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Torsional defects, dielectric response and dynamics of comb polymer liquid crystals

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Nematically and smectically ordered teeth of comb polymers are known to be coupled to the backbone. We speculate that if suitable chemistry can make this coupling torsional as well, then dipolar correlations can be induced in addition to quadrupolar order. We then predict an activated dielectric response mirroring the creation of torsional defects in the tooth order. The susceptibility becomes large, eventually proportional to the degree of polymerization, N_p . A model for the diffusional dynamics of these defects can be calculated exactly and gives an exponential variation of the dielectric relaxation time. At low temperatures this relaxation time ultimately varies as N_p^2 . Analogous conclusions are drawn about possible non-linear optical effects in comb polymer liquid crystals.

1. Introduction

Nematogenic rods, connected together as the teeth of a polymer comb, form nematic phases in competition with whatever nematic character the polymer backbone itself might have. Neutron scattering experiments and investigations of nematic networks demonstrate conclusively that there is strong coupling between the teeth and backbone of the comb. We shall be concerned with defects in the ordering of teeth along the backbone when the polymer is in nematic phases or in a particular smectic phase. To fix our ideas, we envisage one of the nematic possibilities, termed N_1 by Wang and Warner [1]. The teeth have a positive nematic order and the backbone, of much weaker nematic strength and attached to the teeth by hinges with a perpendicular tendency, has a negative nematic order. This phase was first investigated by Kirste and Ohm [2] and by Keller *et al.* [3] who found the backbone confined toward the plane normal to the director. The corresponding smectic ordering of the teeth confines the backbone more strongly [4], eventually leading to hops between planes being predicted [5]. An activated form for chain dimensions, characteristic of these defects in molecular order, has now been observed [6]. We sketch the nematic phase N_1 and a smectic phase of combs in figure 1. Studies hitherto have been concerned with the nematic order, with teeth and the chain backbone configurations and with the connection between these properties. This connection is the additional subtlety of polymer liquid crystals since mesogenic order restricts the drive to maximal entropy usual for polymers. The sketch (see figure 1) of the phases shows the teeth ordered nematically and, consistent with this quadrupolar type of ordering, no regard being paid to up or down (dipolar order). This disorder represents a torsional entropy

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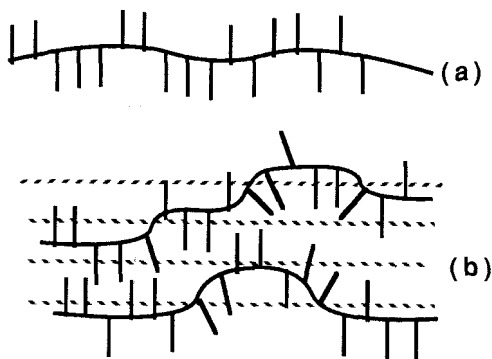


Figure 1. (a) N_1 phase with the main chain forced to explore directions in or close to the plane perpendicular to the ordering director. Torsional energy is sufficiently low that dipolar correlations between teeth are short ranged. (b) Smectic combs with smectic planes dotted in. The chain is strongly confined but the teeth have no dipolar correlations.

along the backbone and that, for molecules with a suitable chemical structure, we propose this entropy can be frozen out at lower temperatures. In backbone polymers, de Gennes [7] proposed hairpins as the molecular defect recovering entropy in the main chain nematic case. They have been discussed in the context of entropy and the current context of dielectric response [8]. Layer hops [5] in a smectic phase are also an attempt to recover some of the entropy lost in confinement in planes. We shall argue that although there is no consequence for the spatial configurations of the polymer from torsional defects, as there is for hairpins and layer hops, there could be an extreme consequence for the low frequency dielectric response as a dipolar correlation within one chain can result, interrupted only by the torsional equivalent of hairpins or layer hops, an abrupt change from an up to down arrangement of teeth. Figure 2(a) sketches the idea of teeth with an isotactic attachment to the backbone. Their lowest energy state has all teeth on one side of the main chain, that is where the main chain is not twisted. This state can be interrupted by defects in the teeth orientation. One such defect involving the relative twist of two successive teeth, discussed later, is shown in figure 2(b). When the tooth dipole has a component always pointing either toward or away from the backbone, then such defects represent large changes of energy of the polymer with respect to an external electric field, \mathbf{E} . Thus, in addition, to the quadrupolar (nematic) order, rotation defines a dipolar sense to the problem, sketched later in figure 4.

Our plan is to describe the conditions for such defects, calculate their energy and hence probability of occurrence, find the static dielectric response and the non-linear optical response, both of which turn out to be extremely large (eventually going as the degree of polymerization), and to introduce a model of diffusion of defects for the dynamics of such combs. The dynamics will allow us to find the low frequency dielectric response. Mapping onto the dynamics of a one dimensional Ising model allows an exact solution to the time evolution. We conclude with a discussion of what aspects of the dielectric and optical response experiments this corresponds to.

Our principal results are (i) a large dielectric susceptibility χ , ultimately scaling like the degree of polymerization N_p , and displaying an activated form betraying the mechanism via torsional defects and (ii) long relaxation times for dielectric response

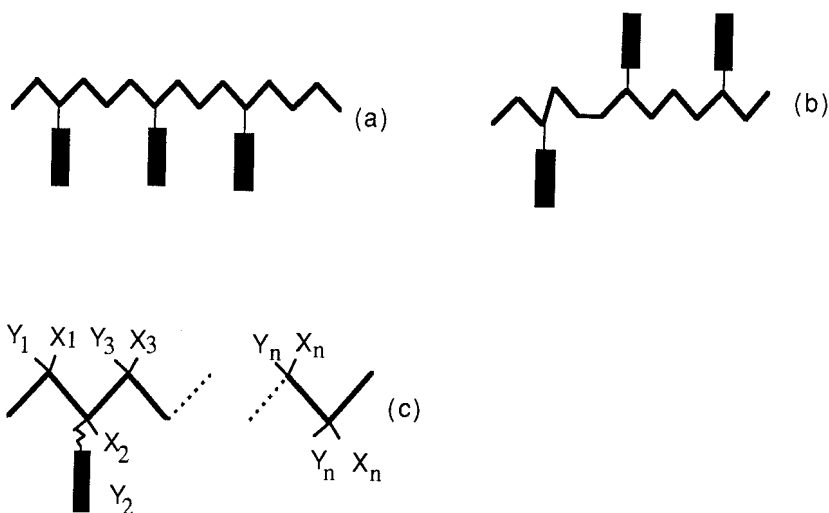


Figure 2. (a) Isotactic nematic comb polymers without defects, i.e. all teeth are on one side. (b) The torsionally defected configuration of isotactic combs, (c) An isotactic comb molecule with a backbone consisting of C-C linkages in the form $[-(CX_1 Y_1)-(CX_2 Y_2)-\dots-(CX_n Y_n)-]$. One repeat with n units is shown; the substituent Y_2 is the tooth.

characteristic of diffusion of defects along the chain in three regions. Relaxation times scale ultimately like N_p^2 . Related results apply for the non-linear optical response.

2 Candidate molecules

The attachment of teeth has a flexibility that depends on the length of the hinge unit. We use the term hinge synonymously with the term attachment spacer. If the hinge is too small, nematic order is entirely destroyed. If it is very long, teeth and backbone are essentially decoupled. We envisage an intermediate case, corresponding to observations [2, 3, 5] of phases where side chain order is sufficiently coupled to the backbone to confine at least partially the backbone, either to a plane perpendicular to the nematic director or within smectic layers. For N_1 however the hinge is sufficiently strong that any nematic tendency of the backbone is insufficient to cause the teeth and backbone to be parallel; these competitions are modelled by Wang and Warner [1], see also the reviews by Warner [9]. The stereochemistry of where the teeth are attached to the backbone is of vital importance for the dielectric analysis that will follow. Imagine for simplicity a backbone consisting of C-C linkages in the form $[-(CX_1 Y_1)-(CX_2 Y_2)-\dots-(CX_n Y_n)-]_N$ where there are $n-(CXY)-$ units in a monomer and one of the $X_1 \dots X_n$ or $Y_1 \dots Y_n$ is a tooth. The all-trans configuration of this is sketched in figure 2(c) with Y_2 the tooth (mesogenic side chain). We also suppose in this example that the substituents X_i and Y_i are such that this all-trans configuration is of lowest energy. Inspection of a simple model shows that, for consecutive teeth to be parallel in the all-trans configuration, attachments have to be made at every second (or multiple of two) carbon atom, that is $n = 2, 4, \dots$ with stereo-regularity inbetween. To twist two consecutive teeth from an initially parallel state to an antiparallel state requires the bonds between successive carbon atoms to rotate from 0° upto around 60° . Within this extent the rotational potential of these bonds increase continuously to its maximum. These angles essentially determine the

rotational potential of bonds [10]. Thus the total rotation potential of two relatively twisted teeth, which is determined by the sum of potentials corresponding to these bonds connecting them, increases to a maximal value when these teeth are anti-parallel. This discussion suggests that, although this process appears to be torsional, it is not: since continuing to twist the teeth can only reduce the relative angles between bonds, further rotation about the backbone in the same direction until the total angle is 2π returns the backbone to the low energy all-trans configuration and a rotation of $\theta = 2\pi$ is equivalent to $\theta = 0$. Two rotations of π have no net effect. On meeting, two such states annihilate each other, independently of the sense in which they were initially rotated by $\theta = \pm\pi$. We shall loosely describe such processes as torsional. As a twist between teeth costs an energy made up of distortions of bonds away from the minimum of their rotational energy states, a less sharp twist will cost less energy and we shall in general model this by a torsional energy proportional to the square of the rate of change of angle of teeth, with θ varying from 0 to π . The points of attachment along the backbone should not be so widely separated that it is easy for the backbone to twist, leaving the torsional states of successive teeth essentially randomly up or down. Since torsion and bend moduli for a backbone have the same stereochemical origin it seems likely, that given bend is sufficiently penalized that a chain can be directionally confined by attached teeth (in N_i phases), this restriction on torsional freedom can also be realized. More complicated is the problem that existing synthetic routes produce combs with no clearly defined tacticity. Obviously these requirements need molecules produced by highly stereospecific polymerization methods, particularly those which produce macromolecules with a high degree of isotacticity (ideally 100 percent). In principle the methods developed for stereospecific polymerization of acrylates and methacrylates could be used [11]. Additionally it is known that by suitable change of solvent polarity the stereochemistry of polydienes prepared by anionic polymerization can be greatly influenced [12]. Our speculations, therefore, relate to molecules yet to be synthesized. For later sections we shall require a dipole in each tooth always pointing in the same direction, that is always toward or always away from the main chain. This is usually the case in comb polymers with on-board tooth dipoles.

3. Torsional defects

As the temperature, T , is reduced in the nematic phase, the order S of the teeth, defined by

$$S = \langle P_2(\cos\theta) \rangle \equiv \frac{3}{2} \langle \cos^2\theta \rangle - \frac{1}{2}, \quad (1)$$

approaches 1. Thus, the angle θ a rod makes with the director n is restricted to values close to 0 or π . We consider a nematic mean field felt by the rods of $-aSP_2(\cos\theta)$ where a is a coupling constant and is related to the transition temperatures of combs [1]. Small excursions from either pole, θ or $\pi-\theta$, are equally likely in each azimuthal direction, but when considering the transition from one pole to the other this is most economically achieved by motion in a plane perpendicular to the local backbone tangent, as sketched in figure 3. We use the angle θ to denote the torsion of the backbone in this plane but keep in mind that in general the rods explore orientations with two Euler angles. In the presence of bend, torsion of the backbone actually has a more complicated definition.

We now follow the de Gennes' argument [7] for hairpins and a simplified version of the argument for layer hops. At $T = 0$ the energy associated with a single twist is

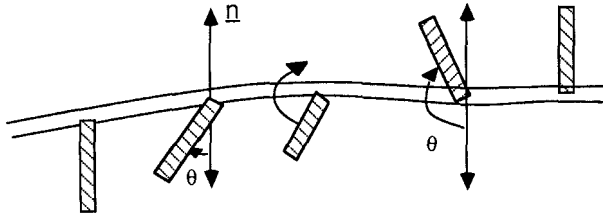


Figure 3. A continuous representation of a defect of width b from the competition between the nematic field and the torsional force resisting rotation perpendicular to the backbone. θ is the angle between tooth and \mathbf{n} .

given by

$$u = \int_{-\infty}^{\infty} ds \left\{ \frac{1}{2} \kappa \left[\frac{\partial \theta(s)}{\partial s} \right]^2 - aP_2(\cos \theta) \right\}, \tag{2}$$

where κ is a torsional modulus and s is the distance along a chain. $\theta(s)$ is the twist angle of the chain at s , with the boundary conditions $\theta(-\infty) = 0$ and $\theta(\infty) = \pi$. The order parameter S normally associated with a has been set equal to 1 at this low temperature. If we subtract the energy associated with the chain at $\theta = 0$ or π and render the arc length dimensionless by $s = by$, with b a length, then we have

$$u = \frac{3ab}{2} \int_{-\infty}^{\infty} dy \left[\left(\frac{\partial \theta}{\partial y} \right)^2 + \sin^2 \theta(y) \right], \tag{3}$$

if $b = \sqrt{(\kappa/3a)}$. Hence the energy scale can only be $ab \equiv \sqrt{(\kappa a/3)}$ and a functional minimization of $\int dy \{ \dots \}$ yields a pure number. The spatial extent of a transition, s_0 , is given by b times a dimensionless number y_0 emerging from the Euler-Lagrange minimization. The results, by an analysis, given explicitly in [5] are

$$\left. \begin{aligned} u &= 2\sqrt{3a\kappa} \\ \theta(s) &= 2 \tan^{-1} \exp\left(\frac{s}{s_0}\right), \\ s_0 &= b = \sqrt{\left(\frac{\kappa}{3a}\right)}. \end{aligned} \right\} \tag{4}$$

Now at finite temperatures we simply say that the probability per unit arc length of finding a torsional defect is given by the Boltzmann weight $\exp\{-u/(kT)\}l_0^{-1}$. Such an analysis can be shown [13] to give the correct exponential behaviour but that the inverse length l_0^{-1} must come from more detailed statistical mechanics, in this case an asymptotic analysis of Mathieu's equation. For layer hops and hairpins such a factor could, in principle, be tested by an independent experiment (neutron scattering) and has been calculated [5, 8]. Here l_0 does not seem to be independently measurable and we do not present its detailed calculation.

4. Static dielectric response

At low temperatures the arc length separating defects is $l_0 \exp\{u/(kT)\}$ (the inverse frequency of defect creation given in §3) and becomes large. This means that if a field \mathbf{E} is applied along the director it couples strongly to a defect since it represents a large section of chain with its dipoles pointing along or against the field. Low temperatures

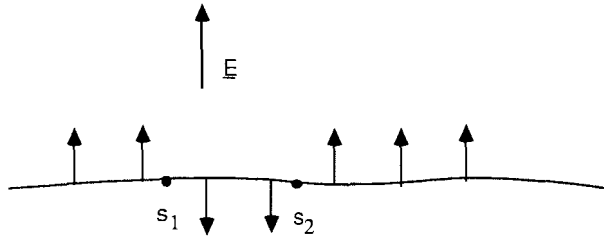


Figure 4. The coordinate system for defects of zero width. E is the applied field and s_1, s_2, \dots , are the positions of defects. Tooth dipoles are denoted by arrows pointing away from the main chain.

also imply that the characteristic region of transition in a defect s_0 , is much less than the distance between them, $l_0 \exp\{u/kT\}$, and hence that defects mostly have a clearly defined identity of their own. This, in turn, suggests using the position of the defects as a coordinate to describe the dielectric response (see figure 4). This was the method of [8] to find the response of the hairpin gas in main chain nematics. If the dipole moment of a monomer, that is of a tooth, is μ and the space between teeth along the backbone is q then the dipole moment per unit length of main chain is $\sigma = \mu/q$. The energy of the polymer in an electric field E directed along \mathbf{n} is

$$V_n = -[s_1 - (s_2 - s_1) + (s_3 - s_2) + \dots (\pm)(L - s_n)]\sigma E, \quad (5)$$

where, as seen in figure 4, the field acts parallel to the dipoles in the interval $(0, s_1)$, anti-parallel to those in (s_1, s_2) and so on. The defect positions are given by s_1, \dots, s_n . The final sign \pm in V_n is $+$ or $-$ according to whether the number of defects n is even or odd. L is the total length of the chain. A sequence starting the other way, that is anti-parallel in $(0, s_1)$ etc. can be obtained by changing the sign of E . Associated with these n defects is a Boltzmann factor $\exp(-n\beta u - \beta V_n)$ with $\beta = 1/(kT)$. An entropy is associated with where the defects are put in along the chain; we must sum over positions $0 < s_1 < s_2 < \dots < s_n < L$. If we turn these sums into integrals $\int ds_1 \dots$ then the correct measure is given by the l_0^{-1} factor introduced when discussing the defect frequency. It is convenient to introduce a dimensionless length $x = s/l_0$ and a dimensionless measure of the electrical energy of a dipole of magnitude $l_0\sigma$; we call this $v = l_0\sigma\beta E$. Denoting the Boltzmann factor $\exp(-\beta u)$ by f , the partition function for a defect comb polymer is then

$$Z = \sum_n \sum_{\pm E} f^n \int_0^N dx_n \dots \int_0^{x_2} dx_1 \exp[vx_1 - v(x_2 - x_1) + \dots v(N - x_n)], \quad (6)$$

where $N = L/l_0$ is the number of sections of length l_0 in the chain. Laplace transformation of the integrals in the n th term of the series turns this Laplace convolution into a product. Z then becomes a geometrical series which can easily be summed and then back-transformed; the result is

$$Z = 2 \left[\cosh AN + \frac{f}{A} \sinh AN \right], \quad (7)$$

with $A^2 = v^2 + f^2$. In the dielectric analysis of hairpins [8] the limit of many defects per chain was taken, that is $fN \gg 1$. That was only for simplicity and we now illustrate the general case here.

The net dipole moment of a chain is

$$p = l_0\sigma[x_1 - (x_2 - x_1) + (x_3 - x_2) - \dots \pm (N - x_n)], \tag{8}$$

which is, of course, the quantity entering the potential (5) and the electrical part of the Boltzmann factor in (6). Since Z is a statistical weight, the mean dipole moment per chain is given by

$$\langle p \rangle = \frac{kT}{Z} \left(\frac{\partial Z}{\partial E} \right) \equiv kT \frac{\partial}{\partial E} \ln Z \equiv - \frac{\partial F}{\partial E} \tag{9}$$

as can be verified by taking the differential of equation (6). F is the free energy of a chain, $F = -kT \ln Z$. The susceptibility χ is $(1/\epsilon_0) (\partial P/\partial E)_{E \rightarrow 0}$ where P is the polarization $P = \langle p \rangle / (Nv)$ with Nv being the volume of a chain. The volume associated with a length l_0 of chain is v . Recalling that $v = l_0\sigma\beta E$ and hence $\partial/\partial E \equiv l_0\sigma\beta\partial/\partial v$, we obtain $\chi = (-\partial^2 F/\partial E^2)/(Nv\epsilon_0)$ from equation (7) as

$$\chi = \frac{(l_0\sigma)^2\beta}{Nv\epsilon_0 f} \left[N \sinh(fN) - \frac{1}{f} \sinh(fN) + N \cosh(fN) \right] \times [\cosh(fN) + \sinh(fN)]^{-1}. \tag{10}$$

In the limit of very few defects per chain on average, $fN \ll 1$ we find [...] $\sim N^2 f$ and

$$\chi \approx \frac{(l_0\sigma)^2\beta N}{v\epsilon_0} \equiv \chi_0 N_p, \tag{11}$$

where $\chi_0 = \mu^2/(a^3 kT\epsilon_0)$ is the susceptibility characteristic of a conventional nematic composed of molecules with the volume a^3 and the dipole μ of the monomers. $N_p = Nl_0/q$ is the degree of polymerization (the number of teeth per chain). We use here the relation $v = a^3(l_0/q)$ where l_0/q is the number of teeth in a length l_0 . Hence an intensive quantity such as χ is seen to become large, eventually becoming proportional to the degree of polymerization N_p , as the teeth act in concert. Rigid combs, probably in this limit and in a new biaxial mesomorphic phase, have been constructed by Ballauff and Schmidt [14] but without reference to possible dielectric anomalies.

The other limit of Gunn and Warner [8] of $fN \gg 1$ can be taken from equation (10) or by returning to equation (7) where since $A > f$, then $AN \gg 1$ also; then we have

$$Z \approx 2 \left(1 + \frac{f}{A} \right) \exp(AN). \tag{12}$$

Directly differentiating and taking the $E \rightarrow 0$ limit we find

$$\chi = \frac{(l_0\sigma)^2\beta}{v\epsilon_0} \exp(\beta u) \equiv \frac{\chi_0 l_0}{q} \exp(\beta u) \equiv \chi_0 \frac{N_p}{n}, \tag{13}$$

where $n \equiv fN$ is the number of defects along one chain. Again there is a large response which is N_p/n times greater than that of conventional nematics since we suppose, in the beginning of this section, that the average distance between two successive defects is much greater than the space between teeth, i.e. $l_0 \exp(u/kT) \gg q$. Comparing these susceptibilities of two different limits given by equations (11) and (13) with each other, we find the χ of the latter case is only one n th of the corresponding value in former. The ratio of these two values $1/n$, shows that the external field

couples to the defects so strongly that the dielectric response in the many defect limit is equivalent to that of molecules with a degree of polymerization equal to N_p/n . Equation (13) shows the tendency of increasing χ , as the frequency n of defects decreases, toward the limiting (11) value $\chi_0 N_p$ where all defects are frozen out. The number $Nl_0/q \equiv N_p$ is the total number of teeth on the chain. Recall that l_0 was an elementary length, not obtainable from our simple Euler-Lagrange argument. In the hairpin case recourse could be made to the full statistical mechanical asymptotic solution of the hairpin problem [13] and l_0 found. It was linear in T thus eliminating all of the temperature dependence in expressions like (13) except in the exponent. We leave the question of l_0 here, remarking simply that χ in equation (13) has a form characteristic of defect activation and is capable of being very large.

In the transition from Z to χ we neglect $O(E^2)$, that is, we looked for the linear response. Examination of the terms thereby discarded shows that they are small provided that $v < f$. Hence fields are small if they satisfy $E < kT \exp(-\beta u)/\sigma l_0$ or $\mu E l_0 \exp(u/kT)/q < kT$ where $l_0 \exp(u/kT)/q$ is the total number of teeth between two successive defects. So this inequality shows that the maximal energy of teeth between two consecutive defects in an external field \mathbf{E} is less than the thermal energy kT . It is consistent with the discussion in the end of this section implying that the electric field is not strong enough to change the average number of defects, only to bias the distribution of teeth up or down toward its mirror images. The response becomes non-linear if the field exceeds this exponentially small value.

For the later interpretation of the dynamical response it is useful to examine χ further. Returning to equation (13) we can work back to the polarization per chain by multiplying by $NvE\epsilon_0$. The result is

$$\langle p \rangle = \sigma^2 l_0 L \beta \exp(\beta u) E \equiv \frac{\mu^2 N_p^2}{n} \beta E \quad (14)$$

which depends on a factor equal to the mean square number of teeth pointing in a particular direction times the square of the dipole moment on a tooth, that is $\mu^2 [l_0 L \exp(\beta u)/q^2]$. The last factor is the equivalent of the mean square spatial extent of a chain in the hairpin case. We can now deduce that a small field, in creating a bulk polarization, does not alter drastically the distribution of lengths of teeth up and down but simply biases it, selecting conformations from their mirror images, a distinction that is imperceptible when considering the number of defects in the defect gas. Changes in the distances between defects are introduced at $O(E^2)$, a result that

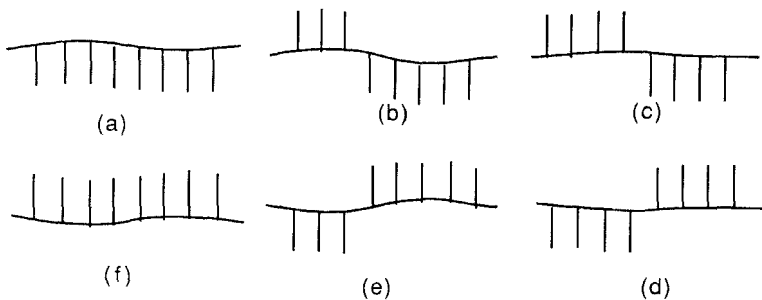


Figure 5. Configuration of defects (a), (b), (c), and their mirror images (f), (e), (d). The population of configurations relative to their images is biased by an applied field, rather than the field changing their shapes.

can be calculated directly or by noting in equation (14) that the mean square net tooth number $(l_0 L/q^2) \exp(\beta u)$ that enters. If this were to be altered at $O(\mathbf{E})$ another vector would have to be found with which to create a scalar from \mathbf{E} . There is no such vector available in the problem, hence the requirement that shape changes enter at $O(E^2)$. Figure 5 illustrates configurations and their mirror images, equal in pairs in energy as far as defects are concerned but different in their electrical energies and thereby biased in number by the field.

5. Dynamics of comb polymers

We shall discuss one limited form of the motion of comb nematics, namely the dynamics of the teeth at low temperatures where the nematic order is strong. The flipping of teeth is not expected to have a strong influence on the spatial motion of the chain, but it will be the relaxation relevant to describe the time dependent aspects of the unusual dielectric response developed in the previous section.

First we give some qualitative arguments for the dynamics by considering the diffusional motion of the torsional defects since it is their motion which leaves a trail of flipped dipoles behind. We have suggested previously that at low temperatures they form a natural set of coordinates for the thermodynamics. It seems they are also natural for the dynamics. We shall then consider how this problem can be made similar to that of the dynamics of a one dimensional Ising chain, a problem solved exactly by Glauber [15]. The results will agree exactly with our qualitative analysis for low temperatures.

At low temperatures all teeth are essentially up or down, such regions of one polarity being connected with one of the other polarity by defects, the width of which is given by equation (4). At low enough temperatures (high nematic order) there are few defects and their width, which is independent of temperature, is small compared with their separation which behaves like $\exp(u/kT)$ thus allowing defects to be considered as separate entities. For a defect to progress an elementary process such as a tooth flip must occur, see figure 6 (a). If this process occurs at a rate α , then in a time t there will be αt steps. Since steps are equally likely in both directions we have

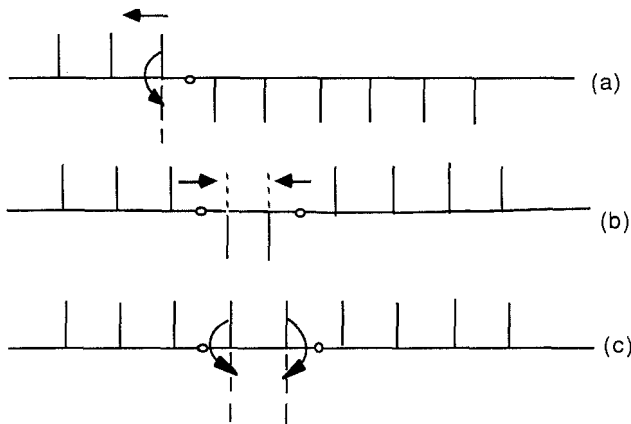


Figure 6. (a) A defect advancing one step by an elementary flip (time $1/\alpha$) (the difference between step lengths l , and l_0 , q or b can be later absorbed into α). (b) The meeting of two defects annihilates the section of the given polarity between them. (c) Generation of a defect pair creates an island of down in a sea of up.

a random walk for the defect. The mean square distance traversed along the backbone is, with l the step length separating effective teeth,

$$\langle s^2 \rangle = l^2 \alpha t \equiv Dt, \quad (15)$$

whereupon the effective diffusion constant, D , is $D = \alpha l^2$.

The problem is how the chains evolve to a state where configurations are biased by the applied field toward their energetically more favourable mirror images. When there are few defects per chain a dynamical question arises. In going from say (*a*) to (*f*) in figure 5, is the rate determined by the diffusion of existing defects from one end of the chain to the other, or is it determined by the rate at which defects are thermally generated at one end of (*a*)? The time for diffusion, τ_d is given simply by the brownian law $L^2 = D\tau_d$, hence

$$\tau_d = \left(\frac{L}{l}\right)^2 \alpha^{-1} \approx \alpha^{-1} N^2, \quad (16)$$

(identifying l with l_0 for simplicity of the algebra).

The thermal activation of defects at the end is $\tau_{th} \sim \alpha^{-1} \exp(u/kT)$ since the attempt frequency α is roughly that involved in the flipping of bonds required to twist teeth, and an activation is required to create a defect of energy u . If thermal generation is the rate determining step, $\tau_{th} > \tau_d$, we have $\exp(u/kT) > N^2$ and the relaxation time is τ_1

$$\tau_1 = \tau_{th} \approx \alpha^{-1} \exp(\beta u). \quad (17)$$

For longer chains, or not such low temperatures, but still few defects per chain, i.e. $N \exp(-u/kT) \ll 1$ but $N^2 \exp(-u/kT) \gg 1$, then $\tau_{th} \ll \tau_d$ and we have a second regime

$$\tau_2 = \tau_d \approx \alpha^{-1} N^2. \quad (18)$$

We can now ask, inspecting the sequence of configurations and their mirror images in figure 5, how long equilibration to (or from) a biased state takes when a field is switched on (or off). A naïve analysis might suggest that relaxation is quick since one defect only has to move a short distance to make it down the cascade to the next configuration in the sequence. The actual time is again $\tau \sim \alpha^{-1} N^2$ since if a defect has a position s along the chain, its energy is $V = -(2s - L) \sigma E$ (see equation (5)) and hence the probability distribution function for defect position s is $P_0(s) \sim \exp(2s\sigma E/kT)$. After the field is switched off, the initial distribution $P_0(s)$ diffuses to the constant value $P \sim l_0/L$ according to the diffusion equation

$$\left(\frac{\partial}{\partial t} - D \frac{\partial^2}{\partial s^2}\right) P(s, t) = 0. \quad (19)$$

The eigen solutions of this are $\sim \cos(n\pi s/L) \exp(-\lambda_n t)$ with $\lambda_n = D(n\pi/L)^2$. The $n = 1$ component gives an eventual exponential decay of any initial distribution with a characteristic time

$$\tau = \frac{L^2}{\pi^2 D} \approx \alpha^{-1} N^2. \quad (20)$$

The many defect relaxation, that is when $N \exp(-u/kT) \gg 1$, can be estimated by recalling that when E is small it does not change the number of defects, but simply biases the distribution between up and down sequences. Thus, the sequence in figure 5

can be thought of as not being for a whole chain, but merely being the dispositions, within a long chain, of a section of chain equal in length to the mean separation between defects. Therefore, in the equilibration time (20) associated with figure 5 we should put, instead of L , the distance $l_0 \exp(u/kT)$ between defects. This yields the third characteristic time, for many defects per chain, $N \exp(-u/kT) \gg 1$, of

$$\tau_3 \approx \alpha^{-1} \exp(2\beta u). \quad (21)$$

The foregoing dynamical model can be pressed into the dynamics of a one dimensional Ising chain by reconsidering the chains; defects have a characteristic width b over which the direction of teeth is reversed. If we consider teeth blocked into groups of b/q then, on this scale, defects will appear to be sharp divisions between regions of effective teeth up and down. Of course, to preserve the static susceptibility and the overall characteristic dynamic scale, μ and α will also have to be scaled. Since we are only interested in the forms of the response we absorb those factors and continue to use μ and α . Since the chain is infinite we are clearly in the many defects per chain limit. Contact can now be made with the Ising model. The energy of two neighbouring spins (teeth) $i, i + 1$ is $-J\sigma_i\sigma_{i+1}$ where $\sigma_i = 1$ or -1 if teeth are up or down and $J > 0$ implies a ferromagnetic ordering. We have, for our blocked teeth $2J \equiv u$. Glauber has solved the dynamics of this problem exactly [15], taking a probability $\alpha/2$ per unit time of flipping i if $i - 1$ and $i + 1$ are oppositely directed to each other. The probabilities of flipping i in the other two cases of $i - 1$ and $i + 1$ parallel to each other and either parallel or anti-parallel to i are related to $\alpha/2$ by detailed balance. Thus $\alpha/2$ describes defect motion, the other two processes being spontaneous generation of defects and their pair-wise annihilation, respectively. In general all three processes occur.

In our diffusion model we took α (not $\alpha/2$) to be the probability per unit time of our defect taking a step in the diffusion process. In Glauber's model the situation is complicated by many defects for finite temperatures. However, at low temperatures, it can be simplified by considering the directions to be equal, i.e. $\alpha/2$, as there is no other defect in the vicinity of the defect considered. Thus when the defect number is low we have a rough correspondence with Glauber if we take the defect motion probability per unit time to be α . We do not repeat Glauber's elegant analysis here but simply quote his result for the decay of bias of up with respect to down set up by a static field E_0 applied until $t = 0$ and then switched off. His result for the mean of σ_i for any tooth i is

$$\langle \sigma(t) \rangle = \frac{\mu E_0 (1 - \gamma \eta)}{kT (1 - \gamma)} \exp[-\alpha(1 - \gamma)t], \quad (22)$$

where

$$\gamma = \tanh(2J/kT) \quad \text{and} \quad \eta = \tanh(J/kT).$$

Gathering together terms we obtain

$$\langle \sigma(t) \rangle = \frac{\mu E_0}{kT} \exp(2JkT) \exp\left\{-\frac{t}{\tau}\right\}, \quad (23)$$

with

$$\tau = \frac{1}{\alpha[1 - \tanh(2J/kT)]} \equiv \frac{1 + \exp(4J/kT)}{2\alpha}. \quad (24)$$

If we take the limit of low T and put $2J = u$ we obtain from equation (23) the mean dipole moment per chain

$$\langle p(t) \rangle = \frac{\mu^2 E_0 N_0}{kT} \exp(\beta u) \exp\left\{-\frac{t}{\tau}\right\}, \quad (25 a)$$

where N_0 is the number of blocked groups of teeth along the chain and τ is derived from equation (24)

$$\tau \approx \frac{1}{2\alpha} \exp(2\beta u). \quad (25 b)$$

The first part of equation (23) is the static response leading to the large values of χ given by equation (13). The low temperature limit of τ given by equation (25 b) yields our result obtained for simple defect diffusion, equation (21). The complicated form of equation (24) for τ away from low temperatures reflects the increase of other processes involved in relaxation, namely the modification of the hopping rate $\alpha/2$ from the presence of other nearby defects and the possibility of defect generation, figure 6(c). For our problem, when this becomes important we probably no longer have a very high underlying nematic order and the dominance of the teeth is lost, thereby invalidating the whole model. We accordingly do not pursue equation (24).

Knowing the relaxation time of a spin (tooth) and the mean square net tooth number allows us to immediately write down the time dependent correlation function for the polarization

$$\langle p(0)p(t) \rangle = \sigma^2 l_0 L \exp(\beta u) \exp\left\{-\frac{t}{\tau}\right\}, \quad (26)$$

with τ given by equation (24). By using equation (26) and fluctuation-dissipation theorem [15] we have the frequency dependent response $\chi(\omega)$ for the case of a harmonic field $E(t) = E_0 \exp(-i\omega t)$

$$\chi(\omega) = \frac{1}{\epsilon_0 k T \tau} \int_0^\infty \langle p(0)p(t) \rangle \exp(i\omega t) dt = \frac{\chi(0)}{1 - i\omega\tau}. \quad (27)$$

The real part of $\chi(\omega)$ yields a lorentzian form $\chi(0)/[1 + (\omega\tau)^2]$. When $\omega \rightarrow 0$, the limit of $\chi(0)$ is that given in §4.

6. Applicability to experiment

We recall that for simple, rod-like nematics there are many dielectric processes possible, the three principal ones being sketched in figure 7. The first two, rotation about the long axis reorientating an outboard dipole (a) and rotation of the rod through the cone of allowed nematic orientations reorientating an onboard dipole (b), are both rapid. The third possibility (c), reversing the rod direction, is slow but obviously contributes most to the decay of polarization built up by a field applied parallel to the direction. It is slow [16, 17] because the rod has to pass through orientations $\theta \sim \pi/2$ highly forbidden by a strong nematic field. This energy is, in fact, one component of the energy required to create a defect and gives a time scale $\tau_f \sim \tau_0 \exp(aS/kT)$ where τ_0 is some underlying time scale, characteristic of the first two processes. We are also proposing a drastic extension of one time scale, that is $\tau = \exp(2\beta u)/2\alpha$, associated with a particular dielectric response. In our case the response can be $\sim N$ times larger than the third possibility (c) for simple nematics. The

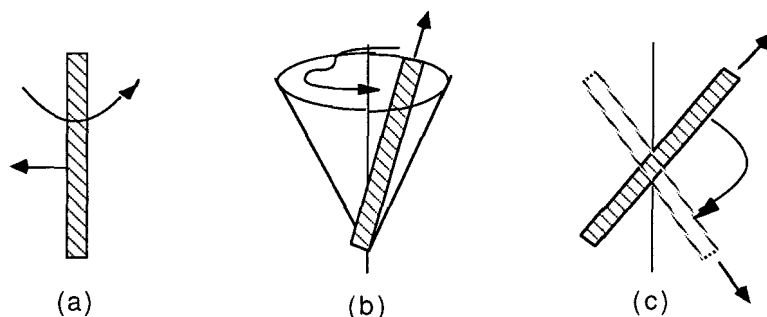


Figure 7. Dielectric processes in simple nematics. (a) rotation about the long axis reorienting an outboard dipole; (b) rotation through the cone of allowed nematic orientations reorientating an onboard dipole; (c) reversing the rod direction.

difference is that our timescale becomes extended because of the cooperative action of the dipoles and the long time required for the defects to arrange this. Because our τ is bounded only by N_p^2 it seems possible that τ could exceed τ_f considerably.

What we are *not* commenting on in this paper is the polymeric equivalent of the first two processes in simple nematics, that is local motions in the chain backbone leading to partial reorientation of dipoles and relatively small responses, all on a relatively fast time scale.

7. Non-linear optical effects

Organic molecules with a donor and acceptor widely separated by a conjugated electron system are very effective, fast and low-loss non-linear optical elements. Their geometry is often cylindrical which makes them nematic or smectic, or at least able to couple strongly to a nematic solvent.

Nematics present a very efficient environment in which to apply a poling field to remove the macroscopic centre of symmetry, a necessary step for achieving a non-linear optical effect [18, 19, 20]. Polymer liquid crystals have been recognized as offering still greater advantages: they can form films and coatings of good mechanical strength and they typically have glassy phases which freeze in the effect of poling. Additionally, sometimes the small solubility of non-linear optical molecules in nematic solvents can be overcome by using nematic comb polymers not as solvents but making the non-linear optical elements themselves the teeth of the comb [18].

We shall point out how the foregoing conclusions about dielectric response could be used to predict an equally large non-linear optical effect and a similar kind of dynamical response. Firstly we sketch this response in simple nematics. We then calculate the response for comb polymers and conclude by discussing a non-linear optical experiment that has seen an anomalously large effect. Assuming, for simplicity, that responses are along the longest principal molecular (z) axis, we have, in the molecular frame (primed),

$$p'_z = \epsilon_0[\alpha E'_z + \beta_2(E'_z)^2 + \dots], \quad (28)$$

where p'_z is the dipole induced by the applied field E'_z . α and β_2 are the molecular linear and first non-linear polarizabilities respectively. If the field E is applied in the laboratory z direction, then $E'_z = E \cos \theta$ when the molecular axis is at an angle θ . The laboratory z component of induced dipole is $p_z = p'_z \cos \theta$ whereupon

$$p_z = \epsilon_0 \beta_2 \cos^3 \theta E^2, \quad (29)$$

where we neglect the linear induced dipole (α) since dipolar effects are stronger with the permanent dipoles in the analysis of §4. Since the macroscopic polarization, P , is the dipole moment per unit volume, we obtain on division by the molecular volume, v , and averaging over angles θ

$$P = \frac{\langle p_2 \rangle}{v} = \frac{\epsilon_0 \beta_2}{v} \langle \cos^3 \theta \rangle E^2 \equiv \epsilon_0 \chi_0^{(2)} E^2, \quad (30)$$

whence the second dielectric constant $\chi_0^{(2)}$ for non-polymeric nematics is defined and is given by

$$\chi_0^{(2)} = \frac{\beta_2}{v} \langle \cos^3 \theta \rangle \equiv \chi_{\text{mol}}^{(2)} \langle \cos^3 \theta \rangle, \quad (31)$$

where $\chi_{\text{mol}}^{(2)}$ is the intrinsic or ideal value obtaining in a sample with perfect dipolar order. In the nematic phase since there is no end-for-end (dipolar) ordering, that is the state of θ is equivalent to that of $\pi - \theta$, then $\langle \cos^3 \theta \rangle = 0$. The centre of symmetry in a nematic fluid of such elements is destroyed by applying a poling field, E_p . In a simple, strongly ordered nematic $\theta \sim 0$ or $\theta \sim \pi$, i.e. molecules can basically be only up or down. It is then easy to show that

$$\langle \cos \theta \rangle \approx \langle \cos^3 \theta \rangle \approx \frac{\mu E_p}{kT}, \quad (32)$$

with the corresponding results for the isotropic state being

$$\langle \cos \theta \rangle = \frac{\mu E_p}{3kT} \quad (33 a)$$

and

$$\langle \cos^3 \theta \rangle = \frac{\mu E_p}{5kT}. \quad (33 b)$$

The rod dipole moment is μ . The result (32) for $\langle \cos \theta \rangle$ gives the conventional nematic susceptibility χ_0 discussed after equation (11). Just as the dielectric response is enhanced by the factor of three from the nematic ordering, so is the non-linear optical response $\chi^{(2)}$ enhanced by a factor of five (in going from equation (33 b) to equation (32)). This is the Ising picture of Williams *et al.* [19], see van der Vorst and Picken [20].

Hence equation (31) gives us the non-linear dielectric susceptibility for conventional nematics as

$$\chi_0^{(2)} = \frac{\beta_2 \mu E_p}{v k T}. \quad (34)$$

The analysis of §4 of the large dielectric response was really a calculation of $\langle \cos \theta \rangle$ when torsional effects induce correlations between teeth. Since in the strong nematic limit $\cos \theta \approx \cos^3 \theta \approx \pm 1$, the calculation of $\langle \cos^3 \theta \rangle$ proceeds in a similar way and we can take over the results. As we suppose a simple case where the nematic is strongly ordered, i.e. $\theta \sim 0$ or $\theta \sim \pi$, the average of $\cos \theta$ or $\cos^3 \theta$ will be given by $\langle \sigma(0) \rangle$ in equation (23)

$$\langle \cos^3 \theta \rangle = \frac{\mu E_p l_0}{k T q} \exp(\beta u) \equiv \frac{\mu E_p}{k T} \frac{N_p}{n}. \quad (35)$$

So the second order susceptibility yields

$$\chi^{(2)} = \frac{\beta_2 \mu E_p l_0}{v k T q} \exp(\beta u) \equiv \chi_0^{(2)} \frac{N_p}{n}, \quad (36)$$

which is exponentially large and is N_p/n times greater than the value for a simple nematic given by equation (34). The enhancement of $\chi^{(2)}$ beyond the value $\chi_0^{(2)}$ is due, as in the dielectric case, to monomers induced to act cooperatively by the nematic field combined with constraints on relative twist. $\chi^{(2)}$ grows exponentially mirroring the growth in distance between twist defects, the second part of equation (35) being so written as N_p/n to emphasize it is the stretches of chain between defects that act together. The ultimate limit of equation (35) is actually $\chi^{(2)} = N_p \chi_0^{(2)}$, the same limit as equation (11) for the dielectric case.

In some respects non-linear optical effects are easier to observe than dielectric effects; there the conduction current obscures the measurement, via polarization current, of the build up of polarization and thus the measurement of χ . In the case of worm polymers it was proposed [8] that the hairpins defects of ordering could be a source of large dielectric response: hairpins represent an abrupt reversal in direction of the worm axis with respect to the nematic field. If each monomer has a dipole pointing in the same sense along the chain backbone then hairpins represent changes in dipole direction, just as twist defects do in the present case. The limit where the chain is stretched with few defects then the limit $\chi \sim N_p \chi_0$ was proposed. The same remark, $\chi^{(2)} \sim N_p \chi_0^{(2)}$ also follows for suitable main chain polymer liquid crystals from the same argument. Unknown to Gunn and Warner the effect of monomers acting cooperatively had long since been observed by Levine and Bethea [21]. They noticed a huge value of $\chi^{(2)}$ in the molecule PBLG which has dipoles and non-linear optic elements pointing in the same direction in each monomer. PBLG is most inflexible and represents an extreme limit of no hairpins.

The example of PBLG has been quoted as an illustration of what is possible when elements of a chain are induced to act cooperatively. In this case it is intrinsic stiffness rather a nematic field and defects that are responsible. It should be noted that the experiment of Levine and Bethea was performed in solution. At higher concentrations the dynamics of response of rigid rods to a poling field is expected [22] to be very slow. Very stiff rods might also be expected to present fewer steric impediments to the anti-ferroelectric ordering expected ultimately in concentrated solution or melts. Antiferroelectric correlation are more difficult to sustain in semi-flexible main chain and comb systems because chains in contact at one point are unlikely to be so at other points.

In contrast to the slow dynamics of rods we expect in combs the dynamics of the build up of the non-linear optic effect $\chi^{(2)}$ in response to the poling field E_p to be the same as the dynamics of the dielectric response. This is again, in terms of the model, because $\sigma^3 = \sigma$ for spin values of $\sigma = \pm 1$. Thus we anticipate three regimes for the characteristic time, τ , of relaxation. For main chain nematics other mechanisms for dynamical response, faster than that for rigid rods, can be envisaged. They do not involve the motion of the whole molecule at one time, as is required for rigid rods, but involves diffusion of conformational defects. In any case side chain or main chain polymer liquid crystals are expected to avoid the difficulties associated with extending the PBLG work to very high concentrations.

8. Conclusions

We have proposed that a particular molecular geometry in comb polymer liquid crystals coupled to strong nematic order can provide a mechanism by which we can have strong dipolar (dielectric) effects in a quadrupolar medium. This is the analogue of the hairpin mechanism proposed for main chain polymers. A defect mediated response leads to static dielectric susceptibilities of an activated form which become very large, eventually scaling like the molecular weight. A large non-linear optic effect is also discussed. The dynamical response is calculated and turns out to be ultimately very slow, scaling like the square of the molecular weight when defect diffusion over the length of the chain is the dominant process. It is hoped that the chemical structures necessary for this unusual behaviour can be soon synthesised.

Dr. J. Deutsch also independently conceived of twist defects and helped clarify ideas of torsion. M. W. thanks Professor H. Finkelmann and Dr. R. W. Richards for illuminating discussions about the synthetic chemistry of comb polymers and Dr. M. E. Cates for help in visualizing the stereochemistry involved in creating twist.

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