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COMPUTER SIMULATION OF THE FIELD-INDUCED ALIGNMENT OF THE SMECTIC A PHASE OF THE GAY-BERNE MESOGEN GB(4.4,20.0,1,1)

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As an aid to understanding the mechanism for the field-induced alignment of the smectic A phase we have attempted to simulate this process for the Gay-Berne model mesogen GB(4.4,20.0,1,1). The results for the quasi-dynamical behaviour of the alignment process obtained from a constant pressure-constant temperature Monte Carlo simulation are discussed. It is found that the molecules realign parallel to the field without destroying the layer structure and, more or less, as a monodomain in the simulations. This is qualitatively in agreement with the results obtained from recent deuterium NMR and small angle X-ray experiments. In addition, the relationship between the box shape and structures formed during the alignment process is discussed. The choice of box is found to be important for the simulation of the field-induced alignment process.

Keywords: field-induced alignment; smectic A; computer simulation; Gay-Berne mesogen; quasi-dynamics

INTRODUCTION

The field-induced alignment of the director in a smectic A phase is a relatively complex process involving the translational as well as the orientational motion of the molecules in order to preserve the layer structure. The complexity of the process has been revealed by deuterium NMR [1] and small angle X-ray scattering [2] studies. An important variable in these experiments proves to be the angle between the aligning field and

We wish to thank Professor M. Neal (University of Coventry) for suggesting that we might use a triclinic box to simulate the field-induced alignment of a smectic A phase. We are grateful to the EPSRC for the award of a Postdoctoral Research Fellowship to K.S. He also thanks the Anglo-Japanese Daiwa Foundation for financial support and the British Council for a travel grant.

the initial director orientation. When these two directions are orthogonal the smectic A phase is not aligned as a monodomain but when the angle is about 45° or less then monodomain rotation does occur. That is the distribution of both the director and the smectic layer normal are more or less uniform during the alignment process. To help understand the results of such experiments we have undertaken a computer simulation investigation analogous to that of the real experiments. In this study, we determine the quasi-dynamical behaviour of the field-induced alignment of a smectic A phase by constant pressure-constant temperature Monte Carlo simulations with conventional periodic boundary conditions in three dimensions. The model liquid crystal used in this study was the Gay-Berne mesogen GB(4.4,20.0,1,1) chosen because the anisotropy in the repulsive and attractive forces are comparable to those for real mesogenic molecules [3]. In addition, the single-site potential function [4] is computationally tractable and so a relatively large number of particles can be studied; further the properties of this mesogen are well-known [5].

SIMULATION DETAILS

The constant pressure-constant temperature Monte Carlo method was used to study the system which was composed of 2048 GB(4.4,20.0,1,1) mesogenic particles. Although it is clearly impossible to determine the dynamic properties directly from a Monte Carlo simulation, some indication of the particle dynamics can be obtained since the configurational update of the previous cycle in a conventional Monte Carlo scheme [6,7] is analogous to the diffusional motion undergone by the particles. In addition our primary concern is not with the details of the particle motion but how their organisation in the sample changes, at least qualitatively, during the field-induced alignment process. The mesogen was studied at the state point $P^* = 1.0$ and $T^* = 1.10$, at which the smectic A phase is stable [5]. The scaled variables P^* and T^* are $P/\varepsilon_0\sigma_0^{-3}$ and $k_B T/\varepsilon_0$ respectively where ε_0 and σ_0 are the well depth and contact distance when the Gay-Berne particles are orthogonal both to each other and to the interparticle vector.

The most important problem for the simulation of a smectic phase is to ensure that the layers in the box are commensurate with those of their periodic images [8,9]. To appreciate the problem it is useful to consider a smectic phase for which the layer normal is confined to the xy plane of the simulation box. The arrangement of the layers in the rectangular area is shown in Figure 1(a) and for these to be commensurate with their periodic images the following two conditions for the box dimensions, L_x and L_y, have to be satisfied [11]

$$L_y = N_y d/\cos\theta_y \tag{1}$$

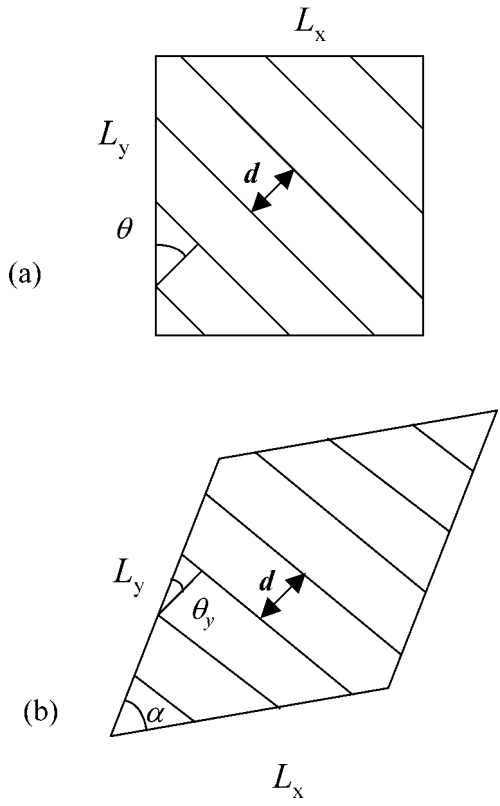

FIGURE 1 Sketches showing the arrangement of the smectic layers in the simulation box when the layer normal is in the plane for (a) an orthorhombic box and (b) a triclinic box.

and

$$L_x = N_x d / \sin\theta_y. \tag{2}$$

Here, N_x and N_y are integers corresponding to the number of layers intersecting an edge of the simulation box, θ_y is the angle made by the layer normal with the y axis of the box and d is the layer spacing. Strictly, of course, the layers in a smectic A phase are not as well-defined as the sketch in Figure 1 suggests. The lines here simply indicate the points midway between the maxima in the singlet translational distribution function or density wave along the layer normal and d is the layer spacing or distance between the maxima. It is clear, from Eqs. (1) and (2), that it will not be difficult for the orthorhombic box to expand or contract so that the structure in the box is commensurate with its images provided θ_y does not

adopt values close to the extremes of 0° or 90° when L_x and L_y, respectively would have to become impossibly large. Thus it is important to select the simulation cell as well as the initial configuration and how the simulation box changes during the simulation. It has also been suggested that an orthorhombic box, able to change its dimensions independently, should be used in the computer simulation of liquid crystal phases [10]. In our study, two simulation box shapes were used in order to simulate the major change in the phase structure and director orientation produced by the magnetic field. One of them had an orthorhombic shape in which each angle of the box is kept at 90° during the simulation which seems entirely appropriate while the phase remains as a smectic A during the alignment process. However, it may also be possible to ensure that the periodic images are commensurate with the layered structure in the simulation box by using a triclinic shape for this. To understand such a choice it is again useful to consider the case when the layer normal is confined to the xy-plane sketched in Figure 1(b). Now the constraints on the box dimensions also depend on the angle, α, between the x and y axes. For the arrangement shown in Figure 1(b) the box length L_y is still given by Eq. (1) but the dimension L_x must satisfy

$$L_x = N_x d/\sin(\alpha - \theta_y), \tag{3}$$

This can now be achieved by changing the angle α as well as L_x provided the difference, $\alpha - \theta_y$, is such that $\sin(\alpha - \theta_y)$ does not become vanishingly small. We have, therefore, also explored the use of this shape in which the dimensions and also the angles can change during the simulation. The triclinic shape has mainly been used for the simulation of phase transitions between crystal phases [12]. Here we are concerned with what kind of cell box is most effective for the simulation of the realignment process of a smectic A structure.

The contribution to the energy from the interaction of the external field with particle i is defined by

$$U_{\text{ext}} = -\lambda P_2(\cos\theta_i), \tag{4}$$

where θ_i is the angle between the symmetry axis for the ith particle and the external field vector which we take to be a magnetic field λ is the strength parameter for the magnetic interaction and is given by

$$\lambda = \Delta\kappa B^2/3\,\mu_0, \tag{5}$$

where $\Delta\kappa$ is the anisotropy in the molecular magnetic polarizability, and μ_0 is the vacuum permeability. In the simulation, a reduced strength parameter, $\lambda^*(\equiv 3\lambda\mu_0/\Delta\kappa B^2\varepsilon_0)$, was used. The director vector was determined via the Q-tensor

$$Q_{\alpha\beta} = N^{-1} \sum_i (3u_\alpha^i u_\beta^i - \delta_{\alpha\beta})/2, \tag{6}$$

where u_α^i is a unit vector defining the component, $\alpha = $ x, y or z, of the orientation of the symmetry axis for particle i, and N is the number of particles in the system. The director was defined as the eigenvector associated with the largest eigenvalue which was obtained by diagonalizing the Q-tensor every cycle. In the case of orthogonal smectic phases, this eigenvector also corresponds to the layer normal vector, **d**. However, these vectors are not equivalent in a tilted structure, as in a smectic C. The layer normal vector for this case was evaluated following the procedure described by Withers *et al.* [13]. In order to calculate **d**, a local layer normal, $\mathbf{d}_i$, was determined for each particle i by diagonalizing the tensor,

$$Q_{\alpha\beta}^{(i)} = \frac{1}{n(n-1)} \sum_j^n \sum_{j \neq k}^n \left[\frac{3}{2} \left(\hat{\mathbf{r}}_{ij} \times \hat{\mathbf{r}}_{ik} \right)_\alpha \left(\hat{\mathbf{r}}_{ij} \times \hat{\mathbf{r}}_{ik} \right)_\beta - \frac{1}{2} \delta_{\alpha\beta} \right], \tag{7}$$

where $\hat{\mathbf{r}}_{i\eta}$ is the unit vector between particle i and one of the n particles neighbouring it. To define the number of neighbouring particles, we used the condition; $|r_{i\eta}| < 2\sigma_0$ which will necessarily select particles in the same layer. These local normals were then used to construct the tensor,

$$Q_{\alpha\beta} = N^{-1} \sum_i (3\mathrm{d}_\alpha \mathrm{d}_\beta - \delta_{\alpha\beta})/2, \tag{8}$$

the system layer normal, **D**, being identified with the eigenvector corresponding to the largest eigenvalue of **Q**. The tilt angle for the director is then obtained from $\cos^{-1}(\mathbf{n} \cdot \mathbf{D})$. The change in the translational order parameter is of particular relevance because it has been suggested that the translational order of the smectic A phase might be reduced during the alignment process [1]. This order parameter was estimated via

$$\tau = |\rho(r^*) \exp(2i\pi r^*/d^*)|, \tag{9}$$

where d^* is the reduced layer spacing, r^* is the reduced position of a particle along the director, and $\rho(r^*)$ is the singlet translational distribution function. This definition has the advantage that it is independent of the choice of the origin for the r^*-coordinates. In the simulation this order parameter, τ, was obtained by averaging $\cos(2\pi r^*/d^*)$ and $\sin(2\pi r^*/d^*)$ over the production run. However, it is necessary to know the reduced layer spacing of the smectic phase. The value of $d^* (\equiv d/\sigma_0)$ was estimated by finding the value which maximized τ [5]. This maximum value was identified as the translational order parameter. As we have seen for an orthorhombic box during the field-induced alignment of the layers the angle θ_y made by the layer normal with the y axis should not be small (see Eq. (2)). Accordingly the starting configuration which we have adopted has the layer

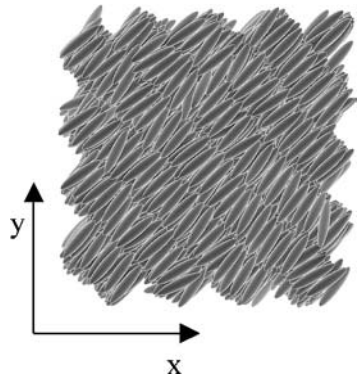

FIGURE 2 The initial configuration for the smectic A phase of GB(4.4,20.0,1,1) for $\lambda^* = 2.0$ and with an orthorhombic box.

normal at an angle of 45° with the y axis; this configuration is shown in Figure 2. The angle between the initial director orientation and the applied field was set at 45° that is the field was applied along the y axis. However, prior to this the external field was applied along the director for the initial configuration so as to obtain an equilibrium structure in the presence of the field, before rotating it along the required direction. Each calculation takes between 2×10^5 to 2×10^6 cycles to simulate the alignment process after equilibration for 1×10^5 cycles. The vectors defining the dimensions of the simulation box were changed every cycle.

RESULTS AND DISCUSSION

The change of the tilt angle, that is between the director and the layer normal, as well as the translational order parameter, τ, for the system with $\lambda^* = 2.0$ using the orthorhombic box are shown in Figure 3. As we can see, the value of the tilt angle increased during the early stages of the simulation from the 0th to the 6,000th cycle. Since the starting structure is not tilted (see Fig. 2), it is confirmed that the molecules tilt with respect to the layer normal in the early stages due to the interaction between the molecules and the magnetic field. However, the tilt angle decreased quickly, returning to the initial value for a non-tilted phase. On the other hand, the translational order parameter decreased rapidly in the early stages of the alignment process, it also recovered to its initial value relatively quickly, and then remained constant. Here we note that the evaluation of τ (see Eq. (9)) has some difficulties based on this definition of the translational order parameter as we shall describe. To begin with, it is useful to examine the

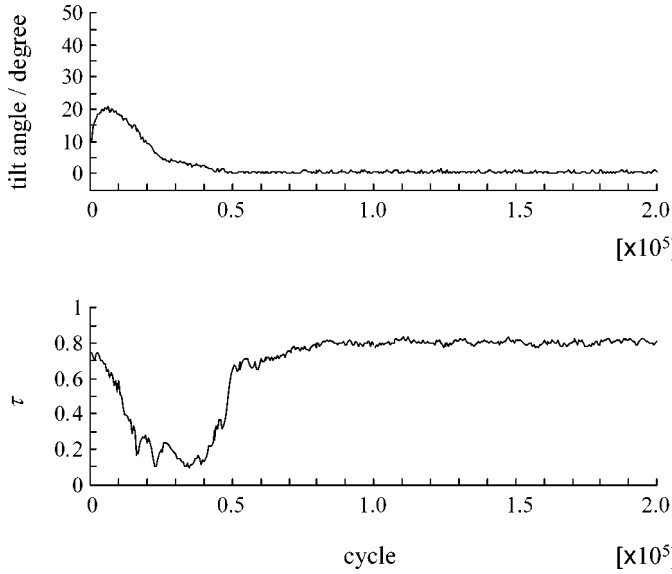

FIGURE 3 The tilt angle and translational order parameter as a function of the number of cycles for GB(4.4,20.0,1,1) with a field strength parameter, λ^*, of 2.0.

instantaneous configurations taken during the alignment process by the magnetic field; the snapshots for these obtained with $\lambda^* = 2.0$ are shown in Figure 4. The molecules are first tilted with respect to the layer normal because of the strong field as we can see from the snapshot for the 2,500th cycle, (see Fig. 4(a)). Then the box expanded along the x* direction in keeping with the decrease in θ_y (see Eq. (1)). Next we can see that the layer starts to rotate towards the applied field at the 10,000th cycle, (see Fig. 4(b)). Some molecules seem to slip towards the upper layer to make up for the reforming layer structure in the configuration at the 15,000th cycle, (see Fig. 4(c)). In other words, the layer structure begins to buckle partially in the vicinity of the 15,000th cycle. After this stage, the smectic phase was rebuilt quickly through the formation of a ripple structure (see Fig. 4(d)) at the 30,000th cycle. As we can see, the layer structure was essentially maintained during the entire process, although a ripple structure formed in the middle of the process. As we have mentioned, however, the translational order parameter shows a lower value for these cycles in apparent contradiction with the snapshots of the configurations shown in Figure 4. The value τ is underestimated because of the difficulty in evaluating the density wave for a ripple structure; the effect of this structure is to reduce significantly the oscillations in $\rho(r^*)$. Therefore, the

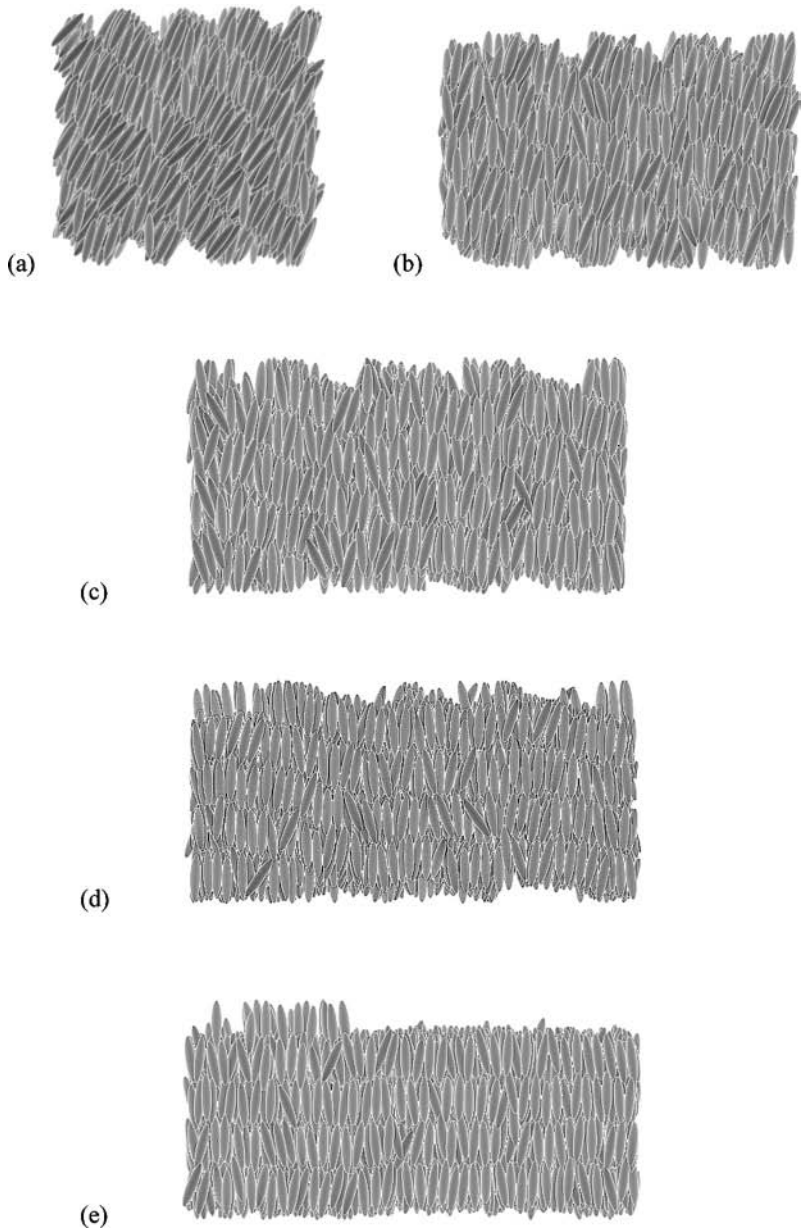

FIGURE 4 Snapshots of the structural changes observed for GB(4.4,20.0,1,1) with $\lambda^* = 2.0$ using an orthorhombic box. (a) 2,500th, (b) 10,000th, (c) 15,000th, (d) 30,000th, and (e) 100,000th cycle.

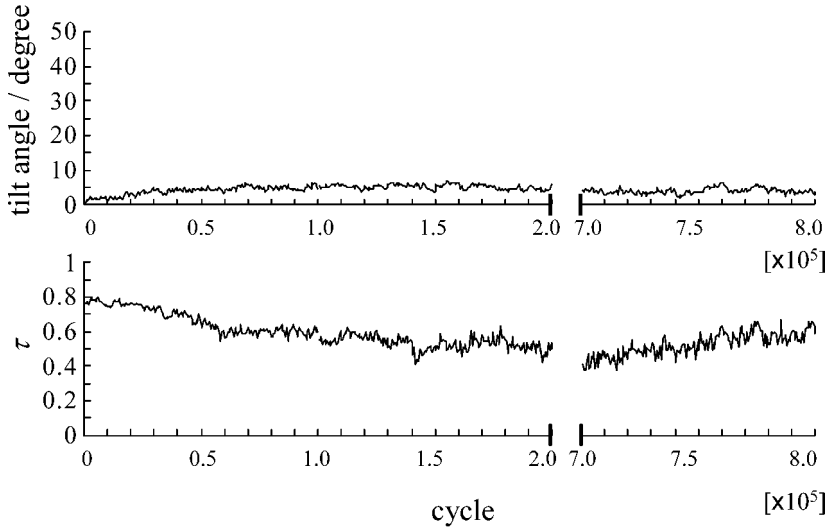

FIGURE 5 The tilt angle and translational order parameter as a function of the number of cycles for GB(4.4,20.0,1,1) with a field strength parameter, λ^*, of 0.1.

translational order parameter is underestimated in the early stages of the simulation following the application of the field. As we see from the configurational snapshots, the layer structure has been retained during the alignment process except for a partial deformation. The result suggests that the sample needs a partial deformation or a slip motion along the layer normal direction in order to reform the smectic structure smoothly. However, this deformation might be caused by the specific simulation box which was used, as we shall describe later.

Next we consider what changes occur when the aligning field strength is reduced significantly from λ^* of 2.0 to 0.1. Figure 5 shows the change of tilt angle and the translational order parameter, τ, for the system with $\lambda^* = 0.1$ using an orthorhombic simulation box. For this weaker field, the particles are scarcely tilted with respect to the layer normal during the field-induced alignment process. However, the translational order parameter decreases gradually, although it never vanishes and eventually seems to start to increase. Some configurational snapshots for the system are shown in Figure 6. It can be seen that the simulation box has been elongated along the x* direction in the simulation frame; this is the same as for the system with the significantly higher field, namely $\lambda^* = 2.0$. This increase in L_x occurs for exactly the same reason as for the larger field, namely to satisfy the condition in Eq. (2). The system also required an enormously larger number of cycles to rotate the molecules towards the applied field.

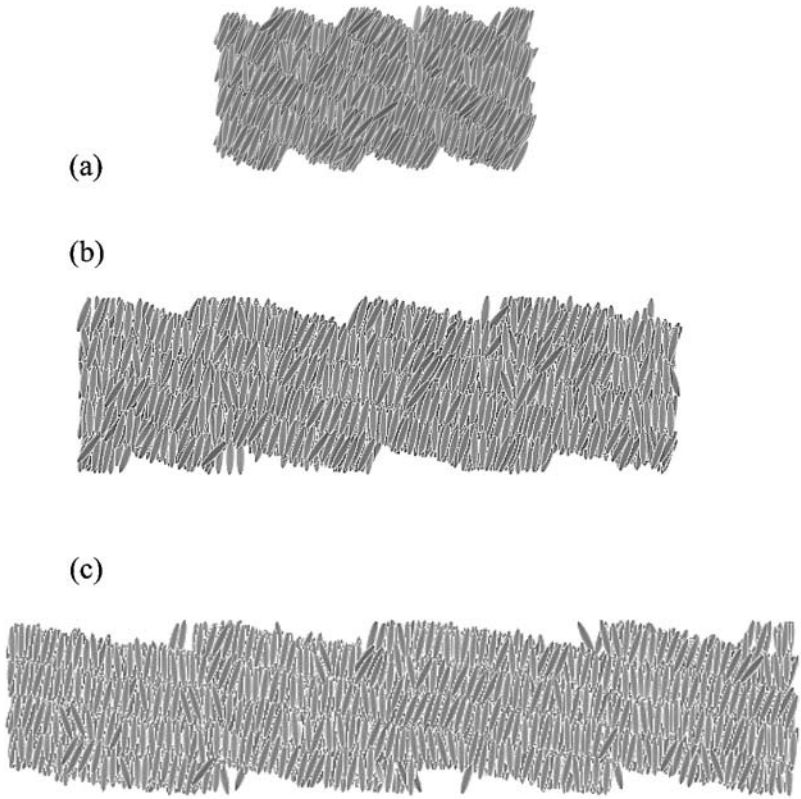

FIGURE 6 Snapshots showing the structural changes for GB(4.4,20.0,1,1) with $\lambda^* = 0.1$ contained in an orthorhombic simulation box. (a) 100,000th, (b) 1,000,000th, and (c) 1,600,000th cycle.

However, the structure could not achieve the most stable alignment even after 2×10^6 cycles, because the molecules appear to be trapped in a local minimum energy structure, this is presumably a result of the huge change of box dimension, L_x, required when the angle, θ_y, is small. Nonetheless, the system with a weaker field realigned smoothly without apparently buckling or breaking the layer structure during the alignment process. According to a recent experimental study by time-resolved small angle X-ray scattering [2], there is no evidence for the formation of a tilted structure during the alignment process. In addition, the director in a smectic A phase was found to be realigned parallel to the electric field, which was applied at 45° to the initial direction of the director, as a monodomain in an experimental study by deuterium NMR for 4-octyl-4′-cyanobiphenyl-d_2 (8CB-d_2) [13].

Consequently, the result obtained from the Monte Carlo simulation with a weaker field, λ^* of 0.1, and with an orthorhombic box seems to reproduce these experimental results, although there are problems in that the molecules are unable to form a final stable structure because they are trapped in a local minimum structure resulting from the inability of the box dimension to change. However, it may be that significant the failure of the system to return to its equilibrium position with the director parallel to the field has been observed for the smectic A phase of a liquid crystal dimer [14].

The significant increase in the number of cycles needed to align the smectic A phase caused by reducing the field strength is to be expected because the magnetic torque is quadratic in the field and so linear in λ^* (see Eq. (5)). Accordingly we might anticipate that the time (i.e. the number of cycles) would increase by a factor of 20 when λ^* is decreased from 2.0 to 0.1; an expectation which is clearly in keeping with our results. The other change in the alignment process which occurs when the field strength is reduced is that the tilt angle initially observed for λ^* of 0.1 is far smaller than the maximal value of 22° found for λ^* of 2.0. This difference in behaviour might be understood in the following way. The first aspect of the process for the field-induced change is in the orientation of the particles with respect to the applied field. Then there is a second feature caused by the interactions between the particles which try to re-establish the layer structure orthogonal to the director; that is with the director and layer normal parallel. The alignment behaviour of the smectic A phase will then depend on the timescales for these two processes. Thus when the field-induced rotation of the particles is faster than their translational diffusion then a tilted structure will be observed. At the other extreme when the translational motion is faster than the rotation of the particles induced by the field then the director and the layer normal will be aligned more or less together. Whereas the translational diffusion is determined by the inter-particle potential the rotational motion also depends on the field strength. From our results it would seem that for λ^* of 2.0 the rotational motion is faster than the translational motion which results in the formation of the tilted structure. However, when λ^* is reduced to 0.1 the smallness of the field-induced tilt angle suggests that the timescales for translational and orientational motions are comparable.

The other notable feature of the simulation results obtained with an orthorhombic box is the observation of the director becoming trapped in a non-equilibrium state with the director tilted with respect to the field. One possible way to avoid such trapping may be to use a triclinic simulation box as we have discussed in the previous section. Here, we present the results of analogous simulations when the simulation box shape as well as its dimensions are allowed to change during the Monte Carlo simulation. The

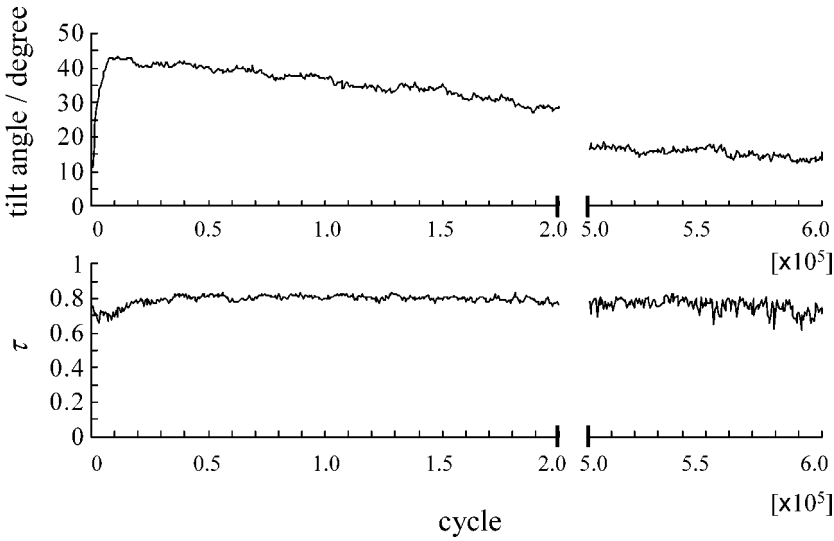

FIGURE 7 The tilt angle and translational order parameter as a function of the number of cycles for GB(4.4,20.0,1,1) with a field strength, λ^*, of 2.0 using a triclinic simulation box.

change of the tilt angle and the translational order parameter, τ, for the system with $\lambda^* = 2.0$ using a triclinic box are shown in Figure 7. In this system with a strong field, the direction of the molecules is quickly rotated parallel to the field, forming a tilted structure as we found for the system with the same field strength when using the orthorhombic box. This tilt angle is, however, close to its maximum value of 45° showing that the smectic layers have not moved. This angle then decreased extremely slowly in contrast to the system using an orthorhombic box, which realigned more or less as a monodomain. Snapshots of configurations taken for the system during the alignment process are shown in Figure 8. It can be seen that the layer structure has not been destroyed during the field-induced alignment process. At an early stage, the simulation box changed to a triclinic shape presumably to ensure that the constraint in Eq. (3) is satisfied. Afterwards the length of the x*-coordinate for the box extended, gradually as found for the system with λ^* of 0.1, in keeping with the constraint in Eq. (2).

As for the orthorhombic simulation box we now consider the field-induced alignment of the smectic A phase with a smaller field corresponding to λ^* of 0.1. Figure 9 shows the change of the tilt angle with respect to the layer normal and the translational order parameter, τ, for the system using a triclinic simulation box. The major difference caused by the lower strength of the field is in the maximum value of the tilt angle. In this

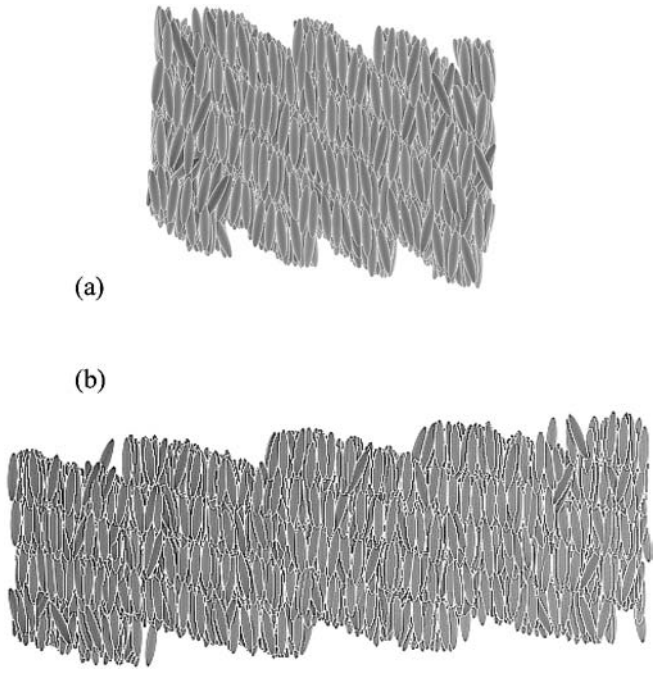

FIGURE 8 Snapshots showing the structural changes for GB(4.4,20.0,1,1) with $\lambda^* = 2.0$ using a triclinic simulation box. (a) 100,000th cycle, and (b) 1,000,000th cycle.

case, the value of the tilt angle was smaller than that for the system with λ^* of 2.0, and the structural change of the system was far slower than that for the system with the stronger field, as for the simulation using an orthorhombic box. We should, however, comment on the variation of the tilt angle with the number of cycles. Unlike the simulation with the stronger field (see Fig. 7) the rate at which the tilt angle grows is extremely slow however the angle continues to grow and after about 240,000 cycles it has reached 30°. Given our previous discussion of the results found with the orthorhombic box the continued growth of the tilt angle is unexpected and may result from a coupling to the variation of the angle in the triclinic simulation box. Figure 10 shows some configurational snapshots for the system with λ^* of 0.1 using a triclinic box. The system behaves in a similar manner to that with the stronger field. The layer structure was retained during the alignment process for both systems with different field strengths. Thus the smectic phase seems to change its structural organisation smoothly. Further, there is no indication of the formation of a rippled

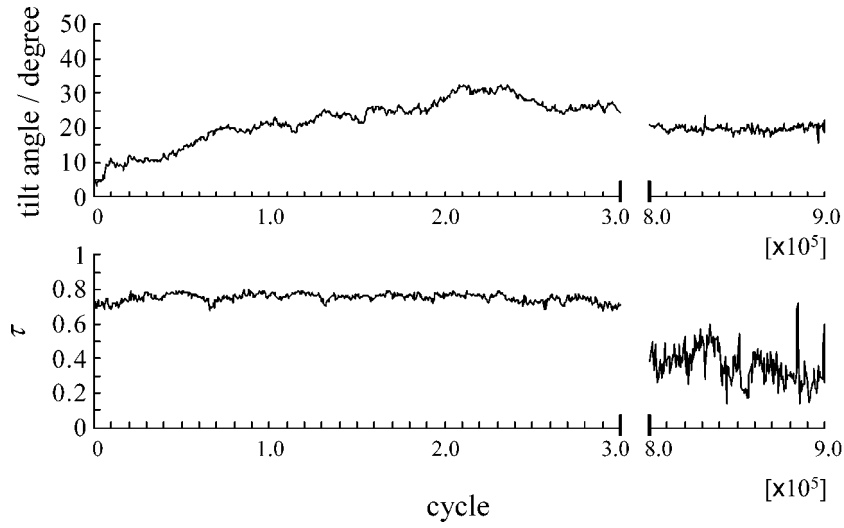

FIGURE 9 The tilt angle and translational order parameter as a function of the number of cycles for the smectic A phase of GB(4.4,20.0,1,1) with a field strength, λ^*, of 0.1 using a triclinic simulation box.

structure. Thus the deformation formed in the system with λ^* of 2.0 using the orthorhombic box might be a consequence of this simulation box, although the system with the weaker field was not affected by the restriction due to the box shape used.

It was found, therefore, that the mechanism for the field-induced realignment depends on both the magnitude of the field and the kind of simulation box used. To explore the dependence on the nature of the simulation box further, we have checked the behaviour using a box in which only two of the three vectors defining the simulation box can change freely. However, the simulations exhibited almost the same behaviour as those for the system using changes to the box shape without any restrictions. One different aspect is that some molecules shifted towards the z-direction in the laboratory frame; this is out of the plane formed by the magnetic field and the original director orientation, presumably this is to escape to local minimum structure in the later stages. Then eventually the molecules became trapped in another local structure for the system when using a triclinic simulation box without any restriction. Therefore, the particles for the system using the triclinic box were unable to achieve the final structure which was the most stable because of the drastic shape change of the simulation box (see Fig. 10(c)). For this reason, the systems investigated with a triclinic simulation box are not stabilised at the later stages where the

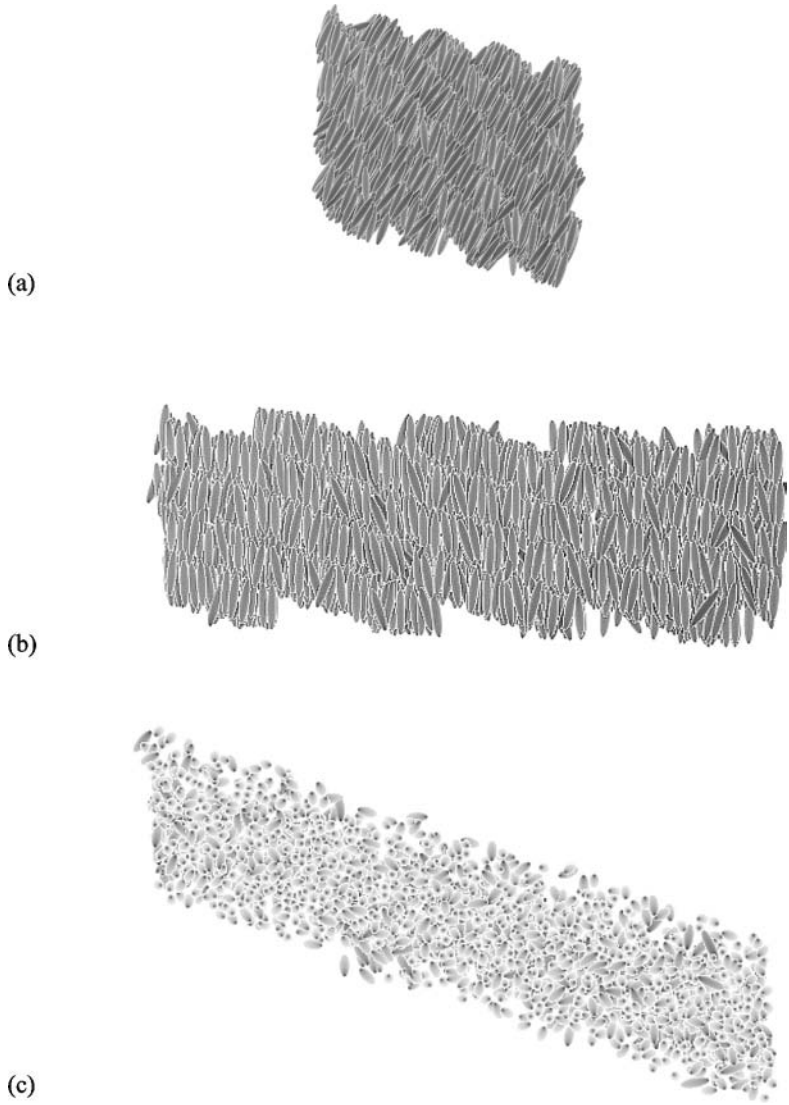

FIGURE 10 Snapshots showing the structural changes for GB(4.4,20.0,1,1) with $\lambda^* = 0.1$ contained in a triclinic simulation box. (a) 10,000th cycle (b) 600,000th cycle, and (c) 600,000th cycle(top view).

translational order parameter, τ, is reduced (see Figs. 7 and 9). However, the simulations in this study have given us some clues as to the microscopic behaviour during the field-induced alignment process and many hints as to how to improve the molecular simulations for the alignment process using model mesogens. In this study, we have used a common displacement value for each component (for example, the x, y and z-components for translation) in the translational and the rotational motion as well as in the change to simulation box dimensions. It may be more effective to use independent values of the displacements for each component in these motions because of the clear anisotropy of the system. In addition we presume that this kind of simulation might give a more realistic behaviour when the translational and rotational moves of the particles and the change in the simulation box dimensions are optimised. In order to investigate this approach, a series of systematic simulations varying parameters for the maximum changes in the translational, rotational and simulation box dimensions would be required. The equivalent idea in a molecular dynamics simulation would be to employ different time steps for the translational and rotational motion and the variation in the box dimensions.

SUMMARY

The results for the quasi-dynamical behaviour of the field-induced alignment process for a smectic A phase obtained from a constant pressure-constant temperature Monte Carlo simulation have been discussed. Two kinds of simulation box were used for the simulation, orthorhombic and triclinic, in an attempt to ensure that the organisation of the particles and their images are commensurate. In the simulation using the orthorhombic box, the molecules aligned parallel to the field without destroying the layer structure of the smectic A phase. The system aligned with a stronger field, λ^* of 2.0, formed a tilted structure at the initial stage of the process, and a perturbed smectic A phase was reformed almost immediately although with a rippled structure. For the weaker field, λ^* of 0.1, the particles aligned smoothly without destroying the layer structure, and without forming any significantly tilted structure. The particles reoriented parallel to the field as a monodomain in the case of the triclinic box. Here both alignment processes were basically the same; that is the particles align parallel to the field first, then the layer normal rotates towards the magnetic field with the sample as a monodomain. According to recent experiments using deuterium NMR for 8CB-d_2, the director was reoriented as a monodomain when the electric field was applied at 45° and 54.5° to the director [15]. Further there has been no evidence of a field-induced tilted structure in recent experiments using time-resolved small angle X-ray scattering [2]. Thus the

experimental results suggest that the structural change for the system with the weaker field strength, λ^* of 0.1, using the orthorhombic box is close to the field-induced alignment process of a real smectic A phase. However, it was found that the alignment process in the simulation was very sensitive to the choice of the simulation box and the strength of the field applied.

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