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MAGNETIC RESONANCE DETERMINATION OF THE ORIENTATIONAL ORDER IN LIQUID CRYSTALS

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Résumé. — On discute les mesures de taux d’orientation moléculaire par résonance magnétique dans les cristaux liquides nématiques. On peut déterminer le paramètre \( S = \frac{1}{2} (3 \cos^2 \theta - 1) \) où \( \theta \) est l’angle entre l’axe de la molécule et la direction d’alignement. Dans les systèmes homogènes, le couplage dipolaire (entre protons par exemple) crée une séparation entre les raies (RMN) qui est proportionnelle à \( S \). Donc en mesurant le spectre en fonction de la température \( T \), on peut déduire \( S(T) \). D’autre part, si l’on dilue des impuretés comportant des radicaux libres, on peut aussi trouver \( S(T) \) par RPE. Cette possibilité provient du fait que le tenseur \( q \) et le couplage hyperfin sont anisotropes. Dans ce cas, les impuretés sont orientées par interactions avec les molécules du solvant.

Abstract. — We discuss magnetic resonance determinations of the alignment in liquid crystals given by \( S = \frac{1}{2} (3 \cos^2 \theta - 1) \) where \( \theta \) is the angle between a molecular axis and the preferred axis. In homogeneous systems, dipolar coupling (e. g. between protons) creates a NMR line splitting proportional to \( S \). Thus by measuring the spectrum as a function of the temperature \( T \) one can deduce \( S(T) \). Furthermore, if the sample is diluted with impurities containing free radicals, \( S(T) \) can also be determined by EPR. This possibility arises from the anisotropy of the \( q \) and hyperfine tensors. In this case, the impurities are oriented by interaction with the solvent molecules.

I. Introduction. — Liquid crystals are characterized by an orientational order of the rod like molecules of which they are composed. It is clearly of interest to measure this order as a function of the various controllable parameters such as the temperature \( T \), magnetic field \( H \), electric field \( E \), and pressure \( P \). Various methods exist to measure this degree of alignment as has been discussed by Saupe and Maier [1] namely : diamagnetic susceptibility, dielectric constant, UV and IR spectra, X-ray scattering, optical dichroism, and magnetic resonance. When applicable the resonance technique is the most accurate. It is the object of this paper to discuss this type of measurement with regard to reviewing the existing experiments and suggesting further extensions.

In part II, we shall briefly consider the physical mechanisms which permit NMR and EPR to be sensitive to the degree of orientational alignment. These results are then immediately applicable to the nematic mesophase.

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The possible information that could be derived from experiments in cholesteric liquid crystals is then discussed in part III.

Throughout this study we shall consider the somewhat simplified model in which the molecules are taken to be rod like entities with the spins of interest (either nuclear or electronic) located on the symmetry axis. More general spin configurations only complicate the notation but do not change the basic physics. Furthermore we limit ourselves to a discussion of radio frequency spectroscopy, i. e. we avoid relaxation effects which may relate to the dynamic orientational fluctuations [2-5]. The advantage of magnetic resonance in the liquid state derives from the fact that inhomogeneous line broadening arising from the random intermolecular dipolar fields is narrowed by the translational and rotational diffusive motion [7].

II. Nematic mesophase. — In the nematic mesophase the application of a magnetic field may create a monodomain specimen through the anisotropic part of the diamagnetic susceptibility [6]. Thus
the magnetic field itself which is necessary for the resonance experiments defines the preferred axis of alignment (of course, this is strictly correct only for bulk samples where boundary effects may be neglected). In figure 1, we sketch the assumed geometry.

![Diagram of nematic phase geometry](image)

**FIG. 1.** — The nematic phase geometry. The molecular axis makes an angle \( \theta \) with the applied field which defines the alignment axis. The spins of interest are taken to be located on the molecular axis.

A convenient choice of parameter describing the degree or orientational order in the liquid crystal is

\[
S = \frac{1}{2} (3 \cos^2 \theta - 1) \quad \text{(II.1)}
\]

where \( < > \) indicates a thermodynamic average. (For complete order \( < \cos^2 \theta > = 1 \) and \( S = 1 \); for complete disorder \( < \cos^2 \theta > = \frac{1}{3} \) and \( S = 0 \).) The purpose of this review is to discuss how magnetic resonance allows one to determine \( S(T) \).

**a) Nuclear Resonance.** — We shall first consider the case of nuclear resonance. For simplicity, we restrict ourselves to the situation of two identical nuclear spins \( I_1 \) and \( I_2 \) located on the molecular axis. As previously noticed, the broadening effect of interactions between spins on different molecules is strongly reduced by the rapid translational diffusion typical of isotropic liquids. Assuming spin one-half nuclei (allowing the neglect of quadrupole interactions) the spin Hamiltonian is then:

\[
\mathcal{H} = - g_n \beta_n \mathbf{H} \cdot (I_1 + I_2) + \\
+ \beta_n^2 a^{-3} (3 I_1 \cdot \mathbf{m} \cdot I_2 - I_1 \cdot I_2) \quad \text{(II.2)}
\]

where \( g_n \) is the nuclear gyromagnetic ratio, \( \beta_n \) the nuclear magnetic moment, \( a \) the nuclear separation, and \( n \) a unit vector directed along the molecular axis. The effective field experienced by one nucleus e.g. (2) is

\[
g_n H_{\text{eff}} = g_n H + \beta_n a^{-3} (I_1 - 3 I_1 \cdot \mathbf{m}) \quad \text{(II.3)}
\]

Thus taking the magnetic field as the direction of quantization, the dipole-dipole coupling between the spins gives a splitting \( (I = \pm \frac{1}{2}) \) of the nuclear resonance [1].

\[
g_n \delta H = | \beta_n a^{-3} (1 - 3 \cos^2 \theta) | \quad \text{(II.4)}
\]

where \( \beta_n a^{-3} \sim 1 \text{ Oe} \). Thus our order parameter \( S \) is directly proportional to the dipolar splitting provided that we may replace the \( \cos^2 \theta \) term in (II.4) by its thermodynamical average. The justification for this is based on the usual motional narrowing type of argument [7]. If during the interaction time, \( (\delta \omega)^{-1} = (g_n \beta_n \beta H)^{-1} \), the molecular orientation remains nearly unchanged (i.e. \( (\delta \omega) \tau \gg 1 \), where \( \tau \) is the characteristic fluctuation rate of the molecular axis), the experiment measures a weighted average of all possible orientations leading to a type of powder pattern spread over a field range \( \beta_n a^{-3} \). On the other hand, if the molecules reorient rapidly \( (\delta \omega) \tau \ll 1 \), the splitting is sensitive only to the mean molecular orientation, i.e. \( S \). Estimates of \( \tau [2] \) based on the dynamical orientational fluctuations in liquid crystals give typical values of \( \sim 10^{-9} \text{ s} \), for which the latter condition is very well satisfied [8]. The nuclear dipolar splitting, then, directly gives the order parameter. Figure 2 gives a typical \( S(T) \) curve obtained in this manner [4].

![Graph of S(T)](image)

**FIG. 2.** — A measurement of \( S(T) \) obtained by Blinc et al [4] for p-anisaldazine from a dipolar proton doublet.
b) **Electron Resonance.** — Typically the molecules forming liquid crystals do not contain unpaired electron spins. Thus there is no possibility of performing electron spin resonances (ESR) directly on the molecules of the mesophase. However, several works [9-10] have added dilute concentrations of molecules, rather similar in form to those of the host liquid crystal, which contain free radicals [9] or biradicals [10]. The impurities are aligned by interaction with the host molecules. In the cases studied [9-10], this impurity alignment is weaker than that of the host. If the free radicals possess anisotropic g tensors or anisotropic hyperfine interactions with neighboring nuclear spins, one may obtain the impurity order parameter $S_i(T)$, in a similar way as discussed in the last section for the case of dipolar coupling between nuclear spins. Figure (3) shows some results obtained by Ferruti et al [9] for nematogen-like probes in p-asoxyanisole (PAA). Falle et al [10] have investigated biradicals in PAA where, in addition to the anisotropic $g$ values and hyperfine couplings, there is the possibility of dipolar or exchange induced zero field splitting which again allows a determination of $S_i(T)$. One must be a bit careful, however, with the condition that $\Delta \omega \tau \ll 1$ ($\Delta \omega$ is the relevant anisotropic shift or splitting) which is necessary if one is to measure $S_i$. Typical hyperfine splittings, for example, are of the order of 10 Oe which leads to $\Delta \omega \approx 10^8$ rd/s. Thus for $\tau \approx 10^{-9}$, one is near the limit $\Delta \omega \tau \approx 1$. In fact, one may expect a broadening of order $(\Delta \omega)^2 \tau$ which is then of order 1 Oe. This may be the origin of the apparent line broadening in the nematic state relative to the isotropic phase observed by Falle et al [10] (Fig. 4).

![Image](image_url)

**FIG. 4.** — Biradical spectra taken by Falle et al [10] in PAA. The upper trace is the hyperfine split EPR in the isotropic liquid while the lower trace is taken in the nematic phase. $\Delta H_1$ is the hyperfine splitting. Note the shift in this splitting arising from the anisotropic contribution to the hyperfine field in the nematic. $\Delta H_2$ is a zero field splitting which is completely averaged out in the isotropic liquid. Note the apparent increase in line width on going from the isotropic-ordered states which may arise from the incomplete averaging of the deviations from thermal equilibrium by the orientational fluctuations.

Erratum: sur la figure, au lieu de $H_1$ et $H_2$ lire $\Delta H_2$ et $\Delta H_1$.

Saupe and Englert [11-12] have also considered the possibility of NMR on impurity molecules. The previous discussion is not sensibly changed for this situation. However the orientation effect by the host molecules may lead to a better understanding of the molecular structure of the impurity, i.e. the non-vanishing alignment $S_i(T)$ allows a measure of the anisotropic part of the spin interactions which is related to the molecular conformation.

Recently it has been suggested [13] that even in the isotropic phase a magnetic field may induce an average alignment through the anisotropic part, $\chi_a$, of the diamagnetic susceptibility. These authors find

\[ S \approx \frac{\chi_a H^2}{k_B(T - T_c)} \]  \hspace{0.5cm} (II.5)

which for $\chi_a \approx 10^{-27}$ cm$^3$, $H \sim 10^4$ Oe, $k_B(T - T_c) \approx 10^{-15}$ gives $S \approx 10^{-3}$, a rather small value. For protons with a dipolar field $\sim 1$ Oe, this would lead to a line broadening proportional to $S$ and of order $10^{-3}$ Oe which should be observable in high resolution spectroscopy. However the technical requirements on the field homogeneity may be too severe when one works very close to the transition temperature $T_c$. 

III. Cholesteric mesophase. — The molecules forming cholesteric liquid crystals are generally optically active, i.e. they distinguish right from left. The orientational ordering of this mesophase may be described as a spiral arrangement of the molecular axes with these axes parallel in a given plane perpendicular to the spiral axis. The distance over which the molecules rotate by \( \pi \) is usually of order \( 10^{-4} \) cm. However this may be lengthened considerably in cholesteric-nematic mixtures. There has not been a great deal of resonance studies in this phase, probably because it is rather difficult to obtain « monodomain » samples. In principle, for molecules with \( \chi_\alpha \) > 0 the application of large magnetic fields can align the spiral axis. Furthermore, as with nematic systems, alignment may be obtained between well polished surfaces. We shall here assume that by some means we may create such « mono-domain » samples and shall only consider their properties. In section a) we treat the case of the external field parallel to the spiral axis, \( C \), while in b) the field is perpendicular to the axis. We shall further restrict our attention to the situation where \( \Delta \sigma \tau \ll 1 \), such that the resonance is sensitive to \( S \). In the cholesteric phase \( S \) is taken to be the order parameter relative to the perfect helical arrangement; i.e. it is the thermodynamic average molecular alignment along a direction which rotates with the spiral. For an undistorted spiral

\[
S = \frac{1}{2} \left\{ x (\mathbf{n} \cdot \mathbf{\sigma}) > ^2 - 1 \right\} \quad \text{(III.1)}
\]

where \( \mathbf{n} \) is a unit vector along the molecular axis and \( \mathbf{\sigma} \) is a unit vector defined by the spiral. If the \( z \) axis is that of the spiral,

\[
\sigma_z = 0; \quad \sigma_x = \cos q_0 z; \quad \sigma_y = \sin q_0 z \quad \text{(III.2)}
\]

where \( \pi q_0^{-1} \) is the distance between identical planes. For a distorted spiral the arguments \( q_0 z \) in (III.2) are replaced by a more general function of \( z, \Phi(z) \). Indeed, the distortion of this structure by the application of a magnetic field has been considered by de Gennes [14]. He finds that when \( H \parallel C \) there is usually no distortion [15]. For \( H \perp C \), the helix distorts and at a certain critical field

\[
H_c \propto q_0 (\sim 10^4 \text{ Oe for } q_0 \approx 3 \times 10^4 \text{ cm}^{-1})
\]

there is a transition to a nematic structure. This untwisting effect has been recently verified by resonance [17] and optically [18-19].

1. \( H \parallel C \). — In this case we assume that the helical structure (III.2) remains undistorted by the magnetic field. We shall restrict our attention to two nuclear dipoles (i.e. protons) on the molecular axis. The ESR situation is essentially identical. Then, since \( H \) is perpendicular to \( S \) for all the molecules, we obtain a splitting \( \Delta \omega = g_s \beta_n \delta H \) as in s. II,

\[
\Delta \omega = h \beta_n a^{-3} S \quad \text{(III.3)}
\]

which allows a direct determination of the order parameter \( S \).

2. \( H \perp C \). — This geometry is clearly more complex for two reasons:

1) because of the spiral structure the molecules in different planes are inequivalent with respect to the applied field and

2) the magnetic field induced distortion modifies the distribution of molecular axes relative to the field direction.

Let us first suppose that the applied field is sufficiently small (compared to \( H_c \)), that the distortion is negligible, and furthermore that the distance over which a molecule diffuses during the times of interest is small compared to \( q_0^{-1} \). Then one should observe a type of « powder pattern » with an ideal shape given in figure 5. The scale of the internuclear dipolar field is given by

\[
H_d = \beta_n a^{-3} \quad \text{(III.4)}
\]

The power absorbed at a field \( \Delta H = (H - \omega/\gamma) \) is proportional to the number of molecules \( n(\Phi) \) making an angle \( \Phi \) with the field direction such that

\[
\Delta H = \frac{1}{2} H_d (3 \cos^2 \Phi - 1) S. \quad \text{(III.5)}
\]

\( n(\Phi) \) is given by

\[
n(\Phi) = \int \rho(\Phi - \Phi') \left( \frac{d\Phi}{d\Phi'} \right) d\Phi' \quad \text{(III.6)}
\]

where \( \rho \) is the number of molecules per unit length along the \( z \) axis. For the case of a uniform spiral (III.2), \( \Phi = q_0 z \) and \( n(\Phi) \) is independent of \( \Phi \). This result together with (III.5) leads to figure 5a. Thus, in this case there is no splitting. However, in principle at least, \( S(T) \) can be deduced from the line width if this is the main broadening mechanism as is likely.

We now turn to a consideration of the possible effect of translational diffusion along the \( z \) axis. Suppose that as a molecule diffuses its direction of alignment adiabatically follows the local order. Then, if during a time \( (\Delta \omega = \gamma \Delta H)^{-1} \) the molecule diffuses a distance much greater than \( \pi/q_0 \) along the \( C \) axis the broade-
P. PINCUS

FIG. 5. - Idealized absorption curves for a cholesteric liquid crystal with \( H \perp C \) in the slow diffusion limit is; \( 5a) \) for \( H/H_c = 0 \); \( 5b) \) for \( H/H_c = 0.6 \); \( 5c) \) for \( H \gg H_c \).

The condition for this motional (diffusive) averaging is:

\[
Dq_0^2 \gg \Delta \omega \quad (\text{III. 7})
\]

where \( D \) is the diffusion constant for motion along the \( C \) axis. For \( D \approx 10^{-5} \text{ cm}^2/\text{s}, \ q_0 \approx 3 \times 10^4 \text{ cm}^{-1} \), we have \( Dq_0^2 \approx 10^4 \text{ s}^{-1} \) which is of order \( \Delta \omega \). Thus for tight spirals this condition may well be realized. Under these circumstances there will be a splitting given by

\[
H_d S \{ 3 < \cos^2 \Phi > -1 \} \quad (\text{III. 8})
\]

which for a uniform spiral is \( \frac{1}{2} H_d S \). The line width will be of order \( \gamma H_d^2 S^2/Dq_0^2 \). Such experiments would thus determine \( S \) and the longitudinal diffusion constant (which, of course, could also be measured by the standard spin echo technique in an inhomogeneous field [7]).

We shall now discuss the effect of magnetic field induced distortion [14] on the NMR signal, both for the cases of slow and fast longitudinal diffusion. As the period of the spiral increases with applied field, the slow diffusion regime remains throughout the field domain (assuming \( D \) independent of \( H \)). On the other hand, at some critical field there will be a transition from fast to slow diffusion behaviors. However as the pitch is initially a slow function of field [14] we shall assume (for simplicity) that the diffusion is either entirely rapid, or entirely slow, up to \( H_c \).

a) Slow diffusion.

From (III.6), \( n(\Phi) \) is proportional to \( \frac{dz}{d\Phi} \) which from de Gennes [14] is given by

\[
\frac{dz}{d\Phi} = \frac{k\xi}{\sqrt{1 - k^2 \cos^2 \Phi}} \quad (\text{III. 9})
\]

where \( \xi = \{ K_{22}/\zeta \}^{1/2} \), \( H^{-1} \) is a characteristic length and \( k \) is a dimensionless constant related to the field and period \( Z \) by

\[
(q_0 \xi)^{-1} = \frac{\pi}{2} k/E(k) \quad (\text{III. 10})
\]

and

\[
Z/Z_0 = (2/\pi)^2 K(k) E(k) \quad (\text{III. 11})
\]

(\( Z_0 = \pi/q_0 \) is the zero field period, \( K(k) \) and \( E(k) \) are elliptic integrals [20]). The critical field for the cholesteric-nematic transition \( (Z \to \infty) \) is given by \( q_0 \xi = 2/\pi \). The parameter \( k \) varies from zero in zero field to 1 at the transition. In figure 5b, c, we sketch some ideal absorption curves for increasing field values, derived from (III.9), (III.10), (III.11). Notice the continuous transition from the uniform spiral behavior of figure 5 to the ideal nematic behavior for \( H \gg H_c \).

b) Rapid diffusion.

As previously discussed, if the self-diffusion along the \( C \) axis is rapid compared to \( (\gamma H_d)^{-1} \), there will exist a splitting given by

\[
\Delta H = H_d S(3 \cos^2 \Phi - 1) \quad (\text{III. 12})
\]
where the « bar » indicates a weighted average over the angles of the local orientation relative to the field:

\[
\cos^2 \Phi = \frac{\int_0^{\pi/2} \cos^2 \Phi \frac{dz}{d\Phi} d\Phi}{\int_0^{\pi/2} \frac{dz}{d\Phi} d\Phi} \quad \text{(III.13)}
\]

with \( \frac{dz}{d\Phi} \) given by (III.9). This gives immediately

\[
\Delta H = H_4 S \left\{ \frac{3}{k^2} \left\{ 1 - E(k/K(k)) \right\} - 1 \right\} \quad \text{(III.14)}
\]

which varies from \( \frac{1}{2} H_4 S \) for \( H = 0 \) to \( 2 H_4 S \) for \( H = H_6 \).

Of course at some field \( H \) the period \( Z \) becomes sufficiently long that a transition is made from the rapid to slow diffusion regimes — this occurs when

\[
D(\pi/Z)^2 \approx \gamma H_4 S \quad \text{(III.15)}
\]

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References

[8] The corresponding linewidth [2] is then of order \( \beta_n a^{-2} g_n \beta_n \tau \sim 10^{-4} \text{ Oe} \). The splitting is thus much larger than the linewidth.
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DISCUSSION

J. MESSIER. — A-t-on essayé de mesurer le taux d'orientation des molécules en observant la résonance électronique associée à leur état triplet ?

P. PINCUS. — Pas à ma connaissance.