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We study theoretically mixtures of liquid crystals (LCs) and nanoparticles (NPs) at a mesoscopic level. Orientational LC ordering is given in terms of a tensor order parameter. We estimate conditions which favor or disfavor phase separation. We show under which conditions topological defect could be exploited as trapping centers for nanoparticles. Influence of Defect Core Replacement *mechanism on phase stability of a structure possessing topological defect is demonstrated.*

Keywords Liquid crystals; mixtures; nanoparticles; phase stability; topological defect

I. Introduction

Recent years witness increased interest in mixtures of various liquid crystal (LC) phases and nanoparticles (NPs) [1–3]. It is of interest to find appropriate combinations yielding quantitatively dramatically enhanced or qualitatively new behavior that individual components do not exhibit on their own. In order to reach these goals it is necessary to avoid agglomeration of NPs and phase separation. One possible path of achieving this is to exploit networks of topological defects in LC ordering as NP trapping centers. Examples of such networks are various blue phases (BP) [1,4] and twist grain boundary (TGB) phases [5,6].

In this contribution we present basic mechanisms which enable this process and related possible advantages. For this purpose we first consider phase separation tendency in a mixture of LC and isotropic NPs focusing on the orientational degree of LC ordering. We emphasize main phase separation driving mechanism. Next we roughly estimate conditions which enable trapping of NPs to topological defects in orientational ordering. Finally, we demonstrate *Defect Core Replacement* (DCR) mechanism [4,7] via which trapped NPs could strongly affect phase stability of a LC host.

The plan of the paper is as follows. In Sec. II we present our mesoscopic model in terms of nematic tensor order parameter. In Sec. III we first discuss a phase separation tendency

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in a mixture of NPs and LC molecules. Then we analyze how NP surface treatment affects trapping tendency of a NP to a topological defect and demonstrate the DCR mechanism. In the last section we summarize results.

II. Model

We consider a mixture consisting of rod-like LC molecules and isotropic NPs, where local volume concentration of the latter component is given by ϕ.

II.1 Order parameter

The LC orientational ordering is expressed in terms of traceless and symmetric tensor order parameter [8]

$$Q = \sum_{i=1}^{3} s_i \vec{e}_i \otimes \vec{e}_i. \tag{1}$$

Here s_i and $\vec{e}_i$ stand for eigenvalues and eigenvectors of $\mathbf{Q}$, respectively, and $|\vec{e}_i| = 1$. In the case of uniaxial LC ordering $\mathbf{Q}$ is commonly expressed as

$$Q = S\left(\vec{n} \otimes \vec{n} - \frac{I}{3}\right), \tag{2}$$

where I stands for the identity tensor. The unit vector $\vec{n}$ is named the nematic director field. It points along the local uniaxial ordering. The head-to-tail invariance of LC molecular orientational ordering at mesoscopic level is reflected in the $\pm\vec{n}$ invariance in Eq. (2). The uniaxial scalar order parameter S quantifies the extent of fluctuations about $\vec{n}$. A degree of biaxiality in Q is measured by the biaxial parameter [9]

$$\beta^2 = 1 - \frac{6(trQ^3)^2}{(trQ^2)^3} \in [0, 1]. \tag{3}$$

A uniaxial ordering yields $\beta^2 = 0$. On the other hand an ordering exhibiting the maximum amount of biaxiality amounts to $\beta^2 = 1$.

II.2 Free Energy

The free energy density f of the system is expressed as a sum [8,10]

$$f = f_m + f_C + f_e + f_i(\vec{r} - \vec{r}_i) \tag{4}$$

of mixing (f_m), condensation (f_C), elastic (f_e) and the interface (f_i) contribution. The position vector $\vec{r}_i$ locates NP-LC interfaces. These terms are in the lowest order approximation given by [8,10]

$$f_m = \frac{k_B T}{v_{LC}}(1-\phi)\ln(1-\phi) + \frac{k_B T}{v_{NP}}\phi\ln\phi + \chi\phi(1-\phi), \tag{5a}$$

$$f_C = (1-\phi)\left(\frac{A_0(T-T_*)}{2}trQ^2 - \frac{B}{3}trQ^3 + \frac{C}{4}(trQ^2)^2\right), \tag{5b}$$

$$f_e = (1-\phi)(L/2) + (Q)^2 + (L_\phi/2)(\phi)^2, \tag{5c}$$

$$f_i = -(1-\phi)\phi w\vec{v}\cdot Q\cdot\vec{v}. \tag{5d}$$

The term f_m describes the isotropic mixing of the two components within the Flory theory [11]. The quantities k_B, T, v_{LC}, v_{NP} stand for the Boltzmann constant, absolute temperature, volume of a LC molecule, and a volume of nanoparticle, respectively. The quantity χ is the Flory-Huggins parameter [11]. If it is large enough it could trigger phase separation. The condensation term enforces uniaxial orientational ordering below the isotropic-nematic phase transition T_{IN}, where A_0, B, C are material constants and T_* is the supercooling temperature which in general depends on ϕ. The elastic term is weighted by positive elastic constants L and L_ϕ which tend to enforce homogenous ordering in $\mathbf{Q}$ and ϕ. The interface term determines conditions at the NP-LC interface [8], where w is a surface anchoring -wetting constant, and $\vec{v}$ is a surface normal unit vector. For illustration purposes we introduced the term enforcing homeotropic anchoring and supporting nematic wetting if the constant w is positive.

II.3 Mechanical Force

In order to compute a mechanical force $\vec{F}$ on a nanoparticle immersed in orientationally ordered LC medium we use the expression [12,13]

$$\vec{F} = \oiint T^{(E)}\vec{v}d^2\vec{r}. \tag{6}$$

Here $T^{(E)}$ is the Ericksen stress tensor and the integration is performed over the NP surface where a local outer unit normal points along $\vec{v}$. The Ericksen stress tensor is expressed in terms of the volume LC free energy density $f = f_c + f_e$ as

$$T^{(e)} = If - \nabla Q \odot \frac{\partial f}{\partial \nabla Q}, \tag{7}$$

where

$$(A\odot B)_{ij} = \sum_{h,k} A_{hki}B_{hkj} \tag{8}$$

applies for any pair of third-rank tensors A and B.

III. Phase and Structural Behavior

In the following we first discuss phase separation tendencies in the system. We proceed by estimating conditions which are required to trap a nanoparticle to a topological defect. Finally, we analyze NP induced stabilization of a LC structure possessing topological defects.

III.1 Phase Behavior

In order to estimate conditions leading towards phase separation we consider average free energy density $\bar{f}$ of the system, where the over-bar ($\bar{\cdot\cdot}$) marks the spatial averaging. We assume that essentially uniaxial orientational order is established which is represented by an average order parameter $\bar{S}$. We further suppose that NPs introduce elastic distortions in the nematic director field. These lead to a domain-type pattern which is roughly estimated

by an average linear domain size length $\bar{\xi}_d$. The average volume concentration of NPs and LC molecules is given by $\bar{\phi} = \frac{N_{NP} v_{NP}}{V}$ and $\bar{\phi}_{LC} = 1 - \bar{\phi}$, respectively, where N_{NP} counts the number of NPs and V is the volume of the sample.

The corresponding contributions in $\bar{f}$ are approximately expressed as

$$\bar{f}_m \sim \frac{k_B T}{v_{LC}}(1-\bar{\phi})\ln(1-\bar{\phi}) + \frac{k_B T}{v_{NP}}\bar{\phi}\ln\bar{\phi} + \chi\bar{\phi}(1-\bar{\phi}), \tag{9a}$$

$$\bar{f}_c \sim (1-\bar{\phi})(a_0(T-T_*)\bar{S}^2 - b\bar{S}^3 + c\bar{S}^4), \tag{9b}$$

$$\bar{f}_e \sim (1-\bar{\phi})\frac{L\bar{S}^2}{\bar{\xi}_d^2}, \tag{9c}$$

$$\bar{f}_i \sim (1-\bar{\phi})\bar{\phi}\bar{S}\frac{w}{R}. \tag{9d}$$

Here $a_0 = 2A_0/9$, $b = 2B/27$, $c = C/9$, and R is the characteristic linear size of a nanoparticle.

In general T_* depends on $\bar{\phi}$. Simple binary modeling suggests [14]

$$T_* \sim T_*^{(0)} - \lambda\bar{\phi}, \tag{10}$$

where positive constants $T_*^{(0)}$and λ are independent of $\bar{\phi}$.

From Eq. (9) one could extract the effective Flory-Huggins parameter χ_{eff} by assembling terms weighted by $(1-\bar{\phi})\bar{\phi}$:

$$\chi_{eff} = \chi + a_0\lambda\bar{S}^2 - \frac{w}{R}\bar{S}. \tag{11}$$

Let us first neglect the interface contribution and let us suppose that a mixture is spatially homogeneous in the isotropic phase. In this case $\chi_{eff} = \chi$ is below the critical value above which phase separation is realized. Note that in most LCs it holds $a_0\lambda \gg \chi$ [15]. For such cases a value of χ_{eff} anomalously increases on entering a nematic phase on lowering temperature because S acquires a finite value. Consequently, in most cases a phase separation takes place. The interface contribution in χ_{eff} suggests that appropriate conditions at the LC-NP interfaces could prevent phase separation providing NPs do not strongly disturb LC ordering (i.e. $\bar{\xi}_d$ entering Eq. (9c) should be large enough).

III.2 Trapping of Nanoparticles

In order to estimate the effects of NP's surface coating on interaction with its surrounding and consequent NP trapping capabilities we study theoretically a force on a nanoparticle immersed in a nematic medium. In particular we are interested in trapping NPs to topological defects the position of which could be in several cases well controlled. For this purpose we analyze a force on a NP immersed in a LC cell possessing a single topological defect. For the latter we choose a fingered boojum which was studied in detail in [16]. We study impact of different NP's surface coatings on interaction with its surrounding. In particular it is of interest under which conditions defect could be efficiently trapped to the finger tip of the boojum.

The geometry of the problem is presented in Fig. 1. For sake of simplicity, which does not affect general validity of results obtained, we consider a nanoparticle immersed

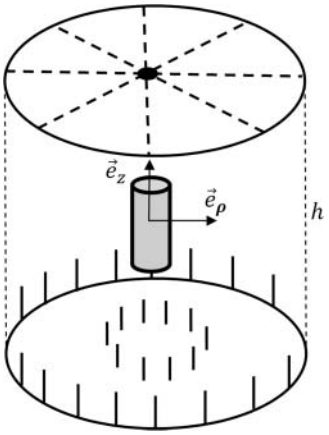

Figure 1. Schematic presentation of the hybrid plan-parallel cell of thickness h hosting NP. The diameter and the height of cylindrically shaped NP is in simulation set to be equal to the biaxial correlation length ξ_b. Furthermore, we used $h = 10\,\xi_b$.

within a planparallel hybrid cell. Both, the nanoparticle and the cell geometry exhibit a cylindrical symmetry. The positive orthonormal triad $\{\vec{e}_\rho, \vec{e}_\varphi, \vec{e}_z\}$ describes the unit vectors of the cylindrical coordinate system. NP is set at an arbitrary position z at the symmetry axis of the cell of thickness h as shown in Fig. 1.

At the top plate ($z = h$) we impose the strong uniaxial radial anchoring. Therefore, we enforce

$$Q(\rho, \varphi, z = h) = S_{eq}\left(\vec{e}_\rho \otimes \vec{e}_\rho - \frac{I}{3}\right) \equiv Q_{rad}, \tag{12a}$$

where S_{eq} stands for the equilibrium nematic order parameter. At the bottom plate ($z = 0$) we impose strong homeotropic anchoring, i.e.

$$Q(\rho, \varphi, z = 0) = S_{eq}\left(\vec{e}_z \otimes \vec{e}_z - \frac{I}{3}\right) \equiv Q_{\mathrm{hom}}. \tag{12b}$$

At the lateral sites free boundary conditions are enforced. In such geometry the boojum topological defect in enforced at the top plate. It is characterized by a finger-like structure, where the finger tip is due to topologically reasons melted (i.e., $Q = 0$). The boojum core structure is shown in Fig. 2 via a $\beta^2(\rho, z)$ plot and analyzed in detail in [16].

Due to the symmetry of the problem the mechanical force on immersed NP points along $\pm\vec{e}_z$ if it is different from zero. Within the cell there exist at least three qualitatively different attractors for NP: i) the melted point at the boojum finger tip, ii) homogeneous ordering along $\pm\vec{e}_z$ at $z = 0$, and iii) radial ordering at $z = h$. We consider three different NP surface coatings. At the NP surfaces we either strongly enforce i) $Q = 0$, ii) $Q = Q_{\mathrm{hom}}$, or iii) $Q = Q_{\mathrm{rad}}$.

The height and diameter of NP is set to be equal to the biaxial order parameter length $\xi_b \sim \sqrt{(Lc/(Sb^2)}$. We vary position of NP along the z-axis. For each position we calculate the equilibrium nematic configuration and the corresponding mechanical force on NP. Mathematical details are given in [17]. In Fig. 3 we plot the force as a function of z-coordinate for the three different surface treatments. We see that a nanoparticle, which

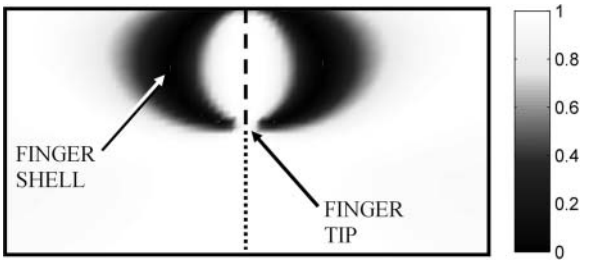

Figure 2. Cross-section through the boojum showing the degree of biaxiality β^2. A biaxial shell joins the isotropic finger tip and the upper surface. Along the cylindrical axis the system exhibits uniaxial ordering due to topological reasons (dashed line: negative uniaxiality, dotted line: positive uniaxiality). In the illustration the anchoring strength at the top plane is finite. The characteristic defect size is comparable to the biaxial correlation length. The grayscale bar of $1-\beta^2$ is shown on the right side of the figure.

locally enforces melted, radial, or homogeneous LC configuration, tends to assemble at the finger tip, top plate, and bottom plate, respectively. Therefore, the key information of this study is that NP tend to assemble at locations which exhibit similar local structure. To efficiently assemble NPs at a disclination core it is essentially to make surface coating such that the effective NP local surrounding resembles the defect core structure.

III.3 Defect Core Replacement Mechanism

We next estimate influence of NPs on the stabilization of a LC structure hosting topological line defects. An example represents either a blue phase (BP) [1,4] or a twist grain boundary phase (TGB) [5,6]. In the former defects exist in the orientational degree of order

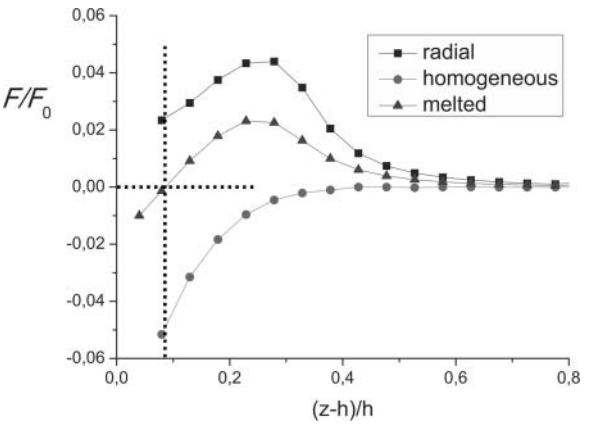

Figure 3. The force F experienced by different NPs as a function of distance z within the cell shown in Fig. 1. The NPs locally enforce either i) melting of LC order (dashed line and triangles), ii) homogeneous ordering (dash-dotted line and circles) along the z-axis, or iii) radial uniaxial order (full line and squares). Note that for the case i) the force equals zero at the boojum finger tip. The characteristic size of NPs used in simulation is comparable to the biaxial order parameter correlation length. This is in the simulation equal to $h/10$. F_0 stands for the reference force. The dotted lines indicate the position of the finger tip.

(i.e., disclinations with the winding number $-1/2$) and in the latter in positional degree of order (i.e., screw dislocations). In the following we illustrate essence of the *Defect Core Replacement* (DCR) mechanism on the case of NP driven stabilization of a BP structure with respect to a competitive chiral nematic phase. For simplicity we assume that the sequence of phases on lowering temperature is isotropic phase (I), a representative blue phase (BP), and a chiral nematic (N*) phase. We label the I-BP and BP-N* phase transition temperatures by $T_C^{(1)}$ and $T_C^{(2)}$, respectively.

We assume that NPs resemble cores of topological defects and therefore exhibit tendency to assemble at their cores. Furthermore, we also assume that in cores of defects the nematic order is essentially melted (i.e. $S \sim 0$). In this approximation we neglect biaxial character of the cores. The average radius of a core is comparable to the relevant (uniaxial or biaxial) order parameter correlation length ξ.

We first estimate the free energy cost ΔF of a representative lattice cell unit of volume V_0 within a BP structure hosting line disclinations of a total length h_{d} in absence of NPs. The condensation free energy penalty ΔF_{C} of introducing the defect is roughly given by

$$\Delta F_C \sim a^0\left(T_c^{(1)} - T\right)S^2\pi\xi^2 h_d. \tag{13}$$

This penalty opposes to formation of a BP structure with respect to the competitive defectless chiral phase N*. However, the former can be stabilized by the saddle splay elastic constant K_{24}. The corresponding elastic term can be via the Gauss theorem expressed as a surface contribution at interfaces facing the LC body. It roughly holds $K_{24} \sim LS^2$. The corresponding free energy gain ΔF_{24} at the interface separating the line disclination core volume and its surrounding is estimated by

$$\Delta F^{24} \sim -\pi L S^2 h_d. \tag{14}$$

Note that the presence of disclinations is accompanied by director field distortions in LC. However, we neglect the corresponding elastic penalties due to their secondary role in the DCR mechanism. The BP-N* phase transition temperature is estimated by the condition

$$\Delta F_C + \Delta F_{24} = 0. \tag{15}$$

It follows $\Delta T = T_C^{(1)} - T_C^{(2)} \sim L/(a_0\xi^2)$.

We next consider that NPs are added to LC medium and that they collect at disclination lines. The condensation free energy penalty is decreased due to the reduced volume occupied by the energetically costly isotropic phase, which is the essence of the DCR mechanism. It roughly holds

$$\Delta F_C \sim a^0\left(T_C^{(1)} - T\right)S^2\left(\pi\xi^{2h_d}d - N_{NP}v_{NP}\right), \tag{16}$$

where N_{NP} counts number of nanoparticles within the defect line of length h_d. Furthermore, we assume that changes in ΔF_{24} and in remaining elastic terms are relatively negligible. From Eq. (15) it follows

$$\frac{\Delta T\,(\phi)}{\Delta T\,(\phi = 0)} \sim \left(1 - \frac{V_0\phi}{\pi\xi^2 h_d}\right)^{-1} \sim 1 + \frac{V_0\phi}{\pi\xi^2 h_d}. \tag{17}$$

Therefore, due to the DCR mechanism the temperature stability interval of a structure possessing topological defects widens with respect to the competitive defectless phase linearly with ϕ in the diluted regime.

IV. Conclusions

We studied theoretically mixtures of liquid crystals and nanoparticles using a simple mesoscopic approach. We demonstrate that entering orientational ordering the phase separation tendency in general strongly increases. However, appropriate surface treatment of NPs could reduce this tendency. Furthermore, we calculate a force on a nanoparticle immersed in a LC cell possessing a topological defect. We demonstrate that NP tends to move to regions which exhibit similar configuration as it is formed in its local surrounding. We also show that nanoparticles of appropriate size and surface-functionalization can induce and stabilize a LC structure possessing a lattice of topological defects. The stabilization is enabled by the *Defect Core Replacement* mechanism [4]. The free energy penalty of forming a topological defect is reduced if a part of its energetically-costly core is replaced by the volume of trapped nanoparticles. This mechanism is believed to efficiently stabilize blue phases possessing disclination lines, and is also responsible for pinning vortices to impurities in type-II superconductors [18]. Its universal character implies that such a mechanism could be utilized towards controlled superstructures in diverse symmetry-broken condensed matter systems, ranging from nanoparticle-decorated liquid crystals to superconductors. By exploiting the trapped nanoparticles as carriers of additional desired physical properties the resulting nanocomposites could exhibit exotic features [19].

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