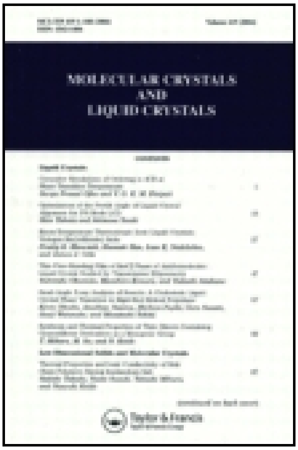

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# On Molecular Structure and Physical Properties of Thermotropic Liquid Crystals

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**Abstract**—Some models for the molecular structures of liquid crystals including a ferroelectric liquid are discussed. It is shown that a smectic liquid with a layered structure, in which the preferred orientation of the molecular axis is inclined against the layers, has some similarities with a nematic liquid. Such a tilted smectic liquid may also have a twisted modification corresponding to a twisted nematic or cholesteric liquid crystal. Attention is drawn to an optically isotropic texture of a cholesteric liquid. A proposal is made for its molecular structure in which a fairly regular, lattice-like arrangement of alignment singularities is assumed. Twist waves in nematic liquids are regarded and numerical estimations are made for their wave velocity and damping in *p*-azoxyanisole. It is concluded that the damping is too strong for an observation of such waves.

## 1. Introduction

After the discovery of liquid crystals about 80 years ago, one of the first and most discussed questions was whether or not liquid crystals correspond to a new state of matter. Later, attention was concentrated on how many different types of liquid crystals exist or are useful to differentiate. That question is still open. Friedel about 45 years ago believed that two liquid crystalline phases that give rise to three types of liquid crystals are enough. His conceptions on the structures of these liquids have proved to be true in the essential points and they helped much in understanding their properties. However, there are more than the three types of liquid crystals that Friedel acknowledged.

Another very useful development followed Friedel's important papers, that is the theory of elastic properties or the continuum theory of liquid crystals. For this development most of the credit is due to Zocher and Oseen. Zocher conceived and supported the continuum theory by direct optical observations. His ideas were not generally accepted because they were in contradiction with the swarm theory which was favored at that time. From a purely theoretical starting point, Oseen arrived essentially at the same result as Zocher at about the same time, but even that did not lead to a general acceptance of the continuum theory.

During the past three months at the Liquid Crystal Institute, I have had many stimulating and interesting discussions with my colleagues and especially with James L. Fergason on molecular structure and elastic properties and I want to pass on to you some of these stimulations and some conceptions which have developed out of these discussions.

## 2. Nematic and Cholesteric Liquid Crystals and Smectic Liquid Crystals of Type A

In Fig. 1 schematic pictures of the molecular structures of some liquid crystalline phases are shown. This list is not complete. Other structures can be thought of and are known to exist. On the other hand, not all structures proposed here have been proven to exist.

In Fig. 1 as in Fig. 4, the molecules are represented as lines, which implies that the molecules may be regarded as possessing a rotational symmetry. The line shows the preferred orientation of the molecular symmetry axis or, in other words, the thermal fluctuation of the molecules are neglected in these pictures.

The lengths of the lines indicate the orientation of the molecular axis with respect to the plane of the drawing. Molecules that are perpendicular to the plane are represented by dots.

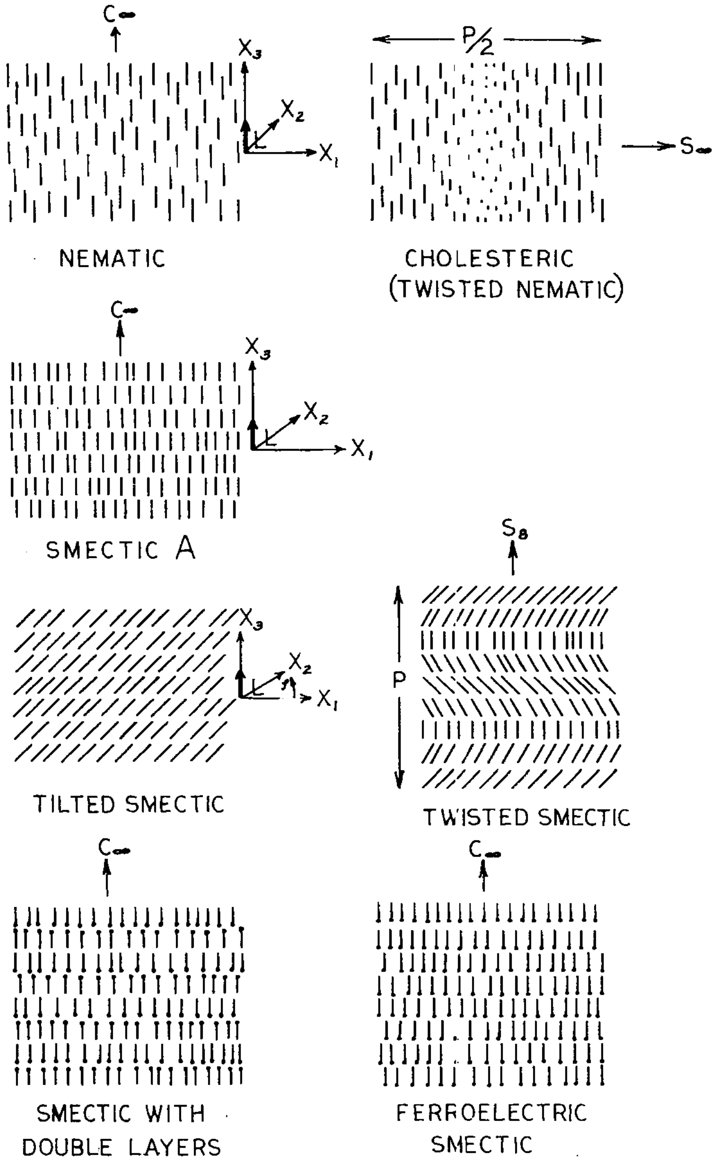


Figure 1. Structures of mesomorphic phases.

Common to all phases shown in Fig. 1 is the parallel orientation of the molecular axes, neglecting the superimposed twist in the cholesteric and in the twisted smectic liquid. The liquid crystalline phases that are most often formed in the melts of organic molecules are the three types to which Friedel[1] limited himself: nematic, cholesteric and smectic *A*.

In nematic and cholesteric liquids the arrangement of the molecular centers is as random as in normal isotropic liquids. The only principle of order is the parallel orientation. There is no entropy difference between the untwisted and the twisted structure. The two liquids are not regarded as different phases although they are very different in their properties.

In smectic *A* we have an additional principle of order. The molecules are arranged in layers. But within the layers the arrangement is random, so that we may speak of a two dimensional isotropic liquid within the layers.

Smectic *A* and the nematic liquid have an infinite fold symmetry axis. Both liquids when uniformly oriented have the optical properties of a uniaxial crystal.

A planar cholesteric structure with a uniform twist as shown in Fig. 1 can easily be obtained in thin layers. It has well-known peculiar optical properties such as a very high optical activity and a selective reflection of circular polarized light.

A general theoretical treatment of its optical properties has not yet been found possible. Only for the particular case of waves with the wave-normal parallel to the twist axis is an exact solution of the Maxwell Equations known. This solution was presented in 1911 by Mauguin[2] and it was applied to cholesteric liquids and discussed in some details by de Vries.[3] The optical properties in this case can be explicitly given as functions of wavelength $\lambda$, pitch $p$, $\epsilon_1$ and $\epsilon_2$.

$\epsilon_1$ and $\epsilon_2$ are equal to the two principle dielectric constants of the untwisted structure. One result of the treatment is that selective reflection of circular polarized light takes place within the wavelength range

$$p\sqrt{\epsilon_2} \leqslant \lambda \leqslant p\sqrt{\epsilon_1} \tag{1}$$

## 3. Elastic Properties of Nematic Liquids and Smectic A

In a nematic liquid and in smectic $A$ the uniform alignment corresponds to an equilibrium structure. However, the uniform alignment is usually not realized in a given sample. We speak then of *deformed* liquid crystals, which means that the preferred orientation changes with the position in space.

Analytically a deformation can be described with the help of a unit vector $L$ which is in any point parallel to the preferred orientation. Following the procedure of Frank[4] we assume that the deformation energy is given by the volume integral

$$E = \int g \, dt \tag{2}$$

where $g$ is an energy density. It is assumed that $g$ is a function of the first derivatives

$$L_{ik} = \frac{\partial L_i}{\partial X_k} \tag{3}$$

When we choose $X_3 \,||\, L_3$ we always have $L_{3k} = 0$ and $g$ as a function of only 6 derivatives

$$g = g(L_{1k}, L_{21}),\ k = 1, 2, 3 \tag{4}$$

An interesting particular case is planar structures in which the preferred orientations are all normal to a given space-fixed axis. Let us choose $X_2$ parallel to this axis and again $X_3 \,||\, L$. For small deformations we find under these conditions

$$g = \tfrac{1}{2}(K_{11}L_{11}^2 + K_{22}L_{12}^2 + K_{33}L_{13}^2) \tag{5}$$

$K_{11}$, $K_{22}$ and $K_{33}$ are the constants introduced by Zocher[5] for splay, twist and bend.

Planar structures are often realized in thin nematic layers with the molecules parallel to the layer plane. The nematic Schlieren texture observable in thin layers is explainable by using the given relation for $g$. This has been shown explicitly for some particular cases by Oseen[6] and Frank.[4]

In smectic $A$ usually only such deformations are admitted in which the layer distances remain unchanged and in which the molecular axes remain normal to the layers. It behaves like a nematic liquid in which $K_{22}$ and $K_{33}$ have very large values, so that for all planar structures with reasonably low deformation energy

$$L_{12} = L_{13} = 0 \tag{6}$$

No twist or bend is allowed, only splay deformations.

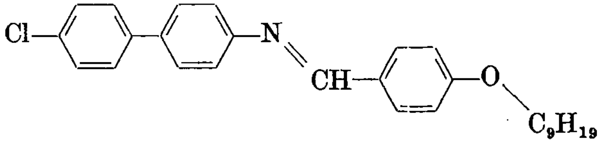
The elastic constants of nematic liquids can be measured. A magnetic field is used for this purpose to induce deformations in a thin layer. The deformations can be observed by the change of the optical properties. The magnitude of the constants[7] is around $10^{-6}$ dyne but they show a remarkable temperature dependence and differ somewhat from one another.

## 4. Some Other Types of Smectic Liquid Crystals

The smectic structures of Fig. 1 are assumed to have three common features: parallel orientation, arrangement of the molecular centers in layers, and within the layers a random arrangement comparable to a two-dimensional liquid. A smectic phase with a tilted structure was first found by Hermann[5] with thallium stearate and thallium oleate. It is a structure with only one plane of symmetry and a two-fold symmetry axis perpendicular to it. This liquid crystal, because of its low symmetry, will be optically biaxial.

The tilted smectic phase does not have a higher kind of molecular ordering than smectic *A*. For a given degree of parallel orientation of the molecules it will have about the same entropy. In fact smectic *A* may be regarded as a special case with vanishing tilt angle. There is no obvious reason why the molecules should generally prefer the normal orientation and we suppose that tilted smectic phases occur fairly often.

The two lower pictures in Fig. 1 represent smectic liquids with a polar orientation of the molecules. Such a polar orientation in thermotropic smectic liquids has been proposed for molecules which are very asymmetrical along their long axes. Gray[9] for instance assumes that 4-*p*-*n*-nonyloxybenzylideneamino-4′-chlorobiphenyl



forms polar layers that are tilted. The molecules may then arrange themselves in double layers without an association in double molecules as is very frequent in lyotropic systems, or in single layers all oriented in the same direction. (The uniform parallel orientation would probably not correspond in the latter case to a stable equilibrium.[4])

Any polar arrangement must have, of course, a strong effect on the electrical properties. In a double layer system a permanent electric dipole moment parallel to the molecular axis will not be influenced by an electric field. It would no longer contribute to the orientation polarization. We may call such a liquid antiferroelectric. In a single layer arrangement the dipole moments along the molecular axes are added. In this case, we have a ferroelectric liquid. But such a ferroelectric liquid has not yet been found.

A polar molecular orientation has a lower entropy than an apolar orientation for the same degree of parallel orientation. It will, therefore, not form so easily. There is not necessarily an entropy difference between a double layer and a single layer system. From this point of view it should also be possible to find ferroelectric smectic liquids. Such a liquid could be formed by a molecule that has a strong tendency to build polar layers and with an interaction between two different molecular ends that is equal to or stronger than the average of the interactions between equal ends.

## 5. On Elastic and Optical Properties of a Tilted Smectic Liquid

The tilted smectic liquid has some interesting similarities with a nematic liquid which are not recognizable at first sight. A unit vector $L$ is not sufficient to describe deformations since there is no longer a rotational symmetry. We have to add at least one additional parameter. We can for instance choose $L$ normal to the layers and use the angle $\phi$ to describe the direction of the tilt.‡ We define $\phi$ as the angle between tilt direction and the coordinate axis $x_1$ (Fig. 1). That means we regard only deformations in which the magnitude of the tilt angle and the layer distance remains fixed.

When we choose again $X_3 \| L_3$ we have

$$g = g(L_{1k}, L_{2k}, \phi_k) \qquad k = 1, 2, 3; \ \frac{\partial \phi}{\partial x_k} = \phi_k \tag{7}$$

The energy density is now a function of 9 derivatives instead of 6.

The interesting particular case is the plane layer structure, that includes only deformation in which the layers remain in equidistant parallel planes. Here $L_{1k} = L_{2k} = 0$ and we obtain for small deformations

$$g = \tfrac{1}{2}(F_{11}\phi_1^2 + F_{22}\phi_2^2 + F_{33}\phi_3^2 + 2F_{13}\phi_1\phi_3) \tag{8}$$

The coordinate system is oriented in such a way that for the chosen point $X_3 \| L_3$ and $\phi = 0$.

One of the cross-terms $F_{13}$ does not generally disappear because of the lower symmetry of this liquid.

When we compare this energy expression with that for a planar nematic structure, we find that the cross-term is the only difference. The tilt direction has taken over the role of the molecular axis. $F_{11}$ is the constant for bend, $F_{22}$ for splay and $F_{33}$ for twist with respect to the tilt direction. We expect that these constants have the same order of magnitude as the elastic constants of nematic liquids, since all of these deformations do not disturb the layer structure.

‡ The tilt direction of a molecular axis at a given position varies due to temperature fluctuations. $\phi$ is the average value over the thermal fluctuations or in other words it gives the tilt direction of the preferred orientation of the molecular axis.

The possible textures in a thin plane layer of such a smectic liquid with the molecular layers parallel to the surface are determined by the derived energy expression. We will expect to find similar Schlieren textures as in planar nematic liquids. The additional cross-term will probably not change the general appearance. Indeed such Schlieren textures can be observed with some smectic liquids[10,11]. We will also expect that the tilt direction at the surfaces can be prescribed by surface action in a similar way to the orientation of the molecular axes in nematic liquids. By rubbing a glass slide, for instance, we should be able to obtain a uniform tilt direction.

Tilted smectic liquids are just as easily twisted as nematic liquids. With enantiomorphic compounds we may accordingly obtain structures with a spontaneous twist corresponding to the twisted nematic or cholesteric liquid.

Both liquids when uniformly twisted have very similar optical properties. For light waves parallel to the twist axis we obtain indeed the same equations for optical activity and selective reflection if the constants $\epsilon_1$ and $\epsilon_2$ are chosen properly. In the smectic liquid we have to set

$$\epsilon_1 = \epsilon_{11} - \frac{\epsilon_{13}^2}{\epsilon_{33}}; \quad \epsilon_2 = \epsilon_{22} \tag{9}$$

$\epsilon_{ik}$ means the components of the dielectric tensor of the untwisted liquid with respect to the indicated coordinate system (Fig. 1).

$$n_1 = \sqrt{\epsilon_1} \quad \text{and} \quad n_2 = \sqrt{\epsilon_2} \tag{10}$$

are, for both liquids, the refractive indices for light propagating along the former twist axis in the untwisted liquid.

It is not possible by observations along the twist axis to distinguish between a twisted nematic and a twisted smectic phase. Or more generally, we cannot easily determine which angle the twist axis with the preferred orientation of the molecular axis forms. So, it may be that some liquid crystals known as cholesteric liquids have a layered smectic structure. It is perhaps appropriate to mention that it has not generally been proven that in cholesteric liquids without a layer structure the twist axis is always normal to the preferred orientation of the molecular axes.

## 6. An " Isotropic " Liquid Crystal

When substances such as cholesteryl nonanoate or cholesteryl myristate, that show a strong twist in the planar structure of their cholesteric phase near the transition to the isotropic liquid, are cooled down from the isotropic liquid phase, they often form a metastable liquid crystal modification that shows no birefringence in thin layers. Gray[10] calls it a homeotropic texture. Lehmann[11] who observed this metastable modification already in 1906 supposed it to be a different type of a liquid crystal. Fergason obtained large quantities of this liquid. It turned out to be optically isotropic.

Figures 2 and 3 show you pictures of an isotropic liquid crystal obtained with cholesteryl *p*-nonylphenylcarbonate.‡ The liquid may remain in this state for weeks and months. Its light scattering at room temperature is much higher than for the normal isotropic liquid state but it is only faintly turbid. Even several centimeters thick layers are still nicely transparent. Its optical activity is also much higher than that of the normal isotropic liquid state. When the liquid is touched with a rod or disturbed as on surfaces, it becomes double refractive (Figs. 2 and 3). These properties show that the optically isotropic liquid crystal has a twisted and deformable molecular structure of high symmetry.

Figure 4 shows an idealized proposal for such a molecular structure. It is assumed that we have an infinite number of singular points at which the molecular orientation is undetermined. The singular points form a space centered cubic lattice. The elementary cell is shown in Fig. 4(a).

The molecular axes of the molecules that are positioned on the edges of the cubes and on the lines through the centers are parallel

‡ *p*-nonylphenylcarbonate, product of ROHM and HAAS COMPANY, Independence Mall, Philadelphia, Pennsylvania.

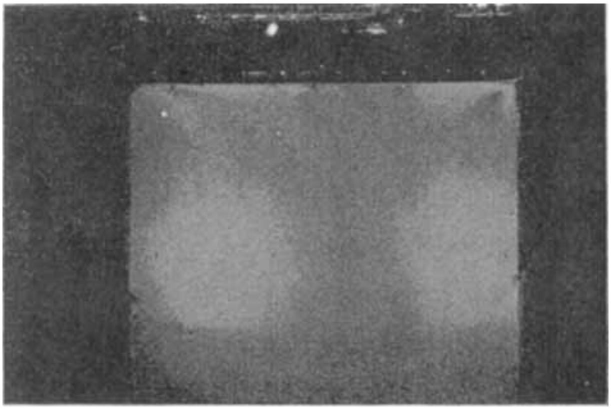


Figure 2. Optically isotropic liquid crystalline phase of cholesteryl *p*-nonylphenylcarbonate in a 2 cm thick glass vessel, observed at room temperature between crossed polarizers with white light, about $\frac{1}{2}$ natural size. It shows a yellow color is due to optical activity. Some double refraction is also present especially around air bubbles and near surfaces. (by J. L. Fergason.)

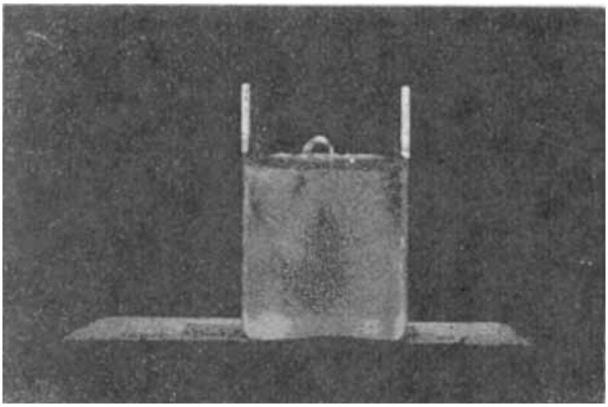


Figure 3. Same as Fig. 2 but in another vessel shortly after touching the surface. (by J. L. Fergason.)

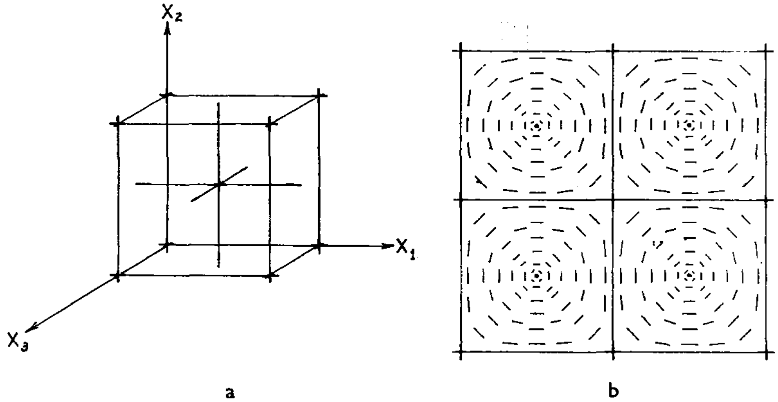


Figure 4. Proposed structure for the optically isotropic modification of a cholesteric liquid crystal.

to those lines. The singular points are the intersections of the lines. In the intermediate space, we will have some twisted arrangement.

A cut parallel to a cube surface and through the singular points is shown in more detail in Fig. 4(*b*). The molecules are normally oriented in the centers of the squares and turn to a parallel orientation when approaching the edges. In this two-dimensional case it is easy to visualize that such an arrangement once formed is relatively stable. If we deform the lattice, it will tend to assume its old regular shape again.

In the three-dimensional case we do not know whether our proposal is near to any structure that really can be assumed by a cholesteric liquid crystal. We are not sure whether it corresponds to a stable solution of the elastic equations of a cholesteric liquid. But there is little doubt that the optically isotropic liquid crystal has some kind of a regular molecular structure with a large elementary cell. The dimension of this cell will probably be neat $p/2$, where $p$ is the pitch of planar cholesteric structure.

The dimensions of an elementary cell will, of course, fluctuate considerably. Thermal motions will cause deformations of the singularity lattice because of the low values of the elastic constants. Such deformations are possible without motion of the molecular centers. The steady thermal fluctuations and the free diffusion of the molecules may also lead to a gradual improvement of the regularity of the lattice after its formation or after a disturbance.

## 7. Twist Waves

In a recent paper[12] on " Liquid Crystal and Living Systems " attention was drawn to twist, splay and bend waves in liquid crystals and it was suggested that a mechanism related to such waves may be important for signal detection and propagation in living systems.

The kind of mechanical waves referred to are unique for liquid crystals. They differ from the familiar mechanical waves in solids and in liquids since no motion of the molecular centers is necessarily connected with them. These are waves in which only the rotational motion of the molecules is essential. Only weak elastic forces come into play in nematic and cholesteric liquids. Correspondingly the wave velocity will be low.

To understand the nature of such waves better, we regard the most simple case: a pure twist wave in a nematic liquid. We start from a uniformly oriented nematic liquid with the optical axis parallel to the $z$-axis of a cartesian coordinate system. The wave propagation shall occur in the $x$-direction which coincides with the twist axis. The molecules remain normal to $x$ during the wave motion. Their position is therefore determined by an angle $\phi$ that describes their inclination against the $z$-axis. This angle is dependent on time and space. It is assumed to follow the equation

$$\phi = \phi_0 e^{-\alpha x} e^{-2\pi i \nu\left(t - \frac{x}{v}\right)} \tag{11}$$

$\alpha$ is the absorption coefficient and $v$ the wave velocity. Each molecule remains in its place but its preferred orientation oscillates with the frequency $\nu$.

The differential equation of this wave can be written

$$K_{22}\frac{\partial\phi}{\partial x^2} - R\frac{\partial\phi}{\partial t} - I\frac{\partial^2\phi}{\partial t^2} = 0 \tag{12}$$

$K_{22}$ is the elastic constant for twist and can be measured. $R$ is a frictional constant. For an estimation of its magnitude we set

$$R = \frac{N}{V}\zeta \tag{13}$$

where $N$ is Avogadro's number, $V$ is the molar volume and $\zeta$ is the frictional constant of a single molecule. It determines the dielectric relaxation time if the influence of the specific potential in a nematic liquid can be neglected. $I$ is an inertial moment density. For its estimation we set

$$I = \frac{N}{V}\theta \tag{14}$$

where $\theta$ is the inertial moment of a single molecule around a transverse axis.

We can now calculate approximately the wave velocity and the absorption coefficient for special substances. With *p*-azoxyanisole, for instance, we have approximately

$K_{22} = .5 \times 10^{-6}$ dyne

$R = 3 \times 10^{-3}$ erg sec/cm$^3$; calculated with $\zeta = 5.5 \times 10^{-25}$ or $\tau = \zeta/2kT = 10^{-11}$ sec

$I = 2 \times 10^{-15}$ erg sec$^2$/cm$^3$

The wave velocity and the absorption coefficient are given by the equations

$$v = \sqrt{\frac{K_{22}}{I}}\frac{\sqrt{2}}{\left(1 + \left(1 + \frac{R^2}{4\pi^2\nu^2 I^2}\right)^{1/2}\right)^{1/2}} \tag{15}$$

$$\alpha = \frac{Rv}{2K_{22}}$$

The wave velocity becomes independent of the frequency for $\nu > 10^{11}$ Hz. We have then approximately

$$V = \sqrt{\frac{K_{22}}{I}} = 1.6 \times 10^4 \text{ cm/sec} \tag{16}$$

$$\alpha = \frac{R}{2\sqrt{K_{22}I}} = 5 \times 10^7 \text{ cm}^{-1}$$

The wave lengths for such high frequencies are already comparable to the molecular dimensions and the continuum theory is no more realistic. In the more interesting lower frequency range with $\nu < 10^9$ Hz we can use the following approximations ($\nu$ in Hz)

$$V = \sqrt{\frac{2K_{22}}{R} 2\pi\nu} = 0.05\sqrt{\nu} \text{ cm/sec} \tag{17}$$

$$\alpha = \sqrt{\frac{R}{2K_{22}} 2\pi\nu} = 140\sqrt{\nu} \text{ cm}^{-1}$$

The inertial forces can be neglected for any accessible frequency because of the extremely strong damping. Within the range of a wavelength, the wave is damped to a very small fraction of its energy ($\alpha = 2\pi/\lambda$).

It means that we will not be able to observe a twist wave in the nematic phase of *p*-azoxyanisole nor probably in any other nematic or cholesteric liquid. Even if the damping should be smaller by several orders of magnitude, it will still be too large for the observation of a wave propagation. The inertial moment density cannot be determined by direct observations, but we can determine $R$, the frictional constant.

Instead of looking for propagation waves, we may ask for the time needed to restore the uniform orientation in a thin layer of a nematic liquid that has been deformed by an external force. If the layer is deformed properly, this time will be equal to the decay time of a standing wave (Equation 18) with a wavelength of twice the layer thickness.

$$\phi = \phi_0 e^{-t/\tau} e^{2\pi i x/\lambda} \tag{18}$$

We find for the time in which such a wave has reduced to $1/e$ of its amplitude.

$$\tau = \frac{R\lambda^2}{4\pi^2 K_{22}} \approx 150\lambda^2 \text{ sec/cm}^2 \tag{19}$$

In a thin layer of 0.1 mm thickness $\tau = 0.06$ sec. In spite of the large damping, the equilibrium will restore itself reasonably fast.

It is well known that normal oriented nematic layers observed with crossed polarizers show light flashes when they are touched. The fast reappearance of darkness shows that the equilibrium is in fact restored in a fraction of a second. It should not be too difficult to make measurements on such layers and determine more reliable data that help to understand the dynamical properties of nematic and cholesteric liquids.

## Acknowledgement

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