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Effective Chiral Interactions between Nonchiral Rigid Macromolecules in a Chiral Solvent and the Induced Cholesteric Liquid Crystal Phase

Mikhail A. Osipov ^{1,*} and Alexey S. Merekalov ^{2,*} 
¹ Department of Mathematics and Statistics, University of Strathclyde, Glasgow G1 1XH, Scotland, UK

² Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 119991 Moscow, Russia

* Correspondence: m.osipov@strath.ac.uk (M.A.O.); alexis@ips.ac.ru (A.S.M.)

Abstract: It has been shown that a nonchiral anisotropic macromolecule embedded in a chiral dielectric solvent possesses an effective optical activity proportional to the optical activity of the solvent. As a result, there exists an effective chiral interaction between the macromolecules, which creates a torque acting on the primary axes of the two interacting molecules. A general expression for the effective chiral interaction potential has been derived in terms of the effective polarizability and the effective gyration tensor of the macromolecule in the chiral solvent. Explicit expressions for the components of the effective polarizability and the gyration have been obtained using the model of a hard rod filled with anisotropic dielectric and embedded into the isotropic chiral dielectric medium. The theory predicts the formation of the cholesteric helical structure in the nematic polymer liquid crystal phase induced by a chiral solvent.

Keywords: anisotropic macromolecule; chiral solvent; chiral interactions



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1. Introduction

Interactions between macromolecules can be very complicated and, in particular, in the case when the macromolecules are embedded into an ionic solvent (see, for example, [1–3]). The major interactions between two isolated molecules include electrostatic, dispersion, and short-range anisotropic repulsion [1,2,4]. At a short separation between the two macromolecules, one also has to take into consideration the hydrogen bonding and the formation of various complexes. In the ionic solvent, one also has to take into account many body interactions between the macromolecules, solvent molecules, and counter ions. Even in the idealized case of a neutral dielectric solvent, its dielectric properties may significantly screen the electrostatic interactions and renormalize the dispersion interactions, as the latter generally depend on the effective polarizabilities of the two molecules in the dielectric medium.

Various anisotropic interactions between macromolecules also play a major role in liquid crystal polymers and block copolymers, which exhibit many different phases with various orientational and translational types of order. However, in the existing molecular theory of polymers, the interactions between macromolecules is taken into consideration only at a basic level. In most theories (see, for example, [5–10] and references therein), only isotropic attraction and/or repulsion between segments of the flexible chains and the model Maier–Saupe orientational interactions between rigid fragments are taken into account. Of particular interest are the chiral intermolecular interactions, which are responsible, for example, for the helical twisting in the cholesteric liquid crystal phase, as well as in more complicated chiral smectic phases. The existing molecular–statistical theory of cholesteric ordering is based either on model interaction potentials or on simple molecular models, including steric repulsion between molecules of helical shape and electrostatic interaction between helical charge distributions of rod-like DNA molecules [11,12]. The effect of the chiral shape and of the molecular biaxiality has recently been taken into consideration in [13–15]. At the same time, as mentioned by a number of authors [2,4], the most general

chiral intermolecular interaction is the dipole–quadrupole dispersion interaction, which in principle exists between chiral macromolecules of any structure. In polymer melts and in nonionic solvents, such a chiral interaction may be predominant if the chiral charge distribution on the macromolecular surface is not very pronounced.

In this paper, we consider the effective dispersion interaction between nonchiral macromolecules in a simple chiral solvent, which is treated as a chiral dielectric medium. It is shown that there exists an effective chiral interaction between nonchiral anisotropic macromolecules embedded in a chiral solvent. Such an interaction potential is determined by the effective optical activity of a nonchiral macromolecule in the chiral dielectric medium. Moreover, even an elongated cavity in the chiral medium possesses an effective optical activity, and hence, any two such cavities will twist with respect to each other. The paper is arranged as follows. In Section 2, we derive a general expression for the effective chiral dispersion interaction between two uniaxial macromolecules in the chiral medium in terms of the effective polarizability and effective optical activity of the macromolecule. The expressions for the effective polarizability and the optical activity are derived in Section 3. Finally, Section 4 contains our discussion and conclusions.

2. Effective Chiral Interaction between Nonchiral Macromolecules in a Chiral Solvent

We assume that the macromolecules are anisotropic and uniaxial, and their orientation is specified by the unit vector \mathbf{a} in the direction of the molecular primary axis. In this case, an arbitrary interaction potential $V(\mathbf{a}_1, \mathbf{r}_{12}, \mathbf{a}_2)$ between the macromolecules “1” and “2” depends on the unit vectors \mathbf{a}_1 and \mathbf{a}_2 and on the intermolecular vector \mathbf{r}_{12} .

In the general case, the interaction between nonpolar neutral macromolecules is dominated by the dispersion (or the so-called van der Waals) 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, [4]):

$$U(\mathbf{R}, \mathbf{a}_1, \mathbf{a}_2) = -\frac{h}{2\pi} \int_0^\infty \text{Tr} \left[\alpha_{\alpha\beta}^*(1, \omega) T_{\beta\gamma}(\mathbf{R}) \alpha_{\gamma\delta}^*(2, \omega) T_{\delta\alpha}(\mathbf{R}) \right] d\omega, \quad (1)$$

where $\alpha^*(i\omega)$ is the effective polarizability tensor of the macromolecules i , h is the Plank constant, and

$$T_{\alpha\beta}(\mathbf{R}) = R^{-5} (3R_\alpha R_\beta - R^2 \delta_{\alpha\beta}) \quad (2)$$

is the dipole–dipole propagator tensor, where $\mathbf{R} = \mathbf{r}_{12}$ is the intermolecular vector.

In this paper, we employ a simple model of a macromolecule, which is considered to be an anisotropic particle filled with a dielectric medium characterized by the anisotropic dielectric susceptibility. It should be noted that if the macromolecule is embedded in the dielectric medium, the molecular polarizability tensor $\alpha_{\alpha\beta}^*(i\omega)$ is the effective quantity renormalized by the dielectric properties of the surrounding medium. For chiral molecules, the effective polarizability also accounts for the molecular optical activity and can be expressed as

$$\alpha_{\alpha\beta}^*(i\omega) = \alpha_{\alpha\beta}^0(i\omega) + \beta_{\alpha\beta\gamma}^*(i\omega) \nabla_\gamma, \quad (3)$$

where $\beta_{\alpha\beta\gamma}^*(i\omega)$ is the effective optical activity tensor, which can generally be expressed as $\beta_{\alpha\beta\gamma}^* = \varepsilon_{\alpha\beta\nu} g_{\nu\gamma}^*$, where $g_{\nu\gamma}^*$ is the effective gyration tensor, and $\varepsilon_{\alpha\beta\nu}$ is the absolute antisymmetric tensor. As shown below in Section 3, even a nonchiral molecule should possess some nonzero effective optical activity if it is embedded into the chiral dielectric medium. This effective optical activity of a macromolecule vanishes together with the optical activity of the solvent. Substituting Equation (3) into Equation (1), one obtains the leading term in the chiral interaction potential between two macromolecules (see, for example, [16]):

$$U^*(\mathbf{R}, \mathbf{a}_1, \mathbf{a}_2) = -\frac{h}{2\pi} \int_0^\infty \text{Tr} \left[\beta_{\alpha\beta\gamma}^*(1, \omega) T_{\gamma\beta\nu}^{dq}(\mathbf{R}) \alpha_{\nu\eta}^0(2\omega) T_{\eta\alpha}(\mathbf{R}) \right] d\omega, \quad (4)$$

where

$$T_{\alpha\beta\gamma}^{dq}(\mathbf{R}) = \nabla_{\gamma} T_{\alpha\beta}(\mathbf{R}) = R^{-7} R_{\gamma} (3R_{\alpha} R_{\beta} - R^2 \delta_{\alpha\beta}) + R^{-5} (3R_{\alpha} \delta_{\beta\gamma} + 3R_{\beta} \delta_{\alpha\gamma} - R_{\gamma} \delta_{\alpha\beta}) \quad (5)$$

is the third rank dipole–quadrupole propagator tensor.

For uniaxial macromolecules, the polarizability tensor $\alpha_{\alpha\beta}^0(2\omega)$ can be expressed in terms of the molecular primary axis \mathbf{a} :

$$\alpha_{\alpha\beta}^0 = \bar{\alpha} \delta_{\alpha\beta} + \Delta\alpha (a_{\alpha} a_{\beta} - \delta_{\alpha\beta}), \quad (6)$$

where $\bar{\alpha}$ is the average molecular polarizability, and $\Delta\alpha = \alpha_{\parallel}^* - \alpha_{\perp}^*$ is the anisotropy of the molecular polarizability. Here, α_{\parallel}^* is the longitudinal polarizability along the axis of the macromolecule, and α_{\perp}^* is the transverse polarizability.

The molecular effective gyration tensor can also be expressed in a similar way:

$$g_{\alpha\beta}^* = \bar{g} \delta_{\alpha\beta} + \Delta g (a_{\alpha} a_{\beta} - \delta_{\alpha\beta}). \quad (7)$$

Substituting Equations (2), (5)–(7) into Equation (4), one obtains the following final expression for the effective chiral interaction potential between two uniaxial macromolecules in the dielectric solvent:

$$U^*(\mathbf{R}, \mathbf{a}_1, \mathbf{a}_2) = -J^* R^{-7} ((\mathbf{a}_1 \cdot \mathbf{a}_2) - 2(\mathbf{a}_1 \cdot \mathbf{u}_{12})(\mathbf{a}_2 \cdot \mathbf{u}_{12}))((\mathbf{a}_1 \times \mathbf{a}_2) \cdot \mathbf{u}_{12}), \quad (8)$$

where

$$J^* = E_0 \frac{\Delta\alpha^* \Delta g^*}{\varepsilon_m^2}, \quad (9)$$

and where \mathbf{u}_{12} is the unit intermolecular vector. Here, $\Delta\alpha^* = \alpha_{\parallel}^* - \alpha_{\perp}^*$ is the anisotropy of the effective polarizability of the macromolecule in the surrounding dielectric medium, $\Delta g^* = g_{\parallel}^* - g_{\perp}^*$ is the anisotropy of the effective gyration tensor of the macromolecule, E_0 is the average excitation energy of the macromolecule, and ε_m is the average dielectric susceptibility of the medium around the macromolecule. One notes that the chiral interaction potential is proportional to the pseudoscalar quantity Δg^* , which possesses opposite signs for macromolecules of opposite handedness. The quantity $((\mathbf{a}_1 \times \mathbf{a}_2) \cdot \mathbf{u}_{12})$ is also a pseudoscalar, which changes sign under space inversion. Hence, the interaction potential itself is a scalar, as it should be.

One can readily see how the chiral interaction potential (8) promotes the mutual twist of the long axes of the two interacting molecules. Indeed, let us consider the simple mutual orientation of the two molecules when $\mathbf{a}_1 \perp \mathbf{u}_{12}$ and $\mathbf{a}_2 \perp \mathbf{u}_{12}$. In this case $(\mathbf{a}_1 \cdot \mathbf{a}_2) = \cos \phi$, and $((\mathbf{a}_1 \times \mathbf{a}_2) \cdot \mathbf{u}_{12}) = \sin \phi$, where ϕ is the angle between the long axes of the two macromolecules. Then, the interaction potential (8) can be written in the simple form:

$$U^*(\mathbf{R}, \mathbf{a}_1, \mathbf{a}_2) = -\frac{1}{2} J^* R^{-7} \sin(2\phi). \quad (10)$$

One can readily see that depending on the sign of the coupling constant J^* , the minimum of the potential (10) corresponds to $\phi = \pi/4$ or $\phi = -\pi/4$. It should be noted, of course, that there exists also the nonchiral dispersion orientational interaction between two rod-like macromolecules, which promotes the parallel orientation of the two molecules. Generally, nonchiral interactions are much weaker than the nonchiral ones; hence, the actual equilibrium twist angle between neighboring rod-like macromolecules should be much smaller than $\pi/4$, which is indeed the case in cholesteric polymer liquid crystals.

It is interesting to note that the chiral interaction potential (8) has the same mathematical form as the first term of the general expansion of the corresponding part of the pair potential. Indeed, let us consider the general pair potential, which depends on the unit vec-

tors \mathbf{a}_1 and \mathbf{a}_2 along the axes of the two uniaxial macromolecules and the intermolecular vector \mathbf{r}_{12} . This potential can be expanded in terms of the so-called spherical invariants

$$U(\mathbf{a}_1, \mathbf{r}_{12}, \mathbf{a}_2) = \sum_{lmk} J_{lmk}(r_{12}) T^{lmk}(\mathbf{a}_1, \mathbf{u}_{12}, \mathbf{a}_2), \quad (11)$$

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 [17,18] that contains 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 [17]. 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 (9)) reads:

$$U^*(\mathbf{a}_1, \mathbf{r}_{12}, \mathbf{a}_2) = J^*(r_{12})((\mathbf{a}_1 \times \mathbf{a}_2) \cdot \mathbf{u}_{12})(\mathbf{a}_1 \cdot \mathbf{a}_2). \quad (12)$$

The potential (Equation (12)) promotes the twist of the long axes of neighboring molecules and is widely used in the statistical theory of cholesteric ordering (see, for example [11,12,17–19]).

3. Effective Optical Activity of a Nonchiral Macromolecule in a Chiral Dielectric Medium

In this section, we use the model of the dielectric ellipsoid embedded into the chiral dielectric medium (see [20]) to express the effective polarizability anisotropy $\Delta\alpha^*$ and the effective anisotropy of the gyration tensor Δg^* of a model macromolecule in terms of the dielectric parameters of the system including the optical activity of the chiral solvent. We assume that the ellipsoid is filled with the anisotropic optically active nonchiral dielectric with the susceptibility ε_n :

$$\varepsilon_{\alpha\beta}^i = \varepsilon_{\perp}^i \delta_{\alpha\beta} + (\varepsilon_{\parallel}^i - \varepsilon_{\perp}^i) a_{\alpha} a_{\beta}, \quad (13)$$

where $\varepsilon_{\parallel}^i$ and ε_{\perp}^i are the longitudinal and transverse components of the dielectric susceptibility of the medium inside the ellipsoid.

The ellipsoid is embedded into the isotropic dielectric medium with the dielectric susceptibility ε_m and the isotropic optical activity $\beta_{\alpha\beta\gamma} = \varepsilon_{\alpha\beta\gamma} g$, where g is the isotropic gyration:

$$\varepsilon_{\alpha\beta}^m = \varepsilon_m \delta_{\alpha\beta} + \varepsilon_{\alpha\beta\gamma} g \nabla_{\gamma}. \quad (14)$$

Then, the electric field \mathbf{E}^i inside the ellipsoid is related to the field \mathbf{E}_m outside the ellipsoid by the following equation:

$$\hat{\varepsilon}_m(\hat{I} - \hat{q})\mathbf{E}^i + \hat{q}\mathbf{D}^i = \hat{\varepsilon}_m\mathbf{E}_m, \quad (15)$$

where the induction $\mathbf{D}^i = \hat{\varepsilon}^i\mathbf{E}^i$, and $q_{\alpha\beta} = q_{\perp} \delta_{\alpha\beta} + (q_{\parallel} - q_{\perp}) a_{\alpha} a_{\beta}$. Here, q_{\parallel}, q_{\perp} are the depolarization coefficients of the ellipsoid of revolution defined, for example, in [20], and \hat{I} is the unit tensor.

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

$$\mathbf{P} = V(\mathbf{P}^i - \mathbf{P}_m), \quad (16)$$

where

$$\mathbf{P}^i = \frac{1}{4\pi}(\hat{\varepsilon}^i - \hat{I})\mathbf{E}^i, \quad \mathbf{P}_m = \frac{1}{4\pi}(\hat{\varepsilon}_m - 1)\mathbf{E}_m, \quad (17)$$

and where V is the NP volume.

On the other hand,

$$\mathbf{P} = (\hat{\alpha}^* + (\hat{\beta}^* \nabla)) \mathbf{E}_m, \quad (18)$$

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

Combining Equations (14)–(18), one obtains the following set of two simultaneous equations, which enable one to determine $\hat{\alpha}^*$ and $\hat{\beta}^*$:

$$\frac{V}{4\pi} (\hat{\epsilon}^i - \hat{\epsilon}_m) \mathbf{E}^i = (\hat{\alpha}^* + (\hat{\beta}^* \nabla)) \mathbf{E}_m, \quad (19)$$

$$\mathbf{E}^i = (\hat{\epsilon}_m - \hat{\epsilon}_m \cdot \hat{q} + \hat{\epsilon}^i \cdot \hat{q})^{-1} \hat{\epsilon}_m \mathbf{E}_m. \quad (20)$$

The optical activity term $(\hat{\beta}_0 \nabla)$ is a small correction to the total susceptibility tensor of the dielectric medium $\hat{\epsilon}_m$, and hence, these equations can be expanded in powers of $(\hat{\beta}_0 \nabla)$ keeping only the linear terms. Finally, one obtains the following expressions for effective polarizability and the effective optical activity in the limiting case of an very long rod-like macromolecule in the isotropic chiral solvent:

$$\alpha_{\perp}^* = \frac{V}{2\pi} \frac{\epsilon_m(\epsilon_{\perp} - \epsilon_m)}{\epsilon_{\perp} + \epsilon_m}, \quad (21)$$

$$\Delta\alpha^* = \frac{V}{4\pi} \frac{[\epsilon_m^2 - \epsilon_m(\epsilon_{\parallel} - 3\epsilon_{\perp}) + \epsilon_{\perp}\epsilon_{\parallel}]}{\epsilon_{\perp} + \epsilon_m}, \quad (22)$$

$$g_{\perp}^* = -\frac{V}{2\pi} \beta_0 \frac{[\epsilon_m(\epsilon_{\perp} + \epsilon_m) - \epsilon_{\perp}(2\epsilon_{\perp} - \epsilon_{\parallel})]}{(\epsilon_{\perp} + \epsilon_m)^2}, \quad (23)$$

$$\Delta g^* = \frac{V}{4\pi} \beta_0 \frac{[\epsilon_m(\epsilon_m - \epsilon_{\perp} + \epsilon_{\parallel}) - \epsilon_{\perp}(3\epsilon_{\perp} + \epsilon_{\parallel})]}{(\epsilon_{\perp} + \epsilon_m)^2}. \quad (24)$$

Substituting the expressions for $\Delta\alpha^*$ and Δg^* into Equation (9), one obtains the following expression for the pseudoscalar coupling constant of the effective chiral interaction potential between nonchiral macromolecules in a chiral solvent:

$$J^* = E_0 \beta_0 \left(\frac{V}{4\pi} \right)^2 \frac{[\epsilon_m^2 - \epsilon_m(\epsilon_{\parallel} - 3\epsilon_{\perp}) + \epsilon_{\perp}\epsilon_{\parallel}][\epsilon_m(\epsilon_m - \epsilon_{\perp} + \epsilon_{\parallel}) - \epsilon_{\perp}(3\epsilon_{\perp} + \epsilon_{\parallel})]}{(\epsilon_{\perp} + \epsilon_m)^3 \epsilon_m^2}. \quad (25)$$

According to Equation (25), the coupling constant of the effective chiral interaction potential is proportional to the optical activity β_0 of the chiral solvent. The coupling constant is also a complicated function of the components of the dielectric susceptibility of the medium inside the rod-like macromolecule. The dependence of the normalized coupling constant $J_{norm}^* = J^* \epsilon_m / E_0 \beta_0 \left(\frac{V}{4\pi} \right)^2$ on $\epsilon_{\parallel} / \epsilon_m$ and $\epsilon_{\perp} / \epsilon_m$ is presented in Figure 1. One can readily see that the effective coupling constant may even change sign depending on the relation between the transverse dielectric susceptibility of the macromolecule and susceptibility of the solvent. One notes also that the effective chiral coupling constant is rather small when $\epsilon_{\parallel} < 2\epsilon_m$. Then, the effective coupling constant is rapidly increasing with the increasing $\epsilon_{\parallel} / \epsilon_m$; hence, one concludes that the sufficiently strong effective chiral interaction can exist only when the longitudinal susceptibility of the macromolecule is significantly larger than the solvent dielectric constant. At the same time, the effective chiral interaction constant is sufficiently large only when the transverse susceptibility of the macromolecule is smaller than the solvent dielectric constant.

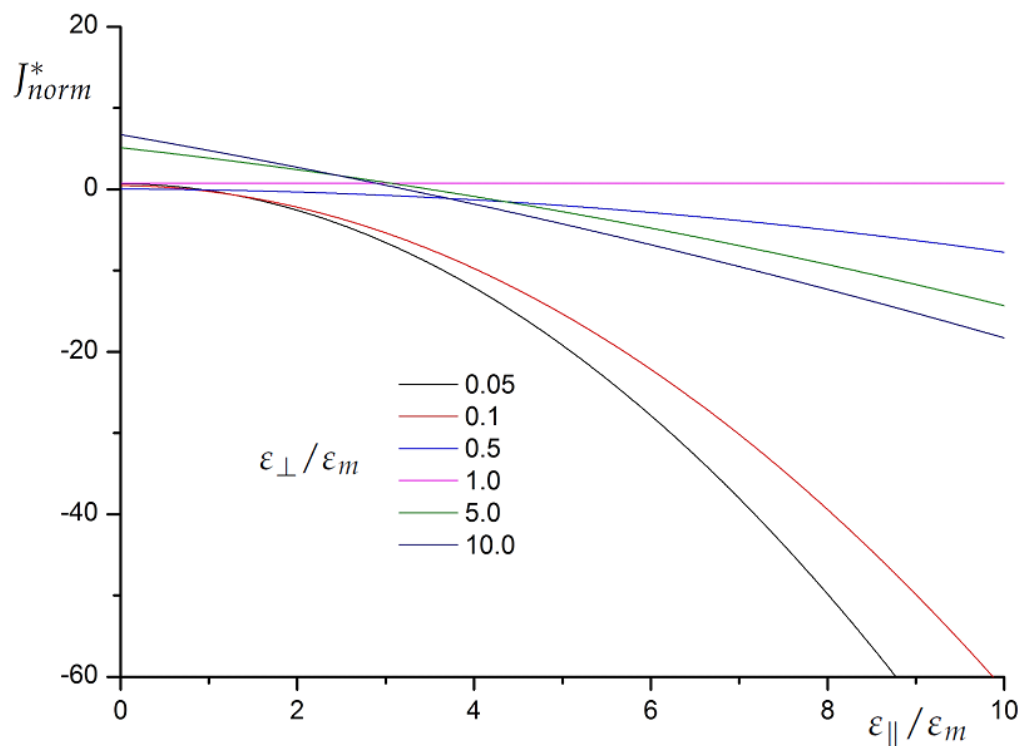


Figure 1. The dependence of the coupling constant on $\epsilon_{\parallel}/\epsilon_m$ and $\epsilon_{\perp}/\epsilon_m$.

It is also interesting to note that even an anisotropic cavity in the chiral dielectric medium possesses an effective optical activity, which can be written in the following simple form, taking into account that in this case $\epsilon_{\parallel} = \epsilon_{\perp} = 1$:

$$\Delta g_{cavity}^* = \frac{V}{\pi} \beta_0 \frac{\epsilon_m - 1}{(1 + \epsilon_m)^2}. \quad (26)$$

The effective polarizability anisotropy of the rod-like cavity is also given by a simple expression:

$$\Delta \alpha_{cavity}^* = \frac{V}{4\pi} \frac{(\epsilon_m - 1)^2}{1 + \epsilon_m}. \quad (27)$$

Thus, one concludes that two neighboring elongated cavities in the chiral dielectric medium should also twist with respect to each other, although the equilibrium twist angle can be relatively small.

4. Conclusions

In this paper, we derived a general expression for the effective chiral interaction potential between two nonchiral rod-like macromolecules in the chiral nonionic solvent, which was modeled as an isotropic chiral dielectric medium. The effective chiral interaction potential was expressed in terms of the anisotropy of the effective polarizability and the effective gyration tensor (which determines the optical activity) of a macromolecule in the chiral solvent. The macromolecules were modeled as long hard rods filled with anisotropic nonchiral dielectric medium. It was shown that a nonchiral macromolecule embedded in a chiral solvent possesses an effective optical activity, which is proportional to the optical activity of the solvent. Explicit analytical expressions for the effective polarizability and effective gyration tensor of a rod-like macromolecule in a chiral solvent were also obtained. A change in the dielectric susceptibility of the solvent may cause the sign inversion of the effective chiral interaction coupling constant. At the same time, strong effective chiral interaction between nonchiral macromolecules can exist only when the longitudinal susceptibility of the macromolecule is significantly larger than the solvent

dielectric constant while the transverse susceptibility is smaller than the solvent dielectric constant. This means that this effect can be observed in nonpolar solvents with relatively low dielectric constant.

The effective chiral interaction between nonchiral macromolecules in a chiral solvent creates a torque acting on the long axes of the two molecules resulting in their mutual twist. Such a twist, however, is expected to be relatively small because the same macromolecules interact also via strong nonchiral dispersion forces which promote parallel orientation of elongated macromolecules. At the same time, such a twist may be of the same order as the one in typical cholesteric polymers where similar chiral and nonchiral intermolecular interactions are also present. Thus, one may conclude that cholesteric twisting in the nematic polymer liquid crystal phase can be induced by a simple chiral solvent. The pitch of the macroscopic helical structure of the existing cholesteric polymer phase can also be modified by adding a low molecular weight chiral dopant, which may be important for practical applications. A similar effect may also be observed in the cholesteric phase exhibited by chiral cellulose nanocrystals [21,22].

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