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Monte Carlo lattice simulations of the elastic behaviour of nematic liquid crystals

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A pairwise additive potential, which approximately reproduces the free energy density for the elastic deformations of a nematic liquid crystal, originally proposed by Gruhn and Hess, has been investigated by simulating the three Fréedericksz transitions as well as that of the Schadt–Helfrich cell. The pair potential depends on the three elastic constants K_1, K_2 and K_3 for the splay, twist and bend deformations, respectively. The results of the simulations are compared with the analytical solutions obtained from continuum theory in order to test the accuracy of the model potential at a quantitative level. This comparison is also made for different temperatures to explore the influence of director fluctuations on the elastic behaviour.

1. Introduction

The elastic behaviour of nematic liquid crystals is of particular interest for technological applications as in nematic liquid crystals displays (LCDs), in which the transmission of light is determined by the director distribution; this, in turn, is associated with the structure having the minimum free energy. In addition, the relative stability and structure of disclinations is influenced by the elastic properties of the sample [1, 2]. Computer simulation studies as well as theoretical investigations have been used to elucidate the elastic behaviour of nematic liquid crystals in LCDs [3–5], liquid crystal droplets [6, 7], capillary tubes [8–10], hybrid nematic films [11] and polymeric liquid crystals [12]. Computer aided techniques have also been employed to study the kinetics of the formation of disclinations and their evolution [3, 13] as well as for classical experiments such as the Fréedericksz transitions and that of the Schadt–Helfrich cell [12, 14].

The elastic free energy density for a nematic phase can be expanded in powers of the gradient of the director, **n**; retaining only the quadratic terms gives the Zocher–Oseen–Frank expression [1]

$$\Psi = \frac{1}{2}\{K_1(\nabla \cdot \mathbf{n})^2 + K_2[\mathbf{n} \cdot (\nabla \times \mathbf{n})]^2 + K_3[\mathbf{n} \times (\nabla \times \mathbf{n})]^2\}, \tag{1}$$

where K_1, K_2 and K_3 are the elastic constants for the splay, twist and bend deformations, respectively. For simple geometries and boundary conditions, equation (1) can be solved analytically [1, 2]. However, in most cases of practical interest it is necessary to resort to numerical integration. Usually the director distribution is calculated by minimizing the free energy numerically, by finite difference methods, on a discrete grid of points [3, 4, 7, 8, 14]. Alternatively a Monte Carlo approach has been implemented. In some cases the method is used to minimize the free energy given by equation (1) [9, 12, 13] and the Metropolis algorithm is employed only to offer the system a way to escape from becoming trapped in local minima. In other cases, an interaction potential between neighbouring sites is used [5, 6, 10, 11]. For example, Zannoni and coworkers, have simulated LCDs [5], droplets [6] and hybrid nematic films [11] by using a Metropolis Monte Carlo algorithm for a

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Lebwohl–Lasher model [15] and at a scaled temperature of a few tenths of the scaled transition temperature, T^*_{NI}, of the model system. In this model the objects are fixed on a cubic lattice and two neighbouring objects, i and j, interact through an orientation dependent potential Φ^{LL}_{ij} given by

$$\Phi^{\mathrm{LL}}_{ij} = -\varepsilon P_2(\cos\beta_{ij}), \qquad (2)$$

where β_{ij} is the angle between the symmetry axes of the two objects and ε is the energy scaling parameter; the interaction is extended only to nearest neighbours on the cubic lattice. In the original development of the Lebwohl–Lasher model [15] the interacting objects were taken to be molecules and so the model was used to investigate properties such as the nematic–isotropic transition temperature and the orientational order at the molecular level. More recently it has been realized that there is an alternative interpretation of the Lebwohl–Lasher model in which the objects on the lattice sites are taken to be directors. Then, provided the system is large and the scaled temperature ($\equiv k_{\mathrm{B}}T/\varepsilon$) is well below the nematic–isotropic transition, the simulations provide a valuable way to study the macroscopic behaviour of a nematic [5, 6, 11]. However, a limiting factor in the use of the Lebwohl–Lasher model to simulate the elastic behaviour of liquid crystals, is the fact that the interaction energy depends only on the relative orientation of the two particles and so it is not possible to distinguish between splay, twist and bend deformations. That is, the model corresponds to the single elastic constant, or so-called spherical, approximation.

Bedford and Windle [10] have proposed an extension of the Lebwohl–Lasher potential which allows a dependence on the three elastic constants. However, there are doubts about the gauge invariance of their potential [16]. Subsequently an alternative potential has been proposed by Gruhn and Hess [9]. In their approach, a model potential for a pairwise additive interaction between directors, which approximately reproduces the elastic free energy density of the system, is derived by mapping equation (1) onto a suitable expansion of the interaction potential. The space is discretized onto a cubic lattice, each site representing a director, and the free energy of the system is defined as the sum of pairwise additive interactions between nearest neighbouring sites. This procedure will only give an approximate representation of the elastic free energy since this is not pairwise additive [9], as we assume for the model potential. The system could then be investigated by means of a Monte Carlo method, based on the usual Metropolis algorithm, in which, now, the total free energy obtained as a sum of the pair interactions plays the same role as the total potential energy in a Monte Carlo simulation of a molecular system [17]. The relationship between the coefficients in the potential and the elastic constants has been given by Romano [18]. Its formulation also differs from the original one [9] by numerical multiplicative and additive constants chosen in order to have the isotropic average of the potential equal to zero. It is of considerable interest to investigate the use of this potential model with typical elastic constants in order to test its reliability in describing complex director distributions such as those in certain LCDs, or in the proximity of disclinations. It is the aim of this work to test the quantitative predictions of the model potential for some director distributions for which analytical solutions exist but in the absence of director fluctuations. To do so we have simulated the three Fréedericksz transitions as well as that for the Schadt–Helfrich cell when an external field is applied to the nematic sample. The dependence on the thickness of the cell has been studied as well as the effect of varying the scaled temperature. We shall see that the model potential which we are using establishes a correspondence between the scaled temperature used in the Metropolis scheme and the size of the unit cell of the lattice. This relation will be used to bridge the gap between the molecular interpretation of the Lebwohl–Lasher model and continuum theory, for which the potential used here is an approximate representation.

The paper is organized as follows: in the next section we present the model potential used for the simulations; in Sec. 3 we give the details of the simulations, while in Sec. 4 we present and discuss the results for the three Fréedericksz experiments and the Schadt–Helfrich cell. Finally, our conclusions are reported in Sec. 5.

2. The pair potential

Following the procedure presented by Luckhurst and Romano in [16], we can expand the pair potential between two directors on neighbouring sites j and k, representing the orientation of the directors in two different points in space, in terms of a complete set of basis functions depending on the orientation of the two directors $\mathbf{n}_j$ and $\mathbf{n}_k$ and the orientation of the vector joining them, $\mathbf{r}$. A suitable set of functions for such an expansion are the S-functions $S_{L_jL_kJ}(\mathbf{n}_j, \mathbf{n}_k, \mathbf{r})$ [19]. The index L_j refers to the j-th director, the index L_k to the k-th director and the index J to the inter-director vector; J takes values from $(L_j + L_k)$ to $|L_j - L_k|$. It can be shown that the S-functions depend only on the scalar invariants $a_j = \mathbf{n}_j \cdot \mathbf{r}$, $a_k = \mathbf{n}_k \cdot \mathbf{r}$, $b_{jk} = \mathbf{n}_j \cdot \mathbf{n}_k$ and $c_{jk} = \mathbf{n}_j \cdot \mathbf{n}_k \times \mathbf{r}$. When the total rank of the S-function, $L_j + L_k + J$ is even only a_j, a_k and b_{jk} are involved and the S-functions are invariant for an inversion of coordinates. Consequently, the terms of even total rank are the only ones needed to describe the interaction energy between neighbouring sites, due to the symmetry properties of the nematic phase for which $\mathbf{n} = -\mathbf{n}$. The invariant c_{jk} appears in S-functions of odd total rank and should be included if chiral effects need to be described. We can, therefore, express the pair potential between two neighbouring sites j and k as

$$\Phi_{jk} = \sum_{L_j L_k J} \varphi_{L_j L_k J} S_{L_j L_k J}(a_j, a_k, b_{jk}), \tag{3}$$

where the $\varphi_{L_j L_k J}$ are the coefficients of the expansion, and the summation is restricted to terms with even total rank. This expansion has the advantage that the powers of the scalar invariants appear in a systematic manner; in addition it may be expected that the series is rapidly convergent. Such a pair potential can then be mapped onto the expression for the free energy density. Assuming small displacements of the director, we can replace the gradients in equation (1) by finite increments and by considering some well-defined deformations, both in equation (1) as well as in equation (3), it is possible to derive the relation between the coefficients $\varphi_{L_j L_k J}$ and the elastic constants. The procedure has been described in detail in [16] and we report here only the final expression for the pair potential

$$\Phi_{jk} = \lambda[P_2(a_j) + P_2(a_k)] + \mu\left(a_j a_k b_{jk} - \frac{1}{9}\right) + \nu P_2(b_{jk}) + \rho[P_2(a_j) + P_2(a_k)]P_2(b_{jk}), \tag{4}$$

where, for example, $P_2(a_j)$ is the second rank Legendre polynomial. This form of the potential can be obtained after rearranging the explicit expansion in terms of the S-functions, which is reported in the Appendix. It has, however, a more convenient form for coding into a program. The coefficients of the expansion are related to the elastic constants by [18]:

$$\begin{cases} \lambda = \frac{1}{3}\Lambda(2K_1 - 3K_2 + K_3) \\ \mu = 3\Lambda(K_2 - K_1) \\ \nu = \frac{1}{3}\Lambda(K_1 - 3K_2 - K_3) \\ \rho = \frac{1}{3}\Lambda(K_1 - K_3), \end{cases} \tag{5}$$

where Λ is the dimension of the unit cell of the cubic lattice. This particular length scale enters the expressions for the expansion coefficients because it is the separation between neighbouring sites which determines the director gradients. Clearly the four expansion coefficients cannot be independent since there are only three elastic constants; in fact we can see from equation (5) that μ is equal to $-3(\lambda + \rho)$. Indeed this relationship ensures that the interaction energy Φ_{jk} is independent of the absolute orientation of two parallel directors. This requirement is essential if the potential given in equation (4) is to describe the elastic interaction between two directors, since only deviations from the ground state geometry (uniform alignment of the director) give contributions to the elastic energy. In contrast, if the model potential of equation (4) is used to describe a molecular interaction [18], such a requirement is not strictly necessary [16], nor indeed is it physically realistic. It is worth noticing that, by setting the three elastic constants to a common value, $K_1 = K_2 = K_3 = K$, the potential is reduced to the same form as in the Lebwohl–Lasher model. In addition we see that the energy parameter, ε, in equation (2) is just equal to ΛK; this definition is only needed if we seek to model the elastic behaviour so that on each site of the lattice there is a director, rather than a molecule. This relationship is helpful since it provides a link between the scaled temperature, T^*, and the dimension of the unit cell:

$$T^* = k_B T/\varepsilon = k_B T/\Lambda K. \tag{6}$$

It is of interest to estimate the order of magnitude of the scaled temperature, T^*, which is needed for realistic simulations of the elastic behaviour for a nematic phase. Assuming a unit cell of dimension, Λ, of 1 μm, a temperature of 300 K and an average elastic constant of 1.0×10^{-12} N, gives a scaled temperature of 4.14×10^{-3}. This should be compared with the scaled transition temperature, T^*_{NI}, of the Lebwohl–Lasher model which is 1.1232 ± 0.0001 [20]; clearly T^* of 4.14×10^{-3} is far removed from the temperature at which the system becomes disordered. Alternatively, for a given temperature and elastic constant of the sample, increasing the scaled temperature corresponds to reducing the size of the unit cell of the lattice. The higher the scaled temperature the larger are the orientational fluctuations of the director associated with each site of the lattice. Of course, for given values of the temperature and average elastic constant there is a limiting value of the scaled temperature above which the size of the lattice cell becomes comparable to the molecular dimension, and the interpretation of the scaling parameter ε as ΛK no longer holds. That is, the use of the model potential to describe the elastic behaviour of a nematic should no longer be valid.

To describe the Fréedericksz transitions and the Schadt–Helfrich cell we need to include the interaction of the sample with an external field. This can be done by adding a second rank term to the energy for each site j:

$$\Phi_f = \gamma P_2(\cos \beta_j), \tag{7}$$

where γ is the strength parameter, which for a magnetic field is given by [2]

$$\gamma = -\Lambda^3 \Delta\tilde{\chi} B^2 / 2\mu_0. \tag{8}$$

The factor Λ^3 occurs here because the anisotropic magnetic susceptibility $\Delta\tilde{\chi}$ is a volume susceptibility and we require the magnetic energy for each unit cell [2]. The total free energy of the system is then given by

$$\Psi = 1/2 \sum_{j=1}^{N} \sum_{i=1}^{6} \Phi_{ij} + \gamma \sum_{j=1}^{N} P_2(\cos \beta_j), \tag{9}$$

where N is the number of sites. In the Fréedericksz experiments an external field is applied to a nematic sample which is subject to certain boundary conditions, in order to induce a deformation which depends on only one of the three elastic constants. For the splay deformation the sample is contained between two planar surfaces which we take to be parallel to the xy plane; these are treated in order to favour uniform planar alignment (e.g. along the y direction) of the nematic director. An external field is then applied perpendicular to these surfaces, that is in the z direction, which induces a pure splay deformation in the nematic sample. However, until the field reaches a critical value, the sample remains with the director uniformly aligned parallel to the surfaces; then a second order transition occurs and the director deviates from the unperturbed orientation, the largest deviation occurring in the middle of the cell. A similar experiment can be performed to induce a pure twist deformation if the field is now applied perpendicular to the original director orientation, but still in the plane defined by the surfaces for the same boundary conditions as before, that is the field is applied along the x direction. Finally, a pure bend deformation can be induced if the surfaces are treated in order to favour homeotropic alignment (perpendicular to the surfaces) and the field is applied parallel to the surfaces.

For these three Fréedericksz transitions, continuum theory, in the absence of director fluctuations, predicts a critical value of the external field, given by [1]

$$B_{c,i}^2 = (\pi/d)^2 \mu_0 K_i / \Delta\tilde{\chi}, \tag{10}$$

where the index i refers to splay (1), twist (2) and bend (3). The field-induced deformation has its maximum in the middle of the cell, where the effect of the surfaces is weakest, and the deformation angle, δ, is symmetric on going across the cell, where δ is the angle between the director and the direction of the easy axis in the surfaces. The deformation angle in the middle of the cell, $\delta_{\max}$, is clearly zero below the critical field ($B < B_{c,i}$), while for $B > B_{c,i}$ the following expression, relating $\delta_{\max}$ to the field, has been derived by Saupe [21]:

$$B = B_c (2/\pi) \Pi(\alpha^2, k) / (1 + k \sin^2 \delta_{\max})^{1/2} \tag{11}$$

for the splay and bend deformations, where

$$\alpha^2 = \kappa \sin^2 \delta_{\max} / (1 + \kappa \sin^2 \delta_{\max}) \tag{12}$$

$$k^2 = (1 + \kappa) \sin^2 \delta_{\max} / (1 + \kappa \sin^2 \delta_{\max}) \tag{13}$$

and $\Pi(\alpha^2, k)$ is the complete elliptic integral of the third kind. The parameter κ is given by $(K_3/K_1 - 1)$ for a splay transition and $(K_1/K_3 - 1)$ for a bend transition. Although the critical field for a Fréedericksz transition depends only on the corresponding elastic constant (see equation (10)) the deformation for fields higher than B_c is determined by both K_1 and K_3. In contrast, the twist deformation does not involve any mixing with the two other fundamental deformations and the field is related to the maximum twist in the middle of the cell by

$$B = B_c (2/\pi) K(\sin^2 \delta_{\max}), \tag{14}$$

where $K(\sin^2 \delta_{\max})$ is the complete elliptic integral of the first kind [21].

In the Schadt–Helfrich cell, on which twisted nematic displays are based, the surfaces are also treated to favour a parallel alignment of the director, but they are rotated by $\pi/2$ with respect to each other. Consequently in the absence of any field the director adopts a helical structure. When the field is applied perpendicular to the surfaces the induced deformation depends on a combination of the three elastic constants, in contrast to the Fréedericksz transition. The critical value of the field, for this transition, is given by [2]

$$B_{c,SH}^2 = (\pi/d)^2 \mu_0 [K_1 + (K_3 - 2K_2)/4] / \Delta\tilde{\chi}. \tag{15}$$

There is, however, no analytical expression for the deformation angle in the centre of the cell.

3. Simulation details

The scaled potential used in the simulations is obtained from equation (4) by dividing by $|v|$. This means that the scaled temperature used in the Metropolis scheme is given by

$$T^* \equiv k_B T / |v| = 3 k_B T / (\Lambda |K_1 - 3K_2 - K_3|) \tag{16}$$

which reduces to equation (6) in the limit of the spherical approximation. We have studied samples of dimension $10 \times 10 \times N_z$, with N_z of 12 and 16, where the first and last plane of the lattice contain the directors at the surfaces of the cell. These have a definite orientation which is not changed during the Monte Carlo chain, while there are periodic boundary conditions in the x and y directions. The thickness of the cell is given by $(N_z - 1)\Lambda$. At first sight this expression for the thickness may seem unexpected since the sample appears to contain N_z unit cells between the two surfaces which would give a thickness of $N_z\Lambda$. However, for the two unit cells containing the director at the surfaces only half of their dimension is to be included in the cell thickness; in other words the perfectly pinned directions are exactly at the surfaces. For the three Fréedericksz experiments and for the Schadt–Helfrich cell, the critical fields have been determined by running simulations for different values of the applied field. For each case two sets of simulations have been run in cascade, equilibrating each configuration starting from the final configuration of the previous production run. The first set has an increasing field strength parameter, γ, and the second has a decreasing field strength, in order to check for any hysteresis about the critical field. In all cases the two sets of results are practically indistinguishable. Each simulation took typically 200 000 cycles for the equilibration as well as for the production stage. The Markov chain of configurations is generated as in [16]: each cycle consists of a random orientational displacement of N randomly chosen sites, followed by $N/2$ random orientational displacements of each site of even parity and then $N/2$ random orientational displacements of each site of odd parity; the parity of a site is defined as the parity of the sum of its coordinates (i, j, k) representing the (x, y, z) position of the site in the three-dimensional cubic lattice. The Barker–Watts technique [22] has been used to change the director orientation. The ratio between accepted and rejected configurations during the Monte Carlo sampling was kept between 0.48 and 0.52, by changing the maximum rotational displacements allowed.

The property used to characterize the transitions is the orientation of the director in each xy plane of the lattice. Accordingly, for each plane of the lattice parallel to the surface we have calculated the instantaneous ordering tensor $\mathbf{Q}(k)$, where k represents the position in the lattice along the z coordinate, and averaged $\mathbf{Q}(k)$ over the number of configurations generated in the production stage, as well as over the number of sites in each plane. The averaged ordering tensor $\bar{\mathbf{Q}}(k)$ was then diagonalized to obtain the order parameter for the directors, in each plane, $\overline{P_2^{\mathrm{d}}}(k)$ and the director components $n_x(k)$, $n_y(k)$ and $n_z(k)$. This appoach is valid only in the limit of a narrow distribution of directors, i.e. a large order parameter $\overline{P_2^{\mathrm{d}}}(k)$. If the orientational fluctuations are relatively large, then it would be more appropriate to diagonalize the $\mathbf{Q}$ tensor at each step, in order to follow possible changes in the director orientation during the production stage. Such motions do not take place for the systems we have studied. This has been checked by running a sequence of simulations for the twist Fréedericksz transition, first 10 runs of 1000 cycles each, then 10 runs of 10 000 cycles each and finally a run of 100 000 cycles; all gave the same results for the director distribution within the simulation error.

4. Results and discussion

To determine the expansion coefficients in the pair potential we have used the elastic constants of 4,4′-dimethoxyazoxybenzene (or p-azoxyanisole, PAA). The values are $K_1 = 7.0 \times 10^{-12}$ N, $K_2 = 4.3 \times 10^{-12}$ N and $K_3 = 17.0 \times 10^{-12}$ N at 120°C. This parametrization has already been studied by Romano [18], where the model potential has been used to investigate the bulk properties of the system at a molecular level. In particular the scaled nematic–isotropic transition temperature, T^*_{NI}, was found to be 1.368. To test the range of validity of the model potential for the elastic behaviour we have chosen three different scaled temperatures. One of these is T^* of 7.8981×10^{-5}, corresponding to a unit cell dimension, Λ, of 9 μm, and at this low value we expect the model potential to give results in quantitative agreement with continuum theory, since the simulation corresponds to a straightforward minimization of the energy. An apparently similar value of the scaled temperature was also selected by Gruhn and Hess [9]; however an exact comparison with their simulations is not straightforward because they used a rectangular unit cell which contrasts with the cubic unit cell used here. For real nematic cells whose thickness is of the order of a few microns, Λ should be of the order of 10^{-1} μm for a lattice with N_z between 12 and 16. In fact we have used such a unit cell dimension namely 0.07108 μm which corresponds to a scaled temperature of 0.01. In this case the thickness of the simulated samples is of the order of a micron and we expect the model potential at this scaled temperature to be in almost quantitative agreement with the continuum theory predictions. Finally, we have set the scaled temperature, T^*, to 0.1, corresponding to a size for the unit cell of the lattice of 0.007108 μm where we expect to find some deviations between the results of the simulations and continuum theory because of the greater importance of director fluctuations. A similar value of the scaled temperature is used in the simulation of disclinations described by Chiccoli *et al.* [11].

The first set of simulations at a scaled temperature of 7.8981×10^{-5} has been performed with a lattice of $10 \times 10 \times 16$. The value of the deformation angle $\delta_{\max}$ in the middle of the lattice, obtained from the simulations, was calculated by a cubic spline interpolation of the values of the angles at the various positions k along the z axis of the lattice. In figure 1 (*a*) we report the dependence of $\delta_{\max}$ on γ for the three Fréedericksz transitions investigated, as open symbols for decreasing field strength and solid symbols for increasing field strength. The step $\Delta\gamma$ in the field strength about the transition point is 0.0001 for the twist geometry, 0.0002 for the splay geometry and 0.0005 for the bend geometry, corresponding to a relative step $\Delta\gamma/\gamma_c$ of *c.* 0.5% in each of the three cases. The results for the transitions show

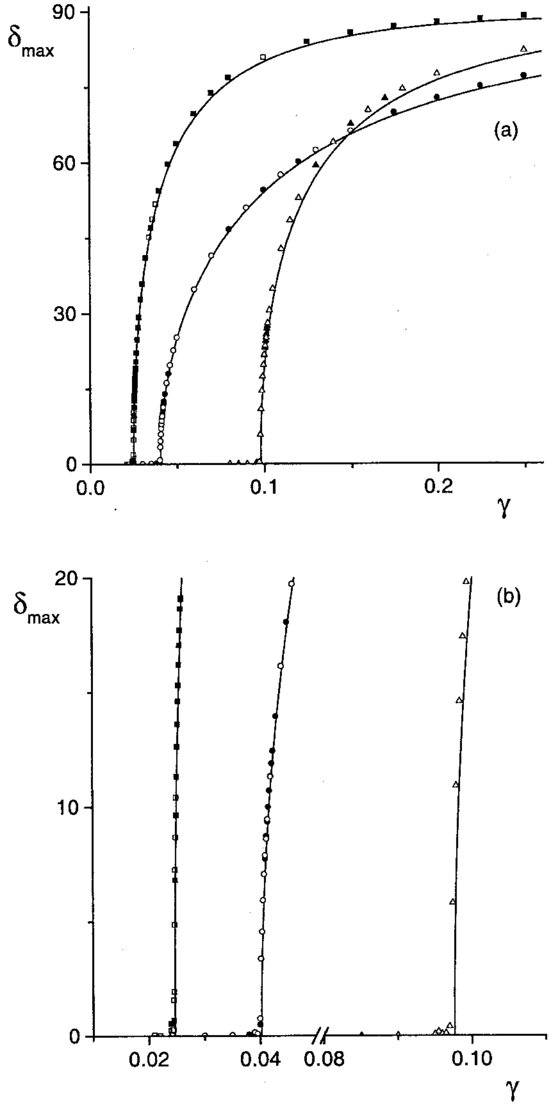

Figure 1. (*a*) The dependence of the deformation angle, $\delta_{\max}$, on the field strength parameter, γ, for a lattice of $10 \times 10 \times 16$ and at a scaled temperature, T^*, of 7.8981×10^{-5}; (circles) splay, (squares) twist, (triangles) bend Fréedericksz experiments. The solid symbols represent a set of simulations for increasing field strength while the open symbols are for decreasing field strength. The solid lines are the analytical solutions given by continuum theory for the three Fréedericksz experiments obtained from equations (11) and (14). (*b*) The same results as in (*a*) but on an expanded scale about the critical fields.

no hysteresis within the error of the simulations. They also show, as expected, that as the field strength parameter, γ, is increased, so the maximum displacement angle remains at zero until a critical value is reached when $\delta_{\max}$ increases continuously, corresponding to a second order transition. The continuous nature of this is clearly apparent from the results shown on an expanded scale in figure 1 (*b*). The angle $\delta_{\max}$ then increases, tending to its limiting value of 90° although clearly at different rates for the three Fréedericksz transitions. We can compare the results obtained from the simulations with the predictions of continuum theory without needing to introduce any adjustable parameters. By using equation (10), and taking account of the scaling of the potential energy by $|\nu|$, the critical field strength parameters predicted by continuum theory are

$$\gamma_{c,i} = 3K_i\pi^2/[|K_1 - 3K_2 - K_3|(N_z - 1)^2] \qquad (17)$$

with $i = 1$, 2 and 3 for the splay, twist and bend transitions, respectively. A similar expression can be derived from equation (15) for the critical field strength parameter $\gamma_{c,SH}$ for the Schadt–Helfrich cell. The predicted dependence of the angle $\delta_{\max}$ on the field strength parameter can be obtained from equations (11) and (14) by replacing B with $\gamma^{1/2}$ and B_c with the appropriate $\gamma_c^{1/2}$. For this case, equation (17), after the appropriate substitutions, gives $\gamma_{c,1} = 0.04023$, $\gamma_{c,2} = 0.02471$ and $\gamma_{c,3} = 0.09769$. The solid lines in figure 1 (*a*) show the predictions of $\delta_{\max}$ obtained in this way. It appears that there is an essentially quantitative agreement between the analytical solutions and the results of the simulations. In figure 1 (*b*) the expanded critical regions for the three experiments are reported and the agreement with the prediction of continuum theory is seen to be very good. The largest error in the values of the critical field strength parameters $\gamma_{c,i}$ occurs for the bend deformation and is estimated to be less than 0.4%. This agreement between the results of the Monte Carlo simulations and continuum theory is especially impressive as the theory does not contain any adjustable parameters. It clearly demonstrates that the Monte Carlo methodology provides a reliable route to the director configuration which minimizes the elastic energy.

We have also investigated the dependence of the critical field on the thickness of the sample by repeating the simulations for a thinner box with N_z of 12. In figure 2 we show the results of the simulations together with the continuum theory predictions given by equations (11) and (14). Again quantitative agreement is obtained for the critical field strength parameters, although there is a slightly worse agreement for large deformations in the case of the twist and bend transitions. This is almost certainly due to the approximation of small displacements between two interacting directors on which the model potential and the continuum theory are based. As the lattice size is reduced the amount of deformation between two consecutive planes of the lattice, for the same total distortion in the middle of the cell, necessarily becomes larger.

For this smaller box size, we have also investigated the Schadt–Helfrich cell. In figure 3 (*a*) we report the azimuthal (α) and polar (β) angles of the director in each

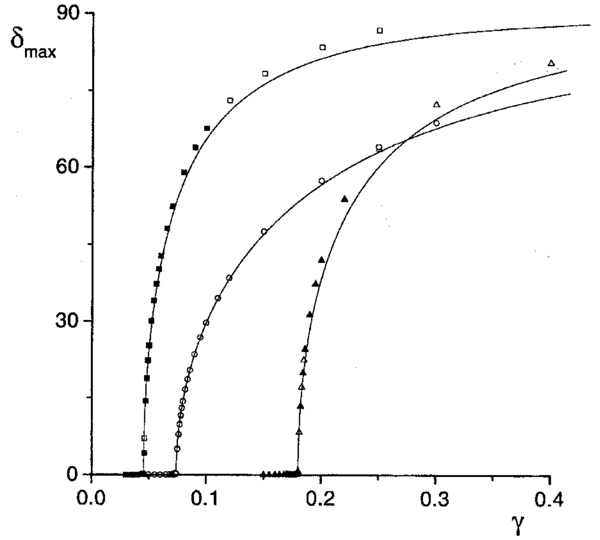

Figure 2. (*a*) The dependence of the deformation angle, δ_{max}, on the field strength parameter, γ, for a lattice of $10 \times 10 \times 12$ and at a scaled temperature, T^*, of 7.8981×10^{-5}; (circles) splay, (squares) twist, (triangles) bend Fréedericksz experiments. The solid symbols represents a set of simulations for increasing field strength while the open symbols are for decreasing field strength. The solid lines are the analytical solutions given by continuum theory for the three Fréedericksz experiments obtained from equations (11) and (14).

plane k for two different values of the field strength parameter, one below ($\gamma = 0.0950$) and the other well above ($\gamma = 0.3500$) the critical field ($\gamma_{c,SH} = 0.0960$). Below the critical field the polar angle is 90° and the azimuthal angle varies linearly across the cell showing that the helical distribution of the director is unperturbed by the field. Above the critical field the polar angle now varies significantly across the cell with the maximum displacement from the original orientation being about 75°. Although there is a large variation in the polar angle on going far above the critical field, the deviation of the azimuthal angle from its linear dependence is relatively small. The helical structure of the director would, therefore, appear to be largely intact. In figure 3 (*b*) the deformation angle in the middle of the lattice, δ_{max}, which is given simply as the deviation from $\pi/2$ of the polar angle of the director, is reported as a function of the field strength parameter γ. The critical field, $\gamma_{c,SH}$, estimated from the simulated results is 0.0960 ± 0.0005. This compares extremely well with the predicted value of 0.0972 obtained from equation (15).

In figure 4 we report the results of the simulations for the field dependence of the maximum displacement angle as a function of the field strength parameter at a scaled temperature T^* of 0.01 and a lattice of $10 \times 10 \times 12$ for the Fréedericksz experiments; these are comparable to the results obtained for the same system size but at the lower scaled temperature of 7.8981×10^{-5} (see figure 2). The solid lines show the continuum theory predictions and, as we can see, the agreement in the vicinity of the critical fields is still almost quantitative. Far above the critical fields the maximum displacements obtained from the simulations are slightly in excess of those predicted by continuum theory for the twist and bend deformations

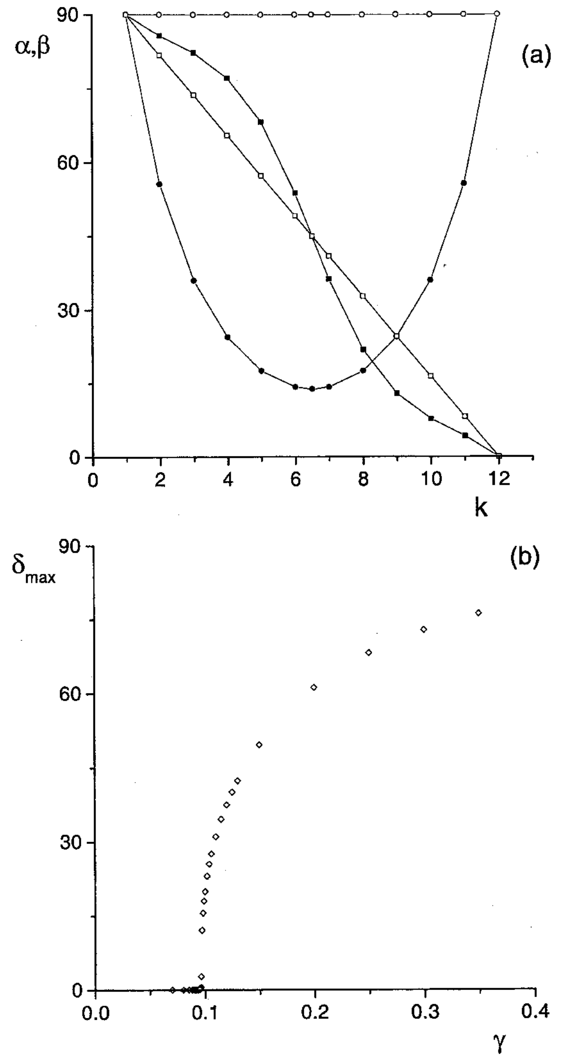

Figure 3. (*a*) The orientation of the director in the Schadt–Helfrich cell as a function of the position k along the z coordinate for a $10 \times 10 \times 12$ lattice at a scaled temperature, T^*, of 7.8981×10^{-5}; (squares) azimuthal, α, and (circles) polar, β, angles. The open symbols indicate the results for a field ($\gamma = 0.095$) below the critical value and the solid symbols for a field ($\gamma = 0.350$) well above the critical value, where the critical value for the field strength parameter, $\gamma_{c,SH}$, predicted by equation (15), is 0.09724. The critical value estimated from the simulations is 0.0960 ± 0.0005. (*b*) The dependence of the deformation angle in the middle of the Schadt–Helfrich cell, δ_{max}, on the field strength parameter γ. The solid symbols are for increasing γ and the open symbols for decreasing γ.

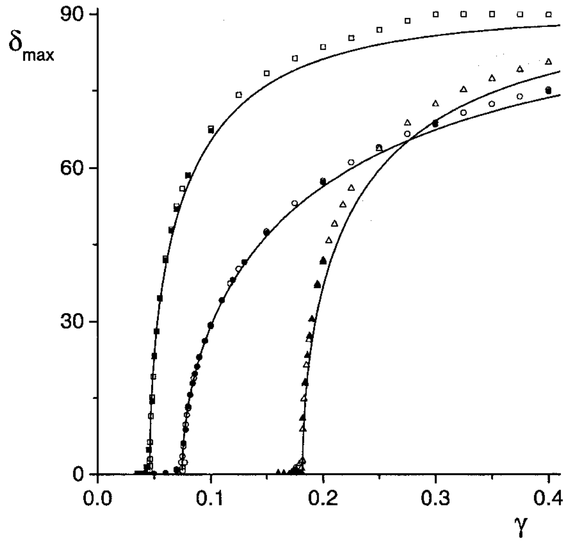

Figure 4. The dependence of the deformation angle, δ_{max}, on the field strength parameter, γ, for a lattice of 10 × 10 × 12 and a scaled temperature, T^*, of 0.01; (circles) splay, (squares) twist, (triangles) bend Fréedericksz experiments. Solid symbols represents a set of simulations for increasing field strength while the open symbols are for decreasing field strength. The solid lines are the analytical solutions given by continuum theory for the three Fréedericksz experiments obtained from equations (11) and (14).

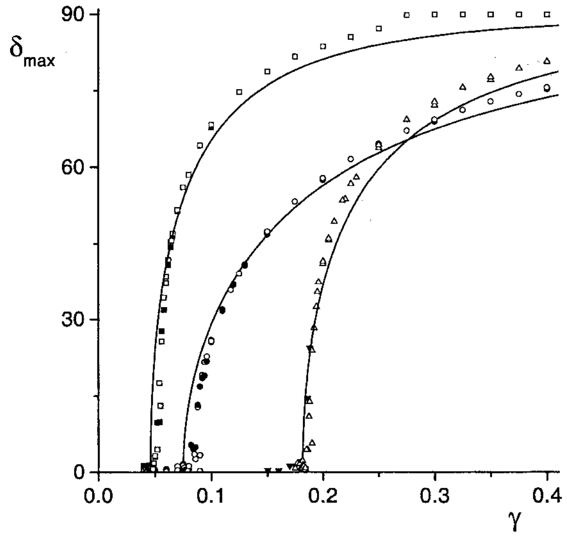

Figure 5. The dependence of the deformation angle, δ_{max}, on the field strength parameter, γ, for a lattice of 10 × 10 × 12 and at a scaled temperature, T^*, of 0.1; (circles) splay, (squares) twist, (triangles) bend Fréedericksz experiments. The solid symbols represents a set of simulations for increasing field strength while the open symbols are for decreasing field strength. The solid lines are the analytical solutions predicted by continuum theory for the three Fréedericksz experiments obtained from equations (11) and (14).

although the agreement for the splay is quite good. Similar agreement was found for the much lower scaled temperature and so it would seem that increasing T^* to 0.01 has little influence on the elastic behaviour of the model, presumably because the director fluctuations are still relatively small.

In order to see how high the scaled temperature used in the Monte Carlo simulation can be before director fluctuations have a significant influence on the results, we have studied the same lattice size (10 × 10 × 12) at T^* of 0.10. As we have seen this would correspond to a unit cell size only ten times larger than the molecular length of PAA [16]. The dependence of the angle in the middle of the box, δ_{max} is shown as a function of the field strength parameter in figure 5 together with the continuum theory predictions. We can see that there is a clear shift of the critical fields to higher values at this higher scaled temperature. For T^* of 0.10 there are small but significant director fluctuations in each *xy* plane of the lattice, which give a director order parameter $\overline{P_2^d}$ that typically is as small as 0.95 ± 0.01, while, for T^* of 7.8981 × 10^{-5}, the director order parameter $\overline{P_2^d}$ is found to be significantly larger at 0.99997 ± 0.00001. The larger director fluctuations at the higher scaled temperature are almost certainly responsible for the quantitative difference in behaviour of the model potential in comparison with the predictions of continuum theory which does not allow for such fluctuations. Moreover, the shift of the critical field strength parameters $\gamma_{c,i}$ to higher values for a scaled temperature of 0.10, can also be interpreted as a result of the larger fluctuations in the orientation of the directors. In fact, they reduce the effective anisotropy in the coupling tensor of the nematic director with the external field, so that a higher field is required, for the same value of the elastic constants, in order to induce the transition to a deformed state. We notice that the amplitude of these fluctuations is consistent with the values of the maximum allowed rotational displacement, $\Delta\phi_{max}$, observed in the simulations, which is ≈0.4° at a scaled temperature of 7.8981 × 10^{-5}, rising to ≈10° at T^* of 0.10. In addition the director fluctuations are similar to, but slightly smaller than those estimated for PAA from the asymmetry in the ESR lineshape of a transition metal complex dissolved in its nematic phase at the same absolute temperature [23].

Finally, a comment about the size of the unit cell of the lattice at the various scaled temperatures can be made. In a recent experimental study the coherence length, ξ, for the director fluctuations in the nematic phase of 4-butyl-4′-cyanophenylcyclohexane has been measured from the NMR spin-lattice relaxometry profile at low Larmor frequencies [24]. The coherence length is related to the dimension of the unit cell of the lattice in our Monte Carlo simulations since both represent the minimum distance over which the orientation of the director is constant. The authors have found that ξ varies from *c.* 200 nm at 41°C, close to the nematic–isotropic transition of the sample, up to a maximum of 1 μm at 29°C, close to the smectic–nematic transition. It is, however, at least one order of magnitude smaller than the dimension of the unit cell of the lattice at the lowest scaled temperature that we have investigated of 7.8981×10^{-5}. In contrast, the dimension of the unit cell for the other two scaled temperatures studied, namely T^* of 0.01 and 0.10, are of the same order of magnitude as the coherence length determined experimentally for the nematic phase of 4-butyl-4′-cyanophenylcyclohexane. This observation provides support for the use of a Monte Carlo simulation in order to include thermal fluctuations when studying director distributions.

5. Conclusions

We have explored the validity of the pairwise additive potential model developed by Gruhn and Hess [9] and parametrized by Romano [18] to describe the elastic behaviour of nematics for which the three elastic constants are not equal. To do this we have simulated, using the Metropolis Monte Carlo algorithm, the three Fréedericksz transitions for two system sizes and at three scaled temperatures. For the larger system where the director gradients are small, and a very low scaled temperature where the director fluctuations are negligible, there is a very good agreement between the simulated results and the predictions of the continuum theory, not only for the critical fields but also for the deformation angles at the centre of the cell. As the scaled temperature is increased so the thermal fluctuations of the director grow and the agreement with continuum theory predictions is less quantitative, presumably because the theoretical calculations ignore such director fluctuations. At the highest scaled temperature, the critical fields are significantly different from those of the continuum theory, as might be expected. An alternative view of this failure is that the dimensions of the unit cell of the lattice at the highest scaled temperature are equivalent to just a few molecular dimensions so that the director gradients are too large for continuum theory to be applicable.

The critical fields for the Fréedericksz transitions depend on a single elastic constant and so to test the model potential in a more complicated situation we have simulated the elastic behaviour of the Schadt–Helfrich twist nematic cell. At the low scaled temperature used there is a very good agreement between the observed critical field and that obtained from continuum theory.

It would seem, therefore, that the Gruhn–Hess potential, parametrized by Romano, with its assumption pairwise additivity provides a good model with which to study the elastic behaviour of nematics having three different elastic constants. Provided some care is exercised in the choice of the system size and scaled temperature the potential can be used with some confidence to explore the director distribution in more complex geometries including those which result in disclinations. In addition the use of the model at relatively high scaled temperatures allows the influence of director fluctuations on the elastic behaviour of a nematic to be readily included.

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Appendix

The S-functions constitute a complete set of basis functions spanning the space Ω defined by the orientational coordinates of triplets of unit vectors: $\Omega \equiv (\alpha_1, \beta_1, \alpha_2, \beta_2, \alpha_3, \beta_3)$ where α and β are the azimuthal and polar angles defining the orientation of the unit vector in a laboratory fixed cartesian frame. They are defined as [19]:

$$S_{L_1,L_2,J}(\Omega) = (i)^{L_1 - L_2 - J} \sum_{M_1 M_2 M} \begin{pmatrix} L_1 & L_2 & J \\ M_1 & M_2 & M \end{pmatrix} \times C_{L_1 M_1}(\alpha_1, \beta_1) C_{L_2 M_2}(\alpha_2, \beta_2) C_{JM}(\alpha_3, \beta_3), \tag{A1}$$

where $C_{LM}(\alpha, \beta)$ is a modified spherical harmonic and

$$\begin{pmatrix} L_1 & L_2 & J \\ M_1 & M_2 & M \end{pmatrix}$$

is a $3j$ symbol. The mapping of equation (1) onto the expansion of equation (3) gives:

$$\Phi_{jk} = \varphi_{202} S_{202} + \varphi_{022} S_{022} + \varphi_{220} S_{220} + \varphi_{222} S_{222} + \varphi_{224} S_{224} + \varphi_{422} S_{422} + \varphi_{242} S_{242} \tag{A2}$$

with

$$\begin{cases} \varphi_{202} = \varphi_{022} = (\Lambda/3\sqrt{5})(K_1 - 5K_2 + 4K_3) \\ \varphi_{220} = (\sqrt{5}\Lambda/21)(2K_1 - 7K_2 - 23K_3) \\ \varphi_{222} = (\sqrt{10}\Lambda/3\sqrt{7})(-5K_1 + 7K_2 - 2K_3) \\ \varphi_{224} = 0 \\ \varphi_{422} = \varphi_{242} = (6\Lambda/\sqrt{70})(K_1 - K_3). \end{cases} \tag{A3}$$

In this expansion for the elastic energy the ranks L_1 and L_2 have to be even because of the director symmetry; in addition the values adopted by J are restricted by those of L_1 and L_2 to the range $|L_1 - L_2|$ to $L_1 + L_2$. We see, therefore, that the Gruhn–Hess model potential includes almost all of the terms of the S-function expansion in a systematic manner, that is with increasing L_1 and L_2. One exception to this is that the term in $S_{224}(\Omega)$ is ignored, whereas the other two members of the set with $L_1 = L_2 = 2$ are included; these are $S_{220}(\Omega)$ and $S_{222}(\Omega)$. The next higher terms with $L_1 = 2$ and $L_2 = 4$ and *vice versa*, are also incomplete for this set, which contains for example $S_{242}(\Omega)$, $S_{244}(\Omega)$ and $S_{246}(\Omega)$, since only the term $S_{242}(\Omega)$ and its counterpart $S_{422}(\Omega)$ are included. Such inclusions and exclusions are made to ensure that the energy is independent of the director orientation to the inter-director vector when the two directors are parallel.

In terms of the invariants a_j, a_k and b_{jk} defined in § 2, the first few S-functions of even rank are:

$$
\begin{aligned}
S_{000}(\Omega) &= 1\\
S_{202}(\Omega) &= (3a_j^2 - 1)/2\sqrt{5}\\
S_{022}(\Omega) &= (3a_k^2 - 1)/2\sqrt{5}\\
S_{220}(\Omega) &= (3b_{jk}^2 - 1)/2\sqrt{5}\\
S_{222}(\Omega) &= [2 - 3(a_j^2 + a_k^2 + b_{jk}^2) + 9a_j a_k b_{jk}]/\sqrt{70}\\
S_{224}(\Omega) &= [1 + 2b_{jk}^2\\
&\quad + 5(-a_j^2 - a_k^2 - 4a_j a_k b_{jk} + 7a_j^2 a_k^2)]/4\sqrt{70}\\
S_{422}(\Omega) &= [1 + 2a_k^2\\
&\quad + 5(-a_j^2 - b_{jk}^2 - 4a_j a_k b_{jk} + 7a_j^2 b_{jk}^2)]/4\sqrt{70}\\
S_{242}(\Omega) &= [1 + 2a_j^2\\
&\quad + 5(-a_k^2 - b_{jk}^2 - 4a_j a_k b_{jk} + 7a_k^2 b_{jk}^2)]/4\sqrt{70}.
\end{aligned}
\tag{A4}
$$

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