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STRONG OPTICAL NONLINEARITIES IN COLLOIDAL SYSTEMS

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A theory dealing with colloidal systems and predicting optical nonlinearities of higher orders probably accounting for the recently observed strong narrowing of laser beams in gold water colloid [1] is proposed. Measurements of the optical birefringence induced in a colloid by strong laser light are suggested as a new method for simple determinations of the anisotropy, shape and nonlinear deformation of colloid particles.

Recently, when studying the propagation of light from a ruby laser in colloid solutions, Kaczmarek [1] observed at sufficiently high power a strong narrowing of the beam. His experiments revealed an important role of optical reorientation of the particles and, moreover, of their geometrical shape and size [1-3]. As shown recently by Askaryan [4], the effects of nonlinear polarizability [3], nonlinear deformation of shape and volume, as well as thermal expansion of the particles can also be of importance.

Colloidal systems acted on by laser light can exhibit strong optical nonlinearity owing to the large dimensions of the particles and their considerable optical anisotropy as given by the principle values of the refractive index n_1, n_2, n_3. The nonlinear change in optical permittivity tensor $n_{\sigma\tau}$ of the colloid can be written as the following expansion in powers of the incident light intensity I:

$$\Delta n^2_{\sigma\tau} = \sum_{l=1} \{Q_l \delta_{\sigma\tau} + B_l(3e_\sigma e_\tau - \delta_{\sigma\tau})\} I^l \qquad (1)$$

with e_σ denoting a unit vector directed as the light vector E_σ and $I = \frac{1}{2}E_0^2$. The indices σ and τ relate to the axes X, Y, Z of the laboratory reference frame and $\delta_{\sigma\tau}$ is the unit Kronecker tensor.

The coefficients Q_l define isotropic optical change in the colloid which can relate to electrostriction, or the electrocaloric effect [5], or nonlinear polarization of the particles [3,4]. Assuming their linear dimensions to be small with respect to the light wavelength ($2r < \lambda/\pi n$), we have in the dipolar approximation, in the absence of optical dispersion and absorption

$$Q_l = \frac{4\pi\rho}{3(l!)^2\, 2^l} A^{(2l+1)}, \qquad (2)$$

ρ being the number density of colloid particles, and $A^{(2l+1)}$ their mean polarizability of order $(2l+1)$ induced by the $(2l+1)$-th power of the optical field E.

The expansion coefficients B_l define the optical birefringence induced in the colloid given with regard to eq. (1) by

$$\Delta n^2_{zz} - \Delta n^2_{xx} = 3 \sum_{l=1}^{\infty} B_l I^l \qquad (3)$$

if the light propagates along the Y-axis and oscillates along the Z-axis.

For particles having the shape of rotational ellipsoids, this birefringence is mainly due to their orientation in the electric field and we obtain (on neglecting the effect of anisotropy of nonlinear polarization)

$$B_l^{\mathrm{OR}} = \tfrac{8}{3}\pi \rho c_l (A_3 - A_1)\left(\frac{A_3 - A_1}{2kT}\right)^l, \qquad (4)$$

where $c_0 = 0$ and, for $l \geq 1$

$$c_l = \frac{l}{l!(2l+1)(2l+3)} - \sum_{k=1}^{l} \frac{c_{l-k}}{k!(2k+1)}. \qquad (5)$$

The linear optical polarizabilities A_1 and A_3 of the particle are given [6,7] as

$$A_s = \frac{v(n_s^2 - n_0^2)n_0^2}{4\pi[n_0^2 + (n_s^2 - n_0^2)L_s]} \qquad (6)$$

with v denoting its volume when immersed in an isotropic medium of refractive index n_0 and L_s is a parameter accounting for its shape.

For ellipsoidal particles one obtains, instead of eq. (4),

$$B_1^{OR} = \frac{2\pi\rho}{45kT}\{(A_1 - A_2)^2 + (A_2 - A_3)^2 + (A_3 - A_1)^2\}, \quad (7)$$

$$B_2^{OR} = \frac{2\pi\rho}{945k^2T^2}\{(A_1 - A_2)^2(A_1 + A_2 - 2A_3) + (A_2 - A_3)^2(A_2 + A_3 - 2A_1) + (A_3 - A_1)^2(A_3 + A_1 - 2A_2)\}, \quad (8)$$

where the principal polarizabilities A_1, A_2, A_3 are given by eq. (6) at $s = 1, 2, 3$.

In the case of spherical optically isotropic particles the orientational effect is absent, and optical birefringence arises owing only to the effect of their nonlinear deformation, according to the formulas

$$B_1^D = \tfrac{2}{3}\pi\rho(A_{33}^{(3)} - A_{13}^{(3)}) = \tfrac{4}{9}\pi\rho A^{(3)}, \quad (9)$$

$$B_2^D = \tfrac{1}{12}\pi\rho(A_{33}^{(5)} - A_{13}^{(5)}) = \tfrac{1}{15}\pi\rho A^{(5)}, \quad (10)$$

where $A^{(3)}$ and $A^{(5)}$ are mean nonlinear polarizabilities of order 3 and 5, respectively.

The coefficient B_1^{OR} is always positive, whereas B_2^{OR} can be positive or negative according to the sign of the particle's anisotropy. Thus, for CS_2 one has $B_1^{OR} = 15.4 \times 10^{-12}$, $B_2^{OR} = 211.1 \times 10^{-24}$, whereas for $C_6H_5NO_2$ $B_1^{OR} = 6.7 \times 10^{-12}$ and $B_2^{OR} = -91.9 \times 10^{-24}$. This latter circumstance can be highly important in the self-focussing of beams propagating in liquids and colloid solutions. Nonlinearities of higher orders can be computed from eqs. (4) and (5). For molecular liquids, one obtains values (table 1) which, at light intensity $I \leq 10^8$ esu, are generally small. On the other hand, even at quite moderate light intensities, a colloidal system can exhibit strong optical nonlinearity, and in more intense fields optical saturation can be achieved. Indeed, denoting by q the ratio of volumes of a colloid particle and molecule, one obtains for the ratio of birefringence constants $B_l^{Coll}/B_l^{Molec} = q^l$. On the assumptions made above $1 \leq q < 10^6$, so that in colloids the values of B_2^{OR}, B_3^{OR}, B_4^{OR} ... increase steeply and can contribute importantly to processes involving propagation of strong laser light in such systems. As can be seen from eq. (1), after an initial steep increase - the refractive index can decrease as negative terms - B_2^{OR}, B_3^{OR}, B_4^{OR} and so forth come to play a part. Thus a laser beam propagating in a colloid solution will at first undergo strong narrowing and can subsequently exhibit divergence; as a matter of fact, this has been observed in certain cases [1,2].

We shall give a demonstration of the foregoing with regard to water containing in suspension gold particles of linear dimensions 300 Å and parameters of shape [6] $L_1 = 0.365$, $L_3 = 0.270$. For $\lambda = 6500$ Å and the preceding values, eq. (6) yields $A_1 = 8 \times 10^{-18}$ cm^3 and $A_3 = 13 \times 10^{-18}$ cm^3, whence the reorientation parameter of the particles appearing in eq. (4) takes the value $b = (A_3 - A_1)/kT = 1.25 \times 10^{-4}$.

By (4), the induced optical anisotropy of eqs. (1) and (3) is given by the series

$$B = B_1 I\left(1 + \frac{b}{21}I - \frac{b^2}{315}I^2 - \frac{b^3}{2079}I^3 + \ldots\right), \quad (11)$$

which for gold colloid becomes

$$B = B_1 I(1 + 6\times10^{-6} I - 5\times10^{-11} I^2 - 9.4\times10^{-16} I^3 + \ldots). \quad (12)$$

One sees that in the present case at laser

Table 1
Calculated values of B_l^{OR} ($l = 1, 2, 3, 4$) for liquids*

Liquid	$B_1^{OR} \times 10^{12}$	$B_2^{OR} \times 10^{24}$	$B_3^{OR} \times 10^{36}$	$B_4^{OR} \times 10^{48}$
Carbon disulphide	15.4	211.1	-1618.6	-14104.8
Chloroform	0.52	-1.5	-24.6	47.5
Benzene	3.3	-23.6	-100.4	452.0

* When applying eq. (4) to molecular liquids, one should replace A_s by the polarizabilities a_s of the isolated molecules and include the factor $[\frac{1}{3}(n+2)]^{2l}$ resulting from the local Lorentz field. Measurements by Kaczmarek [1] in gold-water colloid yielded a value of $B_1 = 1.2 \times 10^{-10}$; this is by two orders of magnitude more than in molecular liquids.

beam intensities $I \geq 10^4$ esu the terms of higher orders begin to play a part, and can no longer be omitted in considerations as it is the case for molecular liquids where nonlinearity is small (cf. table 1). The expansion of eq. (11) shows that in the case of colloidal particles having a negative reorientation parameter b the refractive index can decrease still more steeply with increasing intensity of the beam (in this case B_2^{OR} and B_3^{OR} are negative).

As known, measurements of the Kerr effect induced in colloids by the square of a DC electric field [7] are perturbed by the occurrence of yet other effects, such as the linear electrophoretic effect, and others. Now these effects can be totally eliminated if, instead of a DC electric field, a strong laser beam inducing optical birefringence in the colloid in accordance with eq. (3) is used. Hence this optical Kerr effect can provide an effective and at the same time rather simple method of determining the anisotropy and shape of colloidal particles. Laser technique investigations of these and other nonlinear optical processes in colloids (thus, of nonlinear scattering, nonlinear optical activity, absorption and dispersion) seem very promising, and are accordingly continuing in the Laboratories of this Department. The tunable parametric amplifiers now being rapidly perfected [8] and which provide for easy adaption of the emitted laser light to the wavelength demanded by the regions of transparency or resonance absorption of the colloidal medium under investigation would seem most appropriate for this purpose.

References

[1] F. Kaczmarek, Acta Phys. Polonica 32 (1967) 1003.
[2] S. A. Akhmanov, A. P. Sukhorukov and R. V. Khokhlov, Uspekhi Fiz. Nauk 93 (1967) 19, and references therein;
Y. R. Shen and Y. J. Shaham, Phys. Rev. 163 (1967) 224.
[3] S. Kielich, Acta Phys. Polonica 30 (1966) 683; Proc. Phys. Soc. 90 (1967) 847, and references therein.
[4] G. A. Askaryan, Zh. Eksperim. i Teor. Fiz., Pisma v Redakt. 6 (1967) 672.
[5] Y. R. Shen, Phys. Letters 20 (1966) 378;
S. Kielich, Phys. Letters 24A (1967) 383; J. Chem. Phys. 46 (1967) 4090.
[6] R. Gans, Ann. Physik 37 (1912) 881.
[7] A. Petrlin and H. A. Stuart, Z. f. Physik 112 (1939) 129.
[8] R. L. Garman, J. Hanus and D. L. Weinberg, Appl. Phys. Letters 11 (1967) 250; and other papers.