Nonlinear Coupling between the Mean Polarizability $\bar{\gamma}$ of Molecules and the Local-Field Anisotropy in a Liquid Crystal and Change of the "$\bar{\gamma}$ = const" Paradigm

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Received January 29, 2008

The nonlinear relation between the mean effective polarizability $\bar{\gamma}$ of molecules and the local-field anisotropy in uniaxial liquid crystals is demonstrated. Stringent constraints on $\bar{\gamma}$ from below, indicative of the dependence of $\bar{\gamma}$ on the liquid-crystal state and the change of the "$\bar{\gamma}$ = const" paradigm, are established. The theoretical results are confirmed by experiments with nematic liquid crystals having high and low birefringences.

1. The effective-polarizability tensor γ, which can be determined from refractometric data with correct allowance for the local field of an optical wave, is an important molecular parameter containing information on the polarization, electronic structure, and conformation of a molecule in a condensed medium and the intermolecular interaction. The information on γ is especially important for liquid crystals as a general model of anisotropic statistically ordered molecular media. However, allowance for the anisotropy of the local-field tensor with components $f_j = 1 + L_j(\varepsilon_j - 1)$ for optical waves polarized along ($j = \parallel$) and across ($j = \perp$) the director **n**, where $\varepsilon_j = n_j^2$, n_j are the refractive indices of the liquid crystal, and L_j are the components of the Lorentz tensor, complicates obtaining such information. Owing to the absence of known constraints on the tensor γ in condensed media, the equality

$$\bar{\gamma}_i = \bar{\gamma} = \text{const} \qquad (1)$$

of the mean polarizabilities of the molecules in the isotropic phase ($\bar{\gamma}_i$) and the liquid crystal ($\bar{\gamma}$) was widely used. Since its first introduction [1], formula (1) became the paradigm for a large number of works in molecular optics and liquid-crystal physics. Although some theoretical and experimental studies are indicative of the violation of Eq. (1) due to intermolecular interaction or variations in the conformation or electronic structure of liquid crystal molecules [2, 3], the "$\bar{\gamma}$ = const" paradigm can only be changed if stringent and verifiable constraints are imposed on $\bar{\gamma}$ or $\bar{\gamma}/\bar{\gamma}_i$ for any specific object. A hierarchy of such constraints,

$\bar{\gamma}/\bar{\gamma}_i > \kappa_3 > \kappa_2 > \kappa_1$, where the parameters $\kappa_m(n_i, n_j, \rho_i, \rho)$ depend on the refractive indices and densities of the liquid-crystal and isotropic phase, is pointed out in this paper. These constrains indicate the dependence of $\bar{\gamma}$ on the phase state of the liquid crystal and temperature within the mesophase and exist due to the nonlinear relation between $\bar{\gamma}$ and anisotropy of the tensors f and L in liquid crystals. Until recently, the relation between the dependence $\bar{\gamma}_i(\rho_i)$ and the form of the tensor f_i was known only for isotropic liquid and solid media [4].

2. The proposed approach consists in finding nonphysical consequences of approximation (1) within the framework of refractometry as the simplest and most direct technique involving $\bar{\gamma}$. The criteria of eliminating such consequences will give the desired constraints for $\bar{\gamma}$.

Relation (1) underlies a method [5] for the determination of the components L_j in uniaxial liquid crystals from refractometry data. However, within the framework of this method, the sign of anisotropy, $\Delta f = (f_{\parallel} - f_{\perp}) > 0$, in the visible and IR ranges contradicts experiment [2, 3], the L_j values for individual objects do not correspond to the actual anisotropy of the pair correlation function of liquid-crystal molecules [3], and the temperature dependences $L_j(T)$ for some liquid crystals are nonphysically nonmonotonic [6]. Our goal is to find a formula relating $\bar{\gamma}$ with Δf and $L_j(T)$, clarify the reasons of these nonphysical consequences of Eq. (1), and impose constraints on $\bar{\gamma}$ eliminating these consequences.

Consider a uniaxial liquid crystal with the number density N of uniaxial rod-like molecules with the polarizability components $\gamma_{l,\,t}$, anisotropy $\Delta\gamma = \gamma_l - \gamma_t$, and orientation order parameter S. The components ε_j are related to the quantities $\bar{\gamma} = (\gamma_l + 2\gamma_t)/3$ and $q = S\Delta\gamma/3\bar{\gamma}$ according to the formula [2]

$$(\varepsilon_j - 1)/f_j = 4\pi N \bar{\gamma}(1 + a_j q)$$
$$(a_\parallel = 2,\ a_\perp = -1).$$
(2)

Since $q = 0$, $L_i = 1/3$, and $3(\varepsilon_i - 1)/(\varepsilon_i + 2) = 4\pi N_i \bar{\gamma}_i$ for an isotropic phase, Eq. (1) in view of the relation $\mathrm{Tr}L = 1$ yields the Saupe–Maier–Neugebauer equation for $L_\perp$ [5]

$$\frac{3(\varepsilon_i - 1)}{\rho_i(\varepsilon_i + 2)}$$
$$= \frac{1}{3\rho}\left[\frac{\varepsilon_\parallel - 1}{1 + (1 - 2L_\perp)(\varepsilon_\parallel - 1)} + \frac{2(\varepsilon_\perp - 1)}{1 + L_\perp(\varepsilon_\perp - 1)}\right].$$
(3)

The anomalous solutions of this equation appear due to unknown reasons conventionally related to uncertainties of measuring $n_{i,\,j}$, ρ_i, and ρ [7]. Let us obtain an equation for Δf, which contains the parameter $A = \bar{\gamma}_i/\bar{\gamma}$ by reducing the exact Lorenz–Lorentz equation for liquid crystals [2, 3] to the form

$$(Ar - r_0)(3 + Q)(\bar{\varepsilon} + 2) = 2\Delta f[Q + q(3 + Q)],\quad (4)$$

where $\bar{\varepsilon} = (\varepsilon_\parallel + 2\varepsilon_\perp)/3$, $Q = (\varepsilon_\parallel - \varepsilon_\perp)/(\bar{\varepsilon} - 1)$, $r = C/C_i$,

$$C = \frac{\bar{\varepsilon} - 1}{\rho(\bar{\varepsilon} + 2)},\quad C_i = \frac{\varepsilon_i - 1}{\rho_i(\varepsilon_i + 2)},$$
$$r_0 = 1 - \frac{2Q^2(\bar{\varepsilon} - 1)}{3(3 + Q)(\bar{\varepsilon} + 2)}.$$
(5)

Equation (2) gives the relation $q(\Delta f)$

$$q = \frac{Q(3 + Q)(\bar{\varepsilon} + 2)r_0 - \Delta f(3 - Q)(3 + 2Q)}{3(3 + Q)(\bar{\varepsilon} + 2)r_0 + \Delta f(3 - Q)(3 + 2Q)}.$$
(6)

Substitution of Eq. (6) into Eq. (4) yields the desired equation for Δf:

$$(\Delta f)^2 - \Delta f \frac{(3 + Q)(\bar{\varepsilon} + 2)}{6}[(b_1 b_2)^{1/2} - b]$$
$$+ br_0 \frac{(3 + Q)^2(\bar{\varepsilon} + 2)^2}{2(3 - Q)(3 + 2Q)} = 0,$$
(7)

where

$$b = Ar - r_0,\quad b_1 = \frac{2r_0 Q^2}{(3 - Q)(3 + 2Q)},$$
$$b_2 = b_1[(6 + Q)/Q]^2.$$
(8)

The physically meaningful solution of Eq. (7) obeys the condition $q \geq 0$ and has the form

$$\Delta f = \frac{1}{12}(3 + Q)(\bar{\varepsilon} + 2)$$
$$\times [(b_1 b_2)^{1/2} - b - [(b_1 - b)(b_2 - b)]^{1/2}].$$
(9)

The values of Δf are real for $b_1 \geq b$, while the values $q > 0$ correspond to the condition $r_1 > Ar$, where

$$r_1 = 1 + \frac{6Q^2}{(\bar{\varepsilon} + 2)(3 - Q)(3 + 2Q)}.$$
(10)

This gives the desired first-level constraint

$$\bar{\gamma}/\bar{\gamma}_i > r/r_1.$$
(11)

The more stringent constraint on $\bar{\gamma}/\bar{\gamma}_i$ corresponds to the requirement $L_\perp > 1/3$. This requirement appears because the surface $g_2(\mathbf{R}) = \mathrm{const}$ for the pair correlation function $g_2(\mathbf{R})$ in calamite nematics at mesoscopic scales $R_m < R < R_M$, where R_m and R_M are the molecular and macroscopic scales, respectively, is a spheroid elongated along the director $\mathbf{n}$ [3]. Since $\Delta f = (L_{\perp k} - L_\perp)(\bar{\varepsilon} - 1)(3 + Q)$ and $L_{\perp k} = (1/3)[1 + Q/(3 + Q)]$, it follows from Eq. (9) that

$$L_\perp = L_{\perp k} - \frac{(\bar{\varepsilon} + 2)}{12(\bar{\varepsilon} - 1)}$$
$$\times [(b_1 b_2)^{1/2} - b - [(b_1 - b)(b_2 - b)]^{1/2}].$$
(12)

The requirement $L_\perp > 1/3$ is equivalent to $r_2 > Ar$, where

$$r_2 = 1 + \frac{6Q^2(\bar{\varepsilon} - 1)}{(\bar{\varepsilon} + 2)[(3 - Q)(3 + 2Q)(\bar{\varepsilon} - 1) + 27]}.$$
(13)

This gives the second-level constraint

$$\bar{\gamma}/\bar{\gamma}_i > r/r_2.$$
(14)

The measured values of $L_\perp$ for calamite liquid crystals with high and moderate birefringence $\Delta n = n_\parallel - n_\perp$ in the visible and IR ranges obey the inequalities $L_\perp > L_{\perp k}$ and $\Delta f < 0$ [2, 3] corresponding to $b < 0$ and the third-level constraint

$$\bar{\gamma}/\bar{\gamma}_i > r/r_0.$$
(15)

The experimental values $\Delta f > 0$ in the visible and IR ranges for nematics with anomalously small Δn values and the inversion of the sign of Δf [8] correspond to the constraints

$$r/r_0 > \bar{\gamma}/\bar{\gamma}_i > r/r_2.$$
(16)

The inequalities $r_1 > r_2 > 1 > r_0$ determine the following hierarchy of the constraints:

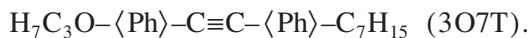$$\bar{\gamma}/\bar{\gamma}_i > r/r_0 > r/r_2 > r/r_1,$$
(17)

which depend only on the refractive indices and densities of the liquid crystal and isotropic phase.
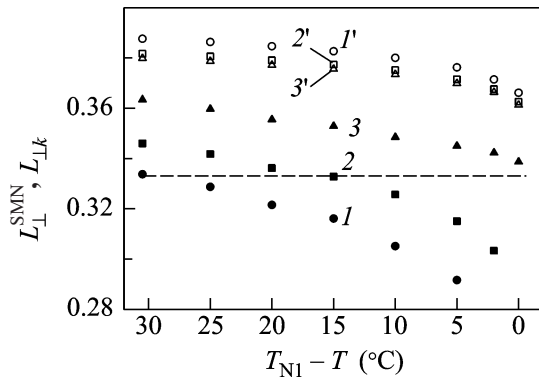
Temperature dependences of $L_\perp^{SMN}$ (*1–3*) and $L_{\perp k}$ (*1'–3'*) in the 3O7T nematic phase calculated by Eq. (12) for $A = 1$ and r_0/r ($b = 0$), respectively, for $\lambda = $ (*1, 1'*) 436, (*2, 2'*) 546, and (*3, 3'*) 644 nm. The dashed line corresponds to $L_\perp = 1/3$.

Note that the dependence $C_i \sim \bar\gamma_i$ is linear for the liquid-crystal isotropic phase, so that the experimental relation $C_i \approx$ const [1–4] corresponds to nonvarying $\bar\gamma_i$. The dependence of Δf (see Eq. (9)) on $b(\bar\gamma)$ for liquid crystals is nonlinear, so that a small variation in b due to varying A (i.e., $\bar\gamma$) and/or C drastically changes Δf. Since Q is small, $Q \ll 3$, and the parameters r_0, r_1, and r_2 are close to unity, the dependence $\Delta f(\bar\gamma)$ becomes even stronger, because r is close to unity according to the experiments [2, 3, 9, 10]. Expression (12) is the solution of equation (3) for $A = 1$. Approximation (1) violates constraint (11) and gives rise to complex-valued solutions of Eqs. (3) and (7) for liquid crystals with $r > r_1$. If $r_1 > r > r_0$, then Eq. (3) has a solution $L_\perp^{SMN} < L_{\perp k}$ for which the dependence $L_\perp^{SMN}(T)$ has a minimum [6]. This minimum is due to the difference $b = r - r_0$ between the almost linear function $r(T)$ [11] and the convex function $r_0(T)$ (see Eq. (5)). The approximation $\bar\gamma/\bar\gamma_i = r$ [10] or $Ar = 1$ corresponds to $b > 0$, $\Delta f > 0$, and constraints (16) for any molecule, Δn value, and wavelength range, which contradicts the experiment [2, 3].

3. The above results were verified for the nematics

$$[H_{2n+1}C_n\!-\!\langle CH\rangle\!-\!COOH]_2 \quad (CHCA),$$

$$H_{11}C_5\!-\!\langle BCO\rangle\!-\!\langle Ph\rangle\!-\!C\!\equiv\!N \quad (5BCO),$$

$$H_7C_3O\!-\!\langle Ph\rangle\!-\!C\!\equiv\!C\!-\!\langle Ph\rangle\!-\!C_7H_{15} \quad (3O7T).$$

Here, $\langle CH\rangle$, $\langle BCO\rangle$, and $\langle Ph\rangle$ are the cyclohexane, bicyclooctane, and phenylic rings. The mixture of CHCA homologues ($T_{NI} = 92°C$ [8, 11]) has the extremely small Δn value, while the nematics 5BCO (101°C [11, 12]) and 3O7T (65°C [13, 14]) have the moderate and high Δn values. Here, T_{NI} is the temperature of the "nematic–isotropic liquid" transition. The temperature

dependences of the densities ρ_i and ρ and the refractive indices $n_{i,j}(\lambda)$ for various optical wavelengths λ are tabulated in the above-cited papers.

The values of ρ_i, ρ, and $n_{i,j}$ at $\lambda = 589$ nm [8, 11] for CHCA in the entire mesophase range $\Delta T = T_{NI} - T = 70°$ yield $r/r_1 > 1$ and complex-valued solutions of Eq. (3). This means a violation of Eq. (1) and the inequality $\bar\gamma/\bar\gamma_i > 1$, which follows from Eq. (11). The experimental values of $L_\perp > 1/3$ obtained independently for CHCA in [8] from the dichroism of the electron absorption band of an impurity probe molecule ($\lambda_{max} = 336$ nm) yield $(\bar\gamma/\bar\gamma_i)_{exp} = \Gamma/3C_i$ for $\lambda = 589$ nm (Γ is the right-hand side of Eq. (3)). This corresponds to Eq. (16) expected for the liquid crystal under consideration with the inversion of the sign of Δf. The quantity $(\bar\gamma/\bar\gamma_i)_{exp}$ ranges from 1.004 to 1.006 in the nematic-phase interval, which shows that Δf is highly sensitive to the value of $\bar\gamma$.

The values of ρ_i, ρ [11], and $n_{i,j}$ ($\lambda = 589$ nm) [11, 12] for 5BCO yield $1 > r > r_0$. Equation (3) has solutions $L_\perp^{SMN} < L_{\perp k}$ and $\Delta f_{SMN} > 0$ for which $L_\perp^{SMN}(T)$ decreases nonmonotonically with an increase in T and has the minimum for $\Delta T \approx 4°$ due to the above-mentioned reason. However, the experimental values of $L_\perp$ obtained independently in [12] from the dichroism of the IR absorption band due to $C\equiv N$ molecular oscillation ($\lambda_{max} = 4.5$ μm) decrease monotonically with an increase in T, obey the inequality $L_\perp > L_{\perp k}$, and correspond to the weak anisotropy $\Delta f < 0$ in the visible and IR ranges. Using these values of $L_\perp$ at $\lambda = 589$ nm yields the ratio $(\bar\gamma/\bar\gamma_i)_{exp}$ that satisfies Eq. (15) and ranges from 1.002 to 1.004 in the mesophase interval $\Delta T = 40°$.

The dependences $L_\perp^{SMN}(T)$ for 3O7T, which follow from Eq. (3) or (12) for $A = 1$, are shown in the figure. The strong dependence of these values on λ contradicts both the meaning of the quantities L_j as the structural characteristics of liquid crystals [5] and the experiment [2, 3]. The experimental values $r/r_1 > 1$ for $\Delta T = 0$ ($\lambda = 546$ nm) and $\Delta T = 0$ and $2°$ ($\lambda = 436$ nm) correspond to complex-valued quantities $L_\perp^{SMN}$ and the inequality $\bar\gamma/\bar\gamma_i > 1$ [see Eq. (11)]. The values $L_\perp^{SMN} < 1/3$ for $\lambda = 436$ (546) nm in the entire nematic phase ($\Delta T < 15°$) contradict constraint (14). These nonphysical consequences of Eq. (1) are eliminated by taking into account that $1/A = \bar\gamma/\bar\gamma_i > 1$ in Eq. (12) increases with ΔT. It is seen in the figure that the increase in $\bar\gamma/\bar\gamma_i$ up to r/r_0 gives the values $L_\perp = L_{\perp k}$ weakly dependent on λ. In this case, the ratio r/r_0 increases monotonically from 1.030 to 1.040 (from 1.007 to 1.011) if $\lambda = 436$ (644) nm and ΔT increases from 0 to 30°. In fact, the ratio r/r_0 is a lower limit for $\bar\gamma/\bar\gamma_i$ in Eq. (15) for 3O7T which is a

homolog of tolans with large Δn values and the anisotropy $\Delta f < 0$ [2, 3] and the actual variation in $\bar{\gamma}/\bar{\gamma}_i$ is even larger.

4. Thus, the appearance of nonphysical solutions of equation (3) expressing condition (1) is explained by the nonlinear relation $\Delta f(\bar{\gamma})$ in uniaxial liquid crystals. The hierarchy of constraints imposed on $\bar{\gamma}/\bar{\gamma}_i$ by Eqs. (11) and (14)–(17) can be verified for any particular object and is confirmed here for liquid crystals with unknown (3O7T) and known (CHCA, 5BCO) experimental values of L_j measured by independent methods. All this means that Eq. (1) is violated and the "$\bar{\gamma} = $ const" paradigm is changed.

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Translated by A. Serber