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Statistical Theory of Helical Twisting in Nematic Liquid Crystals Doped with Chiral Nanoparticles

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Abstract: A molecular field theory of the cholesteric ordering in nematic nanocomposites doped with chiral nanoparticles was developed taking into consideration chiral dispersion interaction between rod-like nanoparticles. It was shown that the inverse pitch of the cholesteric helical structure is proportional to the anisotropy of the effective polarizability and the anisotropy of the effective gyration tensor of a nanoparticle in the nematic host. The theory enables one to predict the helical sense inversion induced by a change of the low-frequency dielectric susceptibility of the nematic host phase. The components of the high-frequency effective polarizability and the effective optical activity of a gold rod-like nanoparticle in a particular nematic solvent were calculated numerically.

1. Introduction

During the past decade, there has been significant interest in LC nanocomposites with metal, dielectric or semiconductor nanoparticles (NPs), which are close to the size of typical mesogenic molecules and can modify and improve the LC properties. It has been shown that the doping of a nematic LC with small NP volume concentration can affect many important nematic phase properties, e.g., a decrease in threshold and switching voltages as well as switching time. In addition, the doping of nematics with ferroelectric NPs is known to enhance dielectric and optical anisotropy, increase the electro-optic response [1,2], and improve the photorefractive properties [3], and the doping of ferroelectric LCs with metal and silica nanoparticles may result in an increase in the spontaneous polarization and dielectric permittivity and enables one to decrease switching times [4–6]. The LC medium may also effect the properties of NPs. For example, the frequency of the localized plasmon resonance of gold NPs can be tuned by modifying the birefringence of the nematic LC medium [7–9].

Chiral NPs may induce a macroscopic cholesteric helical structure in a nematic LC host. In particular, rod-like gold NPs decorated with chiral organic molecules induce a much tighter helical structure than the corresponding chiral molecules doped into the nematic host phase [10,11]. Moreover, the anisometry of a chiral NP appears to be very important. For example, rod-like chirality-decorated gold NPs possess a significantly higher helical twisting power in comparison with the corresponding spherical NPs [11,12]. This is at least partially related to strong long-range chiral interactions between decorated NPs.

In this paper, we develop a statistical theory of cholesteric ordering in nematic nanocomposites doped with rod-like chiral nanoparticles using the general formalism developed by several authors [13–18]. We use a simple model of an NP filled with chiral dielectric medium and embedded into the nematic liquid crystal. We take into account chiral dispersion interaction between such NPs and obtain an explicit expression for the helical pitch in terms of the anisotropy of the effective gyration tensor of the NP and the

anisotropy of the effective polarizability. We also obtain analytical expressions for the effective polarizability and effective gyration of a rod-like NP as functions of the dielectric parameters of the NPs and nematic host phase and present the results of the corresponding numerical calculations for particular nematic hosts.

2. Chiral Interaction between Nanoparticles in the Nematic Host Phase

The distortion free energy density of the cholesteric phase is given by the following well-known general expression:

$$F_d = \lambda(\mathbf{n} \cdot (\nabla \times \mathbf{n})) + \frac{1}{2}K_{22}(\mathbf{n} \cdot (\nabla \times \mathbf{n}))^2, \tag{1}$$

where $\mathbf{n}$ is the director, $(\mathbf{n} \cdot (\nabla \times \mathbf{n}))$ is the twist deformation, K_{22} is the twist elastic constant and λ is the pseudoscalar coefficient which changes sign under space inversion and which vanishes in a nonchiral liquid crystal. Assuming that the director describes a helix along the z axis, i.e., $\mathbf{n} = (\cos(qz), \sin(qz), 0)$ where q is the wave vector of the helical structure. Substituting this expression into the free energy and minimizing with respect to q, one obtains:

$$q = \frac{2\pi}{p} = \frac{\lambda}{K_{22}}, \tag{2}$$

where p is the helical pitch.

One notes that at a relatively small concentration of nanoparticles (NPs), the twist elastic constant is approximately equal to that of the pure nonchiral nematic host. On the other hand, the pseudoscalar quantity λ is determined by the NP chirality and can in principle be evaluated taking into consideration the interaction between chiral nanoparticles. This is the purpose of the molecular statistical theory of cholesteric nanocomposites to calculate the parameter λ starting from the corresponding chiral interaction potential.

We assume that the nanoparticle is anisotropic and uniaxial, and its orientation is specified by the unit vector $\mathbf{a}$ in the direction of the NP primary axis. In this case, an arbitrary interaction potential $V(\mathbf{a}_1, \mathbf{r}_{12}, \mathbf{a}_2)$ between the NPs "1" and "2" depends on the unit vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ and on the intermolecular vector $\mathbf{r}_{12}$. This potential can be expanded in terms of the so-called spherical invariants

$$V(\mathbf{a}_1, \mathbf{r}_{12}, \mathbf{a}_2) = \sum_{lmk} J_{lmk}(r_{12}) T^{lmk}(\mathbf{a}_1, \mathbf{u}_{12}, \mathbf{a}_2), \tag{3}$$

where $\mathbf{u}_{12} = \mathbf{r}_{12}/r_{12}$. The set $T^{lmk}(\mathbf{a}_1, \mathbf{u}_{12}, \mathbf{a}_2)$ is a complete orthogonal set of basis functions [13,14] that contain the vector $\mathbf{a}_1$ to the power l, the vector $\mathbf{u}_{12}$ to the power m, and the vector $\mathbf{a}_2$ to the power k. The explicit expressions for the lower-order invariants have been given, for example, by Van der Meer [13]. The invariants with one zero index are just Legendre polynomials. For example, $T^{202}(\mathbf{a}_1, \mathbf{u}_{12}, \mathbf{a}_2) = P_2((\mathbf{a}_1 \cdot \mathbf{a}_2))$. The invariants with $1 + m + k$ odd are pseudoscalars, and therefore, the corresponding coupling constants J_{lmk} are also pseudoscalars. Such terms may appear in the expansion of the interaction potential only if one of the interacting particles is chiral. The first nonpolar chiral term of the general expansion Equation (3) reads:

$$V^*(\mathbf{a}_1, \mathbf{r}_{12}, \mathbf{a}_2) = J^*(r_{12}) T^{212}((\mathbf{a}_1, \mathbf{u}_{12}, \mathbf{a}_2) \cdot \mathbf{a}_2), \tag{4}$$

where $T^{212}(\mathbf{a}_1, \mathbf{u}_{12}, \mathbf{a}_2) = ((\mathbf{a}_1 \times \mathbf{a}_2) \cdot \mathbf{u}_{12})((\mathbf{a}_1 \cdot \mathbf{a}_2))$.

The potential (Equation 4) promotes the twist of the long axes of neighboring particles and is widely used in the statistical theory of cholesteric ordering (see, for example) [13–15,17,18].

One notes that in the general case the cholesteric stricture may be induced both by the chiral interaction between NPs and by the chiral interaction between NPs and neighboring nonchiral mesogenic molecules. The relative strength of these two types of chiral interaction mainly depends on the size and structure of the chiral particles embedded into the nonchiral nematic host. For example, in the case of low-molecular-weight chiral

dopants, the predominant interaction is the one between a dopant and the neighboring mesogenic molecules which are approximately of the same size. Thus, in this case, the surrounding medium should be considered on the molecular level. By contrast, real chiral NPs are significantly larger than the mesogenic molecules as they contain a long rod-like core coated by the organic chiral ligands. In particular, the volume of such an NP is at least order of magnitude larger than that of a mesogenic molecules. Taking into account that the dispersion interaction between NPs is approximately proportional to the square of the NP volume, one may assume that the chiral interaction between NPs themselves may be predominant in this case, even accounting for a rapid decrease in the interaction potential with the increasing distance between NPs. In the case of relatively large NPs, the surrounding nematic can be treated in the first approximation as a continuous medium which just aligns the rod-like NP along the local director which is a local symmetry axis of the medium. Thus, in the present theory, we neglect the interaction between NPs and the mesogenic molecules. This assumption is obviously not valid in the limit of very low NP concentration, and hence, the present theory is limited to the case of an intermediate concentration range.

Let us now consider in more detail the chiral interaction between two chiral NPs. In the general case, the anisotropic interaction between nonpolar particles 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, [19]):

$$U(\mathbf{R}, \mathbf{a}_1, \mathbf{a}_2) = -\frac{h}{2\pi} \int_0^\infty Tr\left[\alpha^{NP}(1, \omega) \cdot T(\mathbf{R}) \cdot \alpha^{NP}(2, \omega) \cdot T(\mathbf{R})\right] d\omega, \tag{5}$$

where $\alpha^{NP}(i\omega)$ is the polarizabiity tensor of an NP i, 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 $\mathbf{R} = \mathbf{r}_{12}$ is the interparticle vector. In the framework of the dispersion interaction model, the chirality of an NP is determined by its optical activity pseudotensor $\beta_{\alpha\beta\gamma} = \epsilon_{\alpha\beta\nu} g_{\nu\gamma}$ where $g_{\nu\gamma}$ is the NP gyration tensor and $\epsilon_{\alpha\beta\nu}$ is the absolute antisymmetric pseudotensor (which changes the sign under space inversion). One notes that in the isotropic chiral medium the gyration tensor is proportional to the unit tensor, and the corresponding coefficient directly specified the rotation of light. In anisotropic systems, different eigenvalues of the gyration tensor characterize the rotation along the corresponding eigenvalues.

Now, the leading term in the chiral interaction potential between two NPs can be written in the general form similar to Equation (5) (see, for example, [20]):

$$U^*(\mathbf{R}, \mathbf{a}_1, \mathbf{a}_2) = -\frac{h}{2\pi} \int_0^\infty Tr\left[\beta^{NP}(1, \omega) \cdot T^{dq}(\mathbf{R}) \cdot \alpha^{NP}(2\omega) \cdot T(\mathbf{R})\right] d\omega, \tag{6}$$

where $T^{dq}_{\alpha,\beta,\gamma}(\mathbf{R}) = \nabla_\gamma T_{\alpha\beta}(\mathbf{R})$ is the third rank dipole-quadrupole propagator tensor. As shown in [20], Equation (6) can be rewritten in the following approximate form:

$$U^*(\mathbf{R}, \mathbf{a}_1, \mathbf{a}_2) \approx -J^* R^{-7}\left(((\mathbf{a}_1 \cdot \mathbf{a}_2)) - 2(\mathbf{a}_1 \cdot \mathbf{u}_{12})(\mathbf{a}_2 \cdot \mathbf{u}_{12})\right)((\mathbf{a}_1 \times \mathbf{a}_2) \cdot \mathbf{u}_{12}), \tag{7}$$

where

$$J^* = E_0 \frac{\Delta\alpha^* \Delta g^*}{\epsilon_m^2}. \tag{8}$$

where $\Delta\alpha^* = \alpha_\parallel^* - \alpha_\perp^*$ is the anisotropy of the effective polarizability of an NP in the surrounding dielectric medium, $\Delta g^* = g_\parallel^* - g_\perp^*$ is the anisotropy of the effective gyration tensor of the chiral NP (the component $g_\parallel^*$ is along the NP axis), E_0 is the average excitation energy of the NP which is treated as a parameter here and ϵ_m is the average dielectric susceptibility of the medium around the NP.

Real chiral NPs [11,12] are usually composed of the rigid metal or dielectric core coated with the chiral organic ligands. Thus, a more realistic model of strongly anisotropic chiral NP would include a nonchiral cylinder covered with a layer of the effective chiral dielectric of finite thickness. However, the expressions for the effective polarizability and the optical activity of such a two-layer NP in the nematic host are rather complicated and can only be evaluated numerically in the general case. In this paper, we used a more simple model in which the chirality is distributed homogeneously within the volume of the NP. As shown below, this model enables one to derive simple analytical expressions for the components of the effective polarizability and the gyration tensor of the NP and to explicitly express the helical itch in terms of the dielectric constants of the NN and the nematic host phase.

One notes that the effective dielectric properties of a relatively small NP in the nematic medium is determined by the interaction with the first layer of organic molecules around the NP. In particular, gold and silver NPs are usually dressed by organic molecules with chains penetrating into the surrounding LC medium. Such chains can induce a significant orientational disorder around the NP which at least partially justifies the model of an NP in an isotropic dielectric medium with the dielectric susceptibility ϵ_m equal to the average susceptibility of the nematic LC.

$$\varepsilon_m = \frac{1}{3}\left(\varepsilon_{||} + 2\varepsilon_{\perp}\right). \tag{9}$$

were $\varepsilon_{||}$ and $\varepsilon_{\perp}$ are the longitudinal and the transverse susceptibility of the pure nematic phase, respectively.

One notes also that the chiral interaction potential is proportional to the pseudoscalar quantity Δg^*, which possesses opposite signs for NPs of opposite handedness.

3. Helical Pitch of the Cholesteric Nanocomposites

A molecular statistical theory of cholesteric ordering has been developed by several authors [13,15–18,21,22]. In this paper, we employ the molecular-field approximation which enables one to express the free energy of the cholesteric nanocomposite in the following form [14] neglecting the shape chirality of NPs and assuming that the number density of NPs is not extremely small:

$$\begin{aligned} F = F_N + \rho_n \int f((\mathbf{a}_n \cdot \mathbf{n}(\mathbf{r}))) \ln \int f((\mathbf{a}_n \cdot \mathbf{n}(\mathbf{r}))) d\mathbf{a}_n d\mathbf{r} \\ + \frac{1}{2}\rho_n^2 \int U(\mathbf{R}, \mathbf{a}_1, \mathbf{a}_2) f((\mathbf{a}_1 \cdot \mathbf{n}(\mathbf{r}_1))) f((\mathbf{a}_2 \cdot \mathbf{n}(\mathbf{r}_2))) d\mathbf{a}_1 d\mathbf{r}_1 d\mathbf{a}_2 d\mathbf{r}_2 \\ + kT\frac{1}{2}\rho_n^2 \int \Omega(R - \xi_{12}) f((\mathbf{a}_1 \cdot \mathbf{n}(\mathbf{r}_1))) f((\mathbf{a}_2 \cdot \mathbf{n}(\mathbf{r}_2))) d\mathbf{a}_1 d\mathbf{r}_1 d\mathbf{a}_2 d\mathbf{r}_2, \end{aligned} \tag{10}$$

where F_N is the free energy of the pure nematic host, $f((\mathbf{a}_1 \cdot \mathbf{n}(\mathbf{r}_1))$ is the one-particle orientational distribution function of the NPs, $\Omega(R - \xi_{12})$ is the steric cut-off function, $\Omega(R - \xi_{12}) = 0$ if $R > \xi_{12}$ and $\Omega(R - \xi_{12}) = -1$ if $R < \xi_{12}$. Here, ξ_{12} is the closest distance of approach between the centers of the two particles which depends on their relative orientation, and R is the interparticle distance. The last term in Equation (10) is the so-called packing entropy which only depends on the NP shape. We assume that the NP shape is nonchiral, and then, the packing entropy does not contribute to the helical twisting power of the nanocomposite. In this case, the only contribution to the pseudoscalar parameter λ stems from the third term in Equation (10) where the total interaction potential between the NPs should be replaced by its chiral part.

Substituting the chiral interaction potential (7) into the third term of Equation (10) and averaging the overall orientations of the two particles with the corresponding one-particle distribution functions, one obtains:

$$\delta F = -\frac{1}{2}J * S^2 \rho_n \rho_0 \int R^{-7}(((\mathbf{n}(\mathbf{r}_1) \cdot \mathbf{n}(\mathbf{r}_2))) - 2(\mathbf{n}(\mathbf{r}_1 \cdot \mathbf{u}_{12})(\mathbf{n}(\mathbf{r}_2 \cdot \mathbf{u}_{12}))((\mathbf{n}(\mathbf{r}_1 \times \mathbf{n}(\mathbf{r}_2) \cdot \mathbf{u}_{12})d\mathbf{r}_1 d\mathbf{r}_2, \tag{11}$$

where S is the nematic order parameter and $\mathbf{u}_{12}$ is the unit intermolecular vector.

Now, the contribution from Equation (11) to the total distortion free energy can be obtained by performing the Taylor expansion of the director $\mathbf{n}(\mathbf{r}_2)$ at the point $\mathbf{r}_2$ around $\mathbf{n}(\mathbf{r}_1)$ at the point $\mathbf{r}_1$ up to the linear terms in gradients of the director:

$$\mathbf{n}(\mathbf{r}_2) = \mathbf{n}(\mathbf{r}_1) + (\mathbf{R} \cdot \nabla)\mathbf{n}(\mathbf{r}_1) + \dots. \tag{12}$$

Let us now consider the perfect cholesteric helical structure which corresponds to the following director distribution along the z-axis:

$$\mathbf{n}(\mathbf{r}) = (\cos qz, \sin qz, 0) \approx (1, qz, 0), \tag{13}$$

if the helical pitch is sufficiently large compared with the typical range of the intermolecular interaction potential a, i.e., $qa \ll 1$ which is valid for any cholesteric phase.

Substituting Equation (13) into (12), one obtains:

$$\mathbf{n}(\mathbf{r}_2) = \mathbf{n}(\mathbf{r}_1) + Rqu_z\hat{y} + \dots, \tag{14}$$

where $\hat{y}$ is the unit vector along the y axis.

Finally, substituting Equation (14) into Equation (11) and expanding in powers of q, one obtains the following contribution to the distortion free energy which is linear in q:

$$\delta F = \int F_d(\mathbf{r})d\mathbf{r}, \tag{15}$$

where F_d is the distortion free energy density which is expressed as:

$$F_d = -\frac{1}{2}J^*S^2\rho_n^2 \int_D^\infty R^{-4}dR \int u_z^2(1 - 2u_x^2)d^2\mathbf{u} = \frac{4\pi}{45D^3}J^*S^2\rho_n^2 q. \tag{16}$$

Thus, the pseudoscalar parameter $\lambda = \frac{4\pi}{45D^3}J^*S^2\rho_n^2$ and the helical wave number are given by the following expression:

$$q = \frac{4\pi}{45D^3}\frac{1}{K_{22}}J^*S^2\rho_n^2, \tag{17}$$

where the coupling constant J^* is given by Equation (8) and where D is the diameter of the rod-like NP.

Now, let us express the effective polarizability anisotropy $\Delta\alpha^*$ and the effective anisotropy of the gyration tensor Δg^* of an NP in terms of the dielectric parameters of the system. using the model of the dielectric ellipsoid embedded into the dielectric medium considered in [23]. We assume that the ellipsoid is filled with the isotropic optically active dielectric with the susceptibility ε_n and the optical activity $\beta_{\alpha\beta\gamma} = \epsilon_{\alpha\beta\gamma}g$, where g is the isotropic gyration. The ellipsoid is embedded into the effectively isotropic dielectric medium with the dielectric susceptibility ε_m given by Equation (9). In this case, the electric field $\mathbf{E}^n$ inside the ellipsoid is related to the field $\mathbf{E}_m$ outside the ellipsoid by the following equation:

$$\hat{\varepsilon}_m(\hat{I} - \hat{q})\mathbf{E}^n + \hat{q}\mathbf{D}^n = \varepsilon_m\mathbf{E}_m, \tag{18}$$

where the induction $\mathbf{D}^n = \hat{\varepsilon}^n\mathbf{E}^n$, $\varepsilon_{\alpha\beta}^n = \varepsilon^n\delta_{\alpha\beta} + \beta_{\alpha\beta\gamma}\nabla_\gamma$ is the full susceptibility tensor of the optically active medium inside the ellipsoid, $q_{\alpha\beta} = q_\perp\delta_{\alpha\beta} + (q_\parallel - q_\perp)a_\alpha a_\beta$. Here, $q_\parallel, q_\perp$ are the depolarization coefficients of the ellipsoid of revolution defined, for example, in [23], and $\hat{I}$ is the unit tensor.

The induced dipole moment of the ellipsoid embedded in the dielectric medium can be written in the form:

$$\mathbf{P} = V(\mathbf{P}^n - \mathbf{P}_m), \tag{19}$$

where

$$\mathbf{P}^n = \frac{1}{4\pi}(\hat{\varepsilon}^n - \hat{I})\mathbf{E}^n, \quad \mathbf{P}^m = \frac{1}{4\pi}(\varepsilon_m - 1)\mathbf{E}_m, \tag{20}$$

and where V is the NP volume.

On the other hand,

$$\mathbf{P} = \left(\hat{\alpha}^* + (\hat{\beta}^* \nabla)\right)\mathbf{E}_m, \tag{21}$$

where $\hat{\alpha}^*$ and $\hat{\beta}^*$ are the effective polarizability and the optical activity of the ellipsoid in the dielectric medium, respectively.

Combining Equations (18)–(21), one obtains the following set of two simultaneous equations which enable one to determine $\hat{\alpha}^*$ and $\hat{\beta}^*$:

$$\frac{V}{4\pi}\left(\hat{\varepsilon}^n - \varepsilon_m \hat{I}\right)\mathbf{E}^n = \left(\hat{\alpha}^* + (\hat{\beta}^* \nabla)\right)\mathbf{E}_m, \tag{22}$$

$$\mathbf{E}^n = \left(\varepsilon_m \hat{I} - \varepsilon_m \hat{q} + \hat{\varepsilon}^n \cdot \hat{q}\right)^{-1}\varepsilon_m \mathbf{E}_m. \tag{23}$$

The optical activity term $(\hat{\beta}\nabla)$ is a small correction to the total susceptibility tensor $\hat{\varepsilon}^n$, and hence, these equations can be expanded in powers of $(\hat{\beta}\nabla)$ keeping only the linear terms. Finally, one obtains the following expressions for effective polarizability and the effective optical activity of the sufficiently elongated NP in the nematic medium:

$$\alpha_{\perp}^* = \frac{V}{2\pi}\frac{\varepsilon_m(\varepsilon_n - \varepsilon_m)}{\varepsilon_n + \varepsilon_m}, \tag{24}$$

$$\Delta\alpha^* = \frac{V}{4\pi}\frac{(\varepsilon_n - \varepsilon_m)^2}{\varepsilon_n + \varepsilon_m}, \tag{25}$$

$$g_{\perp}^* = \frac{V}{2\pi}\frac{\varepsilon_m g}{\varepsilon_n + \varepsilon_m}, \tag{26}$$

$$\Delta g^* = \frac{V}{2\pi}\frac{\varepsilon_m g(\varepsilon_m - \varepsilon_n)}{(\varepsilon_n + \varepsilon_m)^2}. \tag{27}$$

One notes that relatively simple expressions (24)–(27) were obtained in the limiting case $L \gg D$ where L is the length of the NP and D is the NP diameter, which corresponds to the model of long cylindrical NPs. In the general case, the effective polarizability and the effective gyration tensor depend on the depolarization coefficients of the ellipsoid which, in turn, depend on the NP anisotropy. For arbitrary anisometry, the depolarization coefficients can only be evaluated numerically. It is interesting to note also that in this model the anisotropy of the effective polarizability and their anisotropy of the effective gyration tensor are determined both by the anisometry of the N shape (long cylinders) and the difference between the average dielectric constants of the NP and the nematic medium.

Substituting the expressions for $\Delta\alpha^*$ and Δg^* into Equations (7) and (17), one obtains the following expression for the inverse pitch of the cholesteric helical structure induced by chiral rod-like NPs in the nematic host:

$$\frac{1}{p} = \frac{\rho_n^2 \lambda_0}{K_{22}} S^2 \frac{g(\varepsilon_n - \varepsilon_m)^3}{\varepsilon_m(\varepsilon_n + \varepsilon_m)^3}, \tag{28}$$

where $\lambda_0 = E_0 V^2 (720\pi^3 D^3)^{-1}$

According to Equation (28), the inverse pitch of the cholesteric helical structure is proportional to the anisotropy of the low-frequency effective polarizability of the NP in the nematic liquid crystal medium. The effective polarizability depends on the difference between the average susceptibility of the medium inside and outside the rod-like NP.

Both the pitch P and the inverse pitch $1/p$ are presented in Figure 1 as functions of the ratio $\varepsilon_m/\varepsilon_n$. One notes that the inverse pitch changes sign at a certain value of the average susceptibility of the nematic host, which corresponds to the sense inversion of the cholesteric structure. From the applications point of view, this result paves the way toward the effective control of the pitch by using different nematic hosts and in particular mixtures of several nematic LCs, which enables one to vary the corresponding susceptibility by changing the molar fractions of the components. One notes, however, that from the experimental point of view, no cholesteric structure may be observed in a finite sample in the vicinity of the inversion point because the helical pitch is too large.
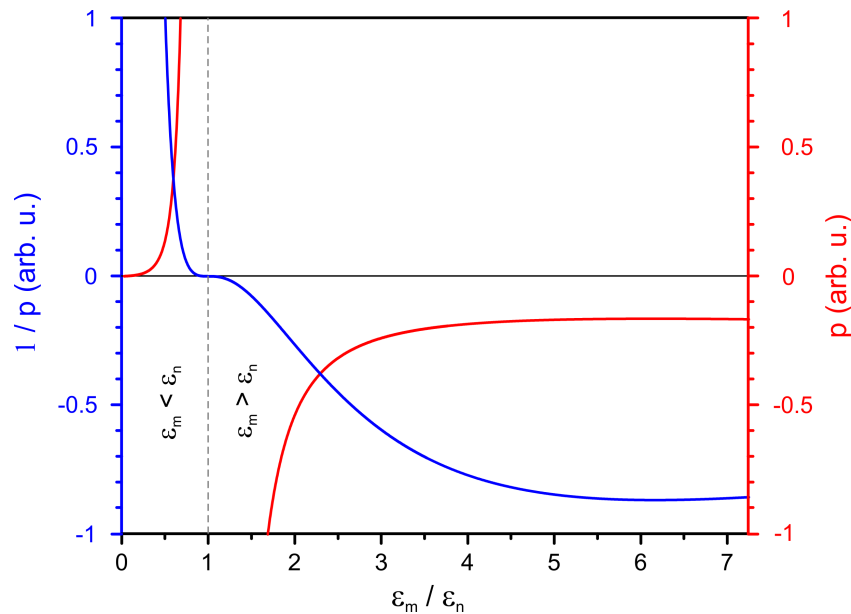

Figure 1. Dependence of the pitch p and of the inverse pitch $1/p$ of the cholesteric structure on the ratio of the average susceptibility of the nematic host phase ε_m and the susceptibility of the nanoparticle ε_n.

4. High-Frequency Effective Polarizability and Gyration of Rod-like NPs in the Nematic Host Phase

The theory presented in the previous section enabled one to obtain relatively simple expressions for the effective polarizability and optical activity of the rod-like NP in the nematic host phase which are also valid at high frequencies. The results of the numerical calculations of these quantities for the nematic host 4-cyano-4'-pentylbiphenyl (5CB) are presented in Figures 2–5 as functions of frequency where the data on the frequency dependent susceptibility of gold [24] and of the nematic 5CB [25] were used. Real and imaginary parts of the effective polarizability of a dressed gold NP in the 5CB are presented in Figure 2. One can readily see that both parts vary significantly within the selected frequency range which is mainly determined by strong dispersion of the susceptibility of the gold NP. For comparison, the components of the effective polarizability of a dressed dielectric NP in 5CB, including fused silica (SiO_2) and cubic zirconia (ZrO_2) ones, are presented in Figure 3. One can readily see that in this case the frequency dependence of the effective polarizability is relatively weak. It would be interesting to verify these theoretical results experimentally.
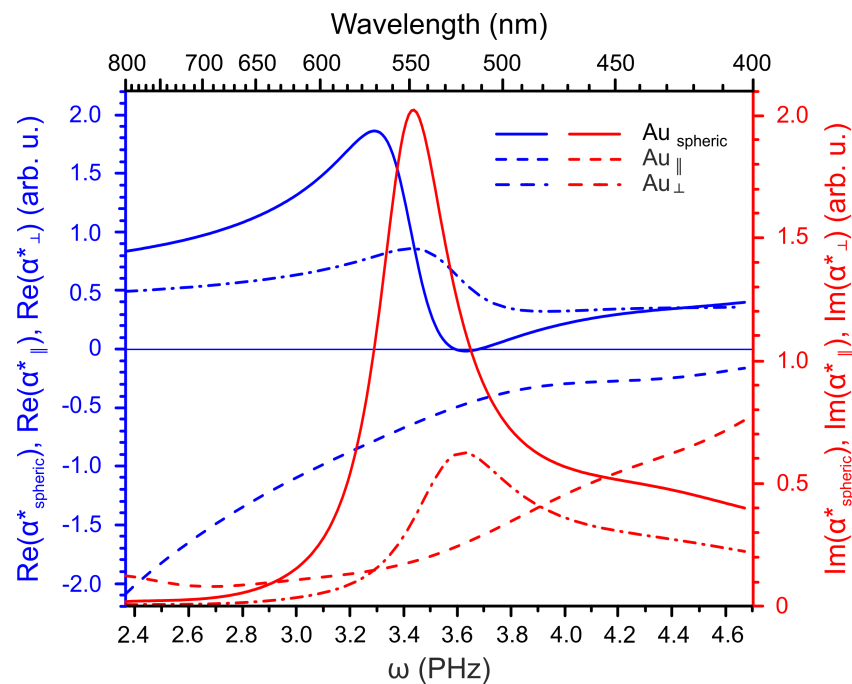
Figure 2. Frequency dependence of real and imaginary parts of the components of the effective polarizability of gold NPs $Re(\alpha*_\parallel)$, $Im(\alpha*_\parallel)$, $Re(\alpha*_\perp)$ and $Im(\alpha*_\perp)$ in the nematic host 5CB.
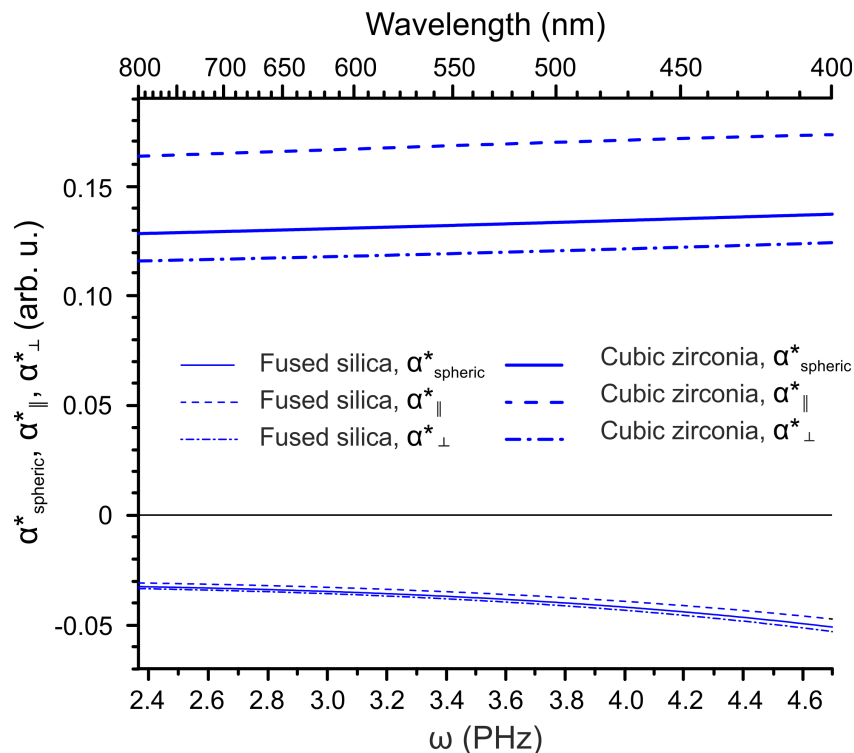

Figure 3. Frequency dependence of the effective polarizability of the fused silica and cubic zirconia NPs in the nematic host 5CB.

The reduced anisotropy of the effective gyration tensor of an NP dressed with chiral organic molecules is presented in Figure 4 for the gold, fused silica and cubic zirconia NPs. It is interesting to note that the effective gyration anisotropy is negative for gold and fused silica NPs and is positive for cubic zirconia NPs, although the sign of the gyration of isolated NPs is assumed to be the same. This is again related to a renormalization of the dielectric properties of an NP in the nematic LC medium. Finally, the reduced anisotropy

of the gyration tensor of a dressed gold NP is presented in Figure 5, together with the corresponding profiles of the effective polarizability.
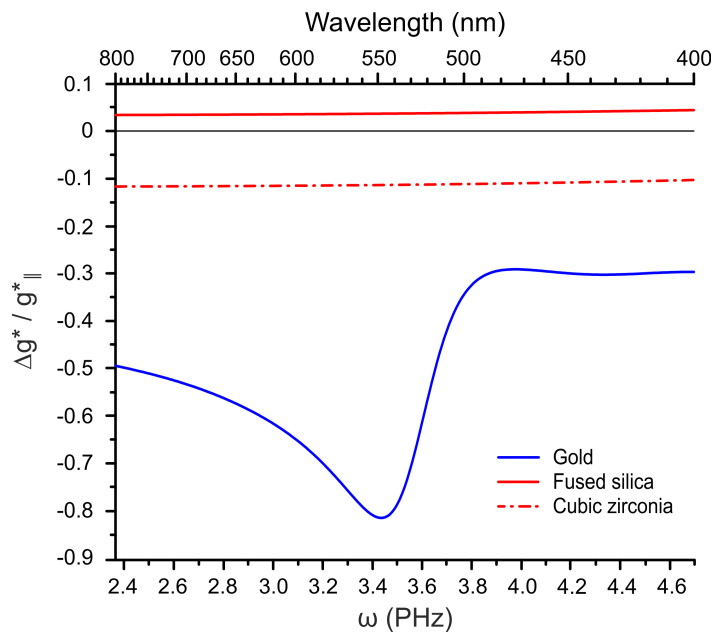

Figure 4. Frequency dependence of the reduced anisotropy of the effective gyration tensor $\Delta g*/g*_{\parallel}$ of the gold, fused silica and cubic zirconia NPs dressed with chiral organic molecules in the nematic host 5CB.
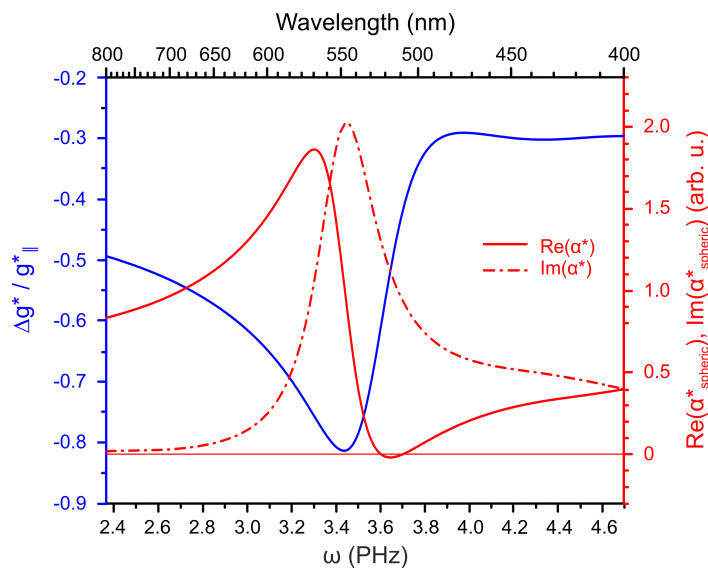

Figure 5. Frequency dependence of the reduced anisotropy of the effective gyration tensor and of the effective polarizability of the gold NPs in the nematic host 5CB.

5. Conclusions

In this paper, we have employed the general molecular field theory of cholesteric ordering to derive an explicit expression for the pitch of the cholesteric helical structure induced by chiral nanoparticles in nematic nanocomposites. The NPs were modeled as long hard rods filled with the dielectric medium characterized by the isotropic dielectric susceptibility and optical activity, and it was assumed that chiral dispersion interaction between NPs is mainly responsible for the helical twisting power. It was shown that in the first approximation the inverse pitch is proportional to the anisotropy of the low-frequency effective polarizability of an NP in the nematic host phase, and the polarizability anisotropy,

in turn, is proportional to the difference between the dielectric susceptibility of the media inside and outside the NP. One concludes that a change of the components of the dielectric susceptibility of the nematic host phase may cause the helical sense inversion in the nematic nanocomposite. This effect is interesting from the applications point of view and can be verified experimentally. The inverse pitch is also proportional to the anisotropy of the effective gyration tensor of an NP which also depends on the average polarizability of the nematic host phase.

The analytical expressions for the effective polarizability and optical activity obtained in this paper are also valid at high frequencies. These quantities were calculated numerically for gold nanorods embedded in a particular nematic host 5CB. The reduced anisotropy of the effective gyration tensor was also calculated for fused silica (SiO_2) and cubic zirconia (ZiO_2) dielectric NPs in the same nematic host phase. The numerical results indicate that the sign of the anisotropy of the effective gyration tensor (which specifies the direction of the rotation of the polarization plane of light) may depend on the average dielectric susceptibility of the dielectric nanorod. A different approach to the theory of cholesteric ordering induced by chiral particles in the nematic host phase was proposed by Ferrarini et al. [21,22]. This approach is based on a coupling between the element of the particle surface and the local director of the surrounding nematic host phase, and the helical pitch is expressed in terms of the parameter which specifies the chirality of the NP shape. By contrast, in the theory developed in this paper, the NP shape chirality is neglected, and the helical ordering is determined by the effective optical activity of chiral NPs. The theory developed in [21,22] is also valid in the limiting case of very low NP concentration.

In this paper, we have used a simple model of a cylindrical NP in which the optical activity is evenly distributed within the NP volume. This model enables one to obtain relatively simple analytical expressions for the effective polarizability and optical activity of the NP. At the same time, real chiral NPs contain a rigid core coated by organic chiral ligands, and hence, it may be more appropriate to use a two-layer model where the nonchiral cylinder is covered by a chiral dielectric layer. In this case, however, the expressions for the effective polarizability and the gyration tensor are significantly more complicated, and the corresponding theory will be presented in our next publication.

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