

## Chapter 1

### Nematic liquid crystals doped with nanoparticles: phase behavior and dielectric properties

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Thermodynamics and dielectric properties of nematic liquid crystals doped with various nanoparticles have been studied in the framework of a molecular mean-field theory. It is shown that spherically isotropic nanoparticles effectively dilute the liquid crystal material and cause a decrease of the nematic-isotropic transition temperature, while anisotropic nanoparticles are aligned by the nematic host and, in turn, may significantly improve the liquid crystal alignment. In the case of strong interaction between spherical nanoparticles and mesogenic molecules, the nanocomposite possesses a number of unexpected properties: The nematic-isotropic co-existence region appears to be very broad, and the system either undergoes a direct transition from the isotropic phase into the phase-separated state, or undergoes first a transition into the homogeneous nematic phase and then phase-separates at a lower temperature. The phase separation does not occur for sufficiently low nanoparticle concentrations, and, in certain cases, the separation takes place only within a finite region of the nanoparticle concentration. For nematics doped with strongly polar nanoparticles, the theory predicts the nanoparticle aggregation in linear chains that make a substantial contribution to the static dielectric anisotropy and optical birefringence of the nematic composite. The theory clarifies the microscopic origin of important phenomena observed in nematic composites including a shift of the isotropic-nematic phase transition and improvement of the nematic order; a considerable softening of the first order nematic-isotropic transition; a complex phase-separation behavior; and a significant increase of the dielectric anisotropy and the birefringence.

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## 1. Introduction

Liquid crystal nanocomposites are considered to be extremely promising materials in which the properties of a liquid crystal (LC), used, for example, in display applications, are modified/improved by the presence of various nanoparticles (NPs). There are many reports showing that doping of a nematic LC with even a small amount of NPs affects nearly all important properties of nematic materials, resulting in a decrease of threshold and switching voltages and reducing the switching times of LC displays (see, for example, Refs. 1–5). Suspensions of metal, dielectric and semiconductor 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<sup>6,7</sup> and improve the photorefractive properties.<sup>8</sup> 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.<sup>9–11</sup> Metal NPs have been also used to widen the temperature range of LC blue phases,<sup>12</sup> which are important for applications, and enhance random lasing in the dye-doped LC medium.<sup>13</sup> Finally, distributing semiconductor quantum dots in smectic LC-polymers enables one to achieve the positional ordering of nanosize particles.<sup>14,15</sup>

At the same time, LC-NP composites are also considered as the building blocks of novel metamaterials. Metamaterials, i.e., arrays of sub-wavelength metallic/semiconductor particles, offer a new degree of freedom in controlling light: they enable tailoring the optical response, achieving very high, very low and negative values of refractive index, permittivity and/or permeability.<sup>16</sup> Combining emerging optical metamaterials with LCs provides a new important quality – tunability, which is of key importance for emerging applications including tunable photonic materials, optically addressed spatial light modulators and dynamic holography. Upon immersing a metamaterial into a nematic LC one can switch the LC alignment by external voltages and modify the overall optical properties of the composite.<sup>17</sup> 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.<sup>18–20</sup>

Many applications of LC nanocomposites require an understanding of how the NPs affect the orientational order in the LC medium and the ther-

modynamic stability of the LC phase. Recently it has been shown<sup>10,11</sup> that the dipolar induction interaction between ferroelectric NPs and the surrounding nematic LC medium may result in a substantial decrease of the nematic-isotropic (N-I) transition temperature. It has also been shown experimentally that the N-I transition temperature can be significantly affected by the presence of other types of NPs. For example, a decrease of the N-I transition temperature is observed in nematics doped with approximately isotropic silver,<sup>21</sup> gold<sup>22</sup> or aerosil particles,<sup>23,24</sup> while the N-I transition temperature increases if the nematic LC is doped with strongly anisotropic NPs including nanotubes,<sup>25</sup> magnetic nanorods<sup>26</sup> and ferroelectric particles.<sup>9,10</sup> Recently a detailed mean-field molecular theory of nematic LCs doped with both isotropic and anisotropic NPs has been developed.<sup>27</sup> The effect of isotropic NPs has also been considered in Ref. 28, while the effect of the external electric field on the nematic nano-composites has been studied in Ref. 29.

In the case of spherical or weakly anisotropic NPs, the N-I transition temperature decreases with the increasing concentration of NPs and as a result the nematic phase is partially destabilized. In such a system the total free energy may be minimized if the system separates into the isotropic phase with an increased concentration of NPs and the nematic phase with lower concentration of NPs. One notes that such a phase separation is very much different from an ordinary demixing, which takes place already in the isotropic phase and does not require the system to undergo a phase transition. Experimentally such a demixing can be suppressed by attaching appropriate organic groups to the surface of the NPs which makes them more compatible with the surrounding fluid. In contrast, the origin of the nematic-isotropic phase separation is intimately related to the phase transition thermodynamics, and we find such a phase separation to be very interesting from both the fundamental and the applications point of view.

It should be noted that a similar phase separation occurs around the N-I transition point in mixtures of different LCs and, in particular, in nematics doped with nonmesogenic molecules (see e.g. Refs. 30,31). The corresponding two-phase region around the N-I transition, however, is usually very narrow. This is related to the fact that properties of the dopant molecules do not differ much from those of the host ones. In contrast, the properties of metal or semiconductor NPs may differ very significantly from those of typical mesogenic molecules, and, as a result, the region of coexistence of the isotropic and the nematic phase may be much wider.<sup>32</sup> The first molecular theory of the nematic-isotropic phase separation in nematic

nano-composites has recently been developed by the authors.<sup>33</sup>

Strong interaction between NPs may also lead to their aggregation including the formation of chains of NPs when the interaction is strongly anisotropic. Aggregates of NPs in general, and polar chains in particular, are expected to modify all major properties of nematic nano-composites, including their dielectric and optical properties. Nematic LCs with polar chains should also be very sensitive to external electric fields which may be used for alignment and switching at very low applied voltage.

It has been shown experimentally (see, for example, Refs. 9,34) that the dielectric anisotropy of nematic LCs doped with strongly polar (ferroelectric) NPs is dramatically increased. Indeed, a very small molar fraction of ferroelectric NPs (of the order of  $10^{-3}$ ) accounts for a contribution of the order of 5 – 6 to the anisotropy of the dielectric constant, which is comparable with the anisotropy of the nematic host. Preliminary estimates indicate that the increase is too strong to be explained without taking into account possible aggregation of NPs and formation of polar chains. There exists some experimental evidence that quantum dots may also form long chains in nematic LCs<sup>35</sup> even though such NPs are nonpolar.

Aggregation of NPs in the nematic phase may occur if the inter-particle interaction potential is not strong enough to induce demixing but is still much stronger than the interaction between mesogenic molecules. Strongly anisotropic interaction between NPs, including in particular dipole-dipole one, will lead to the formation of polar chains. It has been shown<sup>36</sup> that the equilibrium chain length strongly depends on the contact interaction potential normalized by the temperature. Long chains of NPs may occur only if the contact interaction is of the order of  $10k_B T$ <sup>36</sup> which is satisfied, for example, for ferroelectric NPs.<sup>9,34</sup> Polar chains should make a significant contribution to the dielectric anisotropy of nematic composites.

In this chapter we summarize the results of a molecular-field theory of nematic LCs doped with NPs. In Section 2 we consider the effect of both isotropic and anisotropic NPs on the nematic-isotropic phase transition temperature and discuss a softening of the N-I phase transition. In Section 3 the isotropic-nematic phase separation caused by isotropic NPs is studied in detail and the corresponding phase diagrams are presented. Finally, in Section 4 we describe the effect of chains of polar NPs on the dielectric anisotropy and the birefringence of nematic composites.

## 2. Effect of nano-particles on the nematic-isotropic phase transition

### 2.1. Mean-field theory of nematic composites

Consider a composite material formed by  $N_m$  highly anisotropic identical LC molecules and  $N_p$  NPs with possible deviations in physical properties or shape, size and surface structure. To take into account this NP diversity we assume that there are  $L$  different types of NPs in the composite and the number of the NPs of the type  $l$  is  $N_l$  such that  $N_1 + N_2 + \dots + N_L = N_p$ .

Now let  $V_{\text{mol}}$  be the part of the total volume  $V$  occupied by the LC molecules, while the volume  $V_p = V - V_{\text{mol}}$  is occupied by NPs. Then  $\phi = V_p/V$  is the volume fraction of NPs and the number density of NPs  $\rho_p = \phi/v_p$ , where  $v_p$  is the average particle volume. Assuming that the number density of LC molecules in the pure LC is  $\rho_0$ , one may express the number density of LC molecules in the composite as  $\rho = \rho_0(1 - \phi)$ .

Following the classical Maier-Saupe theory of nematic ordering, we specify the orientation of a LC molecule by the unit vector  $\mathbf{a}$  in the direction of its long axis and express the microscopic pair intermolecular interaction potential as  $u_{\text{mol}}(\mathbf{a}_1, \mathbf{a}_2, \mathbf{r})$ , i.e., as depending on the intermolecular vector  $\mathbf{r}$  and the long axes of the two molecules  $\mathbf{a}_1$  and  $\mathbf{a}_2$ .

Macroscopically, the orientational nematic order of the LC is described by the tensor order parameter  $\mathbf{Q} = S(\mathbf{n} \otimes \mathbf{n} - \mathbf{1}/3)$ , which is the macroscopic average of the microscopic molecular tensor  $\mathbf{Q}^M = (\mathbf{a} \otimes \mathbf{a} - \mathbf{1}/3)$ . The conventional scalar nematic order parameter is defined as  $S = \langle 3/2(\mathbf{n} \cdot \mathbf{a})^2 - 1/2 \rangle$ , where  $\langle \dots \rangle$  denotes the statistical average, and  $\mathbf{n}$  is the nematic director, i.e., a unit vector parallel to the nematic symmetry axis.

Generally, the orientation of the anisotropic NP can be characterized by three orthogonal unit vectors: the "primary" axis  $\mathbf{A}_l$ , and the two secondary orthogonal axes  $\mathbf{B}_l$  and  $\mathbf{C}_l$ . In the statistical theory, the orientational ordering of the NPs can be described in a way similar to that established for the orientational ordering of biaxial molecules.<sup>37</sup>

In this Section, we assume that the NP concentration is relatively low and thus we neglect the direct interaction between NPs. In this case, the orientational order of NPs is induced by the uniaxial LC medium and the NPs possess tensor order parameters of the same uniaxial symmetry, i.e.,  $\mathbf{Q}_l = S_l(\mathbf{n} \otimes \mathbf{n} - \mathbf{1}/3)$  and  $\mathbf{D}_l = D_l(\mathbf{n} \otimes \mathbf{n} - \mathbf{1}/3)$ . Here  $S_l = \langle 3/2(\mathbf{n} \cdot \mathbf{A}_l)^2 - 1/2 \rangle$  is the nematic order parameter of the primary axis of  $l$ -th type NP and  $D_l$  is the additional order parameter which describes uniaxial ordering

of short axes of the NPs of the type  $l$ .

The order parameter  $D_l$  is usually much smaller than  $S_l$  and thus it may be neglected. This is equivalent to the assumption that short axes of the particles are distributed randomly in the uniaxial nematic phase and hence the particle may be considered as effectively uniaxial. As a result, one may introduce the uniaxial microscopic pair interaction potential  $u_l(\mathbf{a}, \mathbf{A}_l, \mathbf{r})$  between an LC molecule, which orientation is specified by the long axis  $\mathbf{a}$ , and a uniaxial NP with the axis  $\mathbf{A}_l$ .

Then in the mean-field approximation, the free energy of the composite LC-NP medium reads:

$$\begin{aligned}
 F = & \frac{1}{2V} \sum_{m=1}^{N_m} \sum_{m'=1}^{N_m} \int f(\mathbf{a}_m) u_{\text{mol}}(\mathbf{a}_m, \mathbf{a}_{m'}, \mathbf{r}) f(\mathbf{a}_{m'}) d\mathbf{r} d\mathbf{a}_m d\mathbf{a}_{m'} + \\
 & N_m k_B T \int f(\mathbf{a}) \ln f(\mathbf{a}) d\mathbf{a} + \\
 & \frac{1}{V} \sum_{m=1}^{N_m} \sum_{l=1}^L \sum_{n=1}^{N_l} \int f(\mathbf{a}_m) u_n(\mathbf{a}_m, \mathbf{A}_n, \mathbf{r}) f_l(\mathbf{A}_n) d\mathbf{r} d\mathbf{a}_m d\mathbf{A}_n + \\
 & k_B T \sum_{l=1}^L \sum_{n=1}^{N_l} \int f_l(\mathbf{A}_n) \ln f_l(\mathbf{A}_n) d\mathbf{A}_n, \quad (1)
 \end{aligned}$$

where  $m' \neq m$  in the first term,  $f(\mathbf{a})$  is the orientational distribution function of the LC molecules and where  $f_l(\mathbf{A})$  is the orientational distribution function of the NPs of type  $l$ .

Due to the lack of positional order, the free energy of the nematic phase is determined by the so-called effective orientational pair potentials which are obtained by the integration of the corresponding microscopic pair potentials over the intermolecular vector or the vector between a molecule and a NP. In the mean-field theory of uniaxial nematics, the effective interaction potential is expressed, in the first approximation, as a sum of the isotropic part and the anisotropic potential  $w(\mathbf{a}_m \cdot \mathbf{a}_{m'})^2$  which is a simplest bilinear coupling between the molecular tensors  $(\mathbf{a}_{ml} \otimes \mathbf{a}_{ml} - \mathbf{1}/3)$  and  $(\mathbf{a}_{m2} \otimes \mathbf{a}_{m2} - \mathbf{1}/3)$  which are composed from the components of the molecular long axes  $\mathbf{a}_m$  and  $\mathbf{a}_{m'}$  :

$$U_{\text{mol}}(\mathbf{a}_m, \mathbf{a}_{m'}) = \int d\mathbf{r} u_{\text{mol}}(\mathbf{a}_m, \mathbf{a}_{m'}, \mathbf{r}) = \text{const} + w(\mathbf{a}_m \cdot \mathbf{a}_{m'})^2, \quad (2)$$

The latter term is obviously invariant under the molecular permutation  $m \leftrightarrow m'$  and the head-tail transformations  $\mathbf{a} \leftrightarrow -\mathbf{a}$ . The nematic phase is stable in the pure LC when the constant  $w$  is negative.

Similarly, one can express the effective interaction potential between a NP and an LC molecule as:

$$U_n(\mathbf{a}_m, \mathbf{A}_n) = \int d\mathbf{r} u_n(\mathbf{a}_m, \mathbf{A}_n, \mathbf{r}) = \text{const} + W_n(\mathbf{a}_m \cdot \mathbf{A}_n)^2. \quad (3)$$

Note that this potential is also determined by a coupling between nonpolar molecular tensors of a LC molecule and a NP. Even if NPs are polar, i.e. there is no  $\mathbf{A} \leftrightarrow -\mathbf{A}$  symmetry, the lowest-order anisotropic term in the interaction potential has exactly the same form as in Eq. (2).

In the context of various models of the dominant anisotropic LC-NP interaction, it is possible to obtain particular expressions for the interaction constants  $W$ . For example, according to Ref. 11, dipole-dipole induction interaction between a spherical ferroelectric NP and the nematic LC matrix corresponds to the following constant  $W$

$$W = \frac{\Delta\alpha p^2}{90\varepsilon_0\varepsilon^2 v_p}, \quad (4)$$

where  $p$  is the absolute value of ferroelectric NP permanent dipole,  $\Delta\alpha$  is the dielectric anisotropy of a LC molecule and  $\varepsilon$  is the static LC permittivity. Some expressions for the constants  $W$  determined by the NPs shape anisotropy have been obtained in Ref. 27.

Since all LC molecules are identical, the sums over  $m$  and  $m'$  in the free energy (1) reduce to a multiplication by  $N_m$ . Similarly, summations over the NPs of the same type reduces to the multiplication by the numbers  $N_l$ . Minimizing the free energy one obtains from the Euler-Lagrange equations the following expression for the LC orientational distribution function

$$f(\mathbf{a}) = \frac{1}{Z} \exp \left[ -\frac{U_{\text{mol}}^{MF}(\mathbf{a})}{k_B T} \right], \quad (5)$$

where the molecular partition function  $Z$  is also the normalization constant

$$Z = \int \exp \left[ -\frac{U_{\text{mol}}^{MF}(\mathbf{a})}{k_B T} \right] d\mathbf{a}. \quad (6)$$

The orientational distribution function of the NPs of the  $l$ -th type NPs is similarly given by

$$f_l(\mathbf{A}) = \frac{1}{Z_l} \exp \left[ -\frac{U_l^{MF}(\mathbf{A})}{k_B T} \right], \quad (7)$$

where  $Z_l$  is expressed as

$$Z_l = \int \exp \left[ -\frac{U_l^{MF}(\mathbf{A})}{k_B T} \right] d\mathbf{A}. \quad (8)$$

The mean-field potential for the LC molecules is given by:

$$U_{\text{mol}}^{MF}(\mathbf{a}) = \rho \int f(\mathbf{a}') U_{\text{mol}}(\mathbf{a}, \mathbf{a}') d\mathbf{a}' + \rho_p \sum_{l=1}^L \frac{N_l}{N_p} \int f_l(\mathbf{A}) U_l(\mathbf{a}, \mathbf{A}) d\mathbf{A}, \quad (9)$$

and the mean field potential for the NPs of the  $l$ -th type is expressed as

$$U_l^{MF}(\mathbf{A}) = \rho \int f(\mathbf{a}) U_l(\mathbf{a}, \mathbf{A}) d\mathbf{a}. \quad (10)$$

Using the effective interaction potentials given by (2) and (3) one can express the mean-field potential (9) as

$$U_{\text{mol}}^{MF}(\mathbf{a}) = \rho w(\mathbf{Q}^M : \mathbf{Q}) + \rho_p \sum_{l=1}^L \frac{N_l}{N_p} W_l(\mathbf{Q}^M : \mathbf{Q}_l), \quad (11)$$

while the potential (10) reads

$$U_l^{MF}(\mathbf{A}) = \rho W_l(\mathbf{Q}_l^M : \mathbf{Q}), \quad (12)$$

where the irrelevant isotropic constant terms has been omitted.

Substituting the distribution functions (5) and (7) together with the above expressions for the mean-field potentials into Eq. (1) one can express the free energy of the nematic phase as a function of the scalar nematic order parameters of the LC and NPs:

$$\begin{aligned} \frac{1}{V} F(S, S_1, \dots, S_L) = & -\frac{1}{3} \rho^2 w S^2 - \frac{2}{3} \rho \rho_p S \sum_{l=1}^L \frac{N_l}{N_p} W_l S_l - \\ & \rho k_B T \ln Z - \rho_p k_B T \sum_{l=1}^L \frac{N_l}{N_p} \ln Z_l, \quad (13) \end{aligned}$$

The partition functions can be expressed in terms of the integrals over the polar angles between the long axes of the particles and the director:

$$Z = \int_0^\pi \sin \gamma d\gamma \exp \left[ -\frac{2}{3k_B T} \left( \rho w S + \rho_p \sum_{l=1}^L \frac{N_l}{N_p} W_l S_l \right) P_2(\cos \gamma) \right], \quad (14)$$

$$Z_l = \int_0^\pi \sin \gamma d\gamma \exp \left[ -\frac{2}{3k_B T} \rho W_l S P_2(\cos \gamma) \right], \quad (15)$$

where  $P_2$  is the second Legendre polynomial.

The free energy (13) formally depends on a macroscopic number of variables. Direct numerical minimization of the free energy is possible in

the case of identical particles or in a more general case of a reasonable finite number of types of particles.

Alternatively, one may find the extremum of Eq. (13) by differentiating it with respect to  $S$  and  $S_{1,\dots,L}$ . This yields the system of self-consistent equations:

$$S = \frac{1}{Z} \int_0^\pi d\gamma P_2(\cos \gamma) \sin \gamma \times \exp \left[ -\frac{2}{3k_B T} \left( \rho w S + \rho_p \sum_{l=1}^L \frac{N_l}{N_p} W_l S_l \right) P_2(\cos \gamma) \right], \quad (16)$$

$$S_l = \frac{1}{Z_l} \int_0^\pi d\gamma P_2(\cos \gamma) \sin \gamma \exp \left[ -\frac{2}{3k_B T} \rho W_l S P_2(\cos \gamma) \right], \quad (17)$$

which can also be solved numerically for a finite number of particle types.

## 2.2. Shift of the nematic-isotropic transition temperature caused by nano-particles

In this subsection we first present a general analytical consideration of the mixture of LC with nonidentical particles which is possible in the limit of weak particle anisotropy.

According to the Maier-Saupe mean-field theory of one-component LCs the nematic order parameter satisfies the following equation:

$$S = \frac{1}{Z} \int_0^\pi d\gamma P_2(\cos \gamma) \sin \gamma \exp \left[ -\frac{2\rho_0 w}{3k_B T} S P_2(\cos \gamma) \right], \quad (18)$$

which is known to describe the first order isotropic-nematic phase transition, which occurs at the following transition temperature

$$T_0 \simeq 0.149 \frac{\rho_0 |w|}{k_B}. \quad (19)$$

If the nematic is doped by isotropic spherical NPs, the interaction constants  $W_n$  vanish identically. In this case, Eq. (16) is reduced to the form (18) with  $\rho$  instead of  $\rho_0$ , i.e., in the case of spherical NPs the effective interaction constant  $w$  is renormalized by the factor  $(1 - \phi)$ . Thus the composite LC material with spherical inclusions undergoes the isotropic-nematic phase transition at the lower temperature

$$T_{\text{NI}} = (1 - \phi) T_0. \quad (20)$$

The decrease of the transition temperature by the factor  $(1 - \phi)$  clearly describes the so-called effect of dilution of LC by isotropic particles.

For weakly anisotropic particles, the constants  $W_l$  are small compared to  $w$ . Then in the nematic temperature range one also obtains  $W_l \rho_0 \ll k_B T$  and therefore the exponent in Eq. (17) can be expanded. As a result, the induced order parameter of NPs appears to be linearly related to the LC order parameter:

$$S_l \simeq -\frac{2}{15} \frac{\rho_0(1-\phi)W_l}{k_B T} S. \quad (21)$$

Substituting these small induced parameters  $S_l$  into Eq. (16) one again obtains the self-consistent equation of the form (18), where the interaction constant  $w$  is renormalized by the following factor

$$\left[ 1 - \phi + \phi(1-\phi) \frac{2\langle W^2 \rangle}{15|w|k_B T v_p} \right], \quad (22)$$

and where  $\langle W^2 \rangle = \sum_{l=1}^L W_l^2 N_l / N_p$  is an average square of LC-NP anisotropic interaction constant.

One can readily see that due to the particle anisotropy, the effective nematic interaction constant increases and becomes slightly temperature dependent. This promotes the nematic ordering of the LC matrix and, in the first approximation, this describes the positive feedback from the orientation ordering of anisotropic NPs.

Accordingly, in the case of weakly anisotropic NPs, the transition temperature undergoes the following shift:

$$T_{\text{NI}} \simeq T_0 \left[ 1 - \phi + \phi(1-\phi) \frac{2\langle W^2 \rangle}{15|w|k_B T_0 v_p} \right], \quad (23)$$

where the terms linear in concentration  $\phi$  contain also a positive contribution from the NP anisotropy and can therefore compensate the dilution effect of the LC matrix by NPs. An exact compensation occurs at  $\langle W^2 \rangle = 1.12w^2 v_p \rho_0$ . The terms quadratic in  $\phi$  give rise to a weakly parabolic concentration dependence of the transition temperature  $T_{\text{NI}}(\phi)$ . The sign of the quadratic term is negative in line with the experimental results for nematic LC polymers doped with silver NPs.<sup>21</sup>

### 2.3. Numerical results in the case of strong NP anisotropy

In order to clarify the effects of anisotropic NPs on the nematic-isotropic transition in the general case one has to solve numerically the system of equations (16) and (17). For simplicity, we assume that there is only one

type of NPs in the composite. Then the system of simultaneous equations for the nematic order parameters can be conveniently reduced to the nondimensional form:

$$S = \frac{1}{Z} \int_{-1}^1 dx P_2(x) \exp \left[ \frac{2}{3\tau} [(1 - \phi)S + \phi\xi\omega S_p] P_2(x) \right], \quad (24)$$

$$S_p = \frac{1}{Z_p} \int_{-1}^1 dx P_2(x) \exp \left[ \frac{2}{3\tau} (1 - \phi)\omega S P_2(x) \right], \quad (25)$$

where the partition functions reads:

$$Z = \int_{-1}^1 dx \exp \left[ \frac{2}{3\tau} [(1 - \phi)S + \phi\xi\omega S_p] P_2(x) \right], \quad (26)$$

$$Z_p = \int_{-1}^1 dx \exp \left[ \frac{2}{3\tau} (1 - \phi)\omega S P_2(x) \right], \quad (27)$$

and where the following dimensionless parameters have been introduced:  $\tau = k_B T / (\rho_0 |w|)$  is the dimensionless temperature;  $\omega = W/w$  describes the relative strength of LC-NP anisotropic interaction; and  $\xi = v_m/v_p$ , which is the ratio of the LC molecular volume to the NP volume, characterizes the relative NP size.

Eqs. (24) and (25) have been solved iteratively and the numerical results for the orientational order parameters as functions of temperature and the N-I transition temperature have been obtained.<sup>27</sup>

We first analyze the effect of NPs on the isotropic-nematic transition temperature. Typical profiles of the calculated transition temperatures as functions of the NP volume fraction are presented in Fig. 1 for  $\xi = 0.5$ , i.e., the NP volume is twice larger than the LC molecular volume. Note that the transition temperatures for particles with negative and positive anisotropy are presented on the left and on the right hand side of the chart, respectively. One can readily see that the  $T_{NI}(\phi)$  variations are almost linear, which is very similar to the experimental results in Ref. 21 and the analytical Eq. (23). For smaller  $\omega$ , the addition of NP results in a decrease of the transition temperature, i.e., the effect of LC dilution prevails. For the values  $\omega \simeq -2$  and  $\omega \simeq 1.5$  the transition temperature remains almost constant due to the compensation of the dilution by the effect of NP anisotropy. For stronger anisotropy, the transition occurs at temperatures higher than in the pure LC, and the otherwise hardly noticeable parabolic shape of the curves becomes clearer.

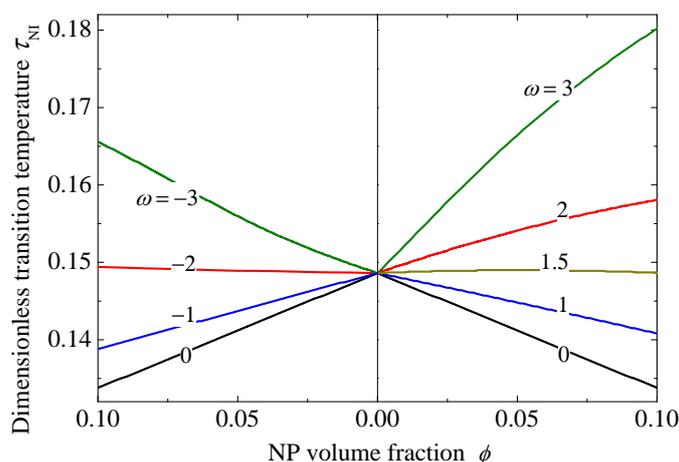


Fig. 1. Isotropic-nematic transition temperature as a function of the NP volume fraction for several negative (on the left) and positive (on the right) values of the NP anisotropy  $\omega$ . Note the reversed direction of the  $\phi$ -axis on the left

Typical variations of the transition temperature as functions of the NP anisotropy are presented in Fig. 2. It can be seen that even far beyond the limit of the weak NP anisotropy, the curves still correspond to the approximately parabolic dependence on  $W$  of Eq. (23). For larger NP concentrations the effect of NPs is more pronounced. According to Fig. 1, in the region of small  $\omega$  the NPs again effectively dilute the LC. At stronger anisotropy, the NPs make a positive effect on the nematic and increase its temperature range. The intersections of different curves take place at the points, which correspond to the lines  $\omega = -2$  and  $\omega = 1.5$  in Fig. 1. The points on these lines correspond to the values of parameters for which the effect of dilution is compensated by that of the anisotropy and as a result the transition temperature is practically independent of  $\phi$ .

In summary, both analytic and numerical results demonstrate the two main mechanisms of the effect of randomly distributed NPs on the nematic LC. Firstly, in the presence of NPs the average separation between mesogenic molecules of the LC matrix is increased, i.e., the LC matrix is effectively diluted. This decreases the average strength of intermolecular interactions, reduces the nematic ordering and decreases the temperature of the transition into the nematic phase. In contrast, partial orientation of NPs along the LC director appears to be an aligning factor for the surrounding LC molecules and provides a positive feedback for the nematic ordering.

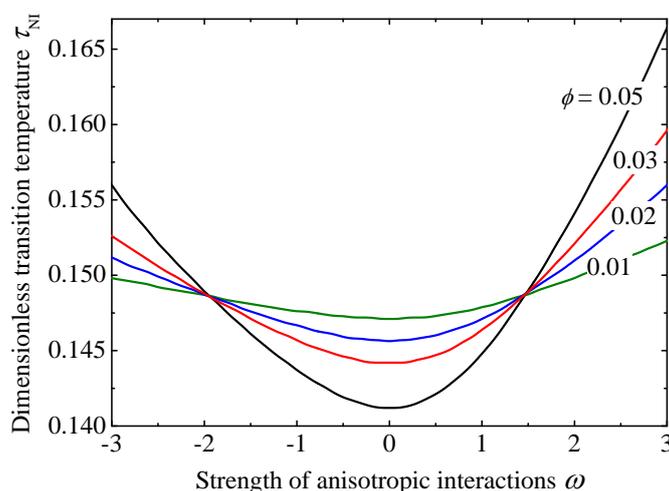


Fig. 2. Isotropic-nematic transition temperature as function of nanoparticle anisotropy for several values of nanoparticle concentration  $\phi$ .

Therefore the nematic ordering improves and the transition temperature increases. At certain values of the NP anisotropy this effect can compensate the negative "dilution" effect, and then the main LC thermodynamic properties remain almost constant independently of the NP concentration. In general, the behavior of a particular composite material is determined by the competition of "dilution" and "orientation" effects.

#### 2.4. Softening of the first order $N$ - $I$ transition

Let us now consider the temperature profiles of the LC order parameter  $S$  and NP order parameter  $S_p$ . As shown in the previous subsection, for small anisotropy, the presence of NPs mainly results in a renormalization of the transition temperature, while the nematic order parameter  $S$  does not experience any qualitative changes. In contrast, for stronger NP anisotropy, NPs may significantly affect the transition scenario. Several examples of such behavior are shown in Figs. 3 and 4, where the profiles are presented for  $\omega = 3$  and  $\omega = -3$ , respectively, and for several values of the concentration  $\phi$  between 0 to 0.1. For an easier comparison, we plot the order parameters as functions of the relative temperature measured from the phase transition point. Clearly, the presence of strongly anisotropic NPs considerably softens the first order phase transition, and at larger NP concentration and anisotropy the profile  $S(T)$  becomes very similar to that characteristic for

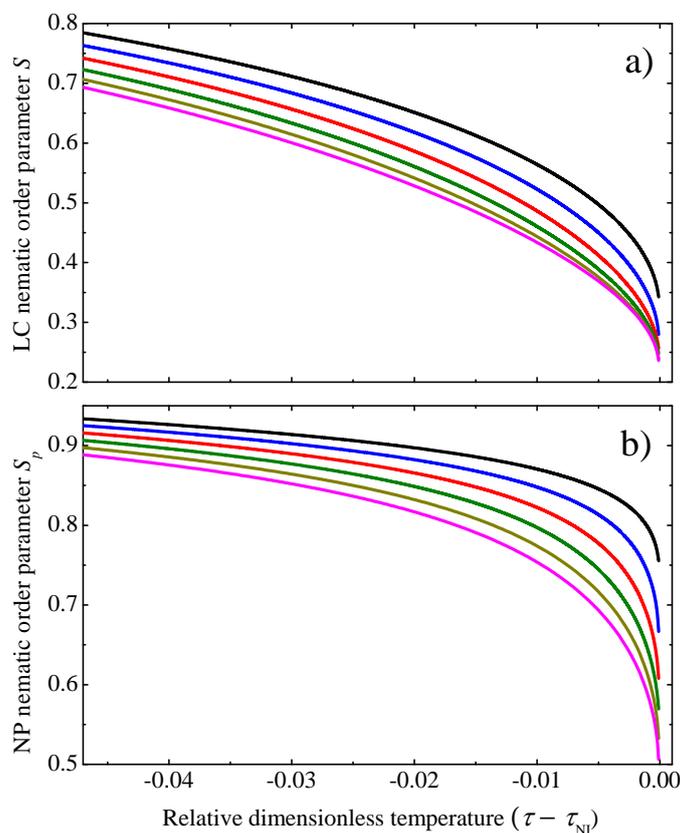


Fig. 3. Temperature dependencies of the nematic order parameters of LC (a) and NP (b) for  $\xi = 0.5$ ,  $\omega = 3$  and  $\phi = 0, 0.02, 0.04, 0.06, 0.08, 0.1$  (from the upper to lower curves respectively).

a second order phase transition.

Comparing the behavior of  $S$  and  $S_p$  one concludes that they tend to follow qualitatively the proportionality given by Eq. (21). The latter cannot be applied here directly, but the main features remain valid: larger  $S$  corresponds to larger  $|S_p|$ , and sign reversal of  $\omega$  reverses the sign of  $S_p$ .

A considerable softening of the first-order nematic-isotropic transition, in the presence of anisotropic NPs, predicted by the theory can be considered as fingerprint of the orientation order effect of such NPs on the LC matrix. One notes that this softening remarkably resembles the softening due to alignment of short molecular axes which has been predicted

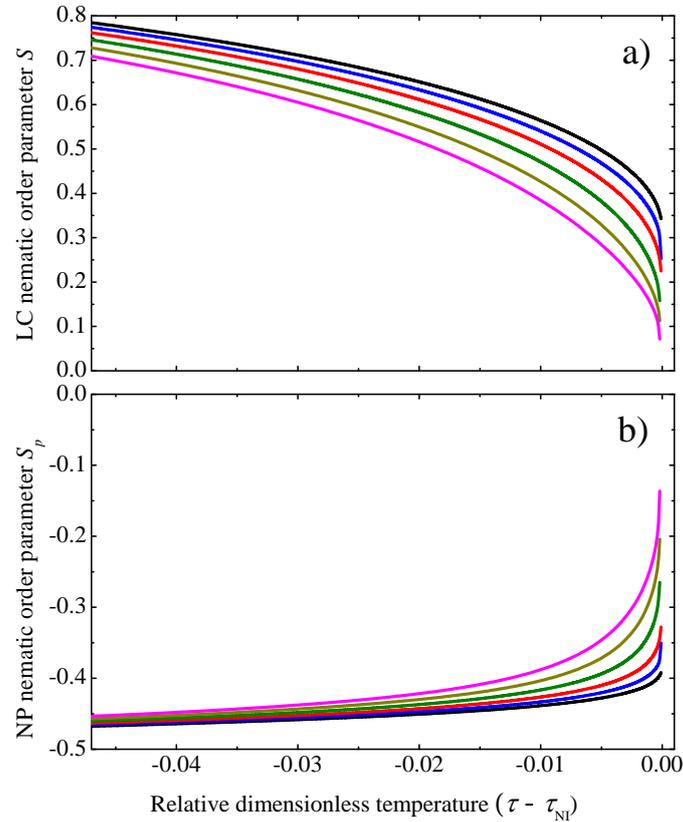


Fig. 4. The same as in Fig. 3 for the negative NP anisotropy  $\omega = -3$ .

recently in the theory of biaxial nematics.<sup>38</sup> Therefore one expects that this may be a general feature of the nematic-isotropic phase transition in systems with additional degrees of freedom, which can be modified/ordered by the conventional uniaxial nematic ordering. Such a softening of the nematic-isotropic transition has not been described in Ref. 11 because the phenomenological theory developed there accounts for the orientational order of the NPs only to the lowest order.

### 2.5. Comparison with existing experimental data

Although there exist relatively few experimental studies of the effect of NPs on the phase behavior of LCs, we believe that our results are in line with

the main established facts. For example, the “dilution”-type decrease of the transition temperature has been found in nematic LC polymers doped with isotropic (at least on average) silver NPs (see Fig. 3 of Ref. 21), in a typical nematic LC doped with gold NPs with the diameter of 3–5 nm and volume fraction of  $10^{-4} - 10^{-3}$  (see Table of Ref. 22), in LCs doped with spherical aerosil particles<sup>23,24</sup> and in dye doped nematics and polymer dispersed nematic LCs (see Table 1 of Ref. 39).

An example of substantially anisotropic NPs are carbon nanotubes which are known to promote the nematic order and increase the transition temperature.<sup>25</sup> The increase of the N-I transition temperature by 3–4 degrees has also been observed in nematics doped with large magnetic nanorods of the average diameter of 40 nm and the average aspect ratio of 10 (see Table 1 of Ref. 26). Also it has been shown experimentally that ferroelectric  $\text{Sn}_2\text{P}_2\text{S}_6$  or  $\text{BaTiO}_3$  nanoparticles at low concentration ( $< 1\%$ ) enhance the orientational order parameter of the host liquid crystal and increase the transition temperature by about 5 K.<sup>9,10</sup>

Very recently a detailed experimental study of the effect of the shape anisotropy of magnetic NPs on the N-I phase transition has been undertaken<sup>40</sup> inspired by the theoretical results presented in Ref. 27. The LC was doped with spherical and rod-like magnetic particles of different size and the measurements have been made for different volume concentrations of NPs. It has been shown that the variation of the phase transition temperature with the increasing the NP concentration depends significantly on the NP shape anisotropy. In full agreement with the theoretical conclusions presented above, ferronematics doped with rod-like magnetic NPs are characterized by a higher  $N_I$  transition temperature  $T_{NI}$  in comparison with the host nematic or the same nematic LC doped with spherical NPs.

In Ref. 41, the effects of the cis and trans forms of 4-OMphenylazobenzene at 1% and 7% mole fraction on the order and stability of the nematic phase of the 5CB LC were studied using the ESR spin probe technique. One notes that in the trans form the dye has approximately the same dimension as the 5CB molecule, and does not influence significantly the nematic ordering of the host. In contrast, the cis isomer is plate-like, i.e. it is characterized by negative anisotropy, using the terminology adopted here. As shown in Fig. 4 of Ref. 41, the jump of the nematic order parameter at the N-I transition point is decreasing with the increasing concentration of cis isomers, and the order parameter becomes more temperature dependent. This behavior corresponds to the results presented in this section which demonstrate a similar softening of the transition.

### 3. Nematic-isotropic separation in liquid crystals doped with spherical nanoparticles

#### 3.1. Simple Molecular theory

Let us consider a nematic LC doped with small amount of spherical NPs. In the appropriate molecular theory one has to take into account both isotropic and anisotropic interactions between LC molecules, isotropic interactions between LC molecules and spherical NPs, and also isotropic interactions between NPs themselves.<sup>33</sup> Then the system can be characterized by the following total interaction potential averaged over all molecule/particle positions:

$$H = \frac{1}{2} \sum_{ij} [V_{mm}(\mathbf{a}_i \cdot \mathbf{a}_j) + U_{nn} + U_{nm} + U_{mm}], \quad (28)$$

where  $U_{nn}$ ,  $U_{mm}$  and  $U_{nm}$  are the average isotropic interaction potential between NPs, LC molecules and between a NP and a LC molecule, respectively.  $V_{mm}(\mathbf{a}_i \cdot \mathbf{a}_j)$  is the anisotropic interaction potential between LC molecules which depends on the unit vectors  $\mathbf{a}_i$  and  $\mathbf{a}_j$  in the direction of the primary axis of the molecules  $i$  and  $j$ , respectively.

In the mean field approximation, the free energy of the nematic phase can be written in the form (see, for example, Ref. 42).

$$\begin{aligned} \frac{1}{V} F_N = & k_B T \rho_n (\ln \rho_n - 1) + k_B T \rho_m (\ln \rho_m - 1) \\ & - \frac{1}{2} \rho_n^2 U_{nn} - \frac{1}{2} \rho_m^2 U_{mm} + \rho_m \rho_n U_{nm} \\ & + \frac{1}{2} \rho_m^2 \int V_{mm}(\mathbf{a}_i \cdot \mathbf{a}_j) f_m(\mathbf{a}_i) f_m(\mathbf{a}_j) d\mathbf{a}_i d\mathbf{a}_j \\ & + k_B T \int f_m(\mathbf{a}) \ln f_m(\mathbf{a}) d\mathbf{a}, \quad (29) \end{aligned}$$

where  $f_m(\mathbf{a})$  is the orientational distribution function of the mesogenic molecules, and  $\rho_m$  and  $\rho_n$  are the number densities of the mesogenic molecules and NPs correspondingly.

The function  $V_{mm}(\mathbf{a}_i \cdot \mathbf{a}_j)$  can be expanded in Legendre polynomials  $P_n(\mathbf{a}_i \cdot \mathbf{a}_j)$  taking into account the first nonpolar term which is responsible for the nematic ordering:

$$V_{mm}(\mathbf{a}_i \cdot \mathbf{a}_j) \approx U_0 + J P_2(\mathbf{a}_i \cdot \mathbf{a}_j). \quad (30)$$

Here  $P_2(x) = 3x^2/2 - 1/3$  is the second Legendre polynomial.

Substituting this expansion into Eq. (29) one obtains the following Maier-Saupe type free energy of the nematic composite:

$$\begin{aligned} \frac{1}{V}F_N = & k_B T \rho_n (\ln \rho_n - 1) + k_B T \rho_m (\ln \rho_m - 1) \\ & - \frac{1}{2} \rho_n^2 U_{nn} - \frac{1}{2} \rho_m^2 U_{mm} + \rho_m \rho_n U_{mn} \\ & + \frac{1}{2} \rho_m^2 J S^2 k_B T \int f_m(\mathbf{a}) \ln f_m(\mathbf{a}) d\mathbf{a}, \end{aligned} \quad (31)$$

where  $S$  is the nematic order parameter of the mesogenic molecules which is expressed as:

$$S = \int P_2(\mathbf{a} \cdot \mathbf{n}) f_m(\mathbf{a}) d\mathbf{a}, \quad (32)$$

where  $\mathbf{n}$  is the nematic director. Minimizing the free energy (31) with respect to the orientational distribution function  $f_m(\mathbf{a})$  and substituting the equilibrium expression for  $f_m(\mathbf{a})$  back into Eq. (31) one obtains:

$$\begin{aligned} \frac{1}{V}F_N = & k_B T \rho_n (\ln \rho_n - 1) + k_B T \rho_m (\ln \rho_m - 1) \\ & - \frac{1}{2} \rho_n^2 U_{nn} - \frac{1}{2} \rho_m^2 U_{mm} + \rho_m \rho_n U_{mn} - \frac{1}{2} \rho_m^2 J S^2 - k_B T \ln Z, \end{aligned} \quad (33)$$

where

$$Z_N = \int_0^\pi \exp[-\beta \rho_m J S P_2(\cos \gamma)] \sin \gamma d\gamma, \quad (34)$$

and where the nematic order parameter  $S$  satisfies the following self-consistent equation:

$$S = \frac{1}{Z_N} \int_0^\pi P_2(\cos \gamma) \exp[-\beta \rho_m J S P_2(\cos \gamma)] \sin \gamma d\gamma, \quad (35)$$

The free energy of the isotropic phase is obtained by setting  $S = 0$ :

$$\begin{aligned} \frac{1}{V}F_I = & k_B T \rho_n (\ln \rho_n - 1) + k_B T \rho_m (\ln \rho_m - 1) \\ & - \frac{1}{2} \rho_n^2 U_{nn} - \frac{1}{2} \rho_m^2 U_{mm} + \rho_m \rho_n U_{mn}. \end{aligned} \quad (36)$$

### 3.2. Nematic-isotropic phase separation

One notes that the concentration of NPs in the nematic phase is generally different from that in the coexisting isotropic phase, and may be strongly temperature dependent. The coexistence between the nematic and the

isotropic phases in the system under consideration is possible only if the chemical potentials of both NPs and mesogenic molecules are the same in the two phases. The pressure must also be the same in the two phases. However, for incompressible LCs only the equations for the chemical potentials are relevant that is  $\mu_{nI} = \mu_{nN}$  and  $\mu_{mI} = \mu_{mN}$  where  $\mu_{nI}$  and  $\mu_{nN}$  are the chemical potentials of the NPs in the isotropic and in the nematic phase, respectively, and  $\mu_{mI}$  and  $\mu_{mN}$  are the corresponding chemical potentials of the mesogenic molecules.

Using the well known general equation for the chemical potential one obtains the following system of two simultaneous equations

$$\frac{1}{V_I} \frac{\partial F_I}{\partial \rho_n} = \frac{1}{V_N} \frac{\partial F_N}{\partial \rho_n}, \quad \frac{1}{V_I} \frac{\partial F_I}{\partial \rho_m} = \frac{1}{V_N} \frac{\partial F_N}{\partial \rho_m}. \quad (37)$$

Substituting Eqs.(36) and (33) for the free energies of the isotropic and the nematic phase into (72) one obtains the following equations:

$$\ln \frac{\rho_{mN}}{\rho_{mI}} = U_1(\rho_{mN} - \rho_{mI}) + U_{12}(\rho_{nN} - \rho_{nI}) + \ln Z_N, \quad (38)$$

and

$$\ln \frac{\rho_{nN}}{\rho_{nI}} = U_2(\rho_{nN} - \rho_{nI}) + U_{12}(\rho_{mN} - \rho_{mI}), \quad (39)$$

where we have introduced the non dimensional interaction constants  $U_1 = U_{mm}/(kT_B)$ ,  $U_2 = U_{nn}^{\text{eff}}/(kT_B)$ ,  $U_{12} = U_{nm}^{\text{eff}}/(kT_B)$  and the number densities of the mesogenic molecules,  $\rho_{mI}$  and  $\rho_{mN}$ , and NPs,  $\rho_{nI}$  and  $\rho_{nN}$ , in the isotropic and nematic phases correspondingly.

Neglecting a small density change at the transition, the number densities of both NPs and mesogenic groups in the nematic and in the isotropic phase can be expressed in terms of the volume fraction  $\phi_i$  of NPs in the corresponding phase  $i$ :

$$\rho_{ni} = \rho_{n0}\phi_i, \quad \rho_{mi} = \rho_{m0}(1 - \phi_i), \quad (40)$$

where  $i = N, I$ ,  $\rho_{m0}$  is approximately equal to the number density of the mesogenic groups in the pure LC and  $\rho_{n0}$  can be estimated as  $\rho_{n0} \sim 1/v_p$  where  $v_p$  is the NP volume.

Now Eqs. (38) and Eqs. (39) can be expressed in terms of the two variables  $\phi_N$  and  $\phi_I$ :

$$\ln \frac{1 - \phi_N}{1 - \phi_I} = w_1(\phi_I - \phi_N) + \ln Z_N, \quad (41)$$

$$\ln \frac{\phi_I}{\phi_N} = w_2(\phi_I - \phi_N), \quad (42)$$

where

$$w_1 = (\rho_{m0}U_1 - \rho_{n0}U_{12}), \quad w_2 = (\rho_{n0}U_2 - \rho_{m0}U_{12}). \quad (43)$$

One notes that Eqs. (41) contain only two constants  $w_1, w_2$ , and it can readily be shown that the phase coexistence is possible only if  $w_2 > 1$ . If the isotropic attraction between NPs and mesogenic molecules is much stronger than that between the mesogenic molecules, the inequality  $\rho_{n0}U_{12} > \rho_{m0}U_1$  is satisfied and hence  $w_1 < 0$ .

Numerical solution of Eqs. (41,42) together with Eq. (34) and the self-consistent Eq. (35) for the nematic order parameter is significantly simplified if the volume fraction of NPs is sufficiently small in both phases, that is  $\phi_I \ll 1$  and  $\phi_N \ll 1$ . In this case Eq. (41) is simplified as:

$$(1 - w_1)(\phi_I - \phi_N) = \ln Z_N, \quad (44)$$

One notes also that the partition function  $Z_N$  is independent of  $\phi_I$ , and therefore  $\phi_I$  can be excluded from the system of simultaneous equations for  $\phi_I \ll 1$  and  $\phi_N \ll 1$  which results in a single equation for  $\phi_N$ :

$$Z_N^{w_2/(1-w_1)} = 1 + \frac{\ln Z_N}{\phi_N(1-w_1)} \quad (45)$$

Now  $\phi_N$  can be found by solving Eq. (45) numerically, and  $\phi_I$  can then be evaluated in terms of  $\phi_N$  as:

$$\phi_I = \phi_N + \frac{\ln Z_N}{1-w_1} \quad (46)$$

Naturally, the volume fractions of NPs in the nematic and the isotropic phases are not completely independent. Indeed, in the experiment one normally controls the total number of NPs  $N_n$  in the volume  $V$  which yields the average volume fraction of NPs  $\phi$ . It follows from the conservation of the total number of NPs that  $\phi V = \phi_I V_I + \phi_N V_N$  where  $V = V_I + V_N$  is the total volume of the system. On the other hand, solutions of the Eqs. (41) and (42) are independent of  $\phi$ . From these equations one obtains the following expressions for the volumes  $V_N$  and  $V_I$ :

$$V_I = V \frac{\phi - \phi_I}{\phi_I - \phi_N}, \quad V_N = V \frac{\phi_N - \phi}{\phi_I - \phi_N}. \quad (47)$$

One can readily see from Eqs. (47) that the phase coexistence is possible only if  $\phi_N < \phi < \phi_I$  as  $\phi_N < \phi_I$ . Taking into account that  $\phi_N$  and  $\phi_I$  are independent of  $\phi$ , one concludes that if  $\phi$  is outside the interval  $(\phi_N, \phi_I)$ , the phase coexistence is impossible and only one phase may be stable at a given

temperature. This condition should be used as an additional constraint imposed on the solutions of the Eqs. (41) and (42).

Finally, coexisting nematic and isotropic phases are globally stable only if the total free energy of the phase-separated system is lower than the free energy of both isotropic and nematic homogeneous phases. This is the second independent condition which should be taken into account in the consideration of the physical meaning of the formal solutions of the Eqs. (41) and (42). This condition can be expressed as:

$$\frac{F_{NI}^{\text{sep}} - F_{\text{hom}}}{Vk_B T} = \frac{1}{Vk_B T} \left[ \frac{V_I}{V} F_I(\phi_I) + \frac{V_N}{V} F_N(\phi_N) - F_{I,N}(\phi) \right] < 0, \quad (48)$$

where  $V_I$  and  $V_N$  are given by Eq. (47) and the free energy densities  $F_I(\phi)$  and  $F_N(\phi)$  can be expressed using Eqs. (33, 36, 40):

$$F_I(\phi)/Vk_B T = \rho_{n0}\phi \ln \phi + \rho_{m0}(1-\phi) \ln(1-\phi) - \frac{1}{2}\rho_{n0}^2\phi^2 U_2 - \frac{1}{2}\rho_{m0}^2(1-\phi)^2 U_1 + \rho_{m0}\rho_{n0}\phi(1-\phi)U_{12}, \quad (49)$$

$$F_N(\phi)/Vk_B T = F_I(\phi)/Vk_B T - \frac{1}{2}\rho_{m0}^2(1-\phi)^2 J^* S_m^2 - \rho_{m0}(1-\phi) \ln Z_N, \quad (50)$$

where  $J^* = J/k_B T$ . Note that for the separated state in Eq. (48) the nematic order parameter is  $S(\phi_N)$  in the nematic phase, which coexists with the isotropic one, and is given by Eq. (35) with  $\rho_m = \rho_{m0}(1-\phi_N)$  and  $Z_N = Z_N(\phi_N)$ . At the same time, the order parameter of the homogeneous nematic phase  $S(\phi)$  is given by the same equation with  $\rho_m = \rho_{m0}(1-\phi)$  and  $Z_N = Z_N(\phi)$ .

### 3.3. Phase diagrams

Let us first consider Eqs. (41) and (42) which enable one to determine the molar fractions of NPs in coexisting phases as functions of temperature. A typical numerical solution of these equations for moderately strong interactions between NPs and mesogenic molecules is presented in Fig. 5. One notes that there exists a bifurcation point which corresponds to a critical temperature  $T_c$ . At higher temperatures there is no solution, that is the phase separation is impossible, and directly below the critical temperature the difference between molar fractions of NPs in the two phases is fairly small.

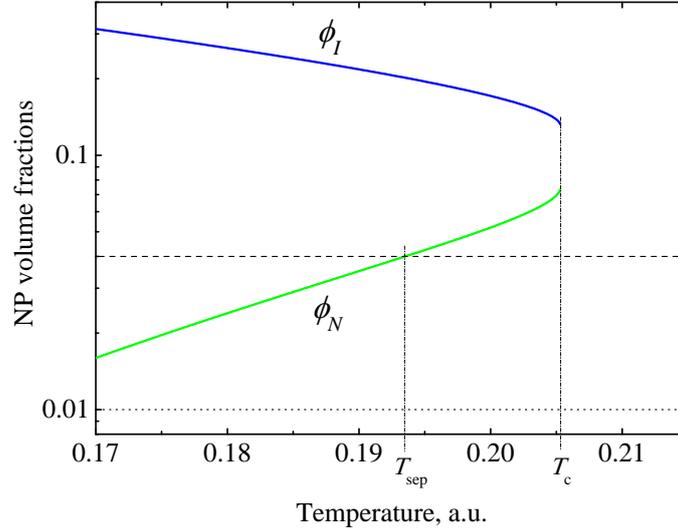


Fig. 5. Nanoparticle volume fractions in coexisting isotropic (upper curve) and nematic (lower curve) phases of the composites with  $w_1 = -5$ ,  $w_2 = 10$

It should be noted, however, that in the general case only part of this solution corresponds to an actual physical state of the system. As discussed in the previous subsection, Eqs. (41) and (42) do not depend on the average molar fraction of NPs  $\phi$  which can be actually controlled in experiments. At the same time, the value of  $\phi$  must lie between the two branches in Fig. 5, as  $\phi_N < \phi < \phi_I$ . If  $\phi$  is different from the critical value of  $\phi_c$  at the bifurcation point, the system separates into the nematic and the isotropic phases with finite difference of NP molar fractions and finite volumes of both phases. In this general case the separation occurs at some temperature  $T_{sep}$  which is below the bifurcation temperature  $T_c$ , and which is an intersection of the horizontal line  $\phi$  and one of the curves representing  $\phi_N(T)$  or  $\phi_I(T)$  (see the intersection of  $\phi_N(T)$  and the horizontal dashed line  $\phi = 0.04$  in Fig. 5).

In principle, even if  $T < T_{sep}$  one cannot finally conclude that the system phase separates, because the separated state is globally stable only if the total free energy of the separated system is lower than that of any homogeneous phase at the same temperature and NP concentration (see Eq. (48)). One notes also that if the value of  $\phi$  is too small or too large (see the dotted line  $\phi = 0.01$  in Fig. 5), there may be no intersection at all, that is the condition  $\phi_N < \phi < \phi_I$  is not satisfied at any temperature and,

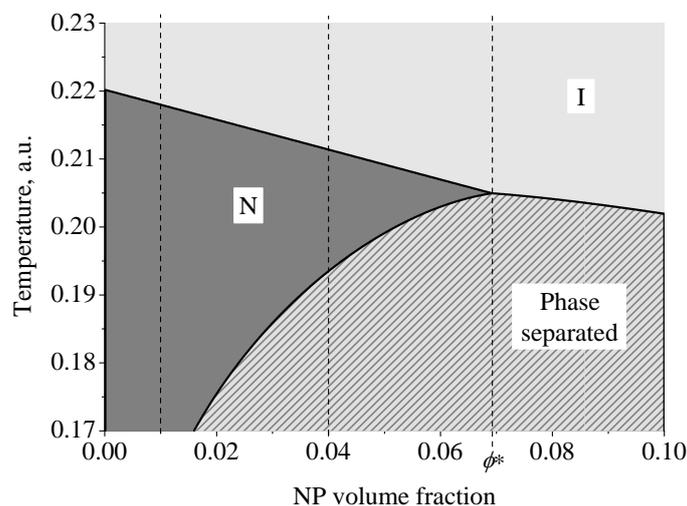


Fig. 6. Phase diagram of the composite calculated from the mean-field theory with interaction constants  $w_1 = -5$  and  $w_2 = 10$ .

therefore, the system never phase separates.

The solutions for  $\phi_N$  and  $\phi_I$  together with Eq. (48) have been used to compose the temperature-concentration phase diagram presented in Fig.6 for the same values of the interaction constants  $w_1$  and  $w_2$  as in Fig. 5. One notes that there is no phase separation at sufficiently low concentration of NPs. In this domain, the N-I transition temperature decreases with the increasing  $\phi$  due to the “dilution” effect considered in Section 2. Above a certain critical concentration, the N-T phase transition is accompanied by the separation between the isotropic and the nematic phase, and the two phases coexist over a significant temperature interval. In this region the transition temperature into the phase-separated state decreases more slowly than the N-I transition temperature at low concentrations. It is interesting to note also, that in this case there exists another critical value  $\phi^*$  of the NP molar fraction shown in Fig. 6. When  $\phi > \phi^*$ , the system undergoes a direct transition from the isotropic into the the phase separated state in which the isotropic and the nematic phases coexist. In contrast, when  $\phi < \phi^*$ , the system first undergoes a transition into the homogeneous nematic phase and then phase separates at some lower temperature.

The solution of Eqs. (41) and (42) and the corresponding phase diagram for a nematic composite with very strong interaction between NPs and the mesogenic molecules are presented in Fig. 7 and Fig. 8 correspondingly.

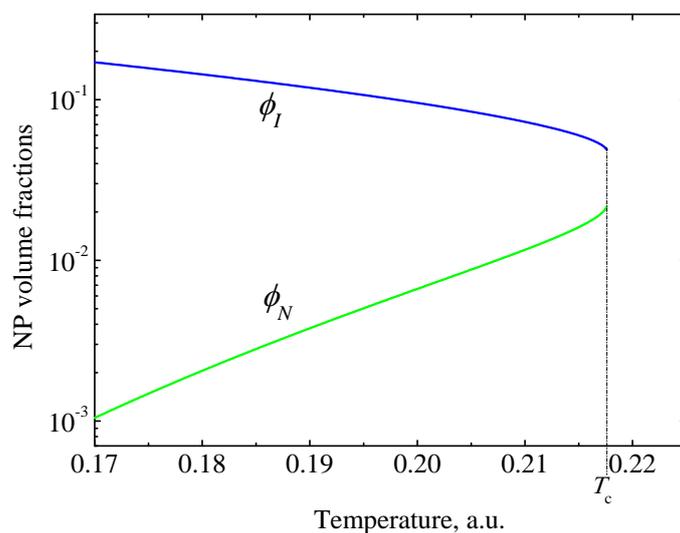


Fig. 7. The same as in Fig. 5 with  $w_1 = -10$  and  $w_2 = 30$

In this case the temperature range of the coexistence between the nematic and the isotropic phase is more narrow, and there is only a relatively small window of NP concentration when the separation takes place at all. One notes also, that in this case a reentrant homogeneous nematic phase may occur within a narrow interval of NP molar fraction.

On the other hand, for weaker interactions between NPs and mesogenic molecules (smaller absolute values of  $w_1$ ), the region of phase separated state expands considerably (compare Figs. 6 and 9). Decreasing  $|w_1|$  results in a proportionate decrease of the critical total concentration  $\phi^*$ . Additionally, in this case the phase separated state dominates over the low-temperature part of the phase diagram and even at small total NP concentrations  $\phi$  the homogeneous nematic phase exists only in a finite temperature range as illustrated by Fig. 9.

These results appear to be rather unusual and are different from what one may expect from the behavior of nematics doped with small nonmesogenic dopants. In particular, the temperature range of the coexisting nematic and isotropic phases may be very large. It is well known, that in mixtures of LCs the N-I coexistence region is typically of the order of 1-2 degrees and can often be neglected. In contrast, the theory indicates that in nematic nano-composites the coexistence region may be as broad as the nematic phase itself. Secondly, the phase separation does not occur at suf-

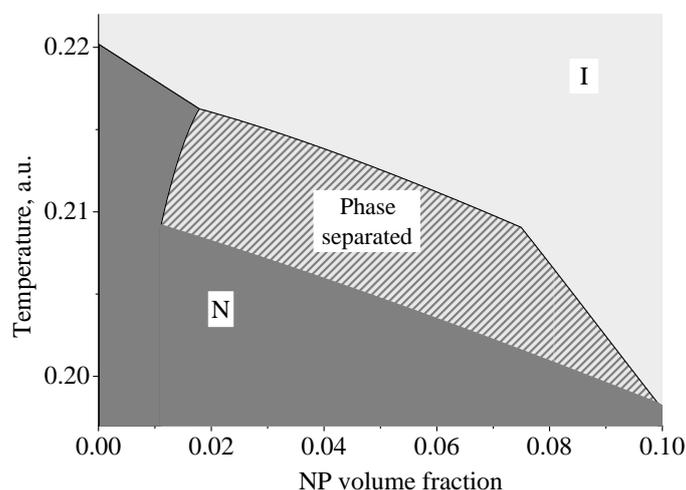


Fig. 8. The same as in Fig. 6 with  $w_1 = -10$  and  $w_2 = 30$

ficiently low concentration of NPs because the entropy of mixing dominates the behavior of the system. Moreover, within a certain range of concentrations of NPs the composite may undergo a direct transition from the isotropic phase into the phase separated state, while at other concentrations of NPs the system first undergoes a transition into the homogeneous nematic phase and then into the phase separated state at lower temperature.

This unexpected behavior of nematic nano-composites is related to the fact that the properties of NPs differ very much from those of typical mesogenic molecules. In particular, the isotropic interaction between NPs and mesogenic groups (and between NPs themselves) is expected to be significantly stronger than that between mesogenic molecules. This is mainly due to the large effective volume of a typical spherical NP which includes also organic chains attached to the surface of metal or semiconductor core.

Isotropic-nematic phase separation has been observed in a few anisotropic soft matter systems<sup>43,44</sup> but it has not been studied in detail experimentally so far. Very recently, however, a two-step decrease of both the N-I transition temperature and the transition heat in few polymer and low molecular weight LCs doped with quantum dots<sup>32</sup> has been interpreted assuming that the system separated into the isotropic and the nematic phase with different concentrations of quantum dots. A different type of phase separation has recently been observed in Refs. 45,46. It has been shown

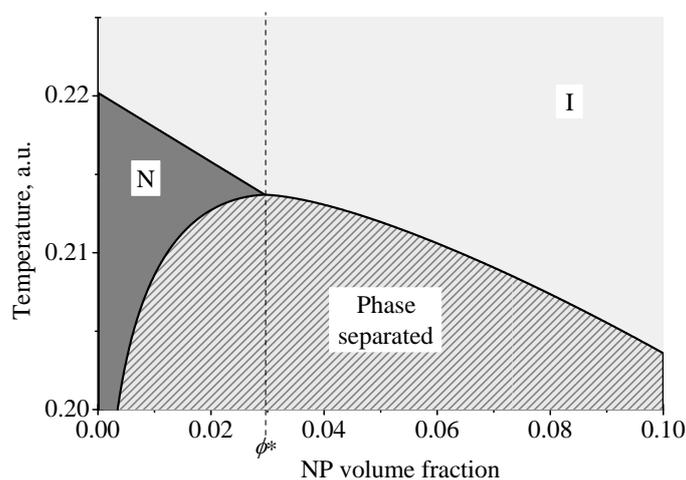


Fig. 9. The same as in Fig. 6 with  $w_1 = -1$  and  $w_2 = 10$

experimentally that gold NPs with mesogenic coatings form reversible networks composed of nematic droplets accompanied by disclination lines and loops as a result of a specific phase separation which results in an enrichment of the NPs at the nematic-isotropic liquid interfaces.

Finally it should be noted that the theory of phase separation in LC nano-composites is at its rudimentary stage and there is much to be done here. Recently phase separation effects in nematics doped with large colloidal particles have been studied theoretically in Refs. 47–49. In particular, very broad N-I coexistence region has been found in Refs. 47,48 using simple mean-field theory of mixtures. This theory, however, is based on a different (and rather oversimplified) model interaction potential which is more suitable for large colloidal particles.

#### 4. Chain formation and dielectric anisotropy of nematic nanocomposites

##### 4.1. Simple theory of chain formation

Nano-particles may form dimers and even long chains in a solution if the interparticle interaction potential is sufficiently anisotropic and strong. In this section we assume that spherical NPs possess relatively large permanent electric dipoles. In this case the minimum of the dipole-dipole interaction energy is achieved when the dipoles of the two adjacent NPs and

parallel to each other and to the interparticle vector  $\mathbf{r}_{12}$ . If this potential minimum is sufficiently deep, the NPs form polar chains which may significantly contribute to the dielectric anisotropy of the nematic composite.

The nematic composite with chains of NPs is characterized by the distribution of chain lengths which can be evaluated using the existing theory of chain formation in the system of polar spheres presented, for example, in Ref. 36. According to this theory, the number density of chains of length  $l$  (i.e. composed of  $l$  NPs) is expressed as:

$$\phi_l = v_p \rho_l = e^{l(U_0 + \Lambda)} e^{-U_0}, \quad (51)$$

where  $\phi_l$  is the volume fraction of chains of length  $l$ ,  $v_p$  is the NP volume and  $U_0$  is the contact energy determined by the dipole-dipole interaction between NPs:

$$U_0 = \ln \left( \frac{\pi \sigma^3 e^{2\lambda}}{18 v \lambda^3} \right). \quad (52)$$

Here  $\lambda = \mu^2 / k_B T \sigma^3$  and  $\sigma$  is the NP diameter and the NP volume  $v$  has been introduced for dimensional correctness.

In Eq. (51),  $\Lambda$  is the Lagrange multiplier (chemical potential) which is determined from the conservation rule for NPs:

$$\rho_p = \sum_{l=1}^{\infty} l \rho_l, \quad (53)$$

where, as above,  $\rho_p$  is the total NP number density which is controlled experimentally.

Substituting Eq. (51) into Eq. (53) and performing the summation one obtains:

$$\rho_p = v_p^{-1} \frac{e^{\Lambda}}{(1 - e^{U_0 + \Lambda})^2}. \quad (54)$$

Accordingly,

$$1 - e^{U_0 + \Lambda} = \frac{-1 + \sqrt{1 + 4\eta}}{2\eta}, \quad (55)$$

where  $\eta = v_p \rho_p e^{U_0}$ . Thus the value of the chemical potential  $\Lambda$  is mainly determined by the order of  $\eta$ .

Finally, one can readily obtain the following expression for the number density of chains of length  $l$ :

$$\rho_l = v_p^{-1} e^{-U_0} \left( 1 - \frac{-1 + \sqrt{1 + 4\eta}}{2\eta} \right)^l. \quad (56)$$

#### 4.2. High frequency permittivity of a nematic composite

At sufficiently high (optical) frequencies the polarization is mainly determined by induced dipoles created by the electric field. Orientational fluctuations of permanent dipoles make a minor contribution because the characteristic times of such fluctuations are much larger than the inverse optical frequency.<sup>50</sup> Relatively simple explicit expressions for the dielectric constant can be obtained in the molecular field approximation in the form of generalized Clausius-Mossotti relation<sup>51</sup> assuming that the composite nematic phase contains mesogenic molecules, NPs and chains of NPs of various lengths  $l$ :

$$(\hat{\epsilon} - 1)(\hat{\epsilon} + 2)^{-1} = \frac{4\pi}{3} \left( \langle \hat{\beta}_m \rangle \rho_m + \langle \hat{\beta}_{np} \rangle \rho_{np} + \sum_{l=2}^{\infty} \langle \hat{\beta}_l \rangle \rho_l \right), \quad (57)$$

where  $\langle \hat{\beta}_m \rangle$ ,  $\langle \hat{\beta}_{np} \rangle$  and  $\langle \hat{\beta}_l \rangle$  are the average polarizabilities of mesogenic molecules, single NPs and chains of NPs of length  $l$ , respectively, and  $\rho_m$ ,  $\rho_{np}$  and  $\rho_l$  are the corresponding number densities.

Introducing the long axes of the molecules  $\mathbf{a}_m$  and the unit vectors of the chain directions  $\mathbf{a}_l$ , and using the corresponding scalar nematic order parameters  $S_\alpha$  one obtains the following expressions for the averaged polarizability tensors:

$$\langle \hat{\beta}_\alpha \rangle = \bar{\beta}_\alpha \hat{I} + S_\alpha \Delta\beta_\alpha \mathbf{n} \otimes \mathbf{n}, \quad (58)$$

where the isotropic polarizabilities are expressed as  $\bar{\beta}_\alpha = \beta_{\alpha\perp} + \Delta\beta_\alpha(1 - S_\alpha)/3$ .

Assuming that moderate dielectric anisotropies  $\Delta\beta_\alpha$  give rise to a relatively small anisotropy of the composite permittivity  $\Delta\epsilon$ , Eq. (57) can be expanded and simplified as follows:

$$\Delta\epsilon = \frac{4\pi}{9} (\epsilon_\perp + 2)^2 \left( \Delta\beta_m \rho_m S_m + \sum_{l=2}^{\infty} \langle \Delta\beta_l \rangle \rho_l \right), \quad (59)$$

while the isotropic part of the composite permittivity satisfies the scalar Clausius-Mossotti relation

$$\frac{\epsilon_\perp - 1}{\epsilon_\perp + 2} = \frac{4\pi}{3} \left( \beta_{m\perp} \rho_m + \beta_{np\perp} \rho_{np} + \sum_{l=2}^{\infty} \beta_{l\perp} \rho_l \right), \quad (60)$$

which includes also the contribution from the isotropic non-aggregated NPs.

One notes that Eqs. (59) and (60) are not expected to be quantitatively precise but they can be used to estimate the dependence of the refractive

indices of the nematic composite on the concentration of NPs, their aggregation and ordering provided that the effective polarizability of a NP in the nematic solvent is known.

#### 4.3. Polarizability of a single chain

Generally, the NP contribution to the composite permittivity (59) and (60) is twofold: both aggregated and non-aggregated NPs affect  $\varepsilon_{\perp}$  while only those NPs which are aggregated into chains contribute to  $\Delta\varepsilon$ .

To sum over chains of different lengths in Eq. (59) one needs to know the quantity  $\langle\Delta\beta_l\rangle$  which can be evaluated as the average dielectric anisotropy of a chain of  $l$  spheres (with the permittivity  $\varepsilon_{np}$ ) immersed into a medium with the permittivity  $\varepsilon_{\perp}$ . Although the exact solution of such a problems can be obtained only numerically, one can obtain useful analytical estimates<sup>52</sup> using a few realistic approximations. Thus taking into account the strongest dipole interactions between NPs and restricting the calculations to the nearest-neighbor contributions (already the next-nearest neighbor ones are at least eight times smaller) and introducing the single NP dielectric polarizability  $\beta_1 = 1/8 \sigma^3(\varepsilon_{np} - \varepsilon_{\perp})/(\varepsilon_{np} + 2\varepsilon_{\perp})$  one can express the dipole moment of the  $k$ -th NP in the chain of the total length  $l$  as

$$\mathbf{p}_k = \beta_1 \mathbf{E} + \beta_1 \hat{T}_{k,k-1} \mathbf{p}_{k-1} + \beta_1 \hat{T}_{k,k+1} \mathbf{p}_{k+1}, \quad (61)$$

where

$$\hat{T}_{k,k\pm 1} = (3\mathbf{u}_{k,k\pm 1} \otimes \mathbf{u}_{k,k\pm 1} - \mathbf{1}) \sigma^{-3}, \quad (62)$$

is the non-singular part of the dipole-dipole propagator,  $\mathbf{u}_{k,k\pm 1}$  are the unit vectors between the centers of the adjacent NPs and the following natural condition is satisfied  $\hat{T}_{1,0} = \hat{T}_{l,l+1} = 0$  at the chain ends.

As shown below, the effect of chain formation on high-frequency permittivity is rather moderate, and one can solve the system (61) by iterations. While in the zeroth order (neglecting the NP interactions) one obtains merely  $\mathbf{p}_k = \beta_1 \mathbf{E}$  and the chain remains dielectrically isotropic, the next iteration yields:

$$\mathbf{p}_k = \beta_1 \left( 1 + \beta_1 \hat{T}_{k,k-1} + \beta_1 \hat{T}_{k,k+1} \right) \mathbf{E}. \quad (63)$$

Since the average chain direction is controlled by the overall composite nematic director  $\mathbf{n}$ , the averaged nearest-neighbor propagator reads

$$\langle \hat{T}_{k,k\pm 1} \rangle = S(3\mathbf{n} \otimes \mathbf{n} - \mathbf{1}) \sigma^{-3}, \quad (64)$$

where we have again assumed that all the scalar nematic order parameters in the composite are equal.

Evaluating the average chain dipole moment as  $\langle \mathbf{P}_l \rangle = \sum_{k=1}^l \langle \mathbf{p}_k \rangle$  one obtains the following expression for the overall average chain polarizability tensor

$$\langle \hat{\beta}_l \rangle = l\beta_1 \mathbf{1} + \frac{2}{\sigma^3} (l-1)\beta_1^2 S(3\mathbf{n} \otimes \mathbf{n} - \mathbf{1}). \quad (65)$$

The anisotropy of this polarizability is given by:

$$\langle \Delta \beta_l \rangle = \frac{6}{\sigma^3} (l-1)\beta_1^2 S. \quad (66)$$

#### 4.4. Contribution of polar chains to the dielectric anisotropy of the nematic composite

Accordingly, the chain contribution to the composite permittivity anisotropy (59) is given by

$$\Delta \varepsilon_{\text{ch}} = \frac{\pi}{24} \left[ \frac{(\varepsilon_{\perp} + 2)(\varepsilon_{np} - \varepsilon_{\perp})}{\varepsilon_{np} + 2\varepsilon_{\perp}} \right]^2 S \sigma^3 \sum_{l=2}^{\infty} (l-1) \rho_l. \quad (67)$$

Substituting the number densities (56) and using the summation rule

$$\sum_{l=2}^{\infty} (l-1)x^l = \frac{x^2}{(1-x)^2} \quad (68)$$

one can express the dielectric anisotropy in terms of the dimensionless NP density  $\rho^* = \rho \sigma^3$  and the parameter  $\lambda$ :

$$\Delta \varepsilon_{\text{ch}} = \frac{\pi}{24} \left[ \frac{(\varepsilon_{\perp} + 2)(\varepsilon_{np} - \varepsilon_{\perp})}{\varepsilon_{np} + 2\varepsilon_{\perp}} \right]^2 S \rho^* \delta_{\eta}. \quad (69)$$

where the function

$$\delta_{\eta} = 2 + \frac{1}{\eta} - \frac{4\eta}{(\sqrt{1+4\eta}-1)^2} \quad (70)$$

effectively describes the dependence on the NP chain formation as  $\eta$  is also expressed in terms of the non-dimensional parameters as  $\eta = \pi \rho^* e^{2\lambda} / (18\lambda^3)$ .

Representative profiles of the factor  $\delta_{\eta}$  as functions of the NP coupling strength, which controls the chain formation, are presented in Fig. 10. One notes that for weaker coupling this factor is very small, as most of the NPs remain single here and do not contribute to the anisotropy. For stronger coupling, the average chain length increases which leads to a pronounced

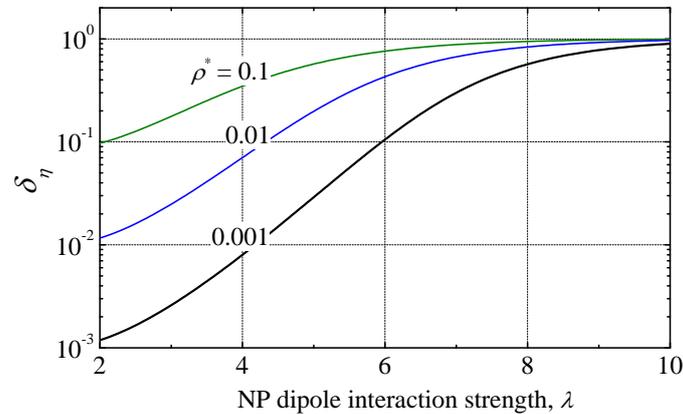


Fig. 10. The effect of chain formation on the high-frequency dielectric anisotropy of the composite: dependences of the factor  $\delta_\alpha$  given by Eq. (70) on the NP coupling strength for NP densities  $\rho^* = 0.1, 0.01$  and  $0.001$  as indicated on the lines.

increase of the anisotropy. The saturation at  $\delta_\eta \approx 1$  for strongly interacting NPs means that in this limit practically all NPs belong to long chains and contribute equally to the anisotropy. Evidently, for higher total NP concentrations this saturation occurs at smaller  $\lambda$ .

The variation of the high frequency dielectric anisotropy as a function of the NP concentration is illustrated by Fig. 11 for different values of the dipole-dipole interaction strength. One notes that this variation is approximately linear when the NP coupling is strong enough, i.e., when all the NPs are aggregated in long chains.

Generally, the high-frequency anisotropy is weak as the factor  $\delta_\eta < 1$  is multiplied in Eq. (69) by a number of other small factors. Thus for the dielectric NPs with  $\varepsilon_{np}$  of the same sign and order of magnitude as  $\varepsilon_\perp$  the factors in the square brackets are of the order of unity, while  $S < 1$  and  $\rho^* \ll 1$ . On the other hand, the variation of  $\delta_\eta$  by three orders of magnitude for low  $\rho^* = 0.001$  in Fig. 10 suggests that this anisotropy can be employed as a sensitive tool for quantitative assessment of the NP chain formation in nematic composites.

#### 4.5. Low frequency dielectric constant of a strongly polar nematic composite

Low frequency dielectric constant of the nematic phase composed of strongly polar molecules is mainly determined by the orientational fluc-

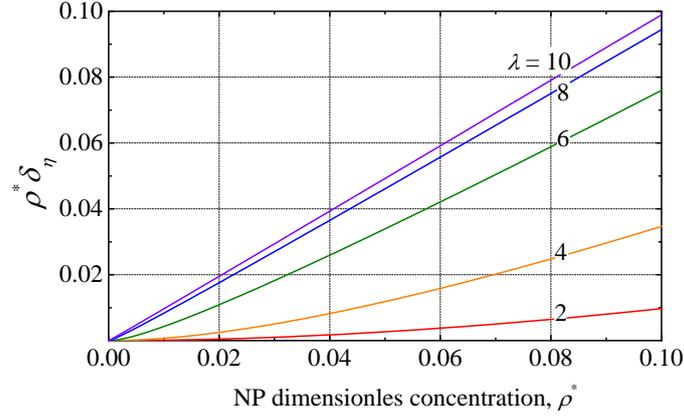


Fig. 11. The effect of chain formation on the high-frequency dielectric anisotropy of the composite: dependences of the factor  $\rho^* \delta_\eta$  in Eq. (69) on the NP concentration for the coupling strength  $\lambda$  varying from 2 to 10 as indicated on the lines.

tuations of permanent molecular dipoles while the molecular polarizability gives a much smaller contribution. Indeed, the static dielectric constant of a strongly polar nematic can be of the order of 100 while a typical contribution from the molecular polarizability is of the order of 3.<sup>50</sup> In this case, the macroscopic polarization can be expressed as a sum of averaged molecular dipoles of all components  $\alpha$  of the mixture in the unit volume:

$$\mathbf{P} = \sum_{\alpha} \rho_{\alpha} \langle \boldsymbol{\mu}_{\alpha} \rangle, \quad (71)$$

where  $\boldsymbol{\mu}_{\alpha}$  is the permanent molecule/particle dipole of the component  $\alpha$ .

In the static case, the average dipole can be expressed as:

$$\langle \boldsymbol{\mu}_{\alpha} \rangle = \int \boldsymbol{\mu}_{\alpha} f_{\alpha}(\theta) d\theta, \quad (72)$$

where  $f_{\alpha}(\theta)$  is the one-particle distribution function which can be written in the following form in the mean-field approximation

$$f_{\alpha}(\theta) = Z^{-1} \exp[-(U_{\text{MF},\alpha}(\theta) + (\boldsymbol{\mu}_{\alpha} \cdot \mathbf{E})) / (k_B T)]. \quad (73)$$

Here  $U_{\text{MF},\alpha}(\theta)$  is the mean-field potential for the component  $\alpha$ ,  $\theta$  specifies the orientation of the particle/molecule and  $\mathbf{E}$  is the external electric field.

The mean-field potential can be written in the form:

$$U_{\text{MF},\alpha}(\theta_1) = \sum_{\beta} \int V_{\alpha,\beta}(\theta_1, \theta_2) f_{\beta}(\theta_2) d\theta_2, \quad (74)$$

where  $V_{\alpha,\beta}(\theta_1, \theta_2)$  is the pair interaction potential between the components  $\alpha$  and  $\beta$ .

Let us now assume that both mesogenic molecules and NPs are uniaxial and their permanent dipoles are parallel to the corresponding long axes. This is also valid for rigid chains of spherical dipolar NPs. In this case, the pair interaction potential  $V$  depends on the unit vectors  $\mathbf{a}_1$  and  $\mathbf{a}_2$  in the direction of the long axes of the molecules “1” and “2”, respectively, and on the intermolecular vector  $\mathbf{r}_{12}$ , i.e.  $V(1, 2) = V(\mathbf{a}_1, \mathbf{r}_{12}, \mathbf{a}_2)$ . The pair potential can now be written as a sum of the nonpolar and the polar parts,  $V(1, 2) = V_{np}(1, 2) + V_{dd}(1, 2)$ , where the nonpolar potential  $V_{np}(1, 2)$  is an even function of  $\mathbf{a}_1$  and  $\mathbf{a}_2$  and where the polar potential  $V_{dd}(1, 2)$  is the electrostatic dipole-dipole interaction potential which can be expressed as:

$$V_{dd}(1, 2) = \boldsymbol{\mu}_1 \cdot \hat{F}(\mathbf{r}_{12}) \cdot \boldsymbol{\mu}_2, \quad (75)$$

where the dipole-dipole propagator can be written in the form:

$$\hat{F}(\mathbf{r}_{12}) = \frac{4\pi}{3} \delta(\mathbf{r}_{12}) + \Theta(r_{12} - D)(\hat{I} - 3\mathbf{u} \otimes \mathbf{u})r_{12}^{-3}, \quad (76)$$

where  $\mathbf{u} = \mathbf{r}_{12}/r_{12}$  and where  $\Theta(r_{12} - D)$  is a step function which is equal to unity if  $r_{12} > D$  and vanishes otherwise. One notes that the first term in Eq. (76) takes into account a singularity of the dipole-dipole potential at the origin (see a detailed discussion of the averaging of the dipole-dipole potential in Refs. 36,53).

Substituting Eq. (76) into Eqs. (75) and (74) and taking into account that the second term in Eq. (76) vanishes after integration over all  $\mathbf{u}$ , one obtains the final expression for the mean-field potential:

$$U_{\text{MF},\alpha}(\theta) = U_{\alpha}^{(0)}(\theta) + \frac{4\pi}{3}(\boldsymbol{\mu}_{\alpha} \cdot \mathbf{P}), \quad (77)$$

Finally this mean-field potential can be substituted into the orientational distribution function (73) and expanding it in powers of the small electric field  $\mathbf{E}$  and field-induced polarization  $\mathbf{P}$  one obtains:

$$f_{\alpha}(\theta) \approx f_{\alpha}^{(0)} \left( 1 + \frac{4\pi}{3} \frac{\boldsymbol{\mu}_{\alpha} \cdot \mathbf{P}}{k_B T} - \frac{\boldsymbol{\mu}_{\alpha} \cdot \mathbf{E}}{k_B T} \right), \quad (78)$$

where the nonpolar distribution function  $f_{\alpha}^{(0)}$  is determined by the nonpolar part  $U_{\alpha}^{(0)}(\theta)$  of the mean field potential, that is  $f_{0,\alpha} = Z_0^{-1} \exp[-U_{\alpha}^{(0)}(\theta)/(k_B T)]$ .

Substituting Eq. (78) into Eqs. (72) and (71) one obtains the following linear equation for the macroscopic polarization  $\mathbf{P}$ :

$$P_i = \sum_{\alpha} \frac{\rho_{\alpha}}{k_B T} \langle \mu_{\alpha,i} \mu_{\alpha,j} \rangle_0 \left( \frac{4\pi}{3} P_j + E_j \right), \quad (79)$$

where the averaging  $\langle \mu_{\alpha,i} \mu_{\alpha,j} \rangle_0$  is performed with the nonpolar orientational distribution function  $f_{\alpha}^{(0)}$ . As a result, one obtains the following expression for the dielectric polarizability tensor  $\hat{\chi}$ :

$$\hat{\chi} = \frac{\hat{\chi}_0}{1 - \frac{4\pi}{3} \hat{\chi}_0} \quad (80)$$

where

$$\hat{\chi}_0 = \sum_{\alpha} \frac{\rho_{\alpha}}{k_B T} \langle \boldsymbol{\mu}_{\alpha} \otimes \boldsymbol{\mu}_{\alpha} \rangle_0. \quad (81)$$

Taking into account that the dipole  $\boldsymbol{\mu}_{\alpha}$  is parallel to the long axis  $\mathbf{a}$  of the corresponding molecule one obtains:

$$\hat{\chi}_0 = \sum_{\alpha} \frac{\rho_{\alpha} \mu_{\alpha}^2}{k_B T} \langle \mathbf{a} \otimes \mathbf{a} \rangle_0 = \sum_{\alpha} \frac{\rho_{\alpha} \mu_{\alpha}^2}{k_B T} [S_{\alpha} (\mathbf{n} \otimes \mathbf{n} - \mathbf{1}/3) + \mathbf{1}/3]. \quad (82)$$

Here  $S_{\alpha}$  is the nematic order parameter of the compound  $\alpha$  in the mixture.

Let us consider the nematic composite in which the permanent dipoles of NPs are sufficiently large and larger than those of the mesogenic molecules. Then the main contribution to the low frequency dielectric constant of the nano-composite stems from the NPs and their chains and can be written using Eq. (81) as:

$$\hat{\varepsilon} \approx 1 + 4\pi \hat{\chi}_0 = 1 + 4\pi \sum_{l=1}^{\infty} \frac{\rho_l \mu_l^2}{k_B T} [S_l (\mathbf{n} \otimes \mathbf{n} - \mathbf{1}/3) + \mathbf{1}/3], \quad (83)$$

where  $\mu_l$  is the total dipole of the chain of length  $l$ ,  $\rho_l$  is the number density of chains of length  $l$  and  $S_l$  is the corresponding nematic order parameter.

One may assume that for short rigid chains of polar NPs the total dipole  $\mu_l = l\mu$  where  $\mu$  is the permanent dipole of a single NP. This assumption is obviously not valid for long flexible chains. However, the concentration of such chains is exponentially small and we will see below that for realistic values of the NP dipole only short chains ( $l = 1 - 4$ ) make a significant contribution to the dielectric constant of the composite. In this approximation Eq. (83) yields the dielectric susceptibility anisotropy:

$$\Delta\chi = \frac{\mu^2}{k_B T} \sum_{l=1}^{\infty} l^2 \rho_l S_l. \quad (84)$$

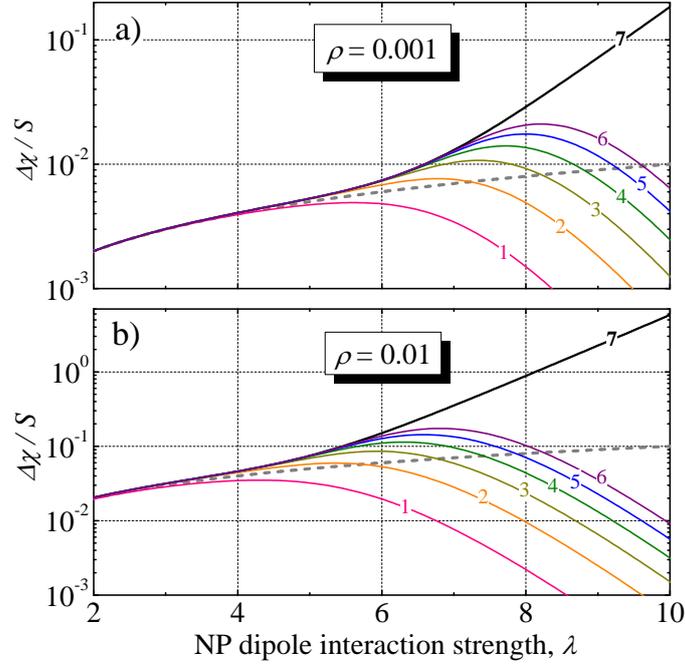


Fig. 12. Anisotropy of the low-frequency composite dielectric susceptibility as a function of NP coupling strength for NP densities  $\rho^* = 0.001$  (a) and  $\rho^* = 0.01$  (b). Solid lines 1 – 6 depict results of partial summation in Eq. (84) neglecting chains with  $l$  higher than 1 – 6 correspondingly. Solid line 7 represents the dependence (86), and the dashed line shows the anisotropy in the absence of chain formation.

By setting  $S_l = S$  and substituting the number densities (56) one can perform the summation over chains of all lengths in Eq. (84). Indeed, using the summation rule

$$\sum_{l=1}^{\infty} l^2 x^l = \frac{x(1+x)}{(1-x)^3} \quad (85)$$

the low-frequency dielectric anisotropy can be expressed explicitly in terms  $\rho^*$  and  $\lambda$ :

$$\Delta\chi = 4\rho^* \lambda S \frac{4\eta^2 + 5\eta + 1 - (3\eta + 1)\sqrt{1 + 4\eta}}{(-1 + \sqrt{1 + 4\eta})^3}. \quad (86)$$

In Fig. 12 the dielectric anisotropy given by Eq. (86) is presented for different NP molar fractions as a function of the parameter  $\lambda$  which describes the strength of the dipole-dipole interaction between NPs. For comparison

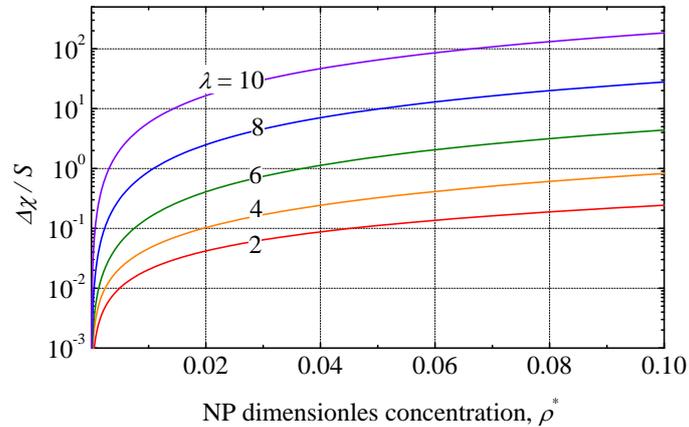


Fig. 13. Anisotropy of the low-frequency composite dielectric susceptibility as a function of the NP concentration for the NP interaction strength  $\lambda$  varying from 2 to 10 as indicated on the lines.

we also present the corresponding variation  $\Delta\tilde{\chi} = \lambda S\rho^*$  of the dielectric anisotropy of the composite without any chains, as well as the results of the partial summation in Eq. (84) which show the relative scale of contributions from chains of different lengths. One can see that the chain formation can modify the dielectric properties by orders of magnitude when the NP interaction (determined by the permanent dipole) is sufficiently strong. At the same time, for weak interaction, the effect of chains is practically negligible and the NPs respond to the electric field independently. For moderate interactions, there exists a noticeable area of  $\lambda$ , where the formation of short chains (dimers and trimers) contributes to  $\Delta\chi$  considerably, while the effect of longer chains is practically absent.

One can readily see in Fig. 12 that the contributions from monomers and dimers (similar to that from monomers and  $l$ -mers for  $l = 3, 4, 5$ ) first increases with the increasing dipolar strength  $\lambda$ , then reaches a maximum and finally begins to decrease. The decreasing stage corresponds to the range of  $\lambda$  which correspond to the formation of longer chains which make a predominant contribution to the dielectric anisotropy. In this range the contribution from dimers, trimers etc. decreases due to a decrease of the corresponding number densities. The increasing stage corresponds to the range of smaller  $\lambda$  where the corresponding short chains make a predominant contribution.

Finally, the variation of the dielectric anisotropy as a function of the NP

concentration for different values of the dipole-dipole interaction strength is presented in Fig. 13. Evidently, the increase of the NP concentration by an order of magnitude results in the increase of the dielectric anisotropy by several orders of magnitude depending on the value of the parameter  $\lambda$ . Thus one can readily see (compare also with Figs. 12a and 12b) that the experimentally observed increase of the dielectric constant<sup>9,34</sup> at very low NP number density  $\rho = 10^{-2} - 10^{-3}$  can be explained by the effect of chain formation only if the dipole-dipole interaction strength is sufficiently high which is the case for ferroelectric NPs with large spontaneous polarization.

One notes that at present there is no direct experimental evidence of the existence of chains of NPs in nematic composites although a number of experimental data cannot be explained without assuming that such chains are actually formed. Recently, however, it has been shown experimentally that in an isotropic fluid doped with an extremely low concentration of magnetic dipolar spherical NPs some birefringence can be induced by the external magnetic field.<sup>54</sup> In such a fluid, the macroscopic magnetic anisotropy can only be determined by the orientational ordering of dimers of magnetic NPs induced by the external field, and theoretical estimates of dimer concentration can be used to explain the experimentally observed dependence of the birefringence on the external magnetic field.<sup>54</sup>

## 5. Conclusions

Molecular theory of nematic nano-composites is at its early stage but, on the other hand, there is a number of interesting theoretical results obtained recently in this area and presented in this review. This includes, in particular, stabilization of the nematic order in the presence of anisotropic NPs, softening of the nematic-isotropic phase transition and peculiar phase diagrams which contain isotropic and nematic phases with different concentration of NPs coexisting over a very broad temperature range. It seems that there is sufficient experimental and theoretical evidence that strongly polar NPs should form at least dimers (but possibly also longer chains) in a nematic host. On the other hand, it is difficult to evaluate the anisotropy of the particle interaction potential and thus the results remain mainly qualitative. In general, there is a significant shortage of systematic experimental studies of the physical properties of LC nano-composites despite the growing interest attracted by these systems. Further development of the molecular theory would strongly benefit from the detailed experimental studies of the shift of the N-I transition temperature as a function of

NP concentration, on the measurements of orientational order parameter of anisotropic NPs and, in particular, on the experimental studies of phase separation effects for different molar fractions of NPs. Finally, some experimental methods should be found to study directly the chain formation in strongly polar nematic nano-composites.

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