Magnetic field effects on the phase-induced biaxiality in cholesteric liquid crystals

Y. R. Lin-Liu
Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106
(Received 19 October 1982)

This paper makes a contribution towards understanding recent nuclear magnetic resonance measurements of biaxiality in cholesteric liquid crystals. We have made use of a simplified version of Landau theory to obtain the magnetic field dependence of the biaxiality parameter η. When the magnetic field H is greater than a critical value H_c, the parameter η vanishes. For $H < H_c$, the ratio $\eta(H)/\eta(0)$ is an almost universal function of H/H_c. The predicted magnetic field dependence is free of adjustable parameters, and comparison with experimental results can be made unambiguously.

In a recent nuclear magnetic resonance (NMR) experiment, Yaniv *et al.* observed sizable biaxiality[1,2] in cholesteric liquid crystals which are binary mixtures of 4-methoxy-benzylidene-4′-*n*-butylaniline (MBBA) and 4-*n*-butyl-oxybenzylidene-4′-*n*-heptyl-d_4-analine. Their experimental results confirmed early theoretical speculations,[3,4] based on symmetry arguments, that cholesteric liquid crystals are biaxial. The observed biaxiality indicates a noncylindrical distribution of the molecular orientation about the average direction, with a larger fluctuation along the pitch axis of the cholesteric helix. The measurements also showed that the biaxiality increases with temperature and has a strong temperature dependence near the cholesteric–blue-phase transition point. Both features of the experimental results can be qualitatively understood in terms of a simple Landau theory[3–5] or a generalized Maier-Saupe molecular-field theory of cholesterics.[6–9] Nevertheless, the magnitude of the biaxiality and its strong temperature dependence near the phase transition are somewhat unexpected.

In this Communication, we consider the effect of external magnetic field on the biaxiality. We will be interested in the case in which the magnetic anisotropy of the material is positive, and in a physical configuration in which the external magnetic field is applied perpendicular to the pitch axis of the cholesteric helix. A very similar problem was studied by de Gennes some years ago[10] without considering the biaxial order. We make use of a simplified version of Landau theory to obtain the magnetic field dependence of the biaxiality parameter η. Within our model, the ratio $\eta(H)/\eta(0)$ is an almost universal function of H/H_c, where H_c is the critical field strength, above which η vanishes.

In the Landau theory of the cholesteric phase, the order parameter which describes the orientational order is a traceless symmetric tensor $Q_{\alpha\beta}(\vec{r})$.[11] Its most general form is given by

$$Q_{\alpha\beta}=S\left[-\left(\frac{1-\eta}{2}\right)l_\alpha l_\beta-\left(\frac{1+\eta}{2}\right)m_\alpha m_\beta+n_\alpha n_\beta\right] \quad . \tag{1}$$

The triad $\hat{l}$, $\hat{m}$, and $\hat{n}$ of unit vectors indicates a set of local principal axes for which the tensor $Q_{\alpha\beta}$ is diagonal. As usual, we use the vector $\hat{n}(\vec{r})$ to designate the *director*, which is the average direction of the molecular long axis over a volume element at position $\vec{r}$. The quantity S is the Maier-Saupe order parameter,[6] and η is a measure of biaxiality. In a uniform nematic liquid crystal, the vectors $\hat{m}$, $\hat{n}$, and $\hat{l}$ are constant vectors and η is zero. The free-energy density, written as a power series in $Q_{\alpha\beta}$,[12] is given by

$$\begin{aligned}F=&\frac{a}{2}Q_{\alpha\beta}Q_{\alpha\beta}-\frac{b}{3}Q_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\alpha}+\frac{c}{4}(Q_{\alpha\beta}{}^2)^2\\&+\frac{L_1}{2}\partial_\alpha Q_{\alpha\gamma}\partial_\beta Q_{\beta\gamma}+\frac{L_2}{2}\partial_\alpha Q_{\beta\alpha}\partial_\alpha Q_{\beta\gamma}\\&-2L_2q_0\epsilon_{\alpha\beta\gamma}Q_{\alpha\mu}\partial_\gamma Q_{\beta\mu}-\chi_{\alpha\beta}H_\alpha H_\beta \quad ,\end{aligned} \tag{2}$$

where the coefficients a, b, c, L_1, L_2, and q_0 are phenomenological parameters, $\chi_{\alpha\beta}$ is the magnetic susceptibility tensor, and repeated indices are summed. We adopt here the standard point of view[11] that the cholesteric is a distorted form of the nematic phase. The constant q_0 has the dimension of an inverse length. If $q_0=0$, the theory describes nematics as well. We assume that the susceptibility tensor $\chi_{\alpha\beta}$ is related to the order parameter $Q_{\alpha\beta}$ by

$$\chi_{\alpha\beta}=\bar{\chi}\delta_{\alpha\beta}+\gamma Q_{\alpha\beta} \quad , \tag{3}$$

where $\bar{\chi}$ is the average susceptibility over all directions and γ is a normalization constant. We shall only consider the case in which $\gamma>0$. The magnetic free energy relevant to orientational order is then reduced to

$$F_H=-\gamma Q_{\alpha\beta}H_\alpha H_\beta \quad . \tag{4}$$

In order to describe the helical arrangement characteristic of cholesterics, we take the $\hat{l}$ vector to be the pitch axis and choose the coordinate axes such that it is along the z axis. The vectors $\hat{n}$ and $\hat{m}$ are parametrized by a single angular variable θ:

$$\hat{m} = (\sin\theta, -\cos\theta, 0) \ , \tag{5}$$

$$\hat{n} = (\cos\theta, \sin\theta, 0) \ . \tag{6}$$

The magnetic field $\vec{H}$ is taken along the y axis. Here we also assume that the order parameters S and η are constants independent of the position vector $\vec{r}$, and θ is a function of z only. With these assumptions, the total free energy is given by

$$\mathfrak{F} = \int d^3r \left\{ \frac{3a}{4} S^2 \left[1 + \frac{\eta^2}{3}\right] - \frac{b}{4} S^3 (1-\eta^2) + \frac{9c}{16} S^4 \left[1 + \frac{\eta^2}{3}\right]^2 + \tfrac{9}{8} L_2 S^2 \left[1 + \frac{\eta}{3}\right]^2 (\theta_z{}^2 - 2q_0\theta_z) - \gamma H^2 S \left[\frac{3}{2}\left[1 + \frac{\eta}{3}\right] \sin^2\theta - \tfrac{1}{2}(1+\eta)\right]\right\} , \tag{7}$$

where θ_z denotes $d\theta/dz$.

A discussion based on the free energy given above is, of course, possible in principle. However, it would not be particularly illuminating, as it would involve consideration of an enormous parameter space. We simplify Eq. (7) by rewriting $\mathfrak{F}$ as

$$\mathfrak{F} = \mathfrak{F}_0(S) + \mathfrak{F}_1 \ , \quad \mathfrak{F}_1 = \int d^3r \left\{ B\eta^2 + K_T \left[1 + \frac{\eta}{3}\right]^2 (\theta_z^2 - 2q_0\theta_z) - \chi_a H^2 \left[\frac{3}{2}\left[1 + \frac{\eta}{3}\right] \sin^2\theta - \tfrac{1}{2}(1+\eta)\right]\right\} , \tag{8}$$

where $F_0(S)$ is the part of the total free energy which depends on S only,

$$B = \frac{9a}{4} S^2 + \frac{b}{3} S^3 + \frac{3c}{8} S^4 \ ,$$

$$K_T = \tfrac{9}{8} L_2 S^2 \ ,$$

and

$$\bar{\chi}_a = \gamma S \ .$$

In making this simplification, we have ignored a term quartic in η. This approximation is justified since the observed biaxiality η is only a few percent except in the small temperature region very close to the phase transition. Furthermore, we assume that the equilibrium value of S will not be significantly affected by textural distortion and external magnetic field. Therefore S is effectively determined by $\mathfrak{F}_0(S)$ only. This assumption is consistent with optical data,[13] and was also made by Yaniv *et al.* in analyzing their NMR data.[1,2] The results of a recent study on biaxiality[9] by Lee and Lin-Liu based on a generalized Maier-Saupe molecular-field theory also support this assertion. We shall proceed in our analysis by treating B as a constant, independent of external magnetic field, and assume that it is positive, since we are not interested in biaxial nematics in the present context. The constant K_T is the Frank twist elastic constant,[11] and χ_a is the anisotropy of the magnetic susceptibility[11] in the uniaxial nematic conformation (i.e., $\eta = 0$). Both quantities can be directly measured.

In the absence of external magnetic field, $\theta = qz + \text{const}$ minimizes the free energy. This solution describes a uniformly twisted helix with pitch $P = \pi/q_0$. The corresponding equilibrium value of η is given, according to Eq. (8), by

$$\eta(0) = \frac{K_T q_0{}^2}{3B - \frac{1}{3} K_T q_0{}^2} \ . \tag{9}$$

This relation can be used to determine the free parameter B, once $\eta(0)$ and $K_T q_0{}^2$ are known from experiment.

For finite H it is convenient to introduce a length scale ξ_H, the magnetic coherence length, which is inversely proportional to H:

$$\xi_H = \left[\frac{K_T}{\chi_a}\right]^{1/2} \frac{1}{H} \ . \tag{10}$$

One of the equilibrium solutions for the angular variable θ is

$$\sin\theta(z) = \mathrm{sn}\left[\frac{z}{d}\middle| k\right] \ , \tag{11}$$

where $\mathrm{sn}(u)$ is the Jacobian sine function, the constants d and k $(0 \leq k < 1)$ are related to the biaxiality parameter η and the magnetic coherence length ξ_H:

$$d = \xi_H (1 + \tfrac{1}{3}\eta)^{1/2} \ , \tag{12}$$

$$q_0 \xi_H = \frac{2}{\pi} \frac{E(k)}{k} \frac{1}{(1+\frac{1}{3}\eta)^{1/2}} \ . \tag{13}$$

Here $E(k)$ is the complete elliptic integral of the second kind. This solution represents a distorted helical configuration. The corresponding result for the case of no biaxiality ($\eta=0$) was originally obtained by de Gennes.[10] To determine the equilibrium value of η for a given H, we minimize the resulting free energy,

$$F_T(\eta)=B\eta^2-\chi_a H^2-\chi_a H^2\left[\frac{1}{k^2}-1\right] . \tag{14}$$

Here k is considered as a function of η through the relation given by Eq. (13). Since the right-hand side of Eq. (13) is bounded from below, for a sufficiently large magnetic field (i.e., $H\rightarrow\infty$, $\xi_H\rightarrow 0$) there is no solution for k, and the distorted helical arrangement is impossible. Another possible equilibrium solution for θ is $\theta=\pi/2$. This solution corresponds to the physical situation in which the director $\hat{n}$ points uniformly along the external magnetic field $\vec{H}$. Substituting this solution into Eq. (8), we find the equilibrium value of η vanishes, and the corresponding free energy is

$$F_n=-\chi_a H^2 . \tag{15}$$

This indicates a uniaxial nematic conformation. When the magnetic field is reduced below a critical value H_c,

$$H_c=\frac{\pi}{2}\left[\frac{K_T q_0^2}{\chi_a}\right]^{1/2} , \tag{16}$$

Eq. (13) admits a solution for k with $\eta=0$. Comparing F_n with $F_T(0)$ in Eq. (14),

$$F_n-F_T(0)=\chi_a H^2\left[\frac{1}{k^2}-1\right]\geq 0 ,$$

it is obvious that the nematic conformation is no longer stable when $H<H_c$. For $H<H_c$, the biaxial parameter $\eta(H)$ can be written as

$$\frac{\eta(H)}{\eta(0)}=\frac{G(k)}{\{1-\frac{1}{3}[1-G(k)]\eta(0)\}} , \tag{17}$$

where

$$G(k)=\frac{\pi^2}{8}\left[1+\frac{E(k)}{K(k)}-k^2\right]\Big/E^2(k) . \tag{18}$$

In writing out this expression, we have eliminated the phenomenological constant B in favor of the directly measurable quantity $\eta(0)$ [see Eq. (9)]. The constant k is determined from Eq. (13), which can also be written as

$$\frac{H}{H_c}=\frac{k}{E(k)}\left[\frac{1+\frac{1}{3}\eta(0)}{1+\frac{1}{3}[1-G(k)]\eta(0)}\right]^{1/2} . \tag{19}$$

In the weak-biaxiality limit, [i.e., $\eta(0)\rightarrow 0$], the ratio $\eta(H)/\eta(0)$ approaches a universal function of H/H_c, which is specified by the function $G(k)$ of Eq. (18) with the value of k determined by the relation $H/H_c=k/E(k)$.

This universal function is shown in Fig. 1. The reduction of the biaxial parameter η at $H=0.5H_c$ is about 15%, and at $H=0.9H_c$, it is about 50%. As $H\rightarrow H_c$, $\eta(H)$ is inversely proportional to $\ln(1-H/H_c)$. We have also numerically evaluated the $\eta(H)/\eta(0)$ for $\eta(0)=0.01$, 0.05, and 0.1. The deviation from the universal curve increases as H approaches H_c. Nonetheless, the maximum derivation at $H=0.9H_c$ is only a fraction of one percent, and at $H=0.95H_c$, it is about 1%. For practical purposes, the ratio $\eta(H)/\eta(0)$ shown in Fig. 1 can be considered universal.

We close by noting that in the standard Landau theory the cholesteric phase is considered as a twisted form of the uniaxial nematic phase. The appearance of biaxiality in such a theory is a natural consequence of the helical texture characteristic of cholesterics. Another possible physical origin of biaxiality related to the manifested molecular asymmetry was also suggested before.[3,14] To distinguish experimentally the above possibilities is certainly of significance. In this paper we have simplified the standard Landau theory on physical plausible grounds, and obtain an almost universal behavior of the phase-induced biaxiality parameter η under the influence of external magnetic field. It should be noted that in the weak-biaxiality limit, results of our calculation are exact within the framework of Landau theory. The predicted magnetic field dependence of the biaxiality parameter η is free of adjustable parameters, and comparison with experimental results can be made unambiguously.

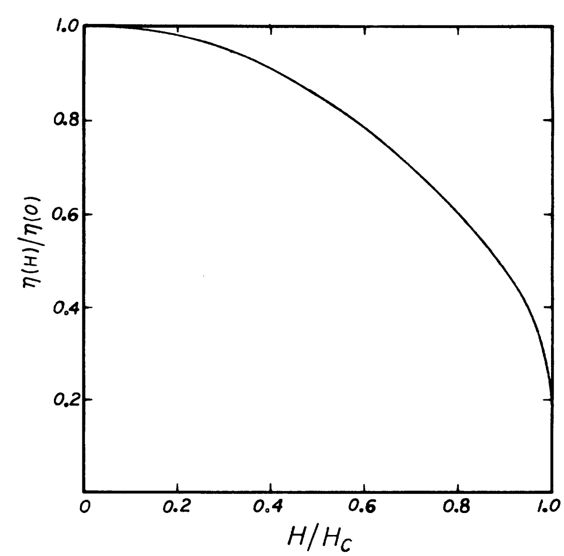

FIG. 1. The magnetic field dependence of the biaxiality parameter η in the weak-biaxiality limit.

ACKNOWLEDGMENTS

I would like to thank Professor J. W. Doane and Dr. Z. Yaniv for discussions of their experimental results. I am also indebted to Professor B. Segall, Professor S. Machlup, and Dr. M. Lee for their comments.

[1]Z. Yaniv, N. A. P. Vaz, G. Chidichimo, and J. W. Doane, Phys. Rev. Lett. 47, 46 (1981).

[2]G. Chidichimo, Z. Yaniv, N. A. P. Vaz, and J. W. Doane, Phys. Rev. A 25, 1077 (1982).

[3]R. G. Priest and T. C. Lubensky, Phys. Rev. A 9, 893 (1974).

[4]A. Wulf, Phys. Rev. A 11, 365 (1975).

[5]H. Schroeder, in *Liquid Crystals of One- and Two-Dimensional Order,* edited by W. Helfrich and G. Hepke (Springer, Berlin, 1980), p. 196.

[6]W. Maier and A. Saupe, Z. Naturforsch. A13, 564 (1958); A14, 882 (1959).

[7]Y. R. Lin-Liu, Y. M. Shih, and C. W. Woo, Phys. Rev. A 15, 2250 (1977); Y. R. Lin-Liu, Y. Shih, C. W. Woo, and H. T. Tan, *ibid.* 14, 445 (1976).

[8]B. W. van der Meer, G. Vertogen, A. J. Dekker, and J. G. J. Yama, J. Chem. Phys. 65, 3935 (1976).

[9]M. Lee and Y. R. Lin-Liu (unpublished).

[10]P. G. de Gennes, Solid State Commun. 6, 163 (1968).

[11]See, for example, P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974).

[12]P. G. de Gennes, Mol. Cryst. Liq. Cryst. 12, 193 (1971).

[13]D. W. Berreman and T. J. Scheffer, Phys. Rev. A 5, 1397 (1974).

[14]B. W. van der Meer and G. Vortogen, Phys. Lett. 59A, 279 (1974).