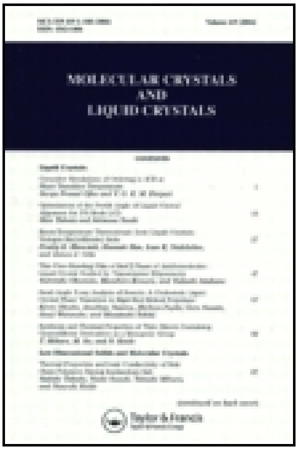

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Structure of the Domain Walls in Soft Ferrocholesterics

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Using the continuum theory the influence of the external magnetic field on the ferrocholesteric – ferronematic phase transition is analyzed. The field being applied normal to the helix. Soft homeotropic coupling between the magnetic particles and the cholesteric molecules is assumed. The diamagnetic anisotropy of the matrix is chosen to be positive. In this case the dipolar and quadrupolar mechanisms of orientational interaction with the external field compete with each other. The transition field as a function of the material parameters of a ferrocholesteric is found. The reentrant ferrocholesteric and ferronematic phases are discussed. It is shown that rising the field strength in the ferronematic phase leads to the change in the coupling between the particles and the director from homeotropic to planar one. A study on the structure of the domain walls in ferronematic phase is undertaken.

Keywords: ferrocholesteric; ferronematic; domain walls

INTRODUCTION

It is well known [1] that a cholesteric liquid crystal (CLC) with positive diamagnetic anisotropy χ_a can be transformed by an applied magnetic field into a nematic state with the director $\boldsymbol{n}$ parallel to the field direction when a magnetic field strength reaches a threshold value. Such a transition corresponds to a cholesteric helix unwinding. The critical field of the transition is large due to small χ_a values. The incorporation of the needle-like ferromagnetic particles into the CLC matrix increases the susceptibility of the system [2]. Such a suspensions are called ferrocholesterics (FC). We study orientational and magnetic properties of the FC in the magnetic field which is perpendicular to the spiral axis. Two mechanisms of the field influence on the FC structure are taken into consideration: dipolar (ferromagnetic) one due to the interaction between the particle magnetic moments $\boldsymbol{\mu} = M_s v \boldsymbol{m}$ and the magnetic field $\boldsymbol{H}$. and quadrupolar (diamagnetic) one conditioned by the interaction between the CLC matrix and $\boldsymbol{H}$ (here M_s is the saturation magnetization of a grain. v is the grain volume. $\boldsymbol{m}^2 = 1$). We consider the case when two mechanisms compete with each other. i.e. diamagnetic anisotropy $\chi_a > 0$ and soft anchoring of the homeotropic type on the particles. In the field absence the magnetic grains are uniformly distributed

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over the FC volume V and their magnetic moments $\boldsymbol{\mu}$ rotate around the z-axis with the director $\boldsymbol{n}$ and FC forms a helical structure with the pitch $p_0 = 2\pi/q_0$. The initial concentration $f_0 = Nv/V$ of the grains is assumed to be small and the magnetic dipolar-dipolar interactions are negligible.

EQUATIONS OF STATE

We assume that the helix axis of the FC is in the z-axis, the magnetic field $\boldsymbol{H}$ in the y-direction and χ_a is positive. Under the action of such a field normal to the helical axis z the distorted director fields are assumed to be:

$$\boldsymbol{n} = (\cos\phi(z), \sin\phi(z), 0), \quad \boldsymbol{m} = (-\sin\psi(z), \cos\psi(z), 0). \tag{1}$$

Deformation of a FC structure can be studied in the framework of continuum theory based on the free energy functional [2, 3]

$$F = \int dV \left[\frac{K_2}{2}\left(\frac{d\phi}{dz} - q_0\right)^2 - \frac{\chi_a H^2}{2}\sin^2\phi - M_s f H \cos\psi + \frac{fw}{d}\sin^2(\phi - \psi) + \frac{f k_B T}{v}\ln f\right]. \tag{2}$$

Here K_2 is the twist elastic constant, w is the anchoring energy, d is the particle diameter, f is the volume fraction of the particles in a suspension, k_B is the Boltzmann constant and T is the temperature. The first term in Eq.(2) represents the free energy density of the orientation - elastic deformation of the director (Frank potential). The second and third terms describe the quadrupolar (diamagnetic) and the dipolar (ferromagnetic) mechanisms of interaction of the diamagnetic CLC matrix and the particle magnetic moments $\boldsymbol{\mu} = M_s v \boldsymbol{m}$ with the magnetic field $\boldsymbol{H}$, respectively. The fourth term describes the coupling between the particle surfaces and CLC molecules and so the angle between $\boldsymbol{n}$ and $\boldsymbol{m}$ can be varied under the action of a magnetic field due to finite anchoring energy w. The last term is connected with the mixing entropy of the ideal solution of noninteracting magnetic particles.

Minimization of the total free energy (2) of a FC over $\phi(z)$, $\psi(z)$ and $f(z)$ (under the condition $\int f dV = Nv$) leads to the equations of orientational and concentration equilibrium

$$\frac{d^2\phi}{d\tilde{z}^2} = -\frac{\Pi^2}{2}\sin 2\phi + G\frac{f}{f_0}\sin 2(\phi - \psi). \tag{3}$$

$$\xi\Pi\sin\psi = G\sin 2(\phi - \psi). \tag{4}$$

$$\frac{f}{f_0} = Q\exp\left\{\frac{\xi\Pi}{\kappa}\cos\psi - \frac{G}{\kappa}\sin^2(\phi - \psi)\right\}, \quad \frac{1}{p}\int_0^p \frac{f}{f_0} = 1. \tag{5}$$

which enables us to determine the dependence $\phi(z)$, $\psi(z)$, $f(z)$ and the pitch p of the FC spiral structure:

$$\tilde{z} = \int_0^{\phi} \frac{d\phi}{\sqrt{A}}, \qquad p = \int_0^{2\pi} \frac{d\phi}{\sqrt{A}}, \tag{6}$$

$$A = C - 2\kappa Q \exp\left\{\frac{\xi \Pi}{\kappa}\cos\psi - \frac{G}{\kappa}\sin^2(\phi - \psi)\right\} - \Pi^2 \sin^2\phi. \tag{7}$$

Here $\tilde{z} = q_0 z$, $\Pi = H q_0^{-1}(\chi_a/K_2)^{1/2}$, and an integration constant C obeys the equation

$$\int_0^{2\pi} d\phi\sqrt{A} = 2\pi. \tag{8}$$

Parameter $\xi = M_s f_0 q_0^{-1}(K_2\chi_a)^{-1/2}$ characterizes the regimes of spiral unwinding [4]: if $\xi \gg 1$, spiral unwinding is realized due to dipolar mechanism and if $\xi \ll 1$ due to quadrupolar one. Parameter $G = w f_0/(d K_2 q_0^2)$ characterizes the anchoring energy of the magnetic particles. This parameter is chosen to be positive and so in the field absence the main particle axes are oriented perpendicular to the director ($\boldsymbol{m} \perp \boldsymbol{n}$), ensuring the homeotropic coupling. The parameter $\kappa = f_0 k_B T/(v K_2 q_0^2)$ characterizes the so-called [2] segregation effect described by Eq.(5): the magnetic particles accumulate in those parts of the helix where the sum of their magnetic and orientational energies takes minimal value. This effect is negligible for $\kappa \gg 1$.

We assume that $\psi = \psi(\phi)$ is single-valued function determined from the Eq.(4). It means that the pitch p corresponds to the distance along the helix axis over which the director and the magnetization $\boldsymbol{M} = M_s f \boldsymbol{m}$ have turned by an angle of 2π. This behavior is realized for $\xi\Pi/G \leq 1$. If $\xi\Pi/G > 1$, then two different helices for the director and magnetization can occur. The analogous behavior occures in hexatic smectics [5].

FERROCHOLESTERIC - FERRONEMATIC TRANSITION

The field $\boldsymbol{H}$, normal to the FC spiral, causes the unwinding of the spiral structure (ferrocholesteric - ferronematic transition) if the field strength Π reaches the critical value Π_c. Thus, for $\Pi > \Pi_c$ the ferronematic (FN) state occurs. Eqs.(3)-(5) have three solutions for ϕ and ψ corresponding to uniform ($f = f_0$) FN phase:

I: $\phi_0 = \psi_0 = 0$, for $\Pi < (2G)^{1/2}$ and $\xi \geq \Pi/(1 - \Pi^2/(2G))$. We call this region of parameters as the region I.

II: $\phi_0(\Pi, \xi, G)$ and $\psi_0(\Pi, \xi, G)$, which are determined by

$$\sin 2\phi_0 = 2\frac{\xi}{\Pi}\sin\psi_0, \quad \sin\psi_0 = \sqrt{1 - \frac{\xi^2}{\Pi^2}\left(1 - \frac{\Pi^2}{2G}\right)^2 \Big/ \left(1 + 2\frac{\xi^2}{G}\right)}. \tag{9}$$

This solution is valid for $\xi \leq \Pi/(\Pi^2/(2G) - 1)$ at $\Pi > (2G)^{1/2}$ and $\xi \leq \Pi/(1 - \Pi^2/(2G))$ at $\Pi < (2G)^{1/2}$ (the region II).

III: $\phi_0 = \pi/2$ and $\psi_0 = 0$, for $\Pi > (2G)^{1/2}$ and $\xi \geq \Pi/(\Pi^2/(2G) - 1)$ (the region III).

Thus, for low field strength, state I is stable, where $\boldsymbol{n} \perp \boldsymbol{m}$ and so the homeotropic coupling between the particles and the director takes place. However, above the boundary between the regions I and II state II occurs, where $\boldsymbol{n}$, $\boldsymbol{m}$ and $\boldsymbol{H}$ are coplanar but each two of these quantities enclose an angle which is different from 0 to $\pi/2$. The angles ϕ_0 and ψ_0 (9) are field dependent. In state II the orientation of the magnetic particles and the director is compromise between the dipolar and quadrupolar alignment. Rising the field strength, ϕ_0 increases monotonically, while ψ_0 is first increasing and then, above a field $\Pi = (2G)^{1/2}$, decreasing. At a boundary field between states II and III $\phi_0 \to \pi/2$ and ψ_0 is going to zero, thus reaching state $\boldsymbol{n} \parallel \boldsymbol{m}$ which is stable for large fields. Therefore, in state II the change in the coupling between the particles and the director from homeotropic ($\boldsymbol{n} \perp \boldsymbol{m}$) to planar ($\boldsymbol{n} \| \boldsymbol{m} \| \boldsymbol{H}$) one takes place, i.e. the director rotates to the field direction due to $\chi_a > 0$ and finite anchoring G.

The critical field of FC - FN transition can be obtained [6] from the equality between the value of free energy for magnetically oriented system and for an untwisting FN sample. It is determined from Eq.(8) where the constants C and Q have the critical values $C_c = C(\Pi_c)$ and $Q_c = Q(\Pi_c)$:

$$C_c = 2\kappa + \Pi^2 \sin^2 \phi_0, \quad Q_c = \exp\left\{ -\frac{\xi \Pi}{\kappa} \cos \psi_0 + \frac{G}{\kappa} \sin^2(\phi_0 - \psi_0) \right\}. \quad (10)$$

The critical field Π_c of the FC - FN transition as a function of ξ for $G = 5$ and two values of κ is depicted in Figure 1 ($\kappa = 3$) and Figure 2 ($\kappa = 2$). The dashed line in these figures corresponds to the boundary between the regions I and II, these regions are marked by "I" and "II" signs. The parameter κ has the critical value $\kappa_c = 2\pi^2 G/(\pi^2 + 8G)$. Thus, for $\kappa > \kappa_c$ the FC - FN transition takes place at $\Pi < \pi/2$ at the dipolar and quadrupolar regime (Figure 1). For $\kappa < \kappa_c$ the equations of state describe two branches (Figure 2) of the $\Pi_c(\xi)$ curve.

As it is seen from Figures 1 and 2 at the dipolar regime ($\xi \gg 1$) and $\kappa > \kappa_c$ the transition field Π_c is small in comparison with its value $\Pi_c = \pi/2$ in pure CLC [1]. At relatively small values of κ, when the segregation effects become significant, two competitive orientational mechanisms of the field influence on the FC lead to the change in the transition behavior at $\kappa < \kappa_c$. One can see from Figure 2, for $\kappa < \kappa_c$ and $\xi \geq 1.5$ there are three critical values Π_c for magnetic field strength $\Pi_{c1} < \Pi_{c2} < \Pi_{c3}$. Then as the field strength increases for $\Pi < \Pi_{c1}$ the FC phase exists, for $\Pi_{c1} < \Pi < \Pi_{c2}$ the

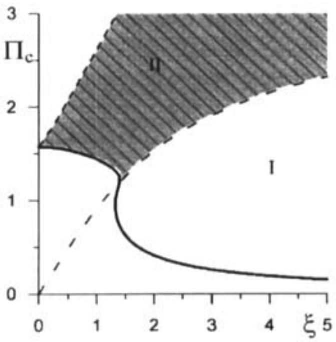

FIGURE 1: Critical field strength Π_c as a function of ξ for $\kappa = 3$ and $G = 5$. The shaded area corresponds to the region of stability for N-domain walls

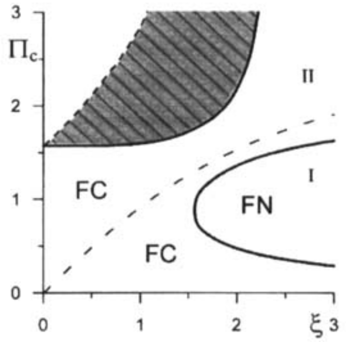

FIGURE 2: Critical field strength Π_c as a function of ξ for $\kappa = 2$ and $G = 5$. The shaded area corresponds to the region of stability for N-domain walls

FN state takes place, for $\Pi_{c2} < \Pi < \Pi_{c3}$ the FC phase takes place ones again (the so-called reentrant FC phase) and for $\Pi > \Pi_{c3}$ the reentrant FN phase occurs. Thus, Π_{c1} and Π_{c3} are the field strength of FC - FN transition, and Π_{c2} corresponds to the field of FN - FC transition. The existence of the reentrant FC phase for $\Pi_{c2} < \Pi < \Pi_{c3}$ is a result of the dipolar and quadrupolar ordering competition. In the region I the dipolar ordering predominates over the quadrupolar one and helps to unwind the helix, but the quadrupolar mechanism hinders the unwinding and so tends to wind the structure in the opposite direction. When Π reaches the value Π_{c2} which is in the vicinity of the boundary between I and II regions, the quadrupolar interactions become comparable with the dipolar ones and then predominate over them, and so the tendency to wind up the structure becomes stronger then the tendency to unwind the structure. As a result, the FC spiral structure appears ones again. For $\Pi_{c2} < \Pi < \Pi_{c3}$ the FC structure has non-monotonic $p(\Pi)$ dependence: the pitch of the helix diverges at $\Pi = \Pi_{c2}$ and $\Pi = \Pi_{c3}$ and takes its minima at $\Pi = \Pi_*(\xi, \kappa, G)$ where $\Pi_{c2} < \Pi_* < \Pi_{c3}$ and $\kappa < \kappa_c$. The behavior of the magnetization $\boldsymbol{M} = M_s f \boldsymbol{m}$ at $\Pi_{c2} < \Pi < \Pi_{c3}$ is more complicated. At $\Pi = \Pi_{c2}$ the dipolar orientational mechanism still predominates over the quadrupolar one and so the magnetic moments of the particles are directed along the field, so $\psi_0 = 0$ and $\langle M_y \rangle \to M_s f_0$ at $\Pi \to \Pi_{c2}$. When $\Pi \to \Pi_{c3}$, then $\langle M_y \rangle \to M_s f_0 \cos\psi_o$, where ψ_0 is determined by Eq.(9) and the angular brackets denote the averaging over the pitch of the structure. Such asymptotic behavior is a result of the competition of the dipolar and quadrupolar ordering.

DOMAIN WALLS

At $\Pi > \Pi_c$ Eqs.(3)-(5) admit a class of nonlinear solutions known as soliton solutions. The soliton describes a domain wall which separates two regions of the uniform FN states with different equilibrium orientation of the particles and the director.

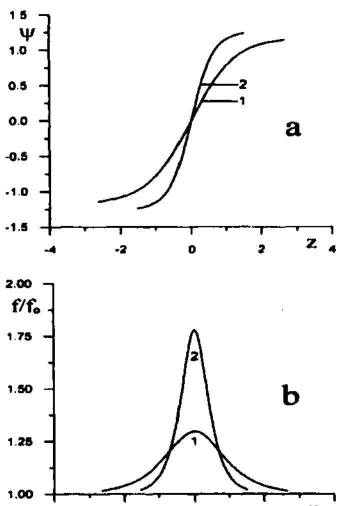

FIGURE 3: The structure of N-domain wall for $\xi = 0.5$, $\kappa = 2$ and $G = 5$: a — $\psi(z)$, b -- $f(z)$. Curves 1 — $\Pi = 1.58$, curves 2 — $\Pi = 3$ ($\Pi_c = 1.572$)

At quadrupolar regime the competition of the orientational mechanisms leads to the possibility of two different kinds of domain walls. In that case the orientation of the director and the particles in the FN phase is compromise (Eq.(9)) between the dipolar and quadrupolar alignment and the change in the coupling on the particle surfaces takes place. In that regime the FN has two permissible states of orientation for the magnetic particles (at $\psi = \pm\psi_0$, where ψ_0 is defined by Eq.(9)) in an external magnetic field. These two permitted states (domains) are separated by so-called [6] N-walls and W-walls. In N-walls ψ changes from $-\psi_0$ to $+\psi_0$ and in the W-walls ψ changes from $+\psi_0$ to $(2\pi - \psi_0)$. Figure 3 shows N-walls for $\xi = 0.5, G = 5$. These walls have the increased concentration of the magnetic particles. N-walls are energetically favoured over W-walls and their energy

$$\mathcal{E}_N = \int_{-\phi_0}^{+\phi_0} d\phi\sqrt{A(\phi, \psi(\phi))} - 2\phi_0 \quad (11)$$

are less than the energy of the uniform FN state in some interval of the field strength values. In Eq.(11) the function $A(\phi, \psi(\phi))$ has the form (7), where the quantities C and Q have their critical values (10). Eq.(4) have been taken into account as well. The regions of stability of the N-walls are shown as shaded areas in Figures 1 and 2. At the dipolar regime Eqs.(3)-(5)

admit a solution corresponded to 2π-domain walls. Here inside the wall the director is confined to a plane and it turns through 2π. Domain structure with such a walls has energy more than that for uniform FN state and so can not be realized. But if the field strength reaches the boundary between the region I and II, N-walls appear and are stable ones.

In conclusion we note that some different possibilities of the FC orientational behavior under the action of magnetic field can occur. For $\kappa > \kappa_c$ (Figure 1) and $\Pi_c < \Pi_{I-II}$ (where Π_{I-II} is the field strength corresponded to the boundary between the regions I and II shown by dashed line) as the field increases the following states are energetically preferable: for $0 < \Pi < \Pi_c$ the helical FC structure, for $\Pi_c < \Pi < \Pi_{I-II}$ the FN state, for $\Pi_{I-II} < \Pi < \Pi_{\mathcal{E}=0}$ — the structure with N-walls, and for $\Pi > \Pi_{\mathcal{E}=0}$ — the uniform FN phase. Here $\Pi_{\mathcal{E}=0}$ — the field strength corresponded to the upper boundary of stability of N-walls, which can be found from the equation $\mathcal{E}_N = 0$ (Eq.(11)). For $\kappa > \kappa_c$ (Figure 1) and $\Pi_c > \Pi_{I-II}$ as Π increases the FC helical structure is changing by the FN state with N-walls, which is stable one for $\Pi_c < \Pi < \Pi_{\mathcal{E}=0}$, and for $\Pi > \Pi_{\mathcal{E}=0}$ the uniform monodomain FN phase is stable one. For $\kappa < \kappa_c$ (Figure 2) and $\Pi_c < \Pi_{I-II}$ as the fields increases the following states are energetically preferable: for $0 < \Pi < \Pi_{c1}$ — the helical FC structure, for $\Pi_{c1} < \Pi < \Pi_{c2}$ — the uniform FN state, for $\Pi_{c2} < \Pi < \Pi_{c3}$ — the reentrant FC structure, for $\Pi_{c3} < \Pi < \Pi_{\mathcal{E}=0}$ the FN structure with N-walls, and for $\Pi > \Pi_{\mathcal{E}=0}$ — the uniform FN phase. For $\kappa < \kappa_c$ (Figure 2) and $\Pi_c > \Pi_{I-II}$ the behavior is the same as for $\kappa > \kappa_c$ and $\Pi_c > \Pi_{I-II}$.

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References

[1] P.G. de Gennes, *The Physics of Liquid Crystals* (Clarendon Press. Oxford 1974).
[2] F. Brochard and P.G. de Gennes, *J. de Physique*, **31**, 691 (1970).
[3] S. Burylov and Yu. Raikher. *Phys. Rev. E*, **50**, 358 (1994).
[4] A.N. Zakhlevnykh and P.A. Sosnin, *J. Magn. and Magn. Mater.*, **146**, 103 (1995).
[5] P. Schiller and F. Zeitler, *Phys. Rev. E*. **56**, 531 (1997).
[6] V. Dmitrienko and V. Belyakov, *Sov. Phys. JETP*, **51**, 787 (1980).