On the Critical Behavior of Phase Changes of a Forward-Scattered Light in a Nonpolar Binary Liquid Mixture

Kyoung-Ran Kim, Young-Soo Kang, and Dong J. Lee*

Department of Chemistry, Pukyong National University, Nam-Gu, Busan 608-737, Korea
Received August 23, 2002

The effect of concentration fluctuations on the changes of azimuth and ellipticity are analytically obtained in a binary chiral liquid mixture, when the incident light is completely linearly polarized above (or below) the horizontal at 45°. The important results are as follows: (1) When the binary liquid is in the critical region far from the critical point, the ellipticity change is proportional to isothermal compressibility factor and the fifth order of frequency. As the system approaches very close to the critical point, the change is proportional to the third order of frequency and shows the logarithmic divergence. (2) In the case that the system is in the critical region far from the critical point, the azimuth change is solely due to the molecular contribution. As the system approaches to the critical point, the effect of fluctuations becomes important. If it is in the extreme close to the critical point, the term due to the concentration fluctuations is comparable to or larger than the molecular contribution.

Key Words : Azimuth, Ellipticity

Introduction

In the previous paper[1] the authors have obtained analytic results for the phase changes of a forward-scattered light in an isotropic fluid, when the incident light is completely linearly polarized above (or below) the horizontal at 45°, using the formalism given by Barron[2] and the theory for the dielectric tensor developed by one of the authors and his coworker.[3] The result is so effective that we could discuss the effect of density fluctuations on the azimuth and ellipticity of the scattered light in the critical region.

In this paper we shall extend the results to a binary liquid mixture composed of an optically active solute and an optically nonactive solvent. The mixture is more suitable for experimental verification than the pure fluid. The basic difference with the latter is that there is one more extra variable in the mixture, *i.e.*, the concentration fluctuations on the phase changes of the forward-scattered light in the critical region of a binary liquid mixture. The form of the correlation function to be used is the Ornstein-Zernike form. In the next section we obtain the explicit results for the azimuth and ellipticity changes are discussed in the limiting cases in the critical region.

Theory

Let us consider monochromatic light propagating along z and incident on a scattering cell, which is assume to be an infinitely wide lamina (xy plane) with the infinitesimal thickness relative to the wavelength of light. If only a small fraction of the wave is scattered by the fluctuating chiral fluid in the scattering cell, the disturbance reaching a point f

at R_0 a large distance from the lamina in the forward direction is essentially the original light plus a contribution due to the scattering by the fluctuating fluid in the lamina. The total light at f is the sum of the primary wave and the scattered light from the lamina, which is given as[1,2]

$$E'_\alpha = \left(\delta_{\alpha\beta} + \frac{1}{2} i c \omega \gamma'_{\alpha\beta} dz \right) E_{0\beta} \exp\left[i\omega\left(\frac{R_0}{c} - t\right) \right]. \quad (1)$$

where c is the light velocity in vacuum; $\gamma'_{\alpha\beta}$ is the forward component of the macroscopic polarizability density tensor of the chiral fluid, which will be discussed in detail later; dz is the thickness and $E_{0\beta}$ is the incident light. From now on we shall take units such that c is unity.

The light $E_{0\beta}$ can be written as the sum of two coherent fields completely linearly polarized in the x and y directions

$$\vec{E}_0 = E_{0x}\hat{x} + E_{0y}\hat{y}. \quad (2)$$

The general pure polarization state can be described in terms of the ellipticity, η and azimuth, θ.[4] Then, the complex amplitude may be written as

$$\vec{E}_0 = E_0[(\cos\theta\cos\eta + i\sin\theta\sin\eta)\hat{x} + (\sin\theta\cos\eta + i\cos\theta\sin\eta)\hat{y}] \quad (3)$$

where

$$-\frac{\pi}{2} \le \theta \le \frac{\pi}{2}, \quad -\frac{\pi}{4} \le \eta \le \frac{\pi}{4}. \quad (4)$$

The six basic polarization states of the incident field are given in the Table 1.

The Stokes' parameters for the incident and scattered lights are defined as[2,5,6]

---

*To whom all the correspondence should be addressed. E-mail: djlee@pknu.ac.kr

Table 1. The definition of six basic polarized lights

Kind of polarized lights	θ	η
horizontally linearly polarized light	$\pi/2$	0
vertically linearly polarized light	0	0
linearly polarized light above the horizontal at 45°	$\pi/4$	0
linearly polarized light below the horizontal at 45°	$-\pi/4$	0
right circularly polarized light	0	$-\pi/4$
left circularly polarized light	0	$\pi/4$

$$M_0 = \langle E_{0x}E_{0x}^* \rangle - \langle E_{0y}E_{0y}^* \rangle, \quad I_0 = \langle E_{0x}E_{0x}^* \rangle + \langle E_{0y}E_{0y}^* \rangle,$$

$$S_0 = -i(\langle E_{0x}E_{0y}^* \rangle - \langle E_{0y}E_{0x}^* \rangle).$$

$$C_0 = -(\langle E_{0x}E_{0y}^* \rangle + \langle E_{0y}E_{0x}^* \rangle). \tag{5}$$

$$M_f = \langle E_x E_x^* \rangle - \langle E_y E_y^* \rangle, \quad I_f = \langle E_x E_x^* \rangle + \langle E_y E_y^* \rangle.$$

$$S_f = -i(\langle E_x E_y^* \rangle - \langle E_y E_x^* \rangle), \quad C_f = -(\langle E_x E_y^* \rangle + \langle E_y E_x^* \rangle).$$

where the subscripts 0 and f in the above definition denote the incident and total forward lights, respectively, and the sharp brackets represent the statistical average.

The Stokes' parameter I_f of the transmitted wave is, using Eq. (1)

$$I_f = \langle E_x' E_x'^* \rangle + \langle E_y' E_y'^* \rangle$$

$$= \left[\left(\delta_{x\beta} + i\frac{\omega}{2}\gamma_{x\beta}'dz \right) \left(\delta_{x\gamma} - i\frac{\omega}{2}\gamma_{x\gamma}'^*dz \right) \right.$$

$$+ \left. \left(\delta_{y\beta} + i\frac{\omega}{2}\gamma_{y\beta}'dz \right) \left(\delta_{y\gamma} - i\frac{\omega}{2}\gamma_{y\gamma}'^*dz \right) \right] \langle E_\beta E_\gamma^* \rangle.$$

Using the definition of Stokes' parameters given in Eq. (5), we obtain I_f and the other parameters up to the first order of dy as follows

$$I_f \approx I_0 - \frac{\omega}{2}\text{Im}[(\gamma_{xx}' + \gamma_{yy}')I_0 + (\gamma_{xx}' - \gamma_{yy}')M_0$$

$$- (\gamma_{xy}' + \gamma_{yx}')C_0 - i(\gamma_{xy}' - \gamma_{yx}')S_0]dz, \tag{6a}$$

$$M_f = \langle E_x' E_x'^* \rangle - \langle E_y' E_y'^* \rangle$$

$$\approx M_0 - \frac{\omega}{2}\text{Im}[(\gamma_{xx}' + \gamma_{yy}')I_0 + (\gamma_{xx}' - \gamma_{yy}')M_0$$

$$- (\gamma_{xy}' + \gamma_{yx}')C_0 - i(\gamma_{xy}' - \gamma_{yx}')S_0]dz. \tag{6b}$$

$$C_f = \langle E_x' E_y'^* \rangle + \langle E_y' E_x'^* \rangle$$

$$\approx C_0 + \frac{\omega}{2}\text{Im}[(\gamma_{xy}' + \gamma_{yx}')I_0 - (\gamma_{xy}' - \gamma_{yx}')M_0$$

$$- (\gamma_{xx}' + \gamma_{yy}')C_0 + i(\gamma_{xx}' - \gamma_{yy}')S_0]dz. \tag{6c}$$

$$S_f = -i\langle E_x' E_y'^* \rangle - \langle E_y' E_x'^* \rangle$$

$$\approx S_0 + \frac{\omega}{2}Re[(\gamma_{xy}' - \gamma_{yx}')I_0 - (\gamma_{xy}' + \gamma_{yx}')M_0$$

$$- (\gamma_{xx}' - \gamma_{yy}')C_0 + i(\gamma_{xx}' + \gamma_{yy}')S_0]dz, \tag{6d}$$

In Eqs. (6) and denote the real and imaginary parts, respectively. The changes of intensity, azimuth and ellipticity are effectively infinitesimal so we can write $I_f - I \approx dI$, $\theta_f - \theta \approx d\theta$ and $\eta_f - \eta \approx d\eta$. The differential equations for the changes of intensity, azimuth and ellipticity with the respect to dy are given as

$$\frac{dI}{dz} = -I\omega[\text{Im}(\gamma_{xx}' + \gamma_{yy}') + \text{Im}(\gamma_{xx}' - \gamma_{yy}')\cos2\eta\cos2\theta$$

$$-\text{Im}(\gamma_{xy}' + \gamma_{yx}')\cos2\eta\sin2\theta - Re(\gamma_{xy}' - \gamma_{yx}')\sin2\eta] \tag{7a}$$

$$\frac{d\theta}{dz} \approx \frac{\omega}{2}\left\{ -[\text{Im}(\gamma_{xx}' + \gamma_{yy}')\cos2\theta - Re(\gamma_{xx}' - \gamma_{yy}')\sin2\theta]\tan2\eta \right.$$

$$+ \frac{[\text{Im}(\gamma_{xx}' - \gamma_{yy}')\sin2\theta + \text{Im}(\gamma_{xy}' + \gamma_{yx}')\cos2\theta]}{\cos2\eta}$$

$$\left. - \text{Im}(\gamma_{xy}' - \gamma_{yx}') \right\} \tag{7b}$$

$$\frac{d\eta}{dz} \approx \frac{\omega}{2}\left\{ -Re(\gamma_{xx}' - \gamma_{yy}')\sin2\theta - Re(\gamma_{xy}' + \gamma_{yx}')\cos2\theta \right.$$

$$+ [\text{Im}(\gamma_{xx}' - \gamma_{yy}')\cos2\theta - \text{Im}(\gamma_{xy}' + \gamma_{yx}')\sin2\theta]\sin2\eta$$

$$\left. + Re(\gamma_{xy}' - \gamma_{yx}')\cos2\eta \right\}, \tag{7c}$$

where we have used the relations

$$\tan2\theta_f - \tan2\theta \approx \frac{2d\theta}{\cos^2 2\theta}.$$

$$\tan2\eta_f - \tan2\eta \approx \frac{2d\eta}{\cos^2 2\eta}, \tag{8}$$

For the linearly polarized light above (below) the horizontal at 45°, we obtain

$$\frac{dI}{dz} = \frac{\omega}{2}I[-\text{Im}(\gamma_{xx}' + \gamma_{yy}') \pm \text{Im}(\gamma_{xy}' + \gamma_{yx}')]. \tag{9a}$$

$$\frac{d\theta}{dz} = \frac{\omega}{4}I[\pm\text{Im}(\gamma_{xx}' - \gamma_{yy}') - \text{Im}(\gamma_{xy}' - \gamma_{yx}')]. \tag{9b}$$

$$\frac{d\eta}{dz} = -\frac{\omega}{4}[\pm Re(\gamma_{xx}' - \gamma_{yy}') - Re(\gamma_{xy}' - \gamma_{yx}')]. \tag{9c}$$

The sign ± corresponds to the lights polarized linearly above and below the horizontal at 45°, respectively. The first equation, Eq. (9a) describes the absorption; Eq. (9b) expresses an azimuth change due to linear dichroism brought about through a differential absorption of the two linearly polarized components of the incident light resolved along the x and y directions and imaginary part of antisymmetric polarizability tensor component; Eq. (9c) shows the corresponding ellipticity change due to linear birefringence, that is, Kerr effect and real part of antisymmetric polarizability tensor component.

Let us consider an isotropic chiral fluid. The antisymmetric part in Eq. (9a) can be neglected, since it is very small

compared with the symmetric part. Also, the part due to the linear dichroism and Kerr effect in Eqs. (9b) and (9c) can be neglected. Integration over a finite path length *l* leads to the following results

$$I = I_0 \exp\left[-\frac{\omega l}{2} \mathrm{Im}(\gamma'_{xx} + \gamma'_{yy})\right], \qquad (10a)$$

$$\Delta\theta = -\frac{\omega l}{4} \mathrm{Im}(\gamma'_{xy} - \gamma'_{yx}). \qquad (10b)$$

$$\Delta\eta = -\frac{\omega l}{4} \mathrm{Re}(\gamma'_{xy} - \gamma'_{yx}). \qquad (10c)$$

where I_0 is the initial intensity and the explicit form of $\gamma'_{\alpha\beta}$ will be given later.

Let us consider the spatial correlations in a binary liquid mixture composed of an optically active solute and an optically nonactive solvent, denoted by 1 and 2, respectively. There are two correlations due to density fluctuations at constant concentration and concentration fluctuations at constant density. Let us define two kinds of fluctuating quantities A and B as

$$A = \sum_{\mu=1}^{2} A_\mu \rho_\mu, \ B = \sum_{\nu=1}^{2} B_\nu \rho_\nu, \qquad (11)$$

where A_n and B_n are the molecular constants of the νth species of the mixture and ρ_ν is the density of the νth component. With the static approximation we may write the correlation function as

$$S_{AB}(\vec{r} - \vec{r}', t - t') = \sum_{\nu,\mu=1}^{2} A_\mu B_\nu \langle \Delta\rho_\mu(\vec{r}, t)\Delta\rho_\nu(\vec{r}', t')\rangle. \qquad (12)$$

Referring to the detailed discussion to ref. 7, the correlation function can be written in terms of two kinds of correlation functions, that is,

$$S_{AB} = \rho_0^2 \bar{A}^0 \bar{B}^0 S_\zeta + \rho_0^2 \bar{A}^1 \bar{B}^1 S_c. \qquad (13)$$

where

$$\bar{A}^0 = A_1 x_1^0 + A_2 x_2^0, \ \bar{A}^1 = (A_1\bar{v}_2 - A_2\bar{v}_1)/\bar{v}. \qquad (14)$$

In Eq. (13) ρ_0 is the density of the mixture at equilibrium and S_ζ and S_c are the correlation functions of fluctuating reduced density $\Delta\zeta$ and mole fraction Δx_1 defined as

$$S_\zeta(\vec{r} - \vec{r}', t - t') = \langle \Delta\zeta(\vec{r}, t)\Delta\zeta(\vec{r}', t')\rangle.$$

$$S_c(\vec{r} - \vec{r}', t - t') = \langle \Delta x_1(\vec{r}, t)\Delta x_1(\vec{r}', t')\rangle. \qquad (15)$$

In Eq. (14) x_1^0 is the mole fraction of the solute at equilibrium and $\bar{v}$ and $\bar{v}_1$ are the equilibrium values of the molar volume of the mixture and the partial molar volume of the solute, respectively. We may use the static approximation for the correlation function in the case that the velocity of a molecule in the fluid is very small compared with the light

velocity. With the aid of the Onstein-Zernike approximation the Fourier transforms for the correlation functions are

$$S_\zeta(\vec{k} - \vec{k}', \omega - \omega') = 2\pi\delta(\omega - \omega') S_\zeta(\vec{k} - \vec{k}').$$

$$S_c(\vec{k} - \vec{k}', \omega - \omega') = 2\pi\delta(\omega - \omega')S_c(\vec{k} - \vec{k}'). \qquad (16)$$

where

$$S_\zeta(\vec{k}) = k_B T \kappa_T [1 + (\xi_\zeta k)^2]^{-1}.$$

$$S_c(\vec{k}) = k_B T \kappa [1 + (\xi k)^2]^{-1}.$$

$$\kappa = (\rho_0 g_{11})^{-1}, \ g_{11} = \left(\frac{\partial^2 g}{\partial x_1^2}\right)_{P,T}. \qquad (17)$$

In Eq. (17) $k_B T$ and κ_T are the Boltzmann factor and isothermal compressibility factor, respectively; ξ_ζ and ξ are the correlation lengths of density and concentration fluctuations, respectively and *g* is the mean molar Gibbs free energy of the mixture. In general S_ζ is small compared to S_c and negligibly small in the critical region of a binary liquid mixture. This is due to the fact that κ_T is finite whereas g_{11}^{-1} becomes infinite. Thus, we only consider the correlation function of concentration fluctuations especially in the critical region of the mixture.

Referring the detailed derivation to Ref. 7, $\gamma'_{\alpha\beta}$ is the forward component of the macroscopic polarizability density tensor of the mixture, which is given as

$$\gamma'_{\alpha\beta}(\vec{k}, \omega) = \overline{\gamma^0_{\alpha\beta}}(\vec{k}, \omega) + \overline{\gamma'_{\alpha\beta}}(\vec{k}, \omega); \qquad (18)$$

$$\overline{\gamma^0_{\alpha\beta}}(\vec{k}, \omega) = \bar{\alpha}_0^0 \rho_0 \delta_{\alpha\beta} - \frac{(\bar{\alpha}_0^0 \rho_0)^2}{(2\pi)^4}$$

$$\times \int d\vec{k}'d\omega' S_c(\vec{k} - \vec{k}', \omega - \omega') K_{\alpha\beta}(\vec{k}', \omega'). \qquad (19a)$$

$$\overline{\gamma'_{\alpha\beta}}(\vec{k}, \omega) = 2\bar{\beta}_0^0 \rho_0 [1 - \bar{\alpha}_0^0 \rho_0 f(ak, a\omega)]\delta_{\alpha\beta,}k_\gamma$$

$$- \frac{2\bar{\alpha}_0^1 \bar{\beta}_0^0 \rho_0^2}{(2\pi)^4}\iint d\vec{k}'d\omega' S_c(\vec{k} - \vec{k}', \omega - \omega')f(ak', a\omega')\delta_{\alpha\beta,}k'_\gamma$$

$$- \frac{2\bar{\alpha}_0^1 \bar{\beta}_0^0 \rho_0^2}{(2\pi)^4}\left[\frac{1}{2} - \bar{\alpha}_0^0 \rho_0 f(ak, a\omega)\right]\iint d\vec{k}'d\omega' S_2$$

$$\times (\vec{k} - \vec{k}', \omega - \omega')K_{\alpha\alpha'}(\vec{k}', \omega')\delta_{\alpha'\beta,}k'$$

$$- \frac{2\bar{\alpha}_0^1 \bar{\beta}_0^0 \rho_0^2}{(2\pi)^4}\left[\frac{1}{2} - \bar{x}_1^0 \bar{\alpha}_0^1 \rho_0 f(ak, a\omega)\right]\iint d\vec{k}'d\omega' S_2$$

$$\times (\vec{k} - \vec{k}', \omega - \omega')\delta_{\alpha\alpha',}k_\gamma' K_{\alpha'\beta}(\vec{k}', \omega')$$

$$+ \frac{2\bar{x}_1^0(\bar{\alpha}_0^1)^2 \bar{\beta}_0^0 \rho_0^3}{(2\pi)^4}\iint d\vec{k}'d\omega' S_2(\vec{k} - \vec{k}', \omega - \omega')$$

$$\times K_1(k', \omega')K_2(k', \omega')[1 - \bar{\alpha}_0^0 \rho_0 f(ak', a\omega')]\delta_{\alpha\beta,}k_\gamma'. \quad (19b)$$

where $\bar{\alpha}_0^0, \bar{\beta}_0^0, \bar{\alpha}_0^1, \bar{\beta}_0^1$ and $\bar{x}_1^0$ are defined as

$$\bar{\alpha}_0^0 = \alpha_{01}x_1^0 + \alpha_{02}x_2^0, \quad \bar{\beta}_0^0 = \beta_{01}x_1^0,$$

$$\bar{\alpha}_0^1 = (\alpha_{01}\tilde{v}_2 - \alpha_{02}\tilde{v}_1)/\tilde{v}, \quad \bar{\beta}_0^1 = \beta_{01}\tilde{v}_2/\tilde{v}. \tag{20}$$

α_{01} and β_{01} are the second and third order polarizability constants of the chiral solute molecule, respectively; α_{02} is the second order polarizability constant of the solvent molecule; $\delta_{\alpha\beta}$ and $\delta_{\alpha\beta\gamma}$ are the Kronecker delta and Levi-Civita tensor, respectively and the explicit forms of the function $f(ak, a\omega)$ and propagators. $K_{\alpha\beta}$ and K_1 are K_2 given in ref. 3.

Results

First let us assume that the light varies slowly over the molecular dimension. This assumption is obviously valid in the nonresonant frequency region where the frequency dependence of the molecular polarizability tensors can be neglected and thus it can be said that the constants are real in the nonresonant region. Since the light intensity was discussed in detail.[8] the phase changes are obtained. The antisymmetric part $\gamma_{\alpha\beta}'$ ($\vec{k}, \omega$) is responsible for the changes of ellipticity and azimuth in an isotropic chiral fluid. With the aid of the explicit forms of propagators and Eq. (17). we may obtain the following results.

(A). The ellipticity change
The ellipticity change is given as

$$\Delta\eta = \frac{\omega l}{4}\mathrm{Re}(\gamma_{xy}' - \gamma_{yx}') = \frac{\omega l}{2}\mathrm{Re}\gamma_{xy}' = -A_c\omega^3 l/[\Delta\eta], \tag{21}$$

where the antisymmetric property of $\overline{\gamma_{\alpha\beta}}$ ($\vec{k}, \omega$) is used and

$$A_c = \frac{1}{24\pi}\Big[\frac{1}{3}(\varepsilon_0+2)(\varepsilon_0-1)\Big]^2\bar{\alpha}_0^1\bar{\beta}_0^1\rho_0^2\Big(\frac{k_BT\kappa}{\xi^2}\Big), \tag{22}$$

$$[\Delta\eta] = [3 - (\bar{\alpha}_0^0 + \bar{x}_1^0\bar{\alpha}_0^1)\rho_0]$$

$$\times \Big[\frac{3}{2} + \frac{1}{p^2} - \Big(1 + \frac{1}{4p^2}\Big)\ln(1+4p^2)\Big]$$

$$+ \bar{x}_1^{0-1}\bar{\alpha}_0^1\rho_0\Big[2 - \frac{1+2p^2}{2p^2}\ln(1+4p^2)\Big]$$

$$+ \frac{\varepsilon_0+2}{4\varepsilon_0}\Big[\frac{4p^2}{1+4p^2} - \ln(1+4p^2)\Big], \tag{23}$$

with

$$p = n_0\xi\omega. \tag{24}$$

When the above result is obtained. we have used the fact that if ak, $a\omega \ll 1$ the function $f(ak, a\omega) \simeq 1/3$ and the dielectric constant at equilibrium ε_0 is given as

$$\varepsilon_0 = \frac{1 + \frac{2}{3}\bar{\alpha}_0^0\rho_0}{1 - \frac{1}{3}\bar{\alpha}_0^0\rho_0}. \tag{25}$$

It should be noted that ω equals 2π over the wavelength of the light in vacuum, since the light velocity in vacuum is taken to be unity. The limiting properties of $[\Delta\eta]$ are as follows:

(i). When $p = n_0\xi\omega \ll 1$. then we have

$$[\Delta\eta] = -\frac{12}{\varepsilon_0+2}p^2(1+4p^2)$$

$$+ 2\bar{x}_1^{0-1}\bar{\alpha}_0^1\rho_0p^2\Big(\frac{2}{3} - \frac{\varepsilon_0+2}{\varepsilon_0}p^2\Big) + \dots \tag{26}$$

so that

$$\Delta\eta(\omega) = -\frac{\varepsilon_0}{6\pi}\Big[\frac{1}{3}(\varepsilon_0+2)\Big]^2\Big(\frac{3}{\varepsilon_0+2} - \frac{1}{3}\bar{x}_1^0\bar{\alpha}_0^1\rho_0\Big)$$

$$\times \bar{\alpha}_0^1\bar{\beta}_0^1\rho_0^3k_BTk\omega^5 l. \tag{27}$$

When the fluid is far from the critical point. the azimuth is proportional to ω^5 and isothermal compressibility factor κ.

(ii). In the extreme critical region where. $p = n_0\xi\omega \to \infty$ we have

$$\Delta\eta(\omega) \sim A_c\Big[\frac{27}{2(\varepsilon_0+2)} + \bar{x}_1^0\bar{\alpha}_0^1\rho_0\Big(\frac{1}{2} + \frac{\varepsilon_0+2}{4\varepsilon_0}\Big)$$

$$-2\Big(\frac{9}{\varepsilon_0+2} + \bar{x}_1^0\bar{\alpha}_0^1\rho_0\frac{\varepsilon_0+2}{4\varepsilon_0}\Big)\ln(2p)\Big]\omega^3 l. \tag{28}$$

$\Delta\eta$ is proportional to ω^3 and shows the logarithmic divergence in the extremely critical region extremely close to the critical point.

(B). The azimuth change. $\Delta\theta(\omega)$ in the critical region is given by

$$\Delta\theta(\omega) = \frac{\omega l}{4}\mathrm{Re}(\gamma_{xy}' - \gamma_{yx}') = \Delta\theta_1(\omega) + \Delta\theta_2(\omega) + \Delta\theta_3(\omega). \tag{29}$$

where denotes the real part and the result of the calculations is written in three terms for convenience. The first term $\Delta\theta_1(\omega)$ due to the molecular contribution given by

$$\Delta\theta_1(\omega) = -\frac{3n_0}{\varepsilon_0+2}\bar{\beta}_0^0\rho_0\omega^3 l. \tag{30}$$

The rest is due to the correlation of the density fluctuations and given by the real part of the integrals in Eq. (19b). These integrals can be calculated when the correlation length is larger than the diameter of the molecule. The results are expressed as $\Delta\theta_2(\omega)$ and $\Delta\theta_3(\omega)$. The term. $\Delta\theta_2(\omega)$ is

$$\Delta\theta_2(\omega) = \frac{1}{48\pi}\Big(\frac{3}{\varepsilon_0+2}\Big)(\varepsilon_0-1)\Big[1 - \frac{1}{3}(\bar{\alpha}_0^0 + \bar{x}_1^0\bar{\alpha}_0^1)\rho_0\Big]$$

$$\times \bar{\alpha}_0^1\bar{\beta}_0^1\rho_0^2\Big(\frac{k_BT\kappa}{\xi^2}\Big)\Big(\frac{1}{5a} - \frac{1}{3\xi}\Big)\omega^3 l. \tag{31}$$

where a is the diameter of a molecule.
The third term $\Delta\theta_3(\omega)$ is given by

$$\Delta\theta_3(\omega) = A_c\omega^3 l\left\{[3 - (\bar{\alpha}_0^0 + \bar{x}_1^0\bar{\alpha}_0^1)\rho_0]\right.$$

$$\times \left[\frac{5}{6p} + \frac{1}{8p^3} - \left(1 + \frac{1}{4p^2}\right)^2 \tan^{-1}(2p) \right]$$

$$+ \left(\frac{\varepsilon_0 + 2}{8\varepsilon_0 |t|}\right)\left(\frac{1 + 2p^2}{2p^2}\right)\cot^{-1}\left(\frac{1}{4p^3 |t|} + \frac{1}{2p|t|} - \frac{1}{2}p|t|\right)\bigg\} + O(t).$$

$$\tag{32}$$

where A_n is given in Eq. (22) and $|t|$ is the absolute value of t defined as

$$t = \left(\frac{\varepsilon_0 + 2}{3n_0}\right)\bar{\beta}_0^0 \rho_0 \omega. \tag{33}$$

The limiting properties of $\Delta\theta_3(\omega)$ are as follows:

(i) When $p = n_0\xi\omega \ll 1$, $\Delta\theta_2(\omega)$ dominates over $\Delta\theta_3(\omega)$. Its magnitude may account to one-tenth of $\Delta\theta_1(\omega)$, depending on the Debye persistence length R defined by $R^{-2} = \rho_0 k_B T \kappa / \xi^2$.

(ii) When $p \gg 1$, $\Delta\theta_3(\omega)$ becomes important. In the case of $1 \ll p \ll |t|^{-1}$, we have

$$\Delta\theta_3(\omega) \simeq -\left(\frac{\varepsilon_0 + 2}{3}\right)^2 (\bar{\alpha}_0^1 \rho_0)^2 (k_B T \kappa / 16\pi n_0 \xi^2) \omega^2 / pt, \tag{34}$$

which may become comparable to or larger than $\Delta\theta_2(\omega)$. It is due to the indirect coupling between two fluctuating parts of dipole densities *via* the equilibrium part of quadrupole density in the middle. In the extreme case where $p|t| \gg 1$, we have

$$\Delta\theta_3(\omega) \simeq -\left(\frac{\varepsilon_0 + 2}{3}\right)^2 (\bar{\alpha}_0^1 \rho_0)^2 (k_B T \kappa / 32\pi n_0 \xi^2) \omega^2 / t, \tag{35}$$

The above result is independent of $\bar{\beta}_0^0$. Its magnitude may become comparable to or larger than the term due to the molecular contribution, $\Delta\theta_1(\omega)$, depending on the Debye persistence length.

Conclusions

The effect of concentration fluctuations has been in detail obtained on the phase changes for a forward-scattered light in a binary chiral liquid mixture, when the incident light is completely linearly polarized above(or below) the horizontal at 45°. Let us summarize some important results:

(1). When the binary liquid is in the critical region far from the critical point, the ellipticity change is proportional to isothermal compressibility factor and the fifth order of frequency (see Eq. (27)). As the system approaches very close to the critical point, the change is proportional to the third order of frequency and shows the logarithmic divergence (Eq. 28). This divergence should not be taken too seriously, since in the extreme critical region we must account for the eventual departure from the Ornstein-Zernike approximation.[9]

(2). In the case that the system is in the critical region far from the critical point, the azimuth change is solely due to the molecular contribution, as shown in Eq. (30). As the system approaches to the critical point, the effect of fluctuations becomes important. If it is in the extreme close to the critical point, the term due to the concentration fluctuations is comparable to or larger than the molecular contribution (see Eq. (35)).

References

1. Kim. Y.; Kim, K. R.; Kang, Y.; Lee, D. J. *Chem. Phys.* in press.
2. Barron. L. D. *Molecular Light Scattering and Optical Activity*, Cambridge University Press: Cambridge. 1982.
3. Kim. S. K.; Lee. D. J. *J. Chem. Phys.* **1981**. *74*. 3591.
4. de Figueiredo. I. M. B.; Rabb. R. E. *Proc. R. Soc. London Ser.* **1981**. *A375*. 425.
5. Lee. D. J.; Kim, K. R. *J. Chem. Phys.* **1996**. *105*. 5341.
6. Born. M.; Wolf, E. *Principle of Optics*, Pergamon: Oxford. 1975.
7. Lee. D. J.; Kim. S. K. *J. Chem. Phys.* **1986**. *84*. 1739.
8. Kim. S. K.; Mazur. P. *Physica* **1974**. *71*. 1027.
9. Stanley. E. H. *Introduction to Phase Transition and Critical Phenomena*. Clarendon: oxford. 1971.