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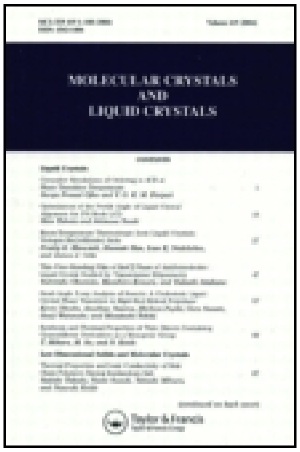

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Introduction

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Introduction

BIAXIAL NEMATICS - FACT OR FICTION?

In his classic paper on the elastic behaviour of nematic liquid crystals published in 1958, Sir Charles Frank hints at the existence of a nematic phase with biaxial symmetry in addition to the conventional nematic phase with its uniaxial symmetry. Little notice appears to have been taken of this intriguing suggestion until 1970 when Freiser presented a molecular theory of nematics formed from biaxial molecules. This predicted that such materials should exhibit isotropic, uniaxial nematic and biaxial nematic phases although for a certain critical biaxiality the system should pass directly from the isotropic phase to a biaxial nematic. Despite these clear predictions it was not until the late 1980s that the claims to have prepared compounds exhibiting a thermotropic biaxial nematic phase began to appear; these originated from the laboratories of Jaques Malthête, S. Chandrasekhar and Klaus Praefcke. However, subsequent studies of some of the materials suggested that the nematic phases claimed to be biaxial were, in fact, uniaxial. Although the formation of real biaxial nematics is in doubt, computer simulators have produced biaxial nematic phases in keeping with the theoretical predictions. In addition, about 17 years ago Alfred Saupe had discovered a biaxial nematic phase formed by a lyotropic system.

Because of the challenge apparently posed by thermotropic biaxial nematics both for their creation and identification it was decided to hold a Workshop on this elusive liquid crystal state. The aim of the organizers, Duncan Bruce, Geoffrey Luckhurst and Demetri Photinos, was to bring together those scientists with interests in the biaxial nematic phase. In the event, 23 scientists drawn from different disciplines and listed at the end of this article were able to gather at St Benet's Hall in Oxford from 20-22 December 1996. During this stimulating 'Oxford Workshop on Biaxial

Nematics' we were able to discuss the major issues, present our latest results and learn from each other. It seemed to those present that it would be of value to make our views as to the present state of knowledge of biaxial nematics and prospects for the future more widely available. To this end the participants agreed the following statement concerning the design and synthesis of biaxial nematics, the identification of this phase, the development of theory to include molecular complexity and the creation of generic models for investigation by computer simulation techniques.

CREATING BIAXIAL NEMATIC PHASES

We begin by noting the following points:

- The only unequivocal demonstration of a biaxial nematic phase is in a lyotropic system (three-component) where repulsive interactions appear to be important (see Yu, L. Y., and Saupe, A., 1980, *Phys. Rev. Lett.*, **45**, 1000).
- There already exists a number of different types of nematic phase, N (including N_D), N_{col}, N_Σ and all ought to be considered as candidate phases to be elaborated.
- That viscosity might play a rôle in helping to stabilize a biaxial nematic phase.
- There appears to be a biaxial nematic phase exhibited by a side-chain polymer system (Hessel, F., and Finkelmann, H., 1986, *Polym. Bull.*, **15**, 349.; Hessel, F., Herr, R. P., and Finkelmann, H., 1987, *Makromol. Chem.*, **188**, 1597; Leube, H., and Finkelmann, H., 1988, *Polym. Bull.*, **20**, 53; Leube, H., and Finkelmann, H., 1991, *Makromol. Chem.*, **192**, 1317).
- At present biaxial nematic phases in low molar mass thermotropic systems remain to be unequivocally demonstrated.

There are two possible approaches to the creation of a biaxial nematic phase, one based on single component systems and the other on mixtures.

It was realized that it was essential to address the issue of phase biaxiality, which we believe requires molecular biaxiality but not necessarily restricted to a shape biaxiality. We also realized that this molecular biaxiality would need to allow for quite pronounced lateral organization, and a shape criterion of 5:3:1 was suggested within the constraints that the molecule ought not to be too large in absolute terms. Molecular biaxility can be promoted by complementary and/or specific intermolecular interactions in the direction perpendicular to the main nematic director, or at least leading to order in that direction. It was felt to be necessary to address the suppression of smectic phase formation, perhaps by suppression of certain intermolecular interactions. It was also realized that the stability of the N_b phase might not be great in thermodynamic terms, and that fluctuations may be a problem. It was felt that problems occurring as a result of fluctuations could be addressed. We then turned our attention to the rôle of chains. Chains might be classified as an external solvent, as in lyotropic systems, or as an internal solvent when they are covalently bound. We refer again to the demonstration of the N_b phase in lyotropic systems (external solvent). We therefore reasoned that the rôle of an external solvent might be transferred to an internal solvent for profit. This would also have the advantage of helping prevent crystallization or the formation of layer structures.

Both molecular field theory and simulation suggest that mixtures of rods and discs represent a positive strategy for the realization of biaxial nematic phases. One of the potential problems is known to be the separation of the mixture into coexisting uniaxial nematic phases. However, a suggestion has been made from simulation that specific interactions between rods and discs can stabilize the mixture and produce biaxial nematics. These interactions could include: chemical (*e.g.*, H bonding), dipolar, geometric, charge-transfer or Lewis acid/Lewis base. These interactions must not be too strong, but this suggests that they will probably be rather temperature dependent. Possible strategies would include both true mixtures, and chemically bound mixtures.

IDENTIFYING BIAXIAL NEMATICS

There are two general approaches to the identification of a biaxial nematic phase. In one, the symmetry of some tensorial property is determined which reflects necessarily the symmetry of the phase while in the other, some indirect behaviour such as the optical texture is employed. There are two features of the texture which can be related to the phase biaxiality; one is the observation of zig–zag defects although care is needed to ensure that they originate from the biaxiality of the phase especially as they have been observed for uniaxial nematics. For a biaxial nematic the angle between the arm of the zig–zag must vary with temperature and equal 180° when the phase becomes uniaxial. It is also possible that only two-brush defects are exhibited by biaxial nematics unlike unaxial nematics which have both-two and four-brush defects; however this important discovery remains to be confirmed. X-ray and neutron diffraction can also be used to determine the phase symmetry but the observation of three length scales in the diffraction pattern is insufficient since this only reflects a local biaxiality. To provide evidence of the phase or long range biaxiality, it is necessary to study a monodomain sample prepared with two external constraints. The availability of a monodomain sample of the biaxial nematic phase is usually a prerequisite for the determination of the three principal components of some tensorial property such as the refractive index or diamagnetic susceptibility. Indeed, conoscopy which has been widely used to characterize biaxial nematics requires the creation of a monodomain which then allows the measurement of the difference in the components of the refractive index orthogonal to the main director. However, some care is needed to ensure that any difference which is observed does not result from a biaxiality induced by some external constraint. As a consequence, it is desirable that studies of monodomain samples should be performed as a function of the constraints controlling the alignment of both major and minor directors, for example the sample thickness and the strength of the applied magnetic field. The magnetic interactions such as the quadrupolar splitting of deuterium observed in NMR spectroscopy have also been employed to determine the phase symmetry. The advantage of this technique, at least for low molar mass materials, is that it is not necessary to prepare a monodomain. Indeed, it is advantageous to study systems in which at least two of the directors are randomly arranged with respect to the applied magnetic field. The NMR spectrum is then determined by the principal components of the quadrupolar tensor and so reflects the phase symmetry. The lower limit which can be placed symmetry. The lower limit which can be placed on the phase biaxiality is controlled by the linewidth and the quadrupolar splitting. A more sensitive technique is to measure the refractive index using a high finesse Fabry–Perot structure but here it is again necessary to have a mondomain sample.

There are other less stringent requirements suggested by theory which a biaxial nematic phase should satisfy. The first is the phase sequence, namely isotropic, uniaxial nematic and biaxial nematic which occurs on lowering the temperature, although reentrant behaviour is possible. Secondly, the biaxial–uniaxial nematic transition should be second order as should the biaxial nematic–isotropic transition. In addition, the phase biaxiality defined in terms of the second rank orientational order parameters should be significant. Although these theoretical requirements are not absolute they are expected to provide a good guide to the behaviour of real systems. Finally, the well-established existence of lyotropic biaxial nematic phases means that any method used to identify a thermotopic biaxial nematic can be validated with the aid of the lyotropic systems.

DESIGNING BIAXIAL NEMATICS

The major feature of the developments in theory and simulation techniques evolved around the molecular attributes that are likely to promote or inhibit phase biaxiality in thermotropic nematics. Molecular biaxiality, more precisely biaxiality of the intermolecular interactions, is an obvious requirement for phase biaxiality in the case of single component systems. There is not, however, a unique way to quantify molecular biaxiality theoretically although an experimental approach may be possible. Molecular flexibility, ever present in real systems, introduces further complications to the quantification of molecular biaxiality. In model biaxial nematics formed by mixing nematogens with non-coincident directions of preferential alignment such as rod–disc mixtures, the stabilization of phase biaxiality essentially reduces to the prevention of decomposition into two uniaxial nematic phases. Such phase separation can, in principle, be prevented by introducing specific molecular interactions which promote association among unlike molecules without perturbing severely the nematic self-organization of the like molecules.

The theory of biaxial phases has a very different outlook from experiments in the sense that a variety of models and theoretical approaches have predicted the existence of a biaxial nematic phase not yet found experimentally. Indeed, there is no fundamental theoretical reason why biaxial nematics should not exist. Molecular field theory has no difficulty in predicting the existence of biaxial nematic phases but it does show that only extremely biaxial molecues can give biaxial nematics. In addition the theory describes biaxial nematic phases only in competition with uniaxial nematic or isotropic phases and does not normally allow for the possible formation of solid and/or smectic phases.

Computer simulation studies of hard biaxial ellipsoids have demonstrated the existence of biaxial nematics. Here the molecular biaxiality is necessarily defined in terms of shape biaxiality. The original version of the Gay–Berne potential which includes attractive as well as repulsive forces was uniaxial and so needed modifications to produce biaxial objects. One route taken is that of combining several Gay–Berne sites to create a biaxial object. The other is to devise a biaxial variant of the single site Gay–Berne potential. Preliminary simulations seem to indicate the formation of biaxial nematics as well as biaxial smectics, although this is less surprising.

Quantification of molecular biaxiality is very desirable, especially for screening target molecules in the search for highly biaxial ones. This could be achieved by using the surface tensor although allowance would need to be made for the many conformational states. There is clearly more than one biaxiality in the problem. For instance the biaxial Gay–Berne potential allows the definition of two biaxiality parameters, one associated with the shape and the other with the attractive forces. Preliminary computer simulation results show that different phase behaviour can be obtained for molecules with the same shape anisotropy but differing biaxiality, hinting that the design of target biaxial molecules should not be based on shape alone. However, the separation of these two aspects for real systems could be difficult.

The use of mixtures rather than pure systems provides, in principle, a good way of preparing biaxial nematics. Mixtures of biaxial rods and discs to avoid the danger of phase separation found in mixtures of uniaxial rods and discs is an interesting possibility. Alternatively the inclusion of hydrogen bonding interactions among rods and discs can stabilize the biaxial nematic phase for aspect ratios in the thermotropic regime. In conclusion computer simulation has an important rôle to play in that it reproduces at least some of the difficulties of real experiments, including the existence of smectic and solid phases. Understanding situations where biaxial nematics are not obtained in the simulations might shed some light on the difficulties apparently faced by experimentalists in creating thermotropic biaxial nematic phases.