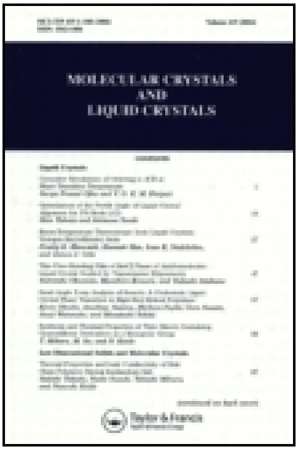


Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

I. Some Topics of Liquid Crystals yet to be Discussed

Hans Zocher [a]

[a] Laboratórios da Produção Mineral Rio de Janeiro, Brasil

Version of record first published: 29 Aug 2007.

To cite this article: Hans Zocher (1969): I. Some Topics of Liquid Crystals yet to be Discussed, Molecular Crystals, 7:1, 165-175

To link to this article: http://dx.doi.org/10.1080/15421406908084870

Molecular Crystals and Liquid Crystals. 1969. Vol. 7, pp. 165–180

Printed in Great Britain

I. Some Topics of Liquid Crystals yet to be Discussed

HANS ZOCHER

Laboratório da Produção Mineral
Rio de Janeiro
Brasil

The science of liquid crystals is a part of general crystallography, which is the physical chemistry of crystals and related objects. Nowadays it is generally accepted that the so-called " liquid crystals " are neither real crystals nor real liquids. Whereas the misunderstandings produced by the name " liquid crystals " may be considered as overcome, this name has become accepted as historically established, indicating the referred matter to all who may be interested. In future denominations closer to the real nature of these objects may become more popular. The name " mesomorphic states " is already widespread. There is no doubt about the accurate meaning of " meso ", the intermediate position between amorphous and crystalline, but " morphic " and " state " mostly indicate the relation to the structure only, the relation to the space coordinates, whereas in physics, physical chemistry and generalized crystallography we have to deal with the time coordinate as well, with processes such as dissolution and growth, with equilibrium and temperature. So, the relation to thermodynamics would be still better expressed by the word " mesophases ", since the definition of " phase " is: a homogeneous system in thermic equilibrium. It is symmetric in relation to time.

Of these so-called " liquid crystals " only two types of phase structure are well known: the nematic and the smectic. In the real crystals the coordinate transfer from one molecule to the next is characterised by the periodicity of all three translations and all three rotations in space. In the smectic state only one translation period and two rotational periods exist. And in the nematic state only the two rotational periods remain. In other words, the smectic phases show a layered structure, and the nematic phases a fibrous one. Some authors[1] maintain that certain substances exhibit a higher number of different phases. Principally it is not excluded that one substance may present more than one smectic or more than one nematic phase. For example in one smectic phase the translation period may be twice that in the other.

" Liquid crystals " exhibit very uncommon phenomena and it is not surprising that some misleading theories have been put forward. C. Hermann,[2] for example, set up the hypothesis that nematic phases consist of chains of molecules and smectic phases of nets of molecules, such as may occur in the space lattices of crystals. Within those chains or nets the molecules would be arranged with definite translational and rotational periods, whereas the chains or nets as such would be merely parallel to each other, but otherwise disposed at random. However such systems would be mere unstable structures, not phases in thermodynamic equilibrium. The lack of thermal motion of the essentially unlimited elements makes the restoration of the supposed disorder impossible. Any transition of two elements into a position of an energy minimum is irreversible. Such systems are time asymmetric. This example shows neatly the necessity to consider movements in crystallography, the reference to the time coordinate.

Another theory[3] not in accordance with the fundamental facts of observation, but even up to this date used for the evaluation of experimental findings, is the " swarm " theory. It refers only to easily movable nematic phases and ignores any relationship to glassy nematic and smectic phases. The basic arguments of this theory are the macroscopically visible turbidity of nematic phases and the Brownian motion seen in the polarising microscope. From these observations was derived the concept that substances in the nematic state consist of swarms of molecules in parallel position, and that these swarms are distributed at random in consequence of the thermic movement. That is to say that the bulk of the nematic mass would be isotropic. The always present optical anisotropy which gave rise to the discovery of the liquid crystals and was studied so intensely, is considered as a small secondary effect, produced by the action of the surrounding walls. This action is supposed to be restricted to a very small reach, perhaps to some few hundredths of a millimeter only. The nature of these forces is not explained. They cannot be molecular forces of the London–van der Waals type, which are known to act only to a distance of a very few Å. Even freely suspended layers, as G. Friedel[4] showed, in contact with air only exhibit the same birefringency of the same orientation.

Indeed, the existence of the supposed isotropic inner layer could never be proved. On the contrary, quantitative measurements[5] showed that the birefringency is the same throughout layers of half a millimeter thickness and more, in homogeneous preparations as well as in simply distorted ones. Therefore, the action of magnetic or electric fields are not to be derived by equations containing the molecular thermic energy kT (Boltzmann's constant times the absolute temperature) in equilibrium with the field energy like in Langevin's theory of ferromagnetism.

A complete picture of the structure of nematic phases and their behaviour under the influence of mechanic, magnetic and electric forces is given by the " distortion " theory.[6] The basic concept is that one has to deal with phases in the sense of thermodynamics. That means that the characteristic molecular structure is the same throughout the whole volume. According to the basic parallel orientation of the molecules, nematic phases may be really liquid against shearing forces producing translational movements only, without changing the direction of the infinitefold symmetry axis. The resistance then is that of viscosity only, anisotropic of course, i.e. different for movements parallel and movements perpendicular to the axis. But forces producing deformations, that is a change of direction, must encounter elastic resistance.

Three types of deformation are possible: (1) torsion, (2) flexion, and (3) divergency of the direction of the axis. Starting from one volume element with fixed axis and the deformation axis perpendicular to it the neighbouring volume elements are situated in the first case upon the deformation axis, in the second upon the symmetry axis, and in the third upon the axis perpendicular both to the deformation and the symmetry axis. A homogeneous torsion is easily produced. Let us consider a circular cylinder of the cross-section q and length l containing a nematic mass with its symmetry axis from top to bottom in one direction in the plane q. Gyration of the bottom plane with respect to the top plane by an angle ϕ (not too large) must produce a torque D, according to a Hooke's law:

$$D = K_t \cdot \frac{q}{l} \cdot \phi \tag{1}$$

The energy for the production of this deformation is

$$E = D \cdot \frac{\phi}{2} = \frac{K_t}{2} \cdot \frac{q}{l} \cdot \phi^2 \tag{2}$$

and the energy density

$$\frac{E}{ql} = \frac{K_t}{2} \left(\frac{\phi}{l}\right)^2 \tag{2'}$$

K_t, a sort of elasticity modulus, has the dimension of a force, or energy divided by length.

For flexion and divergency, occurring mostly together in the same volume element, the analogous moduli K_f and K_d are defined. In a first approximation K_t, K_f and K_d may be considered as nearly equal, whereas in smectic phases K_t and K_f, referring to deformations disturbing the equidistancy of the layers, are much greater than K_d, so that only divergency occurs, producing conic configurations.

The three elasticity moduli of nematic phases are generally very small indeed, of the order of 10^{-6} dynes, comparable to diamagnetic forces on organic substances. In the case of the twisted cylinder, one of 1 cm^2 cross section, of 1 cm length and with the angle 1 radian $\cong 60°$ between top and bottom, the torque would be 10^{-6} dynes times 1 cm, that is, one millionth of the weight of a milligram times 1 cm!

This small value explains the difficulty in obtaining homogeneous layers of more than half a millimeter thickness. Each impurity on the glass surfaces, each tiny particle of dust may produce far-reaching deformations. Furthermore, it is difficult to avoid the formation of the rather stable thread-like discontinuous deformations, the "nemas", from which the name "nematic" was derived. In smectic phases they have the shape of confocal ellipses and hyperbola branches. In crystalline disordered masses, e.g. in rocks like marble, the inhomogeneities are bidimensional interfaces instead of linear nemas. Around each such thread the direction of the anisotropy axis varies continuously by an angle of $\pm n\pi$, n being mostly 1 or 2. The structural inhomogeneity produces strong diffraction of light and may cause macroscopic turbidity.

But even the fluctuations of thermic energy may produce observable deformations in correspondingly small regions, visible as turbidity macroscopically and in the polarising microscope as weakly birefringent scintillations. This phenomenon was studied on acetoxybenzalazine by Tropper[7] experimentally, and by Fürth and Sitte[8] theoretically, who came to the conclusion that the thermic motion prevailed over the general orientation. The authors were not aware of the much stronger birefringency of the investigated layers visible only in directions inclined to the microscope axis.

Summarizing we have to conclude that the thermic fluctuations are of negligible significance compared with the strong inherent anisotropy, which varies according to the elastic constants.

In spite of the difficulty to avoid deformations by impurities or nemas, it is possible to prepare homogeneous layers of half a millimeter thickness or more and over a practically unlimited area. The nematic phases of some substances orient themselves with the symmetry axis perpendicular to the surface of glass, especially if this has previously been treated with acid. Most substances appear in the position of the symmetry axis parallel to the surface. In order to get the same azimuth over the whole area the production of anisotropy of the glass surface by rubbing in one direction with some soft material, such as cottonwool or buckskin for example, proved to be very useful. In such homogeneous nematic layers a uniform deformation may be produced by an external magnetic field from which the elastic moduli K_t, K_f and K_d may be derived. It is evident that these three elastic constants are of fundamental significance for all forces acting upon nematic layers. In spite of this fact only a few measurements to evaluate them have been made up to now. The moduli may be determined by the least magnetic field strength H_0 necessary to produce a deformation of a nematic layer of given thickness. The theory shows, and the experiments—first performed by Fréedericksz[9]—confirm, that the product of field strength H_0 and thickness Z_0 is constant:

$$Z_0H_0 = \pi\sqrt{\frac{K}{\kappa_1 - \kappa_2}} \qquad \text{or} \qquad K = \frac{Z_0{}^2H_0{}^2}{\pi^2}(\kappa_1 - \kappa_2)$$

κ_1 and κ_2 are the magnetic susceptibilities parallel and perpendicular to the symmetry axis. Observing a wedge-shaped layer between a plane slide and a lens placed between crossed polarisers in the position of extinction, one finds that the central part remains dark, whereas separated by a sharp line from the outer part which shows bright interference rings. The case is analogous to the bending point of a solid cylinder under the action of a rising load. Up to a certain force there is no bending, because the elastic deformation energy would be higher than the work done by the applied force. The three constants K result according to the orientation on the glass surface and the direction of the magnetic field applied perpendicularly to the symmetry axis.

With the help of the distortion theory it is possible to calculate the direction of the molecular axis at any distance from the glass surface in a layer under the action of the magnetic field under any angle. And from this, in turn, one may calculate the average electric capacity, as well as the optical anisotropy, that is birefringence and dichroism.‡

The first approximation, obtained supposing that K_f and K_d are equal, gives results already in very satisfactory agreement with the observations.[6] The consideration of differences between K_f and K_d requires the application of the more complicated vector calculus used by C. W. Oseen,[10] starting from the same basic concept of the distortion theory.

As to the thermic fluctuations visible in the absence of a magnetic field, which are to be considered as of secondary importance, the following may be added: The deformations produced by the thermic fluctuations may be estimated by putting the molecular energy kT (k = Boltzmann's constant, T = absolute temperature) equal to the elastic deformation energy of a sphere (radius $= r$) with a deviation of the angle ϕ in the center against its surroundings.

$$E = \frac{4}{3}\pi r^3 \times \frac{K}{2}\left(\frac{\phi}{r}\right)^2 \cong 2r\phi^2 K = kT$$

If $T = 400°$ abs. = 127 °C, then

$$2r\phi^2 \cong \frac{1.6 \times 10^{-16} \times 400}{10^{-6}} \cong 6.4 \times 10^{-8}$$

In the case of a diameter of 10^{-5} cm, corresponding to more or less 100 molecules in a row, ϕ comes to $\sqrt{64 \times 10^{-4}} = 0.08$ radian or nearly 5°. This may produce a well-defined visible light spot between crossed polarisers.

Recent observations showed stronger scintillations in the neighborhood of stronger deformations from impurities and nemas. This perhaps may be due to a deviation from Hooke's law, the elastic resistance being smaller for larger angles between the molecules.

‡ According to the swarm theory the electric capacity of a nematic layer would not be changed by the introduction of a glass lamella dividing it into two layers. This was done by W. Kast in his experiments (*Ann Physik* **83**, 391, 1927), as he told me. The observed influence of the magnetic field strength corresponds indeed to the deformation of two different layers.

It is to be noted that the fluctuations are those of angular deviations only, not those of density. The modulus M of the volume elasticity of liquids is many times higher than these distortion moduli:

$$M = p\frac{V}{\Delta V} \cong 10^{10}\ \mathrm{erg/cm^3}$$

(p = pressure, v = volume, ΔV = diminution of volume)

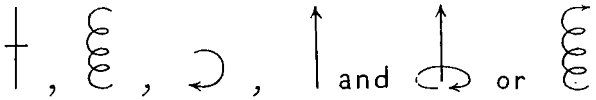
The angular distortion is the reason for the fact that the lateral diffraction of light differs strongly from ordinary light scattering. The total optical density is the same throughout the medium, differences exist only for different directions of vibration. On the same inhomogeneity one vibration is diffracted on a medium of higher optical density, the perpendicular vibration on one of lower. The first ensues under phase reversal, the second without reversal. The resultant of the two is turned against the incident vibration. Indeed Chatelain found that ordinary light is mainly diffracted as extraordinary, and extraordinary light as ordinary.

As to the symmetries or asymmetries of liquid crystals in general, it is to be noted that an asymmetry has not only a geometric significance, but corresponds to a physical effect, whereas symmetry means the absence of this effect.

Since liquid crystals exist always at higher temperatures than crystals, at states of higher entropy, their symmetry is higher than that of the crystals. The second law of thermodynamics is indeed the law of symmetry, of molecular disorder. In this connection symmetry corresponds to disorder, asymmetry corresponds to order. The higher the molecular distances according to temperature or dilution, the more the asymmetries vanish.

The asymmetry classes of crystals[11] are characterized by the five asymmetries—anisotropy, enantiomorphism, circularity or axiality, polarity, and triasymmetry—represented by the symbols on page 173.

Anisotropy, the lowest degree of asymmetry, is characteristic for all liquid crystals. Enantiomorphism, corresponding to optical torsion, mostly arises from the same asymmetry in the



molecules. It may appear in the nematic phases producing the "cholesteric texture". This is not a third type of phase, but a nematic phase with a spontaneous torsion, which may change with temperature or composition from laevo- to dextro-spiral texture, impossible in smectic phases. Here the equidistance of the periodic layer structure excludes torsion and flexion, permitting only divergency. In general one has to distinguish between "phase structure" and "preparation texture", which may be difficult in some cases. The existence of more than two types of mesophases, as indicated by Weygand, is doubtful, and may be simulated by texture differences.

Circularity, not characterized by a simple physical effect, does not appear in liquid crystals. Magnetic dipoles are circularly asymmetric indeed, but it is an asymmetry in time, indicating the rotation of electric charges, independent from any spacial circular structure. Even crystals, which may be ferromagnetic, cannot show pyro- and piezo-magnetism connected to a circular lattice structure. Likewise, liquid crystals exhibit magnetic anisotropy only, but never an inherent magnetic polarity, as M. Born supposed.

Electric polarity, as in crystals like tourmaline, may be considered as essentially possible in liquid crystals. Their molecules certainly may contain electric dipoles, but it is very probable that the number of dipoles in one sense of the symmetry axis and in the opposite is equal, since the energy of compensation is high as compared with other molecular forces. So pyro- and piezoelectric phenomena are not only unknown but very improbable. Therefore, the rotational period of the polar molecule coordinates is probably 180° and not 360°.

A very useful trick to avoid textural inhomogeneity in nematic layers is the production of surface anisotropy of glass[12] and other materials by rubbing in one direction. It is not an effect on soft impurities like fat, as Chatelain[13] believed, but a deformation of the glass surface itself. It may be produced also by breaking, a process spread over areas of several square centimeters and too rapid for any impurity to interfere. Also Tammann[14] showed that at the softening temperature of glass the anisotropy disappears. It results probably from the orientation of —O—Si—O—Si— chains on the surface, possibly fixed on one end only, an action which could be called a "molecular hair combing". Some observations indicated that there exists not only anisotropy but polarity as well: orientation by cleaving or rubbing in one direction and in another perpendicular to the first may produce an anisotropy in the direction of the resultant. This should, however, be more thoroughly investigated, since this result was not obtained in some instances.

The easiest way to prove the surface anisotropy of glass is that by the dichroism of nematic dyestuffs there deposited. Dreyer,[15] the inventor of the Polacoat process, used this method and showed that a great number of dyestuffs exist at least transiently as a nematic phase, afterwards going over into a crystalline state. It may also happen that the film is at first isotropic, revealing dichroism only after breathing at it.

It is easily verified with these nematic dyestuff layers that the rule of the positive birefringence is not always valid. A strong dichroism must always be accompanied by a birefringence of the same sign for frequencies lower than the dichroism maximum, and of the opposite sign in the region of higher frequencies.[14] This rule results from the anomalous dispersion of the refractive index, which shows a maximum on the long wave side and a minimum on the other side of the absorption maximum, where it crosses the index line of the unabsorbed or less absorbed vibration. Babinet's rule, that birefringence and dichroism have the same sign, is valid for yellow dyestuffs only.

Cholesteric phases are generally considered as negatively birefringent, but this refers only to the investigation in the direction of the textural screw axis. The twisted nematic phase itself is of positive double refraction in relation to its molecular structure.

Real negative birefringency occurs in smectic phases of soaps of very short fatty acids and in highly hydrated phases of lecithin and similar substances. The smectic layer structure probably produces a negative birefringence of form prevailing over the positive component, which diminishes more rapidly with rising temperature or rising water content. The complete compensation in one part of the spectrum produces anomalous interference colours with optical isotropy shifting to the blue end of the spectrum.

REFERENCES I

1. Weygand, C. *et al.*, *Z. phys. Chem.* **50B**, 124 (1941).
2. Hermann, C., *Z. Krist.* **79**, 186 (1931).
3. e.g. Ornstein, L. S., *Z. Krist.* **79**, 90 (1931).
4. Friedel, G., *Ann. de phys.* (9) **18**, 273 (1922).
5. Zocher, H. and Ungar, G., *Z. f. Phys.* **110**, 529 (1938).
6. Zocher, H., *Trans. Faraday Soc.* **29**, 945 (1933).
7. Tropper, H., *Ann. d. Phys.* (5) **30**, 371 (1937).
8. Fürth, R. and Sitte, K., *Ann. d. Phys.* (5) **30**, (1937).
9. Fréedericks, V. and Zolina, V., *Z. Krist.* **79** 255 (1931).
10. Oseen, C. W., *Die anisotropen Flüssigkeiten*, Berlin (1929).
11. Zocher, H. and Török, C., *Z. f. Phys.* **139** (1954).
12. Zocher, H. and Coper, K., *Z. phys. Chem.* **132**, 295 (1928).
13. Chatelain, P., *Bulletin Soc. Fr. min.* **66**, 105 (1943).
14. Tammann, G. and Elsner v. Gronow, H., *Z. anorg. allg. Chemie* **201**, 34 (1931).
15. Dreyer, J. F., *Phys. and Coll. Chem.* **52**, 808 (1948).
16. Zocher, H. and Jacoby, F. C., *Kollchem. Beih.* **24**, 365 (1927).