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Invited Lecture. Defects in small-molecule and polymeric nematics

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Invited Lecture

Defects in small-molecule and polymeric nematics

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After a reminder of the essential topological characters of defects in phases with nematic symmetries, a review is given of the observations of textures and defects in polymeric liquid crystals. Emphasis is placed on (a) the diversity of these observations according to the type and character of the polymer, and (b) the differences with small-molecule liquid crystals. However, the topological characters are common. The differences have to be explained in terms of molecular configurations. In this respect, we develop some physical consequences of the scarcity of chain ends, in particular a possible segregation and ordering process that relaxes strong splay deformations and that occurs in the cores of disclinations with a wedge character. After having discussed models of isolated disclinations, we investigate the possibility of the thermodynamical stability of sets of disclinations. We show that this problem has some analogies with the classical Flory–Huggins theory of the stability of polymers in solution, the disclinations playing here the role of the polymeric chains. Finally we indicate the existence of other features specific to polymeric nematics, apart from the question of chain ends, such as the correlations between chains and the related phenomena of frustration.

1. Introduction

Defects and textures in calamitic small-molecule liquid crystals are now well understood, at least as far as their static properties are concerned, and their dynamical properties are today the subject of intense studies [1]. However, the recent synthesis of a large number of compounds possessing completely different architecture and displaying mesogenic properties, such as discotic, bowlic (pyramidic), sanidic and polymeric molecules, offers new prospects for research [2]. We shall restrict ourselves here to some aspects of the question of defects in *thermotropic* and *lyotropic main-chain polymer nematics* (see figure 1). A brief revision of the main concepts that have emerged from the study of small-molecule liquid crystals will be given first in order to illustrate the similarities and differences with polymers. Then we shall describe some of the results concerning the observations of defects in polymers; most of these observations were made with the help of the polarizing microscope. They are remarkable, not only because of the differences they display with respect to the usual liquid crystals, but also because of the diversity they show in polymers of different nature.

The classification of the observations of defects in liquid-crystal polymers should obviously depend on factors such as the flexibility of the chains, the nature of the interactions that dominate the emergence of liquid-crystalline order, the molecular weight, the volume fraction in the case of lyotropics, etc. Our enumeration indicates clearly the nature of the problem: all of these factors refer to molecular properties. This is indeed one of the fascinating features of the study of defects in these

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Figure 1. The architecture of a main-chain mesogenic polymer is made of successive rigid and flexible segments; the monomer is generally mesogenic.

materials—that it relates so directly to local properties, which, as is well known, are quite difficult to grasp in the usual molten polymers or in polymer solutions. Such a situation does not occur, as a matter of fact, in small-molecule liquid crystals. Most of the observations made so far on defects and textures in liquid-crystal polymers have used polarizing microscopy; the resolution of this instrument is, of course, insufficient to offer a direct understanding of molecular properties , and much is expected from the development of methods that go to scales finer than the optical scale, such as freeze fracture or electron microscopy, although a number of interesting problems can already be solved through optical studies. Furthermore, we are far from being able to properly describe (i.e. classify) all of the various kinds of defects and textures observed (in this respect, our summary of the known observations in §3 is quite incomplete, which reflects our personal present knowledge of the subject, and demonstrates the difficulties encountered in combining results of so dispersed a nature), and still less able to relate them to the present theories of nematic order in liquid-crystal polymers.

It is in order, at this stage, to give a brief overview of these theories, which are usually divided into rod-like model theories [3, 4] and worm-like model theories [5–8]. However, the present status of the comparison between experiment and theory is so much in its infancy that such a review could be more confusing than helpful. We have therefore adopted the point of view of classifying the observations according to the nature of the defects (their strength, their contrast, their cores, and the types of deformation they are attended by). We summarize the corresponding situation for small-molecule liquid crystals in §2. From that point of view, the questions of the Frank constants K_1, K_2, K_3, of the bulk compressibility E^{-1}, of the density of chain ends, and of their kinetics of displacement seem to be of some importance. Some of these questions have already been raised by Meyer [9]. Furthermore, we shall see that the relative roles of the elastic terms (the K_i and E^{-1}) and of the entropic terms is of importance. Concerning the kinetic processes of chain ends in the displacement of disclinations, this is a problem that is far from being elucidated, and the thermodynamic (meta)stability of the observed textures must therefore be considered critically.

In rod-like polymer situations [9] theory and experiment agree, giving a K_2 coefficient that has a value of the same order as in small molecule liquid crystals, a K_1 coefficient of the order of $3K_2$, and a K_3 coefficient that is the largest and probably scales with the persistence length (it diverges if the molecule is an infinite rod). In thermotropic media K_2 is still small, and K_3 probably scales in the same way, but the requirement of deformation at constant density forbids splay deformation (K_1 is infinite) if the chain length is infinite: if any splay deformation is necessary, it has to be achieved by hair-pins [10] (see figure 2). Hair-pins of both signs exist in the undisturbed liquid crystal, and might also play a role in the dynamic properties [11]. For chains of finite length, splay deformation can be achieved by a gradient of the density of chain ends (see figure 3); the corresponding splay constant ΔK_1 can be estimated in a model in which the free chain ends are treated like an ideal gas [9] of

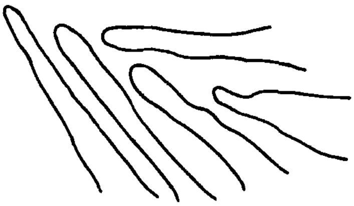


Figure 2. Hair-pins of the same sign create splay deformation.

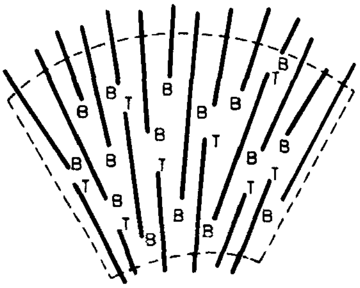


Figure 3. A gradient of chain ends creates splay deformation (redrawn from [9]).

top, t, and bottom, b, particles:

$$\Delta K_1 = \frac{kT}{4d}\frac{L}{d}. \tag{1}$$

Such a model, which allows a mass density that does not vary when the average density ϱ of chain ends of one sign fluctuates ($\varrho \approx (Ld^2)^{-1}$, with d the mean transverse distance between molecules) is valid for any splay deformation $|\operatorname{div} \mathbf{n}|$ smaller than $1/L$. If the splay deformation is larger, we must use a model where the mass density does vary on a small scale, at the expense of some elastic energy and perhaps production of pairs of hair-pins of opposite signs. But if the splay deformation is very large, we might have to consider the possibility of *segregation* and *ordering* of chain ends, a process that leads to an elastic energy smaller than that determined from equation (1) and that depends on the type of ordering in the cluster. This is probably what happens in the disclination cores, as we shall argue.

In polymers the stretching and longitudinal compression of the chains have to be described by a compliance E^{-1}, which must be taken into account in the total elastic energy [12], not only in the infinite-chain limit, as just alluded to, but even for finite chains, as soon as the chain length is larger than

$$\lambda_s = 2\pi(K_1/E)^{1/2} \tag{2}$$

provided, of course, that the persistence length λ_p is also larger than λ_s. If we assume that the deformation created by a free chain end is equivalent to that of an edge dislocation loop of radius d and Burgers' vector d, located in a plane perpendicular to the chain (see figure 4), we find that its elastic energy scales like $Kd(d/\lambda_s)^2 \approx Ed^3$. With $E \approx 10^7\,\mathrm{erg\,cm^{-3}}$ and $K_1 \approx 10^{-6}\,\mathrm{dyn}$, we find $\lambda_s \approx 200\,\text{Å}$ and $Ed^3 \approx 4 \times 10^{-3}(d/\lambda_s)^2\,\mathrm{eV}$, a quantity that is rather small. Therefore entropy factors should always be taken into consideration, although they could be less important at low temperatures, or when E^{-1} is small and d large, or if the pairing of two opposite chains

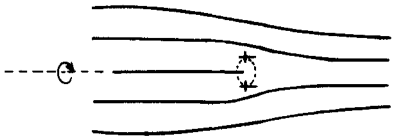


Figure 4. The dislocation model of a free chain end.

ends decreases not only the elastic energy, but also the chemical energy (chemical bonding).

We shall not exclude the possibility of the existence of liquid-crystal polymers in which $\lambda_p < \lambda_s$. This class of system would be extremely flexible, by definition; hair-pin production would therefore be the favoured mechanism of relaxation of the splay deformation.

2. Small-molecule liquid crystals: defects and textures, a brief account

The question of defects and textures can usually be treated under two headings [1, 13]: (a) their classification with regard to the criterion of *topological stability*, which is related to the symmetry properties of the order parameter; and (b) their material-dependent properties, which include their *energetic stability* and the nature of the *order in the core*.

2.1. *Topological stability of defects in nematics*

In *uniaxial nematics*, the *line defects* are of two types; the lines of half-integral strength $S = \pm\frac{1}{2}, \pm\frac{3}{2}, \ldots$, about which the director rotates by an angle of $2\pi S$ and which are topologically stable, and the lines of integral strength $S = \pm 1, \pm 2, \ldots$, about which the director rotates by an angle $2\pi S$ and which are not topologically stable. Specifically, this means that, for an integer line, the director can escape into the third dimension (see figure 5), leaving the core non-singular. If this process occurs (it is material-dependent), the integral lines show up as a blurred contrast under the

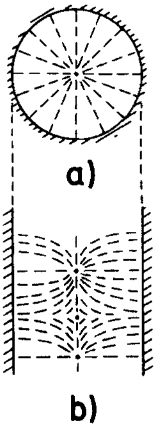


Figure 5. Model of a non-singular core for a line of integral strength in a uniaxial nematic: (*a*) transverse cut; (*b*) meridianal cut with escapes along two opposite directions, and a singular point at the transition between the two escape modes. Radial geometry for the director.

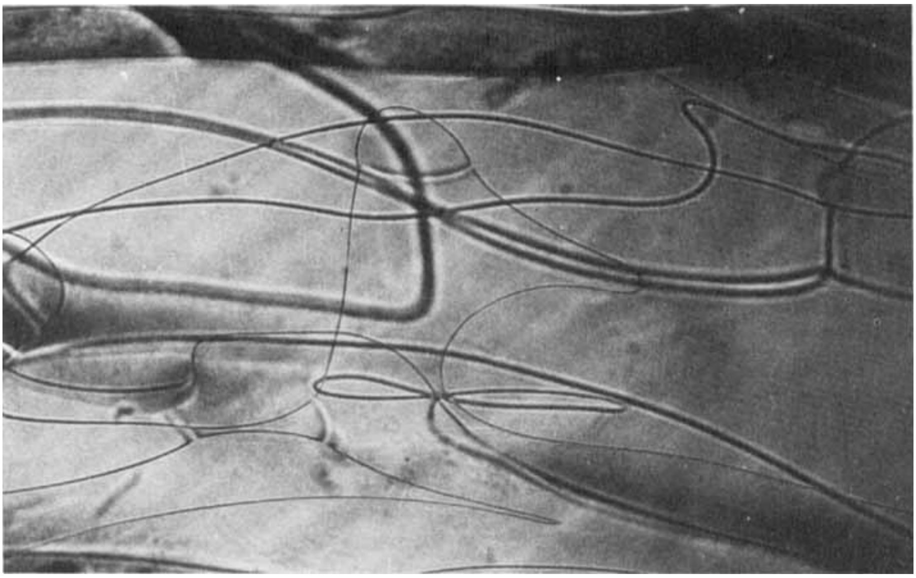


Figure 6. Thicks and thins in a typical small-molecule liquid crystal (polarizing microscopy). Thread texture.

polarizing microscope and appear *thick*, while the half-integral lines appear *thin* because the core region scatters light strongly. All of the half-integral lines are topologically equivalent (it is possible to smoothly transform half-integral line of any strength into a line of opposite strength—for a beautiful illustration of this topological phenomenon see [14]). The same is *a fortiori* true for integral lines. S lines combine and merge according to the rules of addition of the numbers S (see figure 6)—that is, since S is defined mod 1, according to the rules of multiplication of the abelian group with two elements $\mathbb{Z}_2$ [15]. For more details see the approach to topological stability in the homotopy theory of defects [13, 15].

It is usual to make a distinction between *wedge lines*, which are parallel to the rotation vector, and *twist lines*, which are orthogonal to it. Wedge lines are visible in schlieren textures, and twist lines in thread textures (see figure 6). Smoothly transforming a wedge S line to a wedge $-S$ line requires passage through a twist $|S|$ line (see [14]). *Point defects* can be easily visualized as originating on integral lines at the encounter of two opposite escapes (see figure 5 (*b*)).

While the classification and algebra of lines and points in uniaxial nematics [15] is quite easy to grasp physically, this is not the case for defects in *biaxial nematics* and *cholesterics*, which are both locally defined by three directors forming a tripod. In brief, line defects (in both cases) are classified by the quaternion group Q and combine and merge according to the rules of multiplication of this group [16]. However, lines of half-integral strength can still be defined [1, 17] (there are three sets of such lines, each one corresponding to one of the directors), but lines of integral strength divide into two classes: those of strength $S = 2n + 1$ are now topologically stable, those of strength $S = 2n$ are not. Therefore only the latter can appear as non-singular in biaxial nematics. Additional important differences of topological origin between biaxial nematics and uniaxial nematics are (a) the absence of singular points in biaxial nematics (they are not topologically stable), and (b) the obstruction to crossing of two mobile $S = \pm\frac{1}{2}$ lines that do not belong to the same director. None of those properties has ever been used up to now to characterize a biaxial nematic [17].

2.2. *Material-dependent properties in small-molecule liquid-crystal uniaxial nematics*

The energy of a *singular line* of strength S is

$$W = \alpha\pi K_\alpha S^2 \ln\frac{R}{r_c} + w_c, \tag{3}$$

where α is some geometrical coefficient, K_α is some combination of the Frank constants K_i ($i = 1, 2, 3$) R is a typical macroscopic length (a distance between defects), r_c is the size of the region where the order parameter is broken (the core) and w_c is the core energy.

The energy carried by the deformation around a *non-singular line* (necessarily of integral strength) is

$$W = \beta 2\pi K_\beta S \tag{4}$$

and does not depend on any length (the deformation spreads over all of the available space); of course, the core energy vanishes; K_β is a combination of Frank constants, and β is a geometrical coefficient.

It is clear at first sight that any line of *integral* strength will favour a non-singular core, if $K_\beta \gg K_\alpha$. In small-molecular liquid crystals where all of the Frank constants are of the same order of magnitude, this inequality is not satisfied and integral lines are always observed; most often they form Friedel nuclei, and carry singular points. According to Dzyaloskinskii [18], the only wedge, $S = \pm 1$, lines that are stable with respect to three-dimensional perturbations have a circular or a radial geometry; for a circular geometry the line energy is precisely [19]

$$W = \pi\left(K_2 + K_3\frac{k}{\sin k}\right), \quad \sin^2 k = \frac{K_3 - K_2}{K_3}, \tag{5}$$

when assuming $K_3 > K_2$. For a radial geometry we have

$$W = \pi\left(K_1 + K_3\frac{k}{\tanh k}\right), \quad \tanh^2 k = \frac{K_1 - K_3}{K_1} \quad (K_1 > K_3), \tag{6}$$

$$W = \pi\left(K_1 + K_3\frac{k}{\tan k}\right), \quad \tan^2 k = \frac{K_1 - K_3}{K_1} \quad (K_1 < K_3). \tag{7}$$

It is quite plausible that, in the case of equation (6) for example, the disclination might favour a pure circular disclination, with a singular core in the centre, if K_3 is not much smaller than K_1. In order to decide which possibility will be realized, we need only compare $\pi K_3 \ln(R/r_c) + w_c$ and the value in equation (6). Similar comparisons can be made for other situations depicted here and for $S = -1$ lines. We see that the result depends on the nature and size of the core and on the anisotropy of the Frank coefficients. But note immediately that if singular integral lines are favoured, they will have a strong tendency to split into half-integral lines, since the energy now varies like S^2 (see equation (3)). Therefore we expect that in all cases when the Frank constants show a large anisotropy, and if there exist core arrangements of not too prohibitive an energy, half-integral (thin) lines will be much more numerous than integral ones, and that those integral lines will be singular. This is obviously not the case in small-molecule nematics, where non-singular integral lines (and singular points) are predominant over other defects.

We shall not discuss here the question of the core of disclinations in small-molecular liquid crystals (see e.g. [1, 13]), since we shall treat it for liquid-crystal polymers. But let us quickly mention point defects; their energy scales like $K_\gamma R$, where K_γ is a suitable Frank-constant coefficient, and R is a typical macroscopic length. In the isotropic-elasticity case ($K_1 = K_2 = K_3$) the integral of the Frank free energy does not diverge: in other words, there is no *mathematical* core, and the physical core is of atomic dimensions, $w_c = 0$. This is not so in the anisotropic case, when it is necessary to introduce a cut-off for the free-energy integral, i.e. a physical core. This interesting phenomenon has not been studied thoroughly.

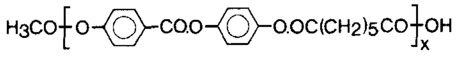
3. Some aspects of defects and textures in polymer nematics

We discuss a certain number of observations according to the concepts just defined.

3.1. *Thins and thicks*; *singular points*

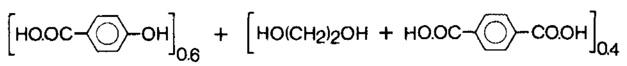
Most of the observations point to the predominance of *thin* line defects, which are $S = \pm\frac{1}{2}$ line defects, or *singular* $S = \pm 1$ lines; this is in agreement with our discussion for anisotropic media. Thick lines are seldom observed.

$S = \pm\frac{1}{2}$ are clearly documented in tobaco mosaic virus (TMV) nematic solutions (freeze-etching observations [20]), where K_3 is much larger than the other Frank constants, and in the C_5 polyester [21, 22]



x ≈ 24

where it is K_1 that is by far the largest Frank constant [23], as well as in certain copolyesters [23, 24, 26], for example of the type designated B-ET (supply by Eastman Kodak as X 7G):



They have also been observed in the schlieren texture of the same copolyesters.

In the C_5 polyester, *thick* integral lines have been observed—but extremely infrequently; in fact their presence has helped to identify the thin lines as being of the half-integral type [21]. Integer lines have been observed in X7G under their thread-like shape [26]; when they are in association with half-integral lines, they obey the algebraic laws required by their merging (see figure 7). Integer lines also form schlieren textures, which are especially conspicuous when the sample is frozen to the nematic state from the isotropic phase [24, 25, 27]. This behaviour seems to be characteristic of the copolyesters cited here. It is difficult to assess without doubt that the integral lines observed in the copolyesters are non-singular. Although their contrast under the polarizing microscope is quite fuzzy (as it should be for any non-singular integral line), it does not disappear completely when the polars are removed (as it would, in principle, if they were non-singular).

Thin threads have been observed [28, 29] in lyotropic solutions (in sulphuric acid) of semiflexible polymers (polyazomethines, polyterephthalamides, etc.) and in a nematic aromatic copolyester [30] of a remarkably high molecular weight and low

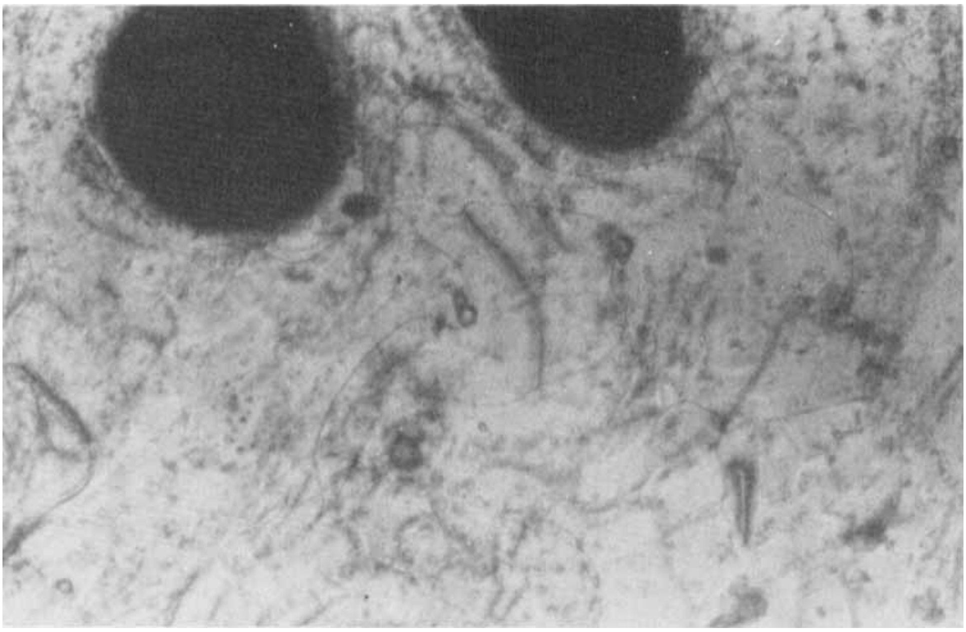


Figure 7. Half-integer and integer lines in the copolyester X7G (see text). Polarizing microscopy. Courtesy of F. Lequeux.

viscosity ($M_w \simeq 220\,000$). These lines might be singular integer lines, as is claimed by the authors. However, direct measurements of the strengths are all lacking, Skoulios *et al.* [28] have argued that K_3 is very large in their sulphuric acid solutions of semi-flexible polymers, and have subsequently devised a model of pure radial integer lines.

Singular points have never been reported in nematic polymers. According to our discussion (concerning the relationship between singular points and integral lines), this might indicate that most of the *thin* lines that are observed are not integral lines.

It is interesting to notice that singular points have not been reported either in those copolyesters where integral and half-integral lines are both visible. It has been claimed by Viney *et al.* [31] that these copolymers are biaxial nematics. This interpretation is perfectly consistent with the present observations of defects: singular points are topologically unstable in biaxial nematics, and non-singular integral lines should have a strength that is an even integer ($S = \pm 2, 4, \ldots$). It is quite possible that, by an extension of the arguments we have developed for the anisotropic uniaxial nematics, those lines are not *energetically* stable, in either their singular or non-singular manifestations, in biaxial nematics.

Samples of *low*-molecular-weight C_5 polyester exhibit textures and defects that are typical of small-molecule liquid crystals [21].

3.2. *Cores of disclinations*

It is evident that, since the order parameter is broken there, the cores of defects should be privileged regions for the presence of chain ends and even for their segregation. In small-molecule liquid crystals [13] the core of disclinations is at least of molecular size, and its radius increases with temperatures, but systematic experimental studies are lacking. We want to comment on two observations of cores in liquid-crystal polymers.

The freeze-fracture experiments of Zasadzinski *et al.* [20] have shown that the $S = \frac{1}{2}$ twist-line cores are of a molecular size in TMV nematic solutions: the virus reorients abruptly by 90° at the core, remaining in the plane of the disclination line. The wedge disclination core is several virus lengths in diameter and much more disordered, the viruses twisting out of the plane perpendicular to the line and into the direction along the disclination line. The twist lines seem more frequent than the wedge lines, which can be related to the smaller value of K_2 (compared with K_1 and K_3, which is the largest Frank coefficient).

The polarizing-microscope observations (see figure 8) of Mazelet *et al.* [22] of the C_5 polyester reveals that in free droplets the cores of the wedge parts of the half-integral lines are very large; the $S = \pm\frac{1}{2}$ and the $S = -\frac{1}{2}$ cases differ widely. In the first the molecules seem to stay in the plane perpendicular to the line, and the chain ends segregate in the core, while the off-core geometry implies essentially bend-and-twist deformation (K_2 is small, K_3 is larger than K_2 but much smaller than K_1). A schematica model is given in figure 9 (*a*). The $S = -\frac{1}{2}$ cores show a typical three-fold symmetry with three spikes emerging from the core; these spikes have been interpreted as three wall-like regions where the chain ends segregate and twist out of the plane perpendicular to the line and into the direction parallel to the line; in the central part of the core itself the molecules are probably along the core (see figure 9 (*b*)). These models are inferred from the contrast observed at large-scale deformation, but the calculations they suggest seem to corroborate them to some extent.

For $S = -\frac{1}{2}$ the basis of the calculation is the Nityananda–Ranganath two-dimensional anisotropic model [32], modified slightly to take into account the vertical components of the director. One of the interesting aspects of this model is that it predicts that the motion of the *configuration* of the $S = -\frac{1}{2}$ requires only a change of direction (by twist) of the molecular directions. This motion can be easy, which might explain the high mobility of these wedge $S = -\frac{1}{2}$ lines.

We discuss in more detail the $S = +\frac{1}{2}$ lines, for which we assume a very special type of segregation of free chain ends in the core. The model is inspired by the geometry of crystals bent under the effect of a density of dislocations, as devised by Nye [33] a long time ago, and we illustrate it in two dimensions (see figure 10). The polymer chains are represented in this figure by half straight lines, which are the analogues of the atomic rows in Nye's model; *d*, the mean distance between chains, plays the role of the lattice parameter in the transverse direction; the chain ends are dislocations of the lattice. Consider now a closed circuit ABCD, in which we have a two-dimensional splayed configuration with splay density

$$|\operatorname{div} \mathbf{n}| = \frac{1}{r},$$

where r is the radius of curvature of the normals to the polymer chains. The quantity

$$\delta = \frac{\mathrm{AB} - \mathrm{CD}}{d}$$

measures the number of chain ends of the same sign, in the area bound by ABCD, unpaired with chain ends of the other sign; this geometry conserves the mass density. Consider now a circuit of infinitesimal side dr, we find that the surface density of chain ends obtained from this relation is $\varrho_s(r) = 1/dr$; the corresponding volume density is

$$\varrho(r) = \frac{1}{d^2 r}. \tag{8}$$

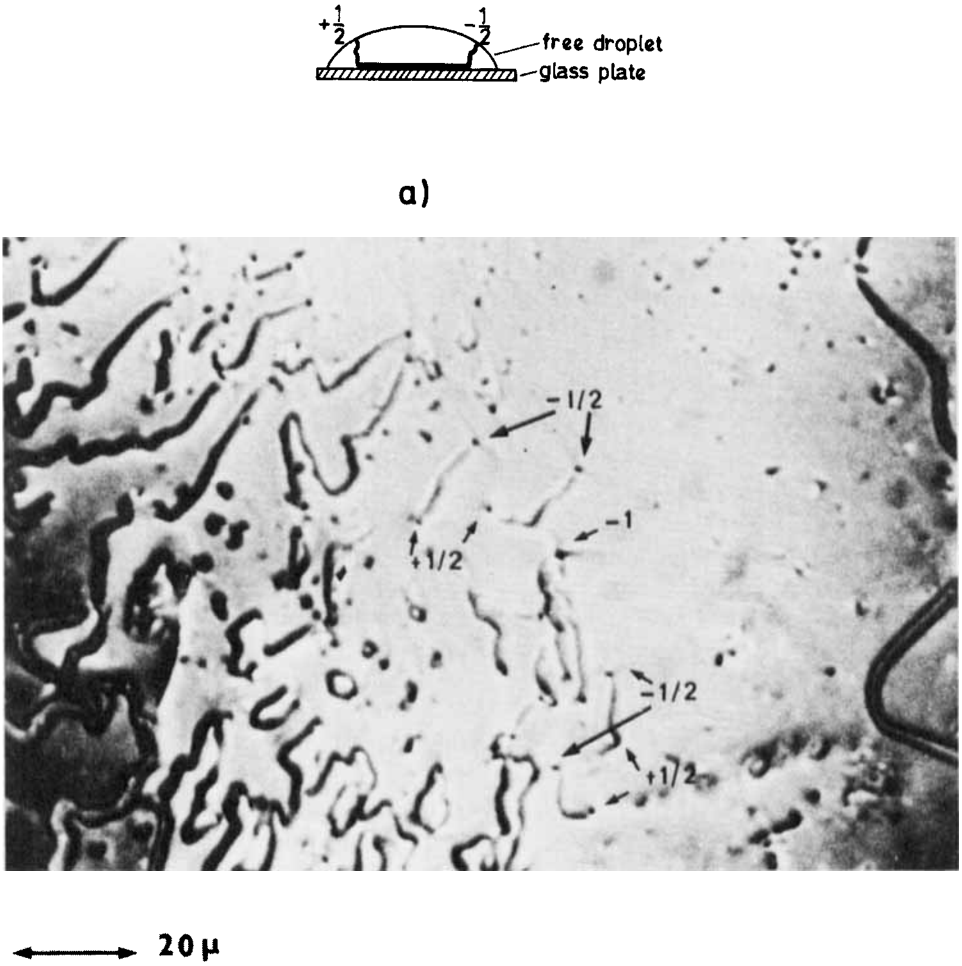


Figure 8. Half-integral lines in a free droplet of the C_5 polyester (see text). (*a*) geometry; (*b*) polarizing microscopy. Courtesy of G. Mazelet-Parizé.

The same calculation can be made for a spherical cluster, with a radial distribution of chains; we now have $|\mathrm{div}\,\mathbf{n}| = 2/r$. The circuit we now have to consider is made of two elements of a sphere, of areas Ωr^2 and $\Omega(r + dr)^2$, subtended by the same solid angle Ω, linked by elements of planes along the radii. The condition of conservation of mass density now requires that

$$\varrho(r) = \frac{2}{d^2 r}, \tag{9}$$

i.e. in fact the same condition as in equation (8), since we have in both cases

$$\varrho(r) = \frac{1}{d^2}|\mathrm{div}\,\mathbf{n}|. \tag{10}$$

This equation can therefore be considered as universal; it relates splay to the density of chain ends of a given sign when the conditions of better clustering (i.e. with conservation of the mass density) are achieved.

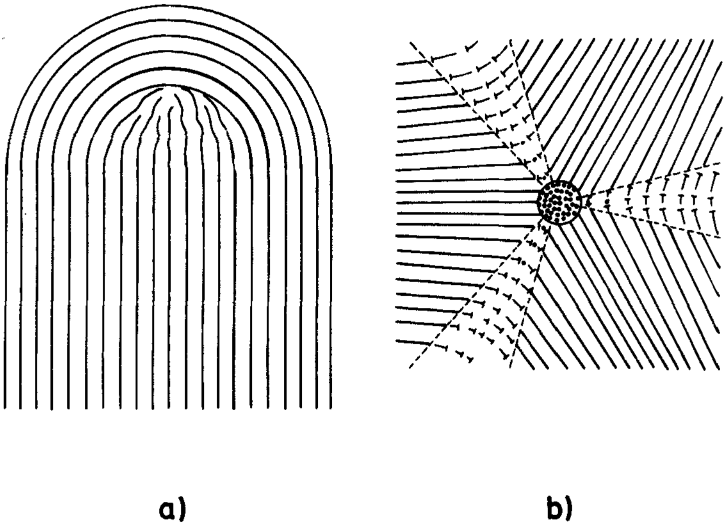


Figure 9. Schematic models for (*a*) a wedge $S = +\frac{1}{2}$ disclination; (*b*) a wedge $S = -\frac{1}{2}$ disclination in a C_5 polyester ($K_1 \gg K_3 > K_2$). Chain ends segregate either in the core in (*a*) or along three quasi-walls in (*b*).

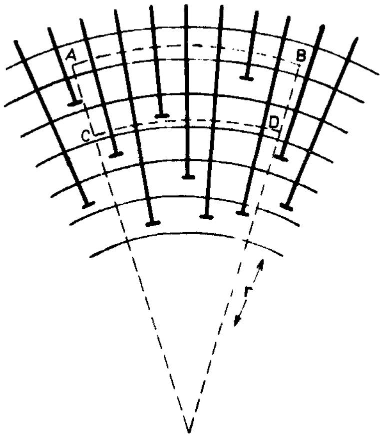


Figure 10. A bent two-dimensional crystal where the bending energy is relaxed by a suitable density of dislocations.

Note at this stage that such clusters cannot be larger than *L*, if the chain ends of opposite signs are free (i.e. contribute to splays of opposite sign). But, of course, opposite chain ends can also be locked in pairs, an effect that leads to a larger effective *L*. Note also that if the chains are polydisperse, the regular arrangement of the chain ends of a given sign in the cluster, as described here, does not yield, fortunately enough, a regular arrangement of the other ends of the same chains. This is the situation we shall assume to exist; the opposite case, with monodisperse chains, would certainly lead to a situation of a quite different physical nature.

We expect the cylindrical arrangement (as in equation (8) for a disclination line) to be of lower energy than the spherical one (as in equation (9) for a singular point). This property results from at least three causes: (a) the density of chain ends is larger in the second case; (b) for the same given volume, the surface that separates the cluster from the normal region is larger in the spherical volume; this surface carries a transition wall of some energy, although this energy is small compared with the other contributions; (c) the elastic energy of an *isolated* free end is of order $\varepsilon = Ed_s^3$, to which must be added a chemical energy that we do not take into account since it does not depend on the neighbourhood of the chain. In a cluster of the cylindrical type the energy, including interactions between chain ends, is of order $(Ed^2/4\pi)\ln(l/d)$ per unit length of cylinder (i.e. for $1/d$ chain ends). This is the energy of a dislocation of Burgers' vector d, located at a mean distance $2l = \langle d\varrho(r)\rangle^{-1/2}$ from its neighbouring dislocations, with a core radius of order d. A simple calculation yields

$$\langle\varrho(r)\rangle = \frac{1}{\pi r_c^2}\int_0^{r_c} 2\pi r\varrho(r)\,dr$$

$$= \frac{2}{d^2 r_c},$$

i.e.

$$l \approx (dr_c)^{1/2}, \tag{11}$$

where r_c is the size of the cluster (and the core radius of the disclination). Since the total number of such dislocations in a cluster is $\frac{1}{2}d\pi r_c^2\langle\varrho(r)\rangle = \pi r_c/d$, for a disclination of strength $S = +\frac{1}{2}$ the total energy per unit length of the cylinder can be estimated as being of order

$$w_c = \frac{1}{2}\frac{\pi r_c}{d}\frac{E}{4}\frac{d^2}{\pi}\ln\frac{r_c}{d}$$

$$= E\frac{dr_c}{8}\ln\frac{r_c}{d} \tag{12}$$

(an exact calculation for a radial $S = +1$ gives

$$\left. w_c = \frac{Edr_c}{4(1-\nu)}\ln\frac{r_c}{ld}\right).$$

For the spherical case (singular point) we expect the total energy per chain end to be proportional to El'^3, where $l' = \varrho^{-1/3}$. The total energy of a radial cluster of size R_c is therefore $\frac{4}{3}\pi ER_c^3$, which is larger by a factor of about $\pi L/d$ than the ground-state energy ($\varepsilon \approx Ed^3$ per chain end), while the energy of the cylindrical region involves a factor of about $L/4r_c$, which, as we shall see, is always much smaller than $\pi L/d$ and even smaller than unity.

Consider, therefore, an isolated disclination, located at some distance R from another; the total energy of the line involves a core energy w_c (see equation (12)); an elastic energy $\frac{1}{4}\pi K\ln(R/r_c)$, where K is some Frank constant including K_2 and K_3 (of order $\frac{1}{2}(K_2 + K_3)$ presumably); a negative contribution, coming from the fact that $\pi r_c/d^2$ previously free ends (per unit length of line) are now involved in the dislocations of the core, and which is of the form $-\varepsilon\pi r_c/d^2$. The total energy of the line is therefore

$$W = \frac{Edr_c}{8}\ln\frac{r_c}{d} + \frac{\pi K}{4}\ln\frac{R}{r_c} - \frac{\varepsilon\pi r_c}{d^2}. \tag{13}$$

We must seek the value of r_c that minimizes W:

$$\frac{\partial W}{\partial r_c} = \frac{Ed}{8}\ln\frac{r_c e}{d} - \frac{\pi K}{4r_c} - \frac{\varepsilon\pi}{d^2}. \tag{14}$$

This expression vanishes only for ε small enough compared with $\frac{1}{8}Ed$. This is the situation that we assume here. The core is large in these conditions (of order $K/Ed \approx \lambda(\lambda/d)$). The positiveness of $\partial^2 W/\partial r_c^2$ ensures that such a situation is (meta)stable. The total energy at equilibrium is

$$\begin{aligned} W_{eq} &= \frac{\pi K}{4}\ln\frac{Re}{r_c} - \frac{Edr_c}{8} \\ &\approx \frac{\pi K}{4}\ln\frac{R}{r_c}, \end{aligned} \tag{15}$$

which is positive (by construction) but quite small. Here $\lambda^2 = 4\pi^2 K/E$.

If ε is larger than $\frac{1}{8}Ed$ then the question of the stability of the disclination is of a very different nature. The chain ends tend to segregate spontaneously, as long as the loss in entropy of the free-end gas is not too large. This is the situation that we contemplate in §4. Another possibility is that twist disclinations are more favoured than wedge disclinations, as observed in TMV solutions [20]. But we have no way to theoretically attack this problem of the nature of the core as a function of the type of defect—wedge or twist—with our present tools.

The large core radius that we have obtained might fit the observations made in a thermotropic material like the C_5 polyester, where d is of order a few Ångströms and λ a few tens of Ångströms. Equation (14) can also be used for a lyotropic polymer, and yields a smaller (d is still the distance between the chains) but still large core radius.

3.3. *Textures*

Individual defects in liquid-crystal polymers show large differences with individual defects in small-molecule liquid crystals of the same symmetry. This is also the case for their textures.

Starting from the isotropic high-temperature phase, the nematic phase that first appear is usually very disordered at the micrometre level, in a sample of a few tens of micrometres thick. This disordered phase relaxes very slowly when the temperature is kept constant. It yields a schlieren texture of a very fuzzy nature in copolyesters, quite often made up of integer lines [24, 27, 30]. In polyesters thin lines appear after some time, but they are more readily obtained when the sample is prepared directly in the nematic phase, by introducing the material by capillarity between the glass plates [21].

Apart from these schlieren textures, two well-characterized types of texture are currently distinguished in liquid-crystal polymers: (1) a threaded (or line) texture made up of individually recognizable disclinations; and (2) an ill-defined texture probably made up of an entanglement of disclinations, and which, when relaxing, gives rise to the first texture. Such textures have been observed and described in detail in lyotropic nematics of the polyazomethine or polyamide type in sulphuric acid [28, 29] and in some copolyesters [34], where the ill-defined texture is designated a worm-texture. The relaxation time τ of the ill-defined texture (which can be obtained by shearing or compressing the specimen) has a remarkable behaviour. It does not seem to depend on any parameter other than the density ϱ of free chain ends and, in thermotropics, on the temperature; for example, it does not depend directly on the viscosity. τ increases when $\varrho \approx (Ld^2)^{-1} \approx \phi/M$ decreases. This behaviour has been critically tested in lyotropics, in which a threshold ratio $(\phi/M)_c \approx 10^{-5}$ has been discovered, below which τ becomes so long that the ill-defined texture does not disappear in the time of an experiment. This is explained tentatively by Millaud *et al.* [28] as being due to a longer time of diffusion of the free ends towards the cores of the defects when ϱ is smaller. But it might well be that below $(\phi/M)_c$ the ill-defined texture is thermodynamically stable. We shall try to discuss this hypothesis in the model presented in §4. In thermotropics the behaviour of τ has been tested with respect to M, the viscosity, and the value of the applied shear. Worm textures that do not decay in the course of time have been observed for large M. Furthermore, τ increases with decreasing temperature, a fact that seems to indicate that the ill-defined texture has to be activated from the line texture. Shear goes in the same direction as temperature, in this respect, since it provides the energy necessary to overcome some barriers. In fact, when shear is increased and then the worm texture (which becomes optically isotropic when the shear is very large, since the defects, which multiply under increasing shear, become so small) is allowed to relax, it transforms to a striated texture perpendicular to the direction of shear. This phenomenon has been observed in copolymers [34, 35] as well as in solutions of semiflexible polymers like PBLG [36] and HPC [37] (hydroxypropylcellulose), which are cholesteric.

4. Cooperative effects between disclinations

We now investigate the stability of sets of disclinations by introducing entropy terms. We shall restrict attention to a two-dimensional model, in the sense that we consider parallel disclinations at a mean distance R. This simplifying hypothesis affects mainly the configurational entropy of the lines, which should be greater in a three-dimensional calculation, therefore enhancing the tendency to stability. However, we shall superimpose on this pure two-dimensional model a phenomenological length L_0, which measures some persistence length along the disclinations, or some mean radius of curvature of the lines.

4.1. *The energy and entropy terms*

Let c be the proportion of free ends that segregate along the disclination cores. We do not care about numerical factors of the order of 2 or $\frac{1}{2}$ coming from the fact that in reality we should consider disclinations of both sign. The total line length per unit volume is

$$\frac{1}{R^2} = \frac{cd^2}{2\pi r_c v_c}. \tag{15}$$

R is again the mean distance between disclinations and $v_c \approx \pi L d^2$ is the volume occupied by a chain. The energy of the disclinations (irrespective of entropy) is the sum of the core energies and of the line energies:

$$\begin{aligned} f_{el} &= \frac{1}{R^2} W \\ &= \frac{cd^2}{2\pi r_c v_c}\left(\frac{\pi}{4} K \ln \frac{2\pi v_c}{c r_c d^2} + \frac{E d r_c}{8} \ln \frac{r_c}{d} - \frac{\varepsilon \pi r_c}{d^2}\right), \end{aligned} \tag{16}$$

where we have taken care to introduce the *gain* in energy due to the fact that some proportion of chain ends are no longer free. With regard to the entropy contributions, they are of three origins: first, the variation of entropy that comes from the fact that the ideal gas of free ends now contains $N(1 - c)$ particles, $N = V/v_c$ for a volume V;

secondly, the configurational entropy of the disclinations; thirdly, the excluded volume due to the cores of radius r_c.

The first contribution is calculated by assuming that the total number of states available to the N (or $N(1 - c)$) particles in volume V (whose variation brings a negligible contribution) is V/v_e where v_e is the effective volume of a free chain end, and is of order d^3 at least, but its precise value does not matter. We then find

$$\Delta S^{(1)} = -Nc \ln\left(\frac{v_c}{v_e} e\right) - N(1 - c)\ln(1 - c), \tag{17}$$

i.e. a free-energy density

$$f_e^{(1)} = \frac{kT}{v_c}\left[c \ln\left(\frac{v_c}{v_e} e\right) + (1 - c)\ln(1 - c)\right]. \tag{18}$$

It is noticeable that it is the *positive* term $c \ln(v_c e/v_e)$ that then prevails. It compensates the ε term in f_{el} and must be larger than or of the same order of magnitude as the ε term in the nematic phase.

The entropy term due to the disclination lines is calculated in the framework of a model for a two-dimensional ideal gas, with $\Sigma/\pi r_c^2$ states available in a surface of area Σ, and Σ/R^2 particles. This yields a number of different states equal to

$$\left(\frac{\Sigma}{\pi r_c^2}\right)^{\Sigma/R^2} \frac{1}{(\Sigma/R^2)!},$$

i.e. an entropy term

$$S^{(2)} = \frac{\Sigma c d^2}{2\pi r_c v_c} \ln \frac{2 v_c e}{c r_c d^2} \tag{19}$$

and a free-energy density

$$f_e^{(2)} = \frac{kT}{v_c} \frac{d^2 c}{2\pi r_c L_0} \ln \frac{c r_c d^2}{2 e v_c}, \tag{20}$$

where L_0 is a typical persistence length along the disclination (it measures its flexibility and cannot be smaller than d, but is certainly much larger than d in a thermotropic nematic). Finally the excluded volume yields a term that we estimate as being of order

$$f_e^{(3)} = \frac{kT}{v_c} \frac{c^2 d^4}{2\pi v_c L_0}, \tag{21}$$

where we have assumed that the volume excluded by a disclination is $u = 4\pi r_c^2 L_0$ and used Onsager's calculation for solid spheres [3], transposed for parallel cylinders of length L_0. $f_e^{(3)}$ provides the only term that is proportional to c^2 in the total free-energy density

$$f = f_{el} + f_e^{(1)} + f_e^{(2)} + f_e^{(3)}.$$

Let us note that c is, up to some irrelevant factor, nothing other than the density of disclinations. It is then interesting to note the analogy between the free energy we have obtained and the free energy of polymer chains in a solvent—the so-called Flory–Huggins free energy [38]—the disclinations playing the role of the Flory–Huggins polymer chains. The analogy can easily be pushed further by examining the entropy terms $f_e^{(1)}$ (in which the term linear in c plays a trivial role) and $f_e^{(2)}$. More precisely, if we perform a Legendre transformation $f \to \varphi = f - c(\partial f/\partial c)_{r_c}$, we find the very simple expression

$$\varphi = \frac{kT}{v_c}\left[c\left(1 - \frac{d^2}{2\pi r_c L_0}\right) + \ln(1 - c)\right] + \frac{Kd^2c}{8r_c v_c} - \frac{kT}{v_c}\frac{c^2d^4}{2\pi v_c L_0}, \qquad (22)$$

where r_c is a function of c obeying the minimization equation

$$\left(\frac{\partial f}{\partial r_c}\right)_c \equiv 0. \qquad (23)$$

In the Flory–Huggins formulation the energy density φ of a solution of chains with σ monomers each has the form

$$\varphi_{\mathrm{FH}} = \frac{kT}{v_c}\left[c\left(1 - \frac{1}{\sigma}\right) + \ln(1 - c) + \chi c^2 + \ldots\right]. \qquad (24)$$

We notice immediately by comparing equations (22) and (24), that $\sigma = 2\pi r_c L_0/d^2$ is the effective length of the disclinations, and that the excluded-volume term provides a negative contribution to χ, i.e. our system has the behaviour of a good solvent (the effect of the excluded volume is of course repulsive). We now estimate the role of the K term in equation (22) by a complete calculation.

We first estimate r_c by using equation (23), and find

$$r_c = 8\frac{kT}{L_0 Ed}\ln\frac{\pi}{e} + \frac{2\pi K^*}{Ed}\ln\frac{2\pi e v_c}{c r_c d^2}, \qquad (25)$$

where $K^* = K - 4kT/\pi L_0$ is of order K, since Kd is much larger than kT in most nematics. We therefore find the same order of magnitude for r_c in this case as for an isolated disclination ($r_c \propto r_c^* = 2\pi K^*/Ed$). However, stability requires that the logarithmic term be positive, i.e. $2\pi e v_c > c r_c d^2$. For the same reason of stability we must have $f_e^{(2)}$ negative, and this condition leads to a quite similar inequality. Since we can show that, at equilibrium (which is obtained by cancelling the other first derivative, $(\partial f/\partial c)_{r_c} \equiv 0$), c is itself large, this implies that L must be sufficiently large in order to obtain this type of cooperative behaviour of disclinations. Note also that both conditions can be written approximately as

$$r_c^2 < R^2,$$

which is the condition for small dilution for disclinations.

Equation (25) allows us to express c as a function of r_c, and hence to evaluate the contribution of the K term (see equation (22)) to the curvature of the free energy φ near any value of r_c. At equilibrium, we have not only $(\partial f/\partial c)_{r_c} = 0$ but also $(\partial f/\partial r_c)_c = 0$. Let r_0 and c_0 be a set of values of r_c and c that satisfy these equations. Let dr_0 and dc_0 be small variations of r_c and c near r_0 and c_0, obeying equation (25). We find from equation (25)

$$d(r_0c_0) = -dr_0\frac{r_0c_0}{r^*}.$$

This equation can also be written, with $r_c c = r_0c_0 + d(r_0c_0)$ as

$$cr_c = r_0c_0\left(1 - \frac{dr_0}{r^*}\right).$$

Therefore the K term in equation (22) also contributes to χ. Comparing

$$\chi_1 = \frac{Kd^2}{4c_0 r_0 kT}$$

and

$$\chi_2 = -\frac{d^4}{2\pi v_c L_0},$$

we see that $|\chi_2|/\chi_1 \sim kT/L_0 K$, which is less than 1. The K term is therefore predominant, except for large temperatures, perhaps in relation to a nematic–isotropic transition driven by defects. But for typical values of $|\chi_2|/\chi_1$ the condition of a good solvent requires $|\chi_1| < \frac{1}{2}$, i.e. approximately

$$Kd^2/L < AkT, \tag{26}$$

where A is some numerical factor of order perhaps 10. Such a condition is generally satisfied.

It remains to consider the complete solution, which satisfies $(\partial f/\partial c)_{r_c} = 0$, and to establish the conditions for stability of this solution ($\partial^2 f/\partial c^2 > 0$, $\partial^2 f/\partial r_c^2 > 0$, $(\partial^2 f/\partial c^2)(\partial^2 f/\partial r_c^2) - (\partial^2 f/\partial c\,\partial r_c)^2 > 0$). The equation $(\partial f/\partial c)_{r_c} = 0$ is easily written in the form

$$kT\left[\ln\frac{v_c}{v_e(1-c)} + \frac{cd^4}{\pi v_c L_0}\right] = \frac{\varepsilon}{2} + \frac{d^2}{4r_c}K^* - \frac{Ed^3}{16\pi}\ln\frac{r_c e}{d}, \tag{27}$$

where use has been made of $(\partial f/\partial r_c)_c = 0$. Taking $r_c = r_c^*$, the quantity

$$\Delta E = \frac{\varepsilon}{2} - \frac{Ed^3}{16\pi}\ln\frac{r_c}{ed},$$

which appears on the right-hand side of equation (27), must be positive since the left-hand side is positive. We therefore see, as expected, that ε must be large enough in order for the existence of cooperative effects of the kind considered here. The condition $\Delta E > 0$ is quite critical, since ε is of order Ed^3. Furthermore, assuming that the second term on the left-hand side is small, we see that

$$1 - c = (1 - c_0)\exp\left(-\frac{\Delta E}{kT}\right), \tag{28}$$

where $1 - c_0 = nv_c/v_e$ cannot be larger than unity; this seems to indicate that we have to take for v_e an effective volume of chain ends that is much larger than d^3; this property is probably related to the fact that the chain ends are not independent, and, strictly speaking, do not form an ideal gas. The most important property of equation (28) is that c *decreases* when the temperature increases. This is in agreement with the physical assumptions involved in this theory (the system does not want to lose too much entropy of free chains at high temperature, since the entropy carried by the lines of defects does not compensate it enough if the rigidity L_0 of the defects is too large) and also in accord with some observations reported earlier [35].

As far as the stability conditions are concerned, they are all of the form

$$\frac{Kd^2}{r_c} < \frac{8BkTc}{1-c}, \tag{29}$$

where B is a coefficient of order unity; this is a condition that is more difficult to satisfy than equation (26), it requires either a high temperature or large $r_c c$, i.e. large L.

Although this last result (large L) is similar to the experimental results quoted previously [29], it is not exactly the same (the threshold in [29] is proportional to Ld^2, and not L).

The transition to the cooperative behaviour of disclinations occurs when the equality is satisfied in equation (29). The free energy (see equation (22)) decreases sharply when this threshold is reached, as can be seen by a calculation of the order of magnitude of f. It is remarkable that, according to out discussion of equation (27), the theory predicts that the density c of segregated chain ends and the density of disclinations decrease as the temperature increases (in other words, we are not considering anything like an ordinary phase transition driven by defects, which could, of course, exist as well). However, we propose this result as an element for discussion, rather than something well established, because of the crudeness of some of our assumptions—in particular, the assumption that the free ends do not interact and the way we have approached the entropy of the lines in a quasi two-dimensional model (the use of L_0). We have also already mentioned the open question of the kinetics of chain ends.

5. Conclusion

We have tried in this paper to indicate the main physical aspects related to the *scarcity* of chain ends in a nematic polymer. Some of these aspects are experimental, and illustrate the importance of the phenomena of segregation of the chain ends in disclination cores at the expense of entropy and the possibility of cooperative phenomena. We have discussed theoretically some of the ingredients of these cooperative phenomena. The discussion shows the limitations always met in all of these types of problems, where we expect a phase transition in the presence of defects [39], but it is expected, owing to the specificity of the mechanisms met here, that such an approach might prove fruitful.

There are other characteristics (apart from free chain ends), not mentioned in this article, that make liquid-crystal polymers fascinating media for the study of defects. One of them is the possible existence of correlations between neighbouring chains, either orientational correlations, which we expect to be at the origin of biaxial phases, or positional correlations (i.e. the tendency to compacity) in competition with a mutual twist. These latter are probably at the origin of the phenomena of *frustration*, which has been invoked to explain some particular geometries of defects in cholesteric polymers of biological origin (DNA in the chromosome of dinoflagellates, precholesteric phases, etc.) [40].

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