

Liquid Crystals

BY holding a conference on "Liquid Crystals and Anisotropic Melts" at the Royal Institution on April 24-25, the Faraday Society has rendered a service not only to the cause of international science but particularly to science in Great Britain, for it has long been a regrettable fact that this interesting and important subject has been practically unknown here. So much so, that in the symposium volume on liquid crystals published by the *Zeitschrift für Kristallographie*, there was not one contribution from an English worker in the field. In part, this neglect has been due to the apparent multiplicity and complexity of the phenomena of liquid crystals, and in part to the prolonged and violent controversies to which their interpretation gave rise. This is a situation to which the holding of the Faraday Society conference has definitely put an end. We now have, as a result of the discussions, a fairly coherent picture of the nature and importance of liquid

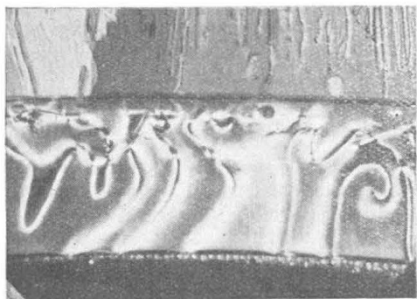


FIG. 1.—Anisaldazine showing solid crystals, nematic liquid crystals with singular points, and isotropic liquid.

crystals: and though differences still remain, they will now, far more than in the past, lead to fresh fields of research rather than to controversy.

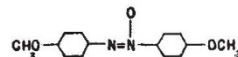
Since their discovery by Reinitzer in 1888, and the pioneer work of Lehmann, Friedel, and Vorländer—of whom the last was present at the conference—liquid crystals have been intensively studied chemically, physically and mathematically, and their essential nature is now well established. The great majority of known chemical substances on melting pass abruptly at a sharp temperature from a crystalline solid with well-defined anisotropic properties to a mobile liquid in every way—optically, magnetically, electrically—isotropic. In some substances, however, a number of intermediate states are interposed between these ultimate ones.

The properties of these states are just as definite as those that distinguish the crystalline and liquid states, but they partake, in different degrees, of the nature of both. Their most striking character, though by no means an essential one, is their optical anisotropy, which betrays itself in their spontaneous turbidity in thick layers, and by the colours they show between crossed nicols. Another

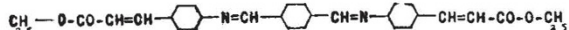
significant property is the possession of a variety—bewildering at first—of internal structures, threads, rods, cones, stepped and faceted drops, oily streaks and iridescent colours, recalling the appearance of biological rather than physical objects.

Direct observation early established two principal types of liquid crystal. The first, apart from optical anisotropy, behaves like a normal liquid of high mobility, with convection currents and Brownian motion. This phase, characterised by the appearance of mobile threads in the body of the liquid, due to lines of optical discontinuity, was called by Friedel *nematic* (from $\nu\eta\mu\alpha$, a thread; Fig. 1). The second type, called *smectic* by Friedel, is much more oily in consistency, and shows only limited internal mobility, but a great complexity of internal structure. When in bulk, it consists entirely of the characteristic focal conic structure (see Fig. 2), but when spreading on surfaces or in small free drops it tends to form flat terraces, the terraces of Grandjean, of unequal thickness and rounded outline (see Fig. 3)¹.

The physical explanation of these two types is now fairly clear. In the first place all liquid crystals have very anisotropic molecules, usually—as emphasised by Prof. Vorländer—with one dimension much greater than the others, for example, the classical *p*-azonyanisole



or the diethyl-*p*-xylylidene-bisamino cinnamate



This leading dimension determines the mutual relation of neighbouring molecules to a greater or less extent, according to the temperature. If we limit our consideration to a very small volume, the following main cases will arise (see Fig. 4): In I the molecules are completely at random: this is the case for the normal isotropic liquid. In II all the molecular axes are parallel, but the centres of the molecule are as irregularly arranged and as free to move as in case I. This corresponds to the *nematic* state. In III as in II the molecular axes are parallel, but the molecular centres have lost one degree of freedom, and are now restricted to a set of regularly spaced parallel surfaces. This corresponds to the typical *smectic* state. In V, which is the case for the crystal, the molecules are parallel, and their centres form a regular three-dimensional network. (Two cases may arise here: either (a) the molecules are arranged in planes, or (b) interleave each other. The first type (smectogenic crystal) tends to give rise to smectic and the second (nematogenic crystal) to nematic.)

That these explanations are essentially correct is proved by the examination of liquid crystals by X-rays; particularly by the work of K. Hermann

and Kast, where sharp Bragg reflections are obtained in the smectic case, but only liquid haloes in the nematic.

A question discussed at the Conference was that of the existence of further liquid crystal states. One other has long been recognised, that typical of cholesterol esters, but which in fact occurs whenever optically active substances form liquid crystals and is called the *cholesteric*. Friedel considers it a variant of the *nematic* type, but it has many properties also of *smectic* states. It is characterised by the production of spectral colours by reflection, with the peculiarity that only right- (or left-) handed circularly polarised light is reflected. This Friedel considers to be Bragg reflection from Grandjean planes regularly spaced, 1000–10000 Å. apart in different cases together with a spiral arrangement of molecules. Oseen, in a paper to the Conference, attempted to prove, by rigorous use of electromagnetic theory, that the latter assumption is sufficient to account for all the phenomena, and that the Grandjean planes are in this case an optical illusion. Friedel maintains that there are no liquid crystal phases apart from nematic, smectic and cholesteric: however, Vorländer has long claimed that he has produced substances with no less than four intermediate states between solid and liquid, and more recently K. Hermann has established that among them there exist, besides normal smectic states, some characterised by faceted drops, showing sharp reflections other than those due to the main plane spacing, and indicating regular arrangement of molecules in each layer of the smectic substance (case IV in Fig. 4).

Such arrangement is geometrically possible; in fact, it is one of C. Hermann's theoretically derived eighteen intermediate forms between crystal and liquid, but whether it should be called 'liquid crystal' may well be only a matter of convention, as it is difficult to draw the line sharply between a liquid with some regular arrangement of molecules and a crystal with some freedom of molecular movement.

The chief business of the Conference was not, however, the discussion of the intermolecular structure of liquid crystals, on which moderate

agreement already exists, but the more intricate problem of explaining the texture of liquid crystals, particularly under the action of surface forces and that of magnetic and electric fields. Two rival views were upheld with some vigour, with the aid of a wealth of experimental and theoretical material. The upholders of the 'swarm' theory—Ornstein and Kast—consider that in nematic substances the strictly parallel arrangement of molecules only holds for groups of about 10^{15} molecules, which form independent swarms in the free interior of the liquid with their axes arranged at random, but can be oriented in parallel by surface or electromagnetic forces. Where such forces are not present, any considerable volume

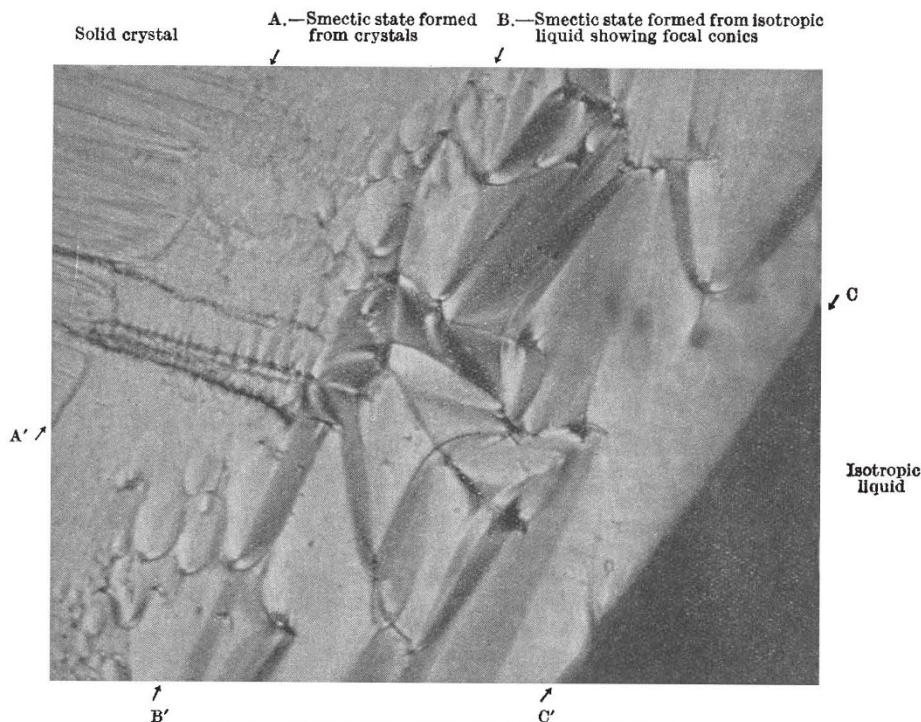


FIG. 2.—Ethylazoxybenzoate showing smectic structures.

(greater than 0.001 cub. mm.) is considered on this theory to resemble a polycrystalline solid, and thus to appear translucent instead of transparent.

The other view, of which the chief protagonist was Zocher, recognises also the limited range of the parallelism of molecules due to their interaction, but considers that the molecular orientation varies continuously from point to point, due not to any intrinsic cause, but to convection currents and Brownian motion in the fluid. The two theories are formally analogous to the ideas of turbulence or stream line motion in hydrodynamics, or to those of mosaic structure or continual deformation in overstrained solids. There are certain ranges of experiment that seem to be more simply explained by one or the other theory. In particular, Kast's work on orientation of pazoxyanisol in alternating electric fields points

to the existence of critical frequencies of 10^5 – 10^6 per sec., above which parallel orientation of the molecules is impossible. This frequency is much too low for simple molecular movement which is usually of the order of 10^{10} per sec., and certainly suggests the existence of swarms.

As Foëx points out, there is an extremely close parallel between the phenomena of orientation in liquid crystals and those of magnetism, a nematic liquid corresponding to a ferromagnetic, and a normal liquid to a paramagnetic substance, with the transition point between the two corresponding to the Curie point. The basis for this comparison is plainly geometrical and not physical, and depends on the existence in both cases of blocks in parallel orientation, such as in magnetism give rise to a Barkhausen effect.

On the other hand, the deformation theory is more suited to account for the phenomena in the

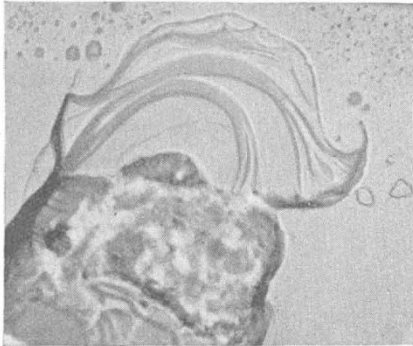


FIG. 3.—Drop of thallium stearate showing Grandjean planes.

neighbourhood of surfaces. Liquid crystals in all their phases exhibit the range of influence of surface forces to a far greater extent than either true liquids or crystalline solids, a range of 10^{-2} instead of 10^{-6} cm. In general, there is a strong tendency to orientation of molecules parallel to the surface, or further, in the case of crystal or rubbed glass surfaces, to certain directions in it. The strength of this force can be measured by opposing to it magnetic or electric forces, as has been done particularly in the beautiful and ingenious experiments of Freedericksz and Zolina. The theoretical treatment of these cases by Zocher shows that they can be explained by continuous distortion up to a point beyond which the structure breaks down sharply as in an overloaded pillar. It became plain as the Conference progressed that the swarm and distortion theories were merely apparently antagonistic, and needed only an effort of synthesis to weld them into a more comprehensive theory.

The nature of smectic structures was not discussed in any paper presented, but the Conference was delighted by the unexpected intervention of Sir William Bragg, who in a few words, explained the *raison d'être* of the focal conic structures which has so long remained a puzzle to students of liquid crystals. These structures consist in general of a pair of cones inclined to a

common elliptical base, and having as a singular line a hyperbola in a plane at right angles to the ellipse, each conic having its focus at the vertex of the other (Figs. 2 and 5). Friedel had shown that the molecular axes lay on lines joining the ellipse to the hyperbola, and that the smectic planes lay in surfaces normal to these lines, the so-called cycloids of Dupin. Sir William now showed that this arrangement is a structure that combines minimum surface and minimum inclination of molecular axes, avoiding the great divergence that would occur at the centre of a simple sphere of

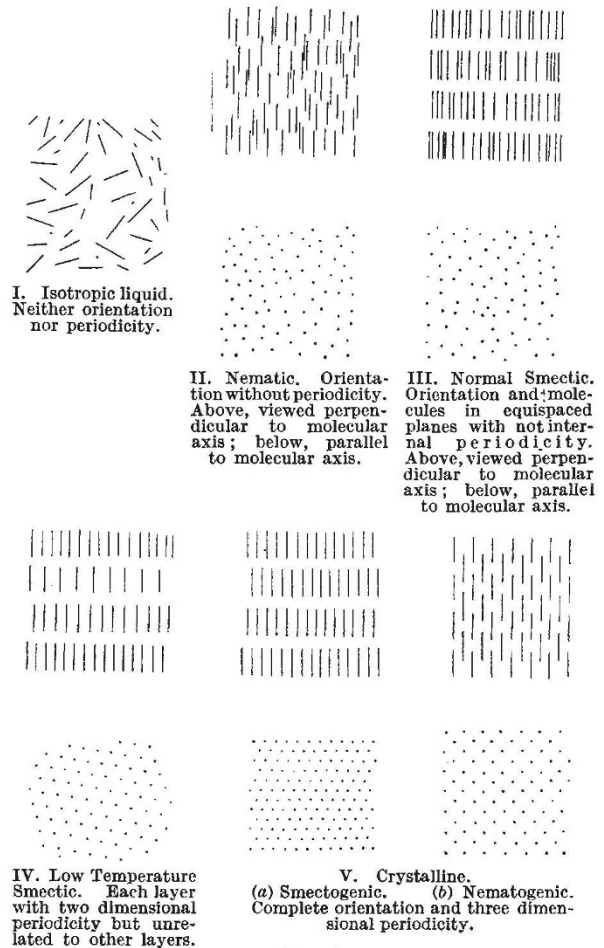


FIG. 4.

radial molecules, by spreading it along the two singular lines of ellipse and hyperbola. Such structures will not, of course, fill space, but the interstices are filled with smaller and smaller focal conics, down to submicroscopic dimensions.

The behaviour of such smectic liquids in motion is naturally quite different from that of true liquids. It is misleading in this case to speak of a viscosity. As Lawrence has shown, the distribution of velocity follows a law much more complicated than that of Newton, in some cases even elastic forces coming into play. The practical values of such studies are obviously great, as many lubricants approximate to liquid crystal conditions.

It remains to point out the widespread importance of liquid crystals in Nature. This was considered in a paper by Prof. Rinne, whose recent lamented death overclouded the proceedings at the beginning of the Conference. The liquid crystals mostly studied are provided by melts of pure substances: far more, however, are to be found in two-component systems, where greater or less concentration in a solvent is equivalent to a rise in temperature. Such liquid crystals show all the phenomena observed in melts, besides others due to their disperse nature, and are widespread, indeed universally found in biological structures.

Most of the protein, fat and myelinic substance of living bodies exists in liquid crystals, but this is only directly visible as such when all the molecules are oriented in definite directions, as in spermatozoa, muscles, nerves and their myelinic sheaths. Indeed the liquid crystal state seems the most suited to biological functions, as it combines the fluidity and diffusibility of the liquid while preserving the possibility of internal structure of crystalline solids.

The spontaneous structures—threads, cones, etc.—of liquid crystals have dimensions intermediate between those of molecules and those of living cells, so that we may say that the liquid crystal has as much right as the colloid to be considered the basis of vital activity.

The existence of this virtually new state of matter will have to be taken into account in any modern comprehensive picture of the material world, whether physical, chemical or biological.

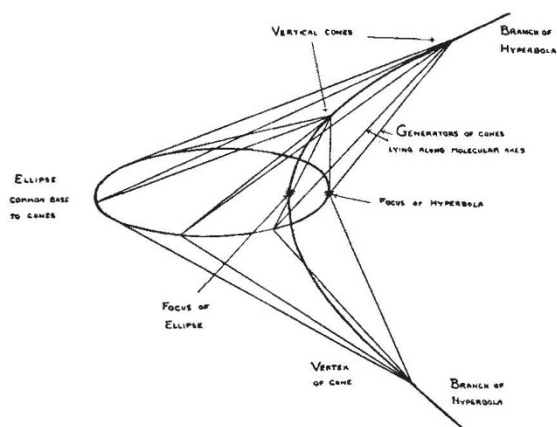


FIG. 5. Focal conic structure. The ellipse and hyperbola must be imagined in planes at right angles. Each cone has its vertex on the hyperbola and its base on the ellipse.

The Faraday Society Conference will have well fulfilled its purpose if it succeeds in provoking further research in the field of liquid crystals.

¹ The photographs reproduced as Figs. 1, 2 and 3, were taken by Dr. Lawrence at the Colloid Physics Department, Cambridge.

Royal Cornwall Polytechnic Society

THE Royal Cornwall Polytechnic Society was instituted in 1833 to encourage and stimulate the ingenuity and inventive faculties of Cornishmen and others, with the view of introducing new inventions and improving the mechanical appliances of the age, also of discovering and assisting persons talented in the fine arts and those showing aptitude in the study of natural history and its allied subjects.

The credit for the Society's inception must be given to Robert Were Fox, F.R.S. and his daughters, Anna Maria and Caroline Fox, who were ably and enthusiastically supported by Lord de Dunstanville, M.P., F.R.S., Sir R. R. Vyvyan, M.P., F.R.S., and a company of the most distinguished gentlemen of the county. Lord de Dunstanville was elected its first patron. In 1835, His Majesty King William IV graciously consented to become patron, and from that date the Society has enjoyed the patronage of succeeding sovereigns. Davies Gilbert, president of the Royal Society, was its first vice-patron. Since 1856 the Society has been honoured by Royal vice-patrons, the present holder being H.R.H. the Prince of Wales and Duke of Cornwall. Viscount Clifden of Lanhedrock, the president, follows in office many distinguished and learned men.

At the time of the Society's foundation there was great mining activity in Cornwall, some four

hundred mines working, chiefly for copper. The county was the world's chief producer of this metal, the exploitation of which was attended by considerable financial gain. The lodes contained minerals rich in copper, comprising chiefly oxides, arsenides and grey sulphides, these passing in depth to yellow sulphides below which the lodes became tin-bearing. The richest mines were in the Gwennap, Camborne, and St. Just districts, and millions of pounds sterling were paid in dividends. John and Richard Taylor, and members of the Williams of Scorrier House, Bolitho, and the Fox families, were the principal mine owners; these men joined the Society at its foundation, thereby assuring its close association with the mining industry.

Early in the Society's history, its attention was attracted to the extreme exertion demanded of miners who, in the deep mines, had to descend and ascend 1,200–1,500 ft. by means of ladders. This daily recurring exercise materially impaired the miner's energies, and was very detrimental to his physical well-being. In view of this, valuable premiums were offered for inventions devised to eliminate these conditions and thereby make the lot of the miner less laborious. Interest in this subject was greatly stimulated and led to the invention of the 'man-engine' by Michael Loam. This appliance was first installed at Tresavean