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Theories of Nematic Order [and Discussion]

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Theories of nematic order

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The paper starts with a description of the molecular alignment that characterizes nematic liquid crystals, and a brisk review of the classic mean field theories of this alignment and of recent attempts to improve on the mean field approach by introducing the direct correlation function. It is argued that such theories are unsatisfactory on two grounds: (*a*) because they fail to recognize that correlations of orientation between adjacent molecules are of very much longer range than the intermolecular potential – they fall off, indeed, only as fast as $1/R$ – and (*b*) because they fail to allow for director fluctuations. The author's continuum theory, which attributes entirely to director fluctuations the fact that molecules in nematics are not perfectly aligned, is free from these particular objections, and it seems to give the most complete description currently available, especially at low temperatures, for the behaviour of simple model nematics that have been studied by computer simulation. Its failure to match completely the behaviour of real nematics such as 5CB may be due to their polar character.

1. Description of nematic order

In nematic liquid crystals the molecules are preferentially aligned with respect to a local axis of symmetry, known as the director. Since the symmetry is in practice uniaxial (though nematics that are locally biaxial are not difficult to imagine) the degree of alignment may be described for rigid molecules by two order parameters

$$S_{zz} = \langle P_2(\cos\beta)\rangle = \langle \tfrac{1}{2}(3\cos^2\beta - 1)\rangle \tag{1}$$

and

$$(S_{xx} - S_{yy}) = \langle \tfrac{3}{2}\sin^2\beta\cos 2\gamma\rangle. \tag{2}$$

In such expressions the angled brackets indicate an ensemble average for molecules in the neighbourhood of interest, and α, β and γ are Euler angles describing the orientation with respect to the director of (x, y, z) axes fixed in each molecule. The molecular axes might be chosen, for example, to coincide with the principal axes for the moment of inertia tensor for a single molecule, I_{ij}. If so, the conventional labelling (not wholly rational!) would be such as to ensure that

$$I_{yy} > I_{xx} > I_{zz}.$$

Thus the z axis is the 'long' axis of the molecule, and β is the angle between this and the director, while γ is the angle through which the molecule is rotated about its long axis, starting from an orientation such that the director lies in the xz plane. It seems that, given this labelling, $(S_{xx} - S_{yy})$ may in practice be of order $+0.05$ (Emsley *et al.* 1981) and large enough to affect some bulk properties, such as magnetic susceptibility (Faber *et al.* 1983). The parameter S_{zz} is of order $+0.5$, however, and is evidently of much greater significance. In what follows we shall lose sight of $(S_{xx} - S_{yy})$, supposing the molecules to rotate with sufficient freedom about their long axes to be treated as cylinders. We shall also lose sight of the complications that arise with molecules that are not rigid.

The parameter S_{zz} is sometimes denoted by S_2 instead, to emphasize that it is one member of the hierarchy of order parameters that are needed to define the full orientational distribution function, $f(\beta)$. We have

$$f(\beta) = \sum_{n=0}^{n} (2n+1)\, S_n P_n(\cos\beta), \tag{3}$$

with

$$S_n = \langle P_n(\cos\beta)\rangle. \tag{4}$$

It is invariably assumed that S_n vanishes when n is odd, because nematics whose molecules carry an electric dipole moment show no signs of ferroelectric ordering. As regards even n, it is fair to say that for most nematics we know only $S_0\ (=1)$ and S_2; the experimental evidence relating to S_4 is limited and not wholly reliable, except in the case of a few model nematics whose properties have been investigated by the 'experimental' technique of computer simulation.

Nematic order is not completely described by $f(\beta)$, even when the rigid cylinder approximation is sound, for this function tells us nothing about correlations in position and alignment for neighbouring molecules. To describe the correlations in position that characterize a simple isotropic liquid we need, of course, a two-body distribution function $g(R)$. The equivalent distribution function in a nematic needs to be written as

$$g(\boldsymbol{R}_{12}, \alpha_1, \beta_1, \alpha_2, \beta_2) = g(1,2) f(\beta_1) f(\beta_2) \tag{5}$$

(an equation that serves to define the function $g(1,2)$ to which reference is made below). In principle $g(1,2)$ describes correlations of orientation as well as of position, but if we wish to focus attention on the former it may be simpler to discuss what have been termed the short-range order parameters

$$\sigma_n(\boldsymbol{R}_{12}) = \langle P_n(\cos\theta_{12})\rangle, \quad n = 2, 4, \ldots, \tag{6}$$

where θ_{12} is the angle between the z axes of two molecules whose centres are separated by $\boldsymbol{R}_{12}$. Of course, the correlations must disappear, i.e. $g(1,2)$ must tend to unity, for large separations, and it is readily shown that in that limit

$$\sigma_2 = S_2^2. \tag{7}$$

The difference between σ_2 and S_2^2 provides a convenient measure of correlations of orientation at smaller separations.

Finally, we should note that in a macroscopic sample of nematic the director does not necessarily point in the same direction throughout. Various types of distortion, distinguished by the terms splay, twist and bend, may be fed into the director field by distorting the boundary conditions of the sample, at some cost in free energy. The cost is determined by the three Frank stiffness constants, k_{11}, k_{22} and k_{33}. Even when the boundary conditions are consistent with uniform alignment, some distortion always arises in the interior of the sample as a result of fluctuations, and it is for this reason that nematic liquids scatter light as strongly as they do.

2. MEAN FIELD AND OTHER THEORIES

Attempts to understand the occurrence of nematic order have mostly (though by no means exclusively) been based upon the pioneering work of either Onsager (1949) or Maier & Saupe (1958, 1959, 1960). Since developments of Onsager's theory are likely to receive attention elsewhere in this symposium, we may concentrate initially on the Maier–Saupe approach. Its essence may be understood by considering a model rather simpler than the one that Maier &

Saupe initially proposed, i.e. a model in which the intermolecular pair potential contains an anisotropic term of short range, of the form

$$V(1,2) = -\epsilon(\boldsymbol{R}_{12})\,P_2(\cos\theta_{12}). \tag{8}$$

Let us evaluate the free energy for this model, making the approximation that correlations of orientation can be completely ignored, i.e. that $g(1,2)$ depends only on $\boldsymbol{R}_{12}$. This approximation allows one to express the entropy of misalignment as $-Nk\langle\ln f(\beta)\rangle$ and it also allows one to make use of (7) in evaluating the internal energy due to the interaction that (8) describes. The order-dependent terms in the free energy therefore turn out to be

$$-CS_2^2+NkT\langle\ln f(\beta)\rangle, \tag{9}$$

where C should depend only on density. A simple variational argument (de Gennes 1974) shows that to minimize the free energy we need

$$f(\beta)\propto\exp\{-2CS_2P_2(\cos\beta)/kT\}, \tag{10}$$

and a self-consistency relation then serves to fix S_2, once C and T are known. Like the Weiss theory of ferromagnetism, which it closely resembles, the theory of Maier & Saupe is a mean field one. The mean field in question is $-2CS_2$ and it couples with $P_2(\cos\beta)$.

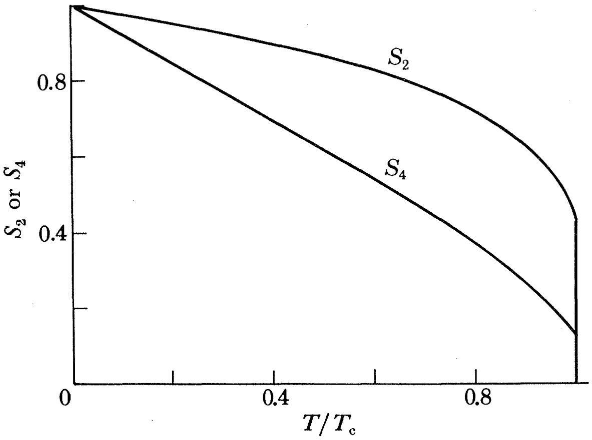

FIGURE 1. The dependence of S_2 and S_4 on T/T_c according to Maier & Saupe.

At constant density the Maier–Saupe theory involves only one adjustable parameter, the constant C in (9) or, if preferred, the temperature T_c at which the nematic phase becomes isotropic on heating. It therefore predicts unique curves, reproduced in figure 1, for the variation of S_2 and S_4 with T/T_c. The agreement with experiment is in some respects quite impressive, but it is certainly not complete. Several attempts have therefore been made to improve the theory, by adding terms to the intermolecular pair potential while retaining the mean field framework (Chandrasekhar & Madhusudana 1971, 1973; Humphries *et al.* 1972; Luckhurst *et al.* 1975; Shen *et al.* 1981). At the expense of one or more additional adjustable parameters, the fit to experiment can indeed be improved.

Unfortunately, the basic assumption that $g(1,2)$ is a function only of $\boldsymbol{R}_{12}$ is not borne out by the results of computer simulation studies. Admittedly these studies have so far been restricted to rather simple models; the most detailed results available are for a $10\times10\times10$ lattice of 'molecules', with periodic boundary conditions, which interact via an anisotropic potential of the sort that (8) describes, ϵ being zero except between nearest neighbours (Zannoni 1979). But if the correlations of orientation between neighbouring molecules are strong in such a lattice, as they seem to be, they are presumably strong in real nematics too.

It has been suggested (e.g. by Luckhurst & Zannoni (1977)) that the mean field arguments of Maier & Saupe should be used to discuss the alignment of *clusters* of molecules rather than of individual molecules, and that the analysis of the mean molecular structure within a cluster should be treated as a separate problem, to be solved exactly as far as possible. The approach is superficially attractive, though to go much beyond the theory of Sheng & Wojtowicz (1976), who considered clusters containing only two molecules, would evidently require much labour.

An alternative approach is that of Stecki & Kloczkowski (1979). In some ways this is more closely related to the theory of Onsager than to that of Maier & Saupe, but the results can be presented in a mean-field-like form, to the extent that an entropic term $NkT\langle \ln f(\beta)\rangle$ can be isolated from the free energy. The residue is expressed, exactly, in terms of a direct correlation function $c(1,2)$, which bears the same relation to $g(1,2)$ that $c(R)$ bears to $g(R)$ for a simple fluid, and similar functions of higher order, $c_3(1,2,3)$ and so on. In simple fluids various approximations are available to link $c(R)$ to the intermolecular pair potential $V(R)$, namely

$$C \approx \exp(-\beta V) - 1, \tag{11}$$

$$C \approx -\beta V, \tag{12}$$

and

$$C \approx g(R)\{1-\exp(\beta V)\}, \tag{13}$$

with $\beta = 1/kT$. The second of these is used in the so-called mean spherical model of simple liquids and the third corresponds to the Percus–Yevick model. Stecki and his coworkers use similar equations to relate $c(1,2)$ to $V(1,2)$ in cases where the potential is anisotropic and where the molecules are perhaps aligned. They have been careful to restrict their calculations so far to circumstances where $c_3(1,2,3)$, etc., can be neglected. This restriction means that while they supply expressions for the change in free energy due to small fluctuations in S_2 about its equilibrium value, or due to gradual changes in the orientation of the director, they do not attempt to calculate curves for S_2 and S_4 in the nematic phase to replace those plotted in figure 1. Other authors have been less cautious (Ruijgrok & Sokalski 1982; Wagner 1981).

It is clear that Stecki's approach is capable in principle of describing correlations of orientation between nearest neighbours. Thus if $V(1,2)$ is such as to favour parallel alignment of molecules 1 and 2, it follows from (11), (12) or (13) that $c(1,2)$, and hence $g(1,2)$, will be enhanced for pairs that are parallel (θ_{12} small) at the expense of pairs that are non-parallel (θ_{12} large). The enhancement would seem to be limited, however, to the range over which $V(1,2)/kT$ is significant. If the range of the correlations proves to be much greater than that, we must surely infer that for nematic liquids (11)–(13) are insufficient.

3. TWO REASONS FOR DOUBT

It is my belief that the correlations of orientation represented by

$$\sigma_2(\boldsymbol{R}_{12}) - S_2^2$$

are in a typical nematic of far longer range than the possible range of $V(1,2)$ – that this quantity diminishes with distance, in fact, only as fast as $1/R$. If this assertion is correct, it not only casts doubt on the approximations on which Stecki and his coworkers have been forced to rely; it also implies that attempts to render the cluster model convincing, by steadily increasing the size of the clusters, are doomed to failure. A second reason for doubting the theories outlined in the previous section is that they include no allowance for the director fluctuations mentioned at the and of § 1. These two points will now be amplified.

Imagine a macroscopic cylinder whose sides have been 'rubbed' longitudinally to favour parallel alignment of the director in any nematic liquid brought into contact with them, and whose ends have been otherwise treated to favour perpendicular alignment. If immersed in a nematic with its axis parallel to the director, this cylinder need cause no distortion of the director field. If it is then tilted through an angle β_1, however, as shown in figure 2, the director will tilt too, by an angle $\beta(\boldsymbol{R})$, where $\boldsymbol{R}$ is measured from the centre of the cylinder. Now it is easily shown that when the three Frank constants are all equal, which is true of the model nematic investigated by Zannoni (1979) and others, though not of any real nematic yet identified, the configuration that minimizes the free energy stored in the nematic is such that $\beta(R)$ satisfies Laplace's equation

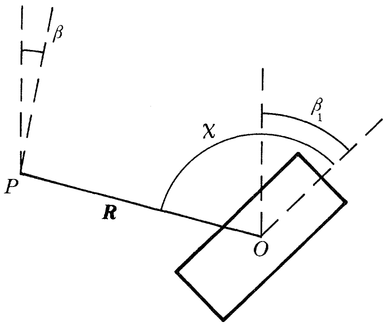

FIGURE 2. Rotation of the cylinder about O through an angle β_1 rotates the director at P through $\beta(R)$.

$$\nabla^2\beta = 0; \tag{14}$$

this is the form that the Euler–Lagrange equation takes for the problem in question. Hence we know that the equilibrium tilt can be expressed as a sum of spherical harmonic functions of the angle χ between $\boldsymbol{R}$ and the cylinder axis, i.e. that

$$\beta/\beta_1 = (a/R) + (b/R)^3\{\tfrac{1}{2}(3\cos^2\chi - 1)\} + O(1/R)^5. \tag{15}$$

At large distances only the first term in this series need be retained, and its coefficient a is clearly a length intermediate between half the length of the cylinder and its radius. Hence if θ is the angle between the axis of the cylinder and the z axis of a molecule at $\boldsymbol{R}$, which is inclined at β_2 to the director at that point, we have

$$\begin{aligned}\langle P_2(\cos\theta)\rangle &= \langle P_2(\cos\beta_2)\rangle P_2[\cos\{\beta_1 - (a\beta_1/R)\}] \\ &= S_2\{P_2(\cos\beta_1) + 3(a\beta_1/R)\sin\beta_1\cos\beta_1 + O(a/R)^2\}.\end{aligned} \tag{16}$$

Now imagine the cylinder to be, in fact, one of the molecules of which the nematic is composed. If correlations of orientation exist between nearest neighbours, any tilt of this central molecule must have some effect on the surrounding nematic, and we may reasonably hope to represent this effect by adjusting the length and radius of the cylinder and by treating everything outside the cylinder as a continuum in which (14) applies. The model suggests, if (16) is averaged over β_1, that at large distances

$$(\sigma_2(R) - S_2^2) = 3(a/R)\, S_2\langle\beta_1\sin\beta_1\cos\beta_1\rangle, \tag{17}$$

with a now a length of molecular dimensions. For well oriented nematics ($S_2 > 0.7$, say) we can expand thus:

$$\begin{aligned} 3\langle\beta_1 \sin\beta_1 \cos\beta_1\rangle &= 3\langle\sin^2\beta_1\rangle - \langle\sin^4\beta_1\rangle + \dots \\ &= 2(1-S_2) - (56 - 80S_2 + 24S_4)/105 + \dots, \end{aligned} \tag{18}$$

in the expectation that higher terms will be negligible. Hence we may estimate, using equation (26) below for S_4, that at large distances

$$\{\sigma_2(R) - S_2^2\} \approx 0.22(a/R) \quad (\text{for } S_2 = 0.867) \tag{19}$$

$$\approx 0.34(a/R) \quad (\text{for } S_2 = 0.753). \tag{20}$$

Evidence for the validity of these predictions is provided by figure 3, reproduced from Faber (1980). In this figure the crosses represent values of $\sigma_2(n)$ computed by Zannoni (1979) for the lattice model described above, plotted in effect against R; n is here the magnitude of R, measured in units of the lattice spacing, d. They are for four different values of (kT/ϵ), and the four horizontal lines represent the corresponding values of S_2^2. From these points alone one might conclude that the correlations of orientation, although appreciable up to $n = 3$, have virtually disappeared by the time $n = 4$ or 5. In this respect, however, results for a relatively small sample, only $10 \times 10 \times 10$ with periodic boundary conditions, give a misleading impression; had we relied on the computer-simulation results of Luckhurst & Romano (1980), who used a sample even smaller than Zannoni's (256 molecules, not confined to a lattice but kept apart by an isotropic Lennard-Jones potential, in a cubic cell with periodic boundary conditions), we would have concluded that the correlations of orientation were negligible beyond about two nearest-neighbour spacings. The open circles in the top two diagrams of figure 3 give a better picture of what $(\sigma_2 - S_2^2)$ should look like in an infinite lattice. Admittedly they are based upon a theory (see below) rather than on computer simulation, but the filled circles show that the theory is to be taken seriously; these filled circles were calculated in just the same way as the open circles but for a $10 \times 10 \times 10$ lattice,

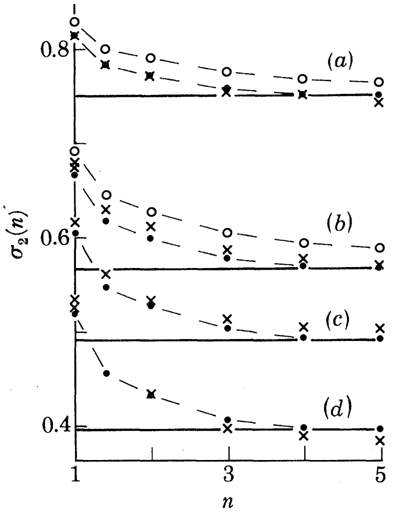

FIGURE 3. The short-range order parameter $\sigma_2(n)$ plotted against n, for a $10 \times 10 \times 10$ lattice of molecules subject to a nearest-neighbour interaction $-\epsilon P_2(\cos\theta_{ij})$: (a) $kT/\epsilon = 0.5$; (b) $kT/\epsilon = 0.8$; (c) $kT/\epsilon = 0.9$; (d) $kT/\epsilon = 1.0$. The filled circles are theoretical predictions, and the horizontal lines to which they converge for large n are predicted values of S_2^2 for the $10 \times 10 \times 10$ lattice at the temperature in question. The crosses show data generated by computer simulation. The open circles are calculated by using the same theory but for an infinite lattice. The values of kT/ϵ for which they apply are slightly different from 0.5 and 0.8, having been chosen to ensure that S_2^2 is the same as for the filled circles just below them. (Redrawn from Faber (1980).)

and they match Zannoni's crosses rather convincingly, considering that no adjustable parameter is involved. In the top two diagrams the open circles are converging for large n onto $(0.867)^2$ and $(0.753)^2$. The rate at which they do so seems to be nicely consistent with (19) and (20) respectively, with a taking the reasonable value of about $\frac{1}{3}d$, virtually independent of temperature.

That is the argument for believing that correlations of orientation in nematics are essentially of long range, varying as $1/R$. The argument for believing that director fluctuations are important in any realistic theory of nematics is equally straightforward. Light-scattering experiments indicate (Orsay Liquid Crystal Group 1969) that these fluctuations may be viewed as the superposition of a spectrum of periodic distortion modes, each of them excited, according to the equipartition theorem, with mean square amplitude

$$\langle \psi^2 \rangle = kT/VKq^2 \tag{21}$$

for $k_{11} = k_{22} = k_{33} = K$; here ψ is the local angle of tilt of the director associated with a mode of wavevector $\boldsymbol{q}$. Because excitation of any one mode may be shown to reduce the overall value of S_2 by a factor

$$\langle P_2(\cos\psi)\rangle = 1 - \tfrac{3}{2}\langle \psi^2 \rangle,$$

it follows that excitation of a spectrum of modes up to some cut-off wave vector q_c should reduce it from $S_2(0)$ to

$$\begin{aligned} S_2 &= S_2(0)\exp\left(-\tfrac{3}{2}\sum_{\boldsymbol{q}}\langle\psi^2\rangle\right) \\ &= S_2(0)\exp\left(-\frac{3kT}{(2\pi)^3}\int_0^{q_c}\frac{4\pi q^2\,\mathrm{d}q}{K(q)\,q^2}\right); \end{aligned} \tag{22}$$

a factor 2 in (22) takes care of the two polarizations that are allowed for each value of $\boldsymbol{q}$. To illustrate the possible importance of the exponential we may take the model nematic discussed by Zannoni as an example. For this it may be shown (Faber 1980) that when $S_2 \approx 0.5$

$$K(q \to 0) \approx (kT/2d). \tag{23}$$

Hence, if we neglect the possible variation of $K(q)$ with q, we find

$$S_2 \approx S_2(0)\exp(-2d/\lambda_c), \tag{24}$$

where λ_c is the cut-off wavelength (i.e. $2\pi/q_c$).

Of course if one is to take into account only those modes for whose reality direct evidence is provided by light-scattering experiments, this means setting λ_c equal to about 200 nm, which is so much larger than the intermolecular spacing in a typical nematic as to make a quantity such as $2d/\lambda_c$ quite negligible. There is no real justification for cutting off the spectrum so soon, however. In Zannoni's lattice model, distortion modes of wavelength down to $2d$ are quite conceivable, and for such modes, indeed, $K(q)$ is likely to be rather smaller than for long wavelengths,† and the mean square amplitude correspondingly greater. Such considerations make the exponential correction factor in (24) look decidedly significant.

The contribution of director fluctuation to S_2 in nematics has been emphasized by a number of people besides myself, e.g. by Berreman (1975) and M. Warner (personal communication 1982). The long-range $(1/R)$ nature of orientation correlations is implicit in some results obtained by de Gennes (1969).

4. An alternative theory

The two criticisms of conventional theories that have been voiced in the previous section are arguably two sides of a single coin: the long-range tail in $(\sigma_2 - S_2^2)$ may be seen as an inevitable

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† Equations quoted by Faber (1980) show that

$$K(q)/K(q \to 0) = 2(1-\cos qd)/q^2d^2.$$

consequence of the contribution that distortion modes of long wavelength make to the destruction of nematic order.

In my alternative theory (Faber 1977*a*, 1980), director fluctuations play the dominant role. It is assumed that but for these fluctuations the molecular alignment would be perfect, i.e. that $S_2(0)$ and likewise $S_4(0)$, etc., are unity. For the simple cubic lattice model of Zannoni the mode spectrum is cut off on the surfaces of a cubic Brillouin zone in $\boldsymbol{q}$-space, i.e. on the planes $q_x = \pm\pi/d$, $q_y = \pm\pi/d$, $q_z = \pm\pi/d$. Otherwise the spectrum is cut off on a spherical surface of radius q_c, of sufficient volume to enclose $2N$ distinct modes, $2N$ being the number of orientational, as opposed to translational, degrees of freedom in a nematic system of N molecules. The theory leads to an expression for S_2 in terms of (kT/ϵ) and N for the lattice model or more generally in terms of the Frank constants k_{11}, k_{22} and k_{33}. It suggests a distribution function $f(\beta)$ such that

$$\ln S_n = \tfrac{1}{6}n(n+1)\ln S_2, \tag{25}$$

which means that

$$S_4 = S_2^{\frac{10}{3}}, \tag{26}$$

$$S_6 = S_2^7, \text{ etc.} \tag{27}$$

It enables quantities such as σ_2 and σ_4 to be worked out, and for the simple cubic lattice model (at any rate for $R = d$ and in the limit $N \rightarrow \infty$) it predicts a relation between these quantities, which may be expressed to a high degree of accuracy by the equation (Faber 1981)

$$\sigma_4 = \sigma_2^{\frac{10}{3}}. \tag{28}$$

It has been used to discuss the order-dependence of the Frank constants (Faber 1977*b*, 1981), with results that differ significantly from those of mean field theories. Finally, it provides a way of calculating time-dependent correlation functions of relevance to the theories of nuclear magnetic relaxation (Faber 1977*c*) and dielectric dispersion in nematics; direct information about the behaviour of these correlation functions in model nematics is beginning to be available from computer-simulation studies (Zannoni & Guerra 1981).

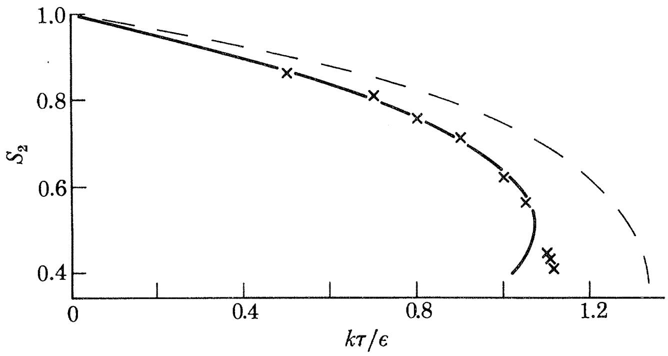

FIGURE 4. Dependence of S_2 on (kT/ϵ) for the $10\times10\times10$ lattice of figure 3. The full curve represents the theoretical prediction and the crosses show data generated by computer simulation. (The broken curve is predicted by mean field theory.)

The success of this so-called 'continuum theory of nematic disorder' in matching, without any adjustable parameter, Zannoni's results for $\sigma_2(n)$ against n in a $10\times10\times10$ sample has been illustrated in figure 2 above. Figure 4 shows that it can also match, again without any adjustable parameter, his results for S_2 against (kT/ϵ) in the same sample, except in the region near $T = T_c$, where S_2 falls below, say, 0.5.

Figure 5 shows how S_4 varies with S_2, not just for the model studied by Zannoni (1979) and Zannoni & Guerra (1981) but for two quite different models – smaller in size, involving different intermolecular potentials, and with no constraining lattice – on which Tsykalo & Bagmet (1978*a*, *b*) have performed computer-simulation experiments. The figure includes points showing how, in Zannoni's model, $\sigma_4(d)$ varies with $\sigma_2(d)$. The data seem to confirm that there is a more or less unique, model-independent, relation between S_4 and S_2 and that the relation between $\sigma_4(d)$ and $\sigma_2(d)$ is very similar. At low temperatures it is accurately described by (20) or (28) as the case may be, but systematic deviations become apparent when S_2 or σ_2 fall below, say, 0.6.

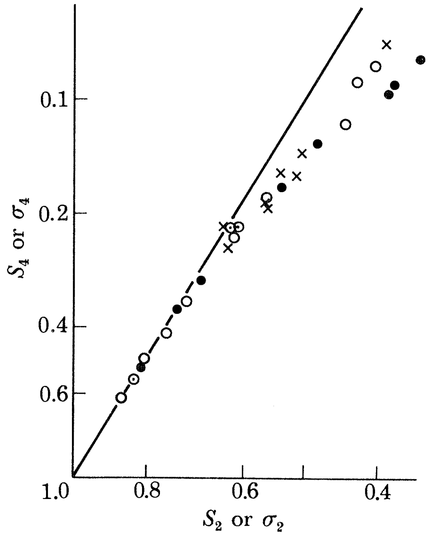

FIGURE 5. Relation between S_4 and S_2, or between $\sigma_4(d)$ and $\sigma_2(d)$, on a logarithmic plot. The points represent data generated by computer simulation by using three distinct models: ○, Zannoni (1979) (S_4 against S_2); ⊙, Zannoni & Guerra (1981) (S_4 against S_2); ×, Tsykalo & Bagmet (1978*a*, *b*) (S_4 against S_2); ●, Zannoni (1979) (σ_4 against S_2). The straight line represents the predicted $\frac{10}{3}$ power law.

Zannoni & Guerra (1981) have provided two values for S_6 in the $10 \times 10 \times 10$ lattice model that may be compared with predictions based on (27). Where S_2 is 0.833 the predicted value is 0.278: the computed value is 0.298 (± ?). Where S_2 is 0.620 (± 0.005) the predicted value is 0.035 (± 0.003): the computed value is 0.05 (± ?). The agreement is not unsatisfactory.

By and large, therefore, the results of computer-simulation studies confirm the reliability of the continuum approach at low temperatures but show that it cannot be trusted to describe the transition into the isotropic phase, at which S_2 is often as low as 0.35. These conclusions are scarcely a surprise. Since the theory takes the perfectly aligned state as its starting point – whereas theories like that of Stecki & Kloczkowski (1979) tend to start from the isotropic phase – it is bound to work best at low temperatures. Since the r.m.s. amplitude of each distortion mode depends (see (21)) on the magnitude of K, and since the magnitude of K depends upon the degree to which all the other modes are excited, an element of approximation enters the theory at an early stage, where the modes are assumed to be independent of one another and therefore excited with random phase. It is presumably this approximation that begins to fail as T_c is approached.

To test the theory against the behaviour of real nematics one needs first to measure, with considerable precision, the three Frank constants k_{11}, k_{22} and k_{33} for small q and then to evaluate the appropriate average of these to use in expressions such as (21) and (22) above. An equation defining the average has been given by Faber (1977*a*), though he has emphasized that it may give too much weight to the 'bend' constant k_{33}, and since this does not necessarily vary with temperature in quite the same way as k_{11} and k_{22} the use of that equation may introduce some error. Then if reliable values of S_2 are available one may plot $\ln S_2$ against $(T\rho^{\frac{1}{3}}/K)$, where ρ is density. A straight line is to be expected, at any rate for temperatures such that $S_2 > 0.5$ or 0.6. The intercept on the $\ln S_2$ axis should tell us $S_2(0)$, and this is expected to be unity. The slope should be given (Bunning *et al.* 1981) by

$$-\ln S_2/(T\rho^{\frac{1}{3}}/K) \approx 0.76k(N/M)^{\frac{1}{3}}. \tag{29}$$

The numerical coefficient in (29) depends upon how $K(q)$ varies with q; the figure 0.76 is based upon a detailed analysis of the lattice model discussed above, and for real nematics it may be in error by 20 % or so.

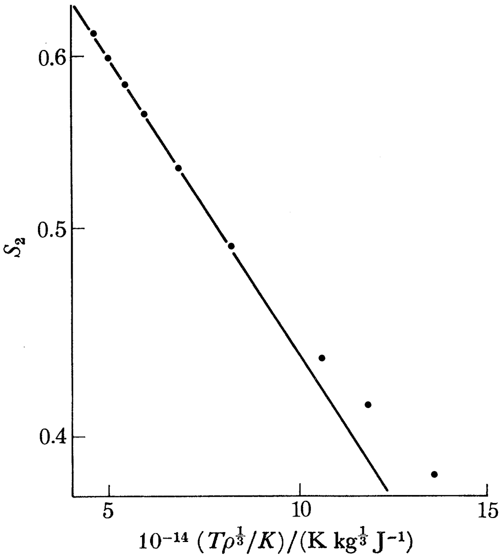

FIGURE 6. Test of continuum theory for nematic 5CB. The scale for S_2 is logarithmic.

Figure 6 shows such a plot for the nematic for which the most reliable information is currently available, 4′-*n*-pentyl-4-cyanobiphenyl or 5CB. It is an updated version of a figure plotted already by Bunning *et al.* (1981), using nine values of S_2 that Emsley *et al.* (1981) have derived from the proton n.m.r. spectrum of a 5CB specimen in which all but the four protons on one of the phenyl rings have been replaced by deuterons, and using our own values of the magnetic anisotropy $\Delta\chi$ to calculate k_{11}, k_{22} and k_{33}, because we now have reason (Faber *et al.* 1983) to prefer these to the Groningen data on which Bunning *et al.* relied. A straight line can indeed be fitted to the points for which $S_2 > 0.5$. Its intercept corresponds to $S_2 = 0.82$ rather than unity, however, and its slope is $0.63 \times 10^{-15}\ \mathrm{J\ kg^{-\frac{1}{3}}\ K^{-1}}$, whereas the slope predicted by (29) is $1.4 \times 10^{-15}\ \mathrm{J\ kg^{-\frac{1}{3}}\ K^{-1}}$. We have enough information available about the properties of other cyanobiphenyl derivatives to know that they would all show similar discrepancies.

All cyanobiphenyl derivatives are strongly polar, of course, and there is evidence from X-ray diffraction (Leadbetter *et al.* 1975) and from dielectric permittivity measurements (Chandrasekhar 1977) that neighbouring molecules associate on this account. One way to explain why the slope of the straight line in figure 6 is about half the expected value is to postulate that the molecules form strongly associated pairs, because pairing would halve the number of orientational degrees of freedom and therefore halve the number of distortion modes contributing to $\sum_q \langle \psi^2 \rangle$ (see (22)).

Pairing would explain the anomalous intercept too, if it could be shown that the two members of a pair are not collinear but lie with their z axes inclined to each other at an angle of about 40°. It is probable, however, that other complicating factors are involved, including the secondary ordering described by $(S_{xx}-S_{yy})$ and the non-rigid character of that part of each molecule that consists of an alkyl chain. Ideally, the theory should be tested against the behaviour of a non-polar nematic without a flexible end chain, for which $(S_{xx}-S_{yy})$ is known to be zero.

5. Conclusions

The idea of pairing between molecules of 5CB brings us back to the cluster model of §2 and may indicate the way forward to a more realistic theory of nematics than any yet discussed. If we could find some way to deal exactly with the correlations of orientation and position to be expected within a cluster of, say, a dozen molecules, we could hope to describe correlations between clusters by using the theory outlined in §4. Complete understanding of the situation near T_c, however, where S_2 is neither small nor close to unity, may remain elusive for many years yet.

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Discussion

Lin Lei (*Institute of Physics*, *Chinese Academy of Sciences*, *Beijing*, *China*). Does Dr Faber's theory produce $\langle P_4 \rangle < 0$, which are observed in some experiments on nematics?

T. E. Faber. No, unless one is prepared to postulate that the quantity that I have called $S_4(0)$ is negative. The sort of model I have suggested in my paper to explain values of $S_2(0)$ as low as 0.82 could in principle be used to explain negative values of $S_4(0)$.

L. G. P. Dalmolen (*Solid State Physics Laboratory*, *University of Groningen*, *The Netherlands*). Recently, negative values of the order parameter $\langle P_4 \rangle$ of different compounds, measured by polarized Raman scattering, have been reported in the literature. Theoreticians seem to be worried about that because mean field and other theories cannot predict such negative results for $\langle P_4 \rangle$. We (Dalmolen & de Jeu, *J. chem. Phys.* (in the press)) measured the order parameters of various compounds, among which some were reported to have a negative $\langle P_4 \rangle$, with polarized Raman scattering. In all cases either a mean field behaviour of $\langle P_4 \rangle$ was observed or lower values between 0.05 and 0.15, but not negative. In our opinion the negative values of $\langle P_4 \rangle$ reported can be ascribed to either inadequate correction of the scattering of the sample or improper calibration. The latter point is evident from large discrepancies in the values of R_{iso}, the depolarization in the isotropic phase. We therefore feel that the problem of the negative values of $\langle P_4 \rangle$ is just an experimental and not a theoretical one.

Sir Charles Frank, F.R.S. (*The University*, *Bristol*). I see no reason to doubt the accuracy of some experimental observations just because they yield a negative value for $\langle P_4 \rangle$. To doubt it because in some other cases $\langle P_4 \rangle$ is positive is like saying 'I have looked at 20 mountains which didn't have craters at the top: therefore there are no volcanoes'. I think so long as one makes theories with cylindrical molecules one will predict a positive $\langle P_4 \rangle$, but if one makes the theory for molecules shaped like dog-bones, negative $\langle P_4 \rangle$ is a likely outcome: and on the whole molecules are rather more like dog-bones than they are like pencils.