

Liquid Crystals

Proceedings of an International Conference

December 3-8, 1979

Edited by

S. CHANDRASEKHAR

LIQUID CRYSTALS

Proceedings of an International Conference held at the
Raman Research Institute, Bangalore, December 3 — 8, 1979.

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P R E F A C E

This volume forms the Proceedings of a Conference on Liquid Crystals organized at the Raman Research Institute, Bangalore, from December 3-8, 1979. About a hundred scientists from sixteen countries, including the USSR and China, participated in the Conference and 84 papers were presented.

The opening paper in the proceedings is by Professor Sir Charles Frank on What is the Director of a Liquid Crystal? - a consideration of the definitional status of some of the basic concepts of liquid crystal theory. This is followed by a paper by Professor W. Helfrich describing the three classes of thermotropic liquid crystals - columnar (or canonic, discovered in 1977), smectic and nematic, representing singly, doubly and triply melted phases - in terms of fluidity and defects. Probably the two most thoroughly discussed topics at the meeting were mesophases of disc-like molecules and the re-entrant phenomenon, and the proceedings contain a number of important and up-to-date contributions on both of them. In addition, the volume includes papers on practically all other aspects of the physics and chemistry of liquid crystalline materials - their preparation, their structures, their thermodynamic, optical and mechanical properties, and their response to external fields. The variety of topics covered emphasizes once again the remarkable growth of activity in this area of research and the impact that it is having on so many disciplines.

I should like to take this opportunity to place on record our sense of gratitude to a number of organizations for their very generous support: the Department of Science and Technology, the Indian Academy of Sciences, the Raman Research Institute, the Department of Atomic Energy, the University Grants Commission, the Council of Scientific and Industrial Research, Bharat Electronics Ltd., Indian Petrochemicals Corporation Ltd., Spectrospin AG, Hindustan Lever Ltd., Larsen & Toubro Ltd., Dadha Pharma Private Ltd., and the Immu-Kimia Laboratory. Finally, it is a pleasure to express my thanks to all my friends at the Institute but for whose encouragement and help this conference would certainly not have taken place.

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WHAT IS THE DIRECTOR OF A LIQUID CRYSTAL?

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The director should not be called the direction of the molecules, nor the average direction of the molecules. The former is a term incapable of exact definition, except when the molecules possess symmetry axes, which is rarely the case: and there are uniaxially ordered sets of directions for which the average direction is indeterminate.

The director, whenever exactly definable, is a symmetry element: the symmetry axis for the orientational distribution of any direction which can be associated with the molecule: or the normal to a mirror plane for these distribution functions.

Where there is a complex curvature, definitions of the director by symmetry fail, and it is only definable by a limiting process: with the consequence that the elastic theory of liquid crystals is strictly speaking limited to being a small strain theory.

For smectic-C, there is no director with any correspondence to "the direction of the molecules".

Several of the concepts commonly used in liquid crystal theory, including order-parameters, are ill-defined unless the molecules possess symmetry axes, which usually they do not. Since there are indications that molecular asymmetry promotes occurrence of mesomorphs, this carries a danger of introducing essential error.

INTRODUCTION

Most publications about liquid crystals will be found to make reference, somewhere or another, to "the direction of the molecules". Sometimes the phrase used will be "the average direction of the molecules". The latter sounds the more careful way of putting it, but in fact raises a second question: "How do you define an average direction?", as well as "How do you define the direction of a molecule?".

Sometimes the term used will be "the director". That is clearly a technical term, and its use carries the implication that it has a precise definition, on which the author and the reader, if properly educated in the subject, would be agreed. But is it so? Often enough, I think, if you asked either the author or the reader, he would tell you it is a synonym for the average direction of the molecules, and take you no further than that.

CONTINUUM THEORY

There is one context in which I suppose the director is well defined. That is in mathematical continuum theories of anisotropic fluids, where it is

assumed, as an axiom of the theory, that in every small neighbourhood of the fluid there is an associated unique direction, determined by molecular arrangement in some unspecified way, which we call a director. It is conveniently represented by a vector, \underline{n} , let us say, with the admission that its sign is ambiguous. We assume that the components of \underline{n} vary continuously in space and time, that the free energy depends on their gradients, which are measures of the curvature of the director field, and that the rate of creation of entropy depends on their time derivatives, together with those of other vectors which are lines connecting neighbouring fluid elements. That way, we obtain a self-consistent system, conforming, at least to a very good approximation, with the real behaviour of, let us say, a nematic fluid. We cannot, however, remain content with this, as our persistent reference to the direction of the molecules shows. We can elaborate the continuum theory, for example by introducing coupling coefficients to electric fields: in doing so we inevitably interpret these by reference to molecular properties and orientations: usually through some simplified assumption about what they might be rather than what they really are. It is easy enough to suppose you know what you are talking about when discussing pictures in which each molecule is represented by a straight line, or a rod, or perhaps a banana: but real molecules are none of these things. We easily get ourselves into sophisticated theories the concepts of which belong to models simulating the liquid crystal, rather than the real thing.

SYMMETRIC MOLECULES

There are some molecules with a unique and precisely definable direction, in which all the atoms lie in a straight line. Such are carbon disulphide, SCS, acetylene, HCCH, diacetylene, HCCCCH: unfortunately, I think none of these form mesomorphs. Quinquephenyl, five benzene rings in a row, is a nematogen in which the molecule has three diad axes of symmetry, one of which may be singled out as the long axis, to be called the direction of the molecule. Para-cyano-diphenyl has one diad, which is also its long axis, but to produce the many valuable mesomorphs based on this molecule we add a symmetry-breaking aliphatic or etheric tail in the para position. This is rather general. I suppose that rigid molecules of high symmetry too readily form true lattice-crystals, and these symmetry breaking rather flexible tails are needed to lower the stability of the true crystal, to permit the mesomorphs to appear.

MOLECULAR AXES

It is certainly the case that the vast majority of mesomorphogenic molecules have no symmetry axes whatever. How then shall we define their direction? For many years "the long axis" has given us an imperfect but useable working concept for this purpose. One always kept in mind the possibility that there might be liquid crystals in which it would be the shortest rather than the longest molecular axes which would be strongly correlated to one direction.

This very likely occurs in the tars of coking-coal, but chemically well-defined examples of it have now been produced here in Bangalore. When the molecule is planar, the shortest axis is well-defined as the normal to the plane: but they won't always be. The long axis might be more precisely defined as the line joining the remotest pair of atoms in the molecule: or, more usefully I think, as the line joining the remotest pair of atoms in the rigid portion of the molecule, without regard to flexible appendages. Moments of inertia are mathematically convenient, but not particularly relevant, I think, to the liquid crystal. The axes of the ellipsoid of diamagnetic susceptibility are well-defined, and truly very relevant to actual experimental observations. The axes of electric polarizability of the molecule are even more directly related to the experimental observations of birefringence etc., which we can make on liquid crystals. But here we have the internal field complications arising from the fact that these electric polarizabilities are large, and each molecule feels not only the applied field but also the induced field from all surrounding molecules. The apparent polarizability of a molecule in the condensed phase is not that of the bare molecule but of a pseudo-molecule, dressed with its environment, and variability in that environment is something we can be interested in. Refractive indices vary with frequency, and so, unless the molecule is symmetric, some variation in the axes of molecular polarizability with frequency must be anticipated. Other optical ways of observing molecular orientation, such as dichroism or fluorescence, are subject to similar complications. Nuclear magnetic resonance experiments give information about the vectors joining pairs of atoms. In a molecule of N atoms there are $N(N-1)$ of these, though only some of them can be readily singled out for NMR study. Diffraction of X-rays, or other short-wave radiation, yields a complex overlay of information about positional correlation of atoms, from which it is hard to extract information about molecular orientation in uncontaminated form: though with neutron scattering intermolecular effects can be eliminated by using a dilute solution of deuterated molecules in a protonated host.

To summarize then, there is an infinite number of ways of defining a molecular axis \underline{M}_i , a direction determined by the orientation of the molecule, and a fairly large subset of these are open to observation of some statistical information about their distribution functions. A number of these \underline{M}_i may merge together into one direction if the molecule is symmetric, but in general they are all distinct. Most mesomorphogenic molecules are asymmetric, and that is probably no accident. Any theory of liquid crystals which eliminates this molecular asymmetry is liable to exclude an essential element of the truth.

What, then, is the director? It is not the average direction of the molecules. Direction of the molecules does not in general have any exact meaning, and we have not yet considered how to define the average of a direction. The director is, whenever it can be precisely defined, a crystallographic symmetry element, the axis of symmetry for the orientational distribution function for any chosen molecular axis \underline{M}_i .

THE SYMMETRY ELEMENTS OF LIQUID CRYSTALS

For a nematic in its ground state that is very straightforward. By every observational test, and therefore we may assume for every statistical property of its internal structure, it is uniaxial, with infinite rotational symmetry about its unique axis, \underline{n} , and every plane normal to that axis is a mirror plane. So is every plane parallel to that axis. The orientational distribution function for any molecular axis \underline{M}_i must therefore be expressible by a series of even zonal spherical harmonics. However, in the elastic theory we consider non-uniformity of \underline{n} , and that implies that the symmetry is spoilt. For curvatures uniformly of one kind enough symmetry is preserved for the purpose of the definition. Uniform bend preserves mirror planes normal and parallel to \underline{n} . Uniform but biaxial splay preserves mirror planes in two orthogonal orientations parallel to \underline{n} . Uniform twist corresponds to the cholesteric case which I shall consider presently: \underline{n} remains well defined, but all mirror planes are necessarily destroyed. Hence with mixed curvatures we are left with no symmetry test strictly applicable for identification of \underline{n} . We can only say, I think, that as we shrink the volume element under consideration it becomes less and less distinguishable from a volume element from a sample with uniform \underline{n} , particularly if the curvatures are not too strong. We have similar subtle difficulties in the elastic theory of solids, where the simpler definitions of strain are only valid in the limit in which strains are small. I think we have to conclude that the elastic theory of nematics is only strictly valid as a small-strain theory. I wish I knew how to improve on that, but I don't.

For the cholesteric in ground state, or the uniformly twisted nematic, the symmetry elements are a continuous screw axis, of pitch p , and a periodic translation of $\frac{1}{2}p$ in the same direction, together with diad axes at intervals of $p/4$ in every plane parallel to the screw axis, alternately of two kinds, respectively parallel and orthogonal to \underline{n} , which is everywhere orthogonal to the screw axis. The $\frac{1}{2}p$ translations, or alternatively the diads orthogonal to \underline{n} , perform the function of ensuring that the sign of \underline{n} is ambiguous, like the diads, or mirror plane orthogonal to \underline{n} in the ground state nematic. The diads parallel to \underline{n} tell us that we are not entitled to expect purely zonal spherical harmonics in the orientational distribution functions for molecular axes, but more general distribution functions of two-fold symmetry about \underline{n} , requiring even-even tesseral spherical harmonics for their description. This applies particularly for cholesterics of very short pitch.

What about smectics? There is no problem about defining \underline{n} for smectic-A: it is both the normal to the layering, and an axis of infinite rotational symmetry for orientational distribution functions as in a nematic. But smectic-C is quite another case. In the conventional models in which molecules are represented as rods, they are presented as parallel and inclined by an angle θ to the layer-normal, and this θ may be employed as a symmetry-breaking variable parameter in theories of the phase-change smectic-A to smectic-C. Here I believe we are introducing a "direction of the molecules" which has no exact definable meaning. The symmetry elements are the periodic translation \underline{l} , normal to the layers, two discrete sets of diads orthogonal to \underline{l} , in a single plane parallel to \underline{l} , one set centring the layers and the other

set between them, and a mirror plane orthogonal to these diads. For smectic-C*, the cholesteric-related optically active equivalent of smectic-C, this mirror plane disappears: but the diads of both kinds are still present, and now recur with a translation period equal to the pitch of the screw rotation, when this is commensurate with the density-layering. The direction of these diad axes is now the only direction we can have as a symmetry axis for orientational distribution functions. These should be of two-fold non-polar symmetry, comprising even-even spherical harmonics, among which the zonal harmonics are present, but cannot be expected to predominate. The symmetry axis of these orientational distribution functions is now orthogonal to the imagined molecular directions in the model with rod-molecules. Whether it is now useful to call it a director I very much doubt. I think it is better to say that for smectic-C neither the director nor the direction of the molecules is an even approximately useful concept, and quite other descriptive parameters should be sought.

AVERAGE DIRECTIONS

I raised the question of defining an average direction. Clearly, when we have equal numbers of vectors pointing opposite ways, we do not do it by adding the vectors and dividing by their number, since that must give zero. We can define an average direction as that from which the sum of the squares of the deviations, θ , is minimum, with the convention that of the two alternative angles between a pair of directions, we always choose $\theta < \pi/2$. A neater avoidance of the 90° discontinuity, with essentially the same result in simple cases, is obtained by choosing that direction which minimises $\sum \sin^2 \theta$, instead of $\sum \theta^2$. That is the same as maximising $\sum \cos^2 \theta$, and likewise the same as maximising

$$S_2 = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle,$$

which is the second zonal spherical harmonic.

Now, quite generally, when we are dealing with orientational distribution functions which have an axis of symmetry, S_2 will either be maximised or minimised on that axis. When it is maximised, meaning that the directions are preferentially parallel to the symmetry axis, the average direction is meaningful, and coincides with the symmetry axis. When it is minimised, the concept "average direction" may have become meaningless, e.g. if the molecular axes concerned are preferentially transverse to the symmetry axis, and S_2 has equal maximal values in every equatorial direction.

ORDER PARAMETERS

S_2 , evaluated on the symmetry axis, is often called "the order parameter". It is an error to suppose that it should have the same value if determined, say for the greatest principal molecular axis of electric polarizability or the least principal axis of diamagnetic susceptibility, except when molecular symmetry causes these molecular axes to coincide. I should suppose that for typical asymmetric mesomorphogenic molecules, 10% discrepancies should be unsurprising, and for some of the potentially observable molecular axes much