. The entries $\boldsymbol{\alpha}_k^{(1)} : \boldsymbol{\alpha}_k^{(1)}$ were obtained previously by Hess[5] and, in somewhat different form, by Landau and Placzek[3].

Each element of the matrix I_{mn} is a sum of terms, every one of which is a product of three factors, one dependent solely upon the polarization and propagation vectors having to do with the geometrical arrangement of the experiment, a second that is determined by the fluctuations of a system in thermodynamic

Table 1. The polarization and propagation vector dependent factors which appear in the expansion Eq. (22) of the scattering function. The entries enclosed by dashed lines are not observable because of the symmetry of the electric permeability tensor.

k	$\boldsymbol{\alpha}_k^{(1)} : \boldsymbol{\alpha}_k^{(1)}$	$\boldsymbol{\beta}_k^{(1)} : \boldsymbol{\beta}_k^{(1)}$	$\boldsymbol{\alpha}_k^{(2)} : \boldsymbol{\alpha}_k^{(2)}$	$\boldsymbol{\beta}_k^{(2)} : \boldsymbol{\beta}_k^{(2)}$
1	$\frac{1}{6}[3 + (\hat{e} \cdot \hat{e}')^2]$	$\frac{1}{6}(\hat{e}' \cdot \hat{f} - \hat{e} \cdot \hat{f}')^2 + (\hat{e}' \cdot \hat{f})(\hat{e} \cdot \hat{f}') - (\hat{e} \cdot \hat{e}')(\hat{f} \cdot \hat{f}') + 1$	$\frac{1}{6}[3 + (\hat{e} \cdot \hat{f}')^2]$	$\frac{1}{6}(\hat{e} \cdot \hat{e}' + \hat{f} \cdot \hat{f}')^2 + (\hat{e} \cdot \hat{f}')(\hat{e}' \cdot \hat{f}) - (\hat{e} \cdot \hat{e}')(\hat{f} \cdot \hat{f}') + 1$
2	$\boxed{\frac{1}{2}[1 - (\hat{e} \cdot \hat{e}')^2]}$	$-\frac{1}{2}(\hat{e}' \cdot \hat{f} - \hat{e} \cdot \hat{f}')^2 - (\hat{e}' \cdot \hat{f})(\hat{e} \cdot \hat{f}') - (\hat{e} \cdot \hat{e}')(\hat{f} \cdot \hat{f}') + 1$	$\boxed{\frac{1}{2}[1 - (\hat{e} \cdot \hat{f}')^2]}$	$-\frac{1}{2}(\hat{e} \cdot \hat{e}' + \hat{f} \cdot \hat{f}')^2 + (\hat{e} \cdot \hat{f}')(\hat{e}' \cdot \hat{f}) + (\hat{e} \cdot \hat{e})(\hat{f} \cdot \hat{f}') + 1$
3	$\frac{1}{3}(\hat{e} \cdot \hat{e}')^2$	$\frac{1}{3}(\hat{e}' \cdot \hat{f} - \hat{e} \cdot \hat{f}')^2$	$\frac{1}{3}(\hat{e} \cdot \hat{f}')^2$	$\frac{1}{3}(\hat{e} \cdot \hat{e}' + \hat{f} \cdot \hat{f}')^2$

k	$\boldsymbol{\alpha}_k^{(1)} : \boldsymbol{\alpha}_k^{(2)}$	$\boldsymbol{\beta}_k^{(1)} : \boldsymbol{\beta}_k^{(2)}$	$\boldsymbol{\alpha}_k^{(1)} : \boldsymbol{\beta}_k^{(2)}$	$\boldsymbol{\alpha}_k^{(2)} : \boldsymbol{\beta}_k^{(1)}$
1	$\frac{1}{6}(\hat{e} \cdot \hat{e}')(\hat{e} \cdot \hat{f}')$	$\frac{1}{3}\left[(\hat{f} \cdot \hat{f}')\left(\hat{e} \cdot \hat{f}' + \frac{\hat{e}' \cdot \hat{f}}{2}\right) - (\hat{e} \cdot \hat{e}')\left(\frac{\hat{e} \cdot \hat{f}'}{2} + \hat{e}' \cdot \hat{f}\right)\right.$	$\frac{1}{2}\left[1 + \frac{(\hat{e} \cdot \hat{e}')^2}{3} + (\hat{e} \cdot \hat{f}')(\hat{e}' \cdot \hat{f}) - \frac{2}{3}(\hat{e} \cdot \hat{e}')(\hat{f} \cdot \hat{f}')\right]$	$-\frac{1}{2}[1 - (\hat{e} \cdot \hat{e}')(\hat{f} \cdot \hat{f}') + \frac{1}{3}(\hat{e} \cdot \hat{f}')^2 + \frac{2}{3}(\hat{e} \cdot \hat{f}')(\hat{e}' \cdot \hat{f})]$
2	$\boxed{-\frac{1}{2}(\hat{e} \cdot \hat{e}')(\hat{e} \cdot \hat{f}')}$	$\frac{1}{2}(\hat{e} \cdot \hat{e}' - \hat{f} \cdot \hat{f}')(\hat{e} \cdot \hat{f}' + \hat{e}' \cdot \hat{f})$	$\boxed{\frac{1}{2}[(\hat{e} \cdot \hat{e}')^2 - (\hat{e} \cdot \hat{f}') \times (\hat{e}' \cdot \hat{f}) - 1]}$	$\boxed{\frac{1}{2}[1 - (\hat{e} \cdot \hat{e}')(\hat{f} \cdot \hat{f}') - (\hat{e} \cdot \hat{f}')^2]}$
3	$\frac{1}{3}(\hat{e} \cdot \hat{e}')(\hat{e} \cdot \hat{f}')$	$-\frac{1}{3}(\hat{e} \cdot \hat{e}' + \hat{f} \cdot \hat{f}')(\hat{e} \cdot \hat{f}' - \hat{e}' \cdot \hat{f})$	$\frac{1}{3}(\hat{e} \cdot \hat{e}') \times (\hat{e} \cdot \hat{e}' + \hat{f} \cdot \hat{f}')$	$\frac{1}{3}(\hat{e} \cdot \hat{f}')(\hat{e}' \cdot \hat{f} - \hat{e} \cdot \hat{f}')$

equilibrium, and a third which is characteristic of the rate of regression of a fluctuation. The angular dependence of the scattering is determined by the first of these factors and its amplitude by the second. The line shape given by the final factor can be observed only in high resolution experiments. Thus, the dynamical information contained within these factors is lost when one measures in place of J_{mn} its integral,

$$\int d\omega' J_{mn} = (c/4\pi)\, 1/2\pi\mathscr{T})\, \langle E_m'(t, \boldsymbol{x})\, E_n'^{*}(t, \boldsymbol{x})\rangle\, x^2 ,$$

over a range of frequencies which is considerably greater than the width of the line. The only observables associated with the scattered beam are then the elements of the "coherence matrix"[6],

$$\begin{aligned} \bar{I}_{mn} &\equiv \langle E_m'(t, \boldsymbol{x})\, E_n'^{*}(t, \boldsymbol{x})\rangle \\ &\cong [\omega^4/(4\pi)^2 c^4]\,(E^2/x^2) \sum_k [\bar{U}_k^{(\varepsilon\varepsilon)}\,(\boldsymbol{\alpha}_k^{(m)} : \boldsymbol{\alpha}_k^{(n)}) + \bar{U}_k^{(gg)}\,(\boldsymbol{\beta}_k^{(m)} : \boldsymbol{\beta}_k^{(n)}) \\ &\qquad + \bar{U}_k^{(\varepsilon g)}\,(\boldsymbol{\alpha}_k^{(m)} : \boldsymbol{\beta}_k^{(n)} - \boldsymbol{\alpha}_k^{(n)} : \boldsymbol{\beta}_k^{(m)})] , \end{aligned} \tag{25}$$

wherein

$$\bar{U}_k^{(\varepsilon\varepsilon)} = \langle \boldsymbol{\Delta\epsilon}(\boldsymbol{q})\, \boldsymbol{\Delta\epsilon}^{*}(\boldsymbol{q})\rangle_k , \quad \bar{U}_k^{(gg)} = \omega^2 \varepsilon \langle \boldsymbol{\Delta}\mathbf{g}(\boldsymbol{q})\, \boldsymbol{\Delta}\mathbf{g}^{*}(\boldsymbol{q})\rangle_k , \quad \bar{U}_k^{(\varepsilon g)} = -\, i\, \omega \sqrt{\varepsilon}\, \mathrm{Re} \langle \boldsymbol{\Delta\epsilon}(\boldsymbol{q})\, \boldsymbol{\Delta}\mathbf{g}^{*}(\boldsymbol{q})\rangle_k . \tag{26}$$

From the components of this matrix one obtains the intensity of depolarized light[6]

$$\bar{I}_{\mathrm{depol.}} = (\bar{I}_{11} + \bar{I}_{22}) - [(\bar{I}_{11} - \bar{I}_{22})^2 + 4|\bar{I}_{12}|^2]^{1/2} \tag{27}$$

and the two angles χ and ψ given by

$$\tan 2\chi = 2\,\mathrm{Re}(\bar{I}_{12})/(\bar{I}_{11} - \bar{I}_{22}) \quad \text{and} \quad \sin 2\psi = 2\,\mathrm{Im}(\bar{I}_{12})/[(\bar{I}_{11} - \bar{I}_{22}) + 4|\bar{I}_{12}|^2]^{1/2} \tag{28}$$

which measure, respectively, the rotation or tilt and the ellipticity of the polarized component of the light. (Any partially polarized beam can be decomposed into the sum of completely unpolarized and completely polarized parts.) Since the $\bar{U}_k^{(\varepsilon\varepsilon)}$ usually will be much greater than $\bar{U}_k^{(\varepsilon g)}$ or $\bar{U}_k^{(gg)}$, the gyration tensor produces a more significant effect upon the ellipticity and tilt than upon the intensity of depolarized light.

III. Discussion

According to Eq. (22) and Table 1 the scattering function

$$I = I_{11} = (4\pi)^{-2} \sum_k [U_k^{(\varepsilon\varepsilon)}\,(\boldsymbol{\alpha}_k^{(1)} : \boldsymbol{\alpha}_k^{(1)}) + U_k^{(gg)}\,(\boldsymbol{\beta}_k^{(1)} : \boldsymbol{\beta}_k^{(1)})] \tag{29}$$

can be resolved into the sum of five distinct contributions the intensities of which depend upon the nature of the target fluid, the arrangement of polarizers and analyzers, and the wavelength of the incident light. The cross correlations $U_k^{(\varepsilon g)}$ make no contributions at all to this function.

In a gas the ratios of intensities due to (scalar) fluctuations of density, given by

$$I_3^{(\varepsilon g)}/I_3^{(\varepsilon\varepsilon)} \approx [\omega \sqrt{\varepsilon}\,(\partial g/\partial \varrho)\,[\partial\varepsilon/[\partial\varrho)\,\Delta\varrho] \approx (\sqrt{\varepsilon}\,\alpha\,(\varepsilon - 1)^{-1}\,(c/\omega) \quad \text{and} \quad I_3^{(gg)}/I_3^{(\varepsilon g)} \approx [I_3^{(\varepsilon g)}/I_3^{(\varepsilon\varepsilon)}]^2$$

with $\alpha = \omega^2 g/c$, seldom will be greater than 10^{-4} and 10^{-8}, respectively. [The values just cited are appropriate to $\Delta^{1(9)}$-10-methyl-2-octalone and $\Delta^{1(9)}$-5-hydroxy-10-methyl-2-octalone for which $\alpha \doteq 5$ radians/cm for 3000 Å light and $\alpha \doteq 6.2$ radians/cm at 2800 Å[9]. In both of these cases $\varepsilon \doteq 1.3$. For the more typical secondary butyl alcohol $\varepsilon \doteq 1.96$, $\alpha \doteq 4 \times 10^{-3}$ radians/cm, and $I_\varepsilon^{(\varepsilon g)}/I_3^{(\varepsilon\varepsilon)} \approx 10^{-7}$ for the sodium D-line (5895 Å).] However, it always should be possible to distinguish between scattering contributions due to fluctuations of $\boldsymbol{\epsilon}$ and $\mathbf{g}$ by the careful selection of sample fluids and of experimental arrangement. For example, it is usual to determine the degree of depolarization by measuring the scattered intensity with polarization such that $\hat{e} \cdot \hat{e}' = 0$, that is, with a polarization to which there is no contribution from scalar fluctuations of $\boldsymbol{\epsilon}$. However, under conditions such that scalar fluctuations are very large (for example, in the vicinity of a phase transition) the major contributions to the scattering function will be $I_1^{(\varepsilon\varepsilon)} = U_1^{(\varepsilon\varepsilon)}\, \boldsymbol{\alpha}_1^{(1)} : \boldsymbol{\alpha}_1^{(1)} = \frac{1}{2}\, U_1^{(\varepsilon\varepsilon)}$, due to the traceless and symmetric part of $\boldsymbol{\Delta\epsilon}$, and $I_3^{(gg)} = U_3^{(gg)}\, \boldsymbol{\beta}_3^{(1)} : \boldsymbol{\beta}_3^{(1)} = U_3^{(gg)}\, \frac{1}{3}\,[(\hat{k} + \hat{k}') \cdot \hat{e} \wedge \hat{e}']^2$, due to the scalar part of $\boldsymbol{\Delta}\mathbf{g}$. The dependence of $I_3^{(gg)}$ upon $\hat{k}$ and $\hat{k}'$ renders it distinguishable from $I_1^{(\varepsilon\varepsilon)}$ and furthermore, $I_3^{(gg)}$ provides a non-zero contribution to the depolarization even when traceless symmetric fluctuations of $\boldsymbol{\epsilon}$ are absent.

The experimental configurations used most frequently are the vv, vh and hh arrangements shown in Figure 1. For these very special situations formula (29) reduces to

$$(4\pi)^2 I^{(\mathrm{vv})} = (\tfrac{2}{3} U_1{}^{(\varepsilon\varepsilon)} + \tfrac{1}{3} U_3{}^{(\varepsilon\varepsilon)}) + (1 - \cos\vartheta)(U_1{}^{(gg)} + U_2{}^{(gg)}),$$

$$(4\pi)^2 I^{(\mathrm{vh})} = (\tfrac{1}{2} U_1{}^{(\varepsilon\varepsilon)} \underline{+ \tfrac{1}{2} U_2{}^{(\varepsilon\varepsilon)})} + \tfrac{1}{6}(\cos^2\vartheta - 4\cos\vartheta + 7)\, U_1{}^{(gg)} + \tfrac{1}{2}\sin^2\vartheta\, U_2{}^{(gg)} + \tfrac{1}{3}(1 + \cos\vartheta)^2\, U_3{}^{(gg)}$$

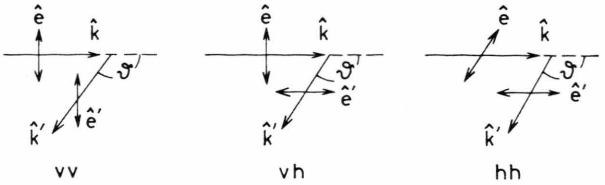
vv vh hh

Fig. 1. Three commonly used scattering arrangements. The single-headed arrows indicate directions of propagation of the incident and scattered beams. The polarization of the incident light and the orientation of the analyzer are indicated by two-headed arrows.

and

$$(4\pi)^2 I^{(\mathrm{hh})} = \tfrac{1}{6}(3 + \cos^2\vartheta)\, U_1{}^{(\varepsilon\varepsilon)} + \underline{\tfrac{1}{2}\sin^2\vartheta\, U_2{}^{(\varepsilon\varepsilon)}} + \tfrac{1}{3}\cos^2\vartheta\, U_3{}^{(\varepsilon\varepsilon)} + (1 - \cos\vartheta)\,[U_1{}^{(gg)} + U_2{}^{(gg)}]$$

where $\vartheta = \cos^{-1}(\hat{k} \cdot \hat{k}')$ is the angle of scattering. The underlined terms are identically zero because of the symmetry of the electric permeability tensor.

As a specific example we apply these formulas to the experimental arrangements with $\hat{e} \cdot \hat{e}' = 0$ which were considered in the preceeding paragraph. The vh and hh cases with $\hat{k} \cdot \hat{k}' = 0$, that is with $\vartheta = \tfrac{1}{2}\pi$, both satisfy this criterion. In the event that there are large scalar fluctuations the major contributions to the scattering functions

$$(4\pi)^2 I^{(\mathrm{vh})} = \tfrac{1}{2} U_1{}^{(\varepsilon\varepsilon)} + \tfrac{7}{6} U_1{}^{(gg)} + \tfrac{1}{2} U_2{}^{(gg)} + \tfrac{1}{3} U_3{}^{(gg)} \quad \text{and} \quad (4\pi)^2 I^{(\mathrm{hh})} = \tfrac{1}{2} U_1{}^{(\varepsilon\varepsilon)} + U_1{}^{(gg)} + U_2{}^{(gg)}$$

will be $U_1{}^{(\varepsilon\varepsilon)}$, due to the symmetric part of $\boldsymbol{\Delta\epsilon}$, and $U_3{}^{(gg)}$, due to the scalar part of $\boldsymbol{\Delta g}$. Therefore, by measuring the difference between $I^{(\mathrm{vh})}$ and $I^{(\mathrm{hh})}$ (which should be zero for an optically inactive fluid) one obtains the value of $U_3{}^{(gg)}$.

What one often measures is the total intensity of light scattered through the angle ϑ, that is, the integral of I_{ii} or of $\bar{I}_{ii}$ over all values of the final polarization $\hat{e}'$. Experiments of this sort focus attention upon the averages $\overline{\boldsymbol{\gamma}_k : \boldsymbol{\gamma}_k} \equiv (4\pi)^{-1} \int \mathrm{d}\hat{e}'\, \boldsymbol{\gamma}_k{}^{(i)} : \boldsymbol{\gamma}_k{}^{(i)} = \tfrac{1}{2}(\boldsymbol{\gamma}_k{}^{(1)} : \boldsymbol{\gamma}_k{}^{(1)} + \boldsymbol{\gamma}_k{}^{(2)} : \boldsymbol{\gamma}_k{}^{(2)})$, with $\boldsymbol{\gamma}_k = \boldsymbol{\alpha}_k$ or $\boldsymbol{\beta}_k$, given by

$$\overline{\boldsymbol{\alpha}_1 : \boldsymbol{\alpha}_1} = \tfrac{1}{12}(6 + \sin^2\phi), \qquad \overline{\boldsymbol{\beta}_1 : \boldsymbol{\beta}_1} = 1 - \cos\vartheta + \tfrac{1}{12}(1 + \cos\vartheta)^2,$$

$$\overline{\boldsymbol{\alpha}_2 : \boldsymbol{\alpha}_2} = \tfrac{1}{4}(1 + \cos^2\phi), \qquad \overline{\boldsymbol{\beta}_2 : \boldsymbol{\beta}_2} = 1 - \tfrac{1}{4}(1 + \cos\vartheta)^2,$$

$$\overline{\boldsymbol{\alpha}_3 : \boldsymbol{\alpha}_3} = \tfrac{1}{4}\sin^2\phi, \qquad \overline{\boldsymbol{\beta}_3 : \boldsymbol{\beta}_3} = \tfrac{1}{6}(1 + \cos\vartheta)^2,$$

The remarkable feature of these results is that the polarization averages of the electric permeability functions $\boldsymbol{\alpha}_k : \boldsymbol{\alpha}_k$ depend only upon the angle $\phi = \cos^{-1}(\hat{k}' \cdot \hat{e})$ whereas the averages of $\boldsymbol{\beta}_k : \boldsymbol{\beta}_k$ are functions of $\vartheta = \cos^{-1}(\hat{k}' \cdot \hat{k})$ alone. Suppose that $\phi = 0$, in which case $\boldsymbol{\alpha}_3 : \boldsymbol{\alpha}_3 = 0$ but $\boldsymbol{\beta}_3 : \boldsymbol{\beta}_3 \neq 0$. Under these circumstances the only scattering due to fluctuations of density is that associated with the gyration tensor.

Finally, let us examine the state of polarization for the special case when $\hat{e}'$ lies in the plane of $\hat{e}$ and $\hat{k}'$. The angles Θ and Φ are defined to equal $\cos^{-1}\hat{e} \cdot \hat{e}'$ and $\cos^{-1}\hat{f} \cdot \hat{f}'$, respectively. Then by neglecting all terms except those proportional to $\bar{U}_1{}^{(\varepsilon\varepsilon)}$, $\bar{U}_3{}^{(\varepsilon\varepsilon)}$ and $\bar{U}_3{}^{(gg)}$ we obtain

$$\bar{I}_{11} \cong \bar{U}_3{}^{(\varepsilon\varepsilon)}\, \tfrac{1}{3}\cos\Theta + \bar{U}_1{}^{(\varepsilon\varepsilon)}\, \tfrac{1}{6}(3 + \cos^2\Theta) + \bar{U}_3{}^{(gg)}\, \tfrac{1}{3}\sin^2\Theta \sin^2\Phi,$$

$$\bar{I}_{22} \cong \qquad + \bar{U}_1{}^{(\varepsilon\varepsilon)}\, \tfrac{1}{2} \qquad + \bar{U}_3{}^{(gg)}\, \tfrac{1}{3}(\cos\Theta + \cos\Phi)^2$$

and so conclude that the depolarization is given approximately by

$$\bar{I}_{\text{depol.}} \approx \bar{U}_1{}^{(\varepsilon\varepsilon)} + \tfrac{2}{3}\,\bar{U}_3{}^{(gg)}(\cos\Theta + \cos\Phi)^2 .$$

When the amplitude of the scalar fluctuation of $\mathbf{g}$ exceeds that associated with the symmetric part of $\boldsymbol{\epsilon}$ the depolarization will be determined solely by $\bar{U}_3{}^{(gg)}$.

For the special arrangement considered here the off-diagonal element

$$\bar{I}_{12} \approx -\,i\,\tfrac{1}{3}\,\omega\sqrt{\varepsilon}\,\mathrm{Re}(\langle \Delta\boldsymbol{\epsilon}(\mathfrak{q})\,\Delta\mathbf{g}^*(\mathfrak{q})\rangle)\cos\Theta\,(\cos\Theta + \cos\Phi)$$

is an imaginary number. Therefore, provided no absorption occurs the ellipticity of the scattered light will be proportional to $\bar{U}_3{}^{(\varepsilon g)}$ and the angle of tilt will be zero.

There are, of course, many similarities between the phenomenological theory presented here and the microscopic theories of Blum and Frisch[10] and of Atkins and Barron[11]. However, we believe that the approach adopted here has several distinct advantages among which is the straightforward way in which it leads from the electromagnetic constitutive relations to a description of the scattered light and the neat way in which it organizes the contributions to the scattering matrix into sums of terms each with a unique dependence upon correlation functions of different symmetries and each with a characteristic dependence upon the polarization and propagation vectors.

Appendix A

Constitutive Relations for an Optically Active Fluid

According to the quantum theory of optical activity first presented by Rosenfeld[7] the induced electric and magnetic moments specific to a molecule in the state "a" are given by

$$\boldsymbol{p}_a = \boldsymbol{\alpha}_a\cdot\boldsymbol{E}_{\mathrm{L}} + \boldsymbol{\gamma}_a\cdot\boldsymbol{H}_{\mathrm{L}} - \boldsymbol{\delta}_a\cdot\partial_t\boldsymbol{E}_{\mathrm{L}} - \boldsymbol{\beta}_a\cdot\partial_t\boldsymbol{H}_{\mathrm{L}}$$

and

$$\boldsymbol{m}_a = \boldsymbol{\varkappa}_a\cdot\boldsymbol{H}_{\mathrm{L}} + \boldsymbol{\gamma}_a{}^{\mathrm{T}}\cdot\boldsymbol{E}_{\mathrm{L}} - \boldsymbol{\zeta}_a\cdot\partial_t\boldsymbol{H}_{\mathrm{L}} + \boldsymbol{\beta}_a{}^{\mathrm{T}}\cdot\partial_t\boldsymbol{E}_{\mathrm{L}} \qquad (\mathrm{A}.1)$$

respectively. Here $\boldsymbol{E}_{\mathrm{L}}$ and $\boldsymbol{H}_{\mathrm{L}}$ denote the effective local fields which generally will differ from the incident field because of polarizations of the medium. The six second rank tensors which appear in these formulas depend upon molecular orientation as well as upon electronic state. They are related in the manner

$$\boldsymbol{\alpha}_a = \mathrm{Re}\,\mathbf{A}_a\,,\quad \boldsymbol{\delta}_a = \mathrm{Im}\,\mathbf{A}_a\,,\quad \boldsymbol{\varkappa}_a = \mathrm{Re}\,\mathbf{B}_a\,,\quad \boldsymbol{\zeta}_a = \mathrm{Im}\,\mathbf{B}_a\,,\quad \boldsymbol{\gamma}_a = \mathrm{Re}\,\mathbf{C}_a\,,\quad \boldsymbol{\beta}_a = \mathrm{Im}\,\mathbf{C}_a\,, \qquad (\mathrm{A}.2)$$

to the three tensors

$$\begin{aligned}
\mathbf{A}_a &= \frac{2}{\hbar}\sum_b \frac{\omega_{ba}}{\omega_{ba}^2-\omega^2}\,\langle a|\boldsymbol{\mu}_{\mathrm{e}}|b\rangle\langle b|\boldsymbol{\mu}_{\mathrm{e}}|a\rangle\,,\\
\mathbf{B}_a &= \frac{2}{\hbar}\sum_b \frac{\omega_{ba}}{\omega_{ba}^2-\omega^2}\,\langle a|\boldsymbol{\mu}_m|b\rangle\langle b|\boldsymbol{\mu}_m|a\rangle\,,\\
\mathbf{C}_a &= \frac{2}{\hbar}\sum_b \frac{1}{\omega_{ba}^2-\omega^2}\,\langle a|\boldsymbol{\mu}_{\mathrm{e}}|b\rangle\langle b|\boldsymbol{\mu}_m|a\rangle\,.
\end{aligned} \qquad (\mathrm{A}.3)$$

The symbols $\boldsymbol{\mu}_{\mathrm{e}}$ and $\boldsymbol{\mu}_m$ denote the molecular electric and magnetic dipole moment operators and $\omega_{ba} = \hbar^{-1}(E_b - E_a)$ where E_a and E_b are (adiabatic) electronic energy eigenvalues.

The polarization and magnetization vectors which occur in the connections $\boldsymbol{D} = \boldsymbol{E} + 4\pi\boldsymbol{P}$ and $\boldsymbol{B} = \boldsymbol{H} + 4\pi\boldsymbol{M}$ are given by $\boldsymbol{P} = \sum_a \int \mathrm{d}\boldsymbol{\Omega}\, n_a(\boldsymbol{\Omega})\,\boldsymbol{p}_a(\boldsymbol{\Omega})$ and $\boldsymbol{M} = \sum_a \int \mathrm{d}\boldsymbol{\Omega}\, n_a(\boldsymbol{\Omega})\,\boldsymbol{m}_a(\boldsymbol{\Omega})$ where $n_a(\boldsymbol{\Omega})$ is the local number density of molecules in electronic state "a" and with orientation $\boldsymbol{\Omega}$. For simplicity let us ignore the difference between the local and incident fields. We then obtain for $\boldsymbol{D}$ and $\boldsymbol{B}$ the constitutive relationships

$$\boldsymbol{D} = \boldsymbol{\epsilon}\cdot\boldsymbol{E} - \boldsymbol{\nu}\cdot\partial_t\boldsymbol{E} + \boldsymbol{\sigma}\cdot\boldsymbol{H} - \mathbf{g}\cdot\partial_t\boldsymbol{H}\,,\quad \boldsymbol{B} = \boldsymbol{\mu}\cdot\boldsymbol{H} - \boldsymbol{\lambda}\cdot\partial_t\boldsymbol{H} + \boldsymbol{\sigma}^{\mathrm{T}}\cdot\boldsymbol{E} + \mathbf{g}^{\mathrm{T}}\cdot\partial_t\boldsymbol{E} \qquad (\mathrm{A}.4)$$

with $\boldsymbol{\epsilon} = \boldsymbol{\delta} + \{\boldsymbol{\alpha}\}$, $\boldsymbol{\nu} = \{\boldsymbol{\delta}\}$, $\boldsymbol{\sigma} = \{\boldsymbol{\gamma}\}$, $\mathbf{g} = \{\boldsymbol{\beta}\}$, $\boldsymbol{\mu} = \boldsymbol{\delta} + \{\boldsymbol{\varkappa}\}$, $\boldsymbol{\lambda} = \{\boldsymbol{\zeta}\}$, and where the symbol $\{\boldsymbol{\theta}\}$ denotes the quantity $4\pi\sum_a \int \mathrm{d}\boldsymbol{\Omega}\, n_a(\boldsymbol{\Omega})\,\boldsymbol{\theta}_a$. (Condon[7] has shown that the terms in (A.4) involving $\boldsymbol{\sigma}$ are of little consequence in connection with optical activity.)

Now it is apparent from (A.3) that the tensor $\mathbf{A}_a$ and $\mathbf{B}_a$ of the Rosenfeld theory are Hermitean. Furthermore, these tensors will be real valued provided that the adiabatic electronic states are eigenstates of the time reversal operator, that is, provided that there is no external magnetic field.

It is well known that in the absence of external magnetic fields the complex dielectric tensor $\boldsymbol{\epsilon}'$ is symmetric and that the imaginary part of this tensor is then the coefficient of extinction or absorption[2]. However, because it neglects the possibility of absorption the Rosenfeld theory predicts that $\boldsymbol{\epsilon}'$ will be real when $\boldsymbol{H}^{\text{ext}} = 0$. On the other hand, when $\boldsymbol{H}^{\text{ext}} \neq 0$ this theory yields for the imaginary part of $\boldsymbol{\epsilon}'$ an antisymmetric tensor $\omega\boldsymbol{\nu}$ which is proportional to $e \cdot \boldsymbol{H}^{\text{ext}}$ (where e denotes the totally antisymmetric third rank isotropic tensor) and which has nothing whatsoever to do with absorption.

Let us now assume that $\boldsymbol{H}^{\text{ext}} = 0$ and neglect in (A.4) terms involving the tensors $\boldsymbol{\sigma}$ and $\mathbf{B}_a$. We then obtain the constitutive relations used in Eq. (2) of the text and are able to identify $\boldsymbol{\epsilon}$ and $\mathbf{g}$, respectively, as symmetric and asymmetric tensors.

Ailawadi, Berne and Forster[12] recently proposed that the "anomalous" splittings of the depolarized Rayleigh spectrum of certain liquids arise from fluctuations of the antisymmetric part of $\boldsymbol{\epsilon}'$ and are coupled (through the antisymmetric portion of the fluid stress tensor) to fluctuations of the molecular angular momentum density. However, in the absence of an external magnetic field $\boldsymbol{\epsilon}'$ is symmetric and so it is impossible for scattering to occur by this mechanism.

Finally, it should be noted that the constitutive equations obtained here appear to be very different from the relationships

$$\boldsymbol{D} = \boldsymbol{\epsilon} \cdot \boldsymbol{E} - (\boldsymbol{\gamma} \cdot \nabla)\,\boldsymbol{E} \quad \text{and} \quad \boldsymbol{B} = \boldsymbol{\mu} \cdot \boldsymbol{H} \tag{A.5}$$

used by Landau and Lifshitz[2]. However, in a recent paper by Bokut' and Serdyokov[13] it is shown that these can be cast into the same form provided that the $\boldsymbol{H}$ and $\boldsymbol{D}$ fields of (A.5) are suitably redefined. The advantages of the Rosenfeld relationships over those of Landau and Lifshitz include their symmetry in $\boldsymbol{D}$ and $\boldsymbol{B}$, that the Poynting vector retains its familiar form in terms of the fields, and that these fields satisfy simple and familiar boundary conditions.

Appendix B

Exact Solution of the Scattering Equation

From Eq. (5) it follows that the time Fourier transform of $\boldsymbol{D}'(t, x)$ satisfies the differential equation

$$(\Delta + k'^2)\,\boldsymbol{D}' + 2\,\alpha \operatorname{curl} \boldsymbol{D}' - \alpha^2 \boldsymbol{D}' = \boldsymbol{F} \tag{B.1}$$

with $k'^2 = \varepsilon\,\omega'^2/c^2$ and $\alpha = g\,\omega'^2/c$. To solve this equation we first perform a spatial Fourier transformation and cast Eq. (B.1) into the form

$$\boldsymbol{\Omega}(\boldsymbol{K}) \cdot \boldsymbol{D}'(\omega', \boldsymbol{K}) = \boldsymbol{F}(\omega', \boldsymbol{K}) \quad \text{with} \quad \boldsymbol{\Omega}(K) = (k'^2 - K^2 - \alpha^2)\,\boldsymbol{\delta} - 2\,i\,\alpha\,\boldsymbol{K} \cdot \boldsymbol{\epsilon} \tag{B.2}$$

and where $\boldsymbol{\epsilon}$ is the familiar totally antisymmetric third rank tensor. We now solve (B.2) for $\boldsymbol{D}'$ and invert the Fourier transform. The electric induction of the scattered field then can be written as the sum of a longitudinal field $\hat{K} D_0'$ and a transverse field $\boldsymbol{D}'^{\perp}$ which is the space Fourier transform of

$$\boldsymbol{D}'^{\perp} = \int \mathrm{d}^3K\, e^{i\,\boldsymbol{K}\cdot\boldsymbol{x}}\, M_+(K)\,(\boldsymbol{\delta} - \hat{K}\hat{K}) \cdot \boldsymbol{F}(\omega', \boldsymbol{K}) - \operatorname{curl} \int \mathrm{d}^3K\, e^{i\,\boldsymbol{K}\cdot\boldsymbol{x}}\, K^{-1}\, M_-(K)\,\boldsymbol{F}(\omega', \boldsymbol{K}) \tag{B.3}$$

with

$$2\,M_{\pm}(K) = [k'^2 - (K + \alpha)^2]^{-1} + [k'^2 - (K - \alpha)^2]^{-1}\,.$$

Next one performs the integrations indicated in (B.3). The asymptotic form of the resulting expression is

$$\begin{aligned} \boldsymbol{D}'^{\perp}(\omega', \boldsymbol{x}) \sim & -(E/4\,\pi)\,(k_+{}^3/2\,k')\,(e^{i\,k_+ x}/x)\,(\hat{x}\hat{x} - \boldsymbol{\delta} + i\,\hat{x} \cdot \boldsymbol{\epsilon}) \cdot (\boldsymbol{\pi}^+ - \boldsymbol{\Gamma}^+) \cdot \hat{e} \\ & -(E/4\,\pi)\,(k_-{}^3/2\,k')\,e^{i\,k_- x}/x)\,(\hat{x}\hat{x} - \boldsymbol{\delta} - i\,\hat{x} \cdot \boldsymbol{\epsilon}) \cdot (\boldsymbol{\pi}^- + \boldsymbol{\Gamma}^-) \cdot \hat{e} \end{aligned} \tag{B.4}$$

with

$$\boldsymbol{\pi}^{\pm} = \int_0^{\infty} \mathrm{d}t\, e^{i\,(\omega' - \omega)\,t} \{\boldsymbol{\Delta\epsilon}(t, \boldsymbol{q}_{\pm}) - i\,\omega \sqrt{\varepsilon}\,\boldsymbol{\Delta}\mathbf{g}(t, \boldsymbol{q}_{\pm}) \cdot (\boldsymbol{\epsilon} \cdot \hat{k})\}\,,$$

$$\boldsymbol{\Gamma}^{\pm} = \int_0^{\infty} \mathrm{d}t\, e^{i\,(\omega' - \omega)\,t} \{-(\omega\,\omega'/k_{\pm})\,(\varepsilon/c)\,\boldsymbol{\Delta}\mathbf{g}^{\mathrm{T}}(t, \boldsymbol{q}_{\pm})\}\,, \quad \boldsymbol{q}_{\pm} = \hat{x}\,k_{\pm} - \boldsymbol{k}\,, \quad \text{and} \quad k_{\pm} = k' + \alpha\,.$$

Finally, we neglect the differences between $k_{\pm}$ and k' except in the phase factors and conclude from (B.4) that

$$\hat{e}'(x) \cdot \boldsymbol{D}'^{\perp}(\omega', x) \sim (E/4\pi)\, k'^2 \,(e^{ik'x}/x)\{[\hat{e}'(\boldsymbol{x}) \cos \alpha x + \hat{x} \wedge \hat{e}'(\boldsymbol{x}) \sin \alpha x] \cdot \boldsymbol{\pi} \cdot \hat{e} + i[\hat{x} \wedge \hat{e}'(\boldsymbol{x}) \cos \alpha x - \hat{e}'(\boldsymbol{x}) \sin \alpha x] \cdot \boldsymbol{\Gamma} \cdot \hat{e}\}. \tag{B.5}$$

Here, $\hat{e}'(\boldsymbol{x})$ is the polarization at the point of observation, $\hat{e}'(\boldsymbol{x}) \cos \alpha x + \hat{x} \wedge \hat{e}'(\boldsymbol{x}) \sin \alpha x \equiv e'$ the polarization of $\boldsymbol{D}'^{\perp}$ in the immediate neighborhood of the scattering element, and $\hat{x} \wedge \hat{e}'(\boldsymbol{x}) \cos \alpha x - \hat{e}'(\boldsymbol{x}) \sin \alpha x$ is equal to $\hat{x} \wedge \hat{e}'$.Therefore, the final result (B.5) is identical in form to that obtained from the simplified wave Eq. (7) but with the polarization altered to account for transmission of the scattered light through the optically active medium.

Acknowledgement

One of us, JSD, gratefully acknowledges the stimulation and help he received during the early stages of this research from several discussions with Dr. Peter Gray.

---

* This research was supported in part by a grant from the National Science Foundation.

[1] M. v. Smoluchowski, Ann. Phys. Leipzig **25,** 205 [1908]; A. Einstein, Ann. Phys. Leipzig **33,** 1275 [1910].

[2] L. D. Landau and E. M. Lifshitz, Electrodynamics of Continuous Media, Pergamon Press, London 1960.

[3] I. L. Fabelinskii, Molecular Scattering of Light, Plenum Press, New York 1968.

[4] D. McIntyre and J. V. Sengers, Study of Fluids by Light Scattering in Physics of Simple Liquids (ed. H. N. V. Temperley, J. S. Rowlinson, G. S. Rushbrooke), North-Holland Publ. Co., Amsterdam 1968.

[5] S. Hess, Z. Naturforsch. **24 a,** 1675 [1969]; **24 a,** 1852 [1969]; **25 a,** 350 [1970].

[6] M. Born and E. Wolf, "Principle of Optics", 2nd edition, The MacMillan Company, New York 1964.

[7] L. Rosenfeld, Z. Physik **52,** 161 [1928]; M. Born and P. Jordan, Elementare Quantenmechanik, Springer, Berlin 1930, p. 250; E. U. Condon, Rev. Mod. Phys. **9,** 432 [1937]; J. G. Kirkwood, J. Chem. Phys. **5,** 479 [1937]; W. J. Kauzmann, J. E. Walter, and H. Eyring, Chem. Rev. **26,** 339 [1940]; A. Moscowitz, Adv. Chem. Physics **4,** 67 [1962].

[8] J. A. R. Coope and R. F. Snider, J. Math. Phys. **11,** 1003 [1970].

[9] P. Crabbe, Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry, Holden-Day, San Francisco 1965, page 205 and 211.

[10] L. Blum and H. L. Frisch, J. Chem. Phys. **52,** 4379 [1970]; **55,** 1188 [1971].

[11] P. W. Atkins and L. D. Barron, Mol. Phys. **16,** 453 [1969].

[12] N. K. Ailawadi, B. J. Berne, and D. Forster, Phys. Rev. A **3,** 1472 [1971].

[13] B. V. Bokut' and A. N. Serdyokov, J. Exp. Theor. Phys. USSR **34,** 962 [1972].