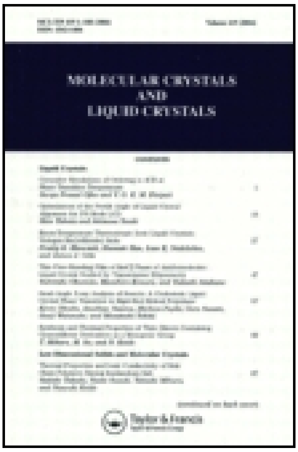

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Magnetoelectrical Effects in Liquid Crystals

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Magnetoelectrical Effects in Liquid Crystals

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Quasiequilibrium states of the liquid crystalline system with added small ferromagnetic particles are discussed. Possible flexomagnetoelectrical effects and a helical twisting under the combined action of electric and magnetic fields are described.

Up to now, liquid crystals with intrinsic ferromagnetic properties are unknown. As a rule, molecules of liquid crystals do not have magnetic moments though paramagnetic liquid crystals can exist in principle (liquid crystals belonging to the class of azoxy-compounds with paramagnetic NO groups were synthesized.[1] It was shown theoretically[2] and experimentally[3] that liquid crystals with anisotropic ferromagnetic particles possess the macroscopic magnetization if the dimensions of the particles are large in comparison with the molecular dimensions. Here we shall discuss the behavior of the liquid crystalline system with added small anisotropic particles under the action of the magnetic and electric fields and also of the mechanical stresses. It is assumed in the case under consideration that in general the particles have the magnetic (m), electric (p) and steric (s) dipole moments, the time of the orientational relaxation of particles is comparable to the time of the molecular orientational relaxation but much smaller than the lifetime of the magnetic state of particles τ.

The magnetic state of particles is determined by the exchange interaction of paramagnetic atoms in them. The magnetic moment m is oriented along the fixed axis of the particle during the long time τ if the exchange energy is larger the temperature and the number of atoms is sufficiently large. It is well known[4,5] that small particles of magnetite Fe_3O_4 and the aerozoles of Ni and $-Fe_2O_3$ with average dimensions 30–100 Å are ferromagnetic monodomains and besides these aerozoles behave as a paramagnetic gas. Thus, one can expect that in some lyotropic and polymer liquid crystals such particles obey the assumptions mentioned above. Consequently, in the appropriate systems the thermodynamically quasi-equilibrium states are possible with the finite macroscopic averages

$$\langle(mp)\rangle,\ \langle(ms)\rangle,\ \langle(m[ps])\rangle \tag{1}$$

though there are zero averages $\langle m\rangle = \langle p\rangle = \langle s\rangle = 0$ in such systems. Here the averaging is made over all the particles and over the time $t < \tau$. It is necessary to note that in full equilibrium state half of particles have, for example, the positive sign of the averages but another half have the negative one because in general the projections $\pm\, m$ of m on s or p are equally probable. But for a time $t < \tau$ one can create the macroscopic nonzero averages [Equation (1)] artificially by appropriate combinations of external actions, these states have the lifetime τ after switching off external fields.

The macroscopic characteristics of the system under consideration enter into coefficients of thermodynamic expansions. The expansions of the density of thermodynamic potential F for described quasi-equilibrium states inside the invariants (relatively for the time inversion and to operations of symmetry for specific liquid crystals) which depend on external fields and order parameters of liquid crystals. The most simple invariants in F are, for example,

$$c\langle(mp)\rangle(EH), \quad c\langle(ms)\rangle H_i \frac{\partial \sigma_{ik}}{\partial \chi_k}, \tag{2}$$

$$c\langle(ms)\rangle(Hn)divn, \quad c\langle(ms)\rangle(H[n \text{ curl } n]), \tag{3}$$

and other, where c is the concentration of particles, σ_{ik} is the stress tensor.

One can see from [Equation (2)] that in the systems under consideration the external electric field or nonhomogeneous mechanical stress can induce the macroscopic magnetization $M = -\partial F/\partial H$:

$$M \sim c\langle(mp)\rangle E, \quad M_i \sim c\langle(ms)\rangle \frac{\partial \sigma_{ik}}{\partial \chi_k}. \tag{4}$$

On the contrary, the homogeneous external magnetic field induces the macroscopic electric polarization $P = -\partial F/\partial E \sim c\langle(mp)\rangle H$ and the surface mechanical deformation $U_{ik} = -\partial F/\partial \sigma_{ik}$. In accordance with [Equation (3)] the external magnetic field can induce the flexomagnetic orientational deformation in the systems, i.e., the nonhomogeneous perturbation of the director distribution $n(r)$:

$$\left|\frac{\partial n_i}{\partial \chi_k}\right| \sim \frac{c}{K}\langle(ms)\rangle H, \tag{5}$$

where K is the Frank constant. This effect is analogous to the flexoelectric effect.

We emphasize that real NCL must consist of achiral molecules and particles with at least one symmetry plane. For this reason, magnetic particles with the same anisotropic form as molecules which give rise, according to Meyer's assumption,[6] to the flexoelectrical effect cannot form NLC if the magnetic moment lies in the plane of these particles (Figure 1). In contrast to chiral particles, shown in Figure 1a, the magnetic particle shown in Figure 1b is achiral, since it has a plane of symmetry (the magnetic moment m is perpendicular to this plane).

The presence of a constant electrical moment p in achiral magnetic particle also

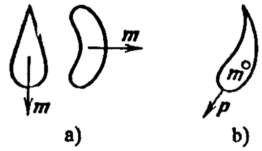

FIGURE 1 Chiral (a) and achiral (b) particles with constant magnetic moments.

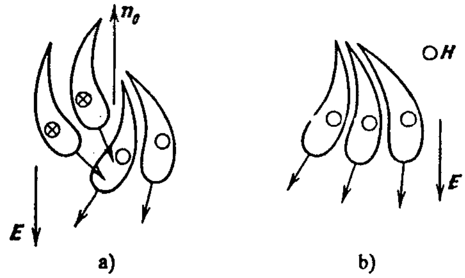

FIGURE 2 Flexomagnetoelectrical effect accompanying the action of an electric field (a) and with simultaneous action of magnetic and electric fields (b) [281].

leads to the qualitative conclusion that simultaneous ordering of electric and magnetic dipole moments is possible as a result of the inhomogeneous orientational deformation of such NLC. It is evident that such deformation must arise under the combined action of electric and magnetic fields (Figure 2). We note that this flexomagnetoelectrical effect is quadratic in the external fields, while the flexoelectrical effect is linear with respect to the electric field. For this reason, the phenomenon examined here can predominate only when the threshold of the flexoelectrical instability is sufficiently high.

The latter possibility arises, for example, when the flexoelectrical coefficients f_1 and f_2 are equal and it is related to an anisotropy of the molecular shape, which consists of a combination of two basic types of anisotropy, corresponding to transverse and longitudinal bending (Figure 2). With an appropriate anisotropy of the molecular shape, a purely flexoelectrical effect is impossible or difficult to achieve, as shown in Figure 2a. However, with the combined action of electric and magnetic fields, a sufficiently strong magnetic field, due to the interaction with magnetic moments, orders the orientation of the planes of the particles and molecules, giving rise to a modulated distribution of the director n under the action of the electric field (Figure 2b).

Formally, from considerations of the symmetry of NLC, the contribution to the free-energy density, linear in E and H and the orientational deformation, can be written in the form

$$\delta F = -f_{m1}([EH]n)divn - f_{m2}(H \text{ curl } n)(En) - f_{m3}(E \text{ curl } n)(Hn) - f_{m4}(EH)(n \text{ curl } n), \quad (6)$$

where f_{m1}, f_{m2}, f_{m3} and f_{m4} are flexomagnetoelectrical coefficients which are proportional to $c(m[ps])$. Analyzing the total free energy of the NLC

$$\tau = \int (F_0 + \delta F)dV,\ F_0 = \frac{1}{2}\{K_1(divn)^2 + K_2(n \text{ curl } n)^2 + K_3[n \text{ curl } n]^2 - \frac{1}{8\pi}\varepsilon_a(nE)^2 - \frac{1}{2}\chi_a(nH)^2\},$$

we arrive at the following results.

The term $-f_{m4}(EH)(n \text{ curl } n)$ from [Equation (6)] is analogous to the invariant arising due to the helicoidal structure of the CLC and describes here the appearance of a macroscopic helical twisting of the director in space under the combined action of electric and magnetic fields. A NLC of the type examined acquires a finite twist under the action of parallel electric and magnetic fields perpendicular to the direction of the unperturbed orientation of the director n_0. In the absence of the other external actions (effect of walls, effects quadratic with respect to E and H related to the dielectric and diamagnetic anisotropy), an orientational helix, whose axis is oriented along the field and which has a pitch $h = 2\pi K_2/(f_{m4}EH)$, where K_2 is the torsional elastic modulus, appears.

In nematic layers with finite thickness d and planar starting orientation of the director n_0, a flexomagnetoelectrical effect of a threshold type, consisting of a formation of a periodic domain structure with small orientational perturbations, is possible. Small deviations of the director from the direction n_0 (x axis) occurs in two planes: by an angle θ in the xz plane and by an angle φ in the xy plane (Figure 3). We shall examine here two limiting cases of the mutual orientation of the fields E and H.

a) $E \perp H$. If the fields are mutually perpendicular and one of them is parallel to the director n_0 (x axis), while the other is parallel to the y axis, then a domain structure is formed with the domain oriented along the direction n_0. In this case the geometry of the domain structure and the threshold characteristics of the effect are analogous to the situation observed with flexoelectric instability.[7] The distributions $\theta(y, z)$ and $\varphi(y, z)$ are given by the equations

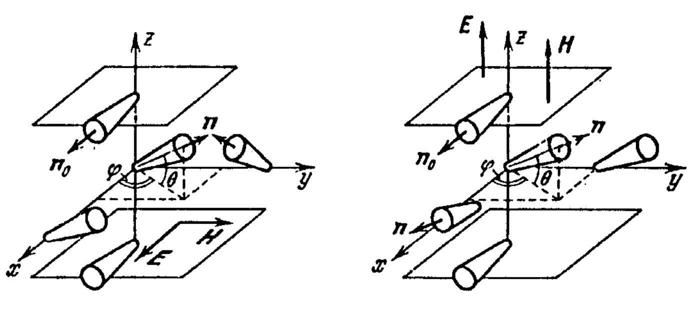

FIGURE 3 Spatial distribution of the director.

$$\theta = \theta_0 \cos(qy)\cos\frac{\pi z}{d}, \quad \varphi = \varphi_0 \sin(qy)\cos\frac{\pi z}{d}$$

with boundary conditions $\theta(y, z = \pm d/2) = \varphi(y, z = \pm d/2) = 0$.

If $H \parallel n_0$, then, repeating the calculations in References 7 and 8 we find that the effect exists for

$$H \geqslant \frac{1}{|f_{m1} + f_{m2}|}\left(\frac{|\varepsilon_a|K}{4\pi}\right)^{1/2},$$

while the threshold values of the electric field intensity $E = E_c$ and wave vector $q = q_c$ equal

$$E_c = \frac{2\pi K}{|f_{m1} + f_{m2}|(1 + \nu_1)dH}, \quad q_c = \frac{\pi}{d}\left(\frac{1 - \nu_1}{1 + \nu_1}\right)^{1/2} \tag{7}$$

where

$$\nu_1 = \frac{\varepsilon_a K}{4\pi(f_{m1} + f_{m2})^2 H^2}, \quad |\nu_1| < 1, \quad K = K_1 = K_2.$$

If $E \parallel n_0$, the effect exists for

$$E \geqslant \frac{1}{|f_{m1} - f_{m3}|}\left(\frac{|\chi_a||K}{4\pi}\right)^{1/2}$$

and is characterized by the threshold value

$$H_c = \frac{2\pi K}{|f_{m1} - f_{m3}|(1 + \nu_2)dE},$$
$$q_c = \frac{\pi}{d}\left(\frac{1 - \nu_2}{1 + \nu_2}\right)^{1/2} \tag{8}$$

where

$$\nu_2 = \frac{\chi_a K}{4\pi(f_{m1} - f_{m3})^2 E^2}, \quad |\nu_2| < 1.$$

Thus, in the cases examined, both fields appear either as a threshold characteristic or as a parameter which, as in the case of the flexoelectrical effect, determines the regions of existence of the phenomenon. We note that if one of the fields E and

H is parallel to the z axis, i.e., perpendicular to the NLC layer, then only the Friedericksz effect can occur.

b) $E \parallel H$. In this case, aside from the helicoidal modulation of the structure of the paramagnetic NLC, a threshold effect similar to that described above can also occur. However, in this case, the domains that arise are perpendicular to the direction n_0. Such a weak distortion of the orientational structure must occur if the fields are perpendicular to the plane of the nematic layer.

In this situation we arrive at the following Euler equations obtained by varying the functional F:

$$K\left(\frac{\partial^2\varphi}{\partial\chi^2} + \frac{\partial^2\varphi}{\partial z^2}\right) - \tilde{f}_m EH\frac{\partial\theta}{\partial\chi}$$

$$= 0, \quad K\left(\frac{\partial^2\theta}{\partial\chi^2} + \frac{\partial^2\theta}{\partial z^2}\right) + \tilde{f}_m EH\frac{\partial\varphi}{\partial\chi} + \left(\frac{\varepsilon_a}{4\pi}E^2 + \chi_a H^2\right) = 0, \quad (9)$$

where $\tilde{f}_m = f_{m2} + f_{m3} + 2f_{m4}$. Equations (9) have solutions of the form

$$\theta = \theta_0 \cos(qx)\cos\frac{\pi z}{d}, \quad \varphi = \varphi_0 \sin(qx)\cos\frac{\pi z}{d},$$

satisfying the boundary conditions $\theta(x, z = \pm d/2) = \varphi(x, z = \pm d/2) = 0$. The corresponding dispersion equation, relating the wave number q and the fields intensities E and H reads as follows:

$$\left[q^2 + \left(\frac{\pi}{d}\right)^2\right]\left[q^2 + \left(\frac{\pi}{d}\right)^2 - \frac{\varepsilon_a}{4\pi}\cdot\frac{E^2}{K} - \chi_a\frac{H^2}{K}\right] - \tilde{f}_m\left(\frac{qEH}{K}\right)^2 = 0 \quad (10)$$

For $\chi_a = 0$ and $\varepsilon_a \neq 0$, it follows from [Equation (10)] that the instability arises with threshold values of the electric field intensity and wave number

$$E_c = \frac{2\pi K}{|\tilde{f}_m|(1 + \nu_3)dH}, \quad q_c = \frac{\pi}{d}\left(\frac{1 - \nu_3}{1 + \nu_3}\right)^{1/2} \quad (11)$$

where

$$\nu_3 = \frac{\varepsilon_a K}{4\pi \tilde{f}_m^2 H^2}, \quad |\nu_3| < 1.$$

In general, threshold characteristics have a more complex dependence on the material parameters, but the qualitative nature of the phenomenon does not change. The situations examined in Equations (7), (8), and (11) do not exhaust all possible flexomagnetoelectrical effects in such NLC. There are combinations of the mutual orientations of the fields E and H and of the director n_0 for which the effects examined interfere and arise simultaneously.

It is necessary to emphasize that all these effects take place in absence of the spontaneous macroscopic magnetization. It is possible to create described macroscopic states with the lifetime τ by the mechanical bend or by the electrical poling of liquid crystalline layers and by the following application of the sufficiently strong magnetic field. If the dimensions of particles are large in comparison with molecular dimensions, the thermal averaging $\langle s \rangle = \langle p \rangle = \langle m \rangle = 0$ does not take place because of large energy of orientational perturbations which should be overcome to reorientate the particles. In the last case the constant macroscopic magnetization $M = c\langle m \rangle$ was observed in lyotropic liquid crystals.[3]

Described phenomena are interesting if one considers physical properties of such complex systems as lyotropic and polymer liquid crystals in biomembranes. For example, changes of the membrane electric potential for nonhomogeneous mechanical deformations of the membrane can induce (in accordance with Equation (4)) the macroscopic magnetization M interacting with the external magnetic field H. One can consider different situations in the biomembranes. The interaction of M and H can influence the spreading of electric and mechanical perturbations. On the other hand, the external magnetic field induce (in accordance with Equation (5)) appreciable macrostructure perturbations and a change of the electric state of the membrane. Assuming that the flexocoefficient $c\langle(ms)\rangle$, for example, is proportional to the magnetic moment of the particle, its magnitude can be estimated from dimensional considerations: $c\langle(ms)\rangle \sim cml$. From here, in the order of magnitude, we obtain the estimate $H_c \sim (K/cmld) \sim 10^2\ A/m$ for $K \sim 10^{11}\ N$, $m \sim 10^{-26}\ J,m/A$, $1 \sim 10^{-7}\ m$, $d \sim 10^{-4}\ m$ and $c \sim 10^{24}\ m^{-3}$, i.e., a weak magnetic field is required to realize the effect.

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