# Introductory Remarks [and Discussion]

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# Introductory remarks

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Liquid crystals have been recognized as such for just about 100 years. The pure substances known to exhibit one or more liquid crystal phases are numbered in thousands: Professor Gray will probably update us on the present score. The liquid crystals give us a very fine object lesson in the interaction of science and application. Their general nature has been well understood since Georges Friedel's great review article in 1921. There was not much written about them in English before the Faraday Society discussion of 1933 – the meeting at which Sir William Bragg brilliantly overnight perceived the geometrical origin of the focal conic texture of smectics, unaware that Friedel had explained it all a dozen years before. After that, most scientists closed the book. The liquid crystals were scientific curiosities, basically understood, and no one had a use for them. Chemists gradually discovered more mesomorphic substances but, on the whole, knowledge of their physics went backwards rather than forwards. The history of the science of liquid crystals is marked with repeated rediscovery of things forgotten. When, in 1958, I published a paper about liquid crystals I was advocating renewed study of them as a source of information about molecular interactions. However, for one thing, that was not too easy, except in terms of severely simplified simulation models; for another, scientific curiosity alone was not sufficient incentive.

In the 1960s there was a fresh appreciation of the need for new methods of display, to make electrically generated signals visible to the eye. Solid state electronics had brought it about that all of a complex electronic system was minute in bulk, weight and power consumption in comparison with its associated display. At last, the science of liquid crystals acquired a sufficient number of target points to engage the attention of the several dozen new research workers needed to advance knowledge and understanding significantly beyond the level attained by the first half-dozen pioneers, and to a considerable extent forgotten in the interim.

The best of the light-valve phenomena exploited so far is that of the electrically switched twisted nematic. The entertaining optical properties of the twisted nematic were elucidated both experimentally and theoretically by Mauguin in 1911. Mauguin's results were to be rediscovered, more than once, about 60 years later, generally by less elegant treatments and without mention of Mauguin. He did not study the electrical switching of the twisted nematic, but with hindsight that was obvious after the work of Freedericksz in 1927. The invention latent in the combination of these two known phenomena lay dormant till the need for application called it forth in 1971.

This is far from being the only useful application of the science of liquid crystals, and we should hear of others in the course of the Discussion but this is the one that has been responsible for the renascence of the science.

## ON TERMINOLOGY

I believe one of the most valuable things I can do by way of introduction to this discussion is to make some comments on the terminology of the subject, which is indeed somewhat confused and confusing. I shall speak dogmatically. You need not agree with me; but I think I may reasonably ask that where what I say gives some indication of possible misunderstanding you take care to define your terms. I first take the term *liquid crystal* and illustrate it by an example of what is *not* a liquid crystal. The *colloid crystal* you obtain with a dilute suspension of negatively charged silica or polystyrene spheres in water at minimal ionic strength is a *crystal*. It is an extreme example of the *plastic crystal*. The particles array themselves on a body-centred cubic lattice that can be seen directly with the microscope or inferred from the coloured Bragg reflexions in visible light. That crystal is liquid in common parlance. It can be poured from one test-tube to another. But it is not liquid: its yield stress is very small, but finite. So it is not a liquid crystal: nor is it a mesomorph. It is a *crystal* belonging to the same structural class as body-centred-cubic iron. The tallest self-supporting uniform column of iron, if the wind didn't blow, would be of the order 10 km in height: the corresponding height for the colloid crystal is of the order of a millimetre, and it is only as large as that because of the buoyant support of the water. A factor of $10^{10}$ is just a large number, and there is still all the difference in the world between a very large number and infinity. A liquid has strictly zero yield stress. Anything having a three-dimensional space-lattice, with its lattice points occupied by material objects, will not have zero yield stress. Dislocations in that lattice structure may lower the yield stress by a factor of $10^3$, say; but $10^{13}$ is just as far short of infinity as $10^{10}$. There is inevitably some anchoring force on the dislocations. If there were none, the dislocations would escape.

Why did I take care to specify that the lattice points were occupied by material objects? I shall answer that question presently.

*Nematic*, *cholesteric*, *smectic*, the three Friedelian classes: etymology gives us little assistance in interpreting those names. 'Nematic' means 'thready', but disclinations, which can look like threads, are not solely confined to nematic phases. 'Cholesteric' derives from the historical fact that the first recognized, the first liquid crystals recognized in fact, were derivatives of cholesterol, but most cholesterics are not. 'Smectic' means 'soapy', but not everything soapy is smectic. Fortunately the first two at least have acquired stable and unquestioned meanings: *nematic*, the simple uniaxial liquid, and *cholesteric* its modification, spontaneously twisting about a single transverse axis, induced by optical activity in the molecules or optically active additives.

'*Smectic*' is the one that gives trouble. Friedel recognized only one smectic structure, layered, with no long-range positional correlation within the layers. We have since learnt that specification does not uniquely define a structure or a phase, and one substance can have more than one distinct phase satisfying that specification. Hence the necessity to subclassify the smectics; but I would allow none to be called smectics of any kind that do not satisfy that specification. And I believe that all those thus misnamed are not even liquid crystals, they are plastic crystals. I would tolerate, and even advocate, a word such as 'smectoid' to recognize their relation to the smectics.

*Thermotropic and lyotropic:* that is a false contrast; but though the naming is illogical, it serves to make a significant and valuable distinction. It is well established and we should tolerate it.

*Blue phases:* I spoke of the cholesteric twisting about a single axis. It is not topologically possible to twist uniformly through many turns about more than one axis: but twisting about two axes at once over a short distance is possible, and there are substances that achieve that condition, making a three-dimensional lattice of twistedness with overall cubic symmetry. They occur in a half-degree temperature range between cholesteric and isotropic in substances giving cholesterics of short pitch, say 300 nm. They are called blue phases. The blue colour is Bragg reflexion from the lattice of twistedness, the lattice parameter of which is of the same order of magnitude as the pitch of the related cholesteric. There are blue phases of other colour than blue – that is entirely in the spirit of liquid crystal etymology. In that $\frac{1}{2}$K temperature range there can be two different cubic phases, and an amorphous one, picturesquely called the *blue fog*, in which the lattice of twistedness melts.

Now, apart from the last of these, we have three-dimensional lattices; so can these materials be liquid, with zero yield stress? I think they can. The lattice points are not occupied by distinct material objects but by states of orientation. I think matter can pass through the lattice points, the body plastically deforming while the lattice does not. So they *are* liquid crystals. What about the amorphous blue phase? Must it be excluded from the liquid crystal family because it is not a crystal? I think not, since locally it is still effectively nematic.

These blue phases make a thermodynamically and structurally distinct class. They were known before Friedel's time, though not structurally interpreted until much later. I think they should be recognized as a fourth class, after the three Friedelian classes of liquid crystals.

I think they may not be mentioned again in this discussion. They are totally useless, I think, except for one important intellectual use, that of providing tangible examples of topological oddities, and so helping to bring topology into the public domain of science, from being the private preserve of a few abstract mathematicians and particle theorists.

*Discotic and columnar:* it is not too late to insist on a little rationality here. 'Discotic' is a word sensibly describing the shape of a molecule rather than a phase. *Discotic nematics* do exist. That was what Chandrasekhar was looking for when instead he discovered the first non-lyotropic columnar phase. His disc-shaped molecules assembled themselves in columns, with no long-range positional correlation along their length, packed parallel in a two-dimensional lattice. That is a distinct structural class, for which I think the best name is *columnar*. Counting the blue phases as the fourth general class, this is the fifth. Like the smectic class, it has subdivisions according to the nature of its two-dimensional lattice.

*Biaxial nematics:* I do not know whether we shall be told anything about biaxial nematics in this Discussion. In case we are, let me remark that the term 'biaxial' belongs to an *optical* classification of symmetries. In crystal optics, homogeneous bodies are biaxial, uniaxial or isotropic. In classifying the liquid crystals, however, we are concerned basically with structural symmetry, which offers more varieties than that. An optically isotropic body may be structurally isotropic, for example glass, or it may be a cubic crystal. An optically uniaxial body may be simply uniaxial, for example the ordinary nematic, or it may be a hexagonal or tetragonal crystal. An optically biaxial crystal may be structurally orthorhombic, monoclinic or triclinic; the two latter may be improbable for nematic symmetries, but I do not know that they are impossible. They will impose different constraints on the possible defects in the structure. When de Gennes speaks of a biaxial nematic I understand him to mean a structure having no long-range positional correlation in any direction, with orthorhombic symmetry for its orientational distribution functions. If so, I think it would be better called *orthorhombic nematic*.

It is a matter for judgement whether this should be considered a sixth class of liquid crystals. I prefer to regard it as a subclass of the nematics, and stick at five.

*Homeotropic*, *homogeneous:* 'homeotropic', to describe either a boundary condition, or a condition throughout a layer between plane parallel walls, in which the director is perpendicular to the wall or walls, is a useful long-established word, with no alternative meaning. 'Homogeneous' to describe the infinite set of converse conditions with the director parallel to the wall, but not necessarily uniformly oriented, is ridiculous. 'Homogeneous' has an ordinary dictionary meaning, for which 'uniform' is a synonym (in French or German, as well as in English): it is unforgivable to give a technical meaning to a word in conflict with its ordinary meaning when the ordinary meaning has applications in the same context. It would be good to have a different technical term: 'planar', 'parallel' and 'horizontal' are each in various ways objectionable but all vastly preferable to 'homogeneous', which should be totally avoided, saying 'uniform' when in any liquid crystal context the ordinary meaning of 'homogeneous' is intended.

*Direction of the molecules*, *molecular long axis*, *director:* I shall be surprised if someone in this Discussion does not make reference to the *direction of the molecules*, or of their *long axes*. Let me remind you that these are concepts having precise meaning only for a simplified model of the liquid crystal, in which the molecules are axisymmetric bodies, which they never really are. These concepts are incapable of precise definition for real molecules. The *director* is a good concept, at least for the nematics. It is the local symmetry axis for the distribution functions of any orientational property of the molecules, or of intermolecular separations. The mean direction of molecular long axes may coincide with the director, but in discotics it may be the direction of their short axes instead. In smectics, a symmetry axis for orientational distribution functions can exist if, and only if, it coincides with the normal to the layers. *Inclination of the molecules* in smectic C has no exact definition except for the simplified models.

*Order parameter* is in general a term well defined only for simplified simulacra of reality. It is true that in phase-transition theory one order parameter can dominate and determine the nature of a transition, but it is an obvious fallacy to suppose that in general the character of molecular order or disorder is simple enough to be described and measured by a single parameter. The order parameters determined by optical, magnetic or n.m.r. measurements are equivalent only for the simplified models. If they differ by 10 %, that reflects reality.

The very word *molecule* can itself be a trap. In mesomorphic polymers it must mean only the whole polymeric long chain, which must not be confused with the orientable entities that give it mesomorphic character.

Enough. I hope I do not sound like a voice crying in the wilderness, but that what I have said does a little to make straight the path of those who are to follow.

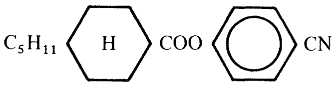
## *Discussion*

M. G. Clark (*R.S.R.E., Malvern, Worcs., U.K.*). I agree that there are difficulties in defining the 'long axis' if only static properties of the nematic are considered. However, there is a natural and unambiguous definition of the long axis if one considers the dynamical theory. The properties of practical interest correspond to timescales longer than those for which molecular inertia is important, with static properties as the long timescale limit. Thus the long axis may be defined as the largest-eigenvalue principal axis of the rotational diffusion tensor

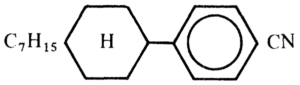
$$\boldsymbol{D}_{\mathrm{rot}} = \int_0^\infty \mathrm{d}t \langle \boldsymbol{\omega}(0)\,\boldsymbol{\omega}(t) \rangle,$$

where $\boldsymbol{\omega}$ is the molecular angular velocity. This means that the 'long axis' is the axis about which rotational diffusion is fastest, which is the natural definition for both elongated and disc-shaped molecules. The definition does not assume any particular molecular symmetry. From the definition we see that the long axis is defined in the molecular frame by the local dynamical structure of the particular fluid, and that its orientation relative to the molecular geometry can and should be determined experimentally. (See M. F. Bone, A. H. Price, M. G. Clark & D. G. McDonnell, in *Liquid crystals and ordered fluids* (ed. J. F. Johnson & A. C. Griffin), vol. 4, Plenum, New York (in the press).)

On the question of agreement between different methods of measuring nematic order parameter, it should be noted that Tough & Bradshaw (in preparation) have been shown that when a well conditioned extrapolation procedure is used, the curves of order parameter against temperature derived from magnetic susceptibility data and refractive index data are in very close agreement. This was shown for both the materials **1** and **2**, which are far from symmetrical.



**1**



**2**

F. C. Frank. I cannot agree with Dr Clark. At best it seems to me that the axis of fastest rotational diffusion is just one more of the directional properties that can be associated with a molecule plus its environment, but I would say it should on no account be called the long axis when it may, as he indicates, alternatively be a short axis of the molecule in the ordinary geometrical sense of short and long.