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Linear and Nonlinear Light Scattering in Colloidal Media

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A theory of the nonlinear light scattering effects producible in colloidal systems by strong laser light is proposed. Two effects are considered: (i) nonlinear scattering due to orientation of colloid particles in the optical field, and (ii) multiharmonic scattering due to nonlinear optical deformation of the particles. Investigation of (i) provides information on the sign and value of the particle's linear optical anisotropy, whereas (ii) shows its nonlinear optical properties and symmetry elements. Since present laser techniques are adequate for revealing higher order scattering effects, we have here a new method of gaining vaster knowledge of the shape and size of particles than by studying linear light scattering only.

Rayleigh (1) and Gans (2) proposed a classical theory of light scattering by colloidal particles, small with respect to the light wavelength and ellipsoidal in shape. Their and later (3) work showed that by studying the state of polarization and depolarization of light scattered by colloidal systems one can gain information on the size and shape of the particles in suspension.

This paper is aimed at giving an extension of the Rayleigh–Gans theory to the case of nonlinear scattering occasioned in colloidal systems by light of high intensity I such as is emitted by lasers. Such a theory for light scattering by molecules of gases (4) and liquids (5) has been proposed by this author earlier, showing that nonlinear scattering can be due to orientation of molecules by the electric field of the light wave, as well as to nonlinear polarization of the molecules by that field. Bersohn (6) proposed a theory of second-harmonic scattering by solutions of macromolecules. Second-harmonic scattering has been recently detected experimentally in liquids by Terhune *et al.* (7) and in gases by Maker (8) recurring to laser technique; it is more sensitive with regard to the type of molecular symmetry than linear Rayleigh scattering and thus constitutes a fine tool for structural and spectroscopical investigations (4–10).

In gases and molecular liquids, the effect of optical orientation is small; in colloidal systems, however, owing to the considerable anisotropy and size of the particles, it can be by several orders of magnitude larger, thus attaining high values. As a consequence, orientation of the particles in the electric field of a laser can cause considerable changes in the optical properties of colloids, leading to self-trapping (autocollimation) of laser beams in gold–water colloid as recently observed experimentally by Kaczmarek (11); but, moreover, such changes should lead to nonlinear light scattering easily accessible to observation by existing laser techniques. Thus laser techniques can be applied to the investigation in colloids of these new nonlinear optical effects as well as of hitherto known optical phenomena (birefringence, activity, dichroism, etc.). The advantages of a laser electric field as compared with the hitherto applied DC electric (12–15) or magnetic fields (16, 17) for producing molecular orientation are obvious, being due to the specific properties of laser light (coherence, monochromaticity, high intensity, etc.) and to the fact that it frees the measurements of

nonlinear effects from various vitiating electric processes such as electrophoresis and electro-osmosis.

The quantum–mechanical theory of harmonic scattering of light has been worked out for scattering by molecules (9) and by macromolecules (6). From the quantum viewpoint, second-harmonic scattering is a process involving three photons: two photons of incident light of frequency ω vanish by absorption as a result of interaction with matter, whereas a third photon is emitted by radiation, with double frequency 2ω, or more generally $2\omega \pm \omega_{kl}$ if the molecule makes a transition from quantum state k to l with frequency ω_{kl}. Quite generally, one can be dealing with multi-harmonic scattering in which n photons of frequency ω are incident on the molecule, which scatters a photon of frequency $n\omega$, or $n\omega \pm \omega_{kl}$ for a quantum transition of the Raman kind (9). The present paper, however, gives a classical theory of nonlinear light scattering by colloidal particles in a phenomenological–statistical approach. Phenomenologically, nonlinear scattering of light consists in the fact that the intensity I_S of scattered light is not a linear function of the intensity I of the incident light if the latter is sufficiently intense, as is the case for lasers. Thus, as will be shown later on, one can write in general

$$I_S = S_1 I + S_2 I^2 + S_3 I^3 + \cdots = \sum_{n=1}^{\infty} S_n I^n,$$

where the quantity

$$S_n = \sum_{k=1}^{n} (k\omega)^4 Q_n^{k\omega},$$

is the phenomenological constant of nth order scattering.

Above, $S_1 = \omega^4 Q_1^{\omega}$ is the constant of linear (or first-order) scattering with ground frequency ω discussed by Rayleigh and Gans for ellipsoidal colloid particles. The constant $S_2 = \omega^4 Q_2^{\omega} + (2\omega)^4 Q_2^{2\omega}$ defines nonlinear scattering of the second order and consists of a constant Q_2^{ω} describing scattering at frequency ω due to orientation of ellipsoidal particles in the optical field and of a constant $Q_2^{2\omega}$ of second-harmonic scattering due to nonlinear deformation of the particle (the latter when in a strong electric field E gains a dipole moment of the second order, i.e., a dipole moment proportional to the second power of E). Similarly, the third-order scattering constant $S_3 = \omega^4 Q_3^{\omega} + (2\omega)^4 Q_3^{2\omega} + (3\omega)^4 Q_3^{3\omega}$ consists of terms involving respectively first-harmonic scattering Q_3^{ω} due to orientation of particles as well as second- and third-harmonic scattering effects $Q_3^{2\omega}$ and $Q_3^{3\omega}$ related moreover with higher-order deformations of the particles. Each of these higher-order scattering effects is in its own way (specifically) sensitive to the shape and type of symmetry of the scattering particle as well as to the structure and thermodynamical state of the scattering medium. They can be resolved into separate contributions by investigating the scattered intensity in its dependence on the temperature, frequency, and angle of scattering.

1. NONLINEAR SCATTERING OF LIGHT DUE TO ORIENTATION OF PARTICLES IN AN OPTICAL ELECTRIC FIELD

Let us consider colloidal particles of ellipsoidal shape, having anisotropic optical properties given by the principal values n_1, n_2, n_3 of their refractive index, and immersed in an extensive isotropic medium of scalar refractive index n_0. Their linear dimensions are assumed small as compared to the wavelength λ of incident light ($2r < \lambda/\pi n$); this assumption allows us to restrict considerations to the dipolar approximation. Let us at first assume for simplicity that, under the influence of the electric field E of the light wave, the particles undergo only linear polarization, i.e., the dipole moment induced in them can be written as follows:

$$m_\sigma = A_{\sigma\tau} E_\tau . \qquad [1]$$

In the preceding equation, the tensor $A_{\sigma\tau}$ describes the linear optical polarizability of the particle; the principal values of $A_{\sigma\tau}$ are given

by the well-known formula (2, 12)

$$A_i = \frac{v(n_i^2 - n_0^2)n_0^2}{4\pi[n_0^2 + (n_i^2 - n_0^2)L_i]}, \quad [2]$$

where the L_i are shape parameters of the particle (of volume $v = 4\pi r_1 r_2 r_3/3$) given as

$$L_i = \frac{1}{2} r_1 r_2 r_3 \int_0^\infty \frac{dS}{(r_i^2 + S)[(r_1^2 + S)(r_2^2 + S)(r_3^2 + S)]^{1/2}}, \quad [3]$$

and fulfilling the condition $L_1 + L_2 + L_3 = 1$; above, r_1, r_2, r_3 are half-axes of the ellipsoid.

With the foregoing assumptions it is sufficient to consider light scattering of only the dipolar kind, described by the tensor (4)

$$I_{\sigma\tau}^S = \frac{\zeta}{c^4} \int \langle (d^2 m_\sigma/dt^2)(d^2 m_\tau/dt^2) \rangle_t \cdot f(\Omega, I)\, d\Omega, \quad [4]$$

where ζ is the number density of scattering particles, whose orientation with regard to the direction of the optical (electric) field E of the light wave (of velocity c and intensity $I = E_0^2/2$) is given by the variables Ω, and whose statistical distribution is given by the Maxwell-Boltzmann function

$$f(\Omega, I) = \frac{\exp\{-\beta u(\Omega, I)\}}{\int \exp\{-\beta u(\Omega, I)\}\, d\Omega}, \quad [5]$$

with $\beta = 1/kT$. A colloid particle, in which the electric field E induces the moment [1], and which undergoes orientation by the field, possesses the potential energy

$$u(\Omega, E) = -\tfrac{1}{2} A_{\sigma\tau} E_\sigma E_\tau . \quad [6]$$

This energy, on time-averaging over one period of oscillations of the field, becomes (4)

$$\langle u(\Omega, E) \rangle_t = u(\Omega, I) = -\tfrac{1}{2} A_{\sigma\tau} e_\sigma e_\tau I, \quad [7]$$

where e_σ is a unit vector in the direction of the electric field E_σ.

If reorientation of particles in the field E is not too strong, we can write in a good approximation (4), with regard to [5] and [7],

$$f(\Omega, I) = f(\Omega, 0)\{1 + \tfrac{1}{6}\beta(3A_{\sigma\tau} - A_{\nu\nu}\delta_{\sigma\tau})e_\sigma e_\tau I + \cdots\}, \quad [8]$$

where $f(\Omega, 0)$ is the distribution function in the absence of light-induced perturbation ($I = 0$).

On introducing [1] and [8] into the fundamental Eq. [4] and on performing an averaging procedure with equal probability over all components of the unit vector e_σ, one has

$$I_{\sigma\tau}^S = V_h^\omega \delta_{\sigma\tau} + (V_v^\omega - V_h^\omega) e_\sigma e_\tau , \quad [9]$$

where we have introduced the well-known intensity components of scattered light:

$$V_h^\omega = H_v^\omega = 3(P_1^\omega I + P_2^\omega I^2 + \cdots), \quad [10]$$

$$V_v^\omega = (Q_1^\omega + 4P_1^\omega)I + (Q_2^\omega + 8P_2^\omega)I^2 + \cdots . \quad [11]$$

Above, the quantities

$$Q_1^\omega = \frac{\zeta}{9}\left(\frac{\omega}{c}\right)^4 (A_1 + A_2 + A_3)^2, \quad [12]$$

$$P_1^\omega = \frac{\zeta}{90}\left(\frac{\omega}{c}\right)^4 \{(A_1 - A_2)^2 + (A_2 - A_3)^2 + (A_3 - A_1)^2\} \quad [13]$$

define, respectively, isotropic and anisotropic linear Rayleigh scattering, whereas the quantities

$$Q_2^\omega = \tfrac{4}{3}\beta(A_1 + A_2 + A_3)P_1^\omega, \quad [14]$$

$$P_2^\omega = \frac{\zeta\beta}{1890}\left(\frac{\omega}{c}\right)^4 \{(A_1 - A_2)^2(A_1 + A_2 - 2A_3) + (A_2 - A_3)^2(A_2 + A_3 - 2A_1) + (A_3 - A_1)^2(A_3 + A_1 - 2A_2)\} \quad [15]$$

define, respectively, the isotropic and anisotropic nonlinear changes in Rayleigh scattering induced by light of high intensity I.

In order to specify the experimental settings, we choose the incident light beam as propagating along the Y-axis of the laboratory coordinate system, with observation of scattered light taking place in the XY-plane at an angle θ to the Y-axis. The general equa-

tion [9] now yields the horizontal component of scattered intensity in the form

$$H_h^{\omega} = V_h^{\omega} + (V_v^{\omega} - V_h^{\omega}) \cos^2 \theta, \quad [16]$$

or

$$H_h^{\omega} = V_v^{\omega} \cos^2 \theta + V_h^{\omega} \sin^2 \theta. \quad [17]$$

In particular, for observation at right angles $\theta = 90°$, we have by [10], [11], and [16]

$$V_h^{\omega} = H_v^{\omega} = H_h^{\omega} \neq V_v^{\omega}, \quad [18]$$

which signifies that the reciprocity principles of Krishnan (3) are fulfilled for linear and nonlinear light scattering alike.

2. SECOND- AND THIRD-HARMONIC SCATTERING DUE TO NONLINEAR POLARIZATION OF THE PARTICLES

Above, we assumed for simplicity that the particles underwent only linear polarization, as given by equation [1], in the electric field $E = E_0 \cos \omega t$ of the incident light wave. This assumption, however, is reasonable only as long as E is not large, and cannot be maintained in the case of a field of intensity sufficiently high for producing nonlinear polarization of the particle as given by the equation (5)

$$\begin{aligned} m_\sigma = {} & A_{\sigma\tau}^{\omega} E_{0\tau} \cos \omega t + \tfrac{1}{4}(B_{\sigma\tau\nu}^{0} \\ & + B_{\sigma\tau\nu}^{2\omega} \cos 2\omega t) E_{0\tau} E_{0\nu} \\ & + \tfrac{1}{24}(3\, C_{\sigma\tau\nu\rho}^{\omega} \cos \omega t \\ & + C_{\sigma\tau\nu\rho}^{3\omega} \cos 3\omega t) E_{0\tau} E_{0\nu} E_{0\rho} \\ & + \cdots, \end{aligned} \quad [19]$$

involving the tensors $B_{\sigma\tau\nu}$, $C_{\sigma\tau\nu\rho}$ of nonlinear polarizability of the particle (second-order and third-order polarizabilities).

On considering the series expansion [19] we see that, under the influence of light of high intensity, the particle radiates not only with the ground frequency ω but moreover with higher harmonic frequencies 2ω, 3ω, and so forth. It is precisely scattering at second and third harmonic frequencies (described by the tensors $B_{\sigma\tau\nu}^{2\omega}$ and $C_{\sigma\tau\nu\rho}^{3\omega}$, respectively) that presents the most interest. In the case now under consideration, in accordance with [4] and the expansion [19], the total scattering tensor can be expressed as the sum of first-, second-, and third-harmonic (and still higher) scattering processes:

$$I_{\sigma\tau}^{S} = I_{\sigma\tau}^{\omega} + I_{\sigma\tau}^{2\omega} + I_{\sigma\tau}^{3\omega} + \cdots = \sum_{n=1}^{\infty} I_{\sigma\tau}^{n\omega}, \quad [20]$$

where, in addition to the tensor $I_{\sigma\tau}^{\omega}$ already discussed, we have the following tensor of second-harmonic scattering

$$I_{\sigma\tau}^{2\omega} = \frac{\zeta}{8}\left(\frac{2\omega}{c}\right)^4 I^2 \cdot \int B_{\sigma\nu\lambda}^{2\omega} B_{\tau\rho\mu}^{2\omega} e_\nu e_\rho e_\lambda e_\mu f(\Omega, I)\, d\Omega. \quad [21]$$

On replacing herein for simplicity the distribution function $f(\Omega, I)$ by the nonperturbated function $f(\Omega, 0)$—which means that we neglect the statistical effect of reorientation of the particles discussed previously—we obtain, after an averaging procedure, an equation analogous to [9] wherein the previous components [10] and [11] have now to be written in the form of

$$V_h^{2\omega} = H_v^{2\omega} = 3P_2^{2\omega} I^2, \quad [22]$$

$$V_v^{2\omega} = (Q_2^{2\omega} + 8P_2^{2\omega}) I^2 \quad [23]$$

involving the following constants of second-harmonic light scattering:

$$Q_2^{2\omega} = \frac{\zeta}{360} \cdot \left(\frac{2\omega}{c}\right)^4 (5B_{\alpha\beta\beta}^{2\omega} B_{\alpha\gamma\gamma}^{2\omega} - 2B_{\alpha\beta\gamma}^{2\omega} B_{\alpha\beta\gamma}^{2\omega}), \quad [24]$$

$$P_2^{2\omega} = \frac{\zeta}{2520} \cdot \left(\frac{2\omega}{c}\right)^4 (4B_{\alpha\beta\gamma}^{2\omega} B_{\alpha\beta\gamma}^{2\omega} - B_{\alpha\beta\beta}^{2\omega} B_{\alpha\gamma\gamma}^{2\omega}), \quad [25]$$

containing the tensor of second-order polarizability $B_{\alpha\beta\gamma}^{2\omega}$, which we have assumed as being totally symmetric. It is thus seen that second-harmonic scattering, too, does not affect the validity of the relations [16–18].

In order to render simpler the discussion of the constants [24] and [25], we assume that the scattering particles have spherical

geometry $L_1 = L_2 = L_3 = \frac{1}{3}$, while being optically anisotropic without a center of symmetry. In this case, the tensor $B_{\alpha\beta\gamma}$ possesses nonzero components. For example, if the symmetry is tetrahedral, there are six such components B_{123}, all equal; the constants [24] and [25] now reduce to the simple form

$$Q_2^{2\omega} = -\frac{\zeta}{30}\left(\frac{2\omega}{c}\right)^4 (B_{123}^{2\omega})^2, \qquad P_2^{2\omega} = \frac{\zeta}{105}\left(\frac{2\omega}{c}\right)^4 (B_{123}^{2\omega})^2. \tag{26}$$

For lower symmetries, the number of independent components of the tensor $B_{\alpha\beta\gamma}$ can be quite considerable. It is only for rotational ellipsoid symmetry that they reduce to two, namely B_{113} and B_{333}, in terms of which the constants [24] and [25] are expressed as follows:

$$Q_2^{2\omega} = \frac{\zeta}{3240}\left(\frac{2\omega}{c}\right)^4 \{31(B_{333}^{2\omega} + 2B_{113}^{2\omega})^2 + 4(13B_{113}^{2\omega} - B_{333}^{2\omega})(B_{333}^{2\omega} - B_{113}^{2\omega})\}, \tag{27}$$

$$P_2^{2\omega} = \frac{\zeta}{22680}\left(\frac{2\omega}{c}\right)^4 \{19(B_{333}^{2\omega} + 2B_{113}^{2\omega})^2 - 8(13B_{113}^{2\omega} - B_{333}^{2\omega})(B_{333}^{2\omega} - B_{113}^{2\omega})\}. \tag{28}$$

Third-harmonic scattering can be discussed along similar lines. But in the general case the resulting formulas are rather intricate, and we refrain from adducing them here. Since the respective tensor $C_{\sigma\tau\nu\rho}^{3\omega}$ has nonzero components $C_{1133}^{3\omega}$ and $C_{1313}^{3\omega}$ even in the case of optical isotropicity, third-harmonic scattering can be exhibited by spherical, optically centro-symmetric particles, for which we obtain the scattering tensor in the form

$$I_{\sigma\tau}^{3\omega} = V_v^{3\omega} e_\sigma e_\tau, \tag{29}$$

with

$$V_v^{3\omega} = \frac{\zeta}{144}\left(\frac{3\omega}{c}\right)^4 (C_{1133}^{3\omega} + 2C_{1313}^{3\omega})^2 I^2 = \frac{\zeta}{144}\left(\frac{3\omega}{c}\right)^4 C_{3\omega}^2 I^2, \tag{30}$$

as $2C_{1313}^{3\omega} = C_{3333}^{3\omega} - C_{1133}^{3\omega}$ with notation $C_{3333}^{3\omega} = C_{3\omega}$. On comparing the preceding result and equation [9], we see that optically isotropic particles, both linearly and nonlinearly polarizable, scatter light only isotropically since by equations [9–15] and [29] one has

$$I_{\sigma\tau}^{S} = (V_v^{\omega} + V_v^{3\omega}) e_\sigma e_\tau \tag{31}$$

where obviously for $A_1 = A_2 = A_3 = A$,

$$V_v^{\omega} = \frac{\zeta}{9}\left(\frac{\omega}{c}\right)^4 (A_1 + A_2 + A_3)^2 = \zeta\left(\frac{\omega}{c}\right)^4 A_\omega^2 I. \tag{32}$$

Consequently, whereas by investigating the linear scattering of equation [32] one can determine the linear polarizability A of an isotropic particle, investigation of the third-harmonic scattering [30] should permit to determine its third-order nonlinear polarizability C.

3. HIGHER-ORDER SCATTERING PROCESSES DUE TO STRONG ORIENTATION OF THE PARTICLES

In Section 1 of this paper, in deriving the scattering tensor [4] we made use of an approximated expansion (Eq. [8]) for the statistical distribution function. We shall now free ourselves of that restriction, valid for weak orientation of the particles, and shall perform calculations with the distribution function in the form [5] with energy given by [7]. However, to carry out calculations to the end, we shall make an additional simplification consisting in the assumption that the particles, linearly polarizable, present the symmetry of rotational ellipsoids so that the polarizability tensor can be written in the form

$$A_{\sigma\tau}^{\omega} = A_\perp^{\omega}\delta_{\sigma\tau} + (A_\parallel^{\omega} - A_\perp^{\omega}) s_\sigma s_\tau \tag{33}$$

with $A_\parallel$ and $A_\perp$ denoting respectively polarizabilities parallel and perpendicular to the symmetry axis of the particle given by the unit vector **s**.

On introducing the energy [7] together

with the polarizability in the form [33] into the distribution function [5] we obtain

$$f(\Omega, I) = \frac{\exp\{(\mathbf{s}\cdot\mathbf{e})^2 y_\omega I\}}{\int \exp\{(\mathbf{s}\cdot\mathbf{e})^2 y_\omega I\}\, d\Omega}, \quad [34]$$

where

$$y_\omega = \frac{1}{2}\beta(A_\parallel{}^\omega - A_\perp{}^\omega) = \frac{A_\parallel{}^\omega - A_\perp{}^\omega}{2kT} \quad [35]$$

denotes a parameter of orientation of the particle.

Similarly, by introducing [1] into [4] and taking into account [33], we obtain

$$I_{\sigma\tau}^S = \zeta\left(\frac{\omega}{c}\right)^4 I\int\{A_\perp{}^2 e_\sigma e_\tau + A_\perp(A_\parallel - A_\perp)(\mathbf{s}\cdot\mathbf{e})(e_\sigma s_\tau + s_\sigma e_\tau) + (A_\parallel - A_\perp)^2(\mathbf{s}\cdot\mathbf{e})^2 s_\sigma s_\tau\} f(\Omega, I)\, d\Omega. \quad [36]$$

Recurring to [34] and [36], we obtain in place of [10] the following expression:

$$V_h{}^\omega = H_v{}^\omega = 3\sum_{n=1}^{\infty} P_n{}^\omega I^n, \quad [37]$$

wherein the constant of nonlinear n-th order scattering has the form

$$P_n{}^\omega = \frac{\zeta}{45}\left(\frac{\omega}{c}\right)^4 (A_\parallel{}^\omega - A_\perp{}^\omega)^2 a_n y_\omega^{n-1}, \quad [38]$$

with expansion coefficients

$$a_n = \frac{15n}{n!(2n+1)(2n+3)} - \sum_{k=1}^{n}\frac{a_{n-k}}{k!(2k+1)}. \quad [39]$$

Likewise, we get instead of [11] the following series expansion for the vertical component:

$$V_v{}^\omega = (Q_1{}^\omega + 4P_1{}^\omega)I + \sum_{n=1}^{\infty}\{Q_{n+1}^\omega + 8S_{n+1}^\omega\} I^{n+1}, \quad [40]$$

where we have introduced the following constants of nonlinear scattering of arbitrary order:

$$Q_{n+1}^\omega = \frac{8\zeta}{135}\cdot\left(\frac{\omega}{c}\right)^4 (A_\parallel{}^\omega + 2A_\perp{}^\omega)(A_\parallel{}^\omega - A_\perp{}^\omega) a_n y_\omega{}^n, \quad [41]$$

$$S_{n+1}^\omega = \frac{2\zeta}{45}\left(\frac{\omega}{c}\right)^4 (A_\parallel{}^\omega - A_\perp{}^\omega)^2 b_n y_\omega{}^n, \quad [42]$$

with the following expansion coefficients:

$$b_n = \frac{4n^2 + n}{n!(2n+1)(2n+3)(2n+5)} - \sum_{k=1}^{n}\frac{b_{n-k}}{k!(2k+1)}. \quad [43]$$

By [38] and [42] we have

$$P_2{}^\omega = S_2{}^\omega = \frac{\zeta\beta}{945}\left(\frac{\omega}{c}\right)^4 (A_\parallel{}^\omega - A_\perp{}^\omega)^3. \quad [44]$$

One readily verifies that the formulas [10–15] derived previously become identical, in a quadratic approximation, to the general formulas [37–44] if applied to particles having the symmetry of rotational ellipsoids.

4. DEPOLARIZATION OF NONLINEARLY SCATTERED LIGHT

Using the expressions obtained in the preceding Sections for the intensity components V_v, V_h, H_v, H_h of scattered light, we can easily calculate various experimentally measured quantities, such as the Rayleigh ratio R, or the depolarization ratio (3): $D_v = H_v/V_v$, $D_h = V_h/H_h$ and $D_u = (H_v + H_h)/(V_v + V_h)$. For the case of linear scattering, the formulas giving these quantities are generally known, so that we shall not cite them here. But we shall discuss D for nonlinear scattering. We begin with second-order scattering due to orientation of the particles. Thus, by [10], [11], and [16], we get

$$D_v^{(2)} = \frac{3P_2{}^\omega}{Q_2{}^\omega + 8P_2{}^\omega}, \quad [45]$$

$$D_h^{(2)} = \frac{3P_2{}^\omega}{3P_2{}^\omega + (Q_2{}^\omega + 5P_2{}^\omega)\cos^2\theta}, \quad [46]$$

$$D_u^{(2)} = \frac{6P_2^{\omega} + (Q_2^{\omega} + 5P_2^{\omega})\cos^2\theta}{Q_2^{\omega} + 11P_2^{\omega}}, \quad [47]$$

with constants Q_2^{ω} and P_2^{ω} defined by [14] and [15] or [44]. If observation is at right angles ($\theta = 90°$), we have similarly as for linear scattering $D_h^{(2)} = 1$ whereas [47] now takes the form

$$D_u^{(2)} = \frac{6P_2^{\omega}}{Q_2^{\omega} + 11P_2^{\omega}}. \quad [48]$$

If the constants [14] and [15] are applied to the case of rotational ellipsoid symmetry, the depolarization ratios [45] and [48] reduce to

$$D_v^{(2)} = \frac{A_{\parallel} - A_{\perp}}{4(3A_{\parallel} + 4A_{\perp})}, \quad [49]$$

$$D_u^{(2)} = \frac{2(A_{\parallel} - A_{\perp})}{13A_{\parallel} + 15A_{\perp}}. \quad [50]$$

These formulas make it immediately apparent that investigation of the depolarization of second-order scattering will permit to determine directly the optical anisotropy $A_{\parallel} - A_{\perp}$ not only as to its magnitude but also as to its sign, i.e., to determine whether the particle has positive anisotropy (like the CS_2 molecule) or negative anisotropy (like C_6H_6). This is an important refinement, since investigation of depolarization of linear (that is first-order) scattering yields information regarding solely the square of the anisotropy, as is seen from the well-known formulas

$$D_v^{(1)} = \frac{3(A_{\parallel} - A_{\perp})^2}{5(A_{\parallel} + 2A_{\perp})^2 + 4(A_{\parallel} - A_{\perp})^2}, \quad [51]$$

$$D_u^{(1)} = \frac{6(A_{\parallel} - A_{\perp})^2}{5(A_{\parallel} + 2A_{\perp})^2 + 7(A_{\parallel} - A_{\perp})^2}, \quad [52]$$

which, by the way, result from [10–13] in a linear approximation. Obviously, the sign of optical anisotropy has been hitherto determined, e.g., by studying orientation of particles due to flow; however, Maxwell's constant is dependent on certain dynamical properties of the liquid which have to be known beforehand (18). Such knowledge is not demanded by formulas [49] and [50], which are thus easy to use for gaining rapid information concerning the sign of optical anisotropy of the colloid particle under investigation.

By [22] and [23], the expressions [45–48] for the depolarization ratios are still of the same mathematical form in the case of second-harmonic scattering if one replaces therein the constants Q_2^{ω} and P_2^{ω} by the constants $Q_2^{2\omega}$ and $P_2^{2\omega}$ given in the general case by the expressions [24] and [25]. In this context, it is of particular interest to consider the case of particles presenting the tetrahedral symmetry, as now formula [26] substituted into [45–47] yields the following, quite simple expressions:

$$D_v^{2\omega} = \frac{2}{3}, \qquad D_h^{2\omega} = \frac{2}{2 + \cos^2\theta} \quad [53]$$

$$D_u^{2\omega} = \tfrac{1}{5}(4 + \cos^2\theta), \quad [54]$$

which are valid for any angle θ of observation of scattered light.

For nonlinearly polarizable axially symmetric particles, we have the expressions [27] and [28], which if substituted into [45] yield:

$$D_v^{2\omega} = \frac{19(B_{333}^{2\omega} + 2B_{113}^{2\omega})^2 - 8(13B_{113}^{2\omega} - B_{333}^{2\omega})(B_{333}^{2\omega} - B_{113}^{2\omega})}{123(B_{333}^{2\omega} + 2B_{113}^{2\omega})^2 - 12(13B_{113}^{2\omega} - B_{333}^{2\omega})(B_{333}^{2\omega} - B_{113}^{2\omega})}. \quad [55]$$

On neglecting herein the anisotropy of nonlinear polarizability of the particle, one gets approximately $D_v^{2\omega} \simeq 19/123 \simeq 0.15$. For strongly nonspherical particles, formula [55] will provide information not only concerning the mean nonlinear polarizability $(B_{333} + 2B_{113})/3$, but also concerning the anisotropy of nonlinear polarizability $B_{333} - B_{113}$ and its sign.

In the general case, for arbitrary symmetry, we obtain with regard to [24], [25], and [45]:

$$D_v^{2\omega} = \frac{4B_{\alpha\beta\gamma}^{2\omega} B_{\alpha\beta\gamma}^{2\omega} - B_{\alpha\beta\beta}^{2\omega} B_{\alpha\gamma\gamma}^{2\omega}}{6B_{\alpha\beta\gamma}^{2\omega} B_{\alpha\beta\gamma}^{2\omega} + 9B_{\alpha\beta\beta}^{2\omega} B_{\alpha\gamma\gamma}^{2\omega}}. \quad [56]$$

5. APPLICATIONS AND DISCUSSION

In concluding, let us still inquire how the intensity of scattered light changes with that

of the very strong incident light wave. For the sake of simplicity, we shall approach the problem from Eq. [37], which we now write as follows:

$$V_h^{\omega} = V_h^{(1)} \sum_{n=1}^{\infty} a_n y_{\omega}^{n-1} I^{n-1}, \qquad [57]$$

where the vertical component

$$V_h^{(1)} = \frac{\zeta}{15} \left(\frac{\omega}{c}\right)^4 (A_{\parallel} - A_{\perp})^2 I, \qquad [58]$$

defines linear (first-order) scattering.

In a satisfactory approximation, we obtain by [39] and [57] the following expression for the nonlinear variation of the vertical intensity component of anisotropically scattered light:

$$\frac{\Delta V_h^{\omega}}{V_h^{(1)}} = \frac{\beta}{21} \delta I - \frac{\beta^2}{315} \delta^2 I^2 - \frac{\beta^3}{2079} \delta^3 I^3 + \cdots \qquad [59]$$

where by $\delta = A_{\parallel} - A_{\perp}$ we have denoted the optical anisotropy of the particle, and $\beta = 1/kT$.

Assuming that the linear dimensions of gold colloid particles in water amount on the average to 300 Å and using the parameters of shape (2) $L_1 = L_2 = 0.365$, $L_3 = 0.270$, we get for $\lambda = 6500$ Å:

$$A_{\parallel} = 13.78 \times 10^{-18} \text{ cm}^3,$$

$$A_{\perp} = 8.31 \times 10^{-18} \text{ cm}^3$$

On substituting the resulting value $\delta = 5.47 \times 10^{-18}$ cm^3 into the expansion [59], we have

$$\Delta V_h^{\omega}/V_h^{(1)} = 6.5 \times 10^{-6} I - 5.7 \times 10^{-11} I^2 - 12 \times 10^{-16} I^3 + \cdots .$$

For comparison, the same calculations applied to benzene yield a value of

$$\Delta V_h/V_h^{(1)} = -7.2 \times 10^{-12} I - 30 \times 10^{-24} I^2 + 137 \times 10^{-36} I^3 + \cdots .$$

We thus see that, whereas the experimental observation of higher-order scattering processes in molecular liquids requires the use of very strong light beams of intensity not less than 10^6 esu, their observation in colloids is quite easy.

It is noteworthy that the optical birefringence inducible in a colloidal system by strong light of intensity I varies by analogy to the nonlinear variation of V_h; we have indeed

$$n_{\parallel} - n_{\perp} = n_0 B I, \qquad [60]$$

where for particles having the symmetry of rotational ellipsoids (19)

$$B = B_1 \sum_{n=1}^{\infty} a_n y_{\omega}^{n-1} I^{n-1}, \qquad [61]$$

with

$$B_1 = \frac{2\pi\zeta}{15 n_0^2 kT} (A_{\parallel} - A_{\perp})^2, \qquad [62]$$

denoting the optical Kerr effect constant; its form is analogous to that of the DC Kerr effect constant K_{DC} calculated by Peterlin and Stuart (12).

Kaczmarek (11), studying experimentally the self-trapping (autocollimation) of laser beams in gold–water colloid, and recurring to Kelley's (20) formula for the critical power of the beam, obtained for the nonlinear change in refractive index $n_{\parallel} - n_0 = \frac{2}{3} n_0 B_1 I = 0.75 \times 10^{-4}$ at a flux density 1.6×10^8 W/cm of the beam, whence $B_1 = 1.2 \times 10^{-10}$ esu whereas for water measurements by Paillette (21) yielded $B_1 = 0.1 \times 10^{-12}$ esu—a value by three orders of magnitude smaller.

Denoting by $\Delta B = B - B_1$ the difference between the constant $B(I)$, dependent on higher-order optical nonlinearities, and B_1, we obtain with regard to [57] and [61] the following relation:

$$\frac{\Delta V_h^{\omega}}{V_h^{(1)}} = \frac{\Delta B}{B_1} = \sum_{n=2}^{\infty} a_n y_{\omega}^{n-1} I^{n-1}, \qquad [63]$$

between the nonlinear variation of the anisotropic scattering component and the constant of optically-induced birefringence. On the basis of the preceding numerical evalua-

tions for gold–water colloid, it should be easy to achieve optical saturation, that is total orientation of the particles, in colloids. In molecular gases and liquids it is essentially not possible to achieve optical saturation, since a laser beam of intensity larger than 10^8 esu will cause electric breakdown (11) as a result, e.g., of multiquantum photoionization. Consequently, one is inclined to consider colloid systems as quite exceptional bodies, in which strong optical nonlinearities can be induced that may find practical applications in the near future.

In addition to various previously investigated nonlinear effects due to orientation of colloid particles in electric (12–15) or magnetic (12, 16, 17) fields, these novel nonlinear optical phenomena (as nonlinear scattering of light, optically-induced birefringence, nonlinear optical activity and dichroism, etc.) will be a source of much fuller data concerning the size, shape as well as the linear and nonlinear optical anisotropies of colloid particles. Based on earlier papers (22–24), the present theory can be extended to comprise particles of arbitrary size and shape, as well as to the dependence of the studied effects on the angle of observation.

The probability of occurrence of multiphoton scattering processes (involving more than three or four photons) is exceedingly small; however, other scattering effects, of multipolar type (25), can occur as a result of strong inhomogeneity of optical fields within the space occupied by a macromolecule or colloid particle. Such multiharmonic scattering effects are expected to be easily detectable in the neighborhood of regions of resonance absorption, where the nonlinear variations of scattered light intensity and of other processes, such as dichroism, can be considerable. Obviously, in proceeding to such experiments, it would be helpful to have two or more incident light waves differing as to their frequencies, wave vectors, and intensities. The tunable parametric amplifiers now being rapidly perfected (26) and which provide for easy adaption of the emitted light to the wavelength demanded by the regions of transparency or resonance absorption of the medium under investigation would seem most appropriate for this purpose. The nonlinear optics of colloidal media thus extended may permit better insight into the finer details of the geometrical and electromagnetic structure of macromolecules and colloid particles than was hitherto possible within the restricted framework of linear optics (27).

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