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Director fluctuations in nematic liquid crystals

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The literature of the past two decades suggests that confusion persists concerning the role of director fluctuations in the theory of nematics. Are these fluctuations necessarily small? If so, the fluctuation spectrum must terminate at a wavevector q_c which is of the order of $10^8\,\mathrm{m}^{-1}$, yet fluctuation modes with wavevectors in excess of $10^9\,\mathrm{m}^{-1}$ are commonly invoked to explain, for example, the frequency dependence of NMR relaxation rates. If the cut-off wavevector exceeds $10^9\,\mathrm{m}^{-1}$ and the fluctuations are not small, are their effects included in standard theories of nematic disorder, or should those theories be renormalized in some way to allow for them? Can we turn to experimental data for nematics, or to the results of computer simulations, in order to learn where q_c lies? This paper suggests answers to these questions, based upon an elementary definition of the director which can be applied to groups of molecules of any size, not necessarily macroscopic. In the course of the argument some widely accepted ideas about nematics are challenged, in particular: (i) the idea that mean field theories of the Maier–Saupe type provide an adequate description of them; (ii) the idea that, in so far as mean field theories are not exact, their deficiencies may be rectified by the cluster-expansion approach; (iii) the idea that the processes whereby molecules in a nematic undergo large changes in orientation, and from time to time experience end-to-end inversion, are essentially distinct from director fluctuations, which do no more than gently rock the cage within which the molecule is constrained.

1. Introduction

Nematic liquid crystals consist of rod-like molecules which are partially aligned, and the direction of the axis of alignment is conventionally described by a unit vector $\mathbf{n}$ which is known as the *director* [1]. The director can be manipulated to some extent, by treating the solid surfaces between which the nematic is contained and by applying magnetic or electric fields. However, no matter how much care is taken to produce single crystals of a nematic, i.e. specimens in which $\mathbf{n}$ is uniform throughout, they are always milky in appearance. This characteristic milkiness is a sign that $\mathbf{n}$ is *not* uniform but is fluctuating in space and time about its mean orientation $\langle\mathbf{n}\rangle$, due to thermal agitation that even the strongest available fields cannot suppress.

There exists a theory of light scattering by nematics which gives quantitative agreement with experimental observations [2, 3]. It is based on the premise, first enunciated by the Orsay Group [4], that director fluctuations in a specimen for which $\langle\mathbf{n}\rangle$ is uniform may be analysed in terms of a set of periodic distortion modes (see also [5]). Each mode is associated with rotation of $\mathbf{n}$ about an axis perpendicular to $\langle\mathbf{n}\rangle$ through an infinitesimal angle ψ which varies sinusoidally with wavevector $\mathbf{q}$. In the one-constant approximation, where no distinction is made between the Frank constants for splay, twist and bend, all three being represented by the same symbol K, the mean square amplitude of each mode in thermal equilibrium at temperature T in a

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specimen of volume V is

$$\langle \psi^2 \rangle = \frac{kT}{VKq^2}. \tag{1}$$

The addition theorem for spherical harmonic functions implies [6] that excitation of many modes should tilt the director through an angle δ which may be finite, such that

$$\langle P_2(\cos\delta) \rangle = \prod_{\text{modes}} (1 - \tfrac{3}{2}\langle \psi^2 \rangle). \tag{2}$$

If terms of order δ^4 are negligible, though not otherwise, equation (2) reduces to

$$\langle \delta^2 \rangle = \sum_{\text{modes}} \langle \psi^2 \rangle. \tag{3}$$

Since there are $V/(2\pi)^3$ allowed values of $\mathbf{q}$ per unit volume of $\mathbf{q}$ space and two polarizations for each of them, it follows from equations (1) and (3) that the mean square tilt due to excitation of all modes for which $\mathbf{q}$ lies within a sphere of radius q_c should be given approximately by

$$\langle \delta^2 \rangle = \frac{2V}{(2\pi)^3} \int_0^{q_c} \frac{kT}{VKq^2} 4\pi q^2 \, dq = \frac{kT}{\pi^2 K} q_c. \tag{4}$$

The degree of alignment of the molecules in a nematic is conventionally described, in terms of the angles (θ,ϕ) which denote the orientations of their long axes relative to $\langle \mathbf{n} \rangle$, by an order parameter

$$S = \langle P_2(\cos\theta) \rangle, \tag{5}$$

and this quantity is liable to be reduced by director fluctuations. That is to say, if the director fluctuations could in some way be suppressed the order parameter would rise to a higher value S_0 related to S by the equation

$$S = S_0 \langle P_2(\cos\delta) \rangle \simeq S_0(1 - \tfrac{3}{2}\langle \delta^2 \rangle). \tag{6}$$

The idea that director fluctuations might be suppressed may seem an artificial one. It may be avoided if preferred by defining S_0 in terms of equation (5) but with the average restricted to regions of space, and to periods of time, within which the fluctuating angle δ happens to be zero, so that $\mathbf{n}$ and $\langle \mathbf{n} \rangle$ coincide. The proof of equation (6) depends upon the fact that all values of the azimuthal angle ϕ are equally likely when $\mathbf{n}$ and $\langle \mathbf{n} \rangle$ coincide and requires, once again, the addition theorem.

Results equivalent to those in equations (1)–(6) are to be found in many places in the literature [6–9] though they are sometimes expressed in terms of the x and y components of $\mathbf{n}$ (the z axis being chosen to coincide with $\langle \mathbf{n} \rangle$) rather than in terms of angles. They evidently command fairly general acceptance. There seems to be rather little agreement, however, about the answers to two questions which arise out of them, namely what value should be chosen for the cut-off wavevector q_c, and do theories which purport to predict the nematic order parameter include the effects of director fluctuations or not? These are the questions to be addressed in §§2–5, the second of them with particular reference to the hierarchy of cluster expansion theories of which the well-known and widely-used theory of Maier and Saupe is the first and simplest member.

The ideas propounded, few of which are particularly novel, form the basis for some comments in §§6, 7 and 8 on various attempts that have been made to determine the magnitude of $\langle \delta^2 \rangle$, or else of q_c, either from experimental data for real nematics or from computer simulation data for the well-known lattice model associated with the names of Lebwohl and Lasher, which is frequently referred to throughout the paper. Section 9 contains a digression concerning the relaxation time for end-to-end inversion of molecules, which determines the dielectric dispersion properties of nematics. The principal conclusions are summarized in § 10.

2. The wavevector cut-off

Several authors make the assumption, in some cases apparently on principle [10] and in others from a desire to simplify [11, 12], that δ is small enough for terms of order δ^2 to be neglected. This attitude implies that $\langle\delta^2\rangle$ is less than say 10^{-2}, which in turn implies, though this is not always recognized, a cut-off at or below say 10^8 m^{-1}, i.e. not very far beyond the range of q for which experimental evidence for director fluctuation modes is provided by light scattering experiments. Authors who belong to this group do not contend that motions which contribute to the molecular misalignment on a finer scale do not exist, but they believe the fine-scale motions to be distinguished from director fluctuations in some way, e.g. by being more rapid [11, 13], and therefore to require separate discussion.

However, we have independent evidence for the existence of director fluctuations from the anomalous dependence of the nuclear magnetic relaxation time T_1 on the strength of the magnetic field B in which it is measured, i.e. on the resonant frequency $\nu_0 = (\gamma B/2\pi)$. For nematic materials $1/T_1$ seems to contain a term which varies like $\nu_0^{-1/2}$ [14, 15], and an explanation for this in terms of director fluctuations was first provided by Pincus [16]. Pincus treated q_c as effectively infinite, but in subsequent analyses of NMR data for nematics it has usually been treated as one of a number of adjustable parameters [17–19], and the values needed to secure reasonable agreement with experimental data seem to be of the order of a^{-1}, where a is a length representing the mean dimensions of a molecule. Throughout the present paper we shall define a in terms of the number of molecules N in volume V by

$$a^3 = V/N, \tag{7}$$

and a typical value for it would be 8×10^{-10} m. Hence there exists a second group of authors for whom q_c is 10^9 m^{-1} or more, i.e. for whom $\langle\delta^2\rangle$ is over 0·1 and by no means negligible. Which group is right?

The answer must surely depend to a great extent upon just how the director is to be defined, in circumstances where it may be a function of both position $\mathbf{R}$ and time t. Most texts are a trifle vague on this matter. They suggest that if we insist on specifying t precisely then we must define $\mathbf{n}(\mathbf{R}, t)$ by reference to the molecules in a macroscopic volume around $\mathbf{R}$, but just how large, or how small, this volume needs to be is not made clear. Does it have to be large enough for us to be able in principle to measure some bulk property such as the birefringence or the dielectric anisotropy within it and to infer the orientation of $\mathbf{n}$ from that? If so, should it include 10 molecules, or 100, or 1000, or what?

This philosophy behind the present paper is that we can define $\mathbf{n}(\mathbf{R}, t)$ on any resolution that we choose. Given the set of angles (θ_i, ϕ_i) $(i = 1, 2, \ldots, m)$ which describe the instantaneous orientations relative to $\langle\mathbf{n}\rangle$ of all the m molecules in the volume of our choice, whether it be macroscopic or microscopic, the direction of $\mathbf{n}(t)$ within this volume is surely such as to maximize the quantity

$$\Sigma(t) = \sum_{i=1}^{m} P_2(\cos\theta'(t)), \tag{8}$$

where θ' denotes the inclination of the ith molecule relative to $\mathbf{n}$ rather than $\langle\mathbf{n}\rangle$. The larger m is, the smaller the fluctuations of $\mathbf{n}$ appear to be, and in the limit $m \to \infty$ they disappear entirely. Now if a specimen which contains N molecules in all is to be treated as an assembly of (N/m) separate domains, within each of which $\mathbf{n}(t)$ may take a different value, we require $2(N/m)$ angles to specify the director field completely. In that case there cannot be more nor less than $2(N/m)$ independent distortion modes for the director. If the domains are chosen to be cubes of sides $(m^{1/3}a)$, say, stacked together to form a simple cubic lattice, then the allowed values of $\mathbf{q}$ for these modes will occupy a cubic Brillouin zone of side $(2\pi/m^{1/3}a)$ [13], and there are other shapes of Brillouin zone associated with other choices of domain shape. It should in many circumstances be an adequate approximation, however, to regard the allowed values of $\mathbf{q}$ as occupying a spherical region in $\mathbf{q}$ space, and in that case the radius of the sphere must be such that

$$\frac{2V}{(2\pi)^3}\frac{4\pi}{3}q_c^3 = \frac{2N}{m},$$

or that

$$q_c a = (6\pi^2/m)^{1/3}. \tag{9}$$

In a series of previous papers [6, 20–24], the present author has put forward a theory of nematic alignment, or misalignment, in which this definition of $\mathbf{n}$ is pursued to the limit in which $m = 1$. In this limit, the way to maximize the quantity expressed by equation (8) is to choose $\mathbf{n}$ to coincide with the long axis of the single molecule within each domain. The quantity S_0 becomes unity, and renormalization for the effects of director fluctuations using equation (6) is essential; the fact that S is less than unity is entirely attributable to these fluctuations. The cut-off wavevector q_c is about $4/a$, or say $5 \times 10^9\ \mathrm{m}^{-1}$ in a typical case. That corresponds, according to equation (4), to values of $\langle\delta^2\rangle$ as large as 0·5. This theory has the merits of internal consistency and relative simplicity, but some of the predictions which it yields are evidently not fulfilled at temperatures near T_c, where S is normally about 0·4. Factors which may be responsible for its failure in this region have been pointed out elsewhere [6]. The theory works extremely well, however, when applied to simple lattice models of nematics for which results have been obtained by computer simulation techniques, at temperatures such that S is greater than about 0·75 [22, 24]. This limited success suggests that in one respect at least the theory is essentially correct: that is to say, in its basic premise that the spectrum of the molecular motions in a nematic is continuous in its variation with q, all the way from zero to its final cut-off at about $4/a$.

Admittedly, we cannot rely on equation (1) at microscopic wavelengths, unless K is allowed to vary with q so as to make it work. That however, is a relatively trivial problem, for which correction is possible. For the simple cubic Lebwohl–Lasher lattice model [5], for example, we expect [22]

$$\frac{K(q)}{K(0)} = \frac{6 - 2\cos q_x a - 2\cos q_y a - 2\cos q_z a}{(q_x^2 + q_y^2 + q_z^2)a^2}, \tag{10}$$

and this ratio varies with q in a smooth and undramatic way. This is nothing in it to suggest that the picture which explains light scattering experiments in terms of distortion modes with q values in the neighbourhood of 10^6 or $10^7\ \mathrm{m}^{-1}$ becomes totally inappropriate when q is $10^9\ \mathrm{m}^{-1}$ or more. And just as the spectrum seems to be a smooth one in terms of wavevector, so also it seems to be smooth in terms of angular frequency, ω. It has been recognized since, the work of the Orsay Group [4], that the modes are overdamped, and that

$$\frac{\langle\psi(t+\tau)\psi(t)\rangle}{\langle\psi(t)^2\rangle} = \exp\left(-\frac{Kq^2\tau}{\eta}\right), \tag{11}$$

where η is an appropriate viscosity coefficient. Thus if the spectrum is continuous in q up to about $4/a$ it should be continuous in ω up to about $16(K/\eta a^2)$, which may amount in a typical case to about $3 \times 10^{10}\,\mathrm{s}^{-1}$. Such frequencies should be high enough to describe the rocking or tumbling motions of individual molecules. Thus we have no obvious need to postulate the existence of modes of motion distinct from director fluctuations that are faster still, quite apart from the fact that if q_c is to be set equal to $4/a$ there are no orientational degrees of freedom left over to be allocated to such modes.

As far as the magnitude of q_c is concerned, therefore, we shall side with those who believe it to be of the order of a^{-1} rather than with those who maintain, if only by implication, that it must be small enough to make $\langle\delta^2\rangle \ll 1$. The remarks in the previous paragraph suggest, however, that the theoretical models which have been used to fit NMR data for nematics are not entirely trustworthy, and that values for q_c which have been estimated by using these models may be of limited significance. We shall return to this point in § 7.

3. Director fluctuations in the Maier–Saupe theory

We now turn to the second of the two questions posed in the introduction, the question of whether theories of nematic alignment take director fluctuations into account or not. In the context of the present author's theory, referred to in § 2, the answer is clear, but in other contexts it is not. Warner [9], who follows Flory in attributing the alignment primarily to steric effects and who has developed mean field theories which reflect this point of view, has argued that director fluctuations are not included in these and that the results should therefore be renormalized using equation (6). The work of Masters [12], however, who follows Stecki and Kloczkowski [25] and others in framing his description of the nematic state in terms of the direct correlation function, suggests that such renormalization may not be needed. Here we address the question in the context of the simplest theory of all, that associated with the names of Maier and Saupe.

This theory can be approached by several paths besides the one used in the original publications [26]. Perhaps the most straightforward approach is to start with a postulate that in so far as the hamiltonian of the system depends upon the orientational coordinates (θ_i, ϕ_i) of the ith molecule it does so through a term which may be written as

$$-uSP_2(\cos\theta), \tag{12}$$

where u is a positive constant; u may be supposed to depend upon density, but here we shall be concerned primarily with lattice models of nematics in which the density cannot vary. Thus every molecule is supposed to see the same mean field uS, which couples with $P_2(\cos\theta)$ in such a way as to favour alignment along the fixed direction $\langle\mathbf{n}\rangle$. All values of the azimuthal angle ϕ are equally likely for each molecule, and there are no correlations between ϕ_i and ϕ_j. The one particle distribution function for $\cos\theta$ is

$$f(\cos\theta) = Z^{-1}\exp(uSP_2(\cos\theta)/kT), \tag{13}$$

where Z is a one particle partition function,

$$Z = \int_0^1 \exp(uSP_2(\cos\theta)/kT)\,d(\cos\theta). \tag{14}$$

The order dependent term in the internal energy of the system is

$$U = -\tfrac{1}{2}NuS^2, \tag{15}$$

where the factor 1/2 is needed because the mean field is due to pairwise interactions which must not be counted twice over, and the order dependent terms in the free energy and entropy are therefore

$$F = \tfrac{1}{2}NuS^2 - NkT\ln Z \tag{16}$$

and

$$-\frac{NuS^2}{T} + Nk\ln Z = -Nk\int_0^1 f\ln f\,d(\cos\theta) \tag{17}$$

respectively. The theory predicts a first order transition to the isotropic state at a temperature T_{NI} such that

$$kT_{\mathrm{NI}}/u = 0{\cdot}2202. \tag{18}$$

The order parameter may be calculated as a function of (T/T_{NI}) by varying it so as to minimize F, or else by using a familiar self-consistency condition which amounts to the same thing.

It may appear at first sight that director fluctuations are entirely suppressed in the Maier–Saupe theory, but this is not the case if we are to define the director, as suggested in § 2, by reference to the orientations which the molecules in the volume of interest actually adopt at time t rather than to the directions which they would most like to adopt. Suppose that $\mathbf{n}$ differs from $\langle\mathbf{n}\rangle$ by two small angles of rotation about axes perpendicular to $\langle\mathbf{n}\rangle$, an angle δ_1 in the plane for which $\phi = 0$ and an angle δ_2 in the plane for which $\phi = \pi/2$. Then it follows from the addition theorem that the quantity Σ defined by equation (8) is

$$\Sigma = \sum_{i=1}^{m} \{P_2(\cos\theta_i)[1 - \tfrac{3}{2}(\delta_1^2 + \delta_2^2)] + 3\sin\theta_i\cos\theta_i[\delta_1\cos\phi_i + \delta_2\sin\phi_i] + \tfrac{3}{4}\sin^2\theta_i[(\delta_1^2 - \delta_2^2)\cos 2\phi_i + 2\delta_1\delta_2\sin 2\phi_i]\}. \tag{19}$$

In supposing that δ_1 and δ_2 are small we are assuming m to be large compared with unity, and it turns out that in the limit of large m the third term on the right hand side of (19) is irrelevant. In that case the value of δ_1 which maximizes Σ is clearly

$$\delta_1 = \frac{\sum(\sin\theta_i\cos\theta_i\cos\phi_i)}{\sum P_2(\cos\theta_i)}. \tag{20}$$

The angles on the right hand side of this expression change with time, of course, and so does δ_1. Its mean value is zero, but its mean square value does not vanish. For large m we find

$$\langle\delta_1^2\rangle \simeq \frac{\langle\sum(\sin^2\theta_i\cos^2\theta_i\cos^2\phi_i)\rangle}{\langle\sum P_2(\cos\theta_i)\rangle^2} = \frac{\langle\sin^2\theta\cos^2\theta\rangle}{2mS^2},$$

and an identical result holds for $\langle\delta_2^2\rangle$. We may use the Maier–Saupe distribution function to establish what $\langle\sin^2\theta\cos^2\theta\rangle$ is, and hence to arrive at the result that

$$\langle\delta^2\rangle = \langle\delta_1^2\rangle + \langle\delta_2^2\rangle = \frac{2kT}{3muS^2}. \tag{21}$$

It follows from equations (19) and (21) that the time average of $\Sigma(t)$, maximized by continuous variation of $\mathbf{n}$ throughout the period over which the average extends, is such that

$$m^{-1}\langle\Sigma_{\max}\rangle = S(1 + \tfrac{3}{2}\langle\delta^2\rangle) = S + \frac{kT}{muS}, \tag{22}$$

and if this is compared with equation (6) it will be seen that $m^{-1}\langle\Sigma_{\max}\rangle$ corresponds to the quantity referred to in the Introduction as S_0. All of these results are valid only when $m \gg 1$. It is possible to improve upon them by expanding in powers of m^{-1}, but the results do not justify the effort required.

It is instructive now to consider the effect on $\langle\delta^2\rangle$ of a small change in our choice of m, and whether this can be explained in terms of the consequent change in the number of periodic modes which are needed to specify the director field completely. Equations (4) and (9) suggest that

$$\frac{d\langle\delta^2\rangle}{dm} = \frac{2V}{(2\pi)^3}4\pi q_c^2\frac{dq_c}{dm}\langle\psi(q_c)^2\rangle = -\frac{2N}{m}\langle\psi(q_c)^2\rangle, \tag{23}$$

whereas equation (21) suggests that

$$\frac{d\langle\delta^2\rangle}{dm} = -\frac{2kT}{3m^2uS^2}. \tag{24}$$

The two results are equivalent for all m provided that

$$\langle\psi^2\rangle = \frac{kT}{3NuS^2} \tag{25}$$

for all q, but not otherwise.

Equation (25), which implies a mean square amplitude independent of q, is obviously completely inconsistent with the results of conventional nematic continuum theory as embodied in equation (1). There is, however, no paradox here. It is well known that mean field theories are only exactly correct when the pairwise interactions which the mean field represents are of a long range nature. The Maier–Saupe theory, for example, is exactly correct for model nematics in which the potential energy shared by the ith and jth molecules is independent of the separation R_{ij} and depends on the orientations of these molecules in such a way that after averaging over these it reduces to

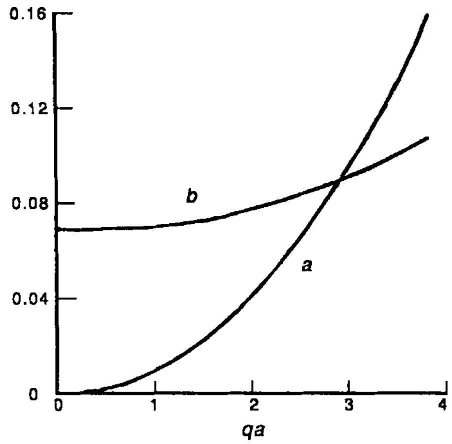
$$-\frac{u}{N}S^2. \tag{26}$$

If the interaction is of this nature, however, its average value is diminished by a factor

$$(1 - \tfrac{3}{2}\langle\psi^2\rangle)$$

when a director fluctuation mode is excited, and the energy stored in the mode is therefore

$$\frac{3uS^2}{2}\langle\psi^2\rangle.$$



Contributions per unit range of qa to the mean square director fluctuation at $T^* = 1$. (a) The Maier–Saupe theory; (b) the Lebwohl–Lasher model, with short range interaction.

We may deduce the mean square mode amplitude by equating this energy to $kT/2$, and equation (25) is the result. Thus in the context of long range interaction models to which Maier–Saupe theory is known to apply, we may calculate $\langle \delta^2 \rangle$ by the direct method employed above or by adding together the effects of periodic distortion modes, and the two approaches yield answers which, for large m at any rate, are precisely the same.

The lessons to be learnt from this analysis are that the Maier–Saupe theory does include the effect of director fluctuations, but that it gives too much weight, for given S, to the fluctuation modes of large q, and correspondingly too little weight to the modes of small q, to provide an accurate description of their effects in real nematics where the interaction is certainly short range. The two curves in the figure show how much the modes contribute per unit range of qa to the magnitude of $\langle \delta^2 \rangle$, or more precisely, if $\langle \delta^2 \rangle$ is not small, to $-(2/3) \ln \langle P_2(\cos \delta) \rangle$ (see equation (2)). The quantity plotted there as a function of qa, from zero up to an ultimate cut-off at $(6\pi^2)^{1/3} = 3{\cdot}90$, is $(Vq^2/\pi^2 a)\langle \psi(qa)^2 \rangle$. The quantity $\langle \psi(qa)^2 \rangle$ has been calculated in two ways, (a) from equation (25), which applies to the long range interaction models which Maier–Saupe theory describes exactly, and (b) from equation (1). To make the comparison specific, curve (b) has been plotted for the simple cubic Lebwohl–Lasher model [5], in which the interaction takes the form

$$-\frac{u}{6} P_2(\cos \gamma_{ij}) \tag{27}$$

but acts between nearest neighbours only; here γ_{ij} is the angle between the long axes in the ith and jth molecules, and $P_2(\cos \gamma_{ij})$ has the property that it averages to S^2 if there are no correlations between ϕ_i and ϕ_j but not otherwise. Curve (b) is based upon equation (10) (with $q_x = q_y = q_z$) in addition to equation (1), and upon an equation for K in the limit of small q which is derived from the present author's earlier work on the Lebwohl–Lasher model [22], namely

$$K(0) = \frac{kT}{a} \frac{1}{\alpha(1) \ln (1/S)}. \tag{28}$$

(This equation may be obtained from equations (17) and (6) in [22], or from the more detailed analysis in [24]. The numerical factor $\alpha(1)$ is close to 1·3 in a very large specimen.) The two curves are plotted for the case $kT = u/6$, which corresponds in the notation used by Zannoni [27] to $T^* = 1$. The values of S that are appropriate at this temperature have been used, namely 0·74 for curve (*a*) and 0·6 for curve (*b*). These values differ because the Maier–Saupe theory, when applied to the Lebwohl–Lasher model, predicts values for S which are significantly higher at given T than those computed for the same model by Zannoni and others; the figure of 0·6 used for curve (*b*) has been read off from figure 1 in [22], where some of Zannoni's results are shown, together with curves based on the present author's theory which are still in good agreement with Zannoni's results at $T^* = 1$, even though S is here less than the limit of 0·75.

Because the two curves in the figure intersect well to the right of its centre, at about $qa = 2{\cdot}9$, we may infer that, if the Maier–Saupe theory is to be used to predict values of S for the Lebwohl–Lasher model, the fact that it underestimates the effects of director fluctuation modes of small q will contribute more error in one direction than the fact that it overestimates the effects of large q modes will contribute in the other. It looks from the figure as though we might end up with about the right value for S by multiplying the raw Maier–Saupe predictions by a renormalization factor to allow for modes up to a cut-off at say $qa = 1{\cdot}5$. At $T^* = 1$ the appropriate factor would, according to equation (6), (4) and (28), be about 0·85, just about what is required to reduce 0·74 to 0·6. Even after such renormalization, however, the description of the Lebwohl–Lasher model which the Maier–Saupe theory would provide would still be defective. The deficiencies of the theory in a situation where the alignment is due to short range interactions are further exposed in the next section.

4. Long range correlations

For a nematic in which the intermolecular interactions are short range, the result equivalent to that in equation (21), obtainable directly from equations (4) and (9), is

$$\langle \delta^2 \rangle = \frac{kT}{Ka}\left(\frac{6}{\pi^4 m}\right)^{1/3}. \tag{29}$$

The fact that $\langle \delta^2 \rangle$ varies like $m^{-1/3}$ rather than like m^{-1} is an indication that in real nematics, as opposed to the idealized models with long range interactions to which Maier–Saupe theory applies, there are significant correlations of orientation between pairs of molecules, correlations, in particular, between ϕ_i and ϕ_j. de Gennes was the first to point out [28] that these correlations must exist and to predict that they decay slowly with separation, like $1/R_{ij}$. A simple physical picture discussed by the present author supports this prediction [29], and it has been more than adequately confirmed by computer simulation work on the Lebwohl–Lasher model [27].

The following argument uses ideas developed here to demonstrate that, if there are no correlations of orientation between well separated molecules in the absence of director fluctuations, then such correlations arise when the fluctuations are switched on. Consider a Lebwohl–Lasher nematic containing N molecules as an assembly of (N/m) domains, with $m \gg 1$. Imagine the $(2N/m)$ modes which are needed to provide a complete description of the director field on this scale of resolution to be in some way suppressed, so that **n** is everywhere coincident with $\langle \mathbf{n} \rangle$ and the order parameter defined by equation (5) is S_0. Suppose that in this state there are no correlations between ϕ_i and ϕ_j as long as the ith and jth molecules inhabit different domains. In that case the excitation of a single mode which rotates the two molecules about the same axis through infinitesimal angles ψ_i and ψ_j will change the average value of $P_2(\cos \gamma_{ij})$ (the average here is over $\phi_{i,j}$ and $\theta_{i,j}$) from S_0^2 to

$$S_0^2(1 - \tfrac{3}{2}(\psi_i - \psi_j)^2). \tag{30}$$

It follows from this result, after a further average over all directions for **q** and over all pairs of molecules which are separated by the same distance R (see [20]) for a fuller explanation), that excitation of all $(2N/m)$ modes reduces $\langle P_2(\cos \gamma(R)) \rangle$ from S_0^2 to

$$\begin{aligned} S_0^2 &\left[1 - \frac{6V}{(2\pi)^3} \int_0^{q_c} \frac{kT}{VKq^2}\left(1 - \frac{\sin qR}{qR}\right) 4\pi q^2 \, dq\right] \\ = S_0^2 &\left[1 - 3\langle \delta^2 \rangle + \frac{3kT}{\pi^2 KR} \int_0^{q_c R} \frac{\sin p}{p} \, \mathrm{d}p\right]. \end{aligned} \tag{31}$$

Excitation of the modes also reduces the order parameter from S_0 to S, and from equations (6) and (31) we may obtain the result

$$\langle P_2(\cos \gamma(R)) \rangle - S^2 = \frac{3kTS_0^2}{\pi^2 KR} \int_0^{q_c R} \frac{\sin p}{p} \, dp, \tag{32}$$

or, if R is appreciably bigger than the domain size (i.e. if $q_c R \gg 1$ as well as $m \gg 1$) and if K is given by equation (28), then

$$\langle P_2(\cos \gamma(R)) \rangle - S^2 = \frac{3S^2 \alpha(1) \ln (1/S)}{2\pi} \left(\frac{a}{R}\right). \tag{33}$$

The difference which equations (32) and (33) describes, which would of course be zero in the absence of correlations in ϕ, constitutes a convenient measure of the strength of the correlations that in fact exist. They are evidently weak under the conditions for which equation (33) is strictly valid, i.e. when $R \gg a$. The computer simulation results of Zannoni [27], however, which are rather well described by the present author's more detailed theory [22], show that the ratio continues to rise, roughly like $1/R$, as we proceed to smaller values of R, and that between nearest neighbours the correlations are quite marked.

In view of these correlations and of the matters discussed in § 3, it is questionable whether we should rely on the Maier–Saupe theory for data-fitting purposes to quite the extent that we do. The theory is so simple and convenient that it is tempting to believe it to be essentially correct. It is tempting to believe that even if the arguments upon which Maier and Saupe constructed their theory in the first place are not reliable, their formula for the orientation-dependent free energy (equation (16)) is nevertheless a fair approximation to the truth, which can be made a better approximation still by adding to the internal energy (equation (15)) some extra terms, involving higher powers of S perhaps, or higher order parameters such as $\langle P_4(\cos \theta) \rangle$; many such modifications of Maier–Saupe theory have been suggested, which yield closer fits to experimental data at the expense of extra adjustable parameters [30–33]. In all of these modifications, however, the Maier–Saupe expression (also attributable to Onsager [34]) for the orientation-dependent entropy, i.e. equation (17), is preserved unchanged and that expression cannot be adequate if the orientations of adjacent molecules are correlated. Sluckin and Shukla [35] have, it is true, succeeded in deriving equation (16) by a powerful analysis based upon the direct correlation function and appear to have conferred respectability upon the mean field approach by doing so. But their derivation depends upon some very drastic approximations, and the point just made about the entropy suggests that these approximations cannot in practice be justified.

5. Cluster expansion theories

There is a recognized procedure for improving upon the mean field descripton of an ordered state, first established on a secure footing by Strieb, Callen and Horwitz [36] in a paper which referred to the Heisenberg ferromagnet. As applied to nematics, this procedure involves an initial postulate that there exists a mean field which favours orientation along $\langle \mathbf{n} \rangle$, but terms are added to the free energy expression to take account in detail of the interactions between molecules within what is called a cluster. For a given cluster size, all possible shapes of cluster are taken into consideration which satisfy the condition that every member has at least one other member among its nearest neighbours. In the context of the Lebwohl–Lasher model the mean field may be written as $u\bar{S}$, and $\bar{S}$ may be found in the same way that S may be found in the Maier–Saupe theory, that is to say by varying it so as to minimize F. Maier–Saupe theory may be regarded as a cluster expansion theory for which the number of particles in the cluster, which will here be denoted by m_1, is unity. In this case $\bar{S}$ and S are the same, but the two are not identical for larger m_1. Clusters are surrounded by cages of m_2 nearest neighbours, and the mean field represents the effects of interactions between members of the cluster and members of the cage. When m_2 is bigger than m_1, as is the case when the clusters are small, these effects are obviously of dominating importance, but in the limit of very large clusters m_2 is much less than m_1, and in that limit $\bar{S}$ clearly tends to zero in a way that S does not. But the cluster expansion approach enables both quantities to be determined, together with other quantities, such as $\langle P_4(\cos\theta)\rangle$.

Cluster expansion theories applicable to lattice models of nematics have been worked out for $m_1 = 2$ [37, 38], 3 [39] and 4 [40]. They clearly provide a much more realistic picture than the Maier–Saupe theory for the correlations of orientation between nearest neighbours, and they predict the nematic–isotropic transition temperature with greater accuracy. The predicted values of (kT_{NI}/u) for the Lebwohl–Lasher model are 0·2202 ($m_1 = 1$), 0·1933 ($m_1 = 2$), 0·1933 ($m_1 = 3$), and 0·1903 ($m_1 = 4$). These are evidently converging, though not very fast, on the best computed value, evaluated for a sample with 30 × 30 × 30 molecules with periodic boundary conditions, which is 0·187 [41]. However, even a four-particle cluster expansion theory cannot describe correlations much beyond the nearest-neighbour range. How good a description may it be expected to provide of the magnitude of S?

The answer to this question surely depends upon how large $\langle \delta_2^2 \rangle$ is, where δ_2 represents the angle between $\langle \mathbf{n} \rangle$ and a director $\mathbf{n}_2$ defined, as in § 3, for the m_2 molecules which constitute the cage. In so far as the mean field $u\bar{S}$ represents interactions with members of the cage, it should presumably favour alignment along $\mathbf{n}_2$ rather than along $\langle \mathbf{n} \rangle$ as is assumed. It is probably an over simplification to say that on this account the results of cluster expansion theory need to be renormalized by a factor of $(1 - 3\langle \delta_2^2 \rangle/2)$, since if low q director fluctuation modes are significant they should really be allowed for in the initial expression for the free energy; the contribution which they make to the free energy will depend upon K, which in turn will depend upon $\bar{S}$ and S, and the value of S which minimizes F may therefore change when this contribution is included. But the results of cluster expansion theory certainly need a correction of some sort, and it seems likely to be a significant one unless $\langle \delta_2^2 \rangle \ll 1$.

The results obtained earlier in this paper allow us to estimate the deviation of $\mathbf{n}_{12}$ from $\langle \mathbf{n} \rangle$, but not the deviation of $\mathbf{n}_2$; here $\mathbf{n}_{12}$ is the director for the domain which includes the cluster as well as the cage. When m_1 is only 4, however, $\mathbf{n}_{12}$ is determined primarily by the orientations of the cage molecules, since these outnumber the cluster molecules by a ratio of over four to one: m_2, when m_1 is 4, may be 16, 17 or 18, depending upon the shape of the cluster. Thus we may plausibly estimate, using equation (29), that

$$\langle \delta_2^2 \rangle \simeq \langle \delta_{12}^2 \rangle = \frac{kT}{\pi^2 Ka}\left(\frac{6\pi^2}{m_1 + m_2}\right)^{1/3}. \tag{34}$$

Equations (34) and (28) suggest that the value of $\langle \delta_2^2 \rangle$ for a four-particle cluster expansion theory in the context of the Lebwohl–Lasher model is liable to be about 0·1 at $T^* = 1$. This is not small enough to be obviously negligible.

6. The cluster Monte Carlo method

Although most computer simulations of the Lebwohl–Lasher model have involved cubic arrays of molecules with periodic boundary conditions, Zannoni [42] has presented results obtained for arrays which are surrounded by a layer of ghost molecules, situated on points of the same simple cubic lattice, whose axes are distributed around a fixed $\langle \mathbf{n} \rangle$ with a Maier–Saupe distribution function consistent with the value of S computed for the array, or cluster, itself. He has called this procedure the cluster Monte Carlo method and has suggested that it is a better way of modelling the behaviour of an infinite array, which generates results that are less dependent on array size. What is of particular interest here about Zannoni's results is that he has computed the quantity $m_1^{-1}\langle \Sigma_{\max} \rangle$ (see equation (22)) or S_0 for his clusters, as well as S, which makes it possible to infer values for $\langle \delta_1^2 \rangle$, the mean square deviation from $\langle \mathbf{n} \rangle$ of the director $\mathbf{n}_1$ within the cluster, with the aid of (6). (In Zannoni's notation, S is $\langle P_2 \rangle$ while S_0 is $\langle P_2 \rangle_\lambda$.) Some of his results are reproduced in the first four columns of the table below.

The boundary conditions used in the cluster Monte Carlo method allow $\langle \mathbf{n} \rangle$ to be predetermined in a way that periodic boundary conditions do not, and for a cluster of $n \times n \times n$ molecules they appear to ensure that, on a coarse scale at any rate, the local director coincides with $\langle \mathbf{n} \rangle$ on the surfaces of a cube of side $(n + 1)a$. (The qualification in that statement is needed because the ghost molecules are not completely ordered, which means that on a fine scale the boundary conditions for the director are not clearly defined.) The allowed values of q_x, q_y and q_z for coarse scale (low q) distortion modes are therefore restricted to a single octant in $\mathbf{q}$ space and take values $(h\pi/(n + 1)a)$, $(k\pi/(n + 1)a)$ and $(l\pi/(n + 1)a)$ respectively, where the integers (h, k, l) may each take values 1, 2, etc. Consider the effect of exciting a single low-q mode in a sample in which $\mathbf{n}_1$ is initially parallel to $\langle \mathbf{n} \rangle$ and in which the order parameter is initially S' say. Following its excitation we have

$$S = S'(1 - \tfrac{3}{2}\langle \overline{\psi^2} \rangle) \tag{35}$$

and

$$S_0 = S'(1 - \tfrac{3}{2}\langle \overline{(\psi - \bar{\psi})^2} \rangle) = S'(1 - \tfrac{3}{2}\langle \overline{\psi^2} - \bar{\psi}^2 \rangle), \tag{36}$$

Results for the Lebwohl–Lasher model computed using the cluster Monte Carlo method [42].

T^*	S	S_0	$\langle\delta_1^2\rangle$ computed	$\langle\delta_1^2\rangle$ calculated
		$m_1 = 125\ (5 \times 5 \times 5)$		
0·90	0·715	0·727	0·011	0·011
0·95	0·688	0·700	0·012	0·012
1·00	0·647	0·660	0·013	0·015
1·05	0·580	0·597	0·020	0·018
1·10	0·508	0·527	0·025	0·023
1·125	0·456	0·477	0·031	0·027
		$m_1 = 1000\ (10 \times 10 \times 10)$		
0·90	0·706	0·710	0·004	0·004
0·95	0·673	0·677	0·004	0·005
1·00	0·630	0·635	0·005	0·006
1·05	0·574	0·579	0·006	0·007
1·10	0·469	0·477	0·011	0·010
1·125	0·375	0·384	0·016	0·013

where the overbars indicated averages over all the molecules in the cluster at a given instant in time, while the angled brackets indicate a time average. Hence the excitation causes S to fall below S_0 by a factor

$$\left(1 - \tfrac{3}{2}\langle\overline{\psi^2}\rangle\right) \tag{37}$$

and causes $\mathbf{n}_1$ to deviate from $\langle\mathbf{n}\rangle$ by a mean square angle $\langle\overline{\psi^2}\rangle$. Now for many of the modes $\langle\overline{\psi^2}\rangle$ vanishes, but it does not do so when (h, k, l) are all odd, and in particular it does not do so for the $(1, 1, 1)$ modes. It is primarily these two modes which are responsible for the distinction between S and S_0 which Zannoni has observed.

Deviation of a formula for $\langle\overline{\psi^2}\rangle$, using ideas discussed in related contexts in earlier papers [22, 24], is straightforward in principle, and only the rather complicated result, which incidentally incorporates results which have been quoted as equations (10) and (28), will be given here. It is (for odd values of h, k and l only)

$$\langle\overline{\psi(h,k,l)^2}\rangle = \frac{4\alpha(1)\ln(1/S)}{(n+1)^3[3 - \cos(h\pi/(n+1)) - \cos(k\pi/(n+1)) - \cos(l\pi/(n+1))]} \times \left[n^3 \tan\left(\frac{h\pi}{2n+2}\right)\tan\left(\frac{k\pi}{2n+2}\right)\tan\left(\frac{l\pi}{2n+2}\right)\right]^{-2}. \tag{38}$$

The right hand side of this may be summed over h, k and l without difficulty because the convergence is rapid; the $(1, 1, 3)$ modes are just about significant but the $(1, 3, 3)$ modes are not. Allowing for the two polarizations for each $\mathbf{q}$ we find

$$\sum_{h,k,l} \langle\overline{\psi(h,k,l)^2}\rangle = C\alpha(1)\ln(1/S), \tag{39}$$

where C is 0·0171 for $n = 5$, and 0·0061 for $n = 10$. The numerical factor $\alpha(1)$ is size dependent. We may use 1·54 when $n = 5$ and 1·44 when $n = 10$ (see table 1 of [24]), though these figures were worked out assuming periodic boundary conditions, and in the present context they may not be entirely appropriate.

Here we have a first estimate for $\langle\delta_1^2\rangle$, but it needs a small correction. Because the $m_2 = 6n^2$ ghost molecules which constitute the cluster's cage are endowed with the

Maier–Saupe distribution function, the director $\mathbf{n}_2$ is not firmly tied to $\langle \mathbf{n} \rangle$ as we have supposed but may fluctuate about it, for reasons explained in § 3. A better estimate for $\langle \delta_1^2 \rangle$ may be obtained by adding to equation (39) an estimate for $\langle \delta_2^2 \rangle$ based upon equation (25), viz.

$$\langle \delta_2^2 \rangle = \frac{T^*}{9(6n^2)S^2}. \tag{40}$$

The figures listed in the final column of the table have been calculated from equations (39) and (40). The agreement with the computed values is good except at the highest temperatures, where the assumptions that lie behind equation (28) for $K(0)$, for example, are certainly breaking down. It is surely good enough to confirm that the analysis presented here is essentially correct, and therefore to call into question Zannoni's claim that the effects which he has computed reveal a limiting length for director fluctuations in his model which is several times larger than a, i.e. a wavevector cut-off such that $q_c a$ is significantly less than 3·9.

It may be added that the values of $\langle \delta_1^2 \rangle$ observed for the cluster Monte Carlo model and predicted by this analysis are smaller by a factor of about 3 when of $n = 5$, and by a factor of about 5 when $n = 10$, than the values of $\langle \delta^2 \rangle$ predicted by equation (29) for clusters which are embedded in an infinite lattice rather than in a cage of ghost molecules which are artificially constrained. When it forms part of an infinite lattice, of course, the cluster can be thought of as being at the centre of an infinite series of cages which enclose one another, like Chinese boxes. Fluctuations of the director within every one of these cages may contribute to the fluctuations of director for the cluster itself.

7. ESR and NMR

Zannoni's suggestion [42] that there may be a limiting length associated with director fluctuations which is several times larger than a echoes a suggestion which is to be found in an earlier paper by Luckhurst [43]. Luckhurst there discusses the asymmetric line shapes observed by Brooks, Luckhurst and Pedulli [44] in their work on the electron spin resonance of probe molecules dissolved in nematic 4,4′-dimethoxyazoxybenzene (PAA) and from the degree of asymmetry he deduces values for a mean square angle which he calls θ_0^2. In the notation of the present paper this appears (though see later) to correspond to $\langle \delta^2 \rangle$. It varies with temperature between 0·011 and 0·025, and such values, if interpreted in terms of equation (4), imply values for $q_c a$ of the order of 0·1. Does this mean, as Luckhurst seems to suggest, that there is a cut-off of absolute significance which lies well below the ultimate limit discussed in § 2 ($q_c a \simeq 3{\cdot}9$)?

Luckhurst's analysis is based upon the fact that ESR lines are symmetric in the fast-motion limit where the hyperfine splitting $\Delta\Omega$ is less than all the angular frequencies ω which are present in the autocorrelation function which describes the rate at which molecules change their orientation. Asymmetries are to be attributed, therefore, to relatively small q director fluctuation modes which contain frequencies such that $\omega < \Delta\Omega$. That being so, we may presumably set out to estimate Luckhurst's θ_0^2 using an extension of equation (4)

$$\theta_0^2 = \frac{2kT}{\pi^3 K} \int_0^{q_c} dq \int_0^{\Delta\omega} \frac{\alpha q^2 \, d\omega}{(\alpha q^2)^2 + \omega^2}, \tag{41}$$

with

$$\alpha = \frac{K}{\eta} + D. \tag{42}$$

Equation (4) includes in the shape of the self-diffusion coefficient D, which does not appear in equation (11), an allowance for some of the effects of diffusion which was first suggested by Pincus [16]. Now if conditions are such that $(\Delta\Omega/\alpha) \gg q_c^2$, the integral on the right hand side of equation (41) does not depend upon the precise magnitude of $\Delta\Omega$; the integral reduces back to equation (4) again, in fact, and the only way to fit this to Luckhurst's estimates of θ_0^2 is indeed to choose a relatively low value for q_c. If $(\Delta\Omega/\alpha) \ll \theta_c^2$, however, q_c becomes the irrelevant quantity; the integral now reduced to

$$\theta_0^2 = \frac{kT}{\pi^2 K}\left[\frac{\Delta\Omega}{2\alpha}\right]^{1/2}. \tag{43}$$

It appears that for the spin probe used by Brooks *et al.* [44] $\Delta\Omega$ was about $5 \times 10^8 \mathrm{~s}^{-1}$, while such viscosity measurements as are available for PAA suggest that η may have been about $3 \times 10^{-9} \mathrm{~m}^2 \mathrm{~s}^{-1}$. Then $(\Delta\Omega a^2/\alpha)^{1/2}$ would have been about 0·3. That is small enough compared with our estimate of about 3·9 for $q_c a$ at the ultimate cut-off to make equation (43) the appropriate version of equation (41) to use, and with $\alpha \simeq 3 \times 10^{-9} \mathrm{~m}^2 \mathrm{~s}^{-1}$ it can be fitted to Luckhurst's data for θ_0^2 quite successfully. We may conclude that, just as the relatively low cut-off suggested by Zannoni's computations is determined by the size of the samples which he has investigated, so the relatively low cut-off suggested by the ESR data of Brooks *et al.* [44] is determined by the viscosity of PAA rather than by anything more fundamental than that .

Since the early work of Brooks *et al.* [44] there have been more intensive studied of ESR line shapes for spin probes dissolved in nematics [45, 46]. The results have been subjected to an analysis which is much more sophisticated than the one outlined above, based on the theoretical model of Polnaszek, Bruno and Freed [47]. Although the fits which have been secured by variation of the principal adjustable parameter in the theory are in many cases quite good ones, the fundamental assumptions (*a*) that director fluctuations are small, and (*b*) that individual molecular reorientation occurs on a time scale that is distinctly more rapid than anything that director fluctuations can describe, are not wholly convincing for reasons that have been stated in § 2.

The problem of how to explain ESR line shapes has much in common with the problem of spin relaxation in NMR, which was one of our starting points in § 2. Reference was made in that section to three early papers on NMR in nematics which concern estimates of q_c which exceed $10^9 \mathrm{~m}^{-1}$. (In one of those papers [19] the cut-off is expressed in terms of a frequency ν_c rather than a wavevector, but the figure of 8·1 GHz quoted for PAA seems to be equivalent, if α is about $3 \times 10^{-9} \mathrm{~m}^2 \mathrm{~s}^{-1}$, to a value for q_c of about $4 \times 10^9 \mathrm{~m}^{-1}$.) Since those papers were published there has been further work on the subject, particularly by Noack and his co-workers who have used elegant field cycling techniques to extend their measurements of T_1, in magnetic fields that may be less than that of the earth, to resonant frequencies ν_0 as low as 100 Hz [48]. This work has made plain that the frequency dependence of T_1 is more complex than was at first appreciated. Thus it is only over the restricted range between 1 and 100 kHz that $1/T_1$ can normally be regarded as proportional to $\nu_0^{-1/2}$. Above this range, according to Noack *et al.* [48], the proton relaxation rate is markedly affected by factors which have little to do with director fluctuations, such as self-diffusion (not fully allowed for by the inclusion of D in equation (42)) and molecular rotation. The data may be fitted by formulae which in principle allow for these extra factors, but the number of adjustable parameters is too large for it to be said that the fit proves the formulae to be correct. Indeed, in so far as these formulae are based on an assumption that the different types of motion allowed for are statistically independent of one another they are almost certainly incorrect; that seems to be the message of a paper by Freed [11], which has relevance both to ESR and to NMR. (See also [10]. The authors of this paper, which is based on the work of Freed, obtain results for the effect of director fluctuations on the alignment of a spin probe which look as though they should apply also to the alignment of a molecule of the nematic solvent, but which bear no resemblance to the equations which have formed the starting point of the present paper, namely equations (4) and (6). The discrepancy appears to have its roots in an assumption made by the authors, though not by Freed, that the potential of mean torque which is seen by a solute molecule fluctuations in magnitude but *not* in direction.) One of the adjustable parameters in the formulae used by Noack *et al.* remains q_c, but its influence on the measurements seems to be fairly small, even at the highest accessible frequencies, and to be masked by other effects. Thus NMR data still suggest that q_c exceeds $10^9 \mathrm{~m}^{-1}$, but they do not warrant a more precise conclusion than that.

Noack *et al.* have found that at low fields, where q_c is totally irrelevant, the curve for $1/T_1$ versus resonant frequency invariably flattens out, and they have interpreted this saturation in terms of a second limit to the director fluctuation spectrum, at a low wavevector (or equivalently at a low frequency) instead of a high one. To match their data, this lower limits needs to be set at roughly $10^6 \mathrm{~m}^{-1}$ for PAA, or else at roughly 1 kHz. It has been suggested by Zupancik *et al.* [49] that it has to do with disclinations, but we would surely expect disclinations to be annealed out by the large fields which are applied during the polarization phase of a field-cycling measurement, and in any case the length scale associated with disclinations, presumably their distance apart, can scarcely be as small as 10^{-6} m. Freed [11] has shown in Appendix B of his paper that field quenching of the director fluctuations (see § 8) is irrelevant, especially at the very low fields which are used during the evolution phase, and that there is no reason to believe that conventional motional narrowing theory breaks down at frequencies of 1 kHz or less. Hence the low frequency saturation phenomenon observed by Noack *et al.* remains unexplained.

Since $1/T_1$ remains proportional to $\nu_0^{-1/2}$ down to 1 kHz at any rate, it follows that the molecules in a nematic can recognize elements of coherence in the director fluctuations that extend over times of up to 1 ms, and this may seem surprising in view of the results of experiments on dielectric dispersion in nematics, which show that the relaxation time $\tau_{\|}$ for end-to-end inversion of a molecule is only about 1 μs [50, 51]. The apparent paradox may be formally resolved by noting that the time dependent correlation functions $J_{0,1,2}$ on which T_1 depends are not affected by a transformation which replaces θ by $(\theta + \pi)$ [52]. However, we need to recognize that molecules cannot invert without passing through states of intermediate θ, and that the motions which lead to inversion are not different in kind from some of the motions with which theories of spin relaxation in ESR and NMR are concerned. It would surely be of interest, therefore, to explore the relation between the theories of spin relaxation in ESR and NMR to which reference has been made and current theories of $\tau_{\|}$ [53, 54]. To date, the two classes of theory seem to have been developed in isolation.

The present author's view is that no theory of $1/T_1$ or of $\tau_\parallel$ can be entirely reliable which does not recognize the existence of the correlations referred to in §4, and that the best hope of taking these into account lies in further development of the idea that all the misalignment of molecules in a nematic can be described in terms of director fluctuations, even on a microscopic scale. Treatment of the $1/T_1$ problem from this point of view is relatively straightforward, at any rate for temperatures which are not too close to T_{NI}, and the corrections which appear to be needed to the results laid down by Pincus [16] and Lubensky [55] are of a relatively trivial nature [21]. A first attempt at a treatment of $\tau_\parallel$ in the same spirit is outlined in §9.

8. Field quenching of director fluctuations

When an electric or magnetic field is applied parallel to $\langle \mathbf{n} \rangle$ the energy associated with a periodic distortion mode of amplitude ψ is affected, and the mean square amplitude in thermal equilibrium may, therefore, be less than the value given by equation (1). In the electric case, for a nematic which has a positive dielectric anisotropy (i.e. $\varepsilon_3 > \varepsilon_1$, where ε_3 is the relative permittivity when the field E is along $\langle \mathbf{n} \rangle$ and ε_1 is the relative permittivity when the field is perpendicular to $\langle \mathbf{n} \rangle$) we have [1]

$$\langle \psi^2 \rangle = \frac{kT}{VK} \frac{\xi^2}{1 + q^2 \xi^2}, \tag{44}$$

where

$$\xi^2 = \frac{K}{\varepsilon_0 (\varepsilon_3 - \varepsilon_1) E^2}. \tag{45}$$

Hence it follows from equation (4) that the field should change $\langle \delta^2 \rangle$ be approximately

$$\Delta\left(\sum \langle \psi^2 \rangle\right) = -\frac{kT}{\pi^2 K} \int_0^{q_c} \left\{1 - \frac{q^2 \xi^2}{1 + q^2 \xi^2}\right\} dq = -\frac{kT}{\pi^2 K |\xi|} \tan^{-1}(q_c \xi). \tag{46}$$

The effect, as de Gennes has noted [1], is proportional to the modulus of the field strength. It has been observed in computer simulation studies of the Lebwohl–Lasher model [56], and the results obtained in that way are closely reproduced by a theoretical analysis based on the ideas outlined here [23]. It has also been observed experimentally; references may be found in a useful review of the subject by Dunmur and Palffy-Muhoray [57].

Experimentally, it is difficult if not impossible to achieve values of ξ that are less than about 10^{-7} m, which means that if q_c is over $10^9\ \mathrm{m}^{-1}$ we may safely replace the factor $\tan^{-1}(q_c \xi)$ in equation (46) by $\pi/2$. *A priori*, the precise magnitude of q_c would then seem to be irrelevant to the results of any field quenching experiment. However, in the course of trying to explain their own measurements of the small increase in the birefringence $(n_3 - n_1)$ shown by thin nematic films with homeotropic alignment when an electric field is applied across them, Dunmur *et al.* [58, 59] have reached a different conclusion. Their argument may be paraphrased as follows. Since the birefringence is very nearly proportional to the order parameter, it seems to follow from equation (6) that

$$\frac{\Delta(n_3 - n_1)}{(n_3 - n_1)} = \frac{\Delta S}{S} = -\frac{3 S_0 \Delta \langle \delta^2 \rangle}{2S}. \tag{47}$$

Then if $\tan^{-1}(q_c\xi)$ can indeed be replaced by $\pi/2$ we have

$$\frac{\Delta(n_3 - n_1)}{(n_3 - n_1)} = \left(\frac{S_0}{S}\right)\frac{3kT}{4\pi K|\xi|}, \tag{48}$$

and equations (6) and (4) allow us to rewrite this result as

$$\frac{\Delta(n_3 - n_1)}{(n_3 - n_1)} = \left(1 - \frac{3kT}{2\pi^2 K} q_c\right)^{-1}\frac{3kT}{4\pi K|\xi|}. \tag{49}$$

Here q_c has re-appeared, because of its influence on the factor (S_0/S). With this argument in mind, Dunmur *et al.* [58, 59] have treated q_c, or equivalently (S_0/S), as an adjustable parameter in fitting their thin film data. They obtain some measure of agreement with theory by choosing values in the range $3 \times 10^9 - 6 \times 10^9\,\mathrm{m}^{-1}$.

Unfortunately, there is a subtle fallacy in this argument. We are not entitled to rely on equation (6) in its approximate form unless $\langle\delta^2\rangle \ll 1$, and in that case the distinction between S_0 and S is negligible. The more exact result, derivable with the aid of equation (2) and the exponential limit theorem, is

$$S = S_0 \exp\left(-\tfrac{3}{2}\sum\langle\psi^2\rangle\right), \tag{50}$$

and differentiation of this result yields

$$\frac{\Delta(n_3 - n_1)}{(n_3 - n_1)} = \frac{3kT}{4\pi K|\xi|}, \tag{51}$$

without the (S_0/S) factor which appears in equation (48). The fact that Dunmur *et al.* [58, 59] need values of (S_0/S) which differ from unity to fit their results is presumably a sign that their observations are affected by factors which the theory does not take into account.

It should be added that the effect observed by Dunmur *et al.* [58, 59] is not linear in the field strength at low fields, and that they have sought to dispose of this discrepancy, with rather limited success, by introducing a second adjustable parameter. They point out [59] that in a film of thickness D the component of $\mathbf{q}$ perpendicular to the film, say q_z, cannot be less than π/D, and suggest that on this account the lower limit of the integral in equation (46) should be some wavevector $q_{\min}$, of the order of π/D, rather than zero.

9. The end-to-end inversion process

At the end of § 7, we touched on the question of how the process which determines the longitudinal dielectric relaxation time $\tau_\parallel$ may be discussed using the language of director fluctuation theory, language which allows the correlations of orientation which exist between neighbouring molecules in a nematic to be recognized. Here the question will be examined with particular reference to the Lebwohl–Lasher model, though the suggested answer may have wider significance.

A fluctuation which locally rotates $\mathbf{n}$ through an angle π may in principle cause the inversion of a number of spins for as long as it persists. In most such fluctuations, however, the inversion is purely temporary; the molecules are carried back to their initial orientations when the distortion associated with fluctuation dies away. Thus, if the molecules carry a longitudinal electric moment, and if the nematic is initially polarized along $\langle\mathbf{n}\rangle$, the excitation and subsequent decay of the fluctuation leaves the polarization unaffected. To explain the relaxation of polarization we are obliged to consider processes in which adjacent molecules reverse their orientation relative to one another in a way that, at any rate until the next fluctuation occurs, is permanent.

Consider therefore a Lebwohl–Lasher model nematic, at such a low temperature that S is close to unity, in which a fluctuation has rotated the molecule with coordinates $(0, 0, +a/2)$ about the x axis through a large angle $+\delta_0$ and the molecule with coordinates $(0, 0, -a/2)$ through $-\delta_0$ about the same axis. If these two molecules were to be regarded as parallel before the fluctuation arose, they become anti-parallel when δ_0 reaches $\pi/2$. The other molecules may be rotated too, of course, and there is one particular pattern for these other rotations which minimizes the energy involved in the fluctuation as a whole. In so far as the nematic may be treated as a continuum, the optimum distortion pattern may be determined by solving the appropriate Euler–Lagrange equation subject to the boundary conditions that $\delta_x = \pm\delta_0$ at $z = \pm a/2$. Since $K_1 = K_2 = K_3$ for the Lebwohl-Lasher model, the Euler–Lagrange equation is $\nabla^2\delta_x = 0$ [29], and the relevant solution is

$$\delta_x = \frac{\delta_0 a^2 z}{4(x^2 + y^2 + z^2)^{3/2}}; \tag{52}$$

it has a singularity at the origin, of course, but there is no molecule at this point. The energy associated with the distortion may now be crudely estimated by integrating the energy density indicated by continuum theory, namely

$$\tfrac{1}{2}K(\nabla\delta_x)(\nabla\delta_x),$$

over all space outside a central sphere of radius say a, which is large enough to contain only the two molecules of $(0, 0, \pm a/2)$, and by adding the energy of interaction between these two. The result is

$$\frac{\pi^2}{12}\delta_0^2 Ka + \tfrac{1}{4}u(1 - \cos^2\delta_0). \tag{53}$$

The low temperature limit for Ka in the Lebwohl–Lasher model is $u/2$ (see for example equation (31) in [22]). Hence (53) describes an energy which passes through a first maximum of $0{\cdot}342u$ when δ_0 is a little over $\pi/4$ and which climbs back up to $0{\cdot}323u$ at $\delta_0 = \pi/2$. Now once δ_0 has reached $\pi/2$ a very small adjustment of the molecules, which should cost a negligible amount of energy, will suffice to shift the singularity from the point $(0, 0, 0)$ to say $(0, 0, a)$ and subsequent relaxation of the fluctuation will leave the molecule at $(0, 0, a/2)$ permanently inverted.

The picture of the inversion process presented here is very different from the picture of rotational diffusion in a mean field which Martin *et al.* [53] assumed, and from the picture of a single jump process made possible by free volume which lies behind the theory of Zeller [54]. It implies that end-to-end inversion in the Lasher–Lebwohl model should be an activated process, and that the activation energy in the low temperature limit should be about $u/3$. This is much less, of course, than the energy of $3u/2$ which is needed to invert a single molecule within a cage of perfectly aligned neighbours whose orientations remain fixed during the process. The activation energy may be expected to decrease on heating as S and K diminish, but a more elaborate calculation would be needed to establish the rate of decrease.

10. Conclusions

The principal conclusions reached in this paper may be summarized as follows.

(i) If the director field of a nematic is regarded as describing how the molecules within it are oriented at any one instant, rather than as describing the constraints to which the nematic is subject, it can be defined on any scale of resolution that is appropriate for the problem in hand. The finer the scale chosen, the larger the director fluctuations appear to be.

(ii) The fluctuations can usefully be discussed in terms of a set of periodic distortion modes, though results obtained in this way are not entirely reliable when the fluctuations are really large, i.e. when the finest scale is chosen and when T is close to T_{NI}. On the finest scale that has physical meaning the fluctuation spectrum cuts off where $q_c a$ is about 3·9.

(iii) Mean field theories such as that of Maier and Saupe include director fluctuations, but for given S they put too much weight on high q modes and too little on low q modes. Put in another way, they ignore the correlations of orientation between neighbouring molecules which characterize nematics (except in the ideal case of a nematic which is aligned by interactions of long range). They therefore overstate the entropy of misalignment.

(iv) Cluster expansion theories offer considerable improvements, but they cannot be expected to converge rapidly with cluster size because the correlations are long range. Predictions of S based upon a four particle cluster expansion theory are likely to need significant correction for the effects of director fluctuations.

(v) Estimate of q_c which appear in the literature, based on computer simulation studies using the cluster Monte Carlo method, or an analysis of line shape anisotropy in ESR, and on field quenching experiments, are not to be trusted. In two out of the three cases examined, the data upon which these estimates are based can be fully explained without cutting off the fluctuation spectrum prematurely.

(vi) It is seriously inconsistent to allow for director fluctuation modes right up to the ultimate cut-off where $q_c a$ is about 3·9 and to suppose at the same time that molecules are free to undergo rotational diffusion about the local director.

(vii) The end-to-end inversion process which determines the longitudinal dielectric relaxation time can be described in terms of director fluctuations alone.

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