Proc. Indian Acad. Sci. (Chem. Sci.), Vol. 94, No. 1, March 1985, pp. 139–179

Molecular interactions and dynamics in liquid crystals

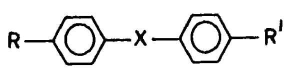
S CHANDRASEKHAR and N V MADHUSUDANA
Raman Research Institute, Bangalore 560 080, India

1. Introduction

The anisotropy of molecular shape is a fundamental requirement for the formation of liquid crystals. Until recently, the rule was that the molecule has to be long and rod-like for mesomorphism to occur, but it has now been established that simple disc-shaped molecules may also form stable mesophases (Chandrasekhar *et al* 1977). Liquid crystallinity may be induced by purely thermal effects (thermotropic mesomorphism) or by the influence of solvents (lyotropic mesomorphism). We shall be concerned here only with the former type of mesomorphism, that too in relatively low molecular weight compounds, and not deal with lyotropics or high molecular weight systems like mesomorphic polymers.

Thermotropic liquid crystals exhibit a rich variety of phases, the broad structural features of which are summarised in table 1. A description of the physical properties of these phases may be found in standard books and articles on the subject (see, for example, Chandrasekhar 1977, 1983; de Gennes 1974). It should be pointed out, however, that the detailed structures are not known with certainty for a number of these phases, and some confusion remains in regard to the structural classification of the more ordered smectic modifications (Gray 1981; Demus *et al* 1980). Recent high resolution x-ray studies have shown that several of these modifications possess three-dimensional positional order, though the interlayer forces are extremely weak, very much weaker than in the ordinary crystalline solid. These highly ordered phases cannot therefore be called liquid crystals in the strict definition of the term. As far as the newly discovered phases of disc-like molecules are concerned, the subject is still very much in its infancy. For these reasons, the discussion in this article will be confined largely to those liquid crystalline phases whose structures are known unambiguously and which have been investigated in detail both experimentally and theoretically from the standpoint of molecular interactions and dynamics, though of course references will be made to the other phases wherever it is relevant.

Typically, the simplest rod-like mesogenic molecules have a structure of the form



where both R and R′ may be hydrocarbon chains, or R a small group like CN, NO_2, Br, etc., and R′ a chain; the middle portion of the molecule is a more or less rigid aromatic core with a central linkage group X, though in some molecules X may be absent altogether. Also, in some cases one or both the phenyl rings may be saturated. Examples of other types of molecules are nona-2,4-dienoic acid, a purely aliphatic compound, and

Table 1. Structural classification of thermotropic liquid crystals.

Rod-like molecules	
Nematic (N)	Long range orientational order but no long range translational order (figure 1a)
Cholesteric (Ch)	Chiral nematic (figure 1b)
Smectic $A(S_A)$	Liquid-like layers with upright molecules (figure 1c)
$B(S_B)$	Two distinct types of S_B have been identified: (i) 3D crystal, hexagonal lattice, upright molecules (Moncton and Pindak 1979), (ii) stack of interacting 'hexatic' layers with in-plane short range positional correlation and long range 3D six-fold 'bond-orientational' order (Pindak *et al* 1981)
$C(S_C)$	Tilted form of S_A (figure 1d)
$C^*(S_{C^*})$	Chiral S_C with twist axis normal to the layers (see figure 7)
$D(S_D)$	Cubic
$E(S_E)$	3D crystal, orthorhombic, upright molecules (Doucet *et al* 1975)
$F(S_F)$	Monoclinic ($a > b$) with in-plane short range positional correlation and weak or no inter-layer positional correlation (Gray 1981; Leadbetter *et al* 1980; Gane *et al* 1981) (tilted hexatic?)
$G(S_G)$	3D crystal, monoclinic ($a > b$) (Gray 1981; Gane *et al* 1981)
$G'(S_{G'})$	3D crystal, monoclinic ($b > a$) (Gane *et al* 1981)
$H(S_H)$	3D crystal, monoclinic ($a > b$) (Leadbetter *et al* 1980; Gane *et al* 1981)
$H^*(S_{H^*})$	Chiral S_H with twist axis normal to the layers
$H'(S_{H'})$	3D crystal, monoclinic ($b > a$) (Gane *et al* 1981)
$I(S_I)$	monoclinic ($b > a$), possibly hexatic with slightly greater in-plane positional correlation than S_F (Gane *et al* 1981; Pindak *et al* 1982)
$I^*(S_{I^*})$	Chiral S_I (Pindak *et al* 1982)
Disc-like molecules (Chandrasekhar 1982; Destrade *et al* 1981a)	
D_{hd}	Columnar structure (D) with a hexagonal packing of the columns and a disordered or liquid-like arrangement of the discs in each column (figure 2a, b)
D_{ho}	hexagonal but with an ordered arrangement of the molecular cores in each column
D_{rd}	rectangular, disordered (figure 2c)
D_t	tilted columnar structure (figure 2d)
N_D	nematic-like arrangement of discs (figure 2e)
N_D^*	Chiral N_D

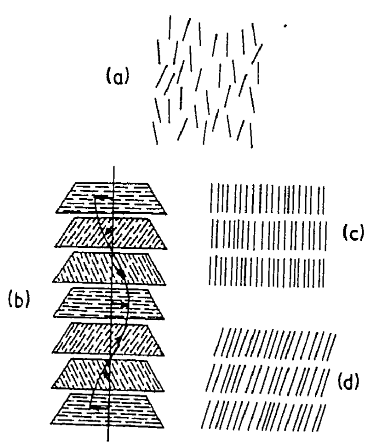


Figure 1. Liquid crystals of rod-like molecules: (a) nematic, (b) cholesteric, (c) and (d) normal and tilted smectic structures.

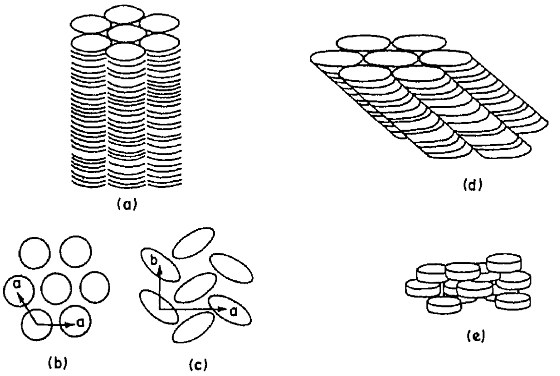


Figure 2. Liquid crystals of disc-like molecules: (a) columnar phase with upright columns; (b) and (c) hexagonal and rectangular modifications of the upright columnar structure; (d) tilted columnar phase; (e) 'nematic' phase.

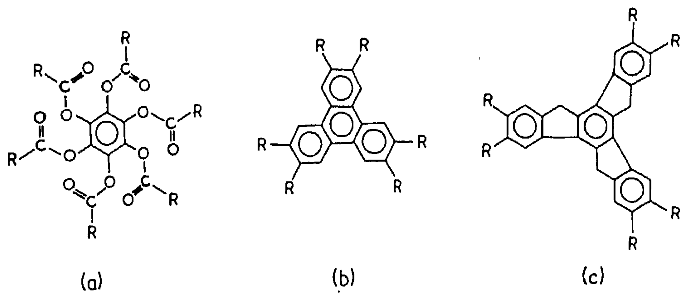


Figure 3. Disc-shaped mesogens: (a) hexa-substituted esters of benzene (Chandrasekhar *et al* 1977); (b) hexa-substituted esters or ethers of triphenylene (Billard *et al* 1978; Destrade *et al* 1979); hexa-*n*-alkyl or alkoxybenzoates of triphenylene (Destrade *et al* 1980); (c) hexa-*n*-alkanoates of truxene (Destrade *et al* 1981b).

p-quinquephenyl, a string of five benzene rings in a row without any end chains. To date, several thousands of mesogens are known (see, for example, Demus *et al* 1974; Demus and Zaschke 1984; Kelker and Hatz 1980) and most of them have rather more complex structures than indicated above. The effect of the central linkage group, the terminal and lateral substituents, and the role of the end chains in determining mesomorphic properties have been extensively discussed (Gray 1976, 1979) and therefore will not be repeated here. The stability of the mesophase is a delicate balance of dispersion forces and steric effects, and, if the molecule is polar, the permanent dipolar forces as well. It is clear that for molecules of such complexity these interactions are by no means easy to calculate.

Comparatively few disc-shaped mesogens have been synthesised so far (Chandrasekhar 1982). Three typical molecular structures are shown in figure 3.

2. Molecular interactions

2.1 *Nematic liquid crystals*

The nematic is the simplest type of liquid crystal and the problem of the molecular interactions responsible for its stability has been the subject of numerous discussions.

The first successful 'mean field' theory of this phase was developed by Maier and Saupe (1958–60), who used a single particle potential of the form

$$U_i = -AsP_2(\cos\theta_i) \tag{1}$$

where A depends on the molecular species and is a function of the density ρ, $s = \langle P_2(\cos\theta)\rangle$ is the orientational order parameter, and $P_2(\cos\theta)$ the Legendre polynomial of the second order. Such a potential is consistent with the fact that the director (or the vector **n** defining the axis of preferred orientation of molecules) is *apolar*. Maier and Saupe assumed that this potential arises from the dipole-dipole part of the anisotropic dispersion forces and thus put $A \propto \rho^2$. However, experiments on the pressure dependence of the order parameter indicate that $A \propto \rho^\gamma$, where $\gamma = 4$ for PAA (*p*-azoxyanisole, McColl and Shih 1972) and in some other cases even greater than 4 (Horn 1978; Horn and Faber 1979). On the other hand, an argument due to Cotter (1977a) shows that thermodynamic consistency of the mean field theory requires that $\gamma = 1$. But, regardless of the magnitude of γ, the theory leads to a universal value of $s \approx 0{\cdot}43$ at T_{NI}, the nematic-isotropic (NI) transition point, for all substances. Experimentally, there are small but systematic deviations from this universal value which can be accounted for by including higher order terms in the potential function (Chandrasekhar and Madhusudana 1971; Humphries *et al* 1972). The principal drawback of the mean field approximation is that it predicts a heat of transition which is much too high, usually by a factor of 2 or 3. The theory can be improved significantly by taking into account near neighbour orientational correlations in terms of a Bethe cluster (Madhusudana and Chandrasekhar 1973a; Madhusudana *et al* 1977; see also Ch. 2 of Chandrasekhar 1977), but quantitatively the agreement is still not too satisfactory.

Another microscopic approach is to treat the system as an assembly of hard rods. The first theory of the phase transition in a hard rod system was developed by Onsager (1949). The properties of such an 'athermal' system depends entirely on the density, and the basic problem is to evaluate φ_N, the excess free energy relative to an ideal gas, with a suitable orientational distribution function of the rods. Onsager made a virial expansion of φ_N and retained only the second virial coefficient. This approximation is valid for low densities and thus for very long rods with a length to breadth ratio ≈ 100. Zwanzig (1963) could evaluate higher virial coefficients by restricting the molecules to take up only three mutually perpendicular orientations. Flory (1956) and Flory and Ronca (1979) used a lattice model and were able to make calculations at relatively high densities. However, these descriptions are useful only for long polymeric molecules (Straley 1973), the predicted s at T_{NI} being $\approx 0{\cdot}85$.

For relatively short rods (of length to breadth ratio $\approx$ 3–5) and high densities, the scaled particle theory provides a convenient method of evaluating φ_N. Cotter (1974, 1979) has developed the most complete form of the theory as applied to nematic liquid crystals. In this scheme, the reversible work $w_i(\alpha, \lambda, \rho)$ of adding a scaled rod (α, λ being the scaling parameters along the length and breadth of the molecule) oriented along Ω_i is evaluated. For $\alpha, \lambda \to 0$, the virial expansion is valid. On the other hand, when $\alpha, \lambda \to \infty$, w_i approaches the PV work to create a macroscopic cavity in the fluid. $w_i(1, 1, \rho)$ is now evaluated by interpolating between these two limits. Calculations (Cotter 1974, 1979; Savithramma and Madhusudana 1980; see also Madhusudana 1981) for rods having the shape of spherocylinders show that many properties predicted by the theory compare favourably with those of a real system, *eg*, PAA. Recently, another method has been used (Savithramma and Madhusudana 1980; Madhusudana 1981) for evaluating φ_N by extending the Andrews (1975) model for calculating the equation of state of a liquid. Basically, this model depends on the recognition that the reciprocal of the thermodynamic 'activity' is merely the probability of being able to insert a particle into the given system such that the extra particle does not overlap with other particles. The model leads to a better description of the nematic phase than that given by the scaled particle theory. Computer simulation studies have also been carried out for hard spherocylinders but till now only for the isotropic phase (Vieillard-Baron 1974; Rebertus and Sando 1977; Nezbeda and Boublik 1978).

It is clear that a realistic theory of nematics should incorporate the attractive potential between the molecules *as well as* their hard rod features. Several hybrid models have been proposed on the basis of the lattice theories (Alben 1971). More recently, equations of state have been derived based on the Percus-Yevick and BBGKY approximations for spherical molecules which are subject to an attractive Maier-Saupe potential (Ypma and Vergoten 1977; Wagner 1981). However, these models lead to $\gamma \approx 1$, where $\gamma = [\ln T/\ln V]_s$ is a measure of the relative importance of volume compared to that of temperature in determining the variation of s near T_{NI}. (In the mean field models which make use of only an attractive potential γ is equal to the exponent of ρ.) The anisotropic shape of the molecule has to be explicitly considered to obtain higher values of γ.

Cotter (1977b; for an up-to-date review, see Cotter 1983) has extended the scaled particle theory to include an attractive potential of the type

$$U_i = -v_0\rho - v_2\rho s P_2(\cos\theta_i).$$

The resulting distribution function is similar to that in the Maier-Saupe theory, except that the coefficient of the potential has the form $[(v_2\rho/kT) + \Lambda(\rho)]$, *ie*, a temperature-dependent attractive part and an 'athermal' part corresponding to the hard particle contribution. The theoretical results can be improved further by using the Andrews model (Savithramma and Madhusudana 1980; Madhusudana 1981). These last two approaches yield promising results—for example, it turns out that $\gamma \approx 4$ for PAA without violating Cotter's thermodynamic consistency condition that the mean field potential should be $\propto \rho$. Certain generalised van der Waals models (Gelbart and Baron 1977; Cotter 1977c) have also been proposed but these lead to results which are essentially similar to the scaled particle theory with a superposed attractive potential. Luckhurst and Romano (1980) have carried out a Monte-Carlo computer simulation study on 256 cylindrically symmetric rigid particles with an attractive potential. They have made calculations for a certain value of an 'anisotropy parameter' and found a weak NI transition, and compared the results with the predictions of the Maier-Saupe theory.

In all these models, the molecules have been taken to be cylindrically symmetric, but most real nematogens have lower symmetry which lowers the order parameter at T_{NI}. Recent calculations (Alben 1973; Straley 1974; Luckhurst *et al* 1975; Gelbart and Barboy 1979) have shown the importance of taking this into consideration. Moreover, the assumption that the molecule is a rigid rod is an oversimplification. Attempts have been made (Marcelja 1974; Martire 1974; Dowell and Martire 1978; Luckhurst 1984) to calculate the contribution of the flexible end chain to the ordering process, and to explain the so-called 'odd-even effect, *ie*, the alternation in T_{NI}, the order parameter and other related properties of successive members of a homologous series. Also, permanent dipolar interactions cannot be neglected, but these give rise to certain special effects which we shall discuss later in greater detail (§3).

Until fairly recently, only $\langle P_2 \rangle$ was accessible experimentally, but now a method is available for measuring both $\langle P_2 \rangle$ and $\langle P_4 \rangle$. The technique, developed by Jen *et al* (1973) involves polarized Raman scattering measurements using aligned samples. A few cyano-compounds have been investigated by this method making use of the C≡N stretching vibration for the Raman measurements. It has been found in most cases studied so far that $\langle P_4 \rangle$ is negative for at least a part of the nematic range (Jen *et al* 1973; Miyano 1978; Prasad and Venugopalan 1980, 1981; Dalmolen *et al* 1984). Using the observed values of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ one can calculate a truncated angular distribution function (Jen *et al* 1973). The results indicate that the molecule has a strong tendency to be tipped away from the nematic axis, which cannot be explained by any of the theories discussed above. More data are needed to confirm these findings, but in any case it would appear that this is an important unsolved problem (Luckhurst and Vitoria 1982; Feng *et al* 1983; de Jeu 1983).

2.2 *Cholesteric liquid crystals*

The cholesteric is also a nematic type of liquid crystal except that the director does not have a uniform orientation in space but is twisted in the form of a helix (figure 1b). Such a structure is obtained when the molecules are chiral, or even when a small amount of an optically active compound is added to a nematic. The energy needed to twist the director is very small compared to the nematic potential. However, to explain the helical structure the chiral nature of the molecules has to be explicitly taken into account. There have been a few attempts to derive a molecular theory of the cholesteric phase. Schröder (1979) has discussed the general potential between chiral molecules based on their symmetry. Goossens (1971) has shown that the dipole-quadrupole part of the dispersion forces is the lowest order contribution to the chiral interaction leading to the helical arrangement of the director. Van der Meer and Vertogen (1979a) have developed a Maier-Saupe type mean field theory by including in the potential a term of the type $-K(\mathbf{a}_i \cdot \mathbf{a}_j)(\mathbf{a}_i \times \mathbf{a}_j \cdot \mathbf{u}_{ij})$, where $\mathbf{a}_i$, $\mathbf{a}_j$ and $\mathbf{u}_{ij}$ are unit vectors along the long axes of the molecules i, j and along the line connecting the two molecules respectively. They have argued that this form of the potential can be obtained by assuming that the molecule can be modelled to have a number of linear polarisabilities which are regularly situated on a twisted cylindrical surface. Contributions to the above form of the potential can also come from the chiral shape of the molecules (for example, a twisted cog-wheel). The two contributions need not have the same sense and may account for the helix inversion found in some nematic-cholesteric mixtures as a function of concentration. They have also shown that a part of the temperature variation of the pitch is connected with the variation of $(k_{11} - k_{33})/k_{22}$, where k_{11}, k_{22} and k_{33} are the splay, twist and bend elastic constants of the material.

2.3 *Smectic and columnar liquid crystals*

Quantitatively speaking, much less is understood about molecular interactions in the smectic phases, and only S_A and S_C have been discussed in any detail.

McMillan (1971, 1972) extended the Maier-Saupe theory of nematics to the S_A phase by assuming a density wave along the director axis. The potential energy of a test particle is then given by

$$V_i = -V_0 P_2(\cos\theta_i)[s + \alpha\sigma\cos(2\pi z/d)]$$

where d is the layer spacing, $\sigma = \langle P_2(\cos\theta)\cos(2\pi z/d)\rangle$ is an order parameter coupling the translational and orientational ordering, and $\alpha \equiv 2\exp[-(r_0/d)^2]$ is a molecular parameter where r_0 is the dimension of the rigid core of the molecules. The theory predicts that for $\alpha > 0{\cdot}98$, the S_A transforms directly to the isotropic phase, while for $\alpha < 0{\cdot}98$ there is an AN transition followed by an NI transition at a higher temperature. For $\alpha \leqslant 0{\cdot}7$ the AN transition is of second order. α increases with the length of the end chain of the molecule. The general conclusions of the theory are in accord with the observed trends. To allow for the fact that real molecules are not cylindrically symmetric but lath-like, the theory has been extended recently to include the possibility of a biaxial S_A phase (Matsushita 1981).

Physically, the strongest attractions between two smectogenic molecules are between their aromatic cores and hence as the end chain length is increased, the cores would prefer to arrange themselves in layers, thus leading to the formation of the smectic phase. However, it must be pointed out that there are some notable exceptions to this rule; for example, *p*-sexiphenyl which has no end chain has been reported to exhibit the S_A phase (Lewis and Kovac 1979).

Generally speaking, the presence of polar groups in the molecule appears to favour the formation of smectic phases. In particular, lateral dipole moments are essential for the occurrence of the S_C phase. Van der Meer and Vertogen (1979b) have shown that the forces between lateral dipoles and the 'induced' dipoles at the centres of neighbouring molecules can lead to a tilted structure as in the S_C phase.

The McMillan model has recently been extended to liquid crystals of disc-like molecules (Kats 1978; Feldkamp *et al* 1981; Chandrasekhar 1983; Chandrasekhar *et al* 1984). The translational order parameter now describes a two-dimensionally periodic

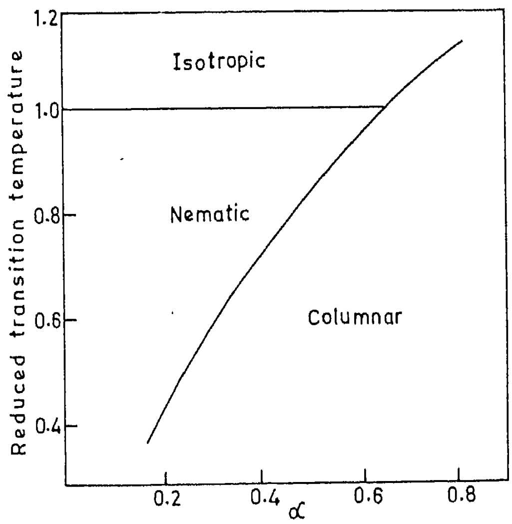


Figure 4. Theoretical diagram showing the hexagonal, nematic and isotropic phase boundaries. All the transitions are of first order (Feldkamp *et al* 1981; Chandrasekhar *et al* 1984).

structure representing the columnar phase. Calculations show that for the hexagonal lattice the transition from the columnar to the isotropic phase may take place either directly or *via* a nematic phase depending on the model potential parameter α (Feldkamp *et al* 1981; Chandrasekhar 1983; Chandrasekhar *et al* 1984) (figure 4). On the other hand, for a biaxial face-centered rectangular lattice (with axial ratio $b/a \neq 3^{1/2}$) the nature of the phase diagram depends on the value of b/a (Chandrasekhar 1983; Chandrasekhar *et al* 1984). When b/a departs only slightly from $3^{1/2}$, the behaviour is very similar to the hexagonal case. Interpreting α to be a measure of the chain length as in McMillan's model, the phase diagram is in broad agreement with the trends exhibited by the hexa-*n*-alkoxy-benzoates of triphenylene. For greater asymmetry of the lattice, the theory predicts the possibility of a columnar-biaxial smectic *A* transition as well. Evidence of a smectic phase in bis-(*p*-*n*-decylbenzoyl)methanato copper(II), a disc-like molecule, has been reported very recently (Ribeiro *et al* 1984). Thus this simple model serves to illustrate that the origin of the two-dimensional translational order in the columnar phase is similar to that of the one-dimensional order in the smectic *A* phase of rod-like molecules in so far as the attraction between the aromatic cores and the role of the end chains are concerned.

3. Some special interactions

In this section we discuss some special types of molecular interactions in liquid crystals which give rise to remarkable effects of fundamental significance, *eg*, flexo-electricity, ferroelectricity, reentrant phenomena, etc.

3.1 *Flexo-electricity*

If the molecule possesses shape polarity as well as a permanent dipole moment, then a splay or bend deformation may polarize the nematic medium, or conversely an electric field may induce a deformation (Meyer 1969; figure 5). This property is known as flexo-

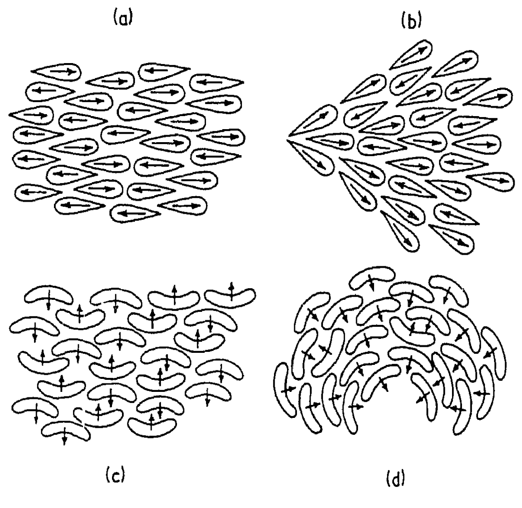


Figure 5. Meyer's model of flexoelectricity. The nematic composed of polar molecules is non-polar in the undeformed state (a and c) but polar under splay (b) or bend (d).

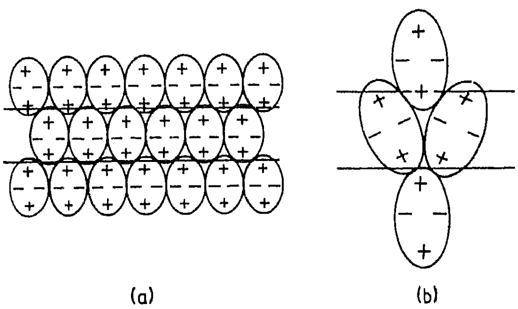


Figure 6. Schematic interpretation of the origin of flexoelectricity in an assembly of quadrupoles (Prost and Marcerou 1977): (a) the symmetry is such that there is no bulk polarization, (b) a splay deformation causes the positive charges to approach the upper plane and to be pushed away from the lower one. This dissymmetry gives rise to a dipole moment pointing upwards.

electricity. The mechanism may be generalised to include induced dipole moments as well. The effect may be looked upon as arising from a coupling of an electric field with a gradient of the director field, but additionally there may be another contribution which comes from a coupling of an electric field gradient with the director. The latter can be attributed to the quadrupole moments of molecules which need not even have shape polarity (Prost and Marcerou 1977). Figure 6 illustrates the physical picture of the origin of flexo-electricity in an assembly of quadrupoles.

The permanent dipolar contribution to the flexo-electric coefficient for pear-shaped molecules may be written as (Marcerou and Prost 1978; Derzhanski and Petrov 1979)

$$f = K_{11} \frac{\varepsilon^{\circ}_{zz} - \varepsilon'_{zz}}{4\pi\alpha},$$

where ε°_{zz} is the static dielectric constant parallel to the director, ε'_{zz} that at a frequency just above the first relaxation (see §4.2), K_{11} the splay elastic constant and α a number relating to the shape polarity. Since $K_{11} \propto s^2$, where s is the order parameter, $f \propto s^2$ to a first approximation. Further, for frequencies beyond that of the relaxation, the permanent dipolar contribution to f is zero.

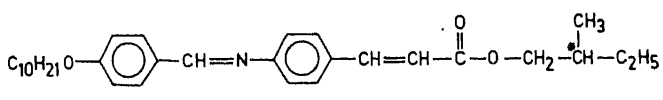
The quadrupolar contribution is (Marcerou and Prost 1978; Derzhanski and Petrov 1979)

$$f \approx -\tfrac{2}{3} n s \theta_a$$

where n is the number of molecules/cc, and θ_a the quadrupole moment. Thus, in this case $f \propto s$ and moreover it will not have the frequency dependence of the permanent dipolar contribution. From experiments in the N as well as S_A phases, it has been shown that it is the quadrupole effect that is most common (Prost and Pershan 1976; Marcerou and Prost 1980), f being usually $\approx 10^{-4}$ esu.

3.2 *Ferroelectricity*

Ferroelectricity in liquid crystals was first demonstrated by Meyer *et al* (1975; see also Meyer 1977) in the S_{C^*} and S_{H^*} phases of DOBAMBC,



which shows the following transitions:

$$\text{crystal} \xleftrightarrow{76°C} S_{C^*} \xleftrightarrow{95°C} S_A \xleftrightarrow{117°C} \text{isotropic}$$
$$S_{C^*} \xrightarrow{63°C} S_{H^*}$$

In the S_A phase, the molecules (which are not only chiral but also have a non-zero dipole moment) are arranged normal to the layers. Since there is no 'head-to-tail' ordering (the director being apolar) there is no polarization normal to the layers. Further, since the molecules are rotating about their long axes the transverse component of the dipole moment is averaged out and there is no net polarization parallel to the layers.

In the S_{C^*} phase the molecules are tilted and their rotation about their long axes is biased. The symmetry plane of the ordinary S_C structure (figure 7a) is now absent because the molecules are chiral. The only symmetry element left is a two-fold rotation axis parallel to the layers and normal to the long molecular axis. This allows the existence of a permanent dipole moment parallel to this axis. Thus in S_{C^*} each layer is spontaneously polarized. The value of this polarization is very small, about 3×10^{-8} C/cm^2 as compared with 5×10^{-6} C/cm^2 for KH_2PO_4. In terms of the dipole moment this turns out to be only $\approx 0{\cdot}25$ debye/molecule. The tilt and the polarization directions rotate from one layer to the next (figure 7b). This implies that there is constant bend around the z-axis which leads to a flexo-electric contribution to the polarization (Durand and Martinot-Lagarde 1980).

When an electric field E is applied normal to the helical axis, the helix gets distorted; above a critical field E_c, it is completely unwound and the sample is poled with the molecules tilted along a preferred direction normal to E. Since this unwinding involves the rotation of the tilt direction, the response is damped by the rotational viscosity of the fluid. Therefore E_c increases with frequency. For the same reason the dielectric

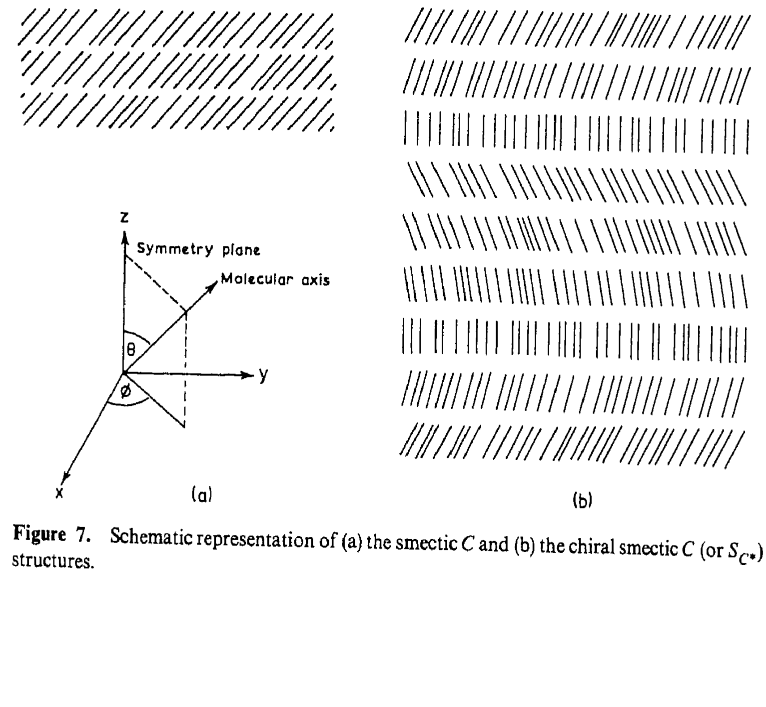


Figure 7. Schematic representation of (a) the smectic C and (b) the chiral smectic C (or S_{C^*}) structures.

constant exhibits a relaxation in the 10^2–10^3 Hz range (Ostrovskii *et al* 1979; Dmitrienko and Belyakov 1980).

Liquid crystalline ferroelectrics may be classified as 'improper' ferroelectrics. Both the tilt angle θ and the polarization P go to zero continuously as the temperature is raised to the $C^* - A$ transition point (T_{C^*A}). Actually T_{C^*A} is itself the Curie point. This coupling between P and θ produces a divergent component in the dielectric constant. It is expected that for $T < T_{C^*A}$ there is in addition to a *soft* mode, a symmetry recovering *Goldstone* mode. Attempts have been made to identify these modes from dielectric relaxation measurements (Garoff and Meyer 1977; Hoffmann *et al* 1978; Levstik *et al* 1979; Zeks *et al* 1979; Martinot-Lagarde and Durand 1981).

The pyroelectric behaviour of these ferroelectric smectics has been studied (Yu *et al* 1976). The pyroelectric coefficient $\gamma(T) = \mathrm{d}P_s/\mathrm{d}T$ increases with increase of temperature and near T_{C^*A} it is $\approx 2 \times 10^{-9}$ C cm^{-2} deg^{-1}, comparable to the values for solid pyroelectrics. Away from $T_{C^*A}, \gamma = 2 \times 10^{-11}$ C cm^{-2} deg^{-1}. The pyroelectric response to a heat pulse exhibits an exponential decay and the time constant is equal to the relaxation time of the dipoles responsible for the spontaneous polarization (Yu *et al* 1976; see also Blinov *et al* 1979).

3.3 *Re-entrant phases and the polymorphism of smectic A*

If the nematic is composed of molecules having a strong longitudinal dipole moment (as will be the case if the molecular end group is CN or NO_2) neighbouring molecules tend to be antiparallel. However, since the mesophase is fluid there can be no long range antiparallel order. The concept of antiparallel near-neighbour correlations (or *antiferroelectric short range order*) was proposed some years ago and its implications were discussed on the basis of the Bethe-Peierls cluster approximation (Madhusudana and Chandrasekhar 1973b; Madhusudana *et al* 1977). An important prediction of the theory is that the mean dielectric constant should increase by a few per cent on going from the nematic to the isotropic phase because of a decrease in the anti-parallel ordering at the transition, and this is borne out by measurements on a number of compounds (Schadt 1972; Ratna and Shashidhar 1976; Bradshaw and Raynes 1981; for a complete list of references, see Chandrasekhar 1984). Neutron diffraction studies on isotopically substituted cyano-compounds have confirmed that the nearest neighbours do indeed prefer to be antiparallel (Leadbetter *et al* 1979a).

A remarkable consequence of this type of antiparallel correlation was discovered by Cladis (1975) in binary mixtures of cyano-compounds. Over a range of compositions, the sequence of transitions on cooling was as follows:

$$I \rightarrow N \rightarrow S_A \rightarrow N \rightarrow \text{solid}.$$

The lower temperature N phase is referred to as the *reentrant* nematic phase (N_R). Examples of more complex behaviour are now known, but we shall first consider this simple type of reentrance. Some relevant experimental facts pertaining to this type of reentrant behaviour are (i) the smectic A phase is a partially bilayer structure, designated as A_d (see figure 9), its layer spacing varying only *very slightly* with temperature or pressure (Guillon *et al* 1978; Chandrasekhar *et al* 1980a, b; Raja and Shashidhar 1984) and (ii) the dielectric anisotropy increases as the sample is cooled from N through A_d into the N_R phase (Ratna *et al* 1980).

From the molecular point of view, only an approximate, qualitative explanation of

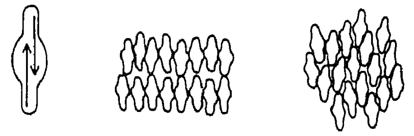
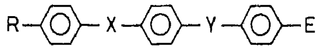


Figure 8. Schematic representation of (a) a dimer unit consisting of two antiparallel molecules, (b) the mechanism of destabilization of the smectic A phase (Cladis 1980).

reentrant behaviour has been possible. The basic idea underlying the molecular model is that because of the antiparallel correlations the molecules form dimers, which are assumed to be somewhat bulgy in the middle (figure 8a). Once the smectic phase is formed the bulgy parts are lined up in a plane, but the alkyl chains cannot fill the rest of the space. With increasing dimer formation (ie with decreasing temperature) and also possibly with the stiffening of the end chains, the packing becomes so unfavourable that the A_d phase is destabilized and the nematic reenters (figure 8b). The elements of the model were proposed by Cladis (1980, 1981) and Cladis *et al* (1981), but a more complete theoretical discussion involving attractive forces and hard core repulsions has been presented by Longa and de Jeu (1982), who showed that there can indeed be a lower temperature nematic phase. Qualitatively this is satisfactory. However, antiferroelectric short range order is a statistical effect, and to look upon the system as a sum of two extreme situations, the perfectly paired dimer with the dipoles compensated and the completely unpaired monomer with the full value of the dipole moment is a rather gross approximation. For example, the model assumes that there is a substantial increase in the dimer concentration with decreasing temperature. If this were so the smectic A layer spacing should increase markedly and the dielectric anisotropy should drop appreciably with decreasing temperature (see Chandrasekhar 1984). Both these predictions are at variance with the experimental facts. One may conclude, therefore, that the appearance of the reentrant phase involves much more subtle structural changes than expected from the current molecular treatments of this phenomenon. Essentially the same conclusions have been drawn from high resolution x-ray studies by Kortan *et al* (1984) who found no detectable change in the lateral intermolecular spacing or in the in-plane correlations in the N, A_d and N_R phases.

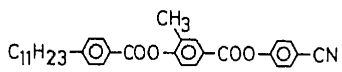
As mentioned earlier, much more complex examples of reentrance have now been found, notably by the Bordeaux group (for recent reviews see Hardouin *et al* 1983 and Tinh 1983). Closely related to this is another interesting effect, *viz*, the occurrence of different types of smectic A and of smectic A-smectic A transitions. It emerges that both reentrant behaviour and smectic A polymorphism are extremely sensitive to the molecular structure. We illustrate this by considering the properties of pure 3-benzene-ring compounds having the structural formula given below. From the data reported to date, the compounds fall into 4 distinct types, the arrows representing the directions of the longitudinal components of the dipole moments of the bridging groups X and Y.



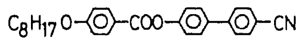
	X	Y	E	
Type I	→	→ or ← or non-polar	CN	Reentrant nematic
Type II	→	→ or ← or non-polar	NO_2	No reentrance; No *A-A* transition
Type III	←	←	CN	*A-A* transitions, no reentrance
Type IV	←	←	NO_2	Reentrance and *A-A* transitions

Examples:

Type I (a) $I \rightarrow N \rightarrow A_d \rightarrow N_R$

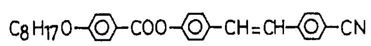


Madhusudana *et al* 1979

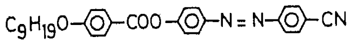


Hardouin *et al* 1979a

(b) $I \rightarrow N \rightarrow A_d \rightarrow N_R \rightarrow A_1$

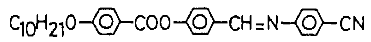


Hardouin *et al* 1979b

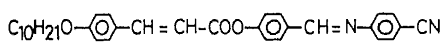


Heppke *et al* 1980

(c) $I \rightarrow N \rightarrow A_d \rightarrow C \rightarrow N_R$

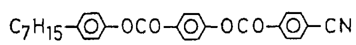


Weissflog *et al* 1980

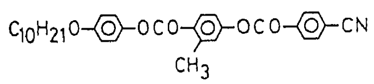


Tinh *et al* 1982

Type III $I \rightarrow N \rightarrow A_d \rightarrow A_2$

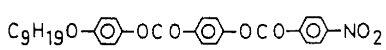


Hardouin *et al* 1981



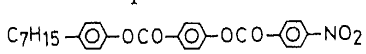
Madhusudana *et al* 1982

Type IV (a) $I \rightarrow N \rightarrow A_d \rightarrow N_R \rightarrow A_d \rightarrow N_R \rightarrow A_1 \rightarrow \tilde{C} \rightarrow A_2 \rightarrow C_2$



Tinh *et al* 1982; Shashidhar *et al* 1985

(b) $I \rightarrow N \rightarrow A_1 \rightarrow \tilde{A}$



Tinh 1983

It is worth mentioning that type IV(a) is an example of a compound showing three nematic, four smectic A and two smectic C phases[1] Schematic representations of the structures of the different A and C phases identified to-date are given in figures 9 and 10 respectively.

Needless to say, we are nowhere near explaining these facts from a molecular theoretical point of view (though a beginning has been made by Longa and de Jeu 1983a, b, to try and develop a molecular model to account for the different types of S_A phases). From the phenomenological point of view, the different phases can be described as arising from a competition between two *incommensurate* lengths, one of them owing its existence explicitly to the antiferroelectric short range order (see Prost and Barois 1983).

Reentrant behaviour has been observed in mesophases of disc-shaped molecules as well (Destrade *et al* 1981b). The higher homologues of the hexa-substituted esters of truxene (figure 3c) show the following sequence of transitions on cooling

$$I \rightarrow D_h \rightarrow N_D \rightarrow D_r \rightarrow D_h \rightarrow \text{crystal}.$$

An important point to be noted here is that the molecule is non-polar Based on the x-ray analysis of the crystal structure of a similar disc-shaped mesogen a triphenylene compound (Cotrait *et al* 1979) it has been suggested that the molecules are associated

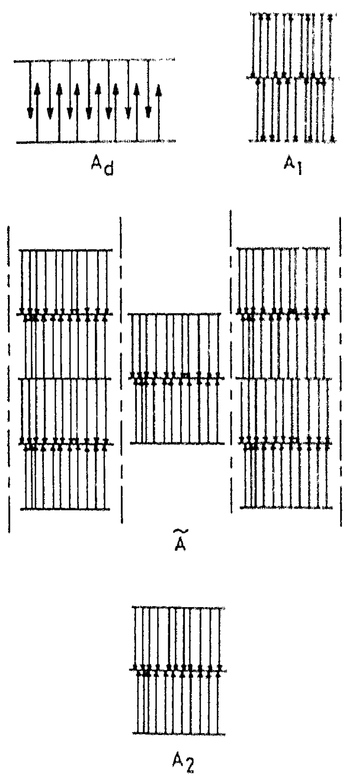


Figure 9. Schematic representation of the structures of the different types of smectic A formed by polar molecules (Hardouin *et al* 1983).

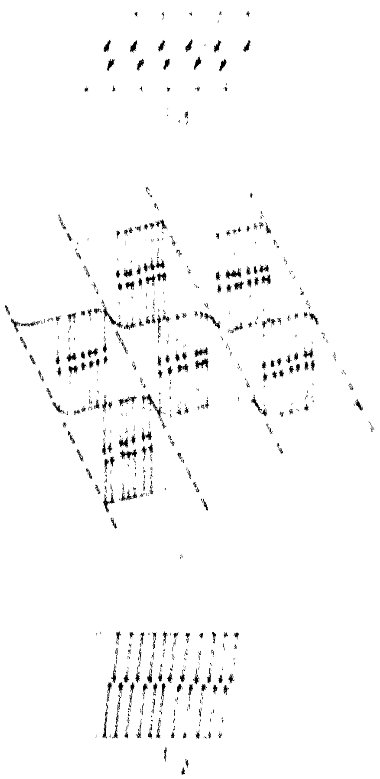


Figure 10. Schematic representation of the structures of the different types of smectic C formed by polar molecules (Hardouin *et al* 1983).

in pairs in each column and that changes in this association are responsible for this effect.

3.4 *The induced smectic phase*

Another interesting example of a special type of molecular interaction in liquid crystals concerns the *induced* smectic phase, *ie*, the appearance of a smectic phase in the temperature-concentration diagram of a binary mixture even though neither component shows this phase in the pure state. This effect occurs most commonly in mixtures with one component having a strongly polar terminal group and the other a non-polar terminal group (Park *et al* 1975; Oh 1977; Griffin *et al* 1978; Bock *et al* 1978; for a complete list of references see Chandrasekhar 1984). An example of a phase diagram showing an induced S_A phase is presented in figure 11. Evidently, dipole-induced dipole interactions play a part in the phase induction. There is also evidence of charge transfer complex formation, the polar molecule acting as the acceptor and the other as the donor (Park *et al* 1975; Sharma *et al* 1980; Araya and Matsunaga 1981). Recently, however, phase induction has been observed in other types of mixtures (Goodby *et al* 1984; Madhusudana *et al* 1984; Suresh 1983). For example mixtures of two cyano-compounds have been found to give rise to an induced S_c phase (Goodby *et al* 1984; Madhusudana *et al* 1984). Thus no generalisations are possible as yet and the precise nature of the molecular interactions and correlations responsible for promoting phase induction is not quite clear.

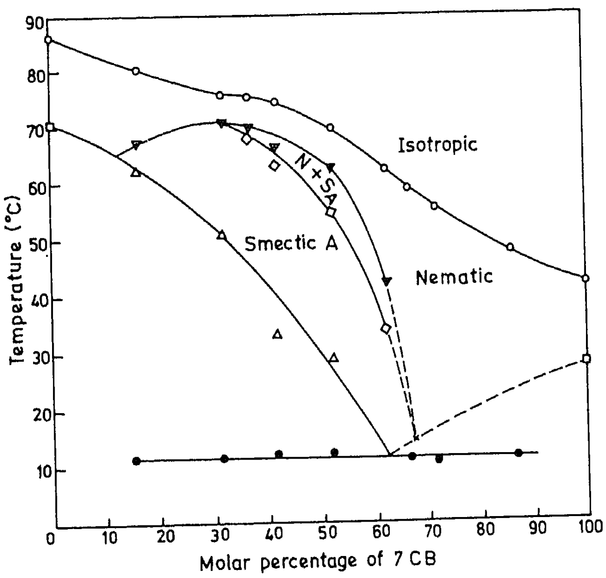


Figure 11. Phase diagram of binary mixtures of (2-hydroxy)-*p*-ethoxybenzylidene-*p*′-butylaniline (OH-EBBA) and 7CB showing the induced smectic *A* phase. (From Moodithaya and Madhusudana 1980, reproduced with permission from Heyden & Son.)

4. Molecular dynamics

4.1 *Introductory remarks*

A complete analysis of the dynamics of molecular motion in the mesophases is a rather complex problem. To begin with, the molecule itself is by no means a rigid rod; there are bonds, often even in the central aromatic core, which allow reorientation of its different parts, and in particular its end chains, which as we have remarked earlier play an important role in determining the mesomorphic properties, are quite flexible. Besides, the molecule as a whole undergoes rapid reorientation about its long axis, though the rotation is probably not completely free for the individual molecule even in the uniaxial nematic and smectic A phases because of the absence of cylindrical symmetry in the molecular shape and the existence of an appreciable degree of short range order. It also executes a much slower and highly hindered rotational (or flipping) motion about its short axes. In addition to all this there are collective motions which depend very specifically on the structure of the mesophase. Thus molecular dynamics in liquid crystals is determined in a complicated way by both intra- and inter-molecular interactions and of course these interactions are strongly temperature dependent.

X-ray diffraction can be used to obtain the molecular distribution functions, but as is well known it does not lend itself to distinguishing between static and dynamic phenomena. In order to gain information on molecular motions, one has to resort to other methods, *eg*, dielectric dispersion, neutron diffraction, Raman, IR, NMR relaxation and light scattering. We shall now review the application of these different techniques.

4.2 *Dielectric dispersion*

As all liquid crystals have orientational order, it is clear that the molecular reorientations about the short axis of the rod-like molecule will be strongly hindered. One can readily visualise two minima in the potential energy curve (bearing in mind that the director is *apolar*) and the molecule can therefore execute a head-to-tail flipping motion. Thus, if the molecule has a component of the dipole moment parallel to its long axis, a relaxation of $\varepsilon_{\parallel}$, the dielectric constant measured parallel to the director, takes place at relatively low frequencies. The first observation of this low frequency relaxation was made in several homologues of the PAA series by Maier and Meier (1961) who correctly attributed it to the influence of the nematic potential. Figure 12 gives the experimental curves for the sixth homologue. Subsequently, Axmann (1966a) made more detailed measurements on several compounds and used the Cole-Cole plot to depict the results. Since then a large number of studies have been made, in pure compounds as well as mixtures, both in the N and S_A phases (de Jeu 1978). The relaxation of $\varepsilon_{\parallel}$ usually lies in the MHz-frequency range, as for the biphenyls, Schiff bases, etc, but for certain esters the viscosities are higher and the relaxation frequencies are lower. At temperatures much below T_{NI}, relaxation frequencies as low as a few kHz have been observed (de Jeu *et al* 1972).

Meier and Saupe (1966) and Martin *et al* (1971) defined a retardation factor $g = \tau_1/\tau_0$ where τ_1 is the observed relaxation time of $\varepsilon_{\parallel}$ in the N phase and τ_0 the ordinary Debye relaxation time (the value extrapolated from the isotropic phase). Extending the Debye model, and assuming that the molecule has only μ_1, the longitudinal component of the dipole moment, these authors were able to relate the retardation factor for $\varepsilon_{\parallel}$ with the nematic potential. As we shall see later this theory is

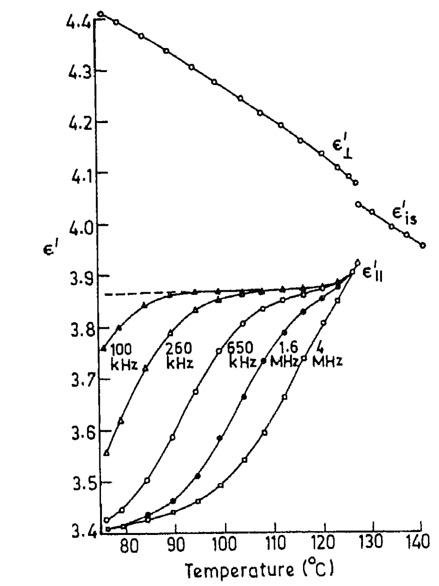


Figure 12. The real part of the principal dielectric constants $\varepsilon'_{\parallel}$, $\varepsilon'_{\perp}$ in the nematic phase and ε'_{is} in the isotropic phase of 4,4′-di-*n*-hexyloxyazoxybenzene at different frequencies between 100 kHz–4 MHz. $\varepsilon'_{\parallel}$ shows a strong dispersion whereas $\varepsilon'_{\perp}$ and ε'_{iso} do not. (From Maier and Meier 1961a, b, reproduced by permission of Verlag der Zeitschrift für Naturforschung.)

able to account for the observed dispersion in cyanobiphenyl compounds in which the dipole moment lies practically along the major molecular axis. However, the absolute value of g estimated on the basis of this theory turns out to be somewhat greater than that obtained from the Maier-Saupe theory using the observed value of the order parameter s. For example for PAA at 121°C, $g \approx 100$ and $q = 0{\cdot}22$ eV, whereas the Maier-Saupe theory gives $q = 0{\cdot}14$ eV. The difference may be attributed to the fact that the dielectric relaxation process is very sensitive to the short-range orientational order which is much stronger than the long-range order measured by s, and which is neglected completely in the mean field theory.

Nordio *et al* (1973a) have pointed out that the correlation time measured in the isotropic phase of PAA from NMR relaxation data (see §4.5) is $\approx 10^{-10}$ sec while dielectric relaxation in the same phase gives $\tau_0 \approx 3{\cdot}2 \times 10^{-11}$ sec. They have attributed this discrepancy to the reorientation of the methoxy groups contributing to the dielectric data and have found that in fact $g = 11{\cdot}5$ and not ≈ 100 as assumed by earlier authors. The strength of the nematic potential thus obtained would agree better with the mean field result than the earlier estimates.

There have been other theoretical approaches to the problem of dielectric relaxation. Nordio *et al* (1973b) have treated it by evaluating the time correlation function of the fluctuating molecular dipole components taking into account the effects of the diffusion tensor. They have used higher order terms of the nematic potential in the theory, and have included both μ_l and μ_t, the longitudinal and transverse components of the molecular dipole moment. Luckhurst and Zannoni (1975) have also developed a relation between the frequency dependent dielectric constant and the autocorrelation matrix of the dipole moment of an ellipsoidal cavity within the dielectric. Moscicki and

Kresse (1981) have proposed a rigid ellipsoid diffusion model to describe the dielectric relaxation in the isotropic phase of liquid crystals.

As remarked by Luckhurst and Yeates (1976) all these theories assume that the orientational motion is diffusional, whereas, in point of fact, changes in molecular orientation can occur through large angle jumps. Moreover, as discussed in earlier sections, the assumption that the molecule is rigid and cylindrically symmetric is certainly not correct. No attempts appear to have been made to take into account these factors in developing a general theory of dielectric relaxation.

The relaxation frequency for $\varepsilon_{\|}$ in the N phase may be expected to decrease, and the corresponding activation energy increase, with increasing molecular length. This has been confirmed by the systematic experiments of Schadt (1972) and Bata *et al* (1977). Indeed even an odd-even effect has been found for the relaxation frequency of successive members of a homologous series (Ratna and Shashidhar 1978).

For the vast majority of compounds that show both N and S_A phases, regardless of whether they are positive or negative dielectric anisotropy materials, it is found that the activation energy for low frequency dielectric relaxation is less in S_A than in the N phase (see Chandrasekhar 1984). In other words, the reorientation of the molecule about its short axis appears to be easier in the S_A phase. On the other hand, the activation energy in the N_R phase is much higher than in the N phase (Ratna *et al* 1980). The reason for the lower activation energy in S_A is still far from clear.

Though in principle $\varepsilon_{\|}$ also contains some information on rotations about the long molecular axis, such a motion would more directly influence the relaxation of $\varepsilon_{\perp}$. If $\mu_l = 0$, *i.e*, $\beta = 90°$ (where β is the angle which the net dipole moment makes with the long axis) both $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ should relax at about the same frequency, as is found to be the case for 4,4′-di-*n*-alkoxyazobenzenes (Axmann 1966b) (figure 13). The relaxation time for these compounds is $\approx 4 \times 10^{-11}$ sec, which corresponds to the rotational time of the (alkoxy) end groups which carry the dipole moment. If $\beta \neq 90°$, $\varepsilon_{\|}$ shows an additional lower frequency relaxation which, as we have already discussed, comes from

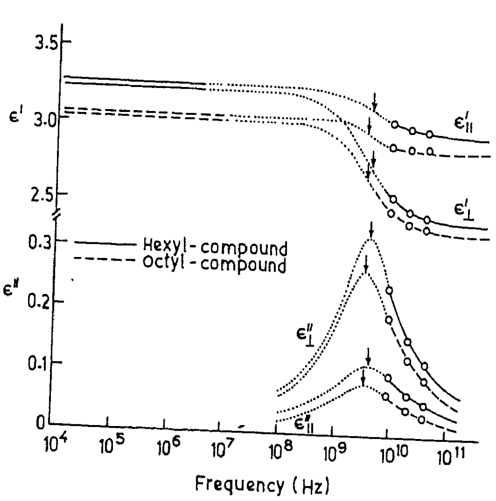


Figure 13. The real and imaginary parts of the principal dielectric constants of 4,4′-di-*n*-hexoxy and octoxyazobenzenes. (From Axmann 1966b, reproduced by permission of Verlag der Zeitschrift für Naturforschung.)

the reorientation of μ_l about the short molecular axis. Figure 12 illustrates this in the case of hexyloxyazoxybenzene for which $\beta \approx 62°$. The relaxation of $\varepsilon_\perp$ is somewhat more complicated and can be due to a superposition of the effect of the reorientation of the central group (if there is one in the molecule) caused by rotations about the long axis, the rotation of the end groups and other mechanisms. For example, measurements (Parneix *et al* 1975) on eutectic mixtures of two isomers of *p*-methoxy-phenylazoxy-*p*′-butylbenzene over the frequency range 1 Hz–26 GHz, show a distribution of relaxation times for $\varepsilon_\perp$. In the MHz region, only $\varepsilon_\parallel$ shows a relaxation. At high frequencies, 0·5–0·7 GHz, both $\varepsilon_\parallel$ and $\varepsilon_\perp$ show a relaxation with an activation energy of $\approx$ 0·2 eV. This relaxation persists in the isotropic phase also and is attributed to the rotations of the molecules about the long axis. Further, a feeble relaxation is found at $\approx$ 3 GHz for $\varepsilon_\perp$, probably arising from the rotation of the end group.

In a recent study of MBBA (4-methoxybenzylidene-4′-butylaniline) up to 18 GHz, Buka *et al* (1979a) have found a high frequency relaxation of $\varepsilon_\parallel$ at 10^9 Hz which arises from reorientation of the *transverse* component μ_t. $\varepsilon_\perp$ also has two relaxations, at $\approx 10^9$ and $\approx 10^{10}$ Hz, the lower frequency one being attributed to the reorientation of the entire molecule and the higher frequency one to internal rotations of the methoxy group.

The case of alkyl cyanobiphenyls (*n*CB) is particularly interesting since the dipole moment lies practically along the long molecular axis and contributes to the dispersion of both $\varepsilon_\parallel$ and $\varepsilon_\perp$. Davies *et al* (1976) found in the case of 7CB that while the dispersion of $\varepsilon_\parallel$ as well as ε_{iso} are characterised by essentially a single relaxation time, the dispersion of $\varepsilon_\perp$ is characterised by a distribution of relaxation times (around 2×10^{-9} sec). According to the theory of Martin *et al* (1971) the librations of the molecules about the director contributes to the relaxation of $\varepsilon_\perp$ at higher frequencies. Since the molecular order and hence the local field is not well defined in the perpendicular direction, and also since the barrier height in this direction is small, a wide range of individual dipole reorientation rates is allowed. Davies *et al* (1976) concluded that the data can be fitted satisfactorily to the theory.

A somewhat more detailed study has since been carried out by Druon and Wacrenier (1977, 1978) and Wacrenier *et al* (1981) on 8 CB, and on 7 CB by Lippens *et al* (1977) in the S_A, N and I phases. In the I phase a relaxation occurs at $\approx$ 25 MHz which indicates that the rotations are due to clusters rather than individual molecules. The relaxation spectrum of $\varepsilon_\perp$ includes frequencies below 10 MHz, which again is evidence of molecular associations. The spectrum has been decomposed into three regions around 10 MHz, 100 MHz and 700 MHz (figure 14). The authors have concluded that while the theory of Martin *et al* (1971) can approximately explain the occurrence of the two higher frequency relaxations, it cannot account for the lowest frequency relaxation at $\approx$ 10 MHz. They have ascribed the low frequency relaxation to associated groups deviating from the director with a short life time of the order 10^{-7} sec. This hypothesis has been incorporated in the Martin *et al* model to account for the low frequency relaxation. The short-range order effect has been estimated to extend over 100–200 molecules. An interesting consequence of this type of short lived association is that in a small range of frequencies, just beyond that corresponding to the relaxation of $\varepsilon_\parallel$ and till the lowest frequency of relaxation of $\varepsilon_\perp$, the dielectric anisotropy of 8 CB is *negative*, even though the molecules have no net dipole moment perpendicular to the long axis (figure 15).

7 CB and 7 OCB (hepoxy cyanobiphenyl) have again been studied very recently by

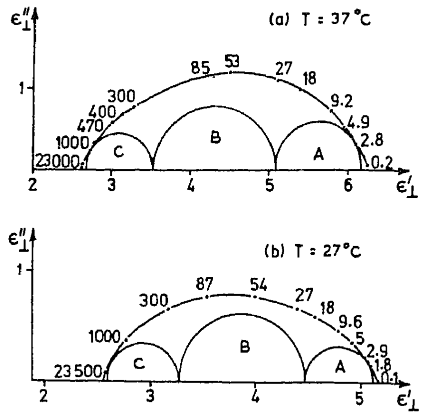


Figure 14. Cole-Cole plot for $\varepsilon_{\perp}$ in (a) the nematic and (b) the smectic *A* phases of 8CB. The frequencies are in MHz. (From Druon and Wacrenier 1978, reproduced by permission of Masson.)

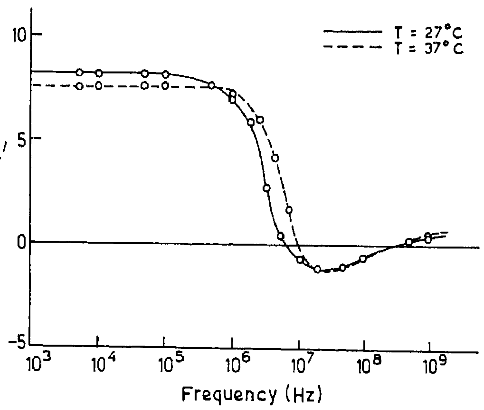


Figure 15. Dispersion of the dielectric anisotropy $\Delta\varepsilon'$ in the nematic (at 37°C) and smectic *A* (at 27°C) phases of 8CB. (From Druon and Wacrenier 1977, reproduced by permission of Commissions des Publications Française de Physique.)

Buka *et al* (1979b) upto 18 GHz. Interestingly, they have observed two relaxations for $\varepsilon_{\parallel}$, the second one occurring at $\approx 10^9$ Hz in both cases (figure 16). This high frequency feature which occurs in the isotropic phase also has been attributed to partial reorientation within short-range ordered groups. In the $\varepsilon_{\perp}$ studies, they observed only one broad absorption band and did not try to resolve it further into different relaxation frequencies. Moreover, in 7 OCB, they did not find any evidence for internal rotation of the heptoxy group. Price and Evans (1980) have tried to explain the high frequency relaxation of $\varepsilon_{\parallel}$ in 7 CB theoretically by developing a model of Brownian motion with a superimposed pairwise orientational interaction potential. The numerical calculations reproduce the high frequency shoulder shown in figure 16.

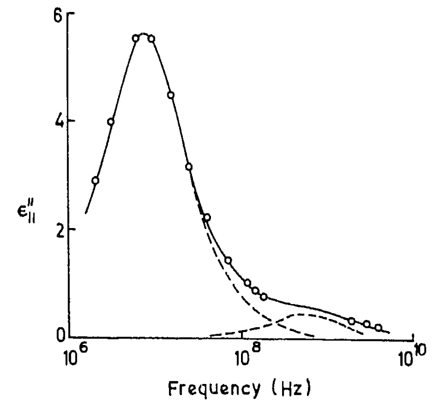


Figure 16. Dielectric absorption $\varepsilon''_{\parallel}$ in 7CB. Circles denote the experimental data, the broken curves the two resolved components whose sum is represented by the solid curve. (From Buka *et al* 1979b, reproduced by permission of Gordon & Breach Science Publishers.)

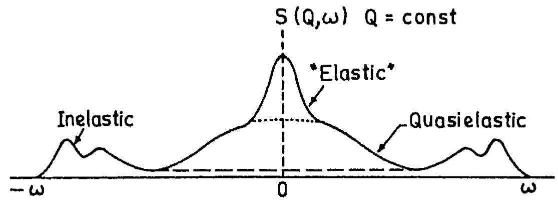


Figure 17. Schematic representation of the incoherent neutron scattering law $S(Q, \omega)$ at constant wavevector **Q**. The contribution to the elastic regime comes mainly from the translational motion, to the quasielastic regime from the translational and rotational motions, and to the inelastic regime from the vibrational, translational and rotational motions (Leadbetter and Richardson 1979).

4.3 *Incoherent quasielastic neutron scattering*

Neutron scattering is particularly suited to the study of rapid motions of the molecule and its constituent parts in condensed systems since the wavelengths of the neutrons used are of the order of molecular dimensions and yet at the same time their energies are low (1 Å corresponds to an energy of about 0·08 eV). The technique has been applied to liquid crystals for over a decade, but the high resolution work necessary for a proper analysis of the data has been undertaken only in the past four or five years. We refer the reader to a review by Leadbetter and Richardson (1979) for a discussion of the theoretical background and the scope of the technique. We present here only a brief summary of the basic ideas and the experimental results on liquid crystalline systems.

In principle, coherent inelastic neutron scattering data can be used to investigate collective modes (see §4.6). However, as far as the motions of individual molecules are concerned, it is the incoherent neutron scattering that offers a direct and powerful tool. A detailed energy analysis at different scattering vectors Q is necessary to delineate the various contributions. The scattering law at any given Q can be broadly separated into three regimes: elastic, quasi-elastic and inelastic. The information contained in these three regimes is shown in figure 17. A high resolution measurement at low enough Q

enables the translational diffusion constant to be defined. This is then used in the analysis of measurements at higher Q to determine the elastic incoherent structure factor (EISF) due to the rotational motion. The rotational correlation time may be derived directly from the width of the quasi-elastic component, though a complete description of the molecular dynamics requires detailed consideration of specific models.

Most mesogenic molecules contain many hydrogen atoms which have a very large incoherent scattering cross-section. By deuterating different parts of the molecule it is possible to study the motion of the undeuterated parts. Thus, from a comparison of the spectra of ring-deuterated and methyl-group deuterated versions of PAA (figure 18) Hervet *et al* (1976) found that even in the solid phase at ≈ 100°C the methyl groups rotate about the O–C bond with a correlation time $\tau_R \approx 0{\cdot}35 \times 10^{-12}$ sec and an activation energy ≈ 10 kJ/mole. From the spectrum in the nematic phase of d_6-PAA, Janik *et al* (1980) concluded that the whole molecule reorients about the long axis with $\tau_R \approx 10^{-11}$ sec, while the benzene rings and O–CH_3 groups have intramolecular rotations with $\tau_R \approx 10^{-12}$ sec. Similar studies have been made Janik *et al* (1980) on d_{30}-HOAB (the seventh homologue of the PAA series) in both the N and S_C phases. It is found that the rotation of the phenyl rings is similar in the N and S_C phases but the end chain rotation is more rapid in the N phase.

A number of high resolution experiments have been carried out in recent years. Some typical spectra obtained from aligned samples are reproduced in figure 19. The broad conclusions of these studies are summarized below (Leadbetter and Richardson 1979; Rustichelli 1978; Volino and Dianoux 1979; Richardson *et al* 1980).

In the N phase the translational diffusion constants (D) are in the range 10^{-7} to

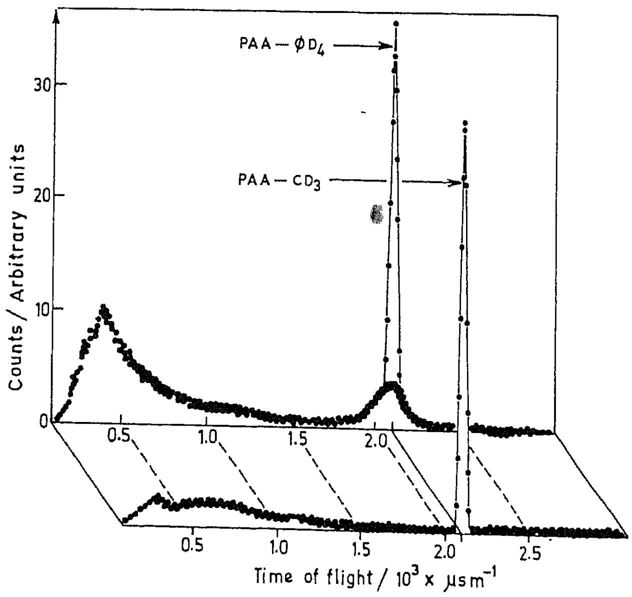


Figure 18. Time of flight spectra for ring (ϕD_4) and methyl (CD_3) deuterated derivatives of solid PAA at 100°C. (From Hervet *et al* 1976, reproduced by permission of Commissions des Publications Française de Physique.)

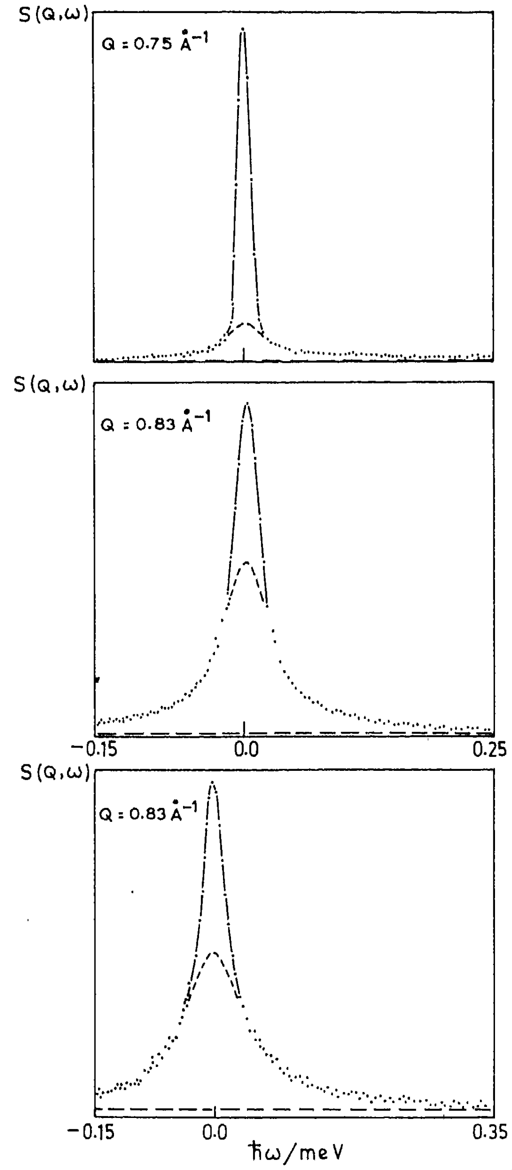


Figure 19. The quasielastic scattering law $S(Q, \omega)$ (in arbitrary units) of partially deuterated isobutyl 4-(4′-phenylbenzylidine amino)cinnamate. The data are shown for $\mathbf{Q} \| \mathbf{n}$ for three smectic phases, from top to bottom (i) S_E phase at 100°C (12 μeV FWHM resolution), (ii) S_B phase at 150°C (20 μeV FWHM resolution) and (iii) S_A phase at 172°C (20 μeV FWHM resolution). The curves show the experimental spectra separated into elastic and quasielastic components. The horizontal dashed lines represent a flat inelastic background. (From Leadbetter *et al* 1979b, reproduced by permission of Commissions des Publications Française de Physique.)

$5 \times 10^{-6}\,\mathrm{cm^2\,sec^{-1}}$, the values being, of course, temperature dependent. In S_A and S_C, D is of the same order of magnitude as in N ($\approx 10^{-6}\,\mathrm{cm^2\,sec^{-1}}$) and is temperature dependent, while in the more ordered smectic phases, *eg*, S_B, S_E, S_H, $D \approx 5 \times 10^{-8}\,\mathrm{cm^2\,sec^{-1}}$ and is temperature independent.

In N, S_A and S_C as well as in S_H and S_B, there is a rapid, uniaxial rotational diffusion about the long axis with a correlation time $\tau_R \approx 10^{-11}$ sec. In S_E, this becomes an overdamped libration of amplitude $\approx 30°$ about the long axis. In S_E, S_B and S_A there is also a rapid localised (or 'bound') diffusive motion ($\tau \approx 10^{-11}$ sec and 1–2 Å RMS amplitude) perpendicular to the layers. In addition, in N and S_A there is a libration about the short axis on a time scale much slower than 10^{-10} sec.

4.4 *Raman and infrared spectroscopy*

While Raman and infrared spectroscopy may not be as powerful as some of the other techniques in elucidating molecular motions in liquid crystals, they do nevertheless yield valuable information. A large number of studies on mesogenic compounds have been reported (see reviews by Bulkin 1976; Chandrasekhar and Madhusudana 1972) the salient results of which will be summarized in this section.

4.4a *Raman studies*: Some interesting changes have been observed in the Raman spectra near the crystal-mesophase transition. For example, in PAA additional bands have been found in the 200–700 cm^{-1} region which have been attributed to new conformations of the molecules especially about the C–OCH_3 bonds in the N phase (Schnur *et al* 1972; Shibata *et al* 1976). The intermolecular Raman mode at $\approx$ 22 cm^{-1} which was observed in the crystalline phase of two smectogenic compounds was found to become weaker and shift towards lower frequencies in the S_A phase and disappear in the isotropic phase (Amer and Shen 1972) (figure 20). This as well as the increase in the line-widths of some higher frequency modes are considered to be due to the rotational freedom of the molecules in the fluid phases. Similar conclusions have been drawn about molecular rotational freedom in the N phase from a study of the low frequency Raman modes in azoxy compounds like PAA and PAP (Sakomoto *et al* 1974). It may be mentioned, however, that these low frequency modes were not observed in simple Schiff base compounds (Sakomoto *et al* 1974).

Vertogen and Fleury (1975a) found that in MBBA the temperature dependence of the bands due to the rigid benzylidene aniline group is substantially different from that of the bands due to the end alkyl group. The phase transition mainly affects the alkyl

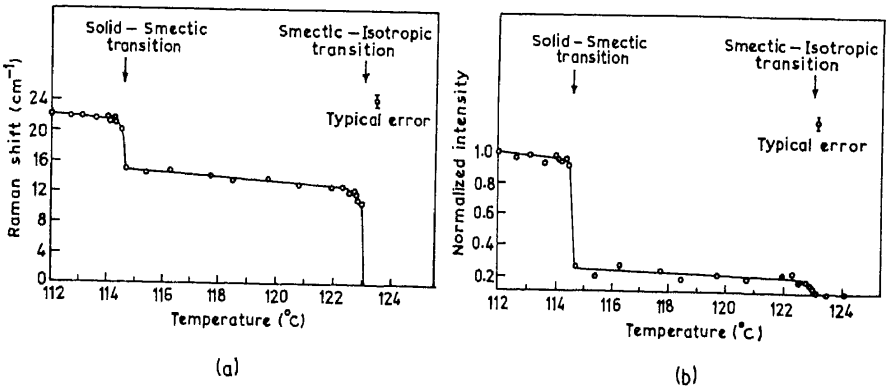


Figure 20. Temperature dependence of (a) the shift, and (b) the intensity of the 22 cm^{-1} Raman mode in the solid, smectic A and isotropic phases of diethylazoxybenzoate. (From Amer and Shen 1972, reproduced by permission of the Pergamon Press Ltd.)

chains. However in the N phase the melting of the chains is not complete (Destrade and Gasparoux 1975).

TBBA is a compound which exhibits many mesophases (Gray 1981; Demus *et al* 1980) and has been the subject of several Raman investigations. The Raman band at 19 cm^{-1} does not change much between the crystalline phases and the S_H (or according to the revised notation of Gray 1981 and Demus *et al* 1980, S_G) phase whereas it totally disappears in the S_C phase (Schnur and Fontana 1974; Schnur *et al* 1973; Dvorjetski *et al* 1975), though in a later study (Takase *et al* 1975, 1977) this band is reported to disappear in the S_H phase as well. This is supposed to indicate 'collective' rotations in the solid reducing in the S_C phase (and very likely also in the S_H phase) to more or less free rotations, probably involving a diffusive process (see §4.3). A broad peak at $\approx$ 130 cm^{-1} in the liquid crystalline phases has been attributed to the torsional motion of the butyl group relative to the phenyl group. There is also evidence of a rotational relaxation of the end chains in the crystal VIII phase which precedes the S_H phase (Fontana and Bini 1976).

The Raman spectra of the higher homologues of the PAA series reveal the accordion vibrations of alkyl chains in the solid phase (Schnur 1973). These disappear in the liquid crystalline phases, which means a partial 'melting' of the chains. Destrade *et al* (1976) have concluded that some intramolecular ordering exists in the end chains of nematogenic materials in the isotropic phase even far away from the NI transition point, while such ordering is not detectable in the case of compounds which are not mesogenic.

From a study of the correlation functions for the Raman scattering associated with the C≡N stretching mode of 8 OCB, Bulkin and Brezinsky (1978) have found that vibrational dephasing rather than 'tumbling' about the short molecular axis is primarily responsible for the bandwidth of this mode.

The low frequency Raman spectra of cholesteryl benzoate and stearate show practically no differences between the cholesteric and isotropic phases, while the smectic phase of the stearate compound has several features similar to those of the crystalline phase (Vertogen and Fleury 1975b).

As mentioned in §3.2, the molecular rotation about the long axis definitely cannot be 'free' in ferroelectric S_{C^*} and an attempt was made by Takezoe *et al* (1979) to study the rotational bias by Raman scattering. However, the measurements were not accurate enough to come to any definite conclusions.

4.4b *Infrared studies*: The earlier studies were mainly in the near IR region and the linewidths of several bands were found to vary with temperature. This was ascribed to combination modes between the lattice vibrations and molecular vibrations/rotations. Attempts have been made to calculate from the widths of these bands the temperature variation of the potential barrier for molecular reorientation (Kirov and Simova 1973). However, it is not usually possible to assert that the motion is that of the entire molecule as these bands may arise from characteristic motions of sub-molecular groups only, and may even be due to more than one type of motion. For example, the far infrared band at 130 cm^{-1} observed in MBBA (and a similar band observed in the next higher homologue, EBBA, at 120 cm^{-1}) can be due to libration modes of the phenyl rings or due to the libration of the entire molecule about its long axis (Sciensinska *et al* 1974; Bulkin and Lok 1973; Davies *et al* 1973; Vertogen *et al* 1976).

Many studies have indicated a strong absorption in PAA at $\approx$ 100 cm^{-1}, which was initially thought to be of intermolecular origin (see Bulkin 1976 and Chandrasekhar and Madhusudana 1972). However, from a detailed and systematic investigation of this and its higher homologues which revealed that the band shifts to lower frequencies and also becomes wider with increasing chain length (figure 21), Venugopalan and Prasad (1979) have concluded that the main contribution to this band comes from the rotational motions of the end alkoxy chains.

From the near IR spectra of the seventh homologue of the PAA series (HOAB) which

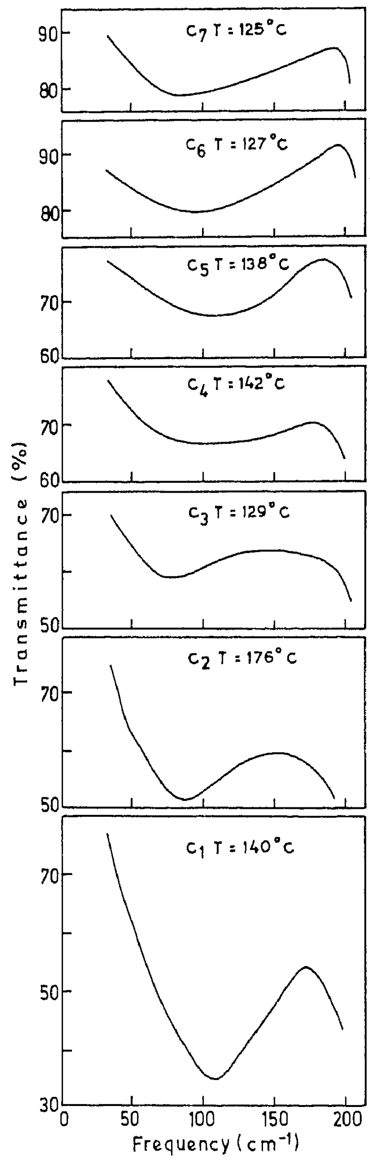


Figure 21. Far-infrared absorption spectra of the first seven homologues (C_1–C_7) of the 4,4′-di-*n*-alkoxyazoxybenzene series. (From Venugopalan and Prasad 1979, reproduced by permission of the Am. Inst. Phys.)

exhibits both N and S_C phases, Lugomer (1974) has estimated the rotational correlation times of benzene rings to be 8×10^{-12} sec in the S_C phase and $4–5 \times 10^{-12}$ sec in the N and I phases. He has also concluded that the average angular rotational jump is $\approx 30°$ in the smectic and $\approx 60°$ in the other two phases. These rotational correlation times are expected to be at least an order of magnitude faster than that for the entire molecule. In the case of MBBA (Evans *et al* 1974) the correlation time for the rotation about the long axis in the isotropic phase is $\approx 7{\cdot}5 \times 10^{-11}$ sec.

The order parameters of the rigid aromatic core and of hydrocarbon chains of several Schiff base derivatives have been determined in the N phase by the use of stationary and modulated infrared attenuated total internal reflection spectroscopy (Fringeli *et al* 1976). The hydrocarbon chains were found to be much less ordered than required by Marcelja's statistical theory (Marcelja 1974).

Fernandes and Venugopalan (1976) have found evidence for increased molecular rotations at the crystal-S_A transition point in CBOOA (4-cyanobenzylidene-4′-octyloxyaniline) by the disappearance of a combination mode at $518\,\mathrm{cm}^{-1}$. The accordion mode of the alkyl chains at $296\,\mathrm{cm}^{-1}$ also disappears at this transition indicating a vibrational 'melting' of the chains in the mesophase.

Venugopalan *et al* (1977) have shown that the band centred at $476\,\mathrm{cm}^{-1}$ in the lower temperature solid phases of TBBA is broadened in smectic H and VI (or, according to the revised notation of Gray (1981) and Demus *et al* (1980), S_G and S_H respectively) (figure 22). This they have attributed to intramolecular reorientations of the butyl chain in the latter two phases. The mean correlation time of the reorientation is estimated to be $1–2 \times 10^{-12}$ sec.

There have been comparatively fewer infrared studies on cholesteric compounds. Myasnikova and Corbatenko (1972) have found that the bands in the $1200–1330\,\mathrm{cm}^{-1}$ region considered to be due to combination modes in six cholesteryl esters disappear at the crystal-cholesteric transition point. Evans *et al* (1975) have ascribed the broad $78\,\mathrm{cm}^{-1}$ band occurring in cholesteryl oleyl carbonate to a libration of the rigid part of the molecule about its long axis.

4.5 *Nuclear magnetic relaxation*

Nuclear magnetic relaxation is another very useful technique for investigating molecular dynamics. A great deal of work has been done particularly on the proton spin relaxation in nematics. However, most of the earlier experiments were confined to small frequency ranges and the results could not therefore be interpreted unambiguously. In the last four or five years Noack and co-workers, using field cycling techniques, have studied the dispersion of the proton spin relaxation time T_1 over a very wide frequency range (a few hundred Hz to 270 MHz) and have carried out a far more complete analysis of the different relaxation mechanisms than was possible previously. We shall limit our discussion to these recent studies as the earlier work has been adequately covered in a review article by Wade (1977) and Doane (1979).

Figure 23 shows the T_1 proton relaxation dispersion in the nematic phase of MBBA at two temperatures, one at 45°C (close to the NI transition) and the other at 18°C in the supercooled nematic phase (Graf *et al* 1977). The curves suggest that there may be three distinct relaxation mechanisms, the one at 10^6 Hz becoming unimportant away from the NI transition.

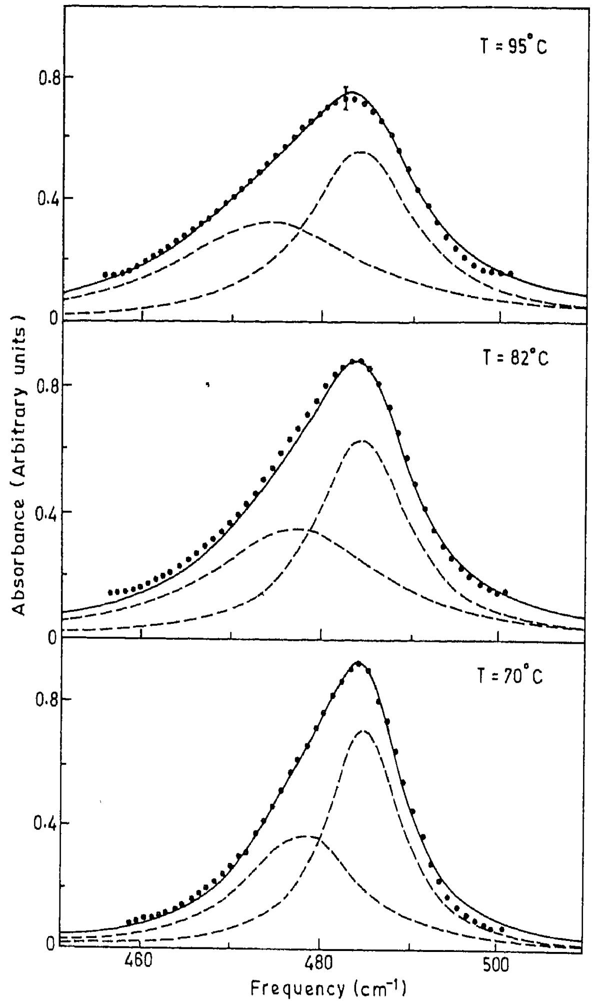


Figure 22. Infrared absorbance of TBBA in the S_G (95°C), S_H (82°C) and VII (70°C, solid) phases in the 460–500 cm^{-1} range. Closed circles denote the experimental values. The typical uncertainty in the data is shown in the top trace. The broken curves denote least squares fitted Lorentzian components and the solid curve represents the sum of the two components. (From Venugopalan *et al* 1977, reproduced by permission of Gordon & Breach Science Publishers.)

Assuming that the net relaxation follows a single exponential law, one may write (Abragam 1962)

$$1/T_1 = \sum_j (P_j/T_{ij})$$

where j stands for the given relaxation mechanism and P_j is the fraction of total number of protons in the molecule which contribute to this mechanism,

$$\frac{1}{T_{ij}} = \left(\frac{H^2}{T_{zj}} + \frac{H_L^2}{T_{dj}}\right) \Big/ (H^2 + H_L^2)$$

where H is the external field, and H_L the dipolar field due to neighbouring protons, T_{zj}

the relaxation time for the Zeeman energy and T_{dj} that for the dipolar energy. Further,

$$1/T_{zj} = \frac{3}{2}\gamma^4\hbar^2 I[I+1][J_j^{(1)}(\omega) + J_j^{(2)}(2\omega)]$$

where I is the spin quantum number, γ the magnetogyric ratio and $R_j = T_{zj}/T_{dj}$ a characteristic ratio. Obviously, the effect of the dipolar relaxation is felt only when $H \approx H_L$, *ie* at low external fields. The $J(\omega)$ coefficients are determined by the dynamical processes involved, and in particular by the Fourier intensities at ω_L and $2\omega_L$ of the fluctuating field arising from molecular motions.

In isotropic liquids the main contributions come from intramolecular dipole-dipole interaction modulated by the rotational tumbling motion ($T_1 \approx \omega^2$) and the intermolecular dipolar relaxation caused by self-diffusion ($T_1 \approx \omega^{3/2}$). While both of these undoubtedly contribute to T_1 in liquid crystals, there is another mechanism unique to the mesophase, namely, the orientational fluctuations (OF) of the director. This is the most important collective motion in nematics. The continuum theory leads to the result that any thermal distortion of size q^{-1} is relaxed in a characteristic time τ_q given by

$$\tau_q^{-1} \approx Kq^2/\eta,$$

where K is an appropriate average of the curvature elastic constants of the nematic and η a viscosity. For $q^{-1} \approx 100$ Å, $\tau_q \sim \mu$ sec. Such distortions modulate the dipole-dipole interactions and contribute very strongly to the NMR relaxation in the MHz region with

$$J_q(\omega) = (2kT/Kq^2V)\, \tau_q/(1+\omega^2\tau_q^2),$$

and taking into account the contribution to the relaxation time from distortions at all possible wavevectors q

$$\frac{1}{T_1} \approx A\omega^{-1/2} + B. \qquad (1)$$

Thus the OF contribution to the relaxation rate shows an unusual frequency dependence. The theory, originally due to Pincus (1969) has been refined by other authors (Sung 1971; Ukleja *et al* 1976; Freed 1977) and extended to include the other mechanisms mentioned earlier, and possible couplings between the different relaxation modes. The most general theory is due to Freed (1977). It is obvious that a formidable amount of analysis is needed to work back from the relaxation data to the dynamical processes involved. As remarked before, the earlier measurements were limited to narrow frequency ranges and led to conflicting interpretations, but the recent wide frequency data of Graf *et al* (1977) make it somewhat easier to delineate the different contributions. Assuming that the OF, self-diffusion (SD) and molecular rotation (R) contributions are not coupled and taking the simplest theoretical expressions for $J(\omega)$ in each case, Graf *et al* reduced the number of parameters to be fitted to six, and found that the dependence of T_1 on temperature and frequency could be accounted for quite satisfactorily on this basis. The frequency variation of the three contributions are shown in figure 23. Two points may be noted: the contribution of T_{1R} is present only close to the transition, and T_{1SD} is strongly temperature dependent (the diffusion constant $D = 0{\cdot}98 \times 10^{-7}$ cm^2/sec at 18°C and $= 3{\cdot}2 \times 10^{-7}$ cm^2/sec at 45°C). A surprisingly good agreement was found with the computer fitted value of A of (1) and that estimated from the known elastic and viscous coefficients and order parameter of MBBA.

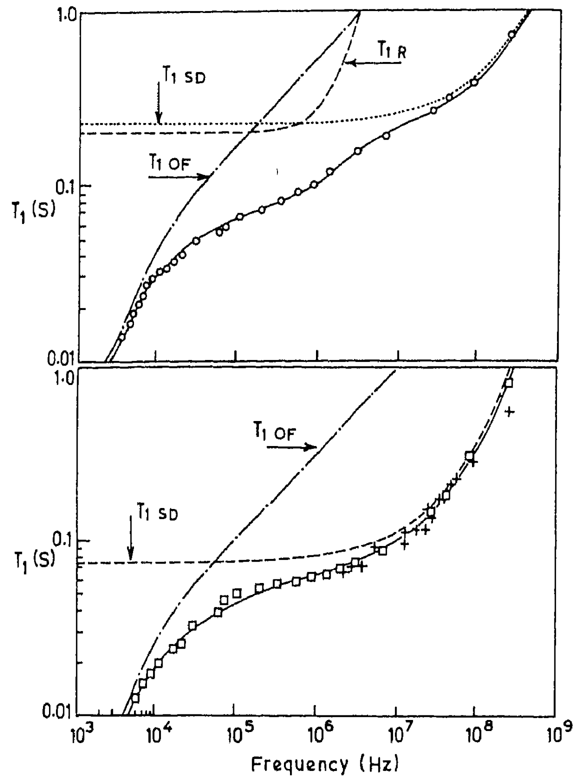


Figure 23. Dispersion of the proton spin relaxation time T_1 in nematic MBBA. Circles and squares are the experimental data of Graf *et al*, crosses the data of Vilfan and Blinc. Full lines represent the computer fitted curves taking into account the contributions of the orientational fluctuations of the director (OF), self-diffusion (SD) and molecular rotation (R). The individual contributions of T_{1OF}, T_{1SD} and T_{1R} are also shown. (From Graf *et al* 1977, reproduced by permission of Verlag der Zeitschrift für Naturforschung.)

In a later study on several homologues of the PAA series, Wolfel *et al* (1980) have given an alternative interpretation of the relaxation which occurs around 10^6 Hz. They have now attributed it to the critical fluctuations of the scalar order parameter s (or the magnitude of s) close to T_{NI}. The theory for this contribution had been worked out earlier by Freed (1977) in his general treatment of T_1 relaxation.

The scalar order parameter fluctuations can be treated in terms of the Landau-de Gennes theory (de Gennes 1974; Chandrasekhar 1977). The critical slowing down of this order parameter fluctuation as the temperature approaches T^*, a hypothetical second order NI transition point slightly above the actual (first order) transition point T_{NI}, has been recently studied by Dong and Tomchuk (1978). By measuring both the laboratory (T_1) and rotating frame ($T_{1\rho}$) relaxation on methyl deuterated PAA, they found that close to T_{NI}, the slowing down of this optical soft mode (Blinc *et al* 1974) follows the mean field result.

Measurements of T_1 at 10 MHz have been reported on MBBA and OHMBBA at low temperatures in the glassy nematic and supercooled nematic phases by Kumagai *et al* (1981). Minima in T_1 have been found at two temperatures (264°K and 140°K for

OHMBBA) which have been interpreted as due to contributions from self-diffusion and end group reorientations respectively.

Proton relaxation in the smectic phases have also attracted a few studies. Blinc *et al* (1975, 1978) studied different phases of TBBA and from the dispersion of T_1 in the 10^5–10^8 Hz range, they concluded that in the S_A and S_C phases OF and fast SD make prominent contributions, while in the smectic *H* and VI phases fast molecular rotations and slow translational self-diffusion determine T_1. The most complete study on TBBA is again due to Mugele *et al* (1980) who covered the range 100 Hz–44 MHz and found that the relaxation dispersion looks very similar in the S_A and S_C phases and further, that it is analogous to that of a high temperature nematic, *eg*, PAA. Figure 24 shows the relaxation dispersion in the S_C, S_A and *N* phases. In both S_A and S_C, there is a strong dispersion between 10^3 and 10^5 Hz. This is mainly due to the OF-contribution, perhaps arising from both the fluctuations of the director and of the tilt angle. T_1 is strongly temperature dependent close to the CA and AN transition points. The data over the entire frequency and temperature range could be well fitted with a combination of OF, SD and another mechanism which is assumed to have a Debye-like power spectrum. It may arise either from the highly hindered molecular rotations about the short axis or the fluctuations of the scalar order parameter referred to earlier. The diffusion constant in S_C (at 156°C) is $1{\cdot}2 \times 10^{-6}$ cm²/sec, in S_A (at 181°C) $2{\cdot}7 \times 10^{-6}$ cm²/sec and in *N* (at 205°C) $5{\cdot}4 \times 10^{-6}$ cm²/sec.

In another study on a few homologues of *p*-alkanoyl-benzylidene-*p*′-aminoazobenzenes, Krüger *et al* (1977) have shown that in the S_B phase the anisotropy of self-diffusion is small and $D_\perp > D_\parallel$. The diffusion in the smectic *A* layers ($D_\perp$) is liquid-like

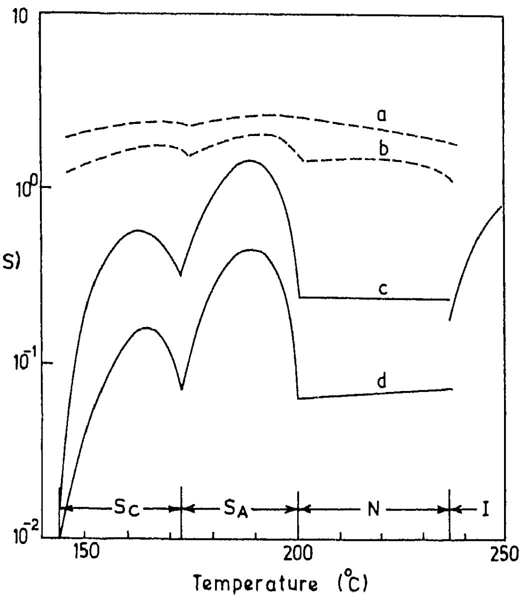


Figure 24. The proton spin relaxation time T_1 *vs* temperature in the smectic *C*, smectic *A*, nematic and isotropic phases of TBBA at four Larmor frequencies (a) 60 MHz (b) 15 MHz (c) 80 kHz and (d) 8·5 kHz. (From Mugele *et al* 1980, reproduced by permission of Verlag der Zeitschrift für Naturforschung.)

whereas $D_\parallel$ (from layer to layer) is to be treated as a pseudo-lattice-jump process, and the corresponding activation energy is a few times larger than that for $D_\perp$.

Dong (1981) has reported proton spin relaxation measurements at 30 MHz in the N, S_A and reentrant N_R phases exhibited by binary mixtures of two cyano-compounds (see §3.3). In the higher temperature nematic, T_1 decreases with decrease of temperature and has been interpreted to be caused by the SD mechanism (activation energy ≈ 4·6 kcal/mole). In the S_A phase, the same trend continues but with a slightly higher activation energy (≈ 5·6 kcal/mole). However in the N_R phase, T_1 is practically temperature independent and is supposed to be because of the domination of the OF mechanism in this phase.

Deuteron relaxation (T_{1Q}) has been studied in a few cases. This technique has the advantage of giving information about intramolecular motion only (Wade 1977; Doane 1979). Emsley *et al* (1976) have determined the relaxation time in the nematic phase of cyano-d_{17}-*n*-octylbiphenyl between 15 and 35 MHz for the CD_3 deuterons (270 msec) as also the CD_2 deuterons from carbon atoms 4 to 7 (≈ 20 msec) in the chain. They could not explain the results on the basis of director fluctuations alone, and in fact concluded that the dominant contribution comes from the internal motions of the alkyl chain. Rutar *et al* (1978) have studied partially deuterated MBBA between 4–41 MHz and concluded that the benzene ring rotation is the dominant mechanism in this frequency range and that the aniline and benzylidene rings reorient at different rates around the para-axis.

As in the deuteron case, ^{13}C relaxation also involves only intramolecular processes (Wade 1977; Doane 1979). Figure 25 shows the temperature dependence of relaxation time for the methyl and ring carbons of PAA as determined by Hayamizu and Yamamoto (1977). It is seen that there is no discontinuity in the relaxation times at T_{NI}. These authors have estimated that the rotation about the long molecular axis is ≈ 10^3 times faster than about the short axis in both the N and I phases. Hutton *et al* (1978) have studied the relaxation of different carbon atoms along the butyl chain of MBBA and found that the flexibility increases as one goes away from the aromatic core. The

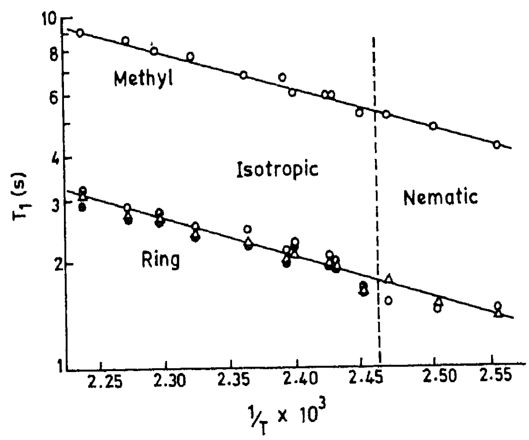


Figure 25. The temperature dependence of the ^{13}C relaxation time in the nematic and isotropic phases of PAA. Open circles, filled circles and triangles in the lower curve represent the data for the three distinguishable species of ring carbons. (From Hayamizu and Yamamoto 1977, reproduced by permission of the Chemical Society of Japan.)

correlation time for rotational diffusion about the short axis was found to be $\approx 4 \times 10^{-9}$ sec in the isotropic phase.

Relaxation measurements have also been used to investigate the dynamics of short-range order fluctuations in the isotropic phase near T_{NI}. As the isotropic phase is cooled towards T_{NI}, these fluctuations slow down. On the basis of the Landau-de Gennes model (de Gennes 1974; Chandrasekhar 1977), the relaxation rate $(1/T_1)$ can be shown to be proportional to $(T-T^*)^{-1/2}$, where T^* is a hypothetical second order transition point slightly below T_{NI}. Many experiments have confirmed this prediction (Cabane and Clark 1970; Ghosh *et al* 1972; Dong *et al* 1974). The relaxation spectrum (from 10^4–10^8 Hz) has recently been studied in the isotropic phase of MBBA and EBBA by Reinhart *et al* (1979). At low frequencies T_1 is independent of the frequency but decreases with temperature, while at high frequencies ($> 10^8$ Hz), T_1 is independent of temperature but increases rapidly with increase of frequency. Rollmann *et al* (1979) have studied the relaxation in the isotropic phase of the same compounds using the NMR pulsed field gradient technique. A superposition of the SD mechanism and the fluctuations of the short-range order appears to give a satisfactory fit with the experimental data. They found that $D = 0{\cdot}9 \times 10^{-6}$ cm^2 sec^{-1} at 50°C for MBBA and $2{\cdot}5 \times 10^{-6}$ cm^2 sec^{-1} at 89°C for EBBA which agree well with the values obtained from the tracer technique. Further, these results demonstrate the inadequacy of the law $D \propto m^{-1/2}$ where m is the mass of the molecule. It indicates that molecular clusters and not individual molecules may be involved in the transport process.

Ghosh *et al* (1980) have made a detailed analysis of the relaxation spectra of MBBA in its isotropic phase, measured between 4 and 20 MHz. They have argued that the nuclear relaxation rate arising from critical fluctuations (CF) close to T_{NI} should be divided into two parts, one arising from the so-called 'non-local' (N) modes with $q = 0$, and the other from the 'local' (L) critical fluctuations wtih $q \neq 0$. According to their analysis, T_1 (CFL) follows the Landau-de Gennes theory, but T_1 (CFN) is properly described only by an extended version of that theory. The authors have drawn an analogy between the NI transition and Bose-Einstein condensation.

4.6 *Collective modes*

We conclude our discussion of molecular dynamics with a brief reference to the problem of collective modes in liquid crystals. This is a major field of study in itself, particularly because it is closely linked with the general problem of phase transitions and pretransition phenomena. A full discussion of this topic is therefore beyond the scope of this article (see de Gennes 1974; Chandrasekhar 1977; Chandrasekhar and Madhusudana 1978). We shall just indicate the methods that are used to investigate the dynamics of these modes.

4.6a *Light scattering*: As liquid crystals are highly anisotropic media, the orientational fluctuations of the director make the predominant contribution to the light scattering, so much so that the effect of the density fluctuations in the fluid can be ignored altogether. Light scattering is therefore a very important tool for studying the dynamics of collective motions in these phases. The technique involves the use of a laser light beat spectrometer to analyse the scattered radiation; the half-width of the scattered spectrum is a direct measure of the relaxation rate of the orientational fluctuations. A large number of studies have been carried out on the N, S_A and S_C phases and the results have been interpreted in terms of the continuum theory. Light scattering may also be used to obtain information on the critical slowing down of the order parameter fluctuations near phase transitions, especially transitions which are weakly first order (*eg*, the NI transition) or quasi-second order (*eg*, the AN or CA transition). These studies are important for estimating the relevant critical exponents associated with these transitions. Here again a number of very careful measurements have been made which have added greatly to our understanding of the nature of these transitions. However we do not propose to discuss any of these experiments here as an excellent, authoritative article on this very topic (covering also the results of the Kerr effect and other studies) has been published recently by Schaetzing and Litster (1979).

4.6b *Coherent neutron scattering*: Coherent inelastic neutron scattering may also be used to study collective motions. In this case, the momentum transfer is typically $\approx 10^{-1}$ Å^{-1}, which is much larger than with the light scattering technique ($\approx 10^{-3}$ Å^{-1}). It is necessary to deuterate the sample fully in order to avoid the large incoherent scattering from protons, and very few studies have so far been carried out.

With fully deuterated nematic PAA, Conrad *et al* (1976, 1977a) and Pepy *et al* (1980) have observed broad inelastic peaks which provide evidence of collective phonon-like excitations in the meV region. Conrad *et al* (1977b, 1980) and Conrad and Mezei (1980) have also studied the AN transition in deuterated CBOOA, and observed a line narrowing near T_{AN} due to the slowing down of the smectic order fluctuations. Further, using neutron-spin-echo spectroscopy they have estimated a characteristic decay time of 0·6 $\times 10^{-8}$ sec for the smectic fluctuations.

Benattar *et al* (1979) have investigated the lattice dynamics of three 3D ordered phases of deuterated TBBA—the room temperature crystal, S_B and S_E (or according to the revised notation of Gray (1981) and Demus *et al* (1980), S_G and S_H) phases—using monodomain samples. They confined their experiments to the a^*c^* plane and found that both longitudinal and transverse phonons propagate in all three phases. However, while the longitudinal mode is practically unaltered in the three phases, the frequency as well as the width of the transverse mode along c^* are larger in the smectic phases.

4.6c *Ultrasonic relaxation*: Though the first ultrasonic studies of the NI phase transition were carried out long ago, accurate relaxation measurements on magnetically aligned samples have been made only recently. The experiments up to 1978 have been reviewed by Candau and Letcher (1978) and we summarize only some of the more recent work on the NI and AN transitions.

Close to these phase transition points, fluctuations of the order parameter contribute to the ultrasonic relaxation. Imura and Okano (1973) and Matsushita (1978) developed the theory for this process by assuming that the temperature oscillations accompanying the sound wave get coupled to the order parameter fluctuations. As the transition point is approached, the fluctuations grow larger and become slower and cannot follow the temperature oscillations. This phase lag produces a frequency dependent heat capacity which results in an additional contribution to the ultrasonic relaxation. While this is the only contribution in the isotropic phase, on the nematic side the order parameter can directly couple to the ultrasonic waves through pressure and temperature variations (the Landau-Khalatnikov process).

The fluctuation contribution leads to the result that $\alpha/f^2 \approx |T-T^*|^{-1.5}$ where α is the attenuation coefficient and f the frequency. This result has been confirmed in the isotropic phase of PAA (Thiriet and Martinoty 1979) and 5CB (Nagai *et al* 1976).

By analysing the attenuation data measured at different angles with respect to the director for temperatures below $(T_{NI}-1)$K, the critical part of the attenuation coefficient in the N phase of PAA was found to vary as $(T_1-T)^{-1}$, where T_1 is a temperature close to T_{NI} (Thiriet and Martinoty 1979). This temperature dependence clearly indicates that the relaxation of the order parameter (and *not* that of its fluctuations) makes the dominant contribution in this phase. One may expect however that fluctuations do make an important contribution very close to T_{NI}, but measurements could not be carried out in this range because of experimental difficulties.

In the case of compounds like MBBA (Castro *et al* 1978) and 5 CB (Nagai *et al* 1976) with relatively long end chains, the relaxation due to rotational isomerism of the chains has to be properly accounted for before the critical part of the relaxation can be analysed. Recent results on MBBA (Castro *et al* 1978) tend to confirm the importance of the Landau-Khalatnikov mechanism in the N phase.

Ultrasonic relaxation studies near the AN transition have been made on CBOOA in both low frequency (0·6–25 MHz) (Kiry and Martinoty 1978) and high frequency (200–1000 MHz) (Bacri 1975) regions. The critical increase in the absorption is apparent on the nematic side as the frequency is lowered. Here both the divergence of some viscosity coefficients and the frequency dependent heat capacity discussed earlier contribute to the relaxation. In the S_A phase, the Landau-Khalatnikov process and the intramolecular (chain reorientation) processes make the analysis somewhat difficult. Much more pronounced attenuation is observed near the AN transition of TBBA (Bhattacharya *et al* 1978). Martinoty (1979) has argued that this is connected with the large value of the excess heat capacity due to fluctuations in TBBA—larger by about an order of magnitude than in the case of CBOOA.

4.6d *Brillouin scattering*: (Schaetzing and Litster 1979). In the S_A phase there are two propagating acoustic modes for any arbitrary direction of the wavevector. One is the usual longitudinal wave whose velocity is practically independent of the direction of propagation. The other is a transverse wave associated with changes in the layer spacing at nearly constant density and is referred to as *second* sound (de Gennes 1974; Chandrasekhar 1977). The velocity of this mode is strongly orientation dependent, becoming zero along as well as perpendicular to the layers. Direct evidence of these two branches has been obtained by Brillouin scattering studies (Bradberry and Vaughan 1977; Ricard and Prost 1979; Liao *et al* 1973; Conrad *et al* 1977b). The velocity of

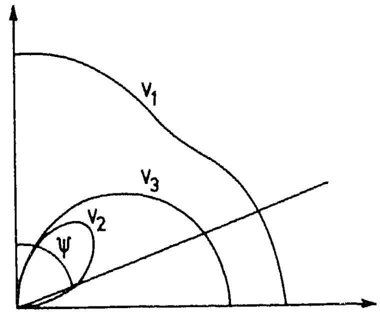


Figure 26. Expected dependence of the sound velocities on polar angle in the columnar phase. Two of the modes, with velocities V_1 and V_2, are similar to the first and second sounds in smectic A (Prost and Clark 1980).

second sound is expected to show critical behaviour near the AN transition, but the experimental data are not quite conclusive on this point.

In the case of columnar liquid crystals, continuum theory shows that there can be three propagating modes (Kats 1978; Prost and Clark 1980). The expected angular dependence of their velocities is shown in figure 26 (Prost and Clark 1980). Two of the modes (with velocities V_1 and V_2) are analogous to the first and second sounds of S_A. There is now another transverse mode which for propagation along the basal plane is polarized in the plane itself and since the two-dimensional lattice can sustain a shear its velocity V_3 does not vanish. For propagation along the columns, this wave becomes the highly damped undulation mode with zero velocity. Consequently, depending on the orientation, there should be one, two or three pairs of Brillouin components, but no experiments have yet been carried out.

References

Abragam A 1962 *The principles of nuclear magnetism* (Oxford: Clarendon)
Alben R 1971 *Mol. Cryst. Liq. Cryst.* **13** 193
Alben R 1973 *Phys. Rev. Lett.* **30** 778
Amer N M and Shen Y R 1972 *Solid State Commun.* **12** 263
Andrews F C 1975 *J. Chem. Phys.* **62** 272
Araya K and Matsunaga Y 1981 *Mol. Cryst. Liq. Cryst.* **67** 153
Axmann A 1966a *Z. Naturforsch.* **A21** 615
Axmann A 1966b *Z. Naturforsch.* **A21** 290
Bacri J C 1975 *J. Phys. (Paris)* **36** C1–123
Bata L, Buka A and Molnar G 1977 *Mol. Cryst. Liq. Cryst.* **38** 155
Benattar J J, Levelut A M, Liebert L and Moussa F 1979 *J. Phys. (Paris)* **40** C3–115
Bhattacharya S, Sarma B K and Ketterson J B 1978 *Phys. Rev. Lett.* **40** 1582
Billard J, Dubois J C, Tinh N H and Zann A 1978 *Nouv. J. Chim.* **2** 535
Blinc R, Lugomer S and Zeks B 1974 *Phys. Rev.* **A9** 2214
Blinc R, Luzar M, Vilfan M and Burgar M 1975 *J. Chem. Phys.* **63** 3445
Blinc R, Vilfan M, Luzar M, Seliger J and Zagar V 1978 *J. Chem. Phys.* **68** 303
Blinov L M, Beresnev L A, Shtukov N M and Elashvili Z M 1979 *J. Phys. (Paris)* **40** C3–269
Bock M, Heppke G, Richter E J and Schneider F 1978 *Mol. Cryst. Liq. Cryst.* **45** 221
Bradberry G W and Vaughan J M 1977 *Phys. Lett.* **A62** 225
Bradshaw M J and Raynes E P 1981 *Mol. Cryst. Liq. Cryst. Lett.* **72** 35, 73
Buka A, Owen P G and Price A H 1979a *Mol. Cryst. Liq. Cryst.* **51** 295
Buka A, Owen P G and Price A H 1979b *Mol. Cryst. Liq. Cryst.* **51** 273
Bulkin B J 1976 in *Advances in liquid crystals* (ed.) G H Brown (New York and London: Academic Press) Vol 2 p. 199
Bulkin B J and Brezinsky K 1978 *J. Chem. Phys.* **69** 15
Bulkin B J and Lok W B 1973 *J. Phys. Chem.* **17** 326
Cabane B and Clark W G 1970 *Phys. Rev. Lett.* **25** 91
Candau S and Letcher S V 1978 in *Advances in liquid crystals* (ed.) G H Brown (New York and London: Academic Press) Vol 3 p. 168
Castro C A, Hikata A and Elbaum C 1978 *Phys. Rev.* **A17** 353
Chandrasekhar S 1977 *Liquid crystals* (Cambridge: University Press)
Chandrasekhar S 1982 *Advances in liquid crystals* (ed.) G H Brown (New York and London: Academic Press) Vol 5 p. 47
Chandrasekhar S 1983 *Philos. Trans. R. Soc. London* **A309** 93
Chandrasekhar S 1984 Plenary Lecture, X Int. Liquid Cryst. Conf., York, July 1984 (to be published in the Proceedings)
Chandrasekhar S and Madhusudana N V 1971 *Acta Crystallogr.* **A27** 303
Chandrasekhar S and Madhusudana N V 1972 *Appl. Spectrosc. Rev.* **6** 189 (and references contained therein)

Chandrasekhar S and Madhusudana N V 1978 in *Progress in liquid physics* (ed.) C A Croxton (Chichester: Wiley) p. 539
Chandrasekhar S, Sadashiva B K and Suresh K A 1977 *Pramana* **9** 471
Chandrasekhar S, Savithramma K L and Madhusudana N V 1984 *Proceedings of the ACS symposium on liquid crystals and ordered fluids, Las Vegas*, 1982 (eds) J F Johnson and A C Griffin (New York: Plenum) p. 299
Chandrasekhar S, Shashidhar R and Rao K V 1980a in *Proceedings of the 3rd liquid cryst. conf., Budapest*, 1979 (ed.) L Bata (Oxford and Budapest: Pergamon and Akademiai Kiado) p. 123
Chandrasekhar S, Suresh K A and Rao K V 1980b *Liquid crystals, Proc. Int. Conf., Bangalore*, 1979 (ed.) S Chandrasekhar (London: Heyden) p. 131
Cladis P E 1975 *Phys. Rev. Lett.* **35** 48
Cladis P E 1980 in *Liquid crystals, Proc. Int. Conf., Bangalore*, 1979 (ed.) S Chandrasekhar (London: Heyden) p. 105
Cladis P E 1981 *Mol. Cryst. Liq. Cryst.* **67** 177
Cladis P E, Guillon D, Bouchet F R and Finn P L 1981 *Phys. Rev.* **A23** 2594.
Conrad H M, Stiller H H and Stockmeyer R 1976 *Phys. Rev. Lett.* **36** 264
Conrad H M, Stiller H H and Stockmeyer R 1977a *Phys. Rev. Lett.* **38** 575
Conrad H M, Stiller H H, Frischkorn C G B and Shirane G 1977b *Solid State Commun.* **23** 571
Conrad H M, Krasser W, Stiller H H and Wergin A 1980 in *Liquid crystals, Proc. Int. Conf., Bangalore*, 1979 (ed.) S Chandrasekhar (London: Heyden) p. 429
Conrad H M and Mezei F 1980 in *Liquid crystals, Proc. Int. Conf., Bangalore*, 1979 (ed.) S Chandrasekhar (London: Heyden) p. 441
Cotrait M, Marsau P, Destrade C and Malthete J 1979 *J. Phys. (Paris) Lett.* **40** L-519
Cotter M A 1974 *Phys. Rev.* **A10** 625
Cotter M A 1977a *Mol. Cryst. Liq. Cryst.* **39** 173
Cotter M A 1977b *J. Chem. Phys.* **66** 1098
Cotter M A 1977c *J. Chem. Phys.* **66** 4710
Cotter M A 1979 in *The molecular physics of liquid crystals* (eds) G R Luckhurst and G W Gray (London and New York: Academic Press) p. 169
Cotter M A 1983 *Mol. Cryst. Liq. Cryst.* **97** 29
Dalmolen L G P, Egberts E and de Jeu W H 1984 *J. Phys. (Paris)* **45** 129
Davies M, Larkin I and Evans M 1973 *J. Chem. Soc. Faraday II* **69** 1011
Davies M, Moutran R, Price A H, Beevers M S and Williams G 1976 *J. Chem. Soc. Faraday II* **72** 1447
de Gennes P G 1974 *The physics of liquid crystals* (Oxford: Clarendon)
de Jeu W H 1978 in *Liquid crystals* (*Solid State Physics Suppl.* 14) (ed.) L Liebert (New York and London: Academic Press) p. 109
de Jeu W H 1983 *Philos. Trans. R. Soc. London* **A309** 217
de Jeu W H, Gerritsma C J, Van Zanten P and Goossens W J A 1972 *Phys. Lett.* **A39** 355
Demus D, Demus H and Zaschke H 1974 Flüssige kristalle in tabellen, VEB Deutscher verlag für grundstoffindustrie, Leipzig
Demus D, Goodby J W, Gray G W and Sackmann H 1980 in *Liquid crystals of one- and two-dimensional order* (eds) W Helfrich and G Heppke (Berlin: Springer-Verlag) p. 31
Demus D and Zaschke 1984 Flüssige kristalle tabellen II, VEB Deutscher verlag für grundstoffindustrie, Leipzig
Derzhanski A I and Petrov A G 1979 *Acta Phys. Pol.* **A55** 747
Destrade C, Bernaud M C, Gasparoux H, Levelut A M and Tinh N H 1980 in *Liquid crystals, Proc. Int. Conf., Bangalore*, 1979 (ed.) S Chandrasekhar (London: Heyden) p. 29
Destrade C and Gasparoux H 1975 *J. Phys. Lett. (Paris)* **36** L-105
Destrade C, Gasparous H, Babeau A, Tinh N H and Malthete J 1981a *Mol. Cryst. Liq. Cryst.* **67** 37
Destrade C, Guillon F and Gasparoux H 1976 *Mol. Cryst. Liq. Cryst.* **36** 115
Destrade C, Mondon M C and Malthete J 1979 *J. Phys. (Paris)* **40** C3–17
Destrade C, Tinh N H and Gasparoux H 1981b *Mol. Cryst. Liq. Cryst.* **71** 111
Dmitrienko V E and Belyakov V A 1980 *Sov. Phys. JETP* **51** 787
Doane J W 1979 in *Magnetic resonance of phase transitions* (New York and London: Academic Press) p. 171
Dong R Y 1981 *Mol. Cryst. Liq. Cryst.* **64** 205
Dong R Y and Tomchuk E 1978 *Phys. Rev.* **A17** 2062
Dong R Y, Wiszniewska M, Tomchuk E and Bock E 1974 *Can. J. Phys.* **52** 766

Doucet J, Levelut A M, Lambert M, Liebert L and Strzelecki L 1975 *J. Phys. (Paris)* **36** C1–13
Dowell F and Martire D E 1978 *J. Chem. Phys.* **68** 1088, 1094
Druon C and Wacrenier J M 1977 *J. Phys. (Paris)* **38** 47
Druon C and Wacrenier J M 1978 *Ann. Phys.* **3** 199
Durand G and Martinot-Lagarde Ph 1980 *Ferroelectrics* **24** 89
Dvorjetski D, Volterra V and Wiener-Avnear 1975 *Phys. Rev.* **A12** 681
Emsley J W, Lindon J C and Luckhurst G R 1976 *Mol. Phys.* **32** 1187
Evans M, Davies M and Larkin I 1974 *J. Chem. Soc. Faraday II* **70** 188
Evans M, Moutran R and Price A H 1975 *J. Chem. Soc. Faraday II* **71** 1854
Feldkamp G E, Handschy M A and Clark N A 1981 *Phys. Lett.* **A85** 359
Feng K, Woo C W and Sheng P 1983 *Phys. Rev.* **A28** 1587
Fernandes J R and Venugopalan S 1976 *Mol. Cryst. Liq. Cryst.* **35** 113
Flory P J 1956 *Proc. R. Soc. London* **A234** 73
Flory P J and Ronca G 1979 *Mol. Cryst. Liq. Cryst.* **54** 289
Fontana M P and Bini S 1976 *Phys. Rev.* **A14** 1555
Freed J H 1977 *J. Chem. Phys.* **66** 4183
Fringeli U P, Schadt M, Rihak P and Günthard Hs H 1976 *Z. Naturforsch.* **A31** 1098
Gane P A C, Leadbetter A J and Wrighton P G 1981 *Mol. Cryst. Liq. Cryst.* **66** 247
Garoff S and Meyer R B 1977 *Phys. Rev. Lett.* **38** 488
Gelbart W M and Barboy 1979 *Mol. Cryst. Liq. Cryst.* **55** 209
Gelbart W M and Baron B A 1977 *J. Chem. Phys.* **66** 207
Ghosh S K, Tettamonti E and Indovina P L 1972 *Phys. Rev. Lett.* **29** 638
Ghosh S K, Tettamonti E and Panatta A 1980 *Phys. Rev.* **B21** 1194
Goodby J W, Leslie T M, Cladis P E and Finn P L 1984 in *Proceedings of the ACS symposium on liquid crystals and ordered fluids, Las Vegas*, 1982 (eds) A C Griffin and J F Johnson (New York: Plenum) p. 89
Goossens W J A 1971 *Mol. Cryst. Liq. Cryst.* **12** 237
Graf V, Noack F and Stohrer M 1977 *Z. Naturforsch.* **A32** 61
Gray G W 1976 in *Advances in liquid crystals* (ed.) G H Brown (New York and London: Academic Press) Vol 2 p. 1
Gray G W 1979 in *The molecular physics of liquid crystals* (eds) G R Luckhurst and G W Gray (London and New York: Academic Press) pp 1 and 263
Gray G W 1981 *Mol. Cryst. Liq. Cryst.* **63** 1
Griffin A C, Britt T R, Buckley N W, Fisher R F, Havens S J and Goodman D W 1978 in *Liquid crystals and ordered fluids* (eds) J F Johnson and R S Porter (New York: Plenum) Vol 3 p. 61
Guillon D, Cladis P E and Stamatoff J 1978 *Phys. Rev. Lett.* **41** 1598
Hardouin F, Levelut A M, Tinh N H and Sigaud G 1979a *Mol. Cryst. Liq. Cryst. Lett.* **56** 35
Hardouin F, Sigaud G, Achard M F and Gasparoux H 1979b *Solid State Commun.* **30** 265
Hardouin F, Levelut A M and Sigaud G 1981 *J. Phys. (Paris)* **42** 71
Hardouin F, Levelut A M, Achard M F and Sigaud G 1983 *J. Chim. Phys.* **80** 53
Hayamizu K and Yamamoto O 1977 *Bull. Chem. Soc. Jpn* **50** 1295
Heppke G, Hopf R, Kohne B and Praefcke K 1980 in *Proceedings of the 3rd liquid cryst. conf., Budapest* 1979 (ed.) L Bata (Oxford and Budapest: Pergamon and Akademiai Kiado) p. 141
Hervet H, Dianoux A J, Lechner R E and Volino F 1976 *J. Phys. (Paris)* **37** 587
Hoffmann J, Kuczynski W and Malecki J 1978 *Mol. Cryst. Liq. Cryst.* **44** 287
Horn R G 1978 *J. Phys. (Paris)* **39** 167
Horn R G and Faber T E 1979 *Proc. R. Soc. (London)* **A368** 199
Humphries R L, James P G and Luckhurst G R 1972 *J. Chem. Soc. Faraday Trans. II* **68** 1031
Hutton H, Bock E, Tomchuk E and Dong R Y 1978 *J. Chem. Phys.* **68** 940
Imura H and Okano K 1973 *Chem. Phys. Lett.* **19** 387
Janik J A, Janik J M and Otnes K 1980 in *Liquid crystals, Proc. Int. Conf., Bangalore*, 1979 (ed.) S Chandrasekhar (London: Heyden) p. 391
Jen S, Clark N A, Pershan P S and Priestley J B 1973 *Phys. Rev. Lett.* **31** 1552
Kats E I 1978 *Sov. Phys. JETP* **48** 916
Kelker H and Hatz R 1980 *Handbook of liquid crystals* (Weinheim: Verlag Chemie)
Kirov N and Simova P 1973 *Spectrochim. Acta* **A29** 55
Kiry F and Martinoty P 1978 *J. Phys. (Paris)* **39** 1019
Kortan A R, Von Kanel H, Birgeneau R J and Litster J D 1984 *J. Phys. (Paris)* **45** 529

Krüger G J, Spiesecke H, Van Steenwinkel R and Noack F 1977 *Mol. Cryst. Liq. Cryst.* **40** 143
Kumagai M, Soda G and Chihara H 1981 *J. Magn. Reson.* **42** 28
Leadbetter A J, Frost J C, Gaughan J P, Gray G W and Mosley A 1979a *J. Phys. (Paris)* **40** 375
Leadbetter A J, Mazid M A and Richardson R M 1980 in *Liquid crystals, Proc. Int. Conf., Bangalore*, 1979 (ed.) S Chandrasekhar (London: Heyden) p. 65
Leadbetter A J and Richardson R M 1979 in *The molecular physics of liquid crystals* (eds) G R Luckhurst and G W Gray (London and New York: Academic Press) p. 451
Leadbetter A J, Richardson R M and Frost J C 1979b *J. Phys. (Paris)* **40** C3–125
Levstik A, Zeks B, Levstik I, Blinc R and Filipic C 1979 *J. Phys. (Paris)* **40** C3–303
Lewis I C and Kovac C A 1979 *Mol. Cryst. Liq. Cryst.* **51** 173
Liao Y, Clark N A and Pershan P S 1973 *Phys. Rev. Lett.* **30** 639
Lippens D, Parneix J P and Chapoton A 1977 *J. Phys. (Paris)* **38** 1465
Longa L and de Jeu W H 1982 *Phys. Rev.* **A26** 1632
Longa L and de Jeu W H 1983a *Solid State Commun.* **46** 693
Longa L and de Jeu W H 1983b *Phys. Rev.* **A28** 2380
Luckhurst G R 1984 Plenary Lecture, X International Liquid Cryst. Conf. York, July 1984
Luckhurst G R and Romano S 1980 *Proc. R. Soc. (London)* **A373** 111
Luckhurst G R and Vitoria F R 1982 *Mol. Cryst. Liq. Cryst. Lett.* **72** 201
Luckhurst G R and Yeates R N 1976 *Chem. Phys. Lett.* **38** 551
Luckhurst G R and Zannoni C 1975 *Proc. R. Soc. (London)* **A343** 389
Luckhurst G R, Zannoni C, Nordio P G and Segre C 1975 *Mol. Phys.* **30** 1345
Lugomer S 1974 *Mol. Cryst. Liq. Cryst.* **29** 141
Madhusudana N V 1981 *Bull. Mater. Sci.* **3** 119
Madhusudana N V and Chandrasekhar S 1973a *Solid State Commun.* **13** 377
Madhusudana N V and Chandrasekhar S 1973b in *Liquid Crystals, Proc., Int. Conf., Bangalore*, 1973 (Pramana Suppl. 1) (ed.) S Chandrasekhar (Bangalore: Indian Acad. Sci.) p. 57
Madhusudana N V, Raghunathan V A and Urs M S R 1984 *Mol. Cryst. Liq. Cryst.* **106** 161
Madhusudana N V, Sadashiva B K and Moodithaya K P L 1979 *Curr. Sci.* **48** 613
Madhusudana N V, Savithramma K L and Chandrasekhar S 1977 *Pramana* **8** 22
Madhusudana N V, Srikanta B S and Urs M S R 1982 *Mol. Cryst. Liq. Cryst. Lett.* **82** 317
Maier W and Meier G 1961 *Z. Naturforsch.* **A16** 470, 1200
Maier W and Saupe A 1958 *Z. Naturforsch.* **A13** 564
Maier W and Saupe A 1959 *Z. Naturforsch.* **A14** 882
Maier W and Saupe A 1960 *Z. Naturforsch.* **A15** 287
Marcelja S 1974 *J. Chem. Phys.* **60** 3599
Marcerou J P and Prost J 1978 *Ann. Phys.* **3** 269
Marcerou J P and Prost J 1980 *Mol. Cryst. Liq. Cryst.* **58** 259
Martin A J, Meier G and Saupe A 1971 *Symp. Faraday Soc.* **5** 119
Martinot-Lagarde Ph. and Durand G 1981 *J. Phys. (Paris)* **42** 269
Martinoty P 1979 *J. Phys. (Paris)* **40** L-291
Martire D E 1974 *Mol. Cryst. Liq. Cryst.* **28** 63
Matsushita M 1978 *Phys. Lett.* **A66** 507
Matsushita M 1981 *Mol. Cryst. Liq. Cryst.* **68** 1
McColl J R and Shih C S 1972 *Phys. Rev. Lett.* **29** 85
McMillan W L 1971 *Phys. Rev.* **A4** 1238
McMillan W L 1972 *Phys. Rev.* **A6** 936
Meier G and Saupe A 1966 *Mol. Cryst.* **1** 515
Meyer R B 1969 *Phys. Rev. Lett.* **22** 918
Meyer R B 1977 *Mol. Cryst. Liq. Cryst.* **40** 33
Meyer R B, Liebert L, Strzelecki L and Keller P 1975 *J. Phys. (Paris)* **36** L-69
Miyano K 1978 *J. Chem. Phys.* **69** 4807
Moncton D E and Pindak R 1979 *Phys. Rev. Lett.* **43** 701
Moodithaya K P L and Madhusudana N V 1980 in *Liquid crystals, Proc. Int. Conf., Bangalore*, 1979 (ed.) S Chandrasekhar (London: Heyden) p. 297
Moscicki J K and Kresse H 1981 *Adv. Mol. Relaxation and Interaction Processes* **19** 145
Mugele Th, Graf V, Wölfel W and Noack F 1980 *Z. Naturforsch.* **A35** 924
Myasnikova T P and Corbatenko L S 1972 *Sb. Dokl. Vses. Nauchn. Konf. Zhidk. Krist. Symp. Ikhor* p. 206

Nagai S, Martinoty P and Candau S 1976 *J. Phys. (Paris)* **37** 769
Nezbeda I and Boublik T 1978 *Czech. J. Phys.* **B28** 353
Nordio P L, Rigatti G and Segre U 1973a *Chem. Phys. Lett.* **19** 295
Nordio P L, Rigatti G and Segre U 1973b *Mol. Phys.* **25** 129
Oh C S 1977 *Mol. Cryst. Liq. Cryst.* **42** 1
Onsager L 1949 *Ann. N.Y. Acad. Sci.* **51** 627
Ostrovskii B I, Pikin S A and Chigrinov V G 1979 *Sov. Phys. JETP* **50** 811
Park J W, Bak C S and Labes M M 1975 *J. Am. Chem. Soc.* **97** 4398
Parneix J P, Chapoton A and Constant E 1975 *J. Phys. (Paris)* **36** 1143
Pepy G, Kroo N and Rosta L 1980 in *Proc. of the 3rd liquid cryst. conf., Budapest*, 1979 (ed.) L Bata (Budapest and Oxford: Akademai Kiado and Pergamon) p. 111
Pincus P 1969 *Solid State Commun.* **7** 415
Pindak R, Moncton D E, Davey S C and Goodby J W 1981 *Phys. Rev. Lett.* **46** 1135
Pindak R, Sprenger W O, Bishop D J, Osheroff D D and Goodby J W (1982) *Phys. Rev. Lett.* **48** 173
Prasad S N and Venugopalan S 1980 in *Liquid crystals, Proc. Int. Conf., Bangalore*, 1979 (ed.) S Chandrasekhar (London: Heyden) p. 381
Prasad S N and Venugopalan S 1981 *J. Chem. Phys.* **75** 3033
Price A H and Evans M W 1980 *J. Chem. Soc. Faraday II* **76** 217
Prost J and Barois P 1983 *J. Chem. Phys.* **80** 65
Prost J and Clark N A 1980 in *Liquid crystals, Proc. Int. Conf., Bangalore*, 1979 (ed.) S Chandrasekhar (London: Heyden) p. 53
Prost J and Marcerou J P 1977 *J. Phys. (Paris)* **38** 315
Prost J and Pershan P S 1976 *J. Chem. Phys.* **47** 2298
Raja V N and Shashidhar R 1984 unpublished
Ratna B R and Shashidhar R 1976 *Pramana* **6** 278
Ratna B R and Shashidhar R 1978 *Mol. Cryst. Liq. Cryst.* **45** 103
Ratná B R, Shashidhar R and Rao K V 1980 in *Liquid crystals, Proc. Int. Conf., Bangalore*, 1979 (ed.) S Chandrasekhar (London: Heyden) p. 135
Rebertus D W and Sando K M 1977 *J. Chem. Phys.* **67** 2585
Reinhart K F, Seeliger R, Graf V and Noack F 1979 *J. Phys. (Paris)* **40** C3–199
Ribeiro A C, Martins A F and Giroud-Godquin A M 1984, 4th Portuguese National Physics Conference, Portugal, 1984 (Preprint)
Ricard L and Prost J 1979 *J. Phys. (Paris)* **40** C3–83
Richardson R M, Leadbetter A J, Bonsor D K and Krüger G J 1980 *Mol. Phys.* **40** 741
Rollmann G, Reinhart K F and Noack F 1979 *Z. Naturforsch.* **A34** 964
Rustichelli F 1978 *Ann. Phys.* **3** 163
Rutar V, Vilfan M, Blinc R and Bock E 1978 *Mol. Phys.* **35** 721
Sakomoto A, Yoshino K, Kubo O and Inuishi Y 1974 *Jpn. J. Appl. Phys.* **13** 1691
Savithramma K L and Madhusudana N V 1980 *Mol. Cryst. Liq. Cryst.* **62** 63
Schadt M 1972 *J. Chem. Phys.* **56** 1494
Schaetzing R and Litster J D 1979 in *Advances in liquid crystals* (ed.) G H Brown (New York and London: Academic Press) Vol 4 p. 147
Schnur J M 1973 *Mol. Cryst. Liq. Cryst.* **23** 155
Schnur J M and Fontana M 1974 *J. Phys. (Paris)* **35** L-53
Schnur J M, Hass M and Adair W L 1972 *Phys. Lett.* **A41** 326
Schnur J M, Sheridan J P and Fontana M 1973 in *Liquid crystals, Proc. Int. Conf., Bangalore*, 1973 (Pramana Suppl. 1 (ed.) S Chandrasekhar (Bangalore: Indian Acad. Sci.) p. 175
Schröder H 1979 in *The molecular physics of liquid crystals* (eds) G R Luckhurst and G W Gray (London and New York: Academic Press) p. 121
Sciensinska E, Sciensinski J, Twardowski J and Janik J A 1974 *Mol. Cryst. Liq. Cryst.* **27** 125
Sharma N K, Pelzl G, Demus D and Weissflog W 1980 *Z. Phys. Chem. (Leipzig)* **261** 579
Shashidhar R, Ratna B R, Raja V N, Nagabhushana C, Krishna Prasad S and Surendranath V 1985 (to be published)
Shibata K, Kutsukabe M, Takahashi H and Higasi K 1976 *Bull. Chem. Soc. Jpn* **49** 406
Straley J P 1973 *Mol. Cryst. Liq. Cryst.* **22** 333
Straley J P 1974 *Phys. Rev.* **A10** 1881
Sung C 1971 *Chem. Phys. Lett.* **10** 35

Suresh K A 1983 *Mol. Cryst. Liq. Cryst.* **97** 417
Takase A, Sakagami S and Nakamizo M 1975 *Chem. Lett.* **792**
Takase A, Sakagami S and Nakamizo M 1977 *Jpn. J. Appl. Phys.* **16** 549
Takezoe H, Usui H, Furuhata K, Nakagiri T, Fukuda A and Kuze E 1979 *J. Phys. (Paris)* **40** C3–217
Thiriet Y and Martinoty P 1979 *J. Phys. (Paris)* **40** 789
Tinh N H 1983 *J. Chim. Phys.* **80** 83
Tinh N H, Hardouin F, Destrade C and Levelut A M 1982 *J. Phys. (Paris)* **43** L-33
Ukleja P, Pirs J, Doane J W 1976 *Phys. Rev.* **A14** 414
Van der Meer B W and Vertogen G 1979a in *The molecular physics of liquid crystals* (eds) G R Luckhurst and G W Gray (London and New York: Academic Press) p. 149
Van der Meer B W and Vertogen G 1979b *J. Phys. (Paris)* **40** C3–222.
Venugopalan S, Fernandes J R and Surendranath V 1977 *Mol. Cryst. Liq. Cryst.* **40** 149
Venugopalan S and Prasad S N 1979 *J. Chem. Phys.* **71** 5293
Vertogen G and Fleury G 1975a *Mol. Cryst. Liq. Cryst.* **30** 213
Vertogen G and Fleury G 1975b *Mol. Cryst. Liq. Cryst.* **30** 223
Vertogen G, Fleury G, Jones R N and Nadeau A 1976 *Mol. Cryst. Liq. Cryst.* **36** 327
Vieillard-Baron J 1974 *Mol. Phys.* **28** 809
Volino F and Dianoux A J 1979 *Mol. Cryst. Liq. Cryst.* **38** 125
Wacrenier J M, Druon C and Lippens D 1981 *Mol. Phys.* **43** 97
Wade C G 1977 *Annu. Rev. Phys. Chem.* **28** 47
Wagner W 1981 *Mol. Cryst. Liq. Cryst.* **75** 169
Weissflog W, Pelzl G, Wiegeleben A and Demus D 1980 *Mol. Cryst. Liq. Cryst. Lett.* **56** 295
Wölfel W, Graf V and Noack F 1980 in *Liquid crystals of one- and two-dimensional order* (eds) W Helfrich and G Heppke (Berlin: Springer-Verlag) p. 156
Ypma J G Y and Vertogen G 1977 *Phys. Lett.* **A60** 212
Yu L J, Lee H, Bak C S and Labes M M 1976 *Phys. Rev. Lett.* **36** 388
Zeks B, Levstik A and Blinc R 1979 *J. Phys (Paris)* **40** C3–409
Zwanzig R 1963 *J. Chem. Phys.* **39** 1714