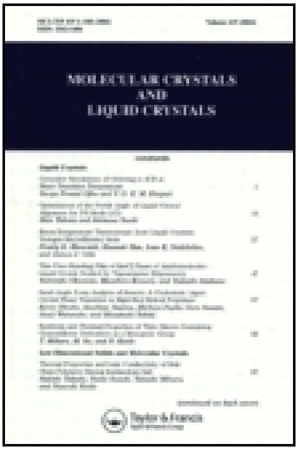

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Structural Transitions in Nematic Filled With Colloid Particles

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Version of record first published: 24 Sep 2006

To cite this article: S. V. Shiyanovskii & O. V. Kuksenok (1998): Structural Transitions in Nematic Filled With Colloid Particles, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 321:1, 45-56

To link to this article: http://dx.doi.org/10.1080/10587259808025075

Mol. Cryst. Liq. Cryst., Vol. 321, pp. 45–56
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Structural transitions in nematic filled with colloid particles

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The theoretical study of the possible structures in nematic with spherical particles with normal boundary conditions on its surface is carried out. Criteria for the structural transitions between the hyperbolic hedgehog, disclination loop and weakly deformed structure are determined.

Keywords: nematic; colloid suspension; structural transitions; anchoring parameter

INTRODUCTION

Colloid suspensions in liquid crystals have interesting structural and optical properties caused by the long-range deformation field created by the director anchoring on particle surface[1,2]. External electric field can change the structure of such systems, that is necessary for using such systems in display engineering, but to interpret the effects like light transmission and scattering a detailed knowledge about the director distribution around a colloid particle suspended in a liquid crystal matrix is required. The director distortion around a spherical particle (SP) with normal boundary conditions on its surface is determined by two competing processes: 1) anchoring tends to align the director along the normal to the surface, 2) elastic energy suppresses this distortion. For the sufficiently high value of anchoring energy the hedgehog structure is created around the SP. The hedgehog either is surrounded by a disclination ring[3-5], or has a hyperbolic satellite hedgehog[6]. For the weak anchoring the hedgehog with satellite defects does not appear, and the director is only slightly distorted around the SP. This paper is devoted to the theoretical study of the possible structures and transitions between them in nematic liquid crystals with SPs.

The task of finding a director distribution around considered spherical particle consists of minimization of the Frank free energy functional and the surface energy. The Frank energy of director distortion is calculated taking into account the divergence K_{24} term

$$F_{Fr} = \int \left[\begin{array}{l} \frac{K_{11}}{2}(\mathrm{div}\mathbf{n})^2 + \frac{K_{22}}{2}(\mathbf{n}\mathrm{curl}\mathbf{n})^2 + \frac{K_{33}}{2}[\mathbf{n}\times\mathrm{curl}\mathbf{n}]^2 \\ - K_{24}\,\mathrm{div}(\mathbf{n}\,\mathrm{div}\mathbf{n} + \mathbf{n}\times\mathrm{curl}\mathbf{n}) \end{array} \right] dV, \qquad (1)$$

and the anchoring energy is calculated in the Rapini approximation

$$F_s = -\frac{1}{2}\int W(\mathbf{n}\,\gamma)^2 dS\ , \qquad (2)$$

with γ being the unit vector normal to the particle surface. An obvious axial symmetry allows to describe the director field in the spherical coordinate system $\{r, \theta, \varphi\}$ by the single distortion angle $\beta(r, \theta)$

$$n_x = \sin\beta\cos\varphi,\ \ n_y = \sin\beta\sin\varphi,\ \ n_z = \cos\beta. \qquad (3)$$

We use two-constant approximation ($K_{11} = K_{33} = K$) as the value of K_{22} does not matter due to the symmetry.

$$F = \frac{K}{2}\int\left[\left(\frac{\partial\beta}{\partial r}\right)^2 + \left(\frac{1}{r}\frac{\partial\beta}{\partial\theta}\right)^2 + \left(\frac{\sin\beta}{r\sin\theta}\right)^2\right]dV + F_{div} + \frac{1}{2}\int W\sin^2(\beta-\theta)\,dS, \qquad (4)$$

where

$$F_{div} = -K\left(k_{24} - \frac{1}{2}\right)\int(\mathbf{P}\ \gamma)dS,\ \ k_{24} = \frac{K_{24}}{K}$$

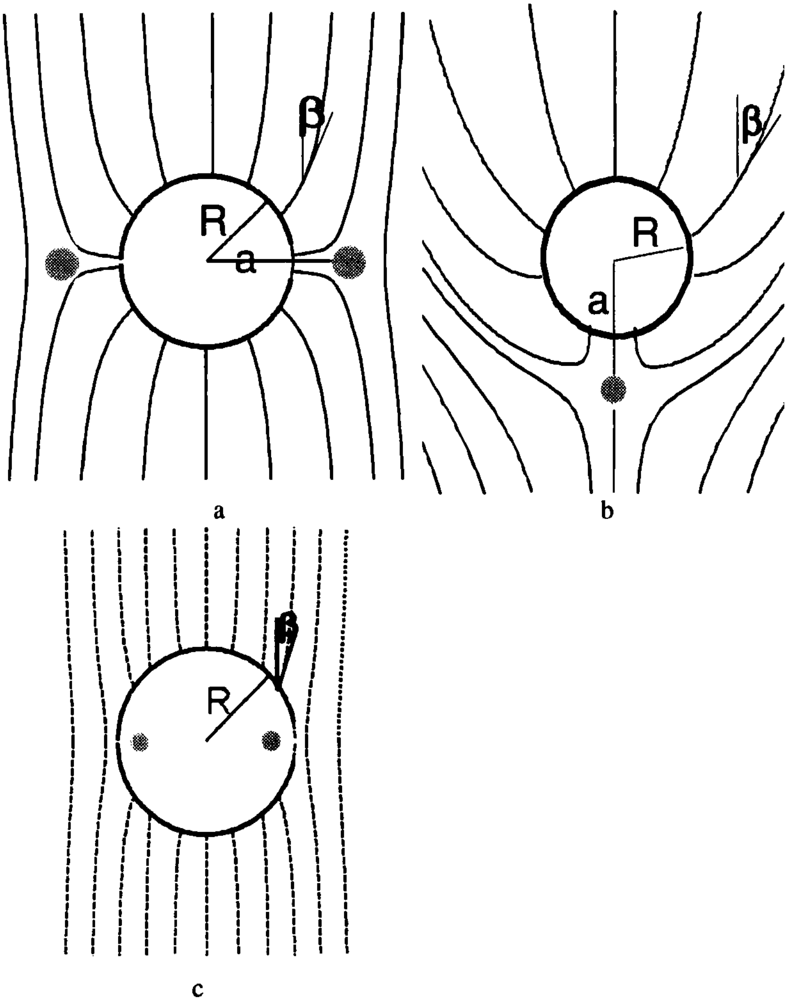

FIGURE 1 Possible structures around SP with radius R, here β is distortion angle:

a. structure with a disclination loop, **a** is a loop radius;
b. structure with a hyperbolic hedgehog, **a** is a distance from the centre of SP to the defect;
c. weak distortion structure.

and

$$\mathbf{P} = \left[\frac{1}{r}\left(\frac{\sin\beta}{\cos\theta}\cos(\beta-\theta) + \frac{\partial\beta}{\partial\theta} \right), \left(\frac{\sin\beta}{r\sin\theta}\sin(\beta-\theta) - \frac{\partial\beta}{\partial r} \right), 0 \right]$$

From the condition of minimum of $\delta F = 0$ we obtain the equilibrium equation

$$\nabla^2\beta - \frac{\sin 2\beta}{2r^2\sin\theta} = 0, \tag{5}$$

and surface terms in the free energy allow to define the appropriate boundary conditions.

WEAK ANCHORING: SMALL DISTORTIONS

In the case of weak anchoring we expect only small deviations of the director and the problem can be linearized. The general solution of the linearized Eq.(5) decaying at infinity is

$$\beta = \sum_k \frac{C_k}{r^{k+1}} P_k^1(\cos\theta), \tag{6}$$

where $P_k^1(\cos\theta)$ are associated Legendre polynomials. The boundary condition on the particle surface selects a particular mode, k=2, with all other coefficients $C_{k\neq 2} = 0$. The director distortion angle dependence on the anchoring parameter $\tilde{w} = WR/K$ takes the form

$$\beta = \frac{\tilde{w}}{1+k_{24}}\left(\frac{R}{r}\right)^3 \sin 2\theta. \tag{7}$$

Obviously, the linear approximation leading to this expression, $\beta << 1$, is satisfied when

$$\tilde{w} << 4(1+k_{24}). \tag{8}$$

STRONG DISTORTIONS–STRUCTURE WITH DISCLINATION LOOP

In the case of strong anchoring on the particle surface one cannot assume that β is small in the vicinity of the particle and there is no straightforward way to obtain the solution.

For rigid radial anchoring on the particle surface the trial function based on the direct superposition of component deformations has been exploited[4,5]. It has been sown that director distribution can be successfully described by means of introduction of an unknown function of distance f(r) in the trial function for distortion angle β

$$\beta = \theta - \frac{1}{2}\operatorname{arccot}\left(\frac{1/f(r) + \cos(2\theta)}{\sin(2\theta)}\right), \quad (10)$$

which must comply with the boundary conditions: $1/f(\infty) = 0$ $(\beta = 0)$ and $f(R) = 0$ for the rigid condition on SP's surface ($\beta = \theta$). Radius of the loop is defined from the condition $f(a) = 1$. It should be noted that the radius of the disclination ring for rigid radial anchoring was shown to depend slightly on the core radius R_c so that $a \approx 1.2R$.

For strong but not rigid anchoring on a SP's surface the trial function β for correct description of director distribution can also be used but we have to change the boundary conditions on the SP's surface to the ones corresponding to the energy minimum $\delta F = 0$.

Integration over the angle θ using trial function $\beta(10)$ gives the free energy as a functional of function $f(r) \equiv f$:

$$F = 2\pi K\left[\int_R^{a_-} \Psi dr + \int_{a_+}^{\infty} \Psi dr + a\tilde{\Sigma}\right] + F_{div} + F_s, \quad (11)$$

here the area $r \in [a_-, a_+]$ (see Fig.2) containing the defect and having the energy $2\pi K a \Sigma$ is cut out and

$$\Psi = \frac{1}{2} U_1(f)(rf')^2 + U_2(f), \quad \frac{\partial f(r)}{\partial r} \equiv f',$$

$$U_1(f) = \frac{(-3+2f-3f^2))}{32(1-f)f^{5/2}} \arctan\left(\frac{2\sqrt{f}}{f-1}\right) - \frac{3}{16}\frac{1}{f^2},$$

$$U_2(f) = \frac{(f-1)(3f+5)}{21(1-f)\sqrt{f}} \arctan\left(\frac{2\sqrt{f}}{f-1}\right) + \frac{1}{2}\ln\left(\left|\frac{1-f}{1+f}\right|\right) - \frac{1}{2\sqrt{f}}\ln\left(\left|\frac{1-\sqrt{f}}{1+\sqrt{f}}\right|\right) + \frac{3}{8}$$

$$F_s = \frac{\pi W R^2}{8}\left[6 - 2f - \ln\left|\frac{1-\sqrt{f}}{1+\sqrt{f}}\right| \frac{(2f-3+f^2)}{\sqrt{f}}\right]_R .$$

It should be noted, that the energy of the thin cut-off area contains its own core energy $2\pi K a \Sigma_0$ as well as the elastic energy of another part of this thin area excluding the core and the divergence elastic term taken at the cut-off surface[7]:

$$\tilde{\Sigma} \approx \Sigma_0 + \frac{1}{2} + \pi(1 - k_{24}). \tag{12}$$

It is convenient to describe the loop by the linear density of loop energy that includes both the core energy of and elastic energy directly caused by presence of the loop (loop energy for the simplicity further on)

$$\Sigma = \Sigma_0 + \pi(1 - k_{24}) - \frac{\pi}{4}\ln\frac{R_c}{R}, \tag{13}$$

where R_c is a core radius.

Solving this problem by variation method with accounting for the possibility of moving boundaries a_+ and a_- we obtained the Euler-Lagrange equation for function $f(r)$ that can be reduced to that of the first order by the substitution

$$y = \ln r, v = \frac{\partial f}{\partial y} = f' r:$$

$$\frac{\partial v}{\partial f} v U_1(f) + v^2 \frac{\partial U_1(f)}{\partial f} + vU_1 - \frac{\partial U_2(f)}{\partial f} = 0 \qquad (14)$$

with a certain condition on the cutting boundary and a condition on SP's surface like

$$\left.\frac{\partial F_s}{\partial f}\right|_R - 2\pi K \left.\frac{\partial \Psi}{\partial f'}\right|_R + \left.\frac{\partial F_{div}}{\partial f}\right|_R = 0 \qquad (15)$$

here $\left.\frac{\partial F_{div}}{\partial f}\right|_R = 4\pi(K_{24} - \frac{K}{2}) R I_1(f)$, and $I_1(f)$

were calculated numerically[7]. Thus we obtained the dependence between the value of the variation function on SP's surface and the anchoring parameter

$$\tilde{w} = \frac{16}{\pi} \left.\frac{\left(U_1(f) w(f) + 2 \cdot (k_{24} - \frac{1}{2}) \cdot I_1(f) \right) f\sqrt{f}}{\left[2f\sqrt{f}(f+1) - \ln\left|\frac{1-\sqrt{f}}{1+\sqrt{f}}\right| (2f - 3 + f^2) \right]}\right|_R . \qquad (16)$$

It should be emphasized that far away from the SP we obtain the director distribution as

$$\beta \sim \left(\frac{R}{r}\right)^3 \sin 2\theta$$

that corresponds to the solution of the weak-distortion case[7].

So the equilibrium loop radius is determined by three independent parameter: anchoring parameter $\tilde{w}$, loop energy Σ end elastic constant k_{24} (see curve 2-5, Fig.2a). We would like to emphasize here that the value of Σ depends on the ratio of the particle radius to that of the core radius. The core radius varies slightly and attains values about $100A^0$. Thus the loop energy Σ is determined by the particle radius to great extent.

It is clear that the director distribution of non-defect structure can been successfully described by the trial function (10), but the unknown function f must satisfy the inequality $f(R) > 1$ on the SP's surface. This approach allows to obtain the director distribution for non-defect structure without approximation of weak distortions (8) as well. In this case the imagine disclination loop inside SP is introduced.

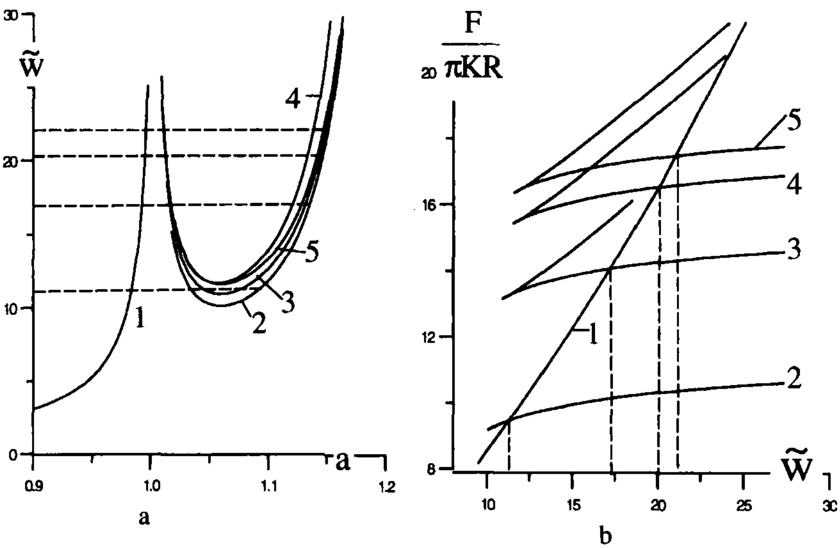

FIGURE 2 Equilibrium radius (a) and energy (b) dependence on the anchoring parameter. Dash lines in the figure (a) denote the restructuring of the system and the dash lines in figure (b) show the critical values of the anchoring parameters: 1 – non-defect structure;
2 - 5 – structure with disclination loop for:
$2 - k_{24} = 0, \Sigma = 5.5$; $3 - k_{24} = 0.5, \Sigma = 5.5$; $4 - k_{24} = 0.5, \Sigma = 6.5$; $5 - k_{24} = 0.9, \Sigma = 6.5$.

Certainly equilibrium equation is solved in the real space outside SP and the distribution for any anchoring is obtained. And it is instructive to find the radius of the imagine disclination loop inside SP corresponding to each structure (see curve 1, Fig.2,a). It should be noted that the weak distortion approximation corresponds to the small loop radius $a < 0.6$.

Thus can be seen in Fig.2,a both structures are possible in a certain interval of anchoring parameter ($\tilde{w} \in [10..25]$). What structure is realized can be found by comparing their energies (Fig.2, b). For the strong anchoring the structure with a loop is more favourable, reduction of anchoring leads to weak reduction of loop radius (down to approximately 1.1R) and at reaching some crucial value of anchoring the structural transition to non-defect structure occurs (see horizontal lines on Fig.2). This critical value is determined from the equality of the energies and depends on the linear loop energy Σ and elastic constant k_{24}. Increasing each of these parameters leads to the increase of critical anchoring.

STRONG DISTORTIONS: DIPOLE STRUCTURE

In the alternative case the director distribution around SP with strong anchoring forms a dipole structure (Fig. 3). We propose the trial function for distortion angle β based on the superposition of component deformations (a radial hedgehog and a hyperbolic hedgehog) similar to the previous case in the form

$$\beta = \theta - \frac{1}{2}\arctan\left(\frac{f(r)\sin\theta}{1+f(r)\cos\theta}\right). \qquad (17)$$

The unknown function of distance f(r) satisfies the boundary condition $1/f(\infty) = 0$ ($\beta = 0$) and position of the hyperbolic hedgehog is defined by the condition $f(a)=1$. The energy of such system is calculated by the equation (4):

$$F=\pi K\int_R^\infty\left[1-\frac{v^2}{f^2}+\frac{1}{2f^3}\left(f^2(f^2-3)-v^2(1+f^2)\right)\ln\left|\frac{1-f}{1+f}\right|\right]dr+ \\ \pi KR(k_{24}-\frac{1}{2})\left[2-\frac{1-f^2}{f}\ln\left|\frac{1-f}{1+f}\right|\right]_R+\pi WR^2\left[\frac{1+f^2}{2}-\frac{(1-f^2)^2}{4f}\ln\left|\frac{1-f}{1+f}\right|\right]_R \quad (18)$$

By minimizing this energy the Euler-Lagrange equation for function f and condition on SP's surface were obtained:

$$\tilde{w}=\left.\frac{\frac{1}{f^2}\ln\left|\frac{1-f}{1+f}\right|\left[(k_{24}-\frac{1}{2})(1+f^2)+\frac{v}{f}(1+f^2)\right]+\frac{v}{f^2}+\frac{2}{f}(k_{24}-\frac{1}{2})}{\left[2f(1-3f^2)-\ln\left|\frac{1-\sqrt{f}}{1+\sqrt{f}}\right|(3f^4-1-2f^2)\right]}8f^2\right|_R \quad (19)$$

Thus the equilibrium structure depends on the values of $\tilde{w}$ and k_{24} (curves 2-4, Fig.3). For the strong radial anchoring we have obtained the position of the hyperbolic hedgehog to be $a\approx 1.46R$. It may be shown that far away from SP the director distribution has a form

$$\beta\sim\left(\frac{R}{r}\right)^2\sin\theta$$

because this structure has no equatorial plane symmetry and has more long range "dipole" term in comparison to the weak distortion solution[7].

STRUCTURAL TRANSITIONS

To compare possible structures and to find transitions between them the corresponding free energies versus anchoring parameters are shown on Fig.3b. Defect structures are preferable for the strong anchoring (large

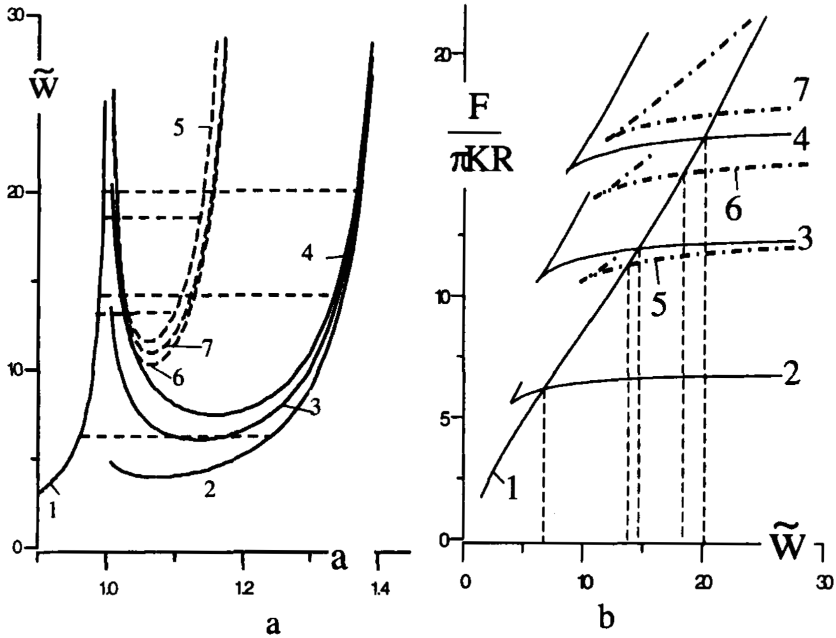

FIGURE 3 Equilibrium radius (a) and energy (b) dependence on the anchoring parameter. Dash lines in the figure (a) denote the restructuring of the system and the dash lines in figure (b) show the critical values of the anchoring parameters. 1 – non-defect structure;
2-4 – structure with hyperbolic hedgehog:
$2 - k_{24} = 0,\ \ 3 - k_{24} = 0.5,\ \ 4 - k_{24} = 0.9.$;
5, 6 – structure with loop:
$5 - \Sigma = 4.5, k_{24} = 0.5, 6 - \Sigma = 4.5, k_{24} = 0.9, 7 - \Sigma = 5.5, k_{24} = 0.9.$

particles), reduction of anchoring (radius) leads to the defect displacement closer to SP and at reaching a certain critical value the structural first order transition to non-defect structure occurs (dash lines on Fig.3). For the strong anchoring the structure with the hyperbolic hedgehog has lesser energy than the structure with the disclination loop for the wide range of values of parameters that corresponds to the experimental data in[6]. The only exception when the structure with the loop may turn out to be more preferable occurs for large values of the elastic constant k_{24} ($k_{24} > 0.5$).

It should be noted that the structure with hyperbolic hedgehog has dipole symmetry whereas ones with disclination loop and without defects have quadruple symmetry. As result the energy barrier for creation of hyperbolic hedgehog can be significantly larger than for disclination loop (curves 4 and 7 in Fig. 3,b) and the disclination loop can occur as a metastable state between non-defect structure and hyperbolic hedgehog

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