

Molecular tilt near nanoparticles in the smectic-*A* phase of a de Vries liquid-crystalline compound

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(Received 15 August 2013; revised manuscript received 18 November 2013; published 21 January 2014)

We show how the inclusions of the nanoparticles or the clusters of nanoparticles in the liquid-crystalline smectic-*A* phase lead to layer deformations and may create a tilt in their vicinity, thus inducing locally a smectic-*A*–smectic-*C* transition. We have studied a freestanding film of “de Vries” compound, which exhibits the smectic-*A*–smectic-*C* transition without layer shrinkage, mixed with functionalized gold nanoparticles. The tilt induced by nanoparticle clusters, which decorate the edge dislocations, has been observed in the smectic-*A* phase. The tilt of liquid-crystal molecules near nanoparticles is a consequence of interaction of liquid-crystalline molecules with the surface of nanoparticles. The observed tilt may prove the concept of existence of a disordered tilt in the smectic-*A* phase of de Vries compounds. The tilt distribution near nanoparticles is discussed using both the smectic-*A* elasticity and local smectic-*A*–smectic-*C* transition.

DOI: [10.1103/PhysRevE.89.012505](https://doi.org/10.1103/PhysRevE.89.012505)

PACS number(s): 61.30.Dk, 61.30.Hn

I. INTRODUCTION

Liquid-crystalline (LC) molecules can create smectic phases, in which molecules are organized in layered systems with a various degree of the orientational and/or positional order. In most studied smectic-*A* and smectic-*C* phases, no inlayer order exists. In the smectic-*A* phase molecules are oriented along the layer normal; in the smectic-*C* phase they are tilted. The main obstacle in the commercialization of devices based on smectic LCs is related to changes of the molecular tilt from the layer normal, which implies shrinkage of the smectic layer spacing at the smectic-*A*–smectic-*C* phase transition. Recently, a number of LC materials displaying low shrinkage of the smectic layer spacing have been identified and these materials were named “de Vries.” Theoretical models for the smectic-*A*–smectic-*C* phase transition in de Vries materials predicted that molecules in the smectic-*A* phase are tilted from the layer normal in azimuthally random directions, so there is a low orientational order [1,2].

Generally, nanoparticles introduced to the smectic liquid crystals can induce a deformation of smectic layers and a perturbation of the molecular director. Layer deformation near a point-like inclusion in the smectic-*A* phase has been already studied in [3–5]. In a series of papers [6–10], elastic effect of an impurity or inclusion embedded between two smectic-*A* layers was investigated in more detail. Perturbation of the director in the smectic-*C* phase near a small inclusion was theoretically investigated in Refs. [11–13]. In recent publications [14–16], aggregating of functionalized golden nanoparticles to clusters visible in the optical microscope has been reported. Besides, in Refs. [15,16] the decoration of edge dislocation lines in the smectic-*A* phase was reported.

In this contribution, specific optical contrast appearing in the vicinity of the nanoparticle clusters dispersed in the smectic-*A* phase of a de Vries compound is reported and discussed. Generally, distribution of the tilt angle near the nanoparticle cluster responsible for the observed contrast can be described by two approaches. In Sec. III we use the elastic model that treats the volume deformation and the molecular tilt

deformation induced by a point-like inclusion in the smectic-*A* phase [4,5]. In Sec. IV we adopt the model of the local transition from the smectic-*A* to smectic-*C* phase based on the Landau free energy with the tilt angle as the transition parameter. In that case the tilt angle distribution near the cluster is not connected with layer deformation but is induced by anchoring on the cluster surface.

The applicability and weight of both attempts for explanation of the phenomena described in the next sections is discussed.

II. OBSERVATION OF THE OPTICAL CONTRAST AROUND THE NANOPARTICLES

The functionalized golden nanoparticles were dispersed in the chiral (*S*)-hexyl-lactate [17–19] abbreviated as 9HL exhibiting the smectic-*A* phase from 138 °C to 64 °C and transition to the chiral smectic-*C* phase takes place. As shown in Ref. [20] the layer thickness does not change significantly at this phase transition. This effect is specific for de Vries phases and used to be explained by the existence of a molecular tilt in the smectic-*A* phase in directions randomly distributed [1,2,18–20], so that the uniaxial state is conserved. The tilt direction becomes ordered in the biaxial smectic-*C* phase.

The preparation of the functionalized nanoparticles and their characterization is published in Ref. [21]. The gold nanoparticles of a diameter of about 1.5 nm were added to 9HL. The nanoparticles were grafted by two kinds of thiols, by an alkyl thiol-S-C₆H₁₃ and then by longer mesogenic molecules, the chemical structure of which is shown in Fig. 1 of Ref. [21]. Grafting layer does not exceed the length of 3.4 nm. Effective dimension of the functionalized nanoparticle is commensurate with the thickness of two smectic-*A* layers, which is about 8.3 nm [18]. Location of the functionalized nanoparticle in the smectic-*A* structure is schematically depicted in Fig. 1.

Free-standing film (ensuring homeotropic alignment) of a typical thickness of 20 μm was prepared from 9HL containing functionalized gold nanoparticles in the concentration of 4.5 w/w%. Observed texture is presented in Fig. 2 at 100 °C, i.e., 36 degrees above the smectic-*A*–smectic-*C* phase transition. We suppose that the visible particles correspond to clusters of nanoparticles preferentially condensed at the

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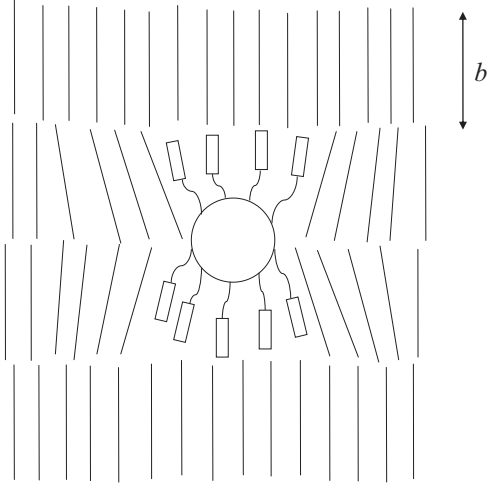


FIG. 1. Schematic drawing of a nanoparticle functionalized by grafted molecular chains embedded in smectic-A layers. Smectic molecules are tilted due to presence of molecular chains on the surface of nanoparticle. The smectic layer thickness is denoted as b .

edge dislocation lines. Similar observation was reported in Refs. [15,16], where the edge dislocations were visualized by nanoparticle clusters in a wedge sample with homeotropic anchoring. Generally, dislocations are not visible in the optical microscope without such a decoration. The only exception is an observation of the edge dislocations during the smectic-A–smectic-C phase transition, when the dislocations represented nucleation centers for the tilted phase and on further cooling the contrast on the dislocation disappeared [22,23].

In Ref. [15] the clusters of nanoparticles were seen in parallel polarizers as dark dots. At crossed polarizers the dark

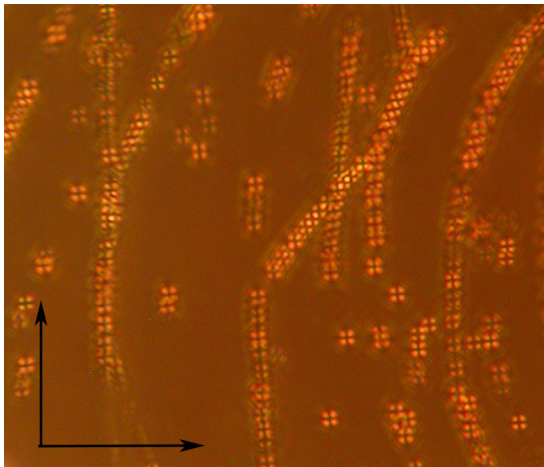


FIG. 2. (Color online) Texture of compound 9HL containing functionalized nanoparticles in the free-standing film of the smectic-A phase observed between crossed polarizers (at temperature $T = 100^\circ\text{C}$). Edge dislocation lines in film are decorated by nanoparticle clusters. Dark background is due to the smectic-A molecules with the mean orientation along the normal to the film. The optical contrast around the clusters indicates cylindrical symmetry of the molecular tilt. The width of micrograph is about $150\ \mu\text{m}$. The arrows mark the direction of the polarizer and analyzer in a crossed position.

dots were hidden in dark background typical for the smectic-A homeotropic sample. On the contrary, in our observations (Fig. 2) one can see a remarkable contrast on particles under the crossed polarizers in the form of Maltese cross. We can interpret this optical contrast as local induction of the molecular tilt on cluster surfaces, the cluster with the liquid crystal in its neighborhood having a cylindrical symmetry. It is worth noting that the same is valid for a single nanoparticle, but in that case the region where the molecules are influenced by the surface is too small to create an observable optical contrast. From our microscope observation the dimension of clusters, which decorate the edge dislocations, is estimated as $0.5\text{--}1\ \mu\text{m}$.

III. POINT DEFECTS DESCRIBED BY SMECTIC-A ELASTICITY

The introduction of point defects into the system of smectic layers generally leads to the volume change near the point defect. This change can be described by displacement of the smectic layers u parallel to the z axis. Models of point-like inclusions in the smectic-A phase [3–10] usually suppose a volume deformation giving rise to interaction either between the edge dislocation and the point defect [4] or between two point defects [5]. These models are based on the elastic energy density of the smectic-A liquid crystal [24]

$$f = \frac{A}{2} \left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right)^2 + \frac{B}{2} \left(\frac{\partial u}{\partial z} \right)^2, \quad (1)$$

the x and y axes being situated in the smectic layers and the z axis along the layer normal. A and B are elastic constants of the smectic-A, namely the curvature modulus and the layer compression modulus, respectively.

Minimization of the free elastic energy Eq. (1) gives a solution describing an isolated point defect (Fig. 3) situated in the origin of the coordinate system [4,5]:

$$u(x, y, z) = \frac{c}{2\lambda z} \exp\left(-\frac{\rho^2}{4\lambda|z|}\right), \quad (2)$$

with $\rho = \sqrt{x^2 + y^2}$ and $\lambda = \sqrt{A/B}$. The constant $c = \zeta \delta S / 4\pi$ has a dimension of volume, $\zeta \delta S$ being volume change due to the presence of the point defect in smectic layers [4].

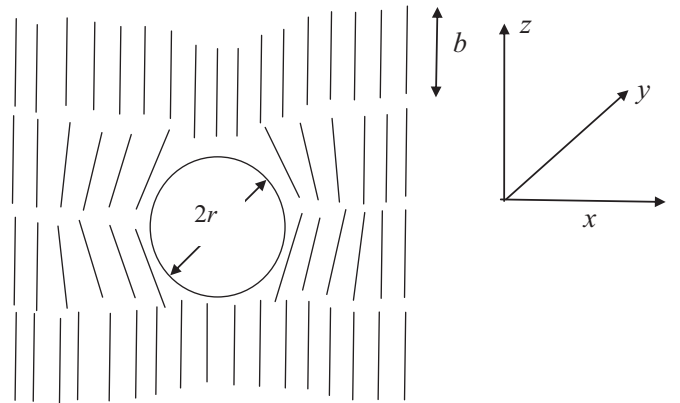


FIG. 3. Schematic drawing of a spherical inclusion embedded in the smectic-A layers. Smectic molecules are tilted due to the interaction with the surface of inclusion. Smectic layer thickness is denoted b and $2r$ is the nanoparticle diameter.

Parameter ζ is oriented along the z axis and the area δS being the cross-section of the point defect in the (x, y) plane. Then the interaction energy E_I of a point defect with an edge dislocation parallel to the y axis can be written as [4,16]:

$$E_I = (\zeta \delta S) \frac{Bbx_i}{8\sqrt{\lambda\pi}} \left(\frac{\exp\left(-\frac{x_i^2}{4\lambda|z_i|}\right)}{|z_i|^{3/2}} \right). \quad (3)$$

Note that the dislocation Burgers vector b is oriented along the z axis and it is equal to the smectic layer thickness. Parameters x_i and z_i describe position of the defect with respect to the dislocation line. For $\zeta > 0$, the defect creates volume dilatation in the system of smectic layers. When $x_i > 0$, it is $E_I > 0$. So the point defect tends to move to the region near the edge dislocation where $E_I < 0$ ($x_i < 0$), i.e., where E_I is minimal. Therefore, to avoid a dilatation imposed on smectic layers, the point defects have a tendency to group themselves near the edge dislocations. This effect represents a driving force for decoration of dislocations by point defects, e.g., by nanoparticles or their clusters [14–16] as is seen in Fig. 2.

Equation (2) also describes a change of the tilt θ around the point defect (Fig. 3). The tilt angle θ is measured from the z axis. For small θ we get $u = b(1 - \cos\theta) \approx b\theta^2/2$. Just to avoid a singularity, let us take the tilt on the nanoparticle surface ($\rho = 0$) and $z \approx b/2$ as $\theta \approx \theta_o$ and $z \approx -b/2$ as $\theta = -\theta_o$. Then the solution $\theta(\rho, z)$ can be written in the form

$$\theta(\rho, z) = \text{sgn}(z)\theta_o \sqrt{\frac{b}{2|z|}} \exp\left(-\frac{\rho^2}{2\lambda|z|}\right). \quad (4)$$

The tilt angle decreases exponentially with the radial distance ρ from the point defect but rather slowly, as $1/\sqrt{|z|}$, along the z axis. It is instructive to estimate the distance on which the exponential function in Eq. (4) falls to e^{-1} . For $z \approx b/2$ we get $\exp\left(-\frac{\rho^2}{4\lambda b}\right) \approx e^{-1}$, which gives

$$\frac{\rho}{b} \approx 2\sqrt{\frac{\lambda}{b}}. \quad (5)$$

For a typical smectic- A phase, the layer compression modulus $B \sim 10^7 \text{ Jm}^{-3}$ and the curvature modulus $A \sim 10^{-11} \text{ Jm}^{-1}$ [25] give $\lambda = \sqrt{A/B} \approx 10^{-3} \mu\text{m}$, which equals about the layer spacing b . Then from relation Eq. (5) one can infer that the tilt angle falls on the distance $\rho \sim 2b$. It is evident that for such fast tilt decay the optical contrast can be hardly observable around the particles or the nanoparticle clusters. It can explain why no optical contrast was observed in the vicinity of clusters embedded in the smectic- A phase in Refs. [15,16]. Attainment of the observable tilt induced by the particle surface would be significantly enlarged for a very soft smectic- A with much lower B , which might happen only in close vicinity of the phase transition to the nematic phase. So the dilatation due to the nanoparticle cluster is responsible for the grouping of clusters near an edge dislocation, but the contribution of this dilatation to the tilt change near clusters is not important. In the following section another contribution to the tilt angle induced by anchoring on the cluster surface is developed.

IV. SURFACE ANCHORING ON CLUSTERS

Due to interaction with the nanoparticles, the liquid crystal molecules located on the surface of clusters can be tilted

(see Fig. 1). In fact, it corresponds to a local transition from the smectic- A structure (optically uniaxial state) to a state reminding the smectic- C structure, the tilt angle θ being the parameter of this transition.

In order to describe the distribution of θ near nanoparticle cluster we use a phenomenological model with the free-energy density development for small θ , including gradient terms [26]

$$f = \frac{a}{2}(T - T_c)\theta^2 + \frac{b}{4}\theta^4 + \frac{K}{2} \left(\left(\frac{\partial\theta}{\partial x} \right)^2 + \left(\frac{\partial\theta}{\partial y} \right)^2 + \left(\frac{\partial\theta}{\partial z} \right)^2 \right), \quad (6)$$

where a , b , and K are the Landau expansion coefficients. Parameters T and T_c are the temperature and the transition temperature from the smectic- A to the smectic- C phase. In this analysis we treat the smectic- A phase, i.e., $T - T_c > 0$. Supposing a , b , and K are positive, the minimum of energy Eq. (6) corresponds to $\theta = 0$ if no external field is applied. The presence of nanoparticle clusters leads to the local transition to smectic- C structure decaying with the distance from the cluster. This local transition can be described by free-energy density Eq. (6) using the development to quadratic terms θ^2 (neglecting the term θ^4).

Then the equilibrium equation following from Eq. (6) in the cylindrical coordinates (ρ, α, z) takes a form

$$\frac{\partial^2\theta}{\partial\rho^2} + \frac{1}{\rho} \frac{\partial\theta}{\partial\rho} + \frac{1}{\rho^2} \frac{\partial^2\theta}{\partial\alpha^2} + \frac{\partial^2\theta}{\partial z^2} = \gamma\theta, \quad (7)$$

with $\gamma = \frac{a}{K}(T - T_c) > 0$.

Note that coordinates ρ and α are polar coordinates in the plane of smectic layer, ρ measuring the distance from the center of the cluster. Coordinate z is oriented along the smectic layer normal.

Let us expect the tilt angle θ not dependent on the angle α so it will be isotropic in the smectic layers. Then we propose the solution of Eq. (7) in the form $\theta(\rho, z) = R(\rho)e^{-|z|/\lambda}$. Parameter λ is the length over which the tilt angle decays to e^{-1} along the z direction. Equation (7) can be rewritten as

$$\frac{\partial^2 R(\rho)}{\partial\rho^2} + \frac{1}{\rho} \frac{\partial R(\rho)}{\partial\rho} + \frac{R(\rho)}{\Lambda^2} = 0, \quad (8)$$

with $\frac{1}{\Lambda^2} = \frac{1}{\lambda^2} - \gamma$. The condition $\frac{1}{\Lambda^2} > 0$ gives $1 > \lambda^2\gamma$ or $K > \lambda^2 a(T - T_c)$.

The solution of Eq. (8) is in the form $\theta(\rho, z) = (C_1 J_0(\frac{\rho}{\Lambda}) + C_2 Y_0(\frac{\rho}{\Lambda}))e^{-|z|/\lambda}$, where $J_0(\frac{\rho}{\Lambda})$ and $Y_0(\frac{\rho}{\Lambda})$ are the Bessel functions of the first and second kind, respectively [27]. From the form of the solution it is seen that the parameter Λ is the scaling length along the radius ρ .

To avoid the divergence of the solution we discard the term $Y_0(\frac{\rho}{\Lambda})$ by taking the integration constant $C_2 = 0$.

The solution $\theta(\rho, z) = C_1 J_0(\frac{\rho}{\Lambda})e^{-|z|/\lambda}$ describes a point-like cylindrical defect at the coordinate origin. Let us suppose a nanoparticle cluster having the radius r and the thickness L_z along the z axis. Then we sum the above solution along the cluster thickness L_z :

$$\theta = C_1 J_0\left(\frac{\rho}{\Lambda}\right) \int_{-L_z/2}^{L_z/2} e^{-\frac{|z-z'|}{\lambda}} dz', \quad (9)$$

where the integral in Eq. (9) can be evaluated as

$$\begin{aligned} & \int_{-L_z/2}^{L_z/2} e^{-\frac{|z-z'|}{\lambda}} dz' \\ &= 2\lambda e^{-\frac{|z|}{\lambda}} \sinh\left(\frac{L_z}{2\lambda}\right) \left(1 + \frac{1}{2} \left(\operatorname{sgn}\left(z - \frac{L_z}{2}\right) - \operatorname{sgn}\left(z + \frac{L_z}{2}\right)\right)\right) \\ & \quad + \lambda \left(1 - e^{-\frac{L_z}{2\lambda}} \cosh\left(\frac{z}{\lambda}\right)\right) \\ & \quad \times \left(\operatorname{sgn}\left(z + \frac{L_z}{2}\right) - \operatorname{sgn}\left(z - \frac{L_z}{2}\right)\right). \end{aligned} \quad (10)$$

Note that this integral approaches the value $2\lambda(1 - e^{-\frac{L_z}{2\lambda}})$ for nearly all z in the interval $z \in (-L_z/2, L_z/2)$ and for $L_z \gg \lambda$. We use this property for determination of the integration constant C_1 .

We expect that the nanoparticles on the cluster surface induce the tilt of liquid-crystal molecules (see Fig. 1). It means $\theta = \pm\theta_o$ at $\rho = r$ in the interval $z \in (-L_z/2, L_z/2)$. From the point of view of optical contrast the sign of θ is not important, and thus we can take $\theta = \theta_o$. Then the integration constant C_1 follows from Eq. (9) as

$$C_1 = \theta_o / 2\lambda (1 - e^{-\frac{L_z}{2\lambda}}) J_o\left(\frac{r}{\Lambda}\right),$$

when $L_z \gg \lambda$.

Observations show that at radial distance, ρ_o , from the cluster the structure is uniaxial, so the tilt angle $\theta \rightarrow 0$. The value ρ_o can be determined from the equation $J_o(\frac{\rho}{\Lambda}) = 0$ as its first root, which is $\frac{\rho_o}{\Lambda} \approx 2.4$. For $\rho \geq \rho_o$ we take $\theta = 0$ approximately. Then solution of Eq. (8) in our approximate form is

$$\begin{aligned} \theta &= \theta_o \frac{J_o\left(\frac{\rho}{\Lambda}\right) \int_{-L_z/2}^{L_z/2} e^{-\frac{|z-z'|}{\lambda}} dz'}{J_o\left(\frac{r}{\Lambda}\right) 2\lambda(1 - e^{-\frac{L_z}{2\lambda}})}, \quad \text{for } \rho \leq \rho_o \quad \text{and} \\ \theta &= 0 \quad \text{for } \rho \geq \rho_o. \end{aligned} \quad (11)$$

The existence of solution Eq. (11) leads to the increase of the energy ΔE in the region near the cluster. This energy ΔE can be determined from Eq. (6) in polar coordinates neglecting the term θ^4 as

$$\begin{aligned} \Delta E &= \int_{-L_z/2}^{L_z/2} dz \int_0^{2\pi} d\alpha \\ & \quad \times \int_r^{\rho_o} \rho d\rho \frac{K}{2} \left[\gamma \theta^2 + \left(\frac{\partial\theta}{\partial\rho}\right)^2 + \left(\frac{\partial\theta}{\partial z}\right)^2 \right]. \end{aligned} \quad (12)$$

As we suppose that the tilt angle θ is not dependent on the angle α , the term $\partial\theta/\partial\alpha \rightarrow 0$ in Eq. (12). For $L_z \gg \lambda$, the function $\int_{-L_z/2}^{L_z/2} e^{-\frac{|z-z'|}{\lambda}} dz' / 2\lambda(1 - e^{-\frac{L_z}{2\lambda}}) \rightarrow 1$ in the interval $z \in (-L_z/2, L_z/2)$. Then this interval $\partial\theta/\partial z \rightarrow 0$ and ΔE can be rewritten in the form

$$\Delta E = \frac{\pi K \theta_o^2 L_z}{J_o^2\left(\frac{r}{\Lambda}\right)} \int_r^{\rho_o} \rho d\rho \left[\gamma J_o^2\left(\frac{\rho}{\Lambda}\right) + \frac{1}{\Lambda^2} J_1^2\left(\frac{\rho}{\Lambda}\right) \right]. \quad (13)$$

Integration in Eq. (13) can be again evaluated by means of Bessel functions but for numerical estimations the form of Eq. (13) is sufficient.

Taking into account geometrical parameters deduced from Fig. 2, namely $r \sim 0.5 \mu\text{m}$ and $\rho_o \sim 2 \mu\text{m}$, we can estimate the length Λ using the relation $\Lambda \approx \rho_o/2.4 \approx 0.8 \mu\text{m}$. Using the relation $\frac{1}{\Lambda^2} = \frac{1}{\lambda^2} - \gamma$, we can also obtain the order of value of the parameter λ as $\lambda = \Lambda/\sqrt{1 + \Lambda^2 a(T - T_o)/K}$.

For a let us take as a typical value $a \approx 1.1 \times 10^4 \text{ Jm}^{-3}\text{K}^{-1}$ [28] and $(T - T_o) \approx 40 \text{ deg K}$. The parameter K has the order of nematic elastic constant, i.e., 10^{-11} Jm^{-1} [24,25]. Then the order of the parameter λ is $\lambda \sim 5 \times 10^{-3} \mu\text{m}$. It means that the angle θ strongly decays already in the smectic layers neighbor to the cluster in z direction. Because the length of L_z is of the order of micrometers, the relation is always valid and we can simplify Eq. (12) to the form of Eq. (13).

The tilt angle θ_o on the surface of nanoparticle cluster was not yet determined. Now we try to discuss its possible values together with the surface anchoring energy. The anchoring of molecules on the cluster surface can be described by the anchoring energy W_A (per unit surface of a cluster). The anchoring keeps on the surface of the cluster molecules tilted by an angle θ_o . The formation of the structure with the nonzero tilt is accompanied with an increase of the energy by ΔE as given by Eq. (13). The energy increase ΔE should be balanced by the anchoring energy W_A .

As the energy ΔE is overcome by the anchoring of molecules on the cluster surface, the energies ΔE and W_A are related as

$$\Delta E \approx 2\pi r L_z W_A. \quad (14)$$

Equation (14) relates the tilt angle θ_o , included in ΔE , and the anchoring energy W_A . So it can give us estimations about their values. The typical values of anchoring energies of the nematic liquid crystals are spanning from 10^{-5} to 10^{-7} Jm^{-2} [29]. For those anchoring energies we obtain small θ_o ; e.g., the higher limit $W_A \sim 10^{-5} \text{ Jm}^{-2}$ gives $\theta_o \sim 0.4^\circ$. With stronger anchoring $W_A \sim 10^{-4} \text{ Jm}^{-2}$, Eq. (14) gives us the estimation $\theta_o \sim 1^\circ$. It is also small tilt angle but it might be recognizable on the background of the surrounding uniaxial structure.

It should be noted that the smectic-A–smectic-C transition observed in the present study resembles polymer stabilized liquid crystals at the paraelectric to ferroelectric smectic-A*–smectic-C* transition [30–33]. The polymer network strands have the size of clusters of nanoparticles. Local transition from smectic-A* to smectic-C* in the vicinity of the network strands is observed, depending on polymerization conditions either in smectic-A* or in smectic-C* phase [30,31]. It was demonstrated both experimentally and theoretically in Refs. [32,33] that this transition takes place due to elastic interactions between the liquid crystal and the polymer strands. It is interesting to note that the penetration length estimated in Ref. [33] as about $0.75 \mu\text{m}$ has a very similar value as our estimation of it is $\Lambda \approx 0.8 \mu\text{m}$. Note that Λ represents the scaling length along ρ .

V. DISCUSSION AND CONCLUSIONS

Microscope observations of the free-standing films in the smectic-A phase made of liquid-crystalline compound 9HL of a de Vries type give evidence that functionalized gold

nanoparticles dispersed in the liquid crystal form clusters. Single gold nanoparticles are too small to be optically detectable when far from each other. It was shown previously [3,5] that interaction of point inclusions is weak but when their concentration is higher, the probability of grouping increases. Conditions for the clustering are given by competing of the surface energy of the contact between nanoparticles and the energy of contact between a nanoparticle and liquid-crystal molecules. Similar to Refs. [15,16], we have found that the clusters created from nanoparticles are concentrated near the edge dislocations. This effect is explained here by volume dilatation due to the presence of nanoparticles interacting with the edge dislocation. We have shown that this dilatation is minimized when the nanoparticles are concentrated at the lines of edge dislocations, where the clustering becomes then more probable.

We have observed optical contrast in the form of Maltese cross on nanoparticle clusters (see Fig. 2). It has to be connected with the de Vries character of 9HL liquid crystal used in our experiment, which is responsible for the induced tilt of the molecules around the clusters. In other systems exploring classical smectic-*A* phase, the tilt angle due to nanoparticle clusters was significantly lower [15,16] and could not be seen by microscope observation. The reason was fast decay of the tilt from the cluster surface due to liquid-crystal elasticity.

It is generally accepted that in de Vries compounds the molecular tilt exists even in the unperturbed smectic-*A* phase, but its orientation in random directions ensures the optically uniaxial state [17–19]. We suppose that due to interaction with the nanoparticles the molecular tilt near the surface of clusters is partially ordered and the cylindrical symmetry (see Fig. 4) of the tilt around the clusters is reflected in the optical contrast in the form of the Maltese cross. In de Vries compounds the reorientation of the tilt direction around the particle clusters is not connected with any changes of the layer thickness, and thus no layer displacement occurs. Thus, it is appropriate to treat the molecular tilt around the clusters on the basis of the anchoring of molecules on the cluster surface. The distance of the oriented (visible) tilt from the clusters is kept by a sufficient anchoring strength.

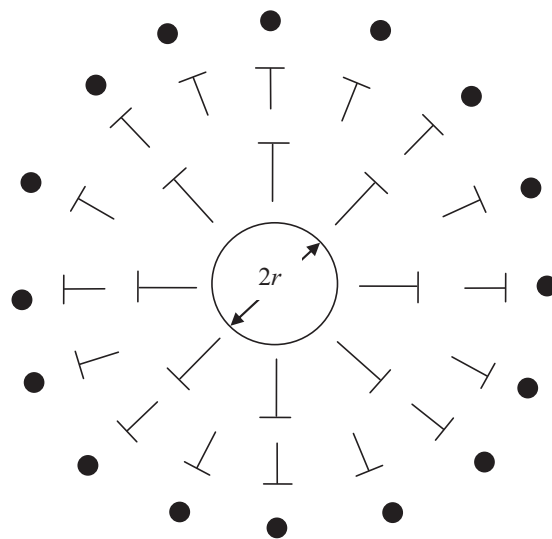


FIG. 4. Schematic drawing of the tilted molecules near an inclusion of the diameter $2r$ in the smectic-*A* liquid crystal observed along the layer normal. Molecules are represented by nails, the points of which are turned toward the observer. The length of the nails is related to the molecular tilt. Black dots are molecules parallel to the layer normal.

In summary, we have documented the tilt of liquid-crystalline molecules in the smectic-*A* phase near the vicinity of nanoparticle clusters. The observed effect was theoretically analyzed and it was shown that the de Vries character of the liquid crystal is responsible for its occurrence. On the other hand, the results may prove the concept of the existence of the disordered tilt of molecules in the smectic-*A* phase of de Vries compounds.

ACKNOWLEDGMENTS

This work was supported by Project No. P204/11/0723 from the Grant Agency of the Czech Republic.

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