Phase Change of Forward-Scattered Light in the Critical Region

Yunsoo Kim, Kyoung-Ran Kim, and Dong J. Lee*

Department of Chemistry, Pukyong National University, Nam-Gu, Pusan 608-737, Korea
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The changes of azimuth and ellipticity due to the linear dichroism and Kerr effect are analytically obtained in the critical region, when the incident light is completely linearly polarized above (or below) the horizontal at 45°. The results are discussed in two extreme cases in the critical region.

Keywords : Azimuth, Ellipticity, Linear dichroism, Kerr effect.

Introduction

When a static uniform field is applied to a fluid perpendicular to the propagation of light, molecules in the fluid are partly oriented. This renders the fluid anisotropy and gives it birefringence, that is, the ability to refract light differently in two directions.[1-8] This effect is called the Kerr effect. One of theoretical methods to discuss the birefringence is based on the Rayleigh theory of scattering. Lord Rayleigh[9] pointed out that the refraction of light is a consequence of light scattering. The individual molecules scatter a small part of the incident light and the forward parts of the resulting waves combine and interfere with the primary wave, resulting in phase change which is equivalent to an alteration of the light velocity. Thus, owing to the anisotropy of the molecular polarizability tensors induced by the external field, there is phase difference between the axes along and perpendicular to the direction of field. Since Kauzmann[7] treated birefringent scattering including optical activity with the aid of quantum mechanical theory, many authors[1,4-6] have studied birefringent phenomena theoretically by considering the interactions between molecular polarizability tensors and light. It is not adequate to discuss the birefringence in the critical region of a fluid by the Rayleigh scattering theory, since correlation between the fluctuating variables becomes important in the critical region near the critical point.[10-12]

The purpose of the present paper is to discuss the critical behavior of the phase change of forward-scattered light due to the linear dichroism and Kerr effect in a chiral fluid. A static electric field is applied to the nonpolar chiral fluid, which is composed of spherical chiral molecules with the same diameter and then some refringence is induced by distorting the molecular shape to some degree. It is, however, assumed that even though the anisotropy of molecular polarizability tensors is induced, the spherical shape is maintained. Then, we may easily extend the result of polarizability density tensor of a nonpolar chiral fluid[11-13] to the present problem.

In section II, the relationships between the changes of azimuth and ellipticity of a scattered light and anisotropy of polarizability tensor of a fluid are obtained with the aid of the Stokes' parameters.[1,14-16] From the relationship we obtain the attenuation intensity, Rosenfeld equation and optical activity[1] when the correlation of density fluctuations is neglected. Subsequently, we introduce a renormalized propagator by using the average polarizabily and dielectric tensors of the fluid. In section III we first obtain the change of azimuth caused by linear dichroism employing the Ornstein-Zernike form of the correlation of density fluctuations. This change is due to the imaginary part of the renormalized propagator of the fluid due to the correlation, since the molecular polarizability tensors are assumed to be real in nonresonant frequency region. The approximate results are given in the two extreme cases in the critical region. Finally, the change of ellipticity due to Kerr effect and density fluctuations is obtained and discussed in the critical region. It is noted that the effects of optical activity on the changes of azimuth and ellipticity are neglected.

Theory

Let us consider monochromatic light propagating along y and incident on a scattering cell, which is assume to be an infinitely wide lamina (xz 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_o 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]

$$E_\alpha^f = \left(\delta_{\alpha\beta} + \frac{1}{2} i c \omega \gamma_{\alpha\beta}^f \, dy\right) E_{o\beta} \exp[i\omega(R_o/c - t)], \qquad (1)$$

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

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

$$\vec{E}_o = E_{ox}\hat{x} + E_{oz}\hat{z}. \qquad (2)$$

The general pure polarization state can be described in terms of the ellipticity, η and azimuth, θ.[15] Then, the

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	$\pi/4$

complex amplitude may be written as

$$\vec{E}_o = E_o\,[(\cos\theta\cos\eta + i\sin\theta\sin\eta)\,\hat{x} + (\sin\theta\cos\eta + i\cos\theta\sin\eta)\hat{z}\,]. \tag{3}$$

where

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

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[1,14-16]

$$\begin{aligned}
&I_o = \langle E_{ox}E_{ox}^*\rangle + \langle E_{oz}E_{oz}^*\rangle,\ M_o = \langle E_{ox}E_{ox}^*\rangle - \langle E_{oz}E_{oz}^*\rangle,\\
&C_o = -(\langle E_{ox}E_{oz}^*\rangle + \langle E_{oz}E_{ox}^*\rangle),\\
&S_o = -i(\langle E_{ox}E_{oz}^*\rangle - \langle E_{oz}E_{ox}^*\rangle),\\
&I_f = \langle E_x^f E_x^{f*}\rangle + \langle E_z^f E_z^{f*}\rangle,\ M_f = \langle E_x E_x^*\rangle - \langle E_z E_z^*\rangle,\\
&C_f = -(\langle E_x E_z^*\rangle + \langle E_z E_x^*\rangle),\ S_f = -i(\langle E_x E_z^*\rangle - \langle E_z E_x^*\rangle),
\end{aligned} \tag{5}$$

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

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

$$\begin{aligned}
I_f &= \langle E_x E_x^*\rangle + \langle E_z E_z^*\rangle\\
&= [(\delta_{x\beta} + i\frac{\omega}{2}\ \gamma_{x\beta}^f dy)(\delta_{x\gamma} - i\frac{\omega}{2}\ \gamma_{x\gamma}^f dy)\\
&\quad + (\delta_{z\beta} + i\frac{\omega}{2}\ \gamma_{z\beta}^f dy)(\delta_{z\gamma} - i\frac{\omega}{2}\ \gamma_{z\gamma}^{f*} dy)]\ \langle E_\beta E_\gamma^*\rangle.
\end{aligned}$$

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

$$\begin{aligned}
I_f &\approx I_o - \frac{\omega}{2} Im[(\gamma_{xx}^f + \gamma_{yy}^f)I_o + (\gamma_{xx}^f - \gamma_{yy}^f)M_o -\\
&\quad (\gamma_{xy}^f + \alpha_{yx}^f)C_o - i(\gamma_{xy}^f - \gamma_{yx}^f)S_o]dy,
\end{aligned} \tag{6a}$$

$$\begin{aligned}
M_f &= \langle E_{fx}\ E_{fx}^*\rangle - \langle E_{fz}\ E_{fz}^*\rangle\\
&\cong M_o - \frac{\omega}{2} Im[(\gamma_{xx}^f + \gamma_{zz}^f)I_o + (\gamma_{xx}^f - \gamma_{zz}^f)M_o - (\gamma_{xz}^f + \gamma_{zx}^f)C_o\\
&\quad - i(\gamma_{xz}^f - \gamma_{zx}^f)S_o]dy,
\end{aligned} \tag{6b}$$

$$\begin{aligned}
C_f &= \langle E_{fx}\ E_{fz}^*\rangle + \langle E_{fz}\ E_{fx}^*\rangle\\
&\simeq C_o + \frac{\omega}{2} Im[(\gamma_{xy}^f + \gamma_{zx}^f)I_o - (\gamma_{xz}^f - \gamma_{zx}^f)M_o - (\gamma_{xx}^f + \gamma_{zz}^f)C_o\\
&\quad + i(\gamma_{xx}^f - \gamma_{zz}^f)M_o]dy,
\end{aligned} \tag{6c}$$

$$\begin{aligned}
S_f &= -i(E_x^f\ E_z^{f*} - E_z^f\ E_x^{f*})\\
&\approx S_o + \frac{\omega}{2} Re[(\gamma_{xz}^f - \gamma_{zx}^f)I_o - (\gamma_{xz}^f + \gamma_{zx}^f)M_o\\
&\quad - (\gamma_{xx}^f - \gamma_{zz}^f)C_o + i(\gamma_{xx}^f + \gamma_{zz}^f)S_o]dy.
\end{aligned} \tag{6d}$$

In Eqs. (2.6) Re and Im 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

$$\begin{aligned}
\frac{dI}{dy} &\cong -I\omega[Im(\gamma_{xx}^f + \gamma_{zz}^f) + Im(\gamma_{xx}^f - \gamma_{zz}^f)\cos 2\eta\cos 2\theta\\
&\quad - Im(\gamma_{xz}^f + \gamma_{zx}^f)\cos 2\eta\cos 2\theta - Re(\gamma_{xz}^f - \gamma_{zx}^f)\sin 2\eta],
\end{aligned} \tag{7a}$$

$$\begin{aligned}
\frac{d\theta}{dy} &\cong \frac{\omega}{2}([Im(\gamma_{xx}^f + \gamma_{zz}^f)\cos 2\theta - Re(\gamma_{xx}^f - \gamma_{zz}^f)\sin 2\theta]\\
&\quad \tan 2\eta + [Im(\gamma_{xx}^f - \gamma_{zz}^f)\sin 2\theta + Im(\gamma_{xz}^f + \gamma_{zx}^f)\cos 2\theta]/\\
&\quad \cos 2\eta - Im(\gamma_{xz}^f - \gamma_{zx}^f))
\end{aligned} \tag{7b}$$

$$\begin{aligned}
\frac{d\eta}{dy} &\cong \frac{\omega}{2}[-Re(\gamma_{xx}^f - \gamma_{zz}^f)\sin 2\theta - Re(\gamma_{xz}^f + \gamma_{zx}^f)\cos 2\theta]\\
&\quad + [Im(\gamma_{xx}^f - \gamma_{zz}^f)\cos 2\theta - Im(\gamma_{xz}^f + \gamma_{zx}^f)\sin 2\theta]\sin 2\eta\\
&\quad + Re(\gamma_{xz}^f - \gamma_{zx}^f)\cos 2\eta],
\end{aligned} \tag{7c}$$

where we have used the relations

$$\begin{aligned}
\tan 2\theta_f - \tan 2\theta &\approx 2d\theta/\cos^2 2\theta,\\
\tan 2\eta_f - \tan 2\eta &\approx 2d\eta/\cos^2 2\eta,
\end{aligned} \tag{8}$$

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

$$\frac{dI}{dy} = I\frac{\omega}{2}[-Im(\gamma_{xx}^f + \gamma_{zz}^f) \pm Im(\gamma_{xz}^f + \gamma_{zx}^f)]. \tag{9a}$$

$$\frac{d\theta}{dy} = \frac{\omega}{4}[\pm Im(\gamma_{xx}^f - \gamma_{zz}^f) - Im(\gamma_{xz}^f - \gamma_{zx}^f)]. \tag{9b}$$

$$\frac{d\eta}{dy} = -\frac{\omega}{4}[\pm Re(\gamma_{xx}^f - \gamma_{zz}^f) - Re(\gamma_{xz}^f - \gamma_{zx}^f)]. \tag{9c}$$

The sign ± corresponds to the lights polarized linearly above and below the horizontal at 45°, respectively. The first equation, Eq. (9a) describes the absorption *via* the absorptive parts of the molecular polarizability tensors and the effect of density fluctuations; 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 z directions and Eq. (9c) shows the corresponding ellipticity change due to linear birefrigence, that is, Kerr effect. We may apply these equations to discuss various kinds of phenomena contained in Eqs. (7).

Let us consider a chiral fluid. The fluid is nonpolar before an external static electric field is applied. The molecules in the fluid are assumed to be spherical with diameter a. The anisotropy in the fluid is generated in the fluid by a partial

orientation of the induced moment due to the field and fluctuations of fluid density, assuming that the molecules are still spherical. Then, extending the previous theory for the macroscopic polarizability density tensor of the nonpolar chiral fluid,[12,13] we may easily obtain the macroscopic polarizability density tensor of an anisotropic chiral fluid as follows;

$$\gamma'_{\alpha\beta}(k,\omega) = \overline{\gamma'_{\alpha\beta}}(k,\omega)+\overline{\gamma'_{\alpha\beta}}(k,\omega); \tag{10}$$

$$\overline{\gamma'_{\alpha\beta}}(k,\omega) = \alpha_{\alpha\beta}\rho_o-\frac{\rho_o^2}{(2\pi)^4}\int dk'd\omega'\ S_2(k-k',\ \omega-\omega')\ \alpha_{\alpha\alpha'}K_{\alpha'\beta'}(k',\omega')\alpha_{\beta'\beta}, \tag{11a}$$

$$\begin{aligned}\overline{\gamma'_{\alpha\beta}}(k,\omega) = {} & \gamma'_{\alpha\beta}(k,\omega)\rho_o \\ & + \frac{\rho_o^2}{(2\pi)^4}\iint dk'd\omega'\ S_2(k-k',\ \omega-\omega')\ \alpha_{\alpha\alpha'}L^{\gamma}_{\alpha'\alpha''}(k',\omega')(\beta-\beta')_{\alpha''\beta\gamma} \\ & - \frac{\rho_o^2}{(2\pi)^4}\iint dk'd\omega'\ S_2(k-k',\ \omega-\omega')\ \alpha_{\alpha\alpha'}K^{\gamma}_{\alpha'\alpha''}(k',\omega')[\gamma'_{\alpha''\beta}(k',\omega')+\gamma_{\alpha''\beta'}(k,\omega)] \\ & - \frac{\rho_o^2}{(2\pi)^4}\iint dk'd\omega'\ S_2(k-k',\ \omega-\omega')\ \alpha_{\alpha\alpha'}K^{\gamma}_{\alpha'\alpha''}(k',\omega')[\gamma''_{\alpha''\beta}(k',\omega')+\gamma''_{\alpha''\beta}(k,\omega)].\end{aligned} \tag{11b}$$

In Eqs. (2.11) we adopted the tensor notation in which the repeated indices mean summation over the indices; $\alpha_{\alpha\beta}$ is the second order molecular polarizability tensor; ρ_o is the density of the fluid at equilibrium; $S_2(\vec{k},\omega)$ is the correlation function of density fluctuations given as

$$S_2(\vec{k}-\vec{k}',\ \omega-\omega') = \rho_o^{-2}\langle\Delta\rho(\vec{k},\omega)\Delta\rho(\vec{k},\omega')\rangle; \tag{12}$$

$\gamma'_{\alpha\beta}$ and $\gamma''_{\alpha\beta}$ are given as

$$\begin{aligned}\gamma'_{\alpha\beta}(k,\omega) &= i(\beta-\beta')_{\alpha\beta\gamma}k_r+\alpha_{\alpha\alpha'}L^{\gamma}_{\alpha'\beta'}(k,\omega)(\beta-\beta')_{\beta'\beta\gamma}, \\ \gamma'_{\alpha\beta}(k,\omega) &= i(\beta-\beta')_{\alpha\beta\gamma}k_r+2\alpha_{\alpha\alpha'}L^{\gamma}_{\alpha'\beta}(k,\omega)(\beta-\beta')_{\beta'\beta\gamma}.\end{aligned} \tag{13}$$

$L^{\gamma}_{\alpha\beta}$ and $K_{\alpha\beta}$ are the propagator due to the existence of discontinuity between molecules at the Lorentz cavity and the renormalized propagator, respectively,[12] and β and β' are the third order molecular polarizability tensors. The α, β and β' are given as[17]

$$\alpha_{\alpha\beta} = \frac{2}{\hbar}\Sigma\rho_n^o\frac{\omega_{nm}Re[(\mu_\alpha)_{nm}(\mu_\beta)_{mn}]}{\omega^2-\omega_{nm}^2+i\lim_{\varepsilon\to 0}\varepsilon\omega}, \tag{14a}$$

$$\beta_{\alpha\beta} = \frac{2}{\hbar}\Sigma\rho_n^o\frac{Im[(\mu_\alpha)_{nm}(M_\lambda)_{mn}]}{\omega^2-\omega_{nm}^2+i\lim_{\varepsilon\to 0}\varepsilon\omega}\delta_{\beta\gamma\lambda} + \frac{2i}{\hbar}\Sigma\rho_n^o\frac{\omega_{nm}Re[(\mu_\alpha)_{nm}(g_{\beta\gamma})_{mn}]}{\omega^2-\omega_{nm}^2+i\lim_{\varepsilon\to 0}\varepsilon\omega}. \tag{14b}$$

$$\beta'_{\alpha\beta\gamma} = \frac{2}{\hbar}\Sigma\rho_n^o\frac{Im[(\mu_\beta)_{nm}(M_\lambda)_{mn}]}{\omega^2-\omega_{nm}^2+i\lim_{\varepsilon\to 0}\varepsilon\omega}\delta_{\beta\gamma\lambda} + \frac{2i}{\hbar}\Sigma\rho_n^o\frac{\omega_{nm}Re[(\mu_\beta)_{nm}(g_{\beta\gamma})_{mn}]}{\omega^2-\omega_{nm}^2+i\lim_{\varepsilon\to 0}\varepsilon\omega}. \tag{14c}$$

where ρ_n^o is defined as

$$\rho_n^o = \exp(-E_n/k_BT)/\sum_n\exp(-E_n/k_BT) \tag{15}$$

ω_{nm} is the circular transition frequency from the n-th state to the m-th state; μ, M and g are the electric dipole moment, magnetic moment and electric quadrapole moment, respectively; ε is an infinitesimal positive real number; $\delta_{\alpha\beta}$ and $\delta_{\alpha\beta\gamma}$ are the Kronecker delta and Levi-Civita tensor, respectively, and k_BT is the Boltzman factor. The above results were obtained by the quantum statisitical method and thus are different from quantum mechanical results in the sense that the tensors show the temperature dependence and the time reversal symmetry is introduced to obtain the tensors.

First let us consider the isotropic fluid, neglecting the effect of density correlation. In this case we may use the orientational average for the tensors, that is,

$$\langle\alpha_{\alpha\beta}\rangle = \frac{1}{3}\alpha_o\beta_{\alpha\beta}\langle\beta_{\alpha\beta\gamma}\rangle = \langle\beta'_{\alpha\beta\gamma}\rangle = \frac{1}{6}\beta_o\delta_{\alpha\beta\gamma}. \tag{16}$$

where[17]

$$\alpha_o = \frac{2}{3\hbar}\Sigma\rho_n^o\frac{\omega_{nm}Re[(\vec{\mu})_{nm}(\vec{\mu})_{mn}]}{\omega^2-\omega_{nm}^2+i\lim_{\varepsilon\to 0}\varepsilon\omega}. \tag{17a}$$

$$\beta_o = \frac{2}{3\hbar}\Sigma\rho_n^o\frac{Im[(\vec{\mu})_{nm}(\vec{M})_{mn}]}{\omega^2-\omega_{nm}^2+i\lim_{\varepsilon\to 0}\varepsilon\omega}. \tag{17b}$$

Substituting Eq. (16) to Eq. (9), we have

$$\frac{dI}{dy} = -\frac{1}{3}Im(\alpha_o)\rho_o\omega I, \tag{18a}$$

$$\frac{d\theta}{dy} = -\frac{1}{6}Im\left[\left(1-\frac{1}{3}\alpha_o\rho_o\right)\beta_o\right]\rho_o\omega^2. \tag{18b}$$

$$\frac{d\eta}{dy} = -\frac{1}{6}Re\left[\left(1-\frac{1}{3}\alpha_o\rho_o\right)\beta_o\right]\rho_o\omega^2. \tag{18c}$$

In Eqs. (2.18b) and (2.18c) the term $(1-\frac{1}{3}\alpha_o\rho_o)$ is the correction for the undue differentiation at the Lorentz cavity. From the Eq. (18a) we obtain for the final attenuation intensity in a cell with a finite path length l

$$I = I_o\exp\left[-\frac{1}{3}Im(\alpha_o)\rho_o\omega l\right]. \tag{19}$$

where I_o is the initial intensity. The Eq. (18b) shows the famous Rosenfeld equation[1] for the azimuth change in an isotropic fluid as follows

$$\Delta\theta = -\frac{1}{6}Im\left[\left(-\frac{1}{3}\alpha_o\rho_o\right)\beta_o\rho_o\right]\omega^2 l. \tag{20}$$

It should be noted that in the original Rosenfeld equation it is

written as

$$\Delta\theta = -\frac{1}{3}G'_{\alpha\alpha}(f)\rho_o\omega l. \tag{21}$$

The expression $Im(\beta_o)\omega$ corresponds to $2G'_{\alpha\alpha}$. The term $(1-\frac{1}{3}\alpha_o\rho_o)$ is not included, when a molecule is considered. The ellipticity change is given as[1]

$$\Delta\eta = \frac{1}{6}Re\left[\left(-\frac{1}{3}\alpha_o\rho_o\right)\beta_o\rho_o\right]\omega^2 l. \tag{22}$$

The results in Eqs. (21) and (22) confirm the fact that the linear dichroism and Kerr effect do not exist for the forward-scattered light in an isotropic achiral fluid and the changes of azimuth and ellipticity are caused by optical activity in an isotropic chiral fluid.

Now let us consider an anisotropy fluid caused by a static uniform electric field applied to an isotropic fluid perpendicular to the propagation direction and at 45° to the azimuth of an incident linearly polarized light (thus the electric field is applied along the x-direction). 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 polarizability tenors can be neglected and thus it can be said that the tensors are real in the nonresonant region. The effect of the term in Eq. (11b) is also neglected compared with that in Eq. (11a), since $\|\beta\cdot k\| << \|\alpha\|$ in optical frequency region, $\|\cdots\|$ being the norm of tensor. Let us define the average of the second order molecular polarizability tensor and dielectric tensor of the fluid as

$$\alpha_o = \frac{\alpha_{xx}+2\alpha_{zz}}{3}; \quad \alpha_{zz}=\alpha_{yy}. \tag{23}$$

Thus the Lorentz-Lorenz formula is given as

$$\alpha_o\rho_o = 3(\varepsilon_o-1)/(\varepsilon_o+2). \tag{24}$$

where ε_o is the average dielectric constant of fluid at equilibrium. The renormalized propagator in a fluid is expressed by the average molecular polarizability tensor and dielectric tensor as[10-11]

$$\begin{aligned}\alpha_o\rho_o K_{\alpha\alpha}(\vec{k},\omega) &= -\frac{1}{3}\Gamma(ak,a\omega)\left(1-\frac{\Gamma(ak,a\omega)+3}{\Gamma(ak,a\omega)+1}\frac{k_\alpha k_\alpha}{k^2}\right)\\ &-\frac{1}{3}[\Psi(ak,a\omega)-1][\Gamma(ak,a\omega)+3]\omega^2\\ &[k^2-(\omega+i\lim_{\varepsilon\to 0}\varepsilon)\times\Psi(ak,a\omega)]^{-1}\left(1-\frac{k_\alpha k_\alpha}{k^2}\right).\end{aligned} \tag{25}$$

where the functions are

$$\begin{aligned}\Gamma(x,y) &= 3\alpha_o\rho_o f(x,y)[1-\alpha_o\rho_o f(x,y)]^{-1},\\ \Psi(x,y) &= \alpha_o\rho_o g(x,y)[1-\alpha_o\rho_o f(x,y)]^{-1}.\\ f(x,y) &= -\frac{1}{x}\frac{d}{dx}\left(\frac{\sin x}{x}\right)(\cos y + y\sin y),\\ g(x,y) &= \cos x\cos y+\frac{y}{x}\sin x\sin y.\end{aligned} \tag{26}$$

When $x, y << 1$, $f(x, y)$ and $g(x, y)$ become approximately 1/3 and 1. 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. We take the Ornstein-Zernike correlation function as the static function, which is given as

$$\begin{aligned}S_2(k-k',\omega-\omega') &= 2\pi\delta(\omega-\omega')S_2(k-k');\\ S_2(k-k') &= \frac{k_B T\chi}{1+\xi^2(k-k')^2}.\end{aligned} \tag{27}$$

where κ is the isothermal compressibility factor and ξ is the correlation length of density fluctuations.

It is very easy to investigate the effect of density fluctuations on the azimuth and ellipticity in the nonresonant frequency region. In this region the molecular polarizability tensors can be considered real and their dependence on frequency can be approximately neglected. Thus, the tensor $\gamma^f_{\alpha\alpha}$ is given as

$$\begin{aligned}\gamma^f_{\alpha\alpha}(k,\omega) &= \alpha_{\alpha\alpha}\rho_o-\frac{1}{(2\pi)^4}\frac{\varepsilon_o+2}{3(\varepsilon_o-1)}\alpha^2_{\alpha\alpha}\rho^2_o\int d\vec{k}'d\omega'\\ &S_2(\vec{k}-\vec{k}',\omega-\omega')\times\alpha_o\rho_o K_{\alpha\alpha}(\vec{k}',\omega').\end{aligned} \tag{28}$$

Results

Now we are ready to give the final results for the changes of azimuth and ellipticity in the critical region.

The change of azimuth in critical region. The linear dichroism is obtained from the imaginary parts of the tensor components given in Eq. (28). Substitution of Eq. (27) into Eq. (25) leads to

$$Im\gamma(k,\omega)^f_{xx} = \frac{1}{32\pi}\left(\frac{\varepsilon_o+2}{3}\right)^2(\alpha_{xx}\rho_o)^2\frac{k_B T\chi}{k\omega\xi^2}\omega^3 f_1(s,r). \tag{29a}$$

$$Im\gamma(k,\omega)^f_{zz} = -\frac{1}{16\pi}\left(\frac{\varepsilon_o+2}{3}\right)^2(\alpha_{zz}\rho_o)^2\frac{k_B T\chi}{k\omega\xi^2}\omega^3 f_2(s,r). \tag{29b}$$

where

$$\begin{aligned}f_1(s,r) &= \frac{1+s^2}{sr}+\left[\left(\frac{1+s^2}{2}\right)^2+1\right]\ln\left(\frac{1+s^2-2sr}{1+s^2+2sr}\right),\\ f_2(s,r) &= \frac{1+s^2}{sr}+\left[\left(\frac{1+s^2}{2}\right)^2-1\right]\ln\left(\frac{1+s^2-2sr}{1+s^2+2sr}\right).\\ s &= \frac{\xi\omega n_o}{[1+(\xi k)^2]^{1/2}},\quad r = \frac{\xi k}{[1+(\xi k)^2]^{1/2}}\end{aligned} \tag{30}$$

The change of azimuth, $\Delta\theta$ is

$$\begin{aligned}\Delta\theta(k,\omega) &= \pm\frac{1}{64\pi}\left(\frac{\varepsilon_o+2}{3}\right)^2\frac{k_B T\chi}{k\omega\xi_2}\omega^4\\ &[\alpha^2_{xx}f_1(s,r)+2\alpha^2_{zz}f_2(s,r)]\rho^2_o l.\end{aligned} \tag{31}$$

where the sign ± corresponds to the lights polarized linearly above and below the horizontal at 45°, respectively. Let us take the zeroth approximation for k, that is,

$$k \cong n_o\omega;\ n_o = \varepsilon_o^{1/2}, \tag{32}$$

where n_o is the refractive index.

When the system is in the critical region far from the critical point, that is, $\xi\omega n_o \ll 1$, we have

$$Im\,\gamma(\omega)^f_{xx} = -\frac{1}{6\pi}\varepsilon_o^{1/2}\left(\frac{\varepsilon_o+2}{3}\right)^2(\alpha_{xx}\rho_o)^2 k_B T\chi\omega^3, \tag{33a}$$

$$Im\,\gamma(\omega)^f_{zz} = -\frac{1}{6\pi}\varepsilon_o^{1/2}\left(\frac{\varepsilon_o+2}{3}\right)^2(\alpha_{zz}\rho_o)^2 k_B T\chi\omega^3. \tag{33b}$$

$$\Delta\theta(\omega) = \mp\frac{1}{24\pi}\varepsilon_o^{1/2}\left(\frac{\varepsilon_o+2}{3}\right)^2 k_B T\chi\omega^4 [(\alpha_{xx}\rho_o)^2-(\alpha_{zz}\rho_o)^2]l. \tag{33c}$$

The $\Delta\theta$ becomes divergent as the isothermal compressibility coefficient κ diverges as ξ^2 and is proportional to ω^4.

If the system is very close to its critical point, the results are

$$Im\,\gamma(\omega)^f_{xx} = \frac{1}{16\pi n_o}\left(\frac{\varepsilon_o+2}{3}\right)^2(\alpha_{xx}\rho_o)^2\frac{k_B T\kappa}{\xi^2}\omega [1-2\ln(2\xi n_o\omega)]. \tag{34a}$$

$$Im\,\gamma(\omega)^f_{zz} = \frac{1}{8\pi n_o}\left(\frac{\varepsilon_o+2}{3}\right)^2(\alpha_{zz}\rho_o)^2\frac{k_B T\kappa}{\xi^2}\omega. \tag{34b}$$

$$\Delta\theta(\omega) = +\pm\frac{1}{16\pi}\frac{1}{\varepsilon_o^{1/2}}\left(\frac{\varepsilon_o+2}{3}\right)^2 k_B T\kappa\xi^{-2}\omega^2 [(\alpha_{xx}\rho_o)^2[1-\ln(2\xi n_o\omega)]-2(\alpha_{zz}\rho_o)^2]l, \tag{34c}$$

if $\xi n_o\omega \gg 1$.

When the system is extremely close to the critical point, the behavior of $\Delta\theta$ is described by Eq. (34c), when $k \cong n_o\omega$. The effect of density fluctuations in the case of $\xi\omega n_o \gg 1$ is quite different from that given in eq. (33c). It is logarithmically divergent. Futhermore the change of azimuth close to the critical point behaves as extinction ω^2 rather than ω^4. It is very interesting that the change of azimuth shows the phenomena of critical opalescence.[9-10]

The critical behavior of the ellipticity change. The real part of $\gamma^f_{\alpha\alpha}$ may be written as.

$$Re\,\gamma^f_{\alpha\alpha}(k,\omega) = \alpha_{\alpha\beta}\rho_o + Re\,\gamma^f_{\alpha\alpha}(k,0) + Re\,\gamma^f_{\alpha\alpha}(k,\omega). \tag{35}$$

The first part in the right hand side of Eq. (34) is due to the anisotropy of molecular polarizability tensor. The second and third terms are due to the static and dynamic parts of the renormalized propagator, respectively. The static part can be analytically obtained in the case that the correlation length is much larger than the diameter of a molecule, that is, $\xi \gg a$. The solutions are given as

$$Re\,\gamma^f_{xx}(k,0) = \alpha_{xx}\rho_o + \frac{1}{27\pi^2}\left[\frac{(\varepsilon_o+2)}{(\varepsilon_o-1)}\right](\alpha_{zz}\rho_o)^2 k_B T\kappa\xi^{-2} \left[\frac{1}{a}Q(\alpha_o\rho_o) - \frac{9}{32}\frac{\pi k}{\varepsilon_o}(\varepsilon_o-1)\left(\frac{\varepsilon_o+2}{3}\right)\Phi(\xi k)\right]. \tag{36a}$$

$$Re\,\gamma^f_{zz}(k,0) = \alpha_{zz}\rho_o + \frac{1}{27\pi^2}\left[\frac{(\varepsilon_o+2)}{(\varepsilon_o-1)}\right](\alpha_{zz}\rho_o)^2 k_B T\kappa\xi^{-2} \left[\frac{1}{a}Q(\alpha_o\rho_o) - \frac{9}{16}\frac{\pi k}{\varepsilon_o}(\varepsilon_o-1)\left(\frac{\varepsilon_o+2}{3}\right)\Phi(\xi k)\right]. \tag{36b}$$

where we have neglected the term proportional to ξ^{-1} and the functions are defined as

$$Q(\alpha_o\rho_o) = \int_0^\infty dx\,\Gamma(x)^2[1+\Gamma(x)]^{-1},$$

$$\Phi(\xi k) = \frac{1}{b^4}\sin^{-1}b - \frac{2b^2+3}{2b^3}(1-b^2)^{1/2};$$

$$b = \frac{\xi k}{(1+\xi k^2)^{1/2}}. \tag{37}$$

The function $Q(\alpha_o\rho_o)$ may be approximated as

$$Q(\alpha_o\rho_o) \cong \frac{3\pi}{5}\left(\frac{3\alpha_o\rho_o}{3+2\alpha_o\rho_o}\right)^2. \tag{38}$$

When the fluid is in the critical region far from the critical point, $\Phi(\xi k)$ becomes

$$\Phi(\xi k) \cong \frac{8}{15}\xi k. \tag{39}$$

If the system is very close to the critical point, the function has the following maximal limit value

$$\Phi(\xi k) \cong \frac{1}{2}\pi. \tag{40}$$

The first term is much larger than the other in the two extreme cases. Thus, $\gamma(k,0)^f_{\alpha\alpha}$ becomes

$$Re\,\gamma(k,0)^f_{\alpha\alpha} = \frac{1}{27\pi^2}\left(\frac{\varepsilon_o+2}{\varepsilon_o-1}\right)(\alpha_{\alpha\alpha}\rho_o)^2 k_B T\kappa\xi^{-2} \times\frac{1}{a}Q(\alpha_o\rho_o). \tag{41}$$

if $a \ll \xi$.

The components of dynamic part are expressed as

$$\Delta\gamma^f_{xx}(k,\omega) = \frac{1}{16\pi}\left[\frac{\varepsilon_o+2}{3}\right]^2(\alpha_{xx}\rho_o)^2 \times k_B T\kappa\xi^{-2}\omega^2 k^{-1}H_1(r,s), \tag{42a}$$

$$\Delta\gamma^f_{zz}(k,\omega) = \frac{1}{8\pi}\left[\frac{\varepsilon_o+2}{3}\right]^2(\alpha_{zz}\rho_o)^2 \times k_B T\kappa\xi^{-2}\omega^2 k^{-1}H_2(r,s). \tag{42b}$$

where the functions H_1 and H_2 are given as

$$H_1(r,s) = \left(1+\frac{1}{2r^2}-\frac{1-s^4}{4s^2r^2}\right)\sin^{-1}r - \frac{1}{2r}(1-r^2)^{1/2} + \left[1+\left(\frac{1+s^2}{2sr^2}\right)^2\right]\times\tan^{-1}\left[\left(\frac{1-s^2}{1+s^2}\right)\frac{r}{(1-r^2)^{1/2}}\right], \tag{43a}$$

$$H_2(r,s) = \left(1-\frac{1}{2r^2}+\frac{1-s^4}{4s^2r^2}\right)\sin^{-1}r - \frac{1}{2r}(1-r^2)^{1/2} +$$

$$\left[1+\left(\frac{1+s^2}{2sr^2}\right)^2\right]\times\tan^{-1}\left[\left(\frac{1-s^2}{1+s^2}\right)\frac{r}{(1-r^2)^{1/2}}\right]. \quad (43b)$$

When the system is in the critical region far from its critical point, the functions become

$$H_1(r,s)=8\xi/k,\ H_2(r,s)=4\xi/k, \quad (44)$$
$$\text{if } \xi k \text{ and } \xi\omega n_o \ll 1.$$

Using these results, we obtain

$$\Delta\gamma^f_{\alpha\alpha}(k,\omega)=\frac{1}{6\pi}\left[\frac{(\varepsilon_o+2)}{3}\right]^2(\alpha_{\alpha\alpha}\rho_o)^2k_BT\kappa\xi^{-1}\omega^2. \quad (45)$$
$$\text{if } \xi k \text{ and } \xi n_o\omega \ll 1.$$

From Eqs. (41) and (45), the change of ellipticity is expressed as

$$\Delta\eta=\mp\frac{\omega}{4}(1+A)(\alpha_{xx}-\alpha_{zz})\rho_o l, \quad (46)$$
$$\text{if } \xi n_o\omega \ll 1 \text{ and } \xi \gg a,$$

where the sign $\mp$ corresponds to the lights polarized linearly above(below) the horizontal at 45°, respectively.

$$A\approx\frac{1}{54\pi}(\varepsilon_o+2)(\alpha_{xx}+\alpha_{zz})\rho_o k_BT\kappa\xi^{-2}$$
$$\left[\frac{2}{\pi(\varepsilon_o-1)}\frac{1}{a}Q(\alpha_o\rho_o)+(\varepsilon_o+2)\xi\omega^2\right]. \quad (47)$$

The parameter A describes the effect of density fluctuations on ellipticity change. The molecular effect on $\Delta\eta$ is larger than the effect of density fluctuations in the case that the system is far from the critical point.

If the system is very close to the critical point, $\Delta\gamma(\omega)^f_{\alpha\alpha}$ is obtained by using the zeroth approximation for k in Eq. (32)

$$\Delta\gamma^f_{xx}(\omega)=\frac{3}{64}\left[\frac{(\varepsilon_o+2)}{3}\right]^2(\alpha_{\alpha\alpha}\rho_o)^2k_BT\kappa\xi^{-1}\omega^2. \quad (48a)$$
$$\text{if } \xi n_o\omega \gg 1.$$

$$\Delta\gamma^f_{zz}(\omega)=\frac{1}{32}\varepsilon_o^{1/2}\left[\frac{(\varepsilon_o+2)}{3}\right]^2(\alpha_{zz}\rho_o)^2k_BT\kappa\xi^{-1}\omega^2. \quad (48b)$$
$$\text{if } \xi n_o\omega \gg 1.$$

$\gamma(r,0)^f_{\alpha\alpha}$ given in Eq. (41) can be neglected compared with $\Delta\gamma(\omega)^f_{\alpha\alpha}$ of Eqs. (48). Thus, $\Delta\eta(\omega)$ in the case of $\xi n_o \gg 1$ is expressed as

$$\Delta\eta=\mp\frac{1}{4}(\alpha_{xx}-\alpha_{zz})\rho_o\omega l\mp\frac{1}{256\pi}\varepsilon_o^{1/2}\left(\frac{\varepsilon_o+2}{3}\right)^2$$
$$[3(\alpha_{xx}\rho_o)^2-(\alpha_{zz}\rho_o)^2]\times k_BT\kappa\xi^{-2}\omega^2 l, \quad (49)$$
$$\text{if } \xi n_o\omega \gg 1.$$

The term due to the density fluctuations is proportional to ω^2, while the molecular contributing term behaves as ω. The effect of density fluctuations becomes important as the system approaches the critical point. Extremely close to the critical point the term can be comparable or larger than the molecular contribution.

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