NONLINEAR CHANGES IN RAYLEIGH LIGHT SCATTERING DUE TO ELECTRIC AND MAGNETIC FIELDS

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Nonlinear changes in elastic light scattering due to reorientation and saturation of reorientation of asymmetric microsystems in an electric, magnetic or optical laser field are discussed. A new, direct method of determining the sign and value of the electric, magnetic and optical anisotropies of asymmetric macromolecules as well as their shape from measurements of these nonlinear changes is proposed.

We consider (immersed in an optically isotropic medium) noninteracting asymmetric microsystems (molecules, macromolecules, colloid particles) of linear dimensions not exceeding the incident light wavelength and sufficiently rigid to present only linear polarizabilities $a_\parallel$ and $a_\perp$ parallel and perpendicular to the symmetry axis respectively. We define the optical anisotropy of a microsystem by the Langevin parameter [1] $\kappa = (a_\parallel - a_\perp)/(a_\parallel + 2a_\perp)$. The scattered light is considered in the dipolar approximation, observed perpendicularly to the incident beam (vertical and horizontal polarisations — lower indices v and h), and is described quantitatively by the usual vertically and horizontally oscillating components [2] V_v, V_h and H_v, H_h.

When the scattering system is acted upon by an externally applied dc electric field E, Langevin reorientation of the microsystems [1] will cause changes in the scattered intensity, the components V_v^E, V_h^E, H_v^E, H_h^E now becoming functions of E. Hitherto, measurements on solutions of polymers [3-5] concerned only variations in the vertical component V_v^E, which were found to be isotropic and functions of E^2. Here, we shall deal with the anisotropic variation in V_v^E as well as with changes in the other anisotropic components V_h^E, H_v^E, H_h^E of the scattered intensity. Our calculations concern weak fields as well as electric fields strong enough to cause complete alignment ("electric saturation of orientation") of the microsystems. We adduce the results for relative changes $\delta V_\mathrm{v}^\mathrm{E} = (V_\mathrm{v}^\mathrm{E} - V_\mathrm{v})/V_\mathrm{v}$, ... of all the components

$$\delta V_\mathrm{v}^\mathrm{E}(5+4\kappa^2) = 10\kappa\{3L_2(p, \pm q) - 1\} + \kappa^2\{1 - 30L_2(p, \pm q) + 45L_4(p, \pm q)\}\,, \tag{1}$$

$$\delta V_\mathrm{h}^\mathrm{E} = \delta H_\mathrm{v}^\mathrm{E} = -1 + (15/2)L_2(p, \pm q) - (15/2)L_4(p, \pm q)\,, \tag{2}$$

$$\delta H_\mathrm{h}^\mathrm{E} = (7/8) - (15/4)L_2(p, \pm q) + (15/8)L_4(p, \pm q)\,, \tag{3}$$

as functions of the parameters

$$p = \frac{\mu E}{kT}\,, \qquad q = \frac{|\alpha_\parallel - \alpha_\perp|}{2kT}E^2 \tag{4}$$

of reorientation of permanent electric dipoles μ and dipoles induced at electric polarizability anisotropy $|\alpha_\parallel - \alpha_\perp|$. The "plus" sign at q in eqs. (1)-(3) is for cigar-like microsystems with positive electric anisotropy ($\alpha_\parallel > \alpha_\perp$), whereas "minus" is for disc-like ones with negative anisotropy ($\alpha_\parallel < \alpha_\perp$).

The scattering components (1)-(3) involve generalized Langevin functions [1] which, for $q \neq 0$ and arbitrary p, have the form [6]

$$L_2(p, \pm q) = \frac{p^2 \mp 2q}{4q^2} \pm \frac{\mathrm{e}^p + \mathrm{e}^{-p}}{4q^{1/2}I(p, \pm q)} - \frac{p(\mathrm{e}^p - \mathrm{e}^{-p})}{8q^{3/2}I(p, \pm q)}\,, \tag{5}$$

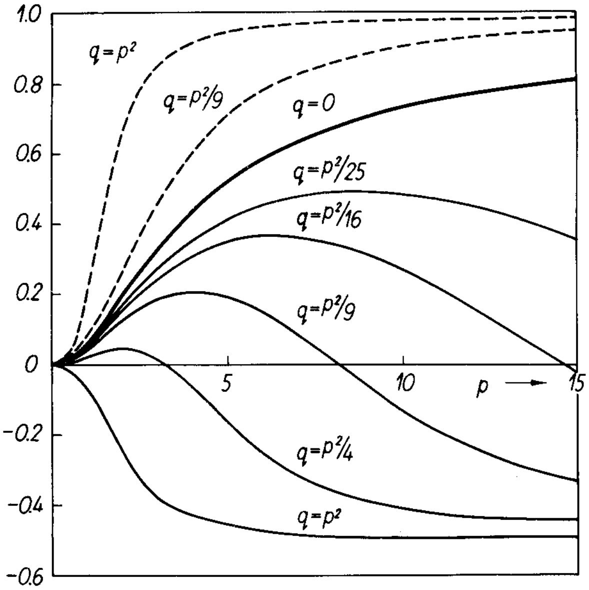

Fig. 1. Variation $\delta V_{\mathrm{v}}^{\mathrm{E}}/4\kappa$ versus the permanent dipole reorientation parameter p. Superposition of induced dipole reorientation (parameter q) enhances the effect in the case of positive anisotropy (dashed curves), but lowers it (with sign reversal) in that of negative anisotropy (continuous curves below the curve for q = 0) .

$$L_4(p, \pm q) = \frac{p^4 + 12q(q, \mp p^2)}{16\,q^4} \pm$$

$$\pm \frac{(p^2 \mp 6\,q + 4\,q^2)(\mathrm{e}^{p} + \mathrm{e}^{-p})}{16\,q^{5/2}\,I(p, \pm q)} -$$

$$- \frac{p(p^2 + 4q^2 \mp 10q)(\mathrm{e}^{p} - \mathrm{e}^{-p})}{32q^{7/2}\,I(p, \pm q)}\,, \qquad (6)$$

involving the numerically tabulated integrals [7, 8]

$$I(p, \pm q) = \frac{1}{2}\exp\left[\mp\left(\frac{p^2}{4q} + q\right)\right] \times$$

$$\times \int_{-\sqrt{q} \pm (p/2\sqrt{q})}^{\sqrt{q} \pm (p/2\sqrt{q})} \exp[\pm t^2]\,\mathrm{d}t\,. \qquad (7)$$

In the case of cigar-like microsystems, the permanent and induced dipoles tend concordantly to orient themselves along E, so that the variations (1)-(3) increase with growing E and increasing ratios q/p^2 (cf. figs. 1-3). Inversely,

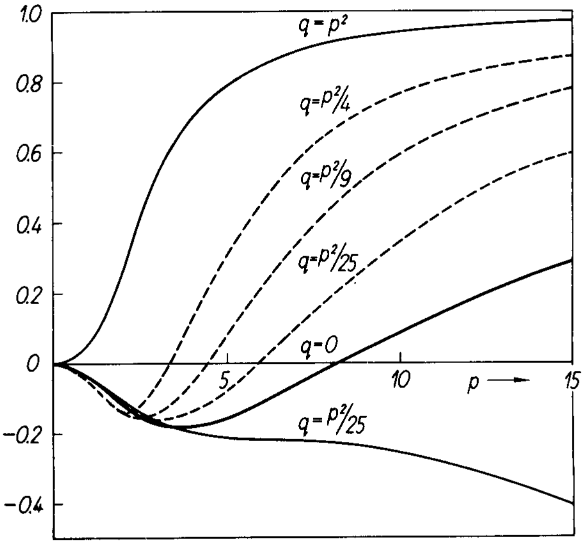

Fig. 2. The cross component variations - $\delta V_{\mathrm{h}}^{\mathrm{E}}$ and - $\delta H_{\mathrm{v}}^{\mathrm{E}}$ increase with growing ratio q/p^2 in the case of positive anisotropy (dashed curves), but exhibit sign reversal in that of negative.

the field E acts on disc-like microsystems with two mutually orthogonal torques simultaneously, since with μ lying along the symmetry axis we have $\alpha_{\perp} > \alpha_{\parallel}$ and a rise in E increases the induced dipole, so that the microsystem changes its orientation from parallel to perpendicular; as a result of this reorientation in the field E, and at a well-defined value of q/p^2, the variations (1)-(3) undergo a reversal of sign (cf. figs. 1-3). The various shapes of the curves 1-3 permit conclusions as to the shape and anisotropies of the microsystem.

At weak reorientation ($p \ll 1$, $q \ll 1$), the following relations hold between the variations (1)-(3) (in eq. (1), small terms in κ^2 will be omitted)

$$\frac{15}{4\kappa}\delta V_{\mathrm{v}}^{\mathrm{E}} = 21\,\delta H_{\mathrm{v}}^{\mathrm{E}} = 21\,\delta H_{\mathrm{h}}^{\mathrm{E}} = -\frac{21}{2}\,\delta H_{\mathrm{h}}^{\mathrm{E}} = p^2 \pm 2q\,, \qquad (8)$$

which, in accordance with (4), now vary quadratically with E.

At electric saturation ($p \to \infty$, $q \to \infty$), the Langevin functions (5) and (6) tend to unity for positive anisotropy, and the intensity variations (1)-(3) take the limiting values [9]

$$\delta V_{\mathrm{v}}^{\mathrm{S}} = 4\kappa, \qquad \delta V_{\mathrm{h}}^{\mathrm{S}} = \delta H_{\mathrm{v}}^{\mathrm{S}} = \delta H_{\mathrm{h}}^{\mathrm{S}} = -1\,, \qquad (9)$$

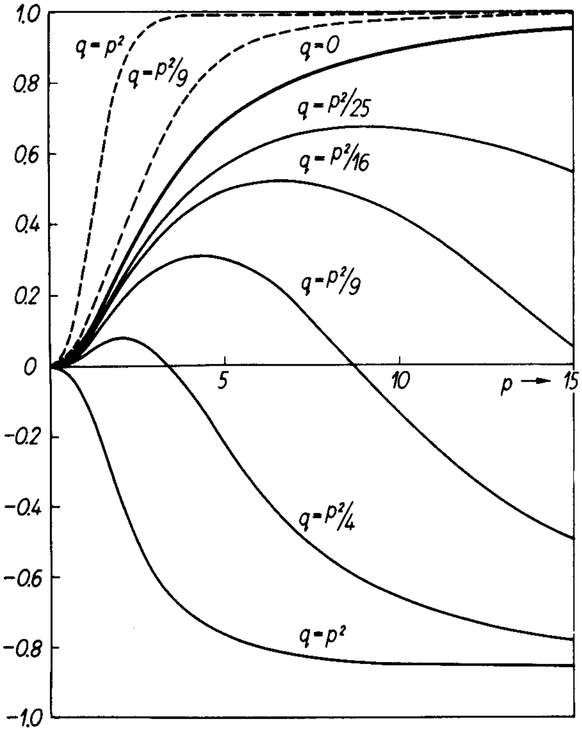

Fig. 3. In the case of positive anisotropy, the variation in horizontal component $-\delta H_{\mathrm{h}}^{\mathrm{E}}$ increases with growing q (dashed curves). In that of negative anisotropy $-\delta H_{\mathrm{h}}^{\mathrm{E}}$ decreases and exhibits reversal of sign with growing q/p^2 (continuous curves).

a result derived independently by Stoylov [10] for needle-like colloid particles.

At complete alignment (oriental saturation) of negatively-anisotropic microsystems, the Langevin functions (5) and (6) tend zero, and the variations (1)-(3) become:

$$\delta V_{\mathrm{v}}^{\mathrm{S}} = -2\kappa, \quad \delta V_{\mathrm{h}}^{\mathrm{S}} = \delta H_{\mathrm{v}}^{\mathrm{S}} = -1, \quad \delta H_{\mathrm{h}}^{\mathrm{S}} = 7/8. \tag{10}$$

Obviously, the results (9) and (10) remain valid in the case of optical saturation [9] (complete alignment caused by the electric field of intense laser light). At incomplete saturation, in the optical case, one has to put $p = 0$ in eqs. (1)-(7) because the permanent electric dipole is not subject to optical orientation (obviously, in the parameter q, one has to replace E^2 by the laser beam intensity I_{L}).

The expressions (9) and (10) show that investigations of electric or optical saturation of the vertical component $\delta V_{\mathrm{v}}^{\mathrm{S}}$ permit determinations of the value of the optical anisotropy κ to be made, whereas studies of the change in horizontal component $\delta H_{\mathrm{h}}^{\mathrm{S}}$ decide the sign of the anisotropy of polarizability since $\delta H_{\mathrm{h}}^{\mathrm{S}}$ is always negative for cigar-shaped microsystems but positive for disc-like ones.

The changes in cross components (2) provide direct information as to the sign and value of the electric anisotropy in the case of weak reorientation, when by (4) and (8) we have for non-dipolar microsystems:

$$\delta V_{\mathrm{h}}^{\mathrm{E}} = \delta H_{\mathrm{v}}^{\mathrm{E}} = \pm \frac{|\alpha_{\parallel} - \alpha_{\perp}|}{21kT} E^2 . \tag{11}$$

If laser light of intensity I_{L} is used in reorienting the microsystems, eq. (11) is still applicable to dipolar substances (with I_{L} instead of E^2). As yet, experiments [11] with strong laser beams have failed to detect univocally, variations in the components of eq. (11) in molecular liquids.

At best, in molecular liquids, $p = 10^{-3} E$ and $q = 10^{-8} E^2$, rendering electric and optical saturation practically inachievable, since dielectric or optical [11] break-down already occurs at at values of $p \geq 1$ or $q \geq 1$.

In polypeptide solutions [7, 8] $p = 0.1\,E$, $q = 10^{-4} E^2$, and in collagen solutions [6] $p = 0.4\,E$, $q = 0.04\,E^2$. Here, consequently, electric saturation begins at as little as $E = 10$ esu and complete electric saturation can be achieved in slightly stronger fields. Clearly, in such macromolecular and colloid solutions, optical saturation can be obtained with strong continuously operating lasers or pulse lasers with a pulse duration sufficiently long for reorientation to follow.

The present theory of nonlinear scattering is automatically applicable to cases when the agent causing reorientation is not E but a magnetic field H [12]. E.g., in colloid solutions of cadmium ferrite [13] $p_{\mathrm{m}} = 10^{-2} H$, $q_{\mathrm{m}} = 10^{-6} H^2$ and magnetic saturation takes place at field strengths $H \geq 10^3$ Oe.

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