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Molecular-theory of high frequency dielectric susceptibility of nematic and cholesteric nano-composites

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Abstract: A molecular-statistical theory of the high frequency dielectric susceptibility of the nematic nanocomposites has been developed and approximate analytical expressions for the susceptibility have been obtained in terms of the effective polarizability of a nanoparticle in the nematic host, volume fraction of the nanoparticles and the susceptibility of the pure nematic phase. A simple expression for the split of the plasmon resonance of the nanoparticles in the nematic host has been obtained and it has been shown that in the resonance frequency range the high frequency dielectric anisotropy of the nanocomposite may be significantly larger then that of the pure nematic host. As a result all dielectric and optical properties of the nanocomposite related to the anisotropy are significantly enhanced which may be important for emerging applications. The components of the dielectric susceptibility have been calculated numerically for particular nematic nanocomposites with gold and silver nanoparicles as functions of the nanoparticle volume fraction and frequency. The splitting of the plasmon resonance has been observed together with the significant dependence on the nanoparticle volume fraction and the parameters of the nematic host phase.

Keywords: liquid crystal; molecular-statistical theory; nanocomposite

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1. Introduction

Nematic liquid crystals LCs have a long history, and numerous contemporary applications. During the past decade there has been significant interest in LC nano-composite, in which metal, dielectric or semiconductor nanoparticles (NPs), which are close to the size of typical mesogenic molecules, modify and improve the LC properties. It has been shown that doping of a nematic LC with small NP volume concentration can affect many important nematic phase properties, e.g. decrease in threshold and switching voltages as well as switching times of LC displays (see, for example, Refs. [1–5]). Suspensions of NPs in various nematic LCs have been investigated by many authors and, in particular, doping of nematics with ferroelectric NPs is known to enhance dielectric and optical anisotropy, increase the electro-optic response [6,7] and improve the photorefractive properties [8]. Suspensions of para- and ferromagnetic particles in nematics are promising candidates for magnetically tunable structures, and doping of ferroelectric LCs with metal and silica nanoparticles enables one to improve the spontaneous polarization and dielectric permittivity and to decrease switching times [9–11]. Finally, distributing semiconductor quantum dots in smectic LC-polymers enables one to achieve the positional ordering of nanosize particles [14,15]. At the same time the LC medium may also effect the properties of NPs including, in particular, their polarizability. For instance, the localized plasmon resonance of gold NPs can be tuned by changing the refractive index and, in particular, the birefringence of the surrounding LC medium [17–19].

The effect of NPs on various properties of nematic LCs is mainly determined by the anisotropic interactions between NPs and mesogenic molecules. Many NPs are approximately spherical or weakly anisometric. In this case the corresponding anisotropic interaction potential is determined by anisotropic charge distribution and the anisotropy of the polarizability of a NP or a mesogenic molecule. For nonpolar particles the anisotropic interaction is dominated by the dispersion interaction which is determined by the dielectric properties of the interacting particles. In particular, the leading contribution is the so-called dipole-dipole dispersion interaction potential which is given by the following general expression (see, for example, [24]):

$$U(\mathbf{R}) = -\frac{h}{2\pi}\int_0^\infty Tr\left[\alpha^{NP}(i\omega)\cdot T(\mathbf{R})\cdot\alpha^{m}(i\omega)\cdot T(\mathbf{R})\right]d\omega, \tag{1}$$

where $\alpha^{NP}(i\omega)$ is the polarizabiity tensor of a NP, $\alpha^{m}(i\omega)$ is the polarizability tensor of a mesogenic molecule, h is the Plank constant and $T_{\alpha\beta}(\mathbf{R}) = R^{-5}\left(3R_\alpha R_\beta - R^2\delta_{\alpha\beta}\right)$ is the dipole-dipole propagator tensor where $\mathbf{R}$ is the intermolecular vector.

One can readily see that the anisotropic interaction (which depends on the direction of the intermolecular vector $\mathbf{R}$) is determined by the anisotropy of the polarizability of both NPs and mesogenic molecules. One notes also that typical NPs have the size of several mesogenic molecues, and in this case the effective polarizability of such a NP is renormalised by the dielectric properties of the surrounding LC medium as the NP is interacting simultaneously with many mesogenic molecules. Thus it is very important to obtain at least qualitative expressions for the effective polarizability of a NP embedded in the LC dielectric medium which is the aim of the present paper.

2. Results

2.1. High frequency dielectric susceptibility of the nematic nano-composite

As shown in [20] the general expression for the tensor dielectric constant of the nematic phase doped with NPs can be expressed in the form of the generalized Clausius-Mossotti equation in which the average polarizability of a single molecule is replaced by the effective renormalized polarizability that depends both on intermolecular interactions and correlations and on interactions and correlations between NPs and neighboring mesogenic molecules:

$$(\hat{\varepsilon}-1)(\hat{\varepsilon}+2)^{-1} = \frac{4\pi}{3}\hat{\alpha}, \tag{2}$$

where

$$\hat{\alpha} = \langle\hat{\gamma}(1+\hat{H}\hat{\gamma})^{-1}\rangle\langle(1+\hat{H}\hat{\gamma})^{-1}\rangle^{-1}, \tag{3}$$

and where $\hat{\gamma}$ is the weighted sum of the microscopic polarizabiities of the mesogenic molecule and the NP which depends on the fluctuating orientation and position of both mesogenic molecules and the NPs:

$$\hat{\gamma}(\omega) = \sum_\alpha \int \hat{\beta}_\alpha(\theta,\omega)\rho_\alpha(\theta,\mathbf{r})d\theta. \tag{4}$$

and ρ_α is the microscopic number density of molecules of type α:

Here the operator $\hat{H} = \hat{F}$ when $|\mathbf{r}-\mathbf{r}| > D$ and $\hat{H} = 0$ when $|\mathbf{r}-\mathbf{r}| < D$, where D is the molecular diameter and the operator $\hat{F}$ is equal to the dipole-dipole propagator if the correlation radius of the nematic is smaller then the wavelength of light:

$$\hat{F}(\mathbf{r}-\mathbf{r}',\omega) = \frac{4\pi}{3}\delta(\mathbf{R}) + (3\mathbf{u}\otimes\mathbf{u}-\hat{I})R^{-3}. \tag{5}$$

The renormalized polarizability $\hat{\alpha}$ can be expanded in powers of the polarizability fluctuation $\Delta\gamma = \gamma - \langle\gamma\rangle$ where $\langle\gamma\rangle$ is the average polarizability:

$$\hat{\alpha} = \langle\gamma\rangle - \langle\Delta\gamma\hat{K}\Delta\gamma\rangle + ..., \tag{6}$$

where $\hat{K} = (1 + \hat{H}\langle\hat{\gamma}\rangle)^{-1}\hat{H}$.

Taking into account Eq. (4), the renormalised weighted polarizability can be written in the form:

$$\hat{\alpha} = \sum_{\alpha}\langle\hat{\beta}_{\alpha}\rangle\rho_{\alpha} - \sum_{\alpha,\beta}\hat{\lambda}_{\alpha,\beta}\rho_{\alpha}\rho_{\beta} + ..., \tag{7}$$

where $\langle\hat{\beta}_{\alpha}\rangle$ is the average polarizability of the component α and

$$\hat{\lambda}_{\alpha,\beta} = \int g_{\alpha,\beta}(\mathbf{R}, \theta, \theta')\hat{\beta}_{\alpha}(\theta)K(\mathbf{R}, \omega)\hat{\beta}_{\beta}(\theta')d\mathbf{R}d\theta d\theta'. \tag{8}$$

Here $\alpha = m, n$ where m denotes the mesogenic molecules of the host nematic phase and n denotes the NPs. The functions $g_{\alpha,\beta}(\mathbf{R}, \theta, \theta')$ are the pair correlation functions between the particles of the components α and β, and $K(\mathbf{R}, \omega)$ is the kernel of the operator $\hat{K}$. The higher order terms in Eqs. (6) and (7) depend on higher order correlation functions.

Usually the volume fraction of NPs in the nematic nano-composite is very small, and then the correlations between NPs can be neglected in the first approximation. As a result Eq.(2) can be written in the following form taking into account also Eq.(7):

$$(\hat{\varepsilon} - 1)(\hat{\varepsilon} + 2)^{-1} = \frac{4\pi}{3}\left((1 - \phi)\hat{\beta}_m^{eff}\rho_m + \phi\hat{\beta}_{NP}^{eff}\right), \tag{9}$$

where ϕ is the volume fraction of the NPs and the effective nondimentional polarizability of a mesogenic molecule is expressed as

$$\hat{\beta}_m^{eff} = v_m^{-1}\left(\langle\hat{\beta}_m\rangle + \hat{\lambda}_{m,m}\rho_m\right). \tag{10}$$

Here v_m is the volume of the mesogenic molecule while $\hat{\lambda}_{m,m}$ is determined by the correlations between neighboring mesogenic molecules and is given by the general Eq.(8).

Similarly the effective nondimentional polarizability of an NP reads:

$$\hat{\beta}_{NP}^{eff} = v_{NP}^{-1}\left(\langle\hat{\beta}_{NP}\rangle + \hat{\lambda}_{NP,m}\rho_m\right), \tag{11}$$

where v_{NP} is the volume of the mesogenic molecule and $\hat{\lambda}_{NP,m}$ is determined by the correlations between the NP and the neighboring mesogenic molecules.

One notes that at small volume fraction of NPs the effective polarizability of the mesogenic molecule $\hat{\beta}_m^{eff}$ is independent on the NPs in the first approximation and hence it can be expressed in terms of the dielectric tensor $\hat{\varepsilon}_{LC}$ of the nematic host phase:

$$(\hat{\varepsilon}_{LC} - 1)(\hat{\varepsilon}_{LC} + 2)^{-1} = \frac{4\pi}{3}\hat{\beta}_m^{eff}. \tag{12}$$

Thus Eq.(9) can be rewritten in the form:

$$(\hat{\varepsilon} - 1)(\hat{\varepsilon} + 2)^{-1} = (1 - \phi)(\hat{\varepsilon}_{LC} - 1)(\hat{\varepsilon}_{LC} + 2)^{-1}\frac{4\pi}{3}\phi v_{NP}^{-1}\hat{\beta}_{NP}^{eff}, \tag{13}$$

where v_{NP} is the nanoparticle volume. From Eq.(12) the dielectric tensor of the nematic composite can be expressed as:

$$\hat{\varepsilon} = \frac{(\hat{\varepsilon}_{LC} + 2\hat{I}) + 2\left[(1 - \phi)(\hat{\varepsilon}_{LC} - \hat{I}) + \frac{4\pi}{3}\phi v_{NP}^{-1}\hat{\beta}_{NP}^{eff}(\hat{\varepsilon}_{LC} + 2\hat{I})\right]}{(\hat{\varepsilon}_{LC} + 2\hat{I}) - \left[(1 - \phi)(\hat{\varepsilon}_{LC} - \hat{I}) + \frac{4\pi}{3}\phi v_{NP}^{-1}\hat{\beta}_{NP}^{eff}(\hat{\varepsilon}_{LC} + 2\hat{I})\right]}. \tag{14}$$

2.2. *Effective polarizability of a nanoparticle in the nematic liquid crystal medium*

We will use a simple model of a spherical metal nanoparticle with a plasmon response which is described in the first approximation by the Drude model:

$$\epsilon_{Me}(\omega) = 1 - \frac{(\omega_p \tau)^2}{\omega\tau\,(\omega\tau + i)}, \tag{15}$$

where ω_p is the metal plasmon frequency and τ is the mean free time of electrons. In the simplest case ω_p can be expressed as $\omega_p = 4\pi n_e e m_e^{-1}$ where n_e is the concentration of the conductivity electrons and m_e is their effective mass. One notes that in the optical range in noble metals $\omega\tau \gg 1$.

Effective dielectric properties of a relatively small NP in the nematic medium is determined by the interaction with the first layer of mesogenic molecules. This layer can be considered isotropic in the first approximation because of the competing tendencies to align along the macroscopic director and parallel (or perpendicular) to the strongly curved surface of an NP. Thus the first molecular layer can be modelled as an isotropic dielectric medium with the average dielectric susceptibility

$$\epsilon_s = \frac{1}{3}\left(\epsilon_{||} + 2\epsilon_{\perp}\right). \tag{16}$$

Here $\epsilon_{||}$ and $\epsilon_{\perp}$ is the longitudinal and the transverse susceptibility of a nematic phase, respectively.

Such an approximation is sufficient to estimate the effective polarizability of a spherical NP renormalised by the interaction with the surrounding medium. In the framework of the quasi static approach the effective polarizability of an NP can be expressed as [25]:

$$\alpha_{NP} = a^3 \epsilon_s \frac{(\epsilon_{Me} - \epsilon_s)}{(\epsilon_{Me} + 2\epsilon_s)}, \tag{17}$$

where a is the radius of the NP. The effective polarizability is characterised by the Mi plasmonic resonance [26] at the frequency which corresponds to the solution of the equation $Re(\epsilon_{Me}) = -2\epsilon_s$ yielding $\omega = \omega_{r0} = \omega_p(1+\epsilon_s)^{-1/2}$.

The real and imaginary parts of the effective polarizability of the AuNPs and silver NPs (AgNPs) in the nematic host 4-cyano-4′-pentylbiphenyl (5CB) are presented in Fig.1 as functions of cyclic frequency. The polarizability has been calculated numerically using the data on the frequency dependendent susceptibility of gold and silver [22] and of the nematic 5CB [23]. The selected frequency range corresponds to the one where the dispersion of both longitudinal and transverse susceptibility of 5CB has been carefully measured [23]. One can readily see that the plasmonic resonance frequency of the AuNP in the nematic host is within the selected frequency range while the resonance frequence of the AgNP is outside the range at higher frequency.

Substituting Eq.(16) into Eq.(13) one obtains the final expression for the dielectric tensor of the nano-composite:

$$\hat{\varepsilon} = \frac{(\hat{\varepsilon}_{LC} + 2\hat{I})(\epsilon_{Me} + 2\epsilon_s) + 2\left[(1-\phi)(\hat{\varepsilon}_{LC} - \hat{I})(\epsilon_{Me} + 2\epsilon_s) + \phi\epsilon_s(\epsilon_{Me} - \epsilon_s)(\hat{\varepsilon}_{LC} + 2\hat{I})\right]}{(\hat{\varepsilon}_{LC} + 2\hat{I})(\epsilon_{Me} + 2\epsilon_s) - \left[(1-\phi)(\hat{\varepsilon}_{LC} - \hat{I})(\epsilon_{Me} + 2\epsilon_s) + \phi\epsilon_s(\epsilon_{Me} - \epsilon_s)(\hat{\varepsilon}_{LC} + 2\hat{I})\right]}. \tag{18}$$

The longitudinal an transverse components of the dielectric tensor can now be expressed as:

$$\varepsilon_{\|} = \frac{(\varepsilon^0_{\|} + 2)(\epsilon_{Me} + 2\epsilon_s) + 2\left[(1-\phi)(\varepsilon^0_{\|} - 1)(\epsilon_{Me} + 2\epsilon_s) + \phi\epsilon_s(\epsilon_{Me} - \epsilon_s)(\varepsilon^0_{\|} + 2)\right]}{(\varepsilon^0_{\|} + 2)(\epsilon_{Me} + 2\epsilon_s) - \left[(1-\phi)(\varepsilon^0_{\|} - 1)(\epsilon_{Me} + 2\epsilon_s) + \phi\epsilon_s(\epsilon_{Me} - \epsilon_s)(\varepsilon^0_{\|} + 2)\right]}, \tag{19}$$

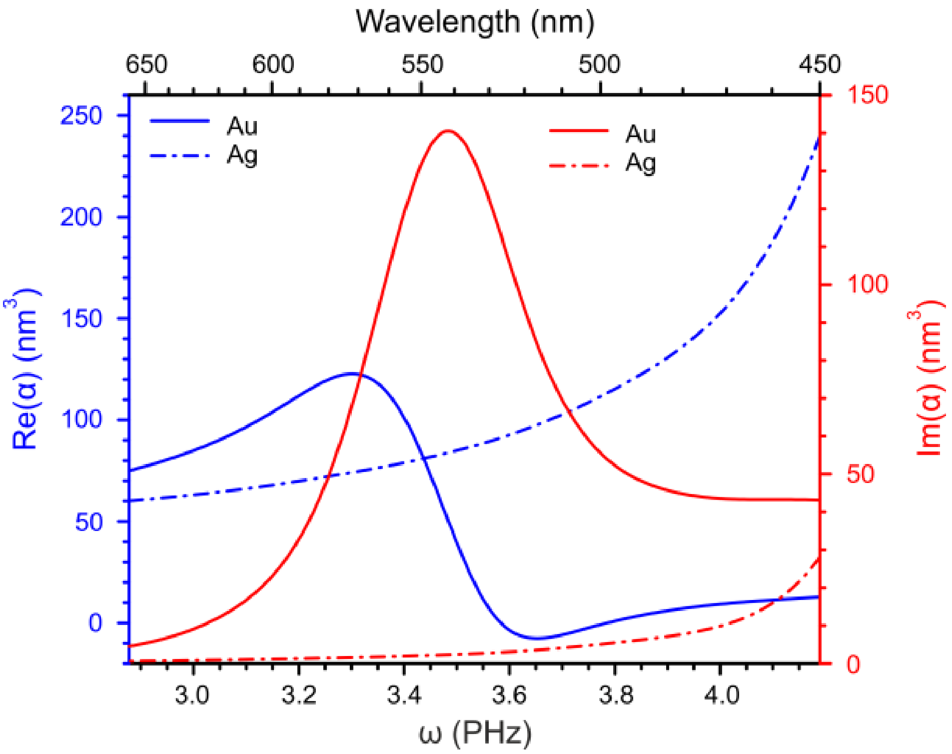


Figure 1. Frequency dependence of the effective polarizability of AuNP and AgNP of the radius $2.5nm$ in the nematic host 5CB.

$$\varepsilon_{\perp} = \frac{(\varepsilon^{0}_{\perp} + 2)(\epsilon_{Me} + 2\epsilon_s) + 2\left[(1-\phi)(\varepsilon^{0}_{\perp} - 1)(\epsilon_{Me} + 2\epsilon_s) + \phi\epsilon_s(\epsilon_{Me} - \epsilon_s)(\varepsilon^{0}_{\perp} + 2)\right]}{(\varepsilon^{0}_{\perp} + 2)(\epsilon_{Me} + 2\epsilon_s) - \left[(1-\phi)(\varepsilon^{0}_{\perp} - 1)(\epsilon_{Me} + 2\epsilon_s) + \phi\epsilon_s(\epsilon_{Me} - \epsilon_s)(\varepsilon^{0}_{\perp} + 2)\right]}. \qquad (20)$$

One notes that Eqs.(19) and (20) can be used both in the nematic and in the smectic A phase because both phases are uniaxial and the smectic positional order does not practically effect the optical properties of the system because the period of the smectic structure is much less then the wavelength of light. On the other hand, in the cholesteric phase the primary axis of the local dielectric tensor is following the helical structure together with the spatially inhomogeneous director $\mathbf{n}(z)$. In this case the inhomogeneous dielectric tensor of the nematic nano-composite can be written in the form:

$$\hat{\varepsilon}(z) = \epsilon_{\perp}\hat{I} + \Delta\epsilon\mathbf{n}(z)\mathbf{n}(z), \qquad (21)$$

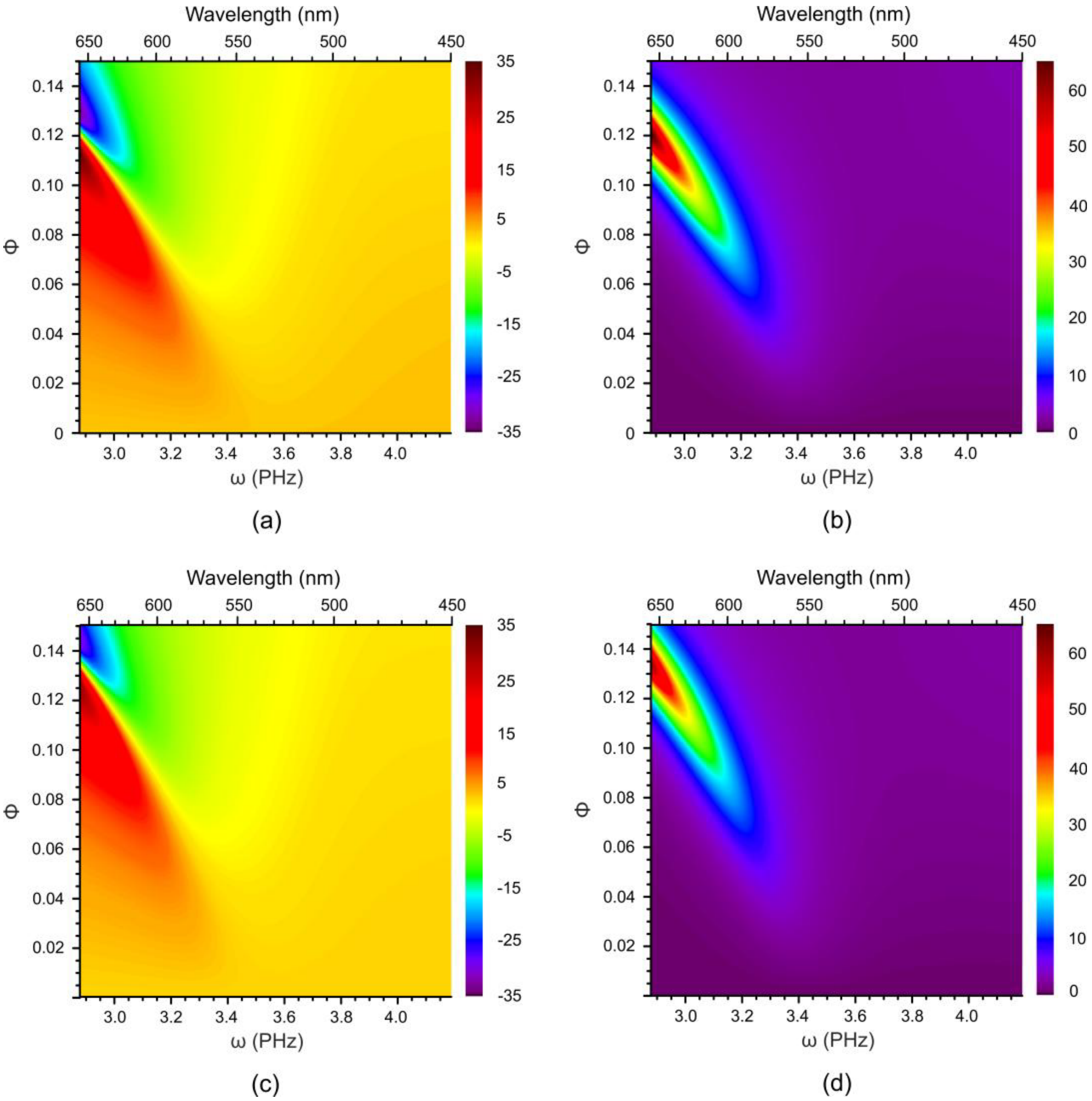
where $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$ and where $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ are given by Eqs.(19),(20). Here the director $\mathbf{n}(z)$ describes the helix according to the equation:

$$\mathbf{n} = \mathbf{x}\cos(qz) + \mathbf{y}\sin(qz). \qquad (22)$$

where q is pitch.

The real and imaginary parts of the longitudinal and the transverse components of the dielectric susceptibility are presented in Figs.2 and 3 as functions of both frequency and the volume fraction ϕ of the NPs for nano-composites based on the nematic host 5CB and AuNPs and AgNPs, respectively. One notes that in both nano-composites the plasmon resonance is visible although its frequency range is significantly wider in the case of AuNPs.

Frequency dependence of the components of the dielectric susceptibility of the same nematic nano-composites with AuNPs and AgNPs is presented separately in Figs.4 and 5 for two different



(a) (b)

(c) (d)

Figure 2. The dependence of $Re(\epsilon_{\|})$ (a), $Im(\epsilon_{\|})$ (b), $Re(\epsilon_{\perp})$ (c) and $Im(\epsilon_{\perp})$ (d) of the nematic nano-composite (host 5CB plus AuNPs) on the volume fraction of AuNPs ϕ and cyclic frequency ω.

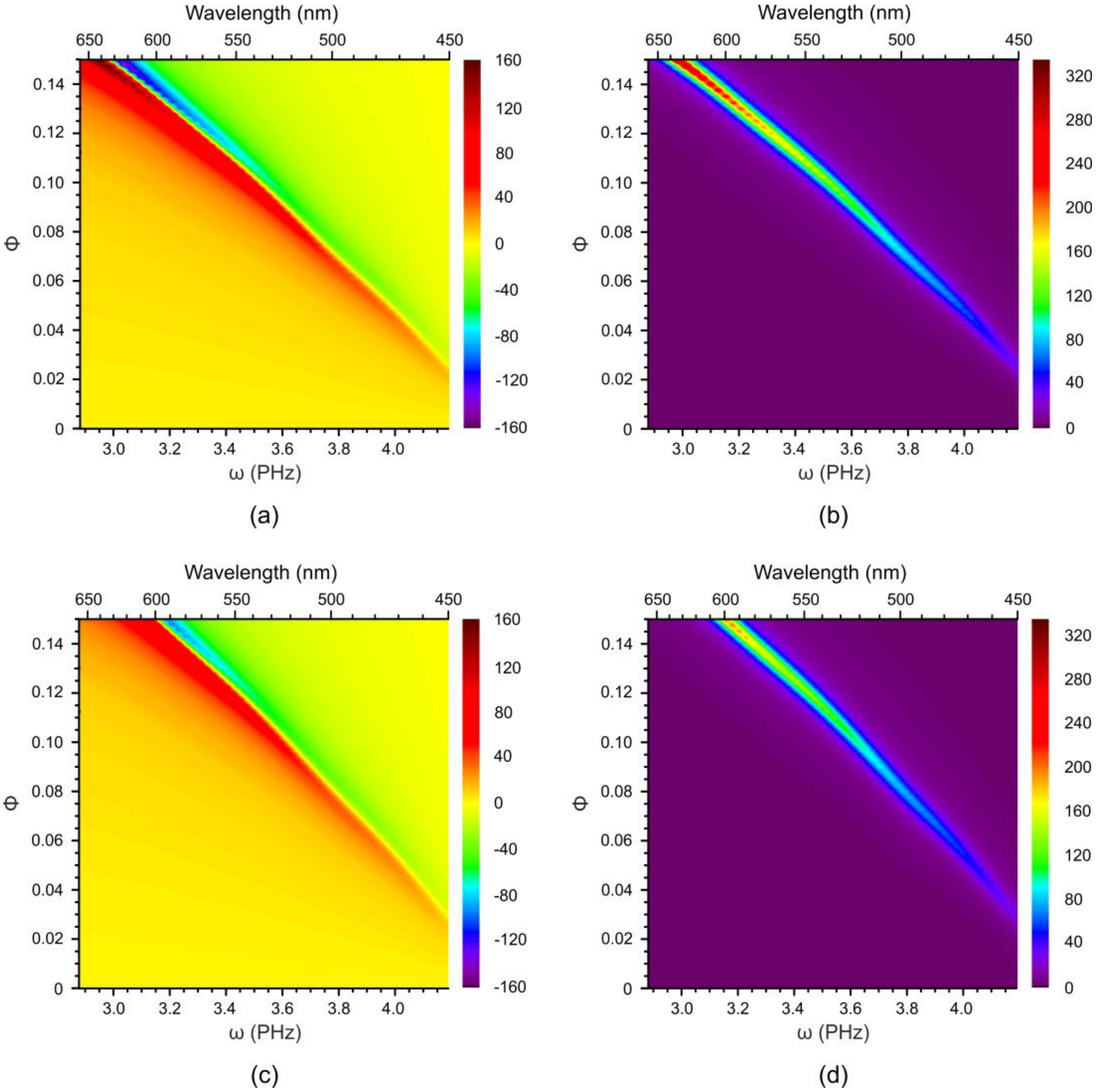


Figure 3. The dependence of $Re(\epsilon_{\|})$ (a), $Im(\epsilon_{\|})$ (b), $Re(\epsilon_{\perp})$ (c) and $Im(\epsilon_{\perp})$ (d) of the nematic nano-composite (host 5CB plus AgNPs) on the volume fraction of AgNPs ϕ and cyclic frequency ω.

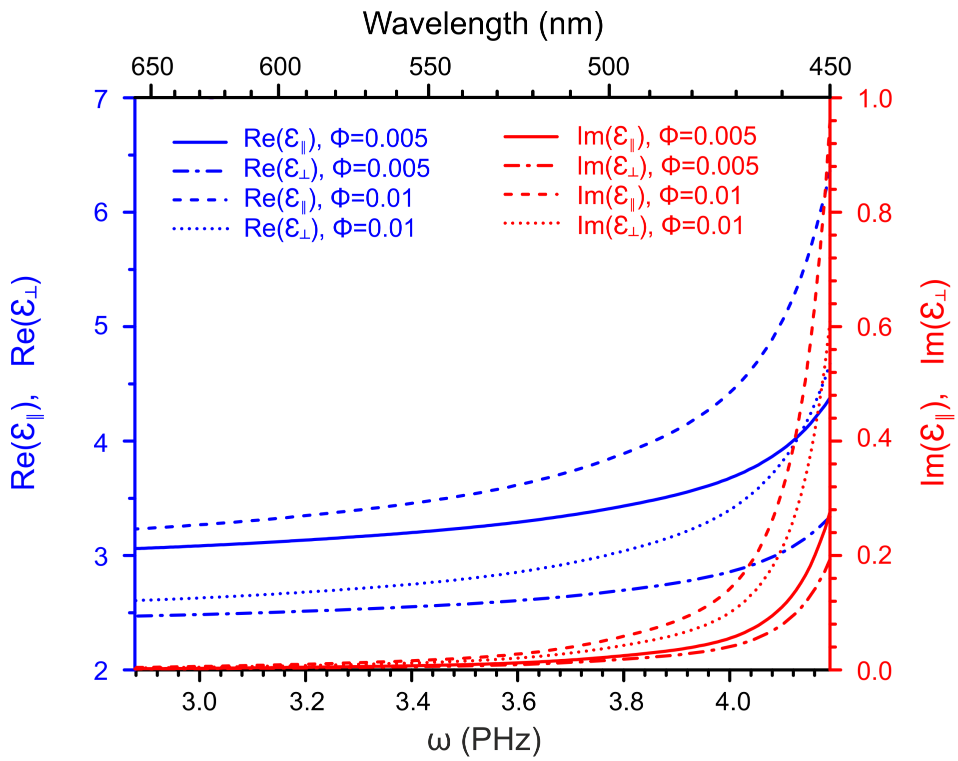


Figure 4. Frequency dependence of $Re(\epsilon_{\|})$, $Im(\epsilon_{\|})$, $Re(\epsilon_{\perp})$ and $Im(\epsilon_{\perp})$ of the nematic nano-composite (host 5CB plus AgNPs) for the two values of the NP volume fraction $\phi = 0.005$ and $\phi = 0.01$.

values of the NP volume fraction ϕ. Again one can readily see that the plasmonic resonance is not observed in the nano-composite with AgNPs because the resonance frequency of the effective polarizability of the AgNP (see Fig.1) is outside the selected frequency range where the dispersion of the susceptibility of the nematic host 5CB has been measured. One can also see the splitting of the plasmon resonance (i.e. the difference between the resonance frequencies of the longitudinal and transverse components of the dielectric susceptibility) and the shift of the resonance caused by the change of the NP volume fraction.

Finally we present the dependence of the real and imaginary components of the dielectric susceptibility on the volume fraction of AuNPs for two different nematic hosts 5CB and NM2, where NM2 is a mixture of various cyanobiphenyls [27]. One notes that the qualitative behaviour of the components of the dielectric susceptibility is similar although the values of the resonant frequencies strongly depend on the parameters of the nematic host.

2.3. Shifting of the plasmon resonance frequency in the nematic matrix

Let us consider now the shift and splitting of the plasmon resonance of the NPs caused by the nematic LC medium. The resonances of the NPs in the nematic medium are determined by the poles of the Eqs.(18) and (19) which are considered as functions of ω. Assuming that the LC medium is transparent one may also assume that the frequency dependence of the dielectric susceptibility of the nano-composite is determined by that of $\epsilon_m(\omega)$ which is a weakly complex number for $\omega\tau \gg 1$ according to Eq.(16).

Substituting Eq.(15) for ϵ_{Me} into Eqs.(18) and (19) and taking into consideration that the volume fraction of NPs is small $\phi \ll 1$, one obtains the following expressions for the resonance plasmon frequencies for the two orientations of the electric field of the light wave (parallel and perpendicular to the local director, respectively):

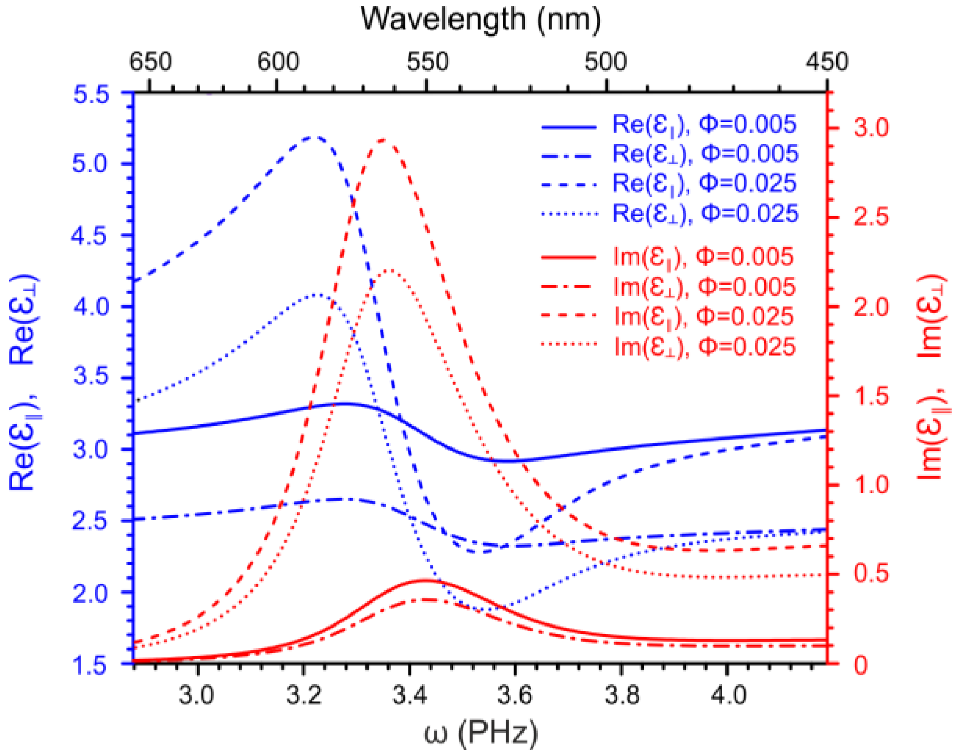


Figure 5. Frequency dependence of $Re(\epsilon_{\|})$, $Im(\epsilon_{\|})$, $Re(\epsilon_{\perp})$ and $Im(\epsilon_{\perp})$ of the nematic nano-composite (host 5CB plus AuNPs) for the two values of the NP volume fraction $\phi = 0.005$ and $\phi = 0.025$.

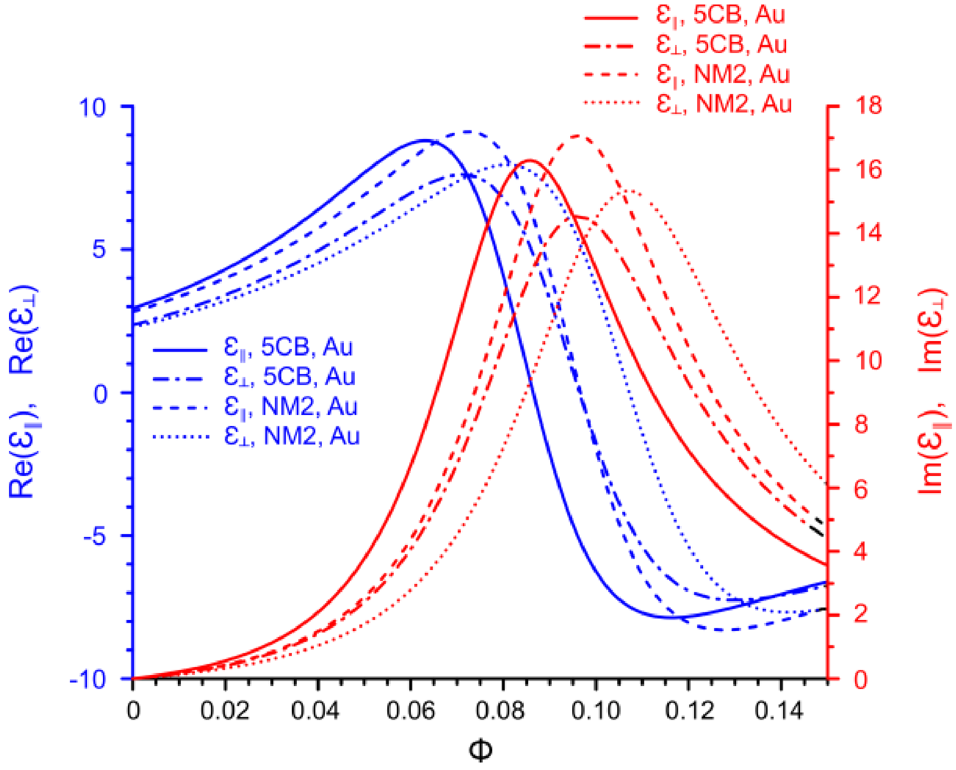


Figure 6. The dependence of $Re(\epsilon_{\|})$, $Im(\epsilon_{\|})$, $Re(\epsilon_{\perp})$ and $Im(\epsilon_{\perp})$ on the volume fraction of AuNPs ϕ for the two different nematic hosts 5CB and NM2 a fixed wavelength of light $\lambda = 589nm$.

$$\omega_{r\parallel} = \omega_{r0}\left(1 - \phi\epsilon_s \frac{\epsilon_\parallel + 2}{2 + 4\epsilon_s}\right), \tag{23}$$

$$\omega_{r\perp} = \omega_{r0}\left(1 - \phi\epsilon_s \frac{\epsilon_\perp + 2}{2 + 4\epsilon_s}\right). \tag{24}$$

Thus, in the framework of the present model the split of the plasmon resonance increases linearly as a function of the NP volume fraction:

$$\Delta\omega_r = \omega_{r\parallel} - \omega_{r\perp} = -\phi\omega_{r0}\frac{\Delta\epsilon\epsilon_s}{2 + 4\epsilon_s}. \tag{25}$$

It is important to find out at what volume fraction of nanoparticles the splitting of the plasmon resonance peak becomes strong. Qualitatively, strong splitting occurs when splitting at least exceeds the full width at half maximum of the plasmon resonance frequency in the nano-composite. Such a width is determined by then light absorption in the NPs which is controlled by the imaginary part of the NP polarizability (17) which should satisfy the inequality $Im(\epsilon_{Me}) < \phi\Delta\epsilon\epsilon_s$. This inequality, in turn, imposes the following lower bound on the mean free time of conductivity electrons in the metal according to Eq.(15):

$$\tau > \frac{1}{\omega_p}\frac{(1 + 2\epsilon_s)^{3/2}}{\phi\epsilon_s\Delta\epsilon}. \tag{26}$$

When this condition is satisfied the split between resonance plasmon frequencies, which correspond to different polarizations of the light wave, is sufficiently large and the anisotropy of the effective polarizability of the nano-composite in the resonance frequency domain is significantly larger then the anisotropy of the pure LC matrix $\Delta\epsilon^0$. As a result all effects related to the local dielectric anisotropy and its helical distribution in the cholesteric phase become particularly pronounced. The split of the plasmon resonance in the nematic nano-composites and its dependence on the NP volume fraction cam be clearly seen in Figs. 4-6.

3. Discussion

A rather general expression for the dielectric susceptibility of the nematic nano-composite has been obtained using the molecular-statistical theory of the dielectric properties of mixtures of LCs developed by one of the authors and M. V. Gorkunov [20,21]. In this theory the local electric field in the anisotropic LC medium is taken into account and the susceptibility of the composite is expressed in terms of the effective polarizability of the NPs, renormalised by the interaction with the first layer of mesogenic molecules, and the susceptibility of the pure nematic host. Simple analytical expression for the frequency dependent effective polarizability of a NP has been obtained using the model of a spherical metal NP embedded into the the dielectric medium.

The final expressions (18),(19) for the components of the high frequency dielectric susceptibility of the nematic composite appear to be nonlinear functions of the NP volume fraction although numerical calculations indicate that the deviation from the linear variation is relatively small. At the same time the rate of change of the susceptibility of the nano-composite with the increasing NP concentration strongly depends on the ratio of the NP polaizability and the average susceptibility of the pure nematic host. The contribution from the NPs to the total dielectric susceptibility of the nematic composite is particularly large when the frequency is in the plasmon resonance range. It has been shown that the split of the plasmon resonance (i.e. the difference between the resonance frequencies corresponding to the parallel and perpendicular orientation of the electric field with respect to the local director) is proportional to the volume fraction of nanoparticles in the first approximation. In the resonance frequency range the anisotropy of the dielectric susceptibility of the nano-composite may become significantly larger then that of the pure nematic phase and as a result all effects related to the anisotropy are strongly enhanced which may be important for optical applications of nano-composites.

Both real and imaginary parts of the longitudinal and the components of the dielectric susceptibility of the nematic nano-composites with gold and silver NPs have been calculated numerically as functions of frequency and the NP volume fraction. The splitting of the plasmon resonance has been observed as well as the dependence on the NP volume fraction. The components of the dielectric susceptibility have also been calculated for nano-composites based on the two different nematic hosts 5CB and NM2 and it has been shown that the resonance frequencies strongly depend on the parameters of the nematic host phase even in the case when the host have similar molecular structure.

One notes also that in the high optical frequency range the expression for the dielectric tensor of the nano-composite is also valid in the smectic A phase because this phase is also uniaxial and the smectic order does not contribute to the optical properties because the smectic periodicity is much smaller then the wavelength of light. In cholesteric nano-composites the present theory describes the local dielectric anisotropy which rotates in space following the helical structure of the inhomogeneous director. Finally it should be noted that a similar formalism can be used to obtain analytical expressions for the dielectric anisotropy of the nematic and cholesteric nano-composites with anisotropic NPs. This will be done in our next publication.

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

MDPI	Multidisciplinary Digital Publishing Institute
DOAJ	Directory of open access journals

References

1. H. Qi, B. Kinkead, and T. Hegmann, Effects of functionalized metal and semiconductor nanoparticles in nematic liquid crystal phases, *Proc. SPIE*. **6911**, 691106 (2008).
2. H. Qi and T. Hegmann, Formation of periodic stripe patterns in nematic liquid crystals doped with functionalized gold nanoparticles, *J. Mater. Chem.* **16**, 4197–4205 (2006).
3. Y. Shiraishi, N. Toshima, H. Maeds, K. Yoshikawa, J. Xu, and S. Kobayashi, Frequency modulation response of a liquid-crystal electro-optic device doped with nanoparticles, *Appl. Phys. Lett.* **81**(15), 2845–2847 (2002).
4. S. Kobayashi and N. Toshima, Nanoparticles and lcds: It's a surprising world, *Information Display*. **23**, 26 (2007).
5. H. Yoshida, K. Kawamoto, H. Kubo, A. Tsuda, T.and Fujii, S. Kuwabata, and M. Ozaki, Nanoparticle-dispersed liquid crystals fabricated by sputter doping, *Adv. Mater.* **22**, 622–626 (2010).
6. S. Kaur, S. P. Singh, A. M. Biradar, A. Choudhary, and K. Sreeniva, Enhanced electro-optical properties in gold nanoparticles doped ferroelectric liquid crystals, *Appl. Phys. Lett.* **91**, 023120 (2007).
7. A. Kumar, J. Prakash, A. M. Mehta, D. S. Biradar, and W. Haase, Enhanced photoluminescence in gold nanoparticles doped ferroelectric liquid crystals, *Appl. Phys. Lett.* **95**, 023117 (2009).
8. O. Buchnev, A. Dyadyusha, M. Kaczmarek, V. Reshetnyak, and Y. Reznikov, Enhanced two-beam coupling in colloids of ferroelectric nanoparticles in liquid crystals, *J. Opt. Soc. Am. B*. **24**(7), 1512–1516 (2007).
9. Y. Reznikov, O. Buchnev, O. Tereshchenko, V. Reshetnyak, A. Glushchenko, and J. West, Ferroelectric nematic suspension, *Appl. Phys. Lett.* **82**(12), 1917–1919 (2003).

10. F. Li, C. Buchnev, O. Cheon, A. Glushchenko, V. Reshetnyak, Y. Reznikov, T. Sluckin, and J. West, Orientational coupling amplification in ferroelectric nematic colloids, *Physical Review Letters*. **97**, 147801 (2006).
11. L. Lopatina and J. Selinger, Theory of ferroelectric nanoparticles in nematic liquid crystals, *Physical Review Letters*. **102**, 197802 (2009).
12. H. Yoshida, Y. Tanaka, H. T. T. Kawamoto, K. Kubo, A. Fujii, S. Kuwabata, H. Kikuchi, and M. Ozaki, Nanoparticle-stabilized cholesteric blue phases, *Applied Physics Express*. **2**, 121501 (2009).
13. S. Wiersma, The physics and applications of random lasers, *Nature Physics*. **4**, 359–367 (2008).
14. G. A. Shandryuk, E. V. Matukhina, R. B. Vasil'ev,A. Rebrov, G. N. Bondarenko, A. S. Merekalov, A. Gas'kov, and R. Talroze, Effect of h-bonded liquid crystal polymers on cdse quantum dot alignment within nanocomposite, *Macromolecules*. **41**, 2178–2185 (2008).
15. R. V. Tal'roze, G. A. Shandryuk, A. S. Merekalov, A. M. Shatalova, and O. A. Otmakhova, Alignment of nanoparticles in polymer matrices, *Polymer Science Ser. A*. **51**(12), 1194–1203 (2009).
16. W. Cai and V. Shalaev, *Optical Metamaterials: Fundamentals and Applications*. Springer (2009).
17. R. Pratibha, K. Park, I. Smalykh, and W. Park, Tunable optical metamaterial based on liquid crystal-gold nanosphere composite, *Optics Express*. **17**(22), 19459–19469 (2009).
18. A. Kossyrev, P. A. Yin, S. G. Cloutier, D. A. Cardimona, D. Huang, P. M. Alsing, and J. M. Xu, Electric field tuning of plasmonic response of nanodot array in liquid crystal matrix, *Nano Letters*. **5**(10), 1978–1981 (2005).
19. C. Y. Chu, K. C.and Chao, Y. F. Chen, Y. C. Wu, and C. C. Chen, Electrically controlled surface plasmon resonance frequency of gold nanorods, *Appl. Phys. Lett.* **89**, 103107 (2006).
20. Osipov, M. A. Gorkunov, M. V. Effect of nanoparticle chain formation on dielectric anisotropy of nematic composites. Phys. Rev. E. **92**, 032501 (2015)
21. Osipov, M. A. and Gorkounov, M. V. Nematic liquid crystals doped with nanoparticles: phase behavior and dielectric Properties Liquid Crystals with Nano and Microparticles. Lagerwall, J. P. F. and Scalia, G. (eds.). Singapore: World Scientific Publishing Company, **41** p, 2016.
22. P. B. Johnson and R. W. Christy. Optical constants of the noble metals. *Phys. Rev. B* **6**, 4370-4379 (1972).
23. J. Li, C. H. Wen, S. Gauza, R. Lu and S. T. Wu. Refractive indices of liquid crystals for display applications, *J. Disp. Technol.* **1**, 51-61 (2005).
24. J. Israelachvili, Intermolecular and Surface Forces, Academic Press, 2011.
25. L. D. Landau, and E. M. Lifshits, Electrodynamics of Continuous Media, Pergamon Press, 1960.
26. G. Mie, *Ann. Phys. (Leipzig)* **330**, 377 (1908).
27. V. S. Bezborodov, S. G. Mikhalyonok, N. M. Kuz'menok, A. S. Arol, G. A. Shandryuk, A. S. Merekalov, O. A. Otmakhova, G. N. Bondarenko, and R. V. Talroze. Anisotropic derivatives of (-)-L-lactic acid and their nanocomposites, *Liquid Crystals* **45**, (8) 1223–1233 (2018).