Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

A supra-molecular approach to the modelling of textures in liquid crystals

S. E. Bedford[a]; T. M. Nicholson[b]; A. H. Windle[a]
[a] Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, England [b] Department of Chemical Engineering, University of Cambridge, Cambridge, England

To cite this Article Bedford, S. E. , Nicholson, T. M. and Windle, A. H.(1991) 'A supra-molecular approach to the modelling of textures in liquid crystals', Liquid Crystals, 10: 1, 63 — 71
To link to this Article: DOI: 10.1080/02678299108028229
URL: http://dx.doi.org/10.1080/02678299108028229

LIQUID CRYSTALS, 1991, VOL. 10, NO. 1, 63–71

A supra-molecular approach to the modelling of textures in liquid crystals

by S. E. BEDFORD, T. M. NICHOLSON†* and A. H. WINDLE
Department of Materials Science and Metallurgy and
† Department of Chemical Engineering, University of Cambridge,
Pembroke Street, Cambridge, England

(*Received 23 November 1990; accepted 18 January 1991*)

We report a simple numerical simulation that can model the evolution of liquid crystal textures from a random isotropic state. Rather than using a molecular description of the mesophase, a lattice of directors is used, corresponding to the supra-molecular orientational organization of the material. By minimizing an interaction energy between these, the development of the optimal structure may be followed. With a suitable choice of energy function this model can begin to predict some textures observed in small molecule liquid crystals.

1. Introduction

The discontinuities and distortions in the director field of a liquid crystal are responsible for the patterns or textures observed in the polarizing microscope. These defects have fascinated scientists for over a century; indeed Friedel first systematically described defect textures in 1922 [1]. Today interest lies in both understanding the abundance of observed topological structures and the influence of these structures on the useful properties of the material. These textures have been extensively categorized and theoretical developments reviewed by Demus [2]. Liquid-crystalline polymers also exhibit characteristic textures, although these may be at a scale too small to be resolved clearly in the optical microscope. The related director fields can affect the usefulness of the final material properties. For example the attainable Young's modulus of fibres drawn from either thermotropic or lyotropic mesophases is believed to be limited by the presence of banded textures [3, 4], while thermotropic liquid-crystalline polymer mouldings are additionally affected by domain boundaries and skin core effects [5].

Therefore an appreciation of the microstructure of both small molecule liquid crystals and liquid-crystalline polymers leads to an understanding of their properties and the possibility of tailoring these for specific requirements. In this paper we discuss an approach to the modelling of liquid-crystalline microstructures by considering the evolution of textures in a material that has been quenched from the isotropic to the mesophase. We develop a simple numerical simulation of the orientational processes caused by isothermal annealing in such a nematic phase.

2. Outline of the model

The disordered liquid crystal is represented by an array of vectors whose centres are fixed on the sites of a primitive cubic lattice while their orientations are free to vary in three dimensional space, representing the variation in director orientation throughout

* Author for correspondence.

0267–8292/91 $3·00

the material. This is not a molecular model since the ordering involved is over a much greater distance than could be efficiently described by existing modelling techniques. The use of a lattice to describe structures has several precedents at both the molecular and microscopic scale. On the molecular level Lebwohl and Lasher [6] and more recently Allen and Wilson [7] and Denham *et al.* [8] have used a lattice to simulate order–disorder transitions for bulk systems of nematics, while at the level of the director, a two dimensional lattice has been used by Cohen *et al.* [9] to test the validity of the Frank–Oseen continuum equations. These equations [10], together with the Leslie–Ericksen theory [11], may be used to predict many of the textures observed in liquid crystals. However these equations are known to be difficult to solve and so a simpler numerical approach based on the preference of the directors for parallel alignment has been chosen here. We assign an interaction energy between adjacent directors that is at a minimum when they are parallel and at a maximum when orthogonal, and simulate the annealing of the material by minimizing the energy of a given director with respect to its nearest neighbours. This method is comparable to the empirical derivations of the liquid-crystalline molecular potential [12] and to the calculation of the exchange energy of magnetic dipoles.

3. The algorithm

If it is assumed that the three elastic constants for the material are equal, and arbitrarily set to unity, and the orientations are confined to a plane, a two dimensional model simulating homogeneous planar textures may be formulated. A suitable energy function for the interaction of two adjacent cells at angles θ and ϕ to a reference direction can be represented by $\sin^2(\theta-\phi)$. Such a function has been used by previous workers [8] and is a good approximation to the strict derivation from tensorial calculus [13]. The contribution to the total energy of the structure, measured in arbitrary units, by one particular cell is the sum of this interaction energy over all the cell's nearest neighbours which for the central cell shown in figure 1 is

$$E=\sum_{i=1}^{4}\sin^2(\theta_i-\phi). \tag{1}$$

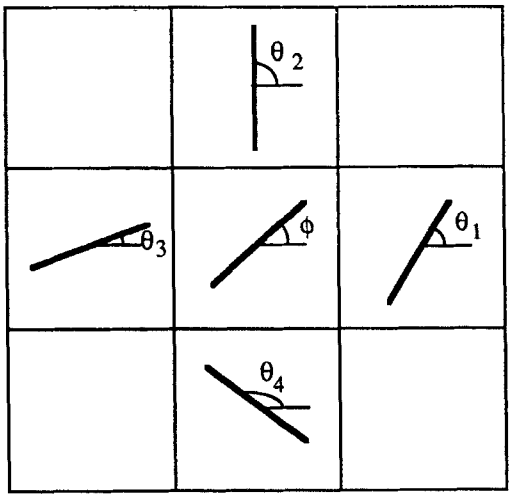


Figure 1. Definition of angles used to calculate the interaction energy in equation 1.

The orientation of the central cell that corresponds to the minimum energy contribution may be calculated by the standard method

$$\frac{dE}{d\phi}=0,$$

which leads to an expression for ϕ (the orientation of the central cell)

$$\tan 2\phi=\frac{\sum_{i=1}^{4}\sin 2\theta_i}{\sum_{i=1}^{4}\cos 2\theta_i}. \tag{2}$$

Cells are picked at random in the array and their orientations altered to the evaluated minimum energy position. After several thousand iterations no further reduction is seen in the total energy associated with the aggregate and a minimum energy configuration has been found.

4. An alternative approach

The energy minimization algorithm discussed already is intensive in computing time since several trigonometric functions need to be calculated at each step. A quicker alternative approach was therefore sought. If the difference in orientation angles between neighbouring cells is not too great, the energy function (see equation (1)) may be rewritten using a Taylor expansion as

$$E=\sum_{i=1}^{4}(\theta_i-\phi)^2. \tag{3}$$

Minimizing this function yields

$$\frac{dE}{d\phi}=0=\sum_{i=1}^{4}2(\theta_i-\phi),$$

or

$$\phi=\frac{1}{4}\sum_{i=1}^{4}\theta_i. \tag{4}$$

Thus the optimum orientation for a particular cell is simply the average orientation of the cells in the neighbourhood.

Since there is a redundancy of 180° in the orientation directions, each angle can be added to the sum in two possible ways. Care must be taken to calculate the correct average orientation by adding the angles (stored as direction cosines) in such a way as to maximize the modulus of the sum. With this proviso the simplified algorithm can be used throughout the whole of the simulation process since the direction in which the cell orientation needs to be moved to minimize both the original energy function (see equation (1)) and the modified energy function (see equation (3)) is the same.

The simulation may be further modified to allow for the possibility of modelling dynamic effects such as the effect of shear fields on the structure, by generating a complete new array of cell orientations at a time, always using the old orientation array to calculate the average neighbourhood orientations. This array then replaces the old array for the next stage of the iteration. Instabilities due to overshooting the minimum

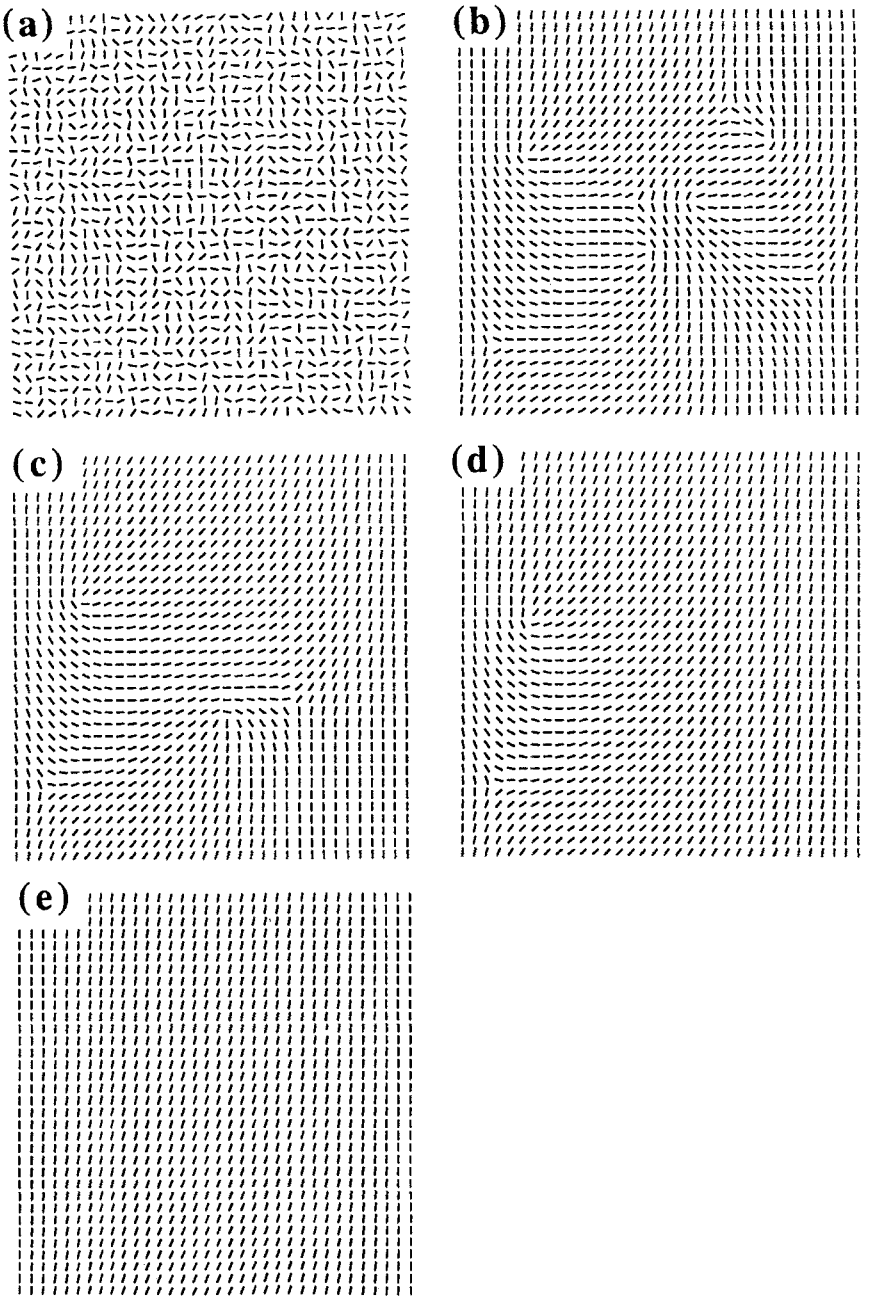


Figure 2. Stages during the relaxation of an initially random structure with no boundary conditions imposed. (*a*) Initial configuration, (*b*) after 1 iteration step, (*c*) after 5 steps, (*d*) after 10 steps and (*e*) after 20 steps.

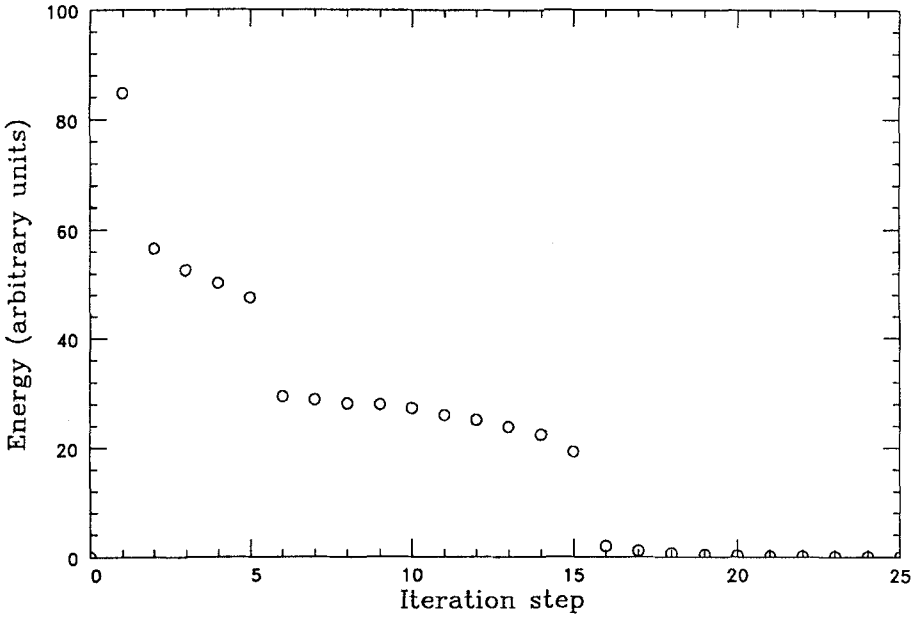


Figure 3. Energy against number of steps for the relaxation illustrated in figure 2. On the same scale the energy of the initial configuration is 2275 units.

energy position are avoided by moving the cell orientation by only a fraction of its deviation from the minimum energy position

$$\mathbf{x}_{n+1} = (1-\rho)\mathbf{x}_n + \rho\bar{\mathbf{x}}, \tag{5}$$

where $\mathbf{x}_{n+1}$ and $\mathbf{x}_n$ are two successive position vectors of the orientation of the considered cell, $\bar{\mathbf{x}}$ is the average neighbourhood orientation and ρ is an orientation parameter.

5. Boundary conditions

The edge cells in the array may be considered in three possible ways. In the first case free boundary conditions are employed, whereby the edge cells are completely ignored, making no contribution to the energy calculations. Here the lowest energy state that may be achieved is uniform orientation. Figure 2 shows stages during the relaxation of an initially random array of cell orientations with these free boundary conditions. It can be seen that the random orientation distribution first segregates into distinct $s = \pm\frac{1}{2}$ disclinations (these have lower energy than disclinations of higher order). These then either annihilate with disclinations of opposite sign, or diffuse to the boundary where they run out of the model. In the corresponding plot of total structure energy against iteration step (see figure 3) it can be seen that the overall energy decreases in steps as each disclination is eliminated.

If periodic boundary conditions are imposed, the lowest energy state that the array can reach remains that of uniform orientation. However, depending on the initial distribution of cell orientations, there will be an inbalance in the number of disclinations of opposite sign and so they will not all be able to annihilate. The periodic boundary conditions imposed prevent these excess disclinations from being lost, and the final annealed state still contains disclinations (see figure 4).

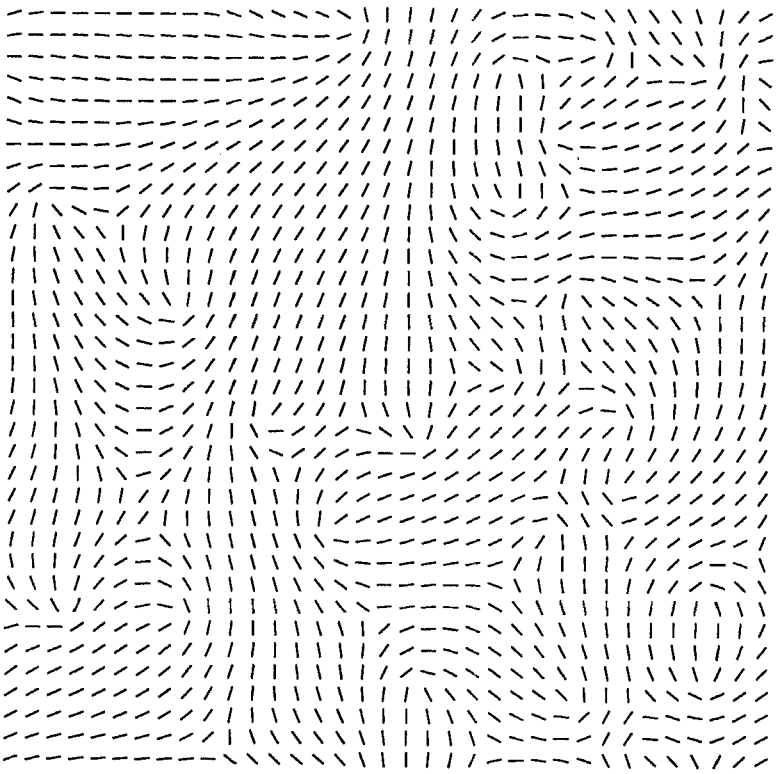


Figure 4. Final structure resulting from the relaxation of an initially random structure with periodic boundary conditions imposed.

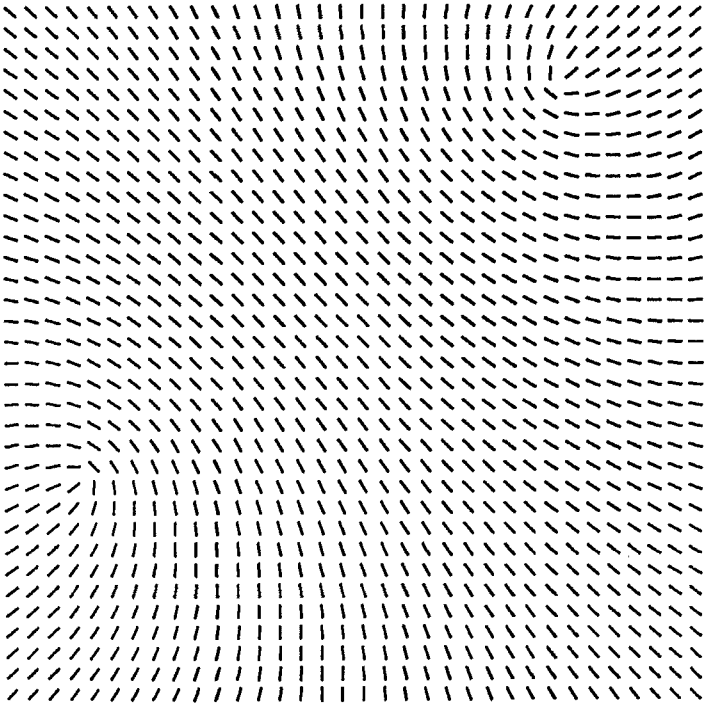
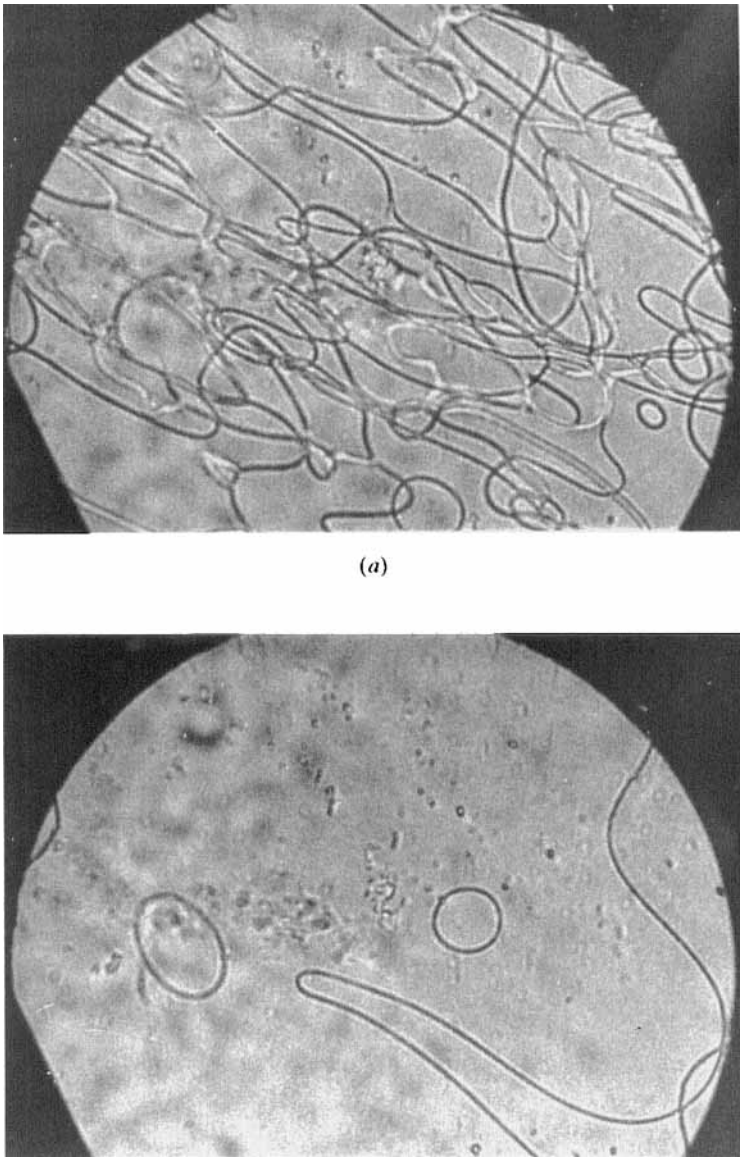


Figure 5. Final structure resulting from the relaxation of an initially random structure with fixed boundary conditions imposed.



(*a*)

(*b*)

Figure 6. Disclination loops in MBBA observed in bright field (*a*) 10 s and (*b*) 60 s after cessation of shear flow.

Alternatively, fixed boundary conditions may be imposed to try to encourage the formation of particular defect structures. An interesting case can be seen if the orientation of the edge cells are fixed to be oriented radially outwards from the centre, as would be expected for a structure with a single $s = 1$ disclination at the centre. In fact (see figure 5) the lowest energy structure that results consists of two $s = \frac{1}{2}$ disclinations. Meyer [14] predicts that the energy of a disclination of strength s is proportional to s^2, so indeed the energy associated with two $s = \frac{1}{2}$ disclinations should be lower than that of one $s = 1$ disclination.

6. Three dimensions

In order to model more general liquid-crystalline structures, the simulation must be extended to three dimensions. This can be achieved quite simply by allowing the directors to move in three rather than two dimensions, and considering the six nearest neighbours of each cell in a three dimensional lattice.

As an illustration, we consider the relaxation of a sample of 4-methoxybenzylidene-4-*n*-butyl aniline (MBBA), after it has been sheared (see figure 6). As has been observed previously [15], just after the cessation of shear the liquid contains a high density of disclination loops, observable in either bright field or between crossed polarizers in the optical microscope. With time these annihilate, until eventually none remain. This process may be simulated using a three dimensional array of $35 \times 35 \times 35$ cells, with no boundary conditions imposed. Slices through the structure resulting after 10 steps were examined to follow the location of disclination cores, and the core positions plotted on a three dimensional perspective view (see figure 7). It can be seen that the simulation has produced realistic disclination lines.

The simulation can thus begin to model textures in real liquid crystal systems, and provides a bridge between the molecular modelling level and the simulation of observed properties. The simulation may be developed in several ways. For instance the splay, twist and bend constants may be separated, by providing a different energy equation, in order to simulate structures with anisotropic elastic energy such as liquid-crystalline polymer textures, or shear induced textures may be modelled by including additional processes to alter the cell orientations.

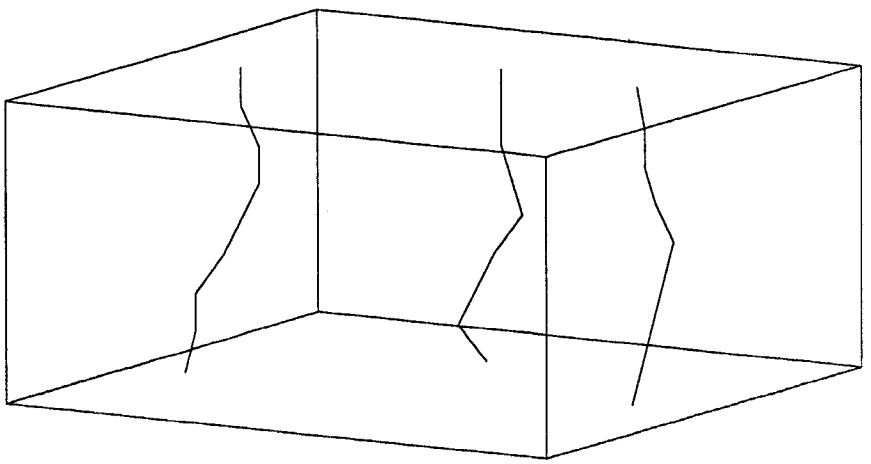


Figure 7. Simulated disclination loops after 10 steps of relaxation of a three dimensional random structure. Nine central slices through the $35 \times 35 \times 35$ array have been analysed.

The authors wish to thank Dr M. R. Mackley and Dr. D. J. Blundell for helpful discussions and the S.E.R.C. and ICI for funding.

References

[1] FRIEDEL, G., 1922, *Annln. Phys.*, **18,** 273.
[2] DEMUS, D., and RICHTER, L., 1978, *Textures of Liquid Crystals* (Verlag Chemie).
[3] DOBB, M. G., JOHNSON, D. J., and SAVILLE, B. P., 1977, *J. Polym. Sci.*, **15,** 220.
[4] DONALD, A. M., VINEY, C., and WINDLE, A. H., 1983, *Polymer*, **24,** 155.
[5] SAWYER, L. C., and JAFFE, M., 1986, *J. Mater. Sci.*, **21,** 1987.
[6] LEBWOHL, P. A., and LASHER, G., 1972, *Phys. Rev.* A, **6,** 426.
[7] ALLEN, M. P., and WILSON, M. R., 1989, *J. Comput. Aided Molec. Design*, **3,** 335.
[8] DENHAM, J. H., LUCKHURST, G. R., ZANNONI, C., and LEWIS, J. W., 1980, *Molec. Crystals liq. Crystals*, **60,** 185.
[9] COHEN, R., HARDT, R., KINDERLEHRER, D., LIN, S. Y., and LUSKIN, M., 1989, *Theory and Applications of Liquid Crystals*, edited by J. L. Ericksen and D. Kinderlehrer (Springer Verlag), p. 99.
[10] FRANK, F. C., 1958, *Faraday Discuss. chem. Soc.*, **25,** 19.
[11] DE GENNES, P. G., 1974, *Physics of Liquid Crystals* (Clarendon Press).
[12] WOJTOWICZ, P. J., 1985, *Introduction to Liquid Crystals*, edited by E. B. Priestly, P. J. Wotjowicz and P. Sheng (Plenum), Chap. 3.
[13] KILIAN, A., and HESS, S., 1989, *Z. Naturf.* (a), **44,** 693.
[14] MEYER, K. B., 1973, *Phil. Mag.*, **27,** 405.
[15] GRAZIANO, D., and MACKLEY, M. R., 1984, *Molec. Crystals liq. Crystals*, **106,** 73.