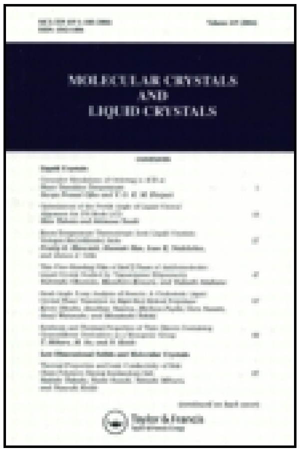

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Discussion. Oxford Workshop on Biaxial Nematic Liquid Crystals December 1996

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DISCUSSION

Oxford Workshop on Biaxial Nematic Liquid Crystals December 1996

Location of Workshop
St. Benet's Hall,
38 St. Giles, Oxford
OX1 31N, UK.
Tel. & Fax: +44(0) 1865 513917.

Organising and Scientific Committee
D. W. Bruce (Univ. of Exeter),
G. R. Luckhurst (Univ. of Southampton),
D. J. Photinos (Univ. of Patras).

FRIDAY 20 DECEMBER

K. Praefcke:

[0.1] As a general recommendation how to represent this meeting afterwards, I think that it is very important that the results of our discussions should be reported to the public. My suggestion is that after the meeting we should publish a summary in a joint paper, *e.g.*, in *Liquid Crystals Today*, with all participants as authors. This will prove the high performance of our network meeting and furthermore such a communication will give us a main level which all of us may refer to. Additionally, all of the lectures then could be published as full papers in a special volume somewhere else.

D. W. Bruce:

[0.2] I suggested that the papers and discussions presented at the workshop should be published as a special issue of Molecular Crystals and Liquid Crystals.

SATURDAY 21 DECEMBER

Session I: *Molecular design: theory and simulations.*
Chair: **S. Chandrasekhar**

[#1] Overview.
G. R. Luckhurst

D. A. Dunmur:

[1.1] With ^{2}H NMR are you probing directly the biaxial order parameters?

G. R. Luckhurst:

[1.2] Yes, the observed components of the quadrupolar splitting are directly proportional to linear combinations of the second rank biaxial order parameters.

S. Chandrasekhar:

[1.3] You could measure the biaxiality as the perturbation due to an external field.

G. R. Luckhurst:

[1.4] This is a good suggestion, that is to estimate the biaxial–uniaxial nematic transition temperature using pretransitional behaviour in the uniaxial nematic phase. To achieve this an external field would need to be applied to the uniaxial phase so as to induce a phase biaxiality; this is then expected to diverge as the transition to the biaxial nematic phase is approached. Since the biaxial–uniaxial nematic transition is predicted to be second order the divergence temperature should equal the transition temperature. Such measurements would then allow the T_{Nb-Nu} to be estimated, even when the biaxial nematic is not formed, and so the relationship between the molecular structure and the transition temperature could be explored.

K. Praefcke:

[1.5] For the Malthête's compound (labelled #1 in GRL transparency) the phase transition sequence was incorrect, so we could skip it from our discussion.

G. R. Luckhurst:

[1.6] Their first identification of the phases gave the sequence isotropic (I) to biaxial nematic (N_b) then to uniaxial nematic (N_u) which is not in accord with theoretical predictions. Moreover a second series of measurements both by Malthête and by Meubert showed that the correct sequence was $I \rightarrow N \rightarrow S_mC$. The question as to identity of the nematic phase remains open.

K. Praefcke:

[1.7] I make a point on the key role molecular rigidity could play for the successful formation of N_b phases, as in the case of compounds labelled #2 (Chandrasekhar's) and #3 in GRL's transparency.

D.W. Bruce:

[1.8] Chandrasekhar's compound is not so rigid since there is a small energy barrier between the square planar and the tetrahedral structure. In addition there is considerable rigidity resulting from the long alkyl chains.

M. Osipov:

[1.9] In lyotropic systems attractive dispersion forces are of minor importance because the dielectric susceptibilities of micelles and of the solvent are similar. The primary anisotropic interaction between micelles is the steric repulsion or the electrostatic repulsion between surface charges or double layers. These examples show the importance of repulsive forces, *i.e.*, that of shape, for biaxial ordering.

G. R. Luckhurst:

[1.10] It is important to recall that the lyotropic biaxial nematic is located between two uniaxial nematics in which the micelles are either rod-like or disc-like. It is possible, therefore, that the biaxial nematic could result either from a mixture of these shapes or that it is formed from single biaxial particles.

Y. Galerne:

[1.11] The anisotropy of the micelles has a small but continuous change moving along the phase diagram.

S. Chandrasekhar:

[1.12] These systems are really sensitive to small external perturbations.

C. Zannoni:

[1.13] In real molecules there is more than one definition of biaxiality at work. It is possible to tune shape biaxiality more easily in micelles.

D. A. Dunmur:

[1.14] I believe we should also consider induced biaxiality. As we know it is possible to induce phase biaxiality using surfaces or external fields. For the latter case if the molecular susceptibility is negative the nematic phase is predicted to be biaxial. Experimental measurements of dielectric anisotropy or birefringence can be used to detect induced phase biaxiality. Another possibility comes from the quenching of major director fluctuations (as predicted by the Landau–de Gennes theory). In this case the off-axis dipoles do not contribute to the formation of biaxial phases. In addition, interactions with the cell surfaces might force an anisotropic cut-off radius for director fluctuations and the nematic phase might become biaxial.

S. Chandrasekhar:

[1.15] ...

C. Zannoni:

[1.16] Is the induction phenomenon observable with NMR?

Y. Galerne:

[1.17] The optical techniques are very sensitive and allow us to measure very small biaxialities provided that they are used with care, *e.g.*, with conoscopy, several rings have to be observed.

G. R. Luckhurst:

[1.18] The sensitivity of deuterium NMR spectroscopy to determine the long range orientational order, either intrinsic or induced, is determined by the linewidth. For example, in the isotropic phase where the spectral lines are sharp, field induced order parameters as small as 10–4 can be observed. However, in the nematic phase the lines are much broader and the accuracy with which an order parameter can be determined is between 10–2 and 10–3.

Y. Galerne:

[1.19] If director fluctuations were big enough they might destroy biaxiality in thermotropic liquid crystals.

D. W. Bruce:

[1.20] What is the role of polymers?

S. Chandrasekhar:

[1.21] ...

D. J. Photinos:

[1.22] What kind of fluctuations? On what time scale?

Y. Galerne:

[1.23] Director and collective fluctuations.

Y. Galerne:

[1.24] NMR works for uniaxial nematics but I do not know if this technique could be used in the biaxial case as well. It depends on the order of magnitude of the biaxial order parameter.

S. Chandrasekhar:

[1.25] Would you then say that the quenching is so important?

Y. Galerne:

[1.26] ...

S. Chandrasekhar:

[1.27] I believe we use the term biaxial in an improper way. It is important to agree on the definition of biaxiality. Furthermore we have to distinguish carefully between phase biaxiality and molecular biaxiality. To measure the two optical axes of a biaxial phase...

G. R. Luckhurst:

[1.28] It is important to recognise that the terms uniaxial and biaxial when applied to phase symmetry have their origins is certain optical properties of the phase. Thus a uniaxial phase is one in which there is a single axis along which a plane polarized light beam can travel without its state of polarization being changed. Similarly for a biaxial phase there are just two axes along which the light beam can travel without change of its state of polarization. Given the origin of the terms uniaxial and biaxial their use to describe the molecular symmetry is not entirely appropriate. However the use in the molecular context is now quite widespread and should not lead to any confusion.

G. Jackson:

[1.29] Have biaxial S_mA phases ever been observed?

Y. Galerne:

[1.30] The biaxial S_mC may really be considered as a biaxial S_mA phase. Just bind two adjacent molecules forming an elementary chevron in neighbouring layers.

G. Jackson:

[1.31] We have seen biaxial S_mA phases in our Monte Carlo simulations of a dipolar model.

D. A. Dunmur:

[1.32] The $S_m\tilde{A}$ has an in-plane modulation of the dipoles. For this point of view it has a biaxial behaviour... Spontaneous polarization in the S_mA phase has been claimed by Watanabe ...

M. Osipov:

[1.33] Ferroelectricity has been observed in a S_mA phase of banana shaped molecules, namely molecules with a moderate electric dipole but with an enormous steric dipole. In this case ferroelectricity is governed by the packing entropy. I believe steric dipoles can promote the formation of phase biaxiality, also in the nematic phase.

K. Praefcke:

[1.34] These molecules are derivatives of phenanthrene; quite a number of them have been studied.

S. Romano:

[1.35] It is known that biaxial molecules usually form uniaxial phases. Does anybody know if conjugated poly-ynes form (uniaxial) nematic phases? Has anybody studied such molecules from this point of view?

G. R. Luckhurst:

[1.36] Poly-ynes do not, as far as I am aware, form liquid crystal phases.

M. Osipov:

[1.37] There is a theory linking nematicity to the persistence length of a semiflexible polymer chain. Thus in this case nematic ordering is also related to the anisotropy in some property.

D. A. Dunmur:

[1.38] An example of an Onsager-like liquid crystal is a colloidal suspension of tobacco mosaic virus.

S. Romano:

[1.39] In that case you have charges.

[#2] *Computer simulations of liquid crystalline phases formed by biaxial Gay – Berne molecules.*

R. Berardi, A. P. J. Emerson and C. Zannoni*

[#3] *Heterogeneous Gay – Berne model for biaxial particles.*

R. Berardi*, C. Fava and C. Zannoni

D. A. Dunmur:

[3.1] What is the contribution of the different order parameters $\langle R^2_{mn} \rangle$ to the total energy?

C. Zannoni:

[3.2] In reality the energy is determined by pair correlations. The order parameters do not appear in general directly as they do in molecular field theories.

G. R. Luckhurst:

[3.3] Is it possible to parametrize the biaxial Gay–Berne potential in order to have shape biaxiality but not an interaction biaxiality?

R. Berardi:

[3.4] Yes. If $\sigma_x \neq \sigma_y$ but $\varepsilon_x = \varepsilon_y$ the energy profiles for the *side-by-side* *aa* and *bb* interactions are not coincident but have the same well depth. Since $\varepsilon(\omega_1, \omega_2)$ depends on shape biaxiality but not on the orientation of the intermolecular vector its value is the same for *aa* and *bb* interactions. Furthermore if the interaction biaxiality is zero even the $\varepsilon(\omega_1, \omega_2, \hat{\mathbf{r}}_{12})$ coefficients are the same for the *side-by-side* interactions.

M. Osipov:

[3.5] The competition of smectic ordering and biaxiality is interesting and has not been discussed before. It is possible that biaxial fluctuations will stabilize smectic phases. If this effect is strong, biaxial ordering can more easily be found in the S_mA phase. What is the effect of the interaction biaxiality?

R. Berardi:

[3.6] It is a parameter we can tune trying to stabilize the biaxial nematic with respect to the smectic phase. For instance, in our biaxial simulations if the parametrization enhances *bb* with respect to *aa side-by-side* interactions ($\lambda_e > 0$) the layering of prolate GB particles ($\lambda_s > 0$) is highly favored and the system eventually forms a highly biaxial smectic phase when the uniaxial nematic is cooled. On the other hand a negative interaction biaxiality ($\lambda_e < 0$) weakens *bb side-by-side* interactions and a biaxial nematic region might appear before the transition to the smectic phase takes place.

[#4] Biaxial nematics: the role of molecular biaxiality and flexibility.

A. Ferrarini and P.-L. Nordio*

D. A. Dunmur:

[4.1] What is the relation between the biaxial shape parameter, other λ parameters and the order parameters measured in NMR experiments?

P. L. Nordio:

[4.2] Molecular biaxiality has the same definition since both properties are second order tensors. Moreover there is no necessary relation between the surface tensor of a molecule and the order parameters measured from NMR experiments.

S. Fan:

[4.3] When you study reentrant systems is one of the two nematic phases more discotic/calamitic than the other one?

P. L. Nordio:

[4.4] Both of them are biaxial phases, one more calamitic, the other more discotic.

S. Chandrasekhar:

[4.5] Did not Bill Doane study chiral cholesteric phases using NMR? What is the comparison with your model?

P. L. Nordio:

[4.6] Under normal conditions the system appears macroscopically uniaxial.

C. Zannoni:

[4.7] If you consider the results of ^{13}C NMR there is not an universal picture for the relation between the observed biaxiality in the ordering matrix of a rigid probe and the various types of molecular biaxiality.

P. L. Nordio:

[4.8] One could devise an infinite number of ways to define the shape tensor. The relation between dimensions of the solute (probe) and solvent may be important. Usually chiral molecules are fairly large. There is a relation between the shape tensor and the molecular biaxiality.

D. J. Photinos:

[4.9] I refer to your remark that the surface tensor approximation works better as the difference between the size of the solvent and the probe molecules gets larger. What does this imply for the accuracy of the results obtained by applying the surface tensor to neat phases, where "*solvent*" and "*probe*" are identical?

P. L. Nordio:

[4.10] ...

D. W. Bruce:

[4.11] The way we think of the molecular shape and the way molecules arrange themselves is not clear. Anyway it seems that the longer the cross section (*e.g.*, the elongation of the lateral groups) is the more calamitic the nematic phase is, whereas a decrease of the cross section leads to disc-like behaviour.

P. L. Nordio:

[4.12] Looking at a molecule and its shape it is not easy to tell how biaxial it is. Looking at certain moieties the shape model works nicely.

K. Praefcke:

[4.13] Generally the influence of the molecular geometry is often underestimated.

P. L. Nordio:

[4.14] This is not the only influence on the mesomorphic behaviour. The molecules thought to form biaxial nematics are very flexible and it is very difficult to define the molecular shape.

K. Praefcke:

[4.15] Very often there is an incomplete view on the possible types of nematic phases. We should not forget that there are four typical classes of nematics N_c (calamitic), N_d (discotic), N_{col} (columnar) and N_Σ (sanidic). Eventually N_{col} might be the best system for studying uniaxial–biaxial nematics, because, so to speak, one of the directions is already fixed.

G. R. Luckhurst:

[4.16] In terms of accepted nomenclature the N_Σ phase should be called a biaxial nematic and denoted by N_b. There is also some doubt as to the additional embellishment of the symbol N to denote other nematics since the long range orientational order is qualitatively the same in all of these. The subscripts describe simply the local structure of the fundamental units and so do not relate to the long range order which should be reflected by the symbol used to denote the phase.

[#5] On the bicritical points in a rod disc mixture.
A. Chrzanowska

Y. Galerne:

[5.1] Do you get phase separation at the intermediate point $x = 0.5$?

A. Chrzanowska:

[5.2] I have not considered the phase stability yet.

L. Longa:

[5.3] I think there should be an additional vertical line in the phase diagram corresponding to $x = 0.5$.

D. J. Photinos:

[5.4] I agree with Lech Longa. At intermediate concentrations you should have either a stable biaxial nematic phase or decomposition into two uniaxial phases. For example, what kind of molecular ordering do you have at an equimolar concentration ($x = 0.5$) and what happens as you increase the pressure at that fixed value of the concentration?

A. Chrzanowska:

[5.5] It is a good question. It is an uniaxial phase; to the left of the diagram there is a mixture rich in rods, to the right a mixture rich in discs.

D. A. Dunmur:

[5.6] In a real system one would always get phase separation in such a case. It is an academic question to change x_a in the ρ *vs* x_a diagram.

G. R. Luckhurst:

[5.7] Is b_{ab} the mean of the b_{aa} and b_{bb} coefficients? What is q exactly?

A. Chrzanowska:

[5.8] q is a scalar number which appears in the free energy equation and belongs to "*strength*" of excluded volume due to the shape anisotropy, but you can also assume that it is due to extra repulsion or attraction. I think that it is not very obvious how to distinguish these two, unless you know exactly what is the reference geometrical shape.

G. Jackson:

[5.9] Why do not you use the exact excluded volume?

A. Chrzanowska:

[5.10] Because I was not interested in the excluded volume but in the phase diagram.

S. Chandrasekhar:

[5.11] Does a larger q mean that b_{ab} is larger? If you have a mixture with longer rods what happens to q?

A. Chrzanowska:

[5.12] With this approximation we cannot distinguish whether a particle is a disc or rod.

S. Romano:

[5.13] What is the role of higher order terms?

A. Chrzanowska:

[5.14] Some effects might disappear.

M. Osipov:

[5.15] It seems that there is no need to put an additional vertical line in the phase diagram as there is no actual transition here. Simply the left hand side of the diagram is rich in rods and they determine the direction of nematic ordering. And to the right there are more discs and they determine the director. But physically the system is the same and the difference is rather formal.

[#6] Stabilisation of phase biaxiality in nematic rod – plate mixtures.

A. G. Vanakaras, S. C. McGrother*,
G. Jackson and D. J. Photinos

C. Zannoni:

[6.1] If the dipoles are axial are not you doing the same thing of Dr. A. Chrzanowska? Should you not use discs with transverse dipoles instead?

S. C. McGrother:

[6.2] We have tried to use transverse dipoles but it did not work.

D. J. Photinos:

[6.3] Dipolar forces influence in more or less the same way the interactions between like and unlike species and therefore do not contribute substantially to the stabilisation of the biaxial mixture. In our calculations we have considered several arrangements of the dipoles, including longitudinal dipoles on the rods and radial dipoles on the discs. In all cases the effect on phase stability was marginal for any realistic size of dipole moment.

C. Zannoni:

[6.4] I expect you should get a different kind of columnar ordering since disc–disc, disc–rod and rod–rod interactions are still different for geometric reasons.

D. J. Photinos:

[6.5] The theory considers only the relative stability of the isotropic, uniaxial nematic and the biaxial nematic phases. It does not address the stability of any of these phases relative to other liquid crystal phases such as the columnar or the smectic.

K. Praefcke:

[6.6] What happens to the length of correlation?

S. C. McGrother:

[6.7] The biaxial phase is not enhanced.

M. Osipov:

[6.8] What about using quadrupoles where you can change the sign and makes dislike interactions stronger than like interactions?

G. R. Luckhurst:

[6.9] The electrostatic quadrupolar interaction could certainly be used to inhibit phase separation. The interaction between disc-like particles with quadrupolar moments opposite in sign is certainly known to induce liquid crystal phases and so should certainly help to prevent phase separation in mixtures of rods and discs.

D. J. Photinos:

[6.10] We have looked into possible ways of stabilising biaxiality; Simon McGrother is about to present some of them.

S. C. McGrother:

[6.11] Another way could be to introduce stronger rod – disc interactions located in the molecular centers (*e.g.*, by hydrogen bonding) to enable stable mixtures. For thermotropics the molecular sizes do not favour the biaxial nematic state.

Session II: *Physical Properties and Characterisation.*
Chair: **D. W. Bruce**

[#7] Overview.
Y. Galerne

C. Zannoni:

[7.1] Can you estimate for the different effects how large observables have to be in order to avoid the "*traps*"?

Y. Galerne:

[7.2] To avoid the "*traps*" the observables have to be larger than the errors of measurements, which naturally strongly depend on the experiment and on the way it is performed.

[#8] Schlieren textures in biaxial nematic liquid crystals.
S. Chandrasekhar*, Geetha G. Nair, K. Praefcke and D. Singer

C. Zannoni:

[8.1] I wonder why you do not see any connecting line between four brushes type defects.

S. Chandrasekhar:

[8.2] I do not know. This is one of many mysteries which remains to be answered.

D. W. Bruce:

[8.3] Would molecular shape eventually affect the appearance of the $S = 1$ disclinations and modify the elastic properties independently on the phase symmetry?

S. Chandrasekhar:

[8.4] There is no evidence of divergence of elastic constants.

Y. Galerne:

[8.5] Do you observe biaxial disclinations making zig-zags with an angle depending on temperature, thus quite different from those observed in MBBA with a constant zig-zag angle?

C. Zannoni:

[8.6] Have you any evidence on the dynamical properties of these defects? (Kibble–Zurek theory....) Sometimes a dependence $t^{1/2}$ is characteristic.

S. Chandrasekhar:

[8.7] We have yet no dynamical properties of defects. We plan to do this sort of study in the future using a video camera.

D. A. Dunmur:

[8.8] How does the nematic director in the plane of the free standing films behave as evidenced by conoscopy?

S. Chandrasekhar:

[8.9] In many samples we have studied there was not a single domain structure as it happens when an external field is applied. Within a few mm the entire sample was a single domain for the cases of high electric fields. For the low voltage case the probe showed domains with differently oriented directors. In addition in the DSC measurements an additional transition peak appears just below the clearing point; this might be the $N_b \rightarrow N_u$ transition.

G. R. Luckhurst:

[8.10] Is there a combination of elastic constants that would generate the optical texture you observe for a uniaxial nematic phase?

Y. Galerne:

[8.11] I think that it is not necessary to adjust precisely the elastic constants to get similar textures.

S. Chandrasekhar:

[8.12] I agree.

S. Romano:

[8.13] How large should the sample be before size effects can be excluded? X-ray scattering gives you only short range information. Have any effects similar to the Kosterlitz magnetic transitions been taken into account?

S. Chandrasekhar:

[8.14] The samples are quite thick. It is impossible to make thin films comparable to smectic thin films containing only one or two layers. Here, the film is much thicker otherwise it would break immediately. It is possible to know from X-ray linewidths if the positional correlations are long range or not. Anyway the X-ray photographs do not provide the ultimate answer. The coherence length ...

K. Praefcke:

[8.15] What do the DSC investigations of Finkelmann show?

S. Chandrasekhar:

[8.16] This was a polymeric sample and so it is not comparable to this one (you cannot produce alignment in more than one direction). They found the biaxial behaviour by conoscopy.

C. Zannoni:

[8.17] How large is the coincidence of conoscopy, DSC and the other measurements? Concerning the homogenity of the temperatures found do you have any evidence if calorimetric and conoscopic measurements have the same temperature dependence?

S. Chandrasekhar:

[8.18] We do not have performed accurate enough investigations and we have not yet reached the precision we would like to have. Anyway, within the accuracy of (1/4)°C of our experiments the two measurements are in agreement. The low temperature peak could resemble the $N_b \rightarrow N_u$ transition.

C. Zannoni:

[8.19] It is interesting that the change of texture and the calorimetric transition happen at the same temperature as they should.

[#9] Molecular dynamics simulation of flow properties of biaxial nematic liquid crystals.

S. Sarman

R. Berardi:

[9.1] It is not unusual that the fluctuations of the principal uniaxial order parameter $\langle R^2_{00} \rangle$ are much bigger than those of the biaxial $\langle R^2_{22} \rangle$? One would expect exactly the opposite behaviour.

S. Sarman:

[9.2] It is hard to draw any definite conclusions about the relative magnitudes of the fluctuations of $\langle R^2_{22} \rangle$ and $\langle R^2_{00} \rangle$ from this simulation. This is a rather short simulation. One would have to perform considerably longer simulations in order to be able to say something more definite.

C. Zannoni:

[9.3] If you reduce the shape biaxiality do you find a uniaxial phase?

S. Sarman:

[9.4] If I reduce the length of the molecules by removing some of the Gay–Berne oblates the biaxial phase vanishes and there is only a uniaxial phase. In this phase the normals of the "*broadsides*" of the molecules are oriented in the same direction.

P. L Nordio:

[9.5] Your model might underestimate the viscosity. If the velocity autocorrelation function has negative parts is this not in contrast to the theory that in nematic phases the motion is overdamped?

S. Sarman:

[9.6] The negative parts of the velocity correlation functions emanates from the rigidity of the molecules. If the molecules are more flexible the "*rebound*" part of the correlation function vanishes. Real molecules are probably more flexible than the rigid Gay – Berne ellipsoids.

P. L. Nordio:

[9.7] My opinion is that the behaviour you have observed is not compatible with the normal properties of a nematic fluid. From this point of view Gay – Berne models may not be compatible with other ones.

S. Sarman:

[9.8] The Gay – Berne fluid might not properly reproduce all of the properties of a real liquid crystal. Thus the viscosities obtained for the Gay – Berne fluid are not exactly the same as those of a real liquid crystal. However, their relative magnitudes and their temperature dependence are similar to those of real systems. If one wants to obtain agreement between simulations and experiments, one should use more sophisticated models. Unfortunately, such models are fairly complicated and very expensive to simulate but it will probably become possible in the future as computers continue to grow in power.

G. R. Luckhurst:

[9.9] The dynamical properties found by your simulations fascinating. However, I am intrigued by the transitional behaviour of your model. This undergoes a transition directly from the isotropic to the biaxial nematic phase. Such behaviour is predicted by previous model/theories when the shape biaxiality is close to the limiting value of $1/\sqrt{6}$. Since the shape biaxiality of your molecules is far from this value I wonder whether you have an interpretation of this unusual behaviour?

S. Sarman:

[9.10] The details of the shape of molecules affect the phase behaviour of liquid crystals. For example, for a liquid crystal consisting of the hard ellipsoids of revolution a length to width ratio of 3:1 is required for the formation of nematic liquid crystal phases. However, for a fluid consisting of hard sphero-cylinders a length to width ratio of 5:1 is required. Therefore it is not unreasonable to assume that the fluid in this simulation, which consists of chains of Gay–Berne oblates, forms biaxial nematic phases at other length to width ratios than a fluid consisting of hard biaxial ellipsoids. These ratios might deviate from the ones obtained from molecular field theory.

S. Chandrasekhar:

[9.11] The theory concludes that the $N_u \rightarrow I$ and $N_b \rightarrow N_u$ transitions should be very close and this is not so for your case. Furthermore you do not observe any uniaxial nematic phase. Can you elaborate on that?

S. Sarman:

[9.12] The phase transition that I observe in the simulation could very well be a $N_u \rightarrow I$ transition followed by a $N_b \rightarrow N_u$ transition. In small system such as a simulation cell which in this case contains only 2000 molecules phase transitions are not very sharp. If they are close they will probably overlap and it will not be possible to resolve them properly. The only way of definitely answering this question is to simulate a larger system and more isotherms.

S. Romano:

[9.13] (to G. R. Luckhurst) You are comparing molecular field theory results obtained for a potential restricted to second order terms with those from a computer simulation based on a pair potential including higher orders as well.

G. R. Luckhurst:

[9.14] Although the Gay–Berne pair potential does indeed contain orientational terms which are of rank higher than two computer simulation studies of Gay–Berne nematogens have shown that the potential of mean torque is indeed of second rank as assumed in the molecular field theories. The estimate of the molecular biaxiality needed to achieve the Landau point where the biaxial nematic phase undergoes a transition directly to the isotropic should, therefore, be quite reliable.

[#10] Determination of phase symmetry using NMR spectroscopy.

G. R. Luckhurst* and B. A. Timimi

Y. Galerne:

[10.1] There could be another "*trap*" related to hydrodynamics. When the sample is rotated there is a magnetic torque compensated by a viscous torque. There could be a flow-dynamical problem in establishing a two-dimensional pattern.

G. R. Luckhurst:

[10.2] In principle I agree with you. There is the possibility that there is diffusion between regions with a different director distribution which is fast on the time scale of the NMR experiment and this could average out the phase biaxiality.

D. A. Dunmur:

[10.3] How about a S_mC phase? Can you do experiments using X-rays?

G. R. Luckhurst:

[10.4] We have not used the NMR technique to investigate the biaxiality in a S_mC phase. However, we have used ESR spectroscopy which requires a paramagnetic probe molecule. Here we find a phase biaxiality for a probe that places itself in close proximity to the alkyl chains but not for one which is located near the mesogenic core.

C. Zannoni:

[10.5] If you use an uniaxial probe you are not able to measure $\langle R^2_{22} \rangle$, the only rather large biaxial order parameter. Acetonitrile is uniaxial so, why did not you use a biaxial probe instead?

G. R. Luckhurst:

[10.6] The simulations of the NMR spectra show that the technique should work well with uniaxial probes as well as biaxial probes. This is especially true for disc-like molecules although even rod-like probes should sense the phase biaxiality provided the solute orientational order is low.

D. J. Photinos:

[10.7] A comment about traps: molecular sites which give small splittings for the aligned sample could provide more sensitive detection of biaxial ordering on the spectra of the rotating sample. In these cases however, one should carefully take into account the coupling between the NMR spectral frequencies and the frequency of the mechanical rotation of the sample. Now a question: How, and how well is the second director aligned in the rotating sample?

G. R. Luckhurst:

[10.8] With respect to thermotropics the alignment of the minor director in a spinning sample is not known, as there are no systems which can be studied. Moreover for lyotropic biaxial nematics one of the minor directors is found to be uniformly aligned along the spinning axis.

S. Chandrasekhar:

[10.9] If you take an nematic and spin it, there are two torques ... In the case of lyotropics high viscous torques ...

G. R. Luckhurst:

[10.10] Continuum theory predicts that for a nematic with a positive diamagnetic anisotropy spun about an axis orthogonal to the magnetic field the director should rotate, on average, with an angular velocity slightly less than that of the sample, provided this is above some critical value. In practice the director is found to be uniformly aligned and to rotate for about ten cycles but then a dephasing process takes place which results in the director being randomly distributed in the plane orthogonal to the spinning axis.

S. Chandrasekhar:

[10.11] What is the criterium you used for your simulation?

G. R. Luckhurst:

[10.12] The observed spectrum is simulated by summing the spectra from all possible orientations of the director.

Session III: *Synthetic search for biaxial nematics.*
Chair: **D. J. Photinos**

[#11] Synthetic search for biaxial nematics
K. Praefcke

D. W. Bruce:

[11.1] Some of the compounds showed some local biaxiality from ESR spectra.

S. Romano:

[11.2] Are there any chiral substituents in the side chains? (triphenylene compounds).

K. Praefcke:

[11.3] No.

K. Praefcke:

[11.4] I believe a stronger collaboration between chemists and theoreticians would be extremely important and fruitful. If chemists knew earlier what their chemical compounds could do they would be more prompted in trying new syntheses. But to this purpose we need to have answers as quickly as possible; not after weeks, months, years, or in most cases never.

D. A. Dunmur:

[11.5] Chemists are focusing on structural single particle properties, while all the others are focusing in cooperative interaction properties.

S. Romano:

[11.6] Could you answer the question if molecules with triple bonds (oligomers of acetylene with suitable terminal groups) form liquid crystalline phases?

[#12] Biaxial nematic phases from metalloporphyrins?
D. W. Bruce* and Q. M. Wang

M. Osipov:

[12.1] You have tried to reduce the temperature of crystallization. Why did you not try to dilute your system using a polarizable non-mesogenic molecule by making a suitable physical mixture?

D. W. Bruce:

[12.2] We have thought about it but is has not been possible to do yet because of the limited amount of product available. We expect to be able to synthesize bigger quantities in the future, then we will try it.

M. Osipov:

[12.3] Can you attach two porphyrin rings with a stiff bridge? The crystallization temperature would not change but the nematic phase would be more stable and with a stronger biaxiality. It is important to have large rings as we need sufficiently strong shape anisotropies in both directions. The molecular length should also be significantly larger then the width.

D. W. Bruce:

[12.4] A nice idea indeed.

G. R. Luckhurst:

[12.5] This is nearly the same as the multi-yne dimers system of Klaus Praefcke.

D. W. Bruce:

[12.6] In principle yes, but these are more rod-like.

S. Romano:

[12.7] What are the simplest ionic mesogens in the literature?

D. W. Bruce:

[12.8] There are in principle two types: the ones we have looked at and fatty acid salts.

S. Fan:

[12.9] Do they form any lyotropic phases?

D. W. Bruce:

[12.10] We have not looked at it yet.

[#13] A possible local biaxiality at the nematic – nematic phase transition of sheet-shaped lyomesogens.

N. Usol'tseva* and K. Praefcke

D. A. Dunmur:

[13.1] Where in these systems could "*local biaxiality*" effects occur? Are you seeing any influences from the surfaces?

N. Usol'tseva:

[13.2] We are actually seeing only the surface influence and we try to understand what is the bulk behaviour in the case of columns formed by tilted molecules. The problem is to separate these effects from surface-induced phenomena.

D. A. Dunmur:

[13.3] Do you have any X-ray data?

N. Usol'tseva:

[13.4] Yes, but it is really difficult to see differences between the two nematic phases.

SUNDAY 22 DECEMBER

Session IV: *General.*

Chair: **G. R. Luckhurst**

[#14] Rods, discs and antinematic interactions.

S. Romano

D. A. Dunmur:

[14.1] We agree about phase separation.

G. R. Luckhurst:

[14.2] Summarizing it seems that unless one does something special to the rods and discs of a given mixture (*e.g.*, enhancing hydrogen bonding interactions) these system will eventually separate into two uniaxial nematic phases rather than form a single biaxial nematic.

[#15] Elastic constants of biaxial nematic liquid crystals.

J. Stelzer and L. Longa*

M. Osipov:

[15.1] It seems that your elastic constants are not independent.

L. Longa:

[15.2] All of the biaxial elastic constants which I was describing are linearly independent. The representation used by us is due to Rainer Trebin [*J. Phys.* (France) **42**, 1573 (1981)].

D. J. Photinos:

[15.3] Is it not a very crude approximation to use the leading term in the high temperature expansion of the Mayer function for the correlation function?

L. Longa:

[15.4] It is a crude approximation as far as absolute values of the elastic constants are concerned. On the other hand relative importance of the various elastic constants is well captured by the Mayer approximation. This has been demonstrated recently by us for uniaxial nematics.

D. J. Photinos:

[15.5] Is it a problem to use a high temperature expansion?

L. Longa:

[15.6] No. Actually we used this expansion (also known in this context as a mean spherical approximation) in our calculations. It is slightly less accurate than the Mayer approach.

D. A. Dunmur:

[15.7] Can you identify any kind of elastic deformation particularly significant for a biaxial liquid crystal?

L. Longa:

[15.8] Generally the ratios of the secondary elastic constants behave as those of primary ones except that they are an order of magnitude smaller.

G. R. Luckhurst:

[15.9] Have you computed the elastic constants for biaxial particles forming a uniaxial nematic phase and checked these results with those for uniaxial particles?

L. Longa:

[15.10] We have not done it yet. But we expect the corrections to be proportional to the square of the molecular biaxiality order parameter.

D. A. Dunmur:

[15.11] If you can switch on and off the molecular biaxiality you could find a large change in the elastic constants.

L. Longa:

[15.12] I do not expect a large change in the Primary Oseen–Zocher–Frank elastic constants. But the elastic constants associated with secondary directors could indeed be strongly affected.

C. Zannoni:

[15.13] Using eighteen orthogonal configurations one would get degenerate elastic constants for the uniaxial case.

L. Longa:

[15.14] Not necessarily. Thermodynamic fluctuations can remove the degeneracy. But in our calculations we have used the mean spherical approximation for the direct pair correlation function which makes the elastic constants proportional to the pair potential. Hence they resemble the degeneracy of the pair potential and only four of them are different.

A. F. Martins:

[15.15] I expect a strong coupling between your elastic constants.

L. Longa:

[15.16] The 12 bulk elastic constants and 3 surface elastic constants I showed are linearly independent. They take care of all restrictions coming from the orthonormality of the directors.

Y. Galerne:

[15.17] Are the elastic constants found to vary approximately linearly with $T_{NI} - T$?

L. Longa:

[15.18] Yes. They are proportional to the square of the order parameters and hence to $T_{NI} - T$.

A. F. Martins:

[15.19] By rotating the molecules you could transform a pure splay into a pure bend distortion and so on. This means that the coupling constants cannot be zero in the biaxial case.

L. Longa:

[15.20] There are general restrictions on the elastic deformations due to the orthonormality of the tripod of the directors which mean that some deformations are not independent. From this, however, we can say nothing about the magnitude of the elastic constants which depend on details of the molecular interactions and on actual thermodynamic parameters like temperature. I accept your point that in general all 12 bulk biaxial elastic constants are non-zero. In the biaxial nematic phase studied by us some of them vanish due to the specific form of the pair interactions and of the approximation imposed for the direct pair correlation function. Using a better theory for the direct correlations, these elastic constants would be non-zero (but very small) and proportional to higher than quadratic powers of the order parameters.

C. Zannoni:

[15.21] If you expand the free energy in eighteen contributions are they orthogonal or independent? What is the minimal basis set for the elastic constants for a biaxial medium?

L. Longa:

[15.22] We have twelve bulk elastic constants, three surface terms and three chiral terms. They are all linearly independent in the sense that none of them can be eliminated by applying the relations that come from the orthonormality conditions of the tripod of the directions. Of course there are many equivalent ways of introducing the 18 elastic constants, but the notation introduced by Rainer Trebin which we have used here seems particularly transparent.

A. Chrzanowska:

[15.23] If you have three sets (x, y and z) of four bulk elastic constants you can express one of them in terms of the other two.

L. Longa:

[15.24] No. All of the biaxial elastic constants which I was discussing are linearly independent.

[#16] Concluding overview.

D. A. Dunmur

D. J. Photinos:

[16.1] I think that we have formed certain guidelines on where and on how to look for phase biaxiality in nematics.

G. R. Luckhurst:

[16.2] I would use a binary mixture or rod-like and disc-like molecules with hydrogen bonding to prevent phase separation.

D. W. Bruce:

[16.3] Besides hydrogen bonding, even interactions based on Lewis acids and bases or charge transfer phenomena could be good choices..

G. R. Luckhurst:

[16.4] In designing a system to form a biaxial nematic phase there are two extreme approaches; one is to create a molecule with the necessary biaxiality while the other is to use a mixture of rod-like and disc-like molecules. Both approaches have their difficulties, for the single component, this is to produce a system with the molecular biaxiality occurring over a very narrow range while for the mixture it is to inhibit the separation into two uniaxial phases. Of these two approaches, I believe that it will be easier to prevent phase separation by using specific molecular interactions than to design molecules with the requisite biaxiality. An extension of this principle is to link the rod-like and disc-like units together chemically, say through a flexible alkyl spacer, which would yield a single component system but with a quite different biaxiality to those which we have been considering.

D. W. Bruce:

[16.5] This way may not be necessarily easier. To finely adjust intermolecular forces could be very difficult. I think it is still worth looking to a single component system.

G. R. Luckhurst:

[16.6] I have said it would be difficult, not impossible.

D. A. Dunmur:

[16.7] We have to distinguish between molecular and phase biaxiality. You can synthesize extremely biaxial molecules of no use at all. The real task lies in stabilizing phase biaxiality.

S. Chandrasekhar:

[16.8] What we are really concerned with is phase biaxiality. We understand that molecular biaxiality is a necessary prerequisite but evidently it is not enough. Furthermore we have realized that if there is phase biaxiality inevitably there will be optical, NMR, ... biaxialities since they are representative of the same phenomena.

C. Zannoni:

[16.9] If you make a mixture using hydrogen bonding you are ending up with a single component system. We are always looking at the molecular shape but I believe the idea of looking at the biaxiality of interaction as well might be rewarding because it could finely tune the effect of shape biaxiality, maybe discouraging the tendency to form smectics.

D. W. Bruce:

[16.10] Do you think would it be possible to form a biaxial phase of uniaxial molecules with a biaxial interaction?

D. A. Dunmur:

[16.11] I do believe so.

D. W. Bruce:

[16.12] What would be the guidelines for the synthesis of such a compound?

S. Chandrasekhar:

[16.13] You may form a biaxial phase using spherical molecules.

D. A. Dunmur:

[16.14] You may form a nematic phase from spherical molecules. ^3He is an example.

C. Zannoni:

[16.15] A fullerene type molecule containing inside a small rod like molecule could be another example.

D. J. Photinos:

[16.16] One is faced with different problems when trying to promote phase biaxiality in pure compounds and in mixtures: in the former case, by increasing the molecular biaxiality (no matter how it is defined it in terms of shape, interactions *etc.*) beyond a certain point one ends up favouring again the uniaxial alignment, only in a different direction. In the case of mixtures there is no requirement of molecular biaxiality but the problem is with phase separation. For mixtures of rods and plates interacting only through hard body forces, Onsager-type theories indicate that phase separation can be avoided if the rods are made sufficiently long and the plates sufficiently thin relative to their diameter, *i.e.*, at large aspect ratios. For intermediate aspect ratios, corresponding to typical thermotropics, separation takes place and there the idea is to promote miscibility by introducing additional interactions between unlike molecules. I do not mean to underestimate the problem of miscibility but I feel that the strategy of mixtures offers more options than the strategy of creating phase biaxiality by "*optimising*" molecular biaxiality in single-component systems.

S. Fan:

[16.17] If we try to learn from the known lyotropic biaxial nematics we should ask what is allowing these systems to express phase biaxiality?

S. Chandrasekhar:

[16.18] You have a shape anisotropy and you can have a dipole ... Since an electric external fields is able to induce biaxiality would it not be possible having suitable biaxial inducing internal fields?

G. R. Luckhurst:

[16.19] My feeling is that it is not possible.

D. A. Dunmur:

[16.20] Field-induced biaxiality with attainable field strengths would be difficult to achieve Stress-induced systems could have the required field strengths. For instance one could think of stress induced biaxiality in polymeric systems.

S. Chandrasekhar:

[16.21] The energy required to produce biaxiality is smaller than that necessary to form alignment. So, the possibility of enhancing biaxiality by hindering the molecular rotations in another synthetic possibility.

C. Zannoni:

[16.22] In magnetic systems you have spherical beads with magnets ... From the point of view of interaction there are examples when molecules behave in this fashion. Some purely sterical models (hard ellipsoids) will not form smectics, so if we put transversal interactions in the correct way we may obtain a biaxial phase. Gay–Berne molecules easily form smectic phases but ...

D. A. Dunmur:

[16.23] There are chemical ways ...

D. W. Bruce:

[16.24] Your analogy is going the opposite direction of what Demetri says.

M. Osipov:

[16.25] There are ways of forming strong interactions without hydrogen bonding. The best ones are induction interactions, for instance dipole – induced dipole. These can be made even larger than k_BT. In this way it is possible to make interactions between unlike molecules to be stronger then those between like ones. Induction forces can be stronger than the corresponding dipole – dipole ones (which are partially averaged out in a fluid) or than the dispersion forces.

P. L. Nordio:

[16.26] I am sure that it is possible from theory and simulation to give suggestions, but there is a weakness in the theory connected with fluctuations. We have to be sure that the biaxial phase is not destroyed by fluctuations. The study of elastic properties is very valuable from this point of view provided there is a long enough coherence length.

L. Longa:

[16.27] From a theoretical point of view biaxial order is legitimate and there are fundamental reasons for its existence. Theory predicts that biaxial order is promoted and I believe fluctuations will not kill it.

D. A. Dunmur:

[16.28] But biaxial elastic constants are at least one order of magnitude smaller than uniaxial ones and their fluctuations could be extremely large.

L. Longa:

[16.29] ...

S. Chandrasekhar:

[16.30] You have to produce a suitable shape anisotropy to have such effects, as in a Gay – Berne model. In a real system things would not be so easy.

D. W. Bruce:

[16.31] This is exactly what I wanted to introduce with the Finkelmann analogue. What if we "*polymerize*" a system of rod – disc biaxial pairs?

A. F. Martins:

[16.32] Unless we are out of equilibrium we cannot produce a continuous stress in a fluid system. I feel biaxiality would be difficult to get. Normally the smectic phase will form before secondary interactions will be strong enough. Dynamic surface charges may favour biaxial alignment of molecules. With associated molecules biaxiality could be produced more easily.

D. W. Bruce:

[16.33] Is it possible that N_b could be below a S_mA phase? Are we crazy enough? Should we look at different behaviour?

G. R. Luckhurst:

[16.34] The importance of a joint report, *e.g.*, in *Liquid Crystals Today*, as suggested by K. Praefcke, and generally the necessity of immediate feedback from the physicists to the chemist and *vice versa* has to emphasized again. This should generally be kept in mind during all of our work.

Acknowledgement:

[16.35] With warm words and on behalf of all participants from ten countries *K. Praefcke* expressed his cordial gratitude to the three organizers (Professors D. W. Bruce, G. R. Luckhurst, and D. J. Photinos) of our brainstorming on biaxial nematics in this beautiful monastery, St. Benet's Hall at Oxford, to its master, Dom. Henry Wansbrough, for the courteous hospitality and stimulating spirit within his convent's own four walls, and to Mrs. Prof. N. Usol'tseva from Russia for the artistic touch she added to this EU-meeting by her wonderful piano playing.

In summary, all these circumstances helped to create the right atmosphere for letting our workshop become such a great success.