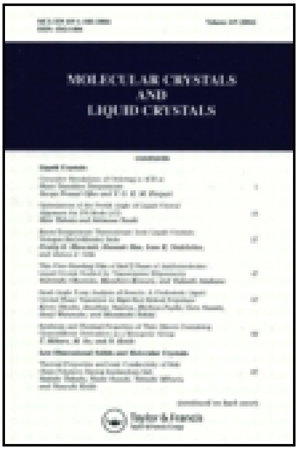

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Solitons in Chiral Liquid Crystalline Systems

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SOLITONS IN CHIRAL LIQUID CRYSTALLINE SYSTEMS

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Abstract The soliton-concept seems to be a valuable tool in interpretation of various phenomena in chiral liquid crystalline systems. Two such phenomena are communicated: the cholesteric phase distorted by magnetic field, and the blue phases.

The de Gennes description of cholesteric phase distorted by magnetic field allows the soliton interpretation. The solitons are considered as concentrated turns of the cholesteric spiral, isolated by nematic-like regions. The deuterium NMR spectra calculated using this soliton concept are in excellent agreement with the measured spectra.

The soliton concept offers an elegant solution of the mystery of the blue phases. These phases are explained here as soliton crystals. Solitons in the blue phases are suggested to be spherical creatures. Their presence is the consequence of the break-down of the nematic ordering below the cholesteric-isotropic transition temperature. The lack of the nematic ordering destabilizes the cholesteric pitches allowing them to have a soliton form representing a small coherence length and rapid inner molecular dynamics. These spherical solitons are able to form the different crystal lattices already observed. The blue fog phase might be a concentrated soliton gas or liquid. Most of the experimental results can be succesfully explained on this basis.

CHOLESTERIC PHASE DISTORTED BY MAGNETIC FIELD

The interaction of cholesteric liquid crystals with magnetic field is a worthwhile way to study orientational processes. De Gennes[1] formulated two basic cases, viz. parallel and perpendicular orientation of the magnetic field (H) to the pitch axis. Parallel orientation is the more simple because in this case all molecules have a common perpendicular orientation to the magnetic field.

With perpendicular orientation of the pitch axis to the magnetic field the molecules will have a continuous orientational distribution of the molecular length axis to the magnetic field (H) in the 0-90 degree interval. The magnetic field will distort the cholesteric structure by unwinding the cholesteric spiral. This process increases the pitch. If the magnetic field is strong enough, it is able to complete this unwinding to the infinite pitch, thus transforming the sample into a nematic structure.

De Gennes[1] calculated Frank's free energy formula[2] for H perpendicular to the pitch axis. The minimization of the free energy of Eq. (2) of Ref. 1 gives the following formula (Eq. (3) of Ref. 1):

$$-K_{22} \frac{\partial^2 \varphi}{\partial z^2} - \chi_a H^2 \sin \varphi \cos \varphi = 0 \qquad (1)$$

where K_{22} is Frank's torsion modulus, χ_a is the magnetic susceptibility of the sample, φ is the angle between the molecular length axis and the orientation of the magnetic field H, and z is the coordinate along the pitch axis. With simple trigonometry this formula has the form:

$$\frac{\partial^2 \varphi}{\partial z^2} = \alpha^2 \sin (2\varphi) \qquad (2)$$

where α contains the constants.

By simple integration of Eq. (2), similarly to Yamashita et al.[3], and Chaves et al.[4] we get:

$$\frac{\partial \varphi}{\partial z} = 2\alpha' \left[\delta^2 + \cos^2\varphi\right]^{1/2} \tag{3}$$

where δ is the integration constant, and α' should keep the whole expression normalised.

On the way of Yamashita et al.[3] equation (2) can be recognized as the sine-Gordon equation, and that is known to describe solitons. The appearance of this equation means an alternative way of explaining the results of de Gennes[1] with a soliton terminology that will be discussed later. The nuclear magnetic resonance (NMR) of the deuterium nuclei is the most widely used experimental method for studying this phenomenon[5-12]. The shape of the NMR spectrum of the perpendicularly oriented cholesteric spiral could be described by the de Gennes formulae without[6], or with biaxial ordering of the molecules[7]. However, a complete description of the experimental results needed a space-modulated diffusion model, in which the local change of pitch determines the diffusion constant[8,9,11].

The line shape of the measured deuterium NMR spectra of the cholesteric phase[6-12] is similar to the usually experienced NMR powder pattern[13], except for the singularities on the outer edges. The spectrum of a completely unwound, or nematic phase has the two singularities at the sites of the outer singularities of the cholesteric spectrum, as can be seen from the experimental results of Yaniv et al.[6]. This fact can only be explained when the angles between the magnetic field and the molecular length axis, φ, and between the magnetic field and the main principal axis with the largest eigenvalue of the electric field gradient tensor at the site of the deuterons, Θ, are equal.

The contribution of the applied magnetic field to the NMR spectrum is of the type

$$\nu(\Theta) = (3 * \cos^2 \Theta - 1) \qquad (4)$$

where Θ is the angle between the main principal axis of the electric field gradient tensor and the magnetic field. Using this assumption we can calculate the spectrum in the way elaborated by Chaves et al.[4]. The line shape of the NMR signal can be calculated using the expression:

$$f(\nu) = \frac{\text{const.}}{d\nu/d\Theta * d\Theta/dz} \cdot \qquad (5)$$

The undistorted cholesteric phase has the dependence

$$\Theta = p^{-1} z \qquad (6)$$

where p is the value of the pitch, is oriented towards the z axis. Taking into account Eq. (4), we get the form:

$$f(\nu) = \frac{\text{const.}}{\cos \Theta \sin \Theta} \cdot \qquad (7)$$

This corresponds to the powder-like spectral pattern with the singularities on both edges, as presented by the measurements in Ref.7. Naturally the broadening of the lines eliminates the singularities, and sharp lines will be found instead.

Having discussed the undistorted cholesteric phase, let us now consider the distorted phase. To describe the phase distorted by a magnetic field we can use Eq. (3), in which we replace φ by Θ; the spectrum will then have the form:

$$f(\nu) = \frac{\text{const.}}{\cos \Theta \sin \Theta (\delta^2 + \cos^2 \Theta)^{1/2}} \cdot \qquad (8)$$

It was mentioned earlier that this distorted cholesteric phase contains solitons. It might be useful here to discuss what we really understand by the word "soliton".

As far as we concerned there is no perfect definition. We can, however, offer a useful one[14], which can be summarized as follows: a soliton is a nonlinear phenomenon, with a wave of permanent form. Solitons are localized, and they interact with each other. We are aware that this definition is possibly too short, but it is usable in our case.

If the cholesteric phase is distorted by a magnetic field its periodicity increases. This is not, however, a normal homogeneous increase of the pitch, as in the case of an expanded helical spring. The increase of the nematic-like component in the NMR spectrum suggests this. The soliton description explains this situation in the following way.

The magnetic field will prefer the nematic-like orientation of molecules, and the regions with such an orientation will be widened with the increasing field. These regions with nematic-like orientation separate the other fractions, the cholesteric spirals. These fractions must have π rotation because of the surrounding nematic neighbourhood. So by the word soliton we will understand these cholesteric droplets, these concentrated cholesteric turns. The increase of the periodicity means the increasing distance between them. This picture roughly agrees with the description of de Gennes[15]. The existence of periodicity is based on the interaction of solitons[16].

This interaction has a strong repulsion character, the solitons cannot go across each other as solitons of shallow water pools usually do[17] because the cholesteric pitch cannot be decreased by a factor of two, which is what the meeting of two solitons at the same place would mean.

This soliton picture fulfils the requirements of the earlier definition. The basic equation is non-linear, its soliton solution has a permanent form, and is localized. The solitons interact with each other.

The function represented by Eq. (3) is plotted in Fig. 1a, for $\delta \ll 1$, where the shape of the soliton can be seen. Figure 1b shows a rough sketch of the orientation of the molecules in the vicinity of the solitons.

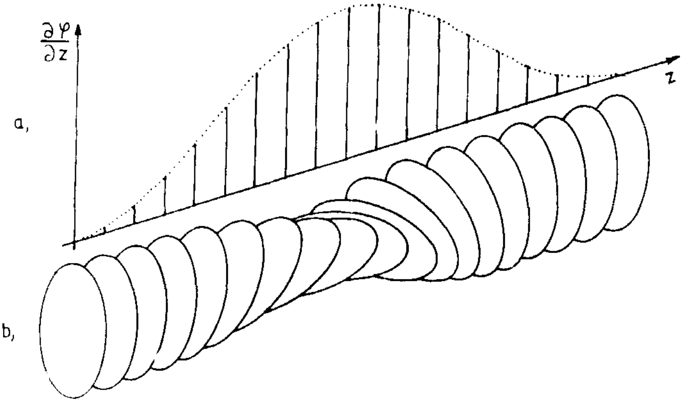

FIGURE 1. Graph of function represented by Eq. (3) (a), and the orientation of the molecules in the vicinity of a soliton (b).

Using Eq. (8) we have calculated different deuterium NMR spectra, characterized with different values of the parameter δ. The theoretical line-shapes have been convoluted with a gaussian profile to provide the broadening presented by the measurements[6-12].

In Fig. 2 we can see three different spectra, presenting the different cases of the soliton formalism. Spectrum A shows the undistorted cholesteric limit, which is characterized by $\delta \gg 1$. The calculated line-shape is in excellent agreement with the experimental spectrum of Yaniv et al.[7]. Spectrum C presents, in agreement with Ref.3, the multi-

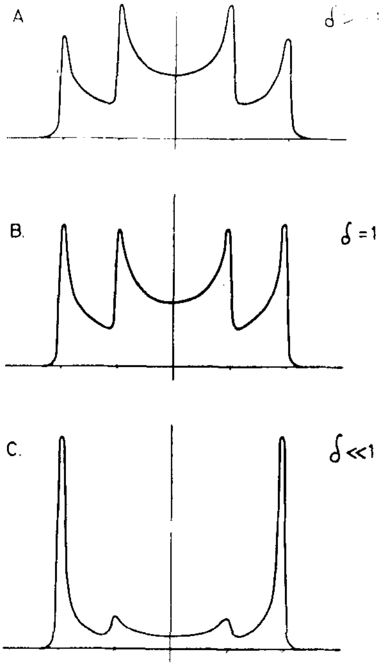

FIGURE 2.

Lineshapes calculated from Eq. 7 at $\delta \gg 1$ (A), $\delta = 1$ (B), and $\delta \ll 1$ (C).

soliton lattice case, the high concentration of solitons, the strongly distorted cholesteric phase, where $\delta = 0$. We have also simulated a medial case (spectrum B), where $\delta = 1$. The basic structure of the spectra does not change, there are two pairs of singularities; however, the ratio of the intensities of the outer pairs to the inner pairs does change. We have made simulations with different δ values, and the ratio of the intensities of the singularities is plotted against δ in Fig. 3.

We can compare our simulated spectra with the measured line shapes of Vaz et al.[10]. Figure 5 displays our results. Spectrum D with $\delta = 0.7$, and spectrum E with $\delta = 0.15$ coincide with the measured spectra in Fig. 1 of Vaz et al.[10]

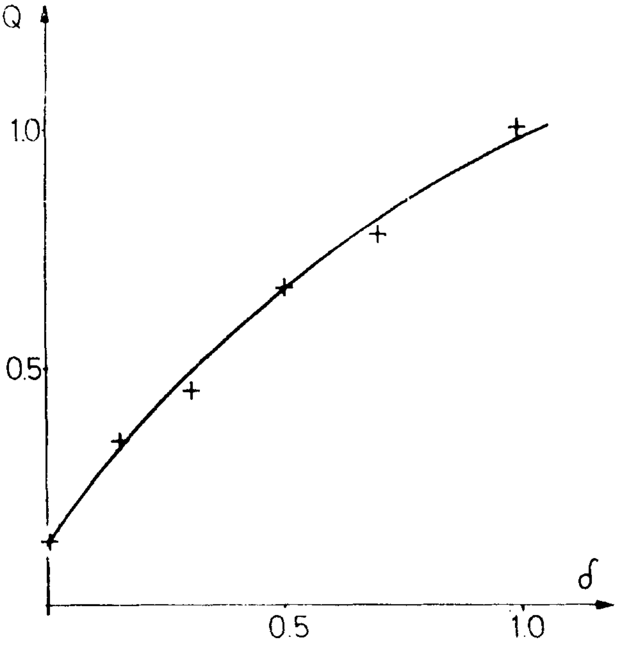

FIGURE 3. Experienced ratio of intensities of the inner and the outer edges, as function of δ. The plotted points are results of the computer simulation of the line-shapes.

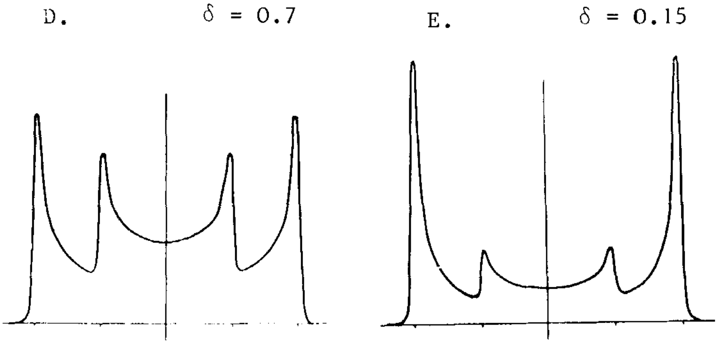

FIGURE 4. Calculated line-shapes with $\delta = 0.7$, (D), and $\delta = 0.15$, (E), which fit the measured line shapes of Vaz et al.[10]

for cholesteric mixtures. Thus our simulation seems to be acceptable, notwithstanding the very simple theory we used.

THE BLUE PHASES

Current liquid crystal research is very much concerned with the blue phases (BP), with their unique features. To describe the structure of the cubic crystalline phases (BP I and BP II) between the cholesteric and isotropic phases and the blue fog (BP III) various theoretical models have recently been suggested[18-25]. Hornreich et al.[26] have investigated the instabilities in BPs, and have found the possibility of solving the free energy minimum problem by means of soliton-like local solutions. They have discussed the existence of the solitons in blue fog phase and mentioned the possibility of condensation of solitons into crystals, forming the other blue phases. The present study discusses the aptness of this idea to describe the blue phases.

De Gennes[27] discusses the similarity between the cholesteric and nematic phases, and he shows that because of the extra term in the free energy expression of the cholesteric phase, there are substantial differences between the various transitional temperatures to the isotropic phase

$$T_{CI} - T_{NI} = \frac{1}{2\,k_B} \int K_2\, q_o^2\, dV \qquad (9)$$

where K_2 is the twist elastic constant, and q_o is the wave vector of the helix, k_B is the Boltzmann constant, T_{CI} and T_{NI} are the transitional temperatures from the cholesteric and nematic phases into the isotropic, respectively. Using typical values as $K = 10^{-6}$ dyn, $q_o = 500$ nm, we get one tenth degree difference, what can be accepted as typical temperature range for BPs.

In between T_{CI} and T_{NI} there might be destabilization in the nematic ordering, which means strongly decreased nematic orientational correlation length. This loss of long range correlation destabilizes the cholesteric ordering too, and instead of the coherent long spirals we will find short cholesteric 'droplets', concentrated cholesteric turns, which droplets may behave as solitons.

If we start from the isotropic liquid, the solitons appear as fluctuations. Because of the extra energy (9) of the cholesteric ordering, these chiral droplets will be stable near the phase transition, and the number of these solitons will increase. These solitons form a soliton gas or liquid with decreasing temperature as a pretransitional phenomenon in the isotropic phase. We think that BP III can be explained as this pretransitional region in the isotropic phase. We discussed earlier what we understand by the word soliton. In the cholesteric phase distorted by magnetic field the solitons there were wall-solitons, perpendicular to the pitch axis. In present case these solitons in the BPs are spherical creatures, having very much in common with the roton excitations in He^3A system[28,29]. The only difference is these chiral character of these BP solitons. The phenomenon can most clearly be demonstrated as a concentrated cholesteric turn, surrounded by disordered regions. Up till recently there were doubts about whether the blue fog phase is a real thermodynamically stable phase or not[24,25,30,31]. New ideas have recently been published about the possible icosahedral structure of this phase[23,25]. We consider the soliton concept is a much simpler model for this phenomenon. We agree with Marcus in this case, who hypothesized BP III as liquid version of of BP I and BP II[32].

The other blue phases, BP I and BP II, appear by virtue of a decrease in temperature by the condensation of these solitons into crystals. Towards lower temperatures these spiral droplets become more strongly correlated, and the cholesteric spiral builds up.

A number of surprising results can successfully be explained using this soliton concept. In the followings we discuss some examples. A more detailed study is in preparation.

A) Electron microscopy have provided very interesting freeze-fracture investigations of the blue phases[33]. There are filament shaped objects a few nm in diameter in BP I, what might be the domain for short range order, observed in isotropic phases as well. What is more interesting, these filaments are ordered alternatively into horizontally and vertically oriented structures, with the typical size in the order of 100 nm (dominantly on Fig. 3a in Ref. 33).

Different cross sections of similar objects are that vortex-like structures at the bottom-centrum of Fig.3a in Ref.33, and at the right side-centrum on Fig.4b in Ref.33. The size of these objects is in the range of 240 nm, the cholesteric pitch-length. This structures might be spherical solitons, fractions of the cholesteric spiral. These vortexes are very much like the roton excitations in He^3A[27,28].

The vortex-like structures on Fig.3a and Fig.4b of Ref. 33 are specially oriented cross sections of these spherical solitons. Even the nearly horizontal dark solid lines, 0.2 μm in length, at the right left corner and the left middle are similar cross sections with different orientation to the fracture-plane of the sample. The changes of vertically and horizontally oriented filaments shows same cross sections as well, with different orientation of fracture-plane, compared to the orientation of the cholesteric pitch within the soliton.

B) Specific heat manifests the main change during isotropic-BP I transition, and there are much smaller ones between the BP phases and the cholesteric phase[31,34,35]. The main ordering process occurs with the creation of the solitons. A vast amount of molecules are already ordered in the solitons in BP's; the changes in soliton ordering (which transforms the sample to the cholesteric phase) have a much smaller effect.

C) Single crystal growth rate with and without blue fog. There is a two orders of magnitude difference between the growth rates of the single crystals starting to grow from blue fog or those directly appearing from isotropic liquid[36,37]. The growth of BP crystals from blue fog needs only the ordering of solitons, which process may have a smaller energy or entropy barrier. The growth from isotropic liquid means the build-up and ordering of solitons, at which a much higher barrier is present.

D) NMR spectra of the BP's have unusually small half-width compared with the cholesteric phase[12,14,38,39]. There are at least two effective processes causing effective motional narrowing. One is the lattice vibration of the soliton lattice, the other is the free reorientational motion of the cholesteric pitch of the soliton. These two types of averaging may be the source of the narrow NMR line.

E) Optical properties of BP's are unusual[23,26,30,31,40,41]. Because of the cubic lattice the loss of biaxiality can easily be accepted, but the sample has optical activity. We explain this phenomenon by means of the structure of the solitons. At the lattice sites we have solitons, which have optical activity because of their helical nature.

F) Red shift is a usually mentioned property of the blue phases[23,31]. The selectively reflected light is shifted towards longer wavelengths, compared with the cholesteric phases. The presence of solitons generates some extra disordered regions thus separating the solitons from each other, and thereby increasing the periodicity compared with the normal cholesteric pitch.

G) Thermal[31,42] and pressure[41,43] dependence of the frequency of the selectively reflected light are unusually strong. The interaction of solitons can be modelled with some attraction-repulsion type potential (Lennard-Jones, or other) which allows the increasing distance between the solitons with increasing temperature and decreasing pressure. The soliton concept explains the strongly increasing periodicity with limited thermal expansion.

H) Viscosity values are by two orders of magnitude larger in BP's than in the neighbouring cholesteric or isotropic phases[44-46]. The stability of solitons creates barrier against their free translational motion. The main feature of these solitons is their strong mutual repulsion. The three dimensional lattice of these barriers hardens the structure. Similar behaviour has been extensively studied by Tabony on microemulsions[47].

K) Electro-optical effects can be explained by the undefined orientation of the cholesteric pitch axis within the soliton[23,48,49]. The electric field can order the local pitch axes generating biaxiality, or cholesteric transition, depending on the dielectric properties of the molecules and the cholesteric spirals.

CONCLUSIONS

The presence of the sine-Gordon equation in the fundamental paper of de Gennes on distorted cholesteric structures is recognized. The solution of this equation contains solitons. The deuterium nuclear magnetic resonance spectra of the distorted cholesteric structures have been successfully calculated using this concept. The success of this simulation may prove the applicability of the soliton picture to liquid crystals.

The explanation of the cholesteric blue phases as a soliton lattice and soliton liquid seems to be well worth considering. Many strange experimental facts concerning the blue phases have been explained supposing the solitons. The soliton concept may help us towards a better understanding of the blue phases.

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