Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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To cite this article: Tom C. Lubensky (1973): Hydrodynamics of Cholesterics in an Extenal Magnetic Field, Molecular Crystals and Liquid Crystals, 23:1-2, 99-109

To link to this article: http://dx.doi.org/10.1080/15421407308083364

Molecular Crystals and Liquid Crystals. 1973. Vol. 23, pp. 99–109

Hydrodynamics of Cholesterics in an External Magnetic Field†‡

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Received September 14, 1972

Abstract—Linearized hydrodynamical equations for a cholesteric liquid crystal with anisotropic magnetic permeability less than zero in an external magnetic field are derived. The mode structure in the absence of dissipation is determined. There is a transverse shear mode for directions of propagation perpendicular to the pitch axis with sound velocity

$$c_t^2 = \frac{\mu_a H^2}{2\rho}\left(1 + \frac{\mu_a H^2}{(K_1 + K_3)q_0^2}\right)^{-1}$$

where H is the external field, ρ the mass density, μ_a the magnitude of the anisotropic permeability, q_0 2π over the pitch, and K_1 and K_3 are Frank elastic constants.

1. Introduction

In this paper, we propose to derive the equations governing linearized hydrodynamics of a cholesteric liquid crystal in an external magnetic field, **H**. We will consider only liquid crystals composed of molecules which align perpendicular to the external field, i.e., systems with $\mu_\parallel < \mu_\perp$ where $\mu_\parallel$ and $\mu_\perp$ are respectively the magnetic permeability for directions parallel and perpendicular to the direction of molecular alignment. In some respects the derivation of hydrodynamical equations in the presence of an external field is more straightforward than the derivation of the same equations in the absence of a field.(1) Molecules arranged in the cholesteric helical pattern have two rotational degrees of freedom: they can rotate in the plane perpendicular to the pitch axis **p** (a unit vector) or they can rotate in a plane containing **p**. In a free cholesteric in the absence of an external

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† Presented at the Fourth International Liquid Crystal Conference, Kent State University, August 21–25, 1972.

‡ Supported in part by grants from the National Science Foundation and the U.S. Office of Naval Research.

field, there is a cancellation in energy between these two degrees of freedom leading to an energy for slowly varying distortions from equilibrium proportional to $k_3^2 + bk_\perp^4$ where k_3 is the component of the wave number $\mathbf{k}$ parallel to $\mathbf{p}$, $\mathbf{k}_\perp$ the component perpendicular to $\mathbf{p}$ and b is a constant. The absence of a $k_\perp^2$ term in this lowest branch of the distortion energy leads to fluctuation distruction of long range helical order in an infinite cholesteric.(1,2,3) The effect of an external field along $\mathbf{p}$ is to inhibit rotations of the molecules in planes containing $\mathbf{p}$ making the cancellation of energy between the two rotational modes of the molecules incomplete and leading to a distortion energy of $K_2 k_3^2 + K_\perp(H) k_\perp^2$ where K_2 is the Frank elastic constant and $K_\perp(H)$ is a function of K_1 and K_3 and tends to zero with H^2. An infinite cholesteric with $\mu_\parallel < \mu_\perp$ in an external field along $\mathbf{p}$ is, therefore, stable and exhibits a shear mode propagating perpendicular to $\mathbf{p}$ with sound velocity $c_t^2 = (q_0^2/\rho) K_\perp(H)$ where q_0 is 2π over the pitch and ρ is the mass density.

We will follow closely the techniques for obtaining hydrodynamical equations in broken symmetry systems developed by Halperin and Hohenberg(4) and applied to cholesterics in the absence of an external field in Ref. 1, and to arbitrary solids and liquid crystals in Ref. 5.

Hydrodynamics describes those modes of a system which are long lived, i.e., those disturbances which persist for times longer than any characteristic collision time τ. Frequencies of hydrodynamical modes tend to zero with some power of the wave-number $\mathbf{k}$. Hydrodynamical variables are associated either with a local conservation law or with some continuous broken symmetry. Local conservation laws for mass, energy and momentum lead to the familiar Navier–Stokes equations for anisotropic fluid. In liquid crystals, there are broken continuous symmetries which give rise to variables which have vanishing restoring forces in the zero k limit. These variables have temporal variations which become infinitely slow as k tends to zero. They are, therefore, hydrodynamical variables. Consider for example a two-dimensional nematic liquid crystal and let $\theta(\mathbf{r})$ be the angle the director $\mathbf{n}(\mathbf{r})$ makes with some fixed axis. If $\theta(\mathbf{r})$ is uniform in space, there is no force tending to change θ, and θ will remain constant in time. If, however, $\theta(\mathbf{r})$ varies slowly in space, there will be forces tending to restore uniformity proportional to gradients of

$\theta(\mathbf{r})$. The Frank free energy for this system, which is an expansion in gradients of $\theta(\mathbf{r})$, is a phenomenological statement of this fact. Now, consider the time for $\theta(\mathbf{r})$ to return to complete uniformity from a distorted state at $t = 0$ in which $\theta(\mathbf{r})$ varied slowly in space. We can picture the distorted state as being composed of a series of cells with $\theta(\mathbf{r})$ uniform in each cell but varying slightly from cell to cell. In order to restore spatial uniformity to θ, one cell must align a cell immediately adjacent which in turn aligns a cell adjacent to it and so on. Clearly the less the mismatch between adjacent cells, the smaller the force tending to align them and the less rapid will be the tendency toward realignment of adjacent cells. The slower the response of adjacent cells to misalignment, the slower information about misalignment will be transmitted to all cells and the slower will be the re-establishment of uniformity. Hence, as spatial variations tend to zero (i.e., $\mathbf{k}$ tends to zero), the time for re-establishment of equilibrium will tend to infinity. Therefore, the frequency of the mode associated with θ must tend to zero with k, and θ must be treated as a hydrodynamical variable along with the conserved variables of the system. As discussed in Ref. 1, a divergent auto-correlation function at zero k is synonymous with a vanishing restoring force at zero k. In cholesterics, auto-correlation functions are easier to calculate than restoring force.

In Sec. 2, we use the Frank free energy in the presence of a field to determine which director auto-correlation function diverges. This tells us what broken symmetry variable must be included in a complete hydrodynamical description of the cholesteric. In Sec. 3, we determine the constitutive relations between the currents and conjugate fields and produce the complete set of hydrodynamical equations. We then analyze the mode structure of these equations in the absence of dissipation.

2. Static Properties

In order to obtain director correlation functions, we need an expression for the Frank Gibbs free energy for a cholesteric as a function of the " external variables " chemical potential μ, temperature T, and magnetic field H. (There should be no confusion between chemical potential μ and magnetic permeabilities $\mu_\parallel$, $\mu_\perp$ and μ_a.)

$$G(\mu, T, H) = G_0(\mu, T) + G_F(\mu, T) + G_H(\mu, T, H) \tag{1}$$

where G_0 is director and field independent, G_F is the Frank free energy

$$G_F(\mu, T, n) = \tfrac{1}{2}\int d^3r[K_1(\nabla\cdot\mathbf{n})^2 + K_2(\mathbf{n}\cdot\nabla\times\mathbf{n} + q_0)^2 + K_3(\mathbf{n}\times(\nabla\times\mathbf{n}))^2] \tag{2}$$

where K_1, K_2 and K_3 are the Frank elastic constants and G_H is given by

$$G_H = -\tfrac{1}{2}\int d^3r\mu_\perp H^2 + \tfrac{1}{2}\int d^3r\mu_a(\mathbf{n}\cdot\mathbf{H})^2 \tag{3}$$

where $\mu_a = \mu_\perp - \mu_\parallel > 0$. The equilibrium state corresponding to this free energy has $\mathbf{n}\cdot\mathbf{H} = 0$ and

$$\mathbf{n}(\mathbf{r}) = (\cos q_0 z, \sin q_0 z, 0) \tag{4}$$

where **H** is along the z axis. Linear deviations of $\mathbf{n}(\mathbf{r})$ from equilibrium can be expressed in the form

$$\delta\mathbf{n}(\mathbf{r}) = (\mathbf{p}\times\mathbf{n}(\mathbf{r}))\,\delta\phi(\mathbf{r}) + \mathbf{p}\delta\psi(\mathbf{r}) \tag{5}$$

where **p** is a unit vector along the pitch axis (the z axis). $\delta\phi(\mathbf{r})$ describes director rotations in the plane perpendicular to **p** and $\delta\psi(\mathbf{r})$ rotations in the plane of **p**. The techniques for finding the $\delta\phi$ and $\delta\psi$ correlation functions are well known and are described in detail in Refs. 1 and 3. Since the derivation is somewhat lengthy, we will merely quote here the results that interest us. Only the $\delta\phi$ correlation function is divergent at zero **k**:

$$\langle\delta\phi(\mathbf{k})\delta\phi(-\mathbf{k})\rangle = \frac{k_B T}{K_2 k_3^2 + K_\perp(H)k_\perp^2} = \frac{\delta\phi(k)}{\delta h_\phi(-k)} \tag{6}$$

where $h_\phi(k)$ is the field conjugate to $\phi(k)$ and

$$K_\perp(H) = \tfrac{1}{2}\,\frac{\mu_a H^2(K_1+K_3)}{(K_1+K_3)q_0^2 + \mu_a H^2} \tag{7}$$

All other correlation functions are well behaved at zero **k**. Hence, the one broken symmetry hydrodynamical variable in a cholesteric in an external field is

$$\mathbf{v}_s(rt) = \nabla\phi(\mathbf{rt}) \tag{8}$$

Using Eq. (6) and the fact that the field h_i conjugate to v_{si} is related to $h_\phi(\mathbf{r})$ via $h_\phi = \nabla \cdot \mathbf{h}$, we obtain

$$\left(\frac{\partial v_{s3}}{\partial h_3}\right)_{\mu, T, H} = \frac{1}{K_2} \tag{9a}$$

$$\left(\frac{\partial v_{s\perp}}{\partial h_\perp}\right)_{\mu, T, H} = \frac{1}{K_\perp(H)} \tag{9b}$$

Changes in v_{s3} are equivalent to changes in q_0. Since q_0 is a function of temperature and pressure

$$\frac{\partial v_{s3}}{\partial h_3} = \frac{\partial q_0}{\partial h_3}$$

depends on which variables are held constant. $v_{s\perp}$ on the other hand, is not affected by changes in pressure temperature or external field. Eq. (9b), therefore, implies that

$$\partial h_\perp(\mathbf{r}, t) = K_\perp(H)\delta v_{s\perp}(\mathbf{r}, t) \tag{10}$$

for small deviations from equilibrium.

The basic thermodynamic relation for cholesterics can, therefore, be written as

$$T\mathrm{d}s = \mathrm{d}\epsilon - \mu \mathrm{d}\rho - \frac{1}{4\pi}\mathbf{H} \cdot \mathrm{d}\mathbf{B} - \mathbf{h} \cdot \mathrm{d}\mathbf{v}_s \tag{11}$$

where T is the temperature, s the entropy per unit volume, μ the chemical potential per unit mass, ρ the mass density, $\mathbf{H}$ the magnetic field and $\mathbf{B}$ the magnetic induction.

3. The hydrodynamical variables for a cholesteric liquid crystal obey the conservation laws

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{g} = 0$$

$$\frac{\partial g_i}{\partial t} + \nabla_j \sigma_{ij} = 0$$

$$\frac{\partial \epsilon}{\partial t} + \nabla \cdot \mathbf{j}^\epsilon = 0$$

$$\frac{\partial v_{si}}{\partial t} + \nabla_i \chi = 0 \tag{12}$$

In the above ρ is the mass density, $\mathbf{g}$ the momentum density, ϵ the energy density, σ_{ij} the stress tensor, $\mathbf{j}^\epsilon$ the energy current and χ the current for $\mathbf{v}_s$. The currents in Eq. (11) can be divided into reactive and dissipative parts (denoted by primes). Conservation of angular momentum can be guaranteed by choosing the stress tensor to be symmetric. This can always be done as long as there are no externally applied volume torques. (For a detailed and elegant discussion of this problem, see Ref. 5.) In an external magnetic field, there are external volume torques and the angular momentum is not necessarily conserved. However, as we shall see, any symmetry in σ_{ij} resulting from these torques dies off in microscopic times and need not be considered in a purely hydrodynamical treatment. It is worth noting here that $\mathbf{g}(\mathbf{rt})$ is the total momentum density at the point $\mathbf{r}$ and not the momentum density associated with center of mass motion only. A theory which chooses to distinguish between momentum due to center of mass motion and momentum due to rotation about the center of mass of the liquid crystals would require an additional angular momentum-like equation to describe the latter motion. However, no additional *hydrodynamical* information is provided by this separation, and such a treatment invariably yields modes which decay in microscopic times and simply cannot be justified to the same level of rigor as the purely hydrodynamical decay times. In our treatment, $\mathbf{v}_s$ describes the subset of possible director rotations which are purely hydrodynamical in character without introducing any extraneous non-hydrodynamical modes. The currents in Eq. (11) can be divided into reactive and dissipative parts (denoted by primes).

$$\begin{aligned} g_i &= \rho v_i \\ \sigma_{ij} &= \sigma_{ij}^R + \sigma_{ij}' \\ j_i^\epsilon &= (\epsilon \delta_{ij} + \sigma_{ji}) v_j + j'^\epsilon \\ \chi &= q_0 \mathbf{p} \cdot \mathbf{v} + \chi' \end{aligned} \tag{13}$$

where v_i is the velocity field. The $q_0 \mathbf{p} \cdot \mathbf{v}$ term in χ is discussed in detail in Ref. 1. It results from the apparent rotation of a helix moving parallel to its pitch axis. σ_{ij}^R includes the pressure and Maxwell stress terms characteristic of an isotropic fluid in an external magnetic(6) and a term proportional to h_i which is characteristic of the cholesteric state (see Ref. 1)

$$\sigma_{ij}^{R} = -\left[\tilde{F} - \rho\left(\frac{\partial \tilde{F}}{\partial \rho}\right)_{T,\, H,\, v_s}\right]\delta_{ij} - \frac{1}{4\pi} H_i B_j + q_0 p_i h_j \tag{14}$$

where $\tilde{F}$ is the free energy per unit volume defined by

$$\tilde{F}(\rho, T, \mathbf{H}, \mathbf{v}_s) = \epsilon - T\mathscr{s} - \frac{1}{4\pi}\mathbf{H}\cdot\mathbf{B} \tag{15}$$

B and **H** are linearly related

$$B_i(r) = \mu_\perp H_i - \mu_a n_i(\mathbf{r})\,(\mathbf{n}(\mathbf{r})\cdot\mathbf{H}) = \mu_{ij}(\mathbf{r}) H_j \tag{16}$$

In equilibrium **n** is perpendicular to **H**. In non-equilibrium situations **n** can have a component parallel to **H**. However, this component will decay to zero in microscopic times and will not contribute to the purely hydrodynamical equations being considered here.(7) We can, therefore set $B_i = \mu_\perp H_i$ and write σ_{ij}^{R} as

$$\sigma_{ij}^{R} = P\delta_{ij} - \frac{1}{4\pi}\mu_\perp H_i H_j + q_0 p_i h_j \tag{17}$$

where

$$P = P_0 + \frac{1}{8\pi} H^2\left[\mu_\perp - \rho\left(\frac{\partial \mu_\perp}{\partial \rho}\right)_{T,\, H,\, v_s}\right] \tag{18}$$

where P_0 is the pressure in the absence of a magnetic field. σ_{ij}^{R} of Eq. (17) can be cast in a manifestly symmetric form by integration by parts, thus insuring conservation of angular momentum.(1) Using Eqs. (14), (15) and (17) the basic thermodynamic relation Eq. (11) can usefully be written as

$$T\mathrm{d}\mathscr{S} = \mathrm{d}\left(\frac{\epsilon'}{\rho}\right) + P\mathrm{d}\left(\frac{1}{\rho}\right) - \frac{1}{4\pi\rho}\mathbf{B}\cdot\mathrm{d}\mathbf{H} - \frac{1}{\rho}\mathbf{h}\cdot\mathrm{d}\mathbf{v}_s \tag{19}$$

where $\epsilon' = \epsilon + (1/4\pi)\mathbf{H}\cdot\mathbf{B}$ and $\mathscr{S}$ is the entropy. From this it follows that

$$\left(\frac{\partial P}{\partial v_{si}}\right)_{H,\, \rho} = \rho\left(\frac{\partial h_i}{\partial \rho}\right)_{H,\, v_{si}} \tag{20}$$

For linear deviations from equilibrium the variable $\delta q(rt)$ defined by

$$\delta q(\mathbf{r}t) = \delta\epsilon(\mathbf{r}t) - \frac{T\mathscr{s} + \mu\rho}{\rho}\,\delta\rho(\mathbf{r}t) - \frac{1}{4\pi} H\cdot\delta B(\mathbf{r}t) \tag{21}$$

magnetic field breaks time reversal invariance and makes such couplings possible. Hence we have

$$
\begin{aligned}
\sigma'_{ij} &= -\nu_{ijkl}\nabla_k v_l - \zeta_{ijk}\frac{\nabla_k T}{T} - \lambda_{ij}\nabla\cdot\mathbf{h} \\
j'^{\epsilon}_i &= -\kappa_{ij}\nabla_j T + \zeta_{kli}\nabla_k v_l - \alpha_i\nabla\cdot\mathbf{h} \\
\chi' &= -\frac{1}{\gamma}\nabla\cdot\mathbf{h} + \lambda_{ij}\nabla_i v_j - \alpha_i\frac{\nabla_i T}{T}
\end{aligned}
\tag{28}
$$

ν_{ijkl} has the same form as an isotropic liquid in an external magnetic field with seven independent coefficients. κ_{ij} has an additional term corresponding to the Rigi–Leduc effect

$$\kappa_{ij} = \kappa_{\perp}\delta_{ij} + (\kappa_{\parallel} - \kappa_{\perp})p_i p_j + \kappa_a \epsilon_{ijk}\hat{H}_k \tag{29}$$

where $\hat{H}$ is a unit vector along $\mathbf{H}$. $\hat{H}$ and $\mathbf{p}$ are parallel in the system we are considering; but since they have different time reversal properties, we will use both symbols when necessary in this section. The coefficient γ is the same as in a free cholesteric. α_i could also be present in a free cholesteric. Its presence would imply a rotation of the helix in a constant temperature gradient—a phenomenon which depends crucially on boundary conditions.$^{(5)}$ If present, it must be of the form $\alpha q_0 p_i$, ζ_{ijk} and λ_{ij} are non-zero only when there is an external field which breaks time reversal invariance. Since σ'_{ij} must be symmetric, λ_{ij} must have the form

$$\lambda_{ij} = \lambda(p_i\hat{H}_j + p_j\hat{H}_i) \tag{30}$$

where λ is scalar under space inversion. ζ_{ijk} would be zero in an isotropic fluid in an external magnetic field because it must be odd under both space and time inversion. Since $\mathbf{H}$ is a pseudo-vector, it is impossible to form a third rank tensor with only δ_{ij} and H_k satisfying both these criteria in an isotropic fluid. A cholesteric, on the other hand, has a pseudoscalar: q_0; so ζ_{ijk} can have the form

$$\zeta_{ijk} = \frac{q_0}{|q_0|}\left(\zeta_1\delta_{ij}\hat{H}_k + \zeta_2(\delta_{ik}\hat{H}_j + \delta_{jk}\hat{H}_i) + \zeta_3\hat{H}_i\hat{H}_j\hat{H}_k\right) \tag{31}$$

This completes the development of hydrodynamical equations for a cholesteric in an external magnetic field. We will not attempt to determine the general dissipative mode structure.

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Molecular Crystals and Liquid Crystals. 1973. Vol. 23, pp. 111–126

Printed in Great Britain

Correlations Orientationnelles dans les Dérivés Hexasubstitués du Benzène

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Received September 5, 1972

Résumé—L'étude, par diffusion des rayons X, des composés hexasubstitués du benzène, montre l'existence d'un " désordre " de structure, accompagné d'un ordre local très anisotrope puisque les substituants forment des chaînes linéaires ordonnées parallèles à l'axe **b**.

Dans le cas de l'hexachlorobenzène, les atomes de chlore sont déplacés de part et d'autre du cycle benzénique: pour des cycles superposés, les déplacements sont coopératifs et l'ordre s'étend sur environ 5 cycles. Par contre, il n'existe aucune corrélation entre les déplacements des substituants de cycles voisins latéralement.

Dans la phase haute température désordonnée des composés chlorométhylés du benzène, il existe à courte distance un ordre local antiferroélectrique limité aux directions parallèles à **b**, bien que l'ordre à grande distance des substituants soit détruit par les sauts orientationnels. De plus, et comme pour l'hexachlorobenzène, les substituants sont déplacés de part et d'autre du cycle benzénique. Au-dessous de la température de transition, l'ordre antiferroélectrique s'étend à trois dimensions; le désordre lié à la disposition des substituants hors du cycle benzénique subsiste cependant et disparaît progressivement par abaissement de la température en même temps que les sauts orientationnels.

Abstract—X-ray diffuse scattering experiments performed on hexasubstituted benzene derivatives give evidence of a somewhat disordered structure characterized by a strongly anisotropic local order with linear correlation chains parallel to the **b** axis.

In the case of hexachlorobenzene, the chlorine atoms are displaced above and below the ring plane: for superposed molecules the displacements are cooperative and the order extends on a range of about 5 mol. There is no correlation between neighbouring rings in a (**a**, **c**) plane.

In the high temperature disordered phase of the chloromethyl derivatives, the molecules reorient about their pseudo-sixfold axis and there is no long range order in the distribution of the chlorine and methyl groups. Nevertheless a local antiferroelectric order exists for rings superposed along the **b** direction. Moreover, as in the case of hexachlorobenzene, the substituted atoms are displaced out of the ring plane.

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Below the transition temperature, the antiferroelectric order extends three-dimensionally; the disorder related to the substituted atoms displacements is always present and disappears progressively when the temperature is lowered below 100 °K.

Les dérivés hexasubstitués chlorométhylés du benzène présentent une transition de phase rotationnelle à une température variable d'un composé à l'autre: 170 °K pour le 12 dichloro 3456 méthylbenzène (DCTMB), 260 °K pour le 123 trichloro 456 triméthylbenzène (TCTMB) ainsi que le montrent les mesures d'analyse thermique différentielle.(1) La transition de phase a été étudiée par différentes méthodes: détermination des structures(2), RMN,(3) mesures diélectriques.(1) Dans tous les cas, elle apparaît liée aux sauts orientationnels du cycle benzénique, les différents composés présentant des structures isomorphes. Toutes les phases ont une structure monoclinique: à basse température, les cycles sont empilés le long de l'axe **b** de manière à former un arrangement antiferroélectrique. Au-dessus du point de transition, les cycles tournent dans leur plan et peuvent prendre 6 positions équivalentes; l'ordre antiferroélectrique disparaît et la période est diminuée de moitié suivant les deux axes **b** et **c**. En fait, il existe déjà un certain désordre d'orientation dans la phase ordonnée de basse température; une mise en rotation de cycles benzéniques est détectée par RMN dès 190 °K pour le DCTMB et 200 °K pour le TCTMB. Ce désordre orientationnel dynamique devient de plus en plus important au fur et à mesure que la température s'élève. Le désordre apparaît complet pour la RMN au-dessus de 250 °K. Parallèlement, les mesures de constante diélectrique statique montrent une disparition de l'ordre antiferroélectrique à mesure que la température s'élève: la constante diélectrique augmente dès 100 °K. L'ensemble de ces résultats expérimentaux et leur comparaison aux résultats d'un calcul de Monte-Carlo a conduit les auteurs à admettre que la phase haute température n'était pas complètement désordonnée. On peut alors se demander quel type d'ordre caractérise la phase " désordonnée ". C'est pourquoi nous avons entrepris des expériences aux rayons X en vue de rechercher l'existence d'un ordre local à *courte distance*, ordre donnant lieu à l'apparition de rayons X diffractés en dehors des taches de diffraction de Bragg: nous avons donc recherché s'il