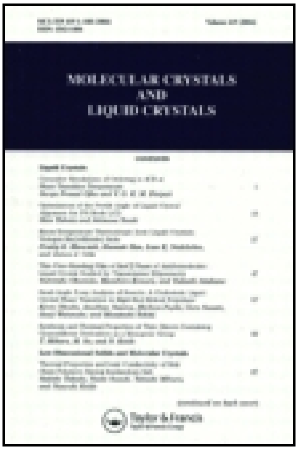

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A Theory of the Cholesteric Mesophase

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Abstract—A theory of the macroscopic twist which is a characteristic feature of the cholesteric liquid crystal phase is proposed. This is based on the presence of anharmonicity in the forces resisting the relative twist of neighboring planes of molecules and views the macroscopic twist as the rotational analog of thermal expansion. On the basis of a simple mode for the harmonic part of the forces, the temperature dependence of the peak reflectance wavelength observed by Fergason *et al.* is well explained.

The dominant feature of the cholesteric liquid crystal phase is the spontaneous macroscopic twist which exists under a wide range of suitable conditions. Such a twist explains[1,2] many of the optical properties of this type of mesophase and now appears to be widely accepted. The source of this twist has not been adequately explained, although " steric effects " are usually considered the reason. In this paper, we present an alternative, somewhat more explicit, explanation of the twist which allows the interpretation of some of the experimental measurements of changes in optical reflectivity with temperature. This theory, which regards the twist as the rotational analog of thermal expansion, is proposed as one possible explanation of the observed twist.

Proposed Model for the Cholesteric Twist

The average twist between planes in a cholesteric liquid crystal is in the order of 10 minutes of arc, or less, which seems to be rather small to be explained by steric hindrance effects. Instead we propose here that the macroscopic twist which is observed via the optical properties is actually an average over much larger instananeous molecular rotations which occur in the liquid crystal due to thermal excitation. In other words, there are normal twist modes which are appreciably excited at the temperatures at which the mesophase exists. Because of anharmonicity in the forces opposing twist, the time-average does not vanish and thus a macroscopic twist results. The molecules are always asymmetric in cholesteric mesophases, and thus the presence of the odd orders of anharmonicity necessary to give a non-zero average is likely. We now consider this theory more quantitatively within the approximation that the anharmonicity is small and that only the lowest-order (i.e., cubic) term need be considered. We shall also show that the same result is obtained from both thermodynamic and microscopic derivations. The theory presented below is not intended as an exhaustive treatment of what is necessarily a complicated problem. Instead, we aim to preserve and exhibit the important physics of the proposed theory and we thus keep the analysis simple and therefore somewhat crude.

We define $\theta = \theta_{\mathbf{q}}$ as the normal coordinate for rotation of the molecules in a plane normal to the associated propagation wave-vector $\mathbf{q}$, which is parallel to the axis of the subsequent macroscopic twist and has the value appropriate to the zone boundary of the virtual crystal in this direction. We take the anharmonic equation of motion for θ as

$$\ddot{\theta} + \omega_0^2\theta - \tfrac{1}{2}A\theta^2 = 0 \tag{1}$$

where the last term is the cubic anharmonicity term. The decoupling of the harmonic part of this equation is, of course, a consequence of the normal coordinate transformation but, in general, the anharmonic part will not be decoupled. However, the normal coordinate θ is proportional to the nearest-neighbor relative rotation since $\mathbf{q}$ belongs to the zone boundary. Thus the decoupling we have used in Eq. (1) not only enables complications which can hide the physics of the problem to be removed, but is equivalent to the approximation that only nearest-neighbor anharmonicity is important—a not altogether unreasonable assumption.

We note that there is no constant term in Eq. (1), which would arise from a linear term in the potential. This is because we have measured the rotation from equilibrium. However, the definition of this rotation is of some importance since the equilibrium value of the rotation is not necessarily zero, because of the same lack of symmetry which allows the cubic anharmonic term to be non-zero. In the present work, however, we shall take the equilibrium value of the relative rotation to be zero since an equilibrium rotation of more than a few degrees will not contribute to the *macroscopic* twist and the experimental data suggests that the pitch of the macroscopic twist does indeed become very long when the anharmonic effect discussed below becomes small. If the anharmonicity is small, then a solution to Eq. (1) is

$$\theta = \theta_0 \cos \omega_0 t - \frac{A\theta_0^2}{12\omega_0^2} \cos 2\omega_0 t + \frac{A\theta_0^2}{4\omega_0^2} \qquad (2)$$

to lowest order in A. Thus, because of the cubic anharmonicity, we have a non-zero time-average

$$\langle\theta\rangle = \frac{A\theta_0^2}{4\omega_0^2} \qquad (3)$$

Now, in a real liquid crystal, θ is not the only twist coordinate and the true situation is a superposition of normal mode rotations. We must therefore give some justification for using such a simple analysis as that above to approximate the true, complex situation. The justification arises from the form of the dispersion curves for the twist modes propagating down the z-direction in the ordered crystal (Fig. 1), where the macroscopic twist axis in the liquid crystal is in the z-direction. We see that the density of states in frequency is high at the zone boundary.[3] We expect the short-range order to be maintained in the liquid crystal, whilst the medium- and long-range order tends to disappear. Theoretical studies[4] have shown that loss of order tends to change the phonon excitation spectrum but the phonon density of states is not

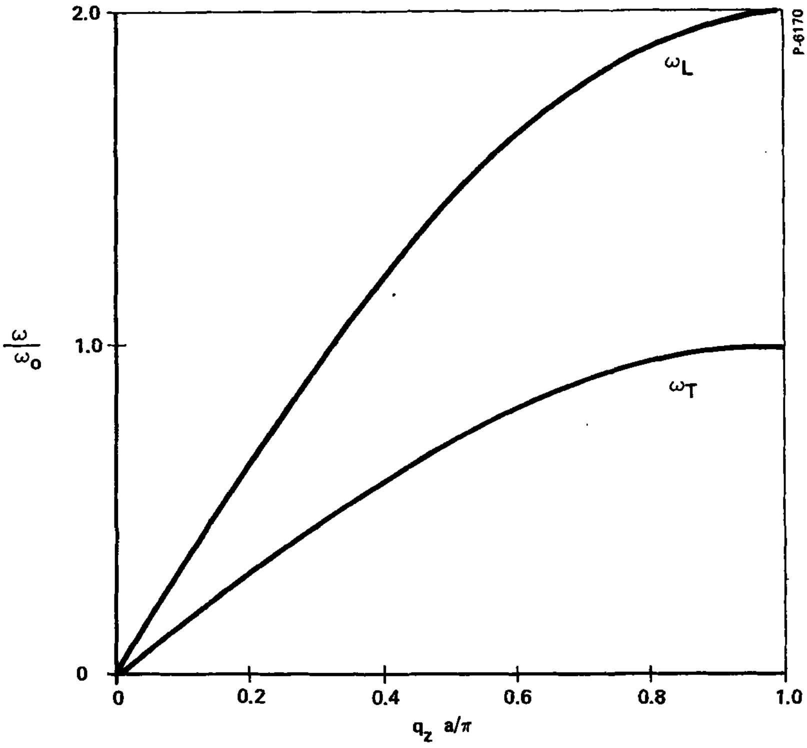

Figure 1. Rotational mode dispersion curves for the virtual crystal along a symmetry direction for near-neighbor forces. The curve ω_L represents the " bending " mode in which the axis of rotation is normal to the propagation direction and ω_T represents the " twist " mode where the rotational axis is parallel.

modified appreciably in regions where this density is not too small. Thus, we can expect a high density of " twiston " states at the zone-boundary of the virtual crystal along the z-axis. Therefore, at high enough temperatures so that classical statistics hold, most of the excited modes will have frequencies in a small frequency range about ω_0. We can then expect[5] Eq. (1) to be a reasonable approximation for the relative twist of nearest-neighbors if the dominant anharmonic forces are between close neighbors, which is reasonable.[6]

Thus, Eq. (3) gives the average relative rotation in going from one plane to the next. If classical statistics hold, then the virial theorem gives

$$\tfrac{1}{2}I\omega_0^2\theta_0^2 = kT \tag{4}$$

where I is proportional to the moment of inertia of the molecule, and we have

$$\langle\theta\rangle = \frac{AkT}{2I\omega_0^4} \tag{5}$$

This same result (Eq. (5)) can also be obtained from purely thermodynamic arguments,[7] using the Boltzmann distribution function (i.e., again assuming classical statistics hold). The equation of motion (1) is derived from a potential

$$V(\theta) = V_0 + \tfrac{1}{2}I\omega_0^2\theta^2 - \tfrac{1}{6}IA\theta^3 = V_0 + v(\theta), \tag{6}$$

where V_0 contains the terms which do not depend on θ. The thermal average value $\langle\theta\rangle$ is given by means of the Boltzmann distribution function as

$$\langle\theta\rangle = {}^1\int_{-\pi}^{\pi} \theta e^{-V(\theta)/kT}\, d\theta$$

where

$$z = \int_{-\pi}^{\pi} e^{-V(\theta)/kT}\, d\theta$$

since integrations over the other normal coordinates merely give a factor unity. If the anharmonic term is small,

$$\int_{-\pi}^{\pi} \theta e^{-v(\theta)/kT}\, d\theta \approx \int_{-\pi}^{\pi} e^{-1/2(I\omega_0^2\theta^2/kT)}\left(\theta + \tfrac{1}{6}\frac{IA\theta^4}{kT}\right)d\theta$$

The first term vanishes through parity and, since $e^{-1/2(I\omega_0^2\pi^2/kT)} \ll 1$, the limits $\pm\pi$ may be approximately replaced by $\pm\infty$. Hence

$$\int_{-\pi}^{\pi} \theta e^{-v(\theta)/kT}\, d\theta \approx \frac{IA}{6kT}\left(\frac{2kT}{I\omega_0^2}\right)^{5/2}\left(\frac{3\pi^{1/2}}{4}\right)$$

Similarly,

$$\int_{-\pi}^{\pi} e^{-v(\theta)/kT}\, d\theta \approx \left(\frac{2\pi kT}{I\omega_0^2}\right)^{1/2}$$

so that

$$\langle\theta\rangle \approx \frac{AkT}{2I\omega_0^4}$$

which is just Eq. (5).

If the frequency ω_0 is independent of temperature, then we note from Eq. (5) that $\langle\theta\rangle$ increases linearly with temperature in a way which is fully analogous to the linear dependence on temperature of thermal expansion—which is due to anharmonicity in the forces resisting *displacements*. The pitch, i.e., the length p over which the twist repeats itself,[1,2] is

$$p = \frac{2\pi a}{\langle\theta\rangle} = \frac{4\pi aI\omega_0^4}{AkT}$$

where a is the mean interplanar distance· Thus the optical wavelength at which maximum reflectivity occurs is[1,2]

$$\lambda_m = pn = \frac{4\pi naI\omega_0^u}{AkT} \tag{7}$$

where n is the mean refractive index. We note that Eq. (7) predicts a $1/T$ temperature dependence for λ_m if ω_0 is temperature independent, although, since λ_m is proportional to ω_0^4, any temperature dependence of ω_0 can be quite important. We also note that the experimental values of λ_m/a are typically in the order of 10^3. Taking $\omega_0^2/A \sim \pi$ as a very rough order-of-magnitude guess and using Eq. (4), we have

$$\theta_0^2 \sim 8\pi^2 n \times 10^{-3}$$
$$\theta_0 \sim 0.35$$

or about 20° of arc, which is a reasonable value. In other words, the molecules instantaneously twist relative to their neighbors through angles of the order of 20° of arc and, because of anharmonicity, have a residual, average twist of about 10 minutes of arc. Furthermore, $A\theta_0/\omega_0^2 \sim 0.1$ if $\omega_0^2/A \sim \pi$, as assumed, and thus the anharmonic contribution to the equation of motion (1) does indeed appear to be fairly small and the analysis is internally consistent in this respect.

Application to Cholesteryl Nonanoate and Decanoate

At this point, we have a tentative crude theory of the macroscopic twist observed in cholesteric liquid crystals which seems reasonable on physical grounds. However, it is necessary to consider the theory further and to examine it in the light of other experimental data in order to give it more credence. In this section, we show how a simple extension of the theory in a physically reasonable way allows a good fit to the experimental data of Fergason *et al.*[8]

As we have already mentioned, Eq. (7) predicts a $1/T$ dependence for λ_m if ω_0 and A are temperature-independent. However, except at the higher temperatures, such a dependence on T is different from that shown by Fergason *et al.*[8] in, for example, Fig. 3 of ref. 8. We believe the reason for this is due to the fact that ω_0 appears to the fourth power and is somewhat temperature-dependent because of the closeness to a transition point, i.e., the smectic-cholesteric transition point. In Cholesteryl Nonanoate and Decanoate, the smectic-cholesteric transition temperatures are[9] 73.9 °C and 75.8 °C respectively with an error in the order of 0.5 °C. If we divide the harmonic forces resisting rotation into (a) short-range and (b) long- and medium-range contributions, then we expect a fairly constant short-range contribution (since the short-range order will be more or less preserved), but a longer-range contribution which changes as the longer-range order decreases with increasing temperature.[10] Although the theory does not rely on this assumption, we wish to suggest that the more " long-range " contribution to ω_0^2 (the harmonic forces are proportional to ω_0^2) is due to the more " long-range " local electric field due to the dipoles on the molecules. There is no evidence of ferroelectric behavior in cholesteric liquid crystals and thus the macroscopic (i.e., average) field, which is proportional to the macroscopic polarization, is zero. In the more ordered liquid crystal (i.e., near the transition point) there is, however, a non-zero long-range contribution to the local electric field, the Lorentz field, acting on each molecule due to the fact that the molecules are ordered on lattice sites. However, as the long- and medium-range order is lost, the molecules begin to see the *average* longer-range contribution to the electric field, which is zero, rather than the microscopic local field of the ordered limiting case.

Thus, we have a constant short-range contribution to ω_0^2 and a longer-range contribution which falls off to zero as we go to temperatures further away from (and above) the phase transition temperature. A common form for such a contribution near a transition point is[11] $\sim (T - T_0)^{-1}$ and thus we write

$$\omega_0^2 = \alpha\left(1 + \frac{\beta}{T - T_0}\right) \qquad (T > T_0)$$

so that

$$\lambda_m = \frac{4\pi n a I \alpha^2}{Akt}\left(1 + \frac{\beta}{T - T_0}\right)^2 \tag{8}$$

is the predicted temperature dependence, where T is in °K and $T > T_0$. We shall ignore dispersion (i.e., the λ-dependence of n) since it has not yet been measured.

In the case of Cholesteryl Nonanoate, there is some excellent data available[0] and we find that the experimental results lie on the curve given by Eq. (8) with

$$\gamma = \frac{4\pi n a I \alpha^2}{AkT_0} = 0.3715 \text{ microns}$$

$$T_0 = 347.25\,°\text{K}\ (74.25\,°\text{C})$$

$$\beta = 0.145\,°\text{K}$$

The agreement between this theoretical curve and the experimental data is shown in Fig. 2 and is seen to be good. The fit is tested more stringently in the upper curve in Fig. 2, where the data between 74.7 °C and 76 °C is shown on an expanded temperature scale, and appears to be excellent. We have also fitted the Cholesteryl Decanoate data of Fergason *et al.*,[8] with

$$\gamma = 0.357 \text{ microns}$$

$$T_0 = 348.5\,°\text{K}\ (75.5\,°\text{C})$$

$$\beta = 0.14\,°\text{K}$$

and the agreement, shown in Fig. 2, is again good. Other similar data on other liquid crystals given in ref. (8) are also well fitted by this expression.

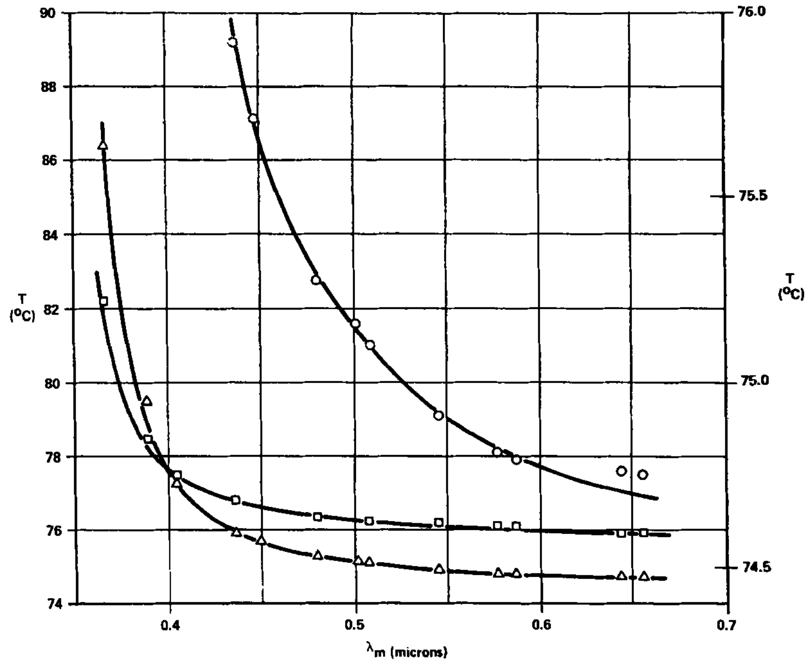

Figure 2. Theoretical fit to the data of Fergason *et al.* (ref. 8). The solid line represents theory (Eq. (8)); △ experimental points for C. Nonanoate; □ experimental points for C. Decanoate; ○ experimental points for C. Nonanoate plotted on expanded temperature scale (at right hand side).

At first sight, the fit involves three adjustable parameters. However, since the T_0 values agree with the experimental values to within the experimental error,[12] the fit essentially requires only two adjustable parameters. Moreover, one of the other parameters (γ) is not completely arbitrary since, as we have seen, the magnitude of θ_0 which arises from the theory is a very reasonable one.

Discussion

We have described a tentative theory for the cholesteric macroscopic twist which is physically reasonable and, so far, is consistent with what we know and expect. With a fairly simple, and again physically reasonable, extension to temperatures near a phase transition point, we have a good fit to some accurate experimental data. In the future, it is hoped that further tests of the proposed theory will be made to show whether it is good, bad, or indifferent, or to suggest improvements to it.

One further interesting explanation the theory provides is the reason for the inverse correlation between temperature and electric-field sensitivity noted earlier by Fergason[9] for cholesteric liquid crystals. The theory explains the fact that the most temperature-sensitive mesophases tend to be the least electric-field sensitive in the following way: The parameter β is a measure of the temperature sensitivity of λ_m since it determines the magnitude of the most temperature-dependent term in λ_m at a given temperature above the phase transition temperature. However, β is also a measure of the internal local electric fields since we have proposed that this temperature-dependent term is the long- and medium-range contribution to the local field. Thus, λ_m is sensitive to temperature but relatively insensitive to an applied electric field if β is large, since an external electric field must then compete with high internal fields.

If the theory proposed here should, in fact, turn out to be substantially correct, then we have the opportunity to separate out short-range and long-range effects. By carrying out plots like those of Fergason *et al.*[8] with different external electric fields or other type of perturbation and analyzing them according to Eq. (8), it should be possible to determine whether the main effect is on the long-range or short-range interactions and thereby facilitate interpretation.

We would also like to comment on one of the more philosophical implications of the theory. It is sometimes implied in the literature that the macroscopic twist encountered in cholesteric liquid crystals represents a higher degree of organization than is present in other types of mesophase. However, the theory proposed here suggests that, in actual fact, the macroscopic twist is a consequence of a *reduction* in order. In the smectic phase below T_0, for example, a macroscopic twist may exist but, because the internal local field appreciably reduces the amplitude of the molecular rotations, the pitch of the twist is so long that it cannot give rise to optical effects in the visible or near-infrared regions. It is only when the long- and medium-range order begins to break down further that the twist can become large enough to give the striking optical effects which are characteristic of this mesophase.

Finally, we are led to the suggestion that the cholesteric liquid crystal may be just a nematic liquid crystal with asymmetric molecules and sufficient anharmonicity and rotational compliance to give an appreciable macroscopic twist. This suggestion is, of course, somewhat similar to the earlier view of Friedel.[13]

Acknowledgments

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REFERENCES

1. de Vries, H., *Acta Cryst.* 4, 219 (1959).
2. Fergason, J. L., p. 89 of " Liquid Crystals," ed. Brown, G. H., Dienes, G. J. and Labes, M. M. (Gordon and Breach, New York, 1966).
3. The dispersion curves shown in Fig. 1 were calculated using only near-neighbor interactions but this result is more general.
4. See, for example, Elliot, R. J., in " Phonons in Perfect Lattices and in Lattices with point Imperfections," ed. Stevenson, R. W. H. (Plenum Press, New York, 1966) and Maradudin, A. A., Montroll, E. W. and Weiss, G. H., " Theory of Lattice Dynamics in the Harmonic Approximation," *Solid State Phys.* Suppl. No. 3 (Academic Press, New York, 1963).
5. These arguments are, of course, very similar to those used to justify the Einstein approximation to the lattice vibrational properties of solids at temperatures which are not too low (see, for example, Schrieffer, J. R., in " Phonons and Phonon Interactions," ed. Bak, T. (Benjamin, W., New York, 1964)).

6. The more-distant-neighbor *harmonic* forces and torques are, of course, included in w_0^2 via the usual normal coordinate transformation.
7. This section is essentially an extension of treatments of thermal expansion (see, for example, Kittel, C., " Introduction to Solid State Physics " (Wiley, New York, 1956)).
8. Fergason, J. L., Goldberg, N. N. and Nadalin, R. J., p. 105 of ref. 2.
9. Fergason, J. L., private communication.
10. The definitions of short-, medium-, and long-range are, of course, somewhat arbitrary. In the present examples, much of the very long-range order is presumably lost in the smectic phase so that it is a break-down in the " medium-range " order which is referred to here. We are indebted to Dr. A. Saupe for this point.
11. This term might also be justified as the lowest order term in an asymptotic expansion above T_0.
12. It is worth noting that the above T_0 values were obtained before the experimental values (ref. 9) were made available.
13. Friedel, M. G., *Ann. Phys.* **18**, 273 (1922).