Two-Dimensional Lattice Model of Disclinations in Liquid Crystals: Choice of Energy Function

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Introduction. Computational modeling has provided a means for predicting liquid crystalline microstructures.[1-4] Models on a supramolecular scale[2,5,6] have enabled equilibrium structures to be predicted for given boundary conditions and also opened up the possibilities of modeling the process of microstructural relaxation.

In a paper published recently in *Macromolecules*,[5] Kimura and Gray predicted textures in liquid crystals using a simple two-dimensional lattice model based on that originally developed by Bedford *et al.*[2] By proposing an alternative iterative procedure, they predicted structures for certain fixed boundary conditions that were closer to the expected minimum-energy arrangement than those which they were able to achieve using the original protocol. In this paper, we show that a careful consideration of the choice of energy functions is necessary if the random cell selection protocol is to give textures that approach equilibrium.

Choice of Energy Function. Meyer[7] predicts that the energy of a disclination of strength S is proportional to the square of the strength. Therefore, any disclination modeled on a two-dimensional mesh (where "escape into the third dimension" is not possible) of higher strength than a half will split into components of strength half resulting in a lower total energy. Similarly, disclinations of opposite sign attract one another and annihilate.[2] It is these interactions between disclinations that control the development of the microstructural relaxation process.

The energy function which has been proposed for the two-dimensional lattice model is

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

where ϕ and θ_i are the angles to the x-axis of the central vector and the ith neighboring vector, respectively.

This function is of the same form as that derived by Lebwohl and Lasher[1] from the Maier–Saupe equation and is the direct consequence of calculations based on tensorial calculus.[3] It has also formed the basis of the lattice models developed by Bedford *et al.*[2]

An approximate form of the function[2] (1) is

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

where the angles between neighboring vectors are small.

In their paper, Kimura and Gray[5] suggest the energy function:

$$E = \sum_{i}^{n} \{(x_c - x_i)^2 + (y_c - y_i)^2 + (z_c - z_i)^2\} \tag{3}$$

where x_c, y_c, and z_c are the components for the central vector along orthogonal axes and x_i, y_i, and z_i are the components of the neighboring n vectors. In two dimensions this has the form:

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

where ϕ and θ_i are defined as above. This function has approximately the same form as (2), and like (2) it tends to (1) at small angles.

Close to a disclination core, and most noticeably in lattice models, the angle between neighboring vectors may be large, and thus the choice between the three functions above (1–3) will be significant. Of the functions described, (1) is unique in having a continuous gradient over 180°.

Consider the orientation distribution around an $S = +1/2$ disclination. At the very center of the core the total energy function (i.e., total energy as the central vector is rotated) will be flat, the director being free to lie in any direction. If a minimum-energy position is found, this director no longer represents the exact core of the disclination. If a square mesh is superimposed on the disclination such that it is represented by four vectors equally spaced around it, the total energy function will be the sum of the individual functions shifted in phase by exactly 45°. The sine-squared relation (1) produces a flat total energy function as required, but the simple squared relation (2) and the Kimura and Gray relation (3) produce four minima at angles halfway between each of the pairs of neighboring vectors. The latter two equations will only produce a flat total energy function if an infinite number of neighbors could be chosen, i.e., if there were no mesh. If the mesh is now rotated with respect to the disclination, the minimum-energy positions predicted by (2) and (3) also rotate, and therefore the resulting orientation of the central director is dependent on the mesh orientation. These arguments are true for any function that does not show diad symmetry about the $\theta_i - \phi = 45°$ point.

In order to explore further the significance of function symmetry, a "sawtooth" energy function was considered. While the symmetry of the function ensures that where the surrounding vectors are at 45° intervals as above the total energy function will be completely flat, addition of four of these functions at *random* phase shifts gives a total energy function (corresponding to four randomly orientated neighbors) where the minima are flat bottomed; i.e., the minimum-energy orientation is not defined. To avoid this effect, the function must have a continuously varying gradient. If the gradient close to the minimum is steeper than that in the sawtooth, then the minimum-energy position will tend to be fixed close to one of the individual minima; i.e., there is a tendency for the central vector to lie nearly parallel to one of its neighbors.

Selecting symmetric functions in this manner can only reveal a certain amount about the criteria for the energy function; however, it does highlight the properties of the sine-squared relation that are specifically relevant to this model.

Comparison of Textures. Kimura and Gray,[5] using the energy relation (3) and the random cell selection protocol, attempted to predict equilibrium structures for a mesh with fixed boundary conditions set to define an $S = +2$ disclination. Figure 1a shows the starting structure used. They report that the structure corresponding to minimum energy was not achieved: the structure, which "locked up" and showed no further relaxation, still contained half-strength disclinations of opposite sign which did not approach each other and annihilate. We have run

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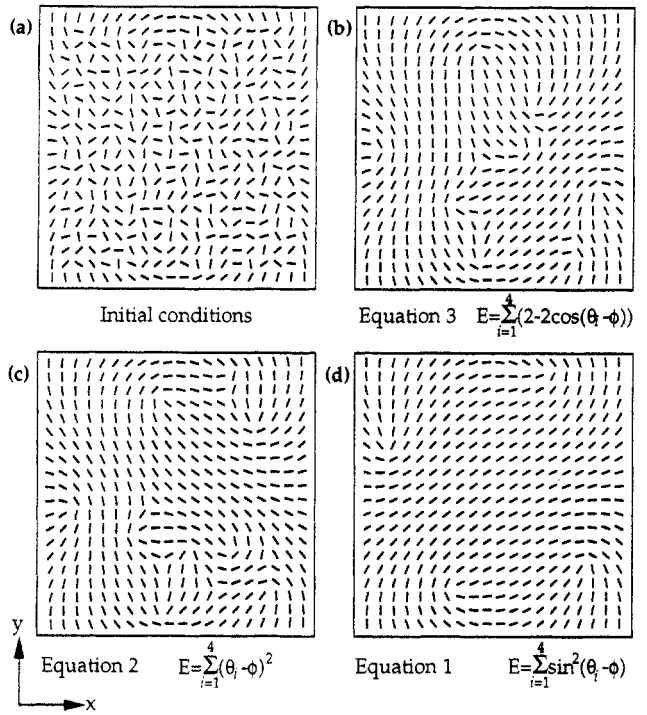

Figure 1. (a) Example of the initial conditions with fixed boundary conditions defining a $S = +2$ disclination and random central vectors and a comparison of the final structures achieved using the different energy functions (b–d). Each final structure shown has undergone 300 000 iterations.

simulations using the function (3) with random cell selection and were able to reproduce the same problem, observing final structures such as Figure 1b. The difficulty was also encountered using the squared function (2), with an example being shown in Figure 1c. In the case of the sine-squared energy function (1), however, the disclinations remain mobile and annihilation between disclinations of opposite sign occurred until the minimum number of disclinations (four $S = +1/2$) remained, as can be seen in Figure 1d. An equilibrium structure was obtained after only about 25 iterations per cell; however, for each plot shown, the simulation had been left to run for many thousands of iterations beyond the point where there was no disnerible movement of the vectors. We emphasize that, in the case of the locked up structures (Figures 1b,c), *each vector* in the final structures is in its minimum-energy position, and in order for disclinations of opposite sign to move toward one another to annihilate, a cooperative movement of several lattice vectors would be required.

In order for the disclinations to be mobile (necessary for separation or annihilation to occur), large rotations of the central vector must be possible as a result of very small movements in one of the neighboring vectors: each vector is influenced by four others, so if a movement in one neighbor only produces a response the same size or smaller in its neighbors, the lattice will eventually become locked up and unable to move. Equation 1 is a *harmonic* function; i.e., the total energy function has the same form as an individual function. This results in the smoothest possible total energy curve. Figure 2 illustrates the effect of using a harmonic function on the mobility of disclinations of the model. Four vectors were chosen with an almost even distribution in orientation representing the neighbors on a mesh around a half-strength disclination core. The vectors are close but do not exactly correspond to a perfectly symmetrical distribution, and so a single minimum-energy orientation is the result using any of the three functions considered above. A small change in angle of one of the neighbors results in a large shift in the minimum-energy position using the sine-squared equation

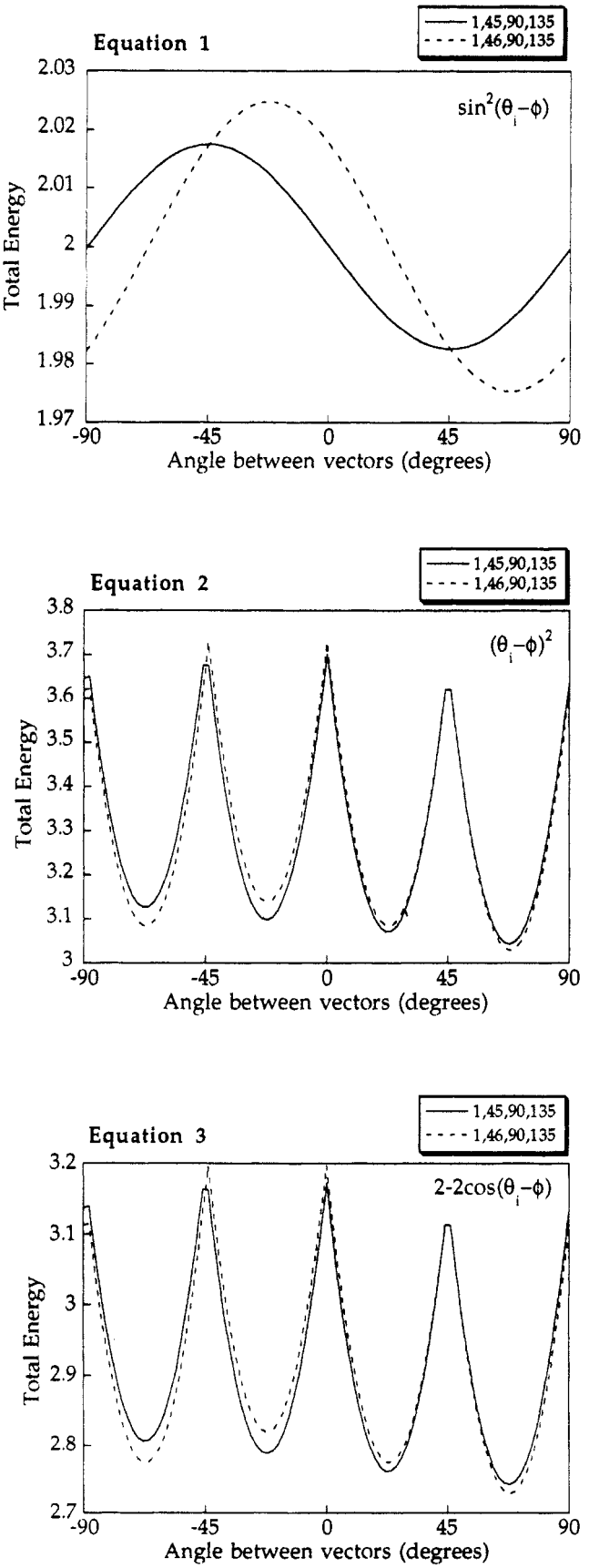

Figure 2. Change in total energy functions resulting from a rotation of 1° in one of the neighboring vectors (set at angles 1°, 45°, 90°, and 135° and shifted by a small amount to 1°, 46°, 90°, and 135°). For the sin-squared (a) the minimum-energy position has moved by 22.5°. In (b) and (c), using the simple squared and the Kimura and Gray functions, respectively, the movement of the minimum is of the same order as the change in orientation of one of the surrounding vectors.

(1), but the shift with the nonharmonic functions is only of the same order as that of the neighbor. Large changes

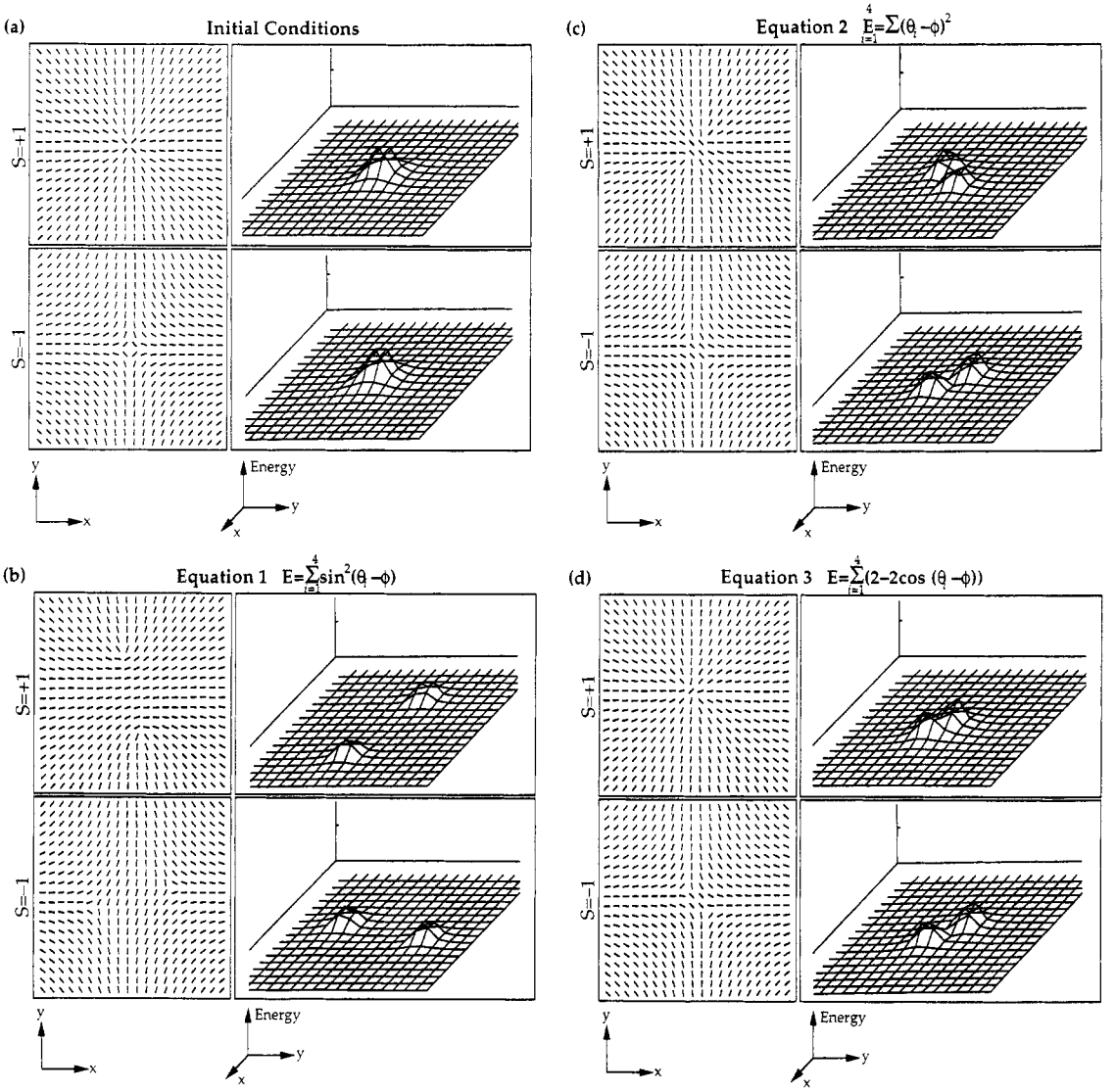

Figure 3. (a) Initial imposed $S = +1$ and $S = -1$ disclinations and its separation into halves (b–d) using each of the three energy functions. On the right-hand side in each case, the energy profile of each structure is plotted.

are only possible if the lowest energy orientation shifts from one minimum to one of the other local minima in the total energy function.

To exemplify further the difference between the three energy equations considered, $S = +1$ and $S = -1$ disclinations were set up and relaxed with fixed boundary conditions. Figure 3 shows the initial conditions used in each case and the final texture observed after relaxation with each of the three energy functions. As predicted, the disclination splits into halves in all cases, but only in the case of the sine-squared relation (1) did they move apart until they reached their equilbrium position, where the interactions between the two disclinations and the boundary conditions are balanced.

Iterative Protocol. Kimura and Gray[5] overcame the locking up difficulty that arises from the approximate energy functions (2) and (3) by introducing a specific cell selection protocol which they called "annealing". In this routine, the cells next to the fixed boundary conditions were visited first and permitted to relax, then the next layer in was allowed to relax also, and so on, so that in effect a front delimiting the progression of relaxation was permitted to grow.

A modeling routine in which the vectors are chosen at random most closely reproduces a system in which all regions are relaxing in parallel. We would urge caution in the use of any more specific cell selection protocol. While it might enable a closer approach to the equilibrium structure with a nonharmonic function than in the case of random selection, it is important to be aware that it may "color" the structure obtained, especially in the intermediate stages of relaxation.

Conclusion. We therefore suggest that the success of energy minimizations such as this depends critically on the choice of energy function. We have found the harmonic function given in (1) to be the most successful. The appropriate choice of energy function ensures that the minimum-energy arrangement for the whole mesh may be reached, without the need to use nonrandom types of protocol.

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