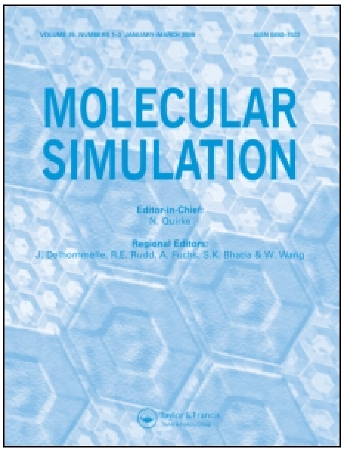

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Computer Simulation of Liquid Crystal Films

Michael P. Allen[a]
[a] H.H. Wills Physics Laboratory, Bristol, United Kingdom

To cite this Article Allen, Michael P.(1989) 'Computer Simulation of Liquid Crystal Films', Molecular Simulation, 4: 1, 61 — 78
To link to this Article: DOI: 10.1080/08927028908021965
URL: http://dx.doi.org/10.1080/08927028908021965

Molecular Simulation, 1989, Vol. 4, pp. 61–78
Reprints available directly from the publisher
Photocopying permitted by license only

COMPUTER SIMULATION OF LIQUID CRYSTAL FILMS

MICHAEL P. ALLEN

H.H. Wills Physics Laboratory, Royal Fort, Tyndall Avenue, Bristol BS8 1TL, United Kingdom

(*Received January, 1989, accepted March, 1989*)

We present the results of extensive Monte Carlo simulations of liquid crystal films of various thicknesses. A simple nearest-neighbour lattice model, the Lebwohl-Lasher model, is employed, with periodic boundaries in two directions and free, planar, surfaces in the third. Particular attention is devoted to locating the temperature of the order-disorder (nematic-isotropic) phase transition. Weak first-order behaviour apparently persists in systems as thin as 8 layers across, but below this the transition cannot be detected. The shift of the transition temperature from its bulk value approaches the expected asymptotic linear dependence on inverse thickness, but significant deviations from this are seen for films of 10 layers thickness and less. These results enable an accurate estimate to be made of the bulk phase transition temperature in the thermodynamic limit, and the result is consistent with that extrapolated from systems with full periodic boundaries.

KEY WORDS: Computer simulation, liquid crystals, surfaces

1. INTRODUCTION

The continuing increase in the computer power available to the simulation research community allows progress to be made in two significant ways. Firstly, it becomes possible to model, in a more realistic fashion, complicated physical systems, such as large organic molecules with long-range interactions. Secondly, it becomes possible to study more complicated physical phenomena, such as phase transitions, and the behaviour of systems with long-range correlations or interfaces. Because liquid crystalline phases fall into both these categories, it is only recently that significant progress has been made in the computer simulation of liquid crystals. Relatively simple models, such as hard ellipsoids and spherocylinders, have been used to model the essential physics of the bulk phases [1, 2]. Simulation runs of sufficient length can be carried out, for example, to study the approach to, and properties of, the nematic liquid crystal phase [3]. Somewhat more realistic soft potentials have also been used [4]. The necessary computer power to carry out full molecular dynamics simulations of liquid crystals, employing realistic atom-atom potentials, is only just coming within reach; most work to date has involved very few molecules, and has used energy minimization techniques rather than molecular dynamics [5].

When inhomogeneity is introduced into the system, through the presence of confining walls, applied external fields, or, in general, coexistence of phases, then problems of long equilibration times and large-scale spatial fluctuations become very taxing. Good examples of this are provided by the study of wetting and related phenomena in Ising spin/lattice gas systems [6, 7], and in Lennard-Jones systems [8]. Also relevant is the earlier work on Ising and Heisenberg spin systems which attempted to assess the effects of finite size and free surfaces on the positions of phase transitions and on order parameters [9, 10, 11]. For a recent review of applications of the Monte Carlo method to problems in surface physics, see [12].

The phase diagrams of molecular systems, and especially nematogenic compounds, in similar circumstances should be very rich, with a variety of orientational wetting and tilt-angle transitions predicted by theory [13]. The prediction of surface-modified and field-modified orientational ordering is also of great technological relevance. However, the realistic simulation of such systems is a great challenge.

In such circumstances, an idealized model may still be of some use. In this paper, we describe simulations of a very simple model of a nematic liquid crystal film with free surfaces. The aim of this study is to determine the influence of film thickness on the isotropic-nematic (I-N) phase transition, and to pave the way for an examination of the surface properties of this system. Here, we describe the simulation techniques and report the primary results: the accurate location of the transition temperatures as a function of film thickness. This is a pre-requisite for the investigation of the surface properties close to the phase transition, and especially the way in which quantities such as the degree of adsorption of the isotropic phase diverge on approach to the transition. These matters will be discussed in a separate paper [14].

In the course of this work, we have found it necessary to conduct simulation runs significantly longer than those used previously. We have made extensive use of a parallel-processing computer, the DAP 510-8, dedicated to simulations of inhomogeneous systems. The Monte Carlo simulation techniques we employ are quite standard, but there are some technical details specific to machines of this kind, and we address these in the appendix.

The layout of this paper is as follows. In section 2 we discuss the model, and refer to recent simulation studies of it. In section 3 we describe the effects of finite system size on models of this kind, and comment on methods of characterizing the phase transition. Our own simulation results are set out in section 4. Finally, section 5 contains a discussion and conclusions.

2. THE LEBWOHL-LASHER MODEL

The Lebwohl-Lasher model [15] is a simple approach to the properties of an interacting set of molecules with orientational degrees of freedom. The molecular centres are fixed on the sites of a simple cubic lattice. Molecular orientations are represented by unit vectors $\boldsymbol{e}_i = (e_{ix}, e_{iy}, e_{iz})$, allowed to vary freely in three-dimensional space. The interaction between nearest-neighbour molecules i and j is given by

$$H_{ij} = -JP_2(\boldsymbol{e}_i.\boldsymbol{e}_j) = -JP_2(\cos\theta_{ij}) \qquad (1)$$

where P_2 is the second Legendre polynomial, $P_2(x) = \frac{3}{2}x^2 - \frac{1}{2}$, and θ the angle between molecular axes. J is a (positive) coupling constant: in this work we set $J = 1$ and measure temperature T in units of J/k_B where k_B is Boltzmann's constant.

This is certainly not a good representation of a liquid crystal, because of the lattice restriction, and the consideration of nearest-neighbour interactions only. However, the interactions have the correct symmetry to describe nematogenic molecules, and the model is closely connected with the Maier-Saupe theory of liquid crystals. Recently, extensive Monte Carlo simulations by Fabbri and Zannoni [16] have shown that the bulk orientational order–disorder transition is weakly first-order (with a transition entropy $\Delta S/Nk_B \approx 0.05$), and so is similar to that seen experimentally for the isotropic-nematic transition. Fabbri and Zannoni studied a 30 × 30 × 30 simple cubic lattice, with run lengths of up to 70000 MC cycles (1 cycle = 1 attempted move per molecule). Shortly afterwards, Luckhurst and co-workers [17] published a study of the surface properties of a thin liquid crystal film, using the same model. They attempted to relate the shift in the bulk transition temperature (due to the effects of finite size and free surfaces), to the measured surface free energy. They also examined the growth in thickness of the surface-adsorbed disordered phase, as the transition was approached from the ordered side. Their simulations were limited, however, to ≈ 1200 MC cycles, and they used a small system of 10 × 10 × 10 sites.

The current investigation is very much in the spirit of these last two papers. We study the Lebwohl-Lasher model on a simple cubic lattice, for system sizes $N = 32 \times 32 \times L$, where L, the thickness, varies from 6–32. Most of the simulations are for a film: periodic boundary conditions are applied in the transverse directions, but top and bottom surfaces (both of area $A = 32 \times 32$) are left free, so that molecules in these layers have only 5 neighbours rather than 6. We have also carried out some related bulk simulations, in which periodic boundary conditions are applied in all three directions.

We use the standard Metropolis Monte Carlo algorithm [18], but adopt a special procedure to allow the updating of 1024 molecular orientations in parallel: this is described in the appendix.

3. FINITE-SIZE EFFECTS AND ANALYSIS

As mentioned earlier, the I-N transition for the bulk system is believed to be weakly first-order. We are considering systems of fixed cross-sectional area, $A = 32 \times 32$, and of different thicknesses L, both in the fully periodic, bulk, case and in the case of a film with two free surfaces. In this section, we outline some of the effects expected in our systems due to finite thickness. For an excellent review of finite-size scaling theory, the reader is referred to reference [19].

The transition temperature T_{NI} for a thin film is expected to be shifted from the bulk value to a lower value. The asymptotic form of the dependence on L follows from a simple thermodynamic argument, analogous to that yielding the Kelvin equation [13, 17]:

$$\Delta T_{\mathrm{NI}} = T_{NI}(\mathrm{L}) - T_{NI}(\infty) = 2\gamma_{\mathrm{NI}} A/N\Delta S_{\mathrm{NI}} = 2\gamma_{\mathrm{NI}}/L\Delta S_{\mathrm{NI}} \qquad (2)$$

Here, ΔS_{NI} is the entropy of transition (per molecule) in the bulk system and γ_{NI} is the surface tension between nematic and isotropic phases. We have assumed that the surfaces are completely wet by the isotropic phase.

This formula is a possible route to the determination of γ_{NI}, which Luckhurst *et al.* also attempted to measure directly. We defer a detailed discussion of the interpretation of this quantity, and the practical difficulties associated with its calculation, to a later publication [14].

It is also predicted that the first-order phase transition will weaken and disappear as the system becomes thinner [13]. In the limit $L = 1$, the system is spatially two-dimensional, and the ordered ground state should be destroyed by spin waves, as for the Heisenberg model [20]. Our hope is to obtain some indication of the value of L at which the already weak first-order transition disappears, presumably at a critical point. However, the situation for the two-dimensional Heisenberg model is still not clear-cut, in that some kind of phase transition may occur [21, 22, 23, 24]. If our model has features in common with the Heisenberg model, then the transition might not vanish as $L \rightarrow 1$ after all.

It should be noted that, in the framework of finite-size scaling theory, the prediction $\Delta T \propto L^{-1}$ is a mean-field result [25] which should not hold in the case of a critical phase transition. In that case, it can be argued [26] that the transition should occur when the bulk correlation length matches the width of the film, and this leads to $\Delta T \propto L^{-1/\nu}$ where ν is the correlation length exponent [26, 25, 19]. For three-dimensional systems $\nu \approx 0.63$–0.72, $1/\nu \approx 1.4$–1.6, so significant differences should be seen from the L^{-1} form. However, once again, the situation is not straightforward for the Heisenberg system [19], with direct series-expansion calculations of the susceptibility suggesting a form $\Delta T \propto L^{-\lambda}$ with $\lambda = 1.1 \pm 0.2$ [23]. If our system is Heisenberg-like, we might still expect to see the naive prediction of equation (2) borne out.

A shift in transition temperature is also expected, due to finite-size effects, even for the fully periodic system. Analysis of the case of a first-order transition leads Challa *et al.* [27] again to an L^{-1} dependence of ΔT. For a critical point, for example in Ising systems, it seems that $\Delta T \propto L^{-\lambda}$ with λ rather higher than 1, perhaps $\lambda = 2$ [25]. For Heisenberg systems [23] the estimate is $\lambda = 2$. The magnitude of this shift is not expected to be as great as that seen in the case of free surfaces, so it may be difficult to test different predictions.

In the first analysis of our results, we follow Challa, Landau and Binder [27]. Away from any phase transition, the probability distribution function for the energy per molecule is expected to have a Gaussian form, with mean-square fluctuations proportional to the specific heat per molecule, C, (defined in the limit of infinite system size):

$$P(E) = \frac{A}{\sqrt{C}} \exp\left\{-\frac{N}{2C/k_{\mathrm{B}}}\left(\frac{E-\bar{E}}{k_{\mathrm{B}}T}\right)^2\right\} \tag{3}$$

Here A is a normalization constant, and $\bar{E}$ is the average energy at the chosen temperature T. Close to a first-order phase transition, Challa *et al.* adopt a double Gaussian form for $P(E)$, which we write

$$\begin{aligned} P(E) = {} & \frac{A_{\mathrm{I}}}{\sqrt{C_{\mathrm{I}}}} \exp\left\{-\frac{N}{2C_{\mathrm{I}}k_{\mathrm{B}}}\left(\frac{E-\bar{E}_{\mathrm{I}}}{k_{\mathrm{B}}T}\right)^2\right\} \\ & + \frac{A_{\mathrm{N}}}{\sqrt{C_{\mathrm{N}}}} \exp\left\{-\frac{N}{2C_{\mathrm{N}}/k_{\mathrm{B}}}\left(\frac{E-\bar{E}_{\mathrm{N}}}{k_{\mathrm{B}}T}\right)^2\right\} \end{aligned} \tag{4}$$

where the subscripts I and N denote isotropic and nematic phases respectively. Following Challa *et al.* we can use the equation $A_{\mathrm{I}} = A_{\mathrm{N}}$ to define the transition temperature in the finite system as the point at which two equally weighted Gaussians contribute to $P(E)$.

Fabbri and Zannoni [16] examined $P(E)$ curves for the 30 × 30 × 30 bulk system, and commented on the doubly-peaked form characteristic of a first-order phase transition. In our work, we determine the position of the phase transition by examining $P(E)$, fitting to the double-Gaussian form, and finding the temperature at which equally-weighted contributions arise. This requires very long runs: we must simulate for long enough that the system samples both phases close to the transition. Challa *et al.* required runs of order 10^7 MC cycles in their study of the 10-state Potts model, largely because the transition is quite strongly first-order, and transitions between the two states occur infrequently. In our case, fluctuations play a larger role, and this is not such a problem. Our difficulties stem from the desire to resolve two closely-spaced peaks in $P(E)$. The hope is that the disappearance of the doubly-peaked structure may be taken as an indication that the first-order transition has disappeared, although this may be impossible to demonstrate convincingly.

Hysteresis does not occur in these circumstances: the curve of average energy $\bar{E}$ vs temperature is smooth and single-valued. However, of course, the positions of the two maxima in the distribution, $\bar{E}_{\mathrm{I}}$ and $\bar{E}_{\mathrm{N}}$ may be interpreted as the two branches of the equation of state.

A method of locating a continuous phase transition is to determine the specific heat, for example from the fluctuation formula

$$C/k_{\mathrm{B}} = \frac{N(\overline{E^2} - \overline{E}^2)}{(k_{\mathrm{B}}T)^2} \qquad (5)$$

and identify the transition temperature with the position of the maximum in C. For a transition which is first-order in the thermodynamic limit, but rendered smooth by finite-size effects, this prescription can again be applied. In fact, Challa *et al.* showed that this is equivalent to determining the point at which $A_{\mathrm{I}} = A_{\mathrm{N}}$. (Note that C should not be confused with the constants C_{I} and C_{N} appearing in equation (4) above). This approach is quite valid, but it still requires runs of sufficient length to sample both phases, otherwise the analysis does not hold. In any case, in our view, examination of the form of the $P(E)$ curves, not just the second moment, is an essential first step in characterizing the transition. A saving grace of the method adopted here is that, once an estimate of the transition temperature has been obtained, runs may be concentrated at relatively few state points to locate it accurately.

We have not used other prescriptions for determining the transition temperature, largely because of the character of the transition. In particular, we have not attempted to calculate free energies $F(T)$ of the two phases, for example by thermodynamic integration, since the determination of the point of intersection of the $F(T)$ curves would be subject to large errors near such a weak transition.

4. RESULTS

Total run lengths and average energies are summarized in Table 1. Run lengths were determined by inspecting the $P(E)$ energy distribution curves for each subrun (typically of 10^5 MC sweeps or longer) and continuing until satisfactory statistics had been accumulated. Typical curves for the $L = 16$ system close to the phase transition are shown in Figure 1, together with double Gaussian fits. To illustrate the dependence on thickness, three curves corresponding to temperatures just below the transition, for thicknesses $L = 10, 24, 32$ are shown in Figure 2. For $L = 32$, the peaks are easily resolved, and the shape of the P(E) curve is quite sensitive to temperature changes. For $L = 10$ fluctuations are relatively more important, and the resolution of the two peaks is more difficult. This makes the precise location of the transition more difficult.

Table 1 Run lengths and average energies

temperature T	*run length* (*k-sweeps*)	*energy* $\bar{E}$
$L = 6$ (film)		
1.00000	50	−1.2902
1.00500	50	−1.2666
1.01000	50	−1.2407
1.01500	50	−1.2203
1.02000	50	−1.1883
1.02500	50	−1.1653
1.03000	50	−1.1369
1.03500	50	−1.1009
1.04000	50	−1.0517
1.04500	50	−1.0197
1.05000	50	−0.9836
1.05500	50	−0.9607
1.06000	50	−0.9287
1.06500	50	−0.9133
1.07000	50	−0.8875
1.07500	50	−0.8708
1.08000	50	−0.8575
1.10000	50	−0.8040
1.10500	50	−0.7908
1.11000	50	−0.7819
1.11500	50	−0.7711
1.12000	50	−0.7620
1.12500	50	−0.7523
$L = 8$ (film)		
1.06000	100	−1.0856
1.06400	720	−1.0452
1.06450	1070	−1.0426
1.06550	850	−1.0295
1.06750	950	−1.0079
1.07000	100	−0.9792
$L = 10$ (film)		
1.00000	40	−1.4138
1.07000	40	−1.1078
1.07750	50	−1.0484
1.08050	200	−1.0188
1.08100	600	−1.0062
1.08200	1200	−0.9971
1.08250	600	−0.9831
1.08300	200	−0.9699
1.08350	200	−0.9673
1.08750	50	−0.9322
1.11000	50	−0.8327
1.11250	50	−0.8241
1.11500	50	−0.8174
1.11750	50	−0.8107
1.12000	50	−0.8060
$L = 16$ (film)		
1.10000	340	−0.9842
1.10200	440	−0.9555
1.10400	340	−0.9271

L = 24 (film)		
1.10700	100	−1.0056
1.10900	110	−0.9776
1.11000	220	−0.9507
1.11100	460	−0.9299
1.11250	100	−0.8963
L = 32 (film)		
1.00000	5	−1.5335
1.05000	35	−1.3579
1.10000	15	−1.0962
1.11000	50	−1.0076
1.11250	50	−0.9604
1.11400	360	−0.9342
1.11500	295	−0.8962
1.11750	50	−0.8681
1.12000	50	−0.8575
L = 10 (bulk)		
1.00000	40	−1.5873
1.07000	40	−1.3397
1.08050	200	−1.2894
1.08150	100	−1.2842
1.08250	100	−1.2797
1.11000	150	−1.0960
1.11250	90	−1.0420
1.11500	200	−1.0063
1.11750	100	−0.9500
1.12000	100	−0.9282
L = 16 (bulk)		
1.11500	150	−1.0507
1.11750	140	−0.9634
1.12000	160	−0.9246

We were able to resolve the peaks in the $L = 8$ case also, but it was apparent that this would not be possible for $L = 6$, and so we could not determine a transition temperature in this case. Our estimates of transition temperatures T_{NI} are collected in Table 2.

We determined the transition entropies from the positions of the two peaks in $P(E)$:

$$\Delta S/k_B = (\overline{E_I} - \overline{E_N})/k_B T_{NI}. \tag{6}$$

Although the widths of the distributions increased as L decreased, as would be expected, we found no evidence that the peak separations were changing. On the contrary, we obtained $\Delta S/k_B = 0.061 \pm 0.002$ for all values of L between 8 and 32.

Average energies for films of various thickness are plotted as functions of temperature in Figure 3. The arrows mark the positions of the transition temperatures, as determined by the procedure described in the last section. The shift in transition temperature with decreasing thickness can clearly be seen. Also shown in the Figure are the curves for a fully periodic system with $L = 10$, 16, and the results of Fabbri and Zannoni [16] for a 30 × 30 × 30 lattice.

In Figure 4, we show the specific heat values, as determined from equation (5). Again the transition temperatures (determined as above) are marked with arrows, and we can see consistency between the two approaches. Note here that the lines in the Figure are to guide the eye: we have made no attempt to independently fit the specific

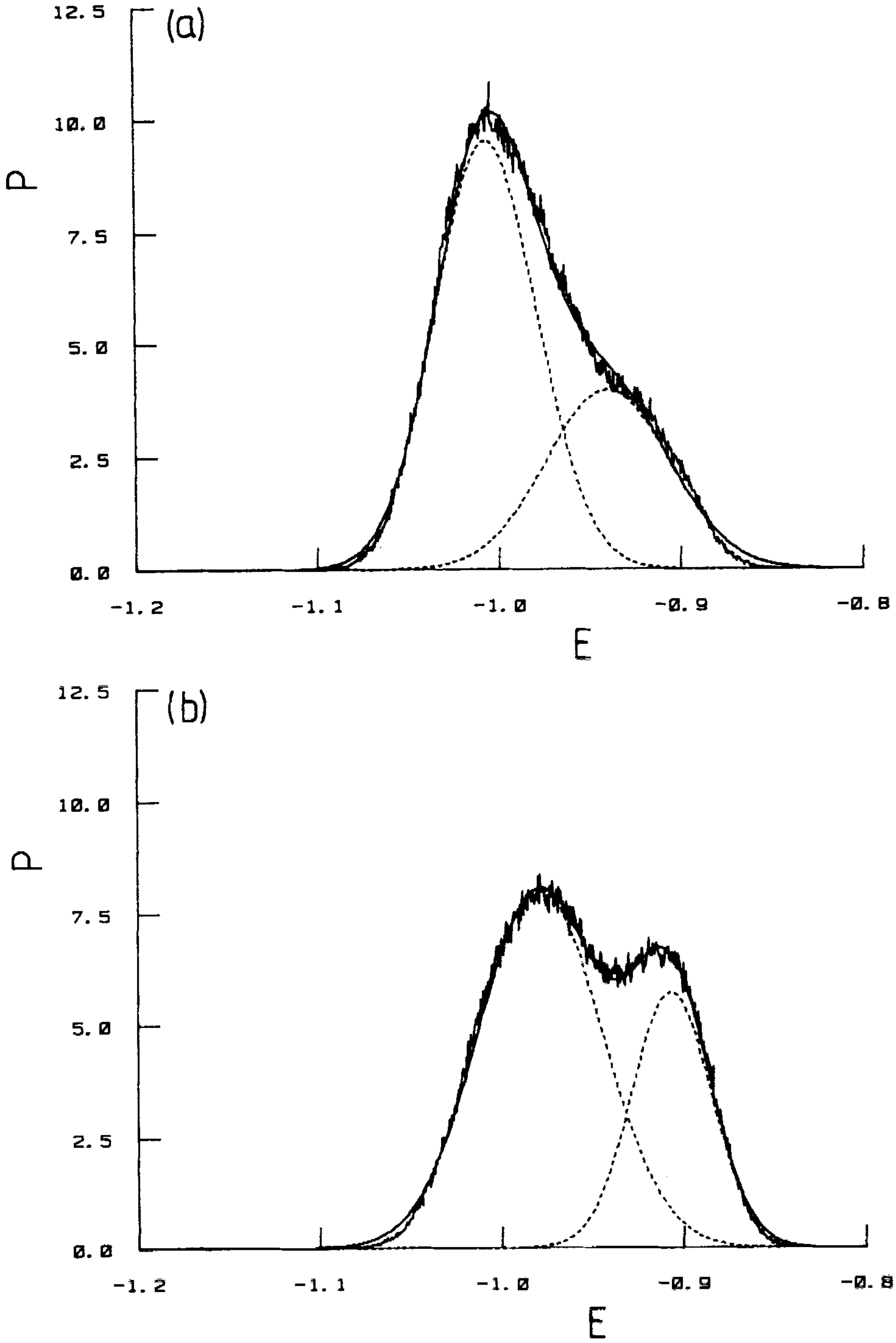

Figure 1 Energy distribution curves P(E) with double-Gaussian fits, for thickness $L = 16$. (a) $T = 1.1000$; (b) $T = 1.1020$.

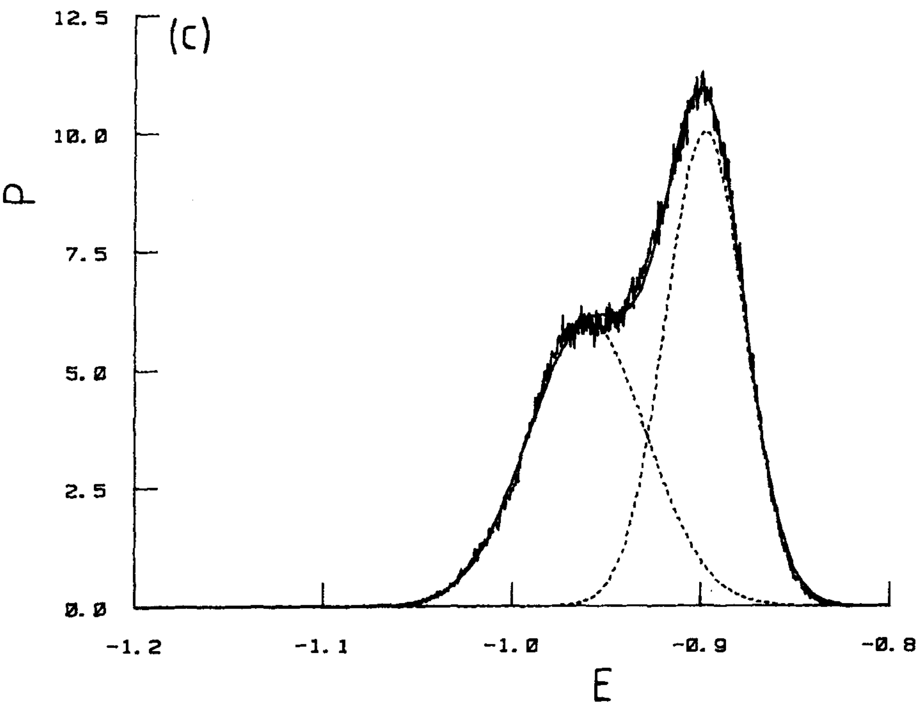

Figure 1 **(continued)**
(c) $T = 1.1040$.

heat data, and indeed if we wished to do so we would probably require more data points. We have also calculated the function

$$1 - \overline{E^4}/3\overline{E^2}^2 \tag{7}$$

recommended by Challa *et al.* [27] as a discriminator between first- and second-order transitions. In our case, unfortunately, this only departs slightly from its trivial limiting value of $\frac{2}{3}$, presumably due to the weakness of the transition, and so we do not plot it here.

Table 2 Transition temperatures

L	T_{NI}
Film systems	
8	1.0665 ± 0.0025
10	1.0830 ± 0.0005
16	1.1025 ± 0.0004
24	1.1115 ± 0.0004
32	1.1145 ± 0.0004
Bulk systems	
10	1.1150 ± 0.0005
16	1.1175 ± 0.0005

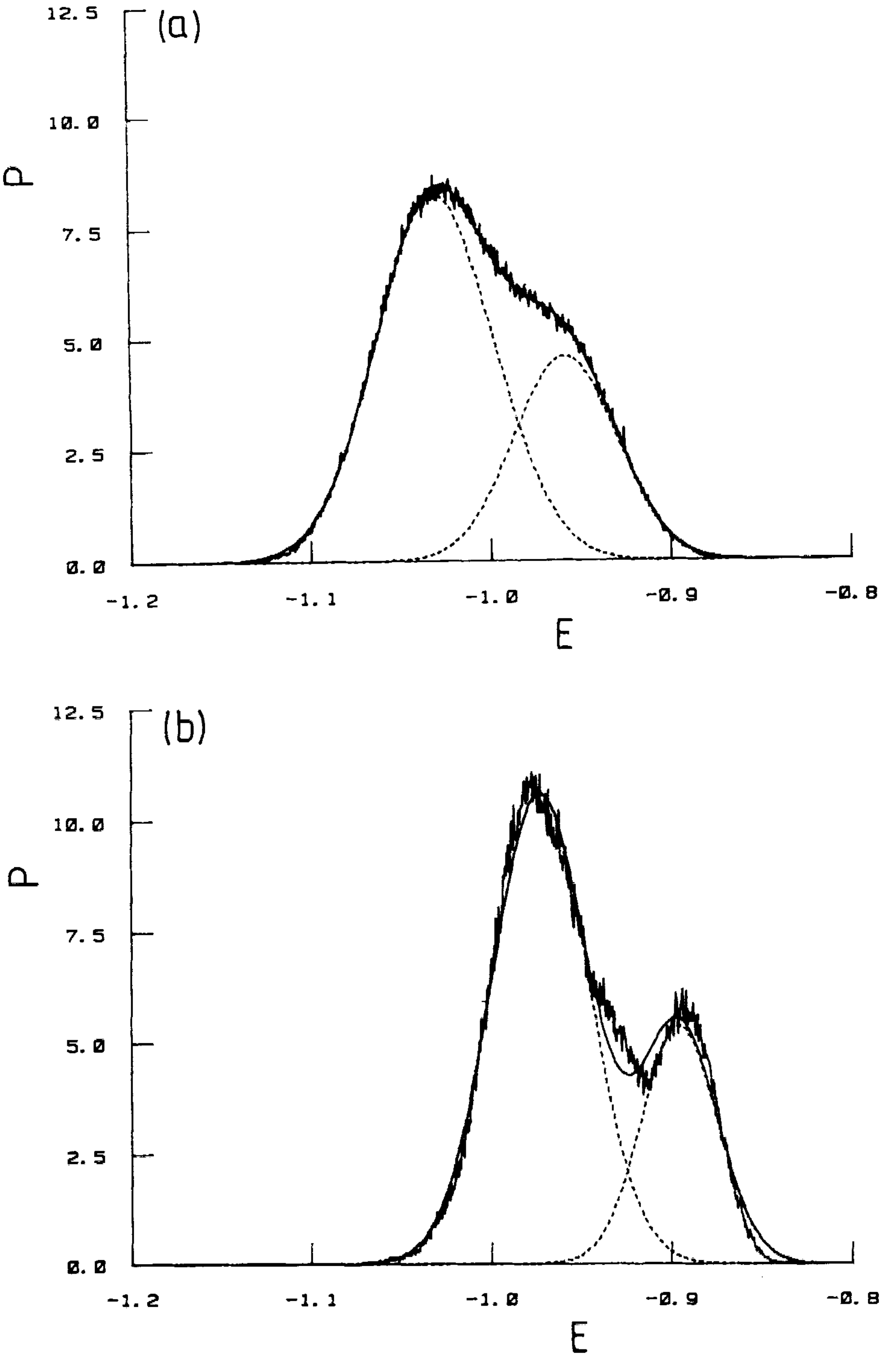

Figure 2 Energy distribution curves P(E) with double-Gaussian fits, for temperatures T just below T_{NI}. (a) $L = 10$, $T = 1.0810$; (b) $L = 24$, $T = 1.1100$.

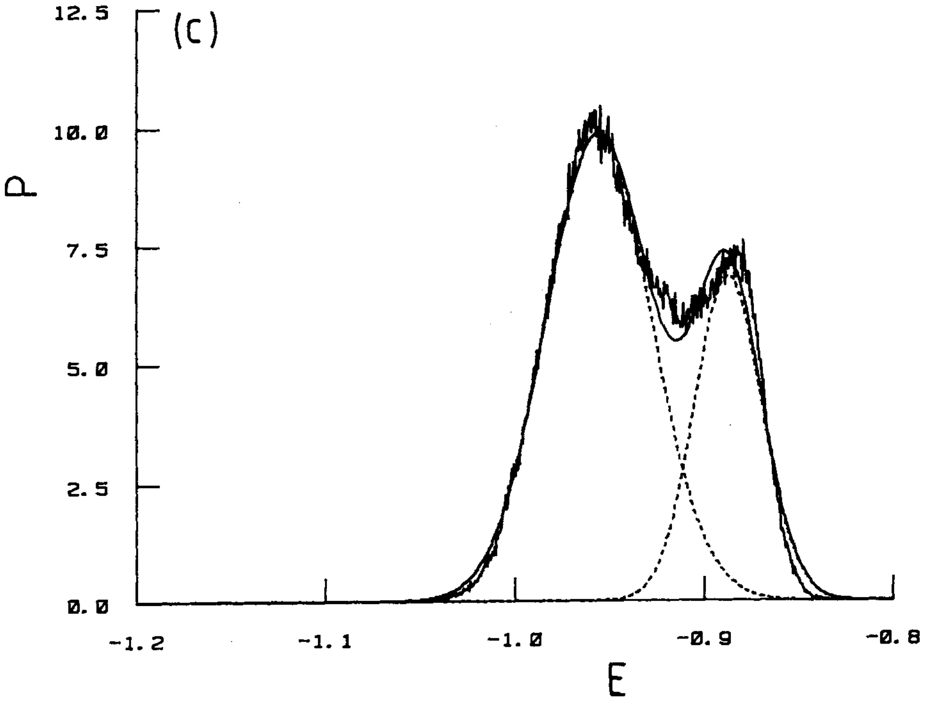

Figure 2 **(continued)**
(c) L = 32, T = 1.1140.

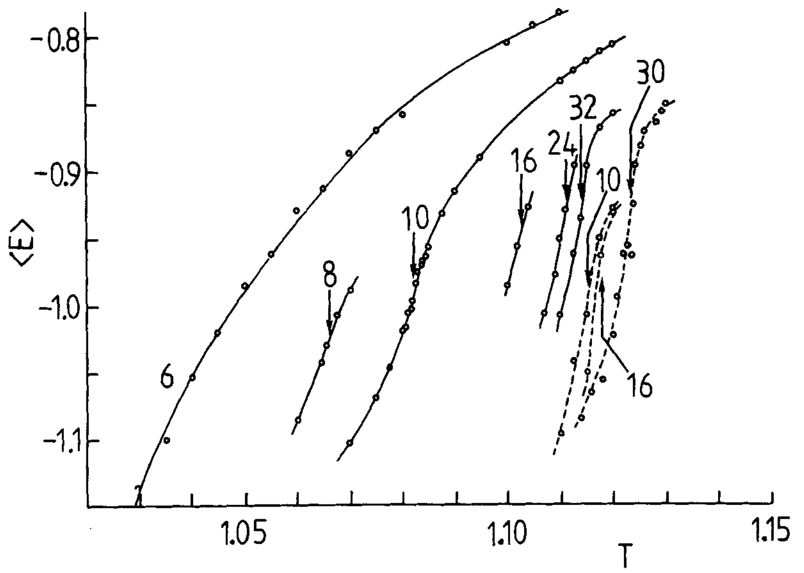

Figure 3 Average energies as functions of temperature for films (solid lines) and bulk systems (dashed lines). The curves are to guide the eye. The numbers denote the thickness L and the arrows indicate the estimated transition temperatures. The curve labelled 30 is from the data of Fabbri and Zannoni [16].

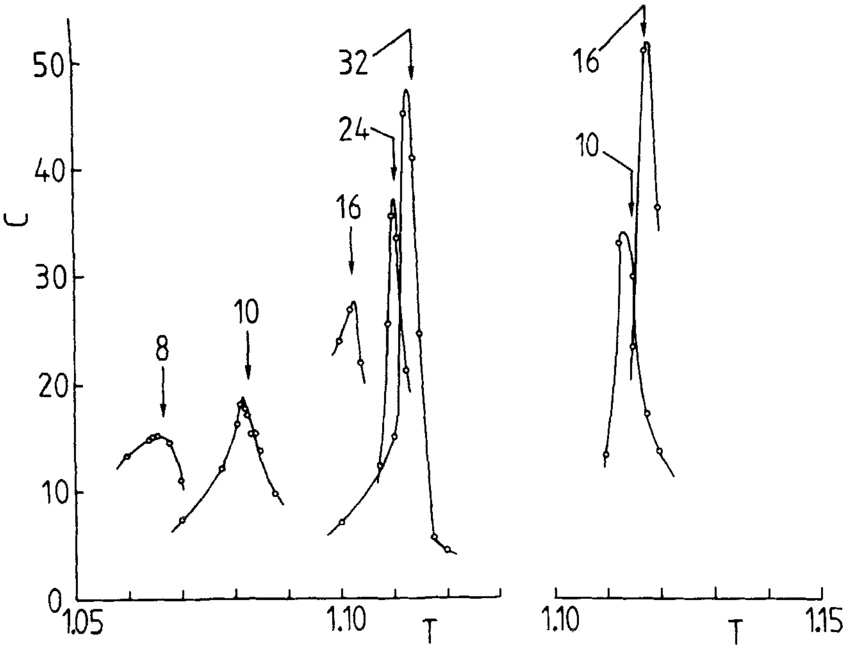

Figure 4 Specific heats calculated from the fluctuation formula, eqn (5), as functions of temperature, for the film systems. The curves are to guide the eye. The numbers denote the thickness L and the arrows indicate the estimated transition temperatures. The bulk and film results are separated for clarity.

Finally, the transition temperatures for both film and bulk systems are plotted as functions of L^{-1} in Figure 5. For the films, we see the expected asymptotic linear dependence. The transition temperatures for the bulk system, including the 30 × 30 × 30 system of Fabbri and Zannoni, are also shown in the Figure. Here, the effects of system size are much less pronounced, and we see a slight decrease in transition temperature as the system becomes thinner. It is not obvious why the change should be in this direction, but we note that similar behaviour is seen in Ising simulations [11]. The important point to note is that both sets of results, for film and bulk, seem to extrapolate to the same transition temperature in the thermodynamic limit $L \rightarrow \infty$: we obtain $T_{\mathrm{NI}}(L \rightarrow \infty) = 1.1255 \pm 0.001$. In the Figure, we also show alternative ways of extrapolating, as discussed above: vs $L^{-1.5}$ (for the films) and vs L^{-2} (for the bulk systems). For the film systems, the $L^{-1.5}$ form fits the data almost as well as L^{-1} in the large-L limit, although the extrapolated value of $T_{\mathrm{NI}}(L \rightarrow \infty)$ then differs quite significantly from that obtained by any sensible extrapolation of the bulk data. For the bulk system, the L^{-2} form is definitely less satisfactory than L^{-1}.

5. DISCUSSION

We have carried out an extensive series of simulations on the Lebwohl-Lasher model, in order to determine as accurately as possible the transition temperatures T_{NI} for a free liquid crystal film as a function of film thickness L. We have attempted to do this,

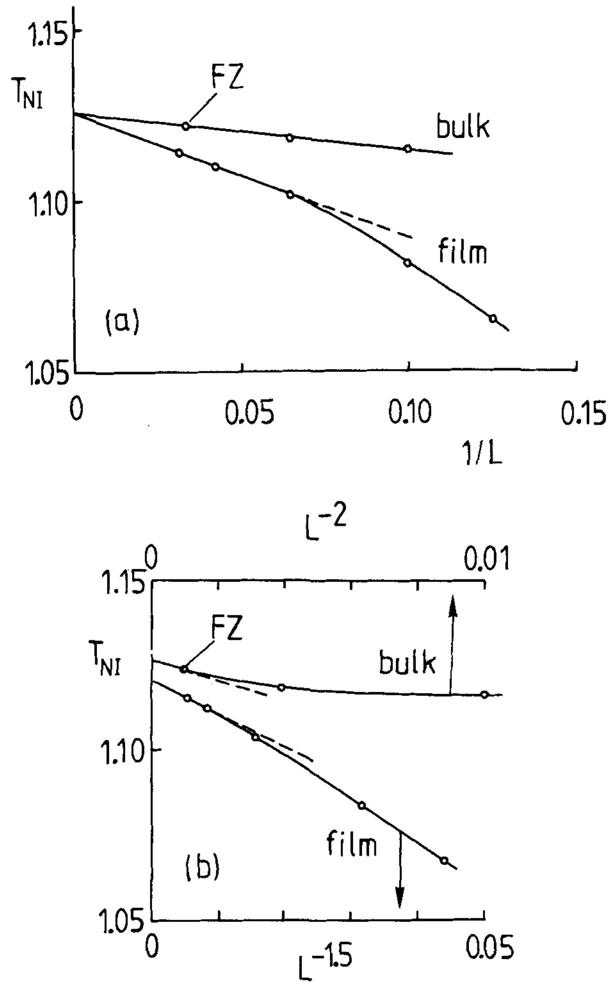

Figure 5 Transition temperatures for film and bulk systems, (a) as functions of inverse film thickness, L^{-1}; (b) as functions, respectively, of $L^{-1.5}$ and L^{-2}. The result of Fabbri and Zannoni [16] is indicated.

and to investigate the character of the transition, using the finite-size analysis of Challa, Binder and Landau [27]. So far as we are able to determine, the transition retains the weakly-first-order nature of the bulk transition, with $\Delta S/k_B \approx 0.061$, down to film thickness $L = 8$, but we have been unable to demonstrate any phase transition at all below this. Our results enable us, for the first time, to extrapolate the transition temperature to the thermodynamic limit: we obtain $T_{NI}(L \rightarrow \infty) = 1.1255 \pm 0.001$. Systems of thickness $L = 10$ and lower deviate quite significantly from the asymptotic inverse-system-size dependence of the shift in transition temperature.

From the limiting gradient of the plot of T_{NI} vs L^{-1}, and the value of $\Delta S/k_B$, an estimate of the surface tension, $\gamma_{NI} = 0.011$, can be obtained from equation (2). This is identical with the estimate of Luckhurst *et al.* [17], based on systems of size

$10 \times 10 \times 10$. Clearly this agreement is partly fortuitous. The transition temperature for our $32 \times 32 \times 10$ system lies significantly off the true asymptotic line, and an estimate of γ_{NI} based on this system size alone should be in error by about 20%. It is possible that the smaller transverse dimensions of the system studied in reference [17] produce a compensating effect.

Although we have carried this investigation to the limit of the computing resources available to us, several questions and reservations remain concerning this system. The whole question of the nature of phase transitions in systems of finite thickness is a tricky one. The fact that we have been unable to demonstrate a doubly-peaked $P(E)$ distribution for $L = 6$ does not mean that longer runs would not find it. We can only tentatively conclude that the transition has vanished below $L = 8$. In the neighbourhood of a critical point, we would expect the double Gaussian formula to break down, although in fact it seems to fit all our data fairly satisfactorily, with minor discrepancies in between the peaks. Moreover, the positions of the two peaks do not seem to be approaching one another, and so the transition entropy does not seem to be changing, even for systems as thin as $L = 8$. If there is a critical point, we have not observed any clear precursors of it.

Ideally we should vary the transverse dimensions, and again study the form of $P(E)$, to determine whether or not the transition can be termed 'first order'. We have not done this, confining our work to the $32 \times 32 \times L$ system for reasons of economy, but we are aware of examples [32] where the peak splitting decreases with increasing system size, indicating that the transition will disappear in the thermodynamic limit. Clearly this merits further investigation.

It is of some interest to relate the simulation run lengths, found necessary here, to the simulation times that would be required for a realistic model. A typical nematogenic molecule (for example N-(p-methoxybenzylidine)-n-butylaniline, MBBA) can be represented roughly as a prolate ellipsoid of length $a \approx 18\,\mathrm{nm}$ and width $b \approx 7\,\mathrm{nm}$. For linear dimensions $\sigma = (ab^2)^{1/3}$, and a molecular mass $m \approx 6 \times 10^{-25}\,\mathrm{kg}$, it is possible to define a typical time for the molecule to move through a distance σ: $t_{\mathrm{trans}} = (m\sigma^2/k_{\mathrm{B}}T)^{1/2} \approx 10\,\mathrm{ps}$ at $T = 300\,\mathrm{K}$. In a similar way, knowing the moment of inertia I, it is possible to calculate a typical rotation time. In this case, it once more turns out to be $t_{\mathrm{rot}} = (I/k_{\mathrm{B}}T)^{1/2} \approx 10\,\mathrm{ps}$. A typical molecular dynamics timestep, then, would have to be an order of magnitude less than this, i.e. ≈ 1 ps. We can identify a single Monte Carlo sweep with this time, very roughly, since it takes of order 10 trial rotational moves per molecule, typically, to achieve a complete rotation. Thus our runs, which needed to be more than 10^6 sweeps long in some cases, correspond to simulating a real system for $\approx 1\,\mu\mathrm{s}$. Only with a very idealized model is this feasible.

In this paper, we have deliberately concentrated on the thermodynamically relevant variables, particularly the energy, in order to focus on the thermodynamic features of this phase transition. Other interesting questions concern the orientational ordering in the system, especially the orientation profile, and the behaviour of this function as the transition is approached. We return to this in a separate paper [14].

NOTE ADDED IN PROOF: After the current paper was submitted, a study of this model in higher dimensions, showing the approach to the mean-field limit, appeared [33].

Acknowledgements

This work was supported by the Science and Engineering Research Council, through the provision of an Active Memory Technology DAP 510-8 parallel processor, under the Computational Science Initiative. The project has also benefitted from computer support within Bristol University, and the author is particularly grateful to J. Alcock and J.-P. Melot for their assistance. Conversations with R. Evans, T.J. Sluckin, and G.R. Luckhurst are gratefully acknowledged.

APPENDIX

This work has been carried out on a fine-grained, massively-parallel computer, the DAP 510-8. The simulation program is written in a straightforward parallel extension of FORTRAN 77, called FORTRAN Plus. In this appendix, we briefly describe the features of the Monte Carlo method specific to this work (for useful background material, see [28]).

We use the standard Metropolis method to generate states in the canonical ensemble. Molecules are rotated using the algorithm of Barker and Watts [29]. Because interactions are nearest-neighbour only, we can use a checkerboard black-white colouring of the molecules, which allows us to make independent moves on an entire sublattice in parallel [30, 31].

In our case, the orientations of all the molecules in the L layers of the system are stored in arrays of DAP matrix variables, $S(\ , \ ,L)$. The first two, blank, dimensions correspond to the fixed transverse dimensions of the DAP, here 32 × 32, but for simplicity we illustrate in Figure 6 the case of a 4 × 4 DAP. Also, for simplicity, we discuss a single orientation variable S, whereas in fact the unit vectors defining the molecular axes are stored in a set of 3 variables SX, SY, SZ.

It can be seen in Figure 6 that just half of the molecules in a single layer belong to one of the sublattices. We use the full parallelism of the DAP by attempting moves on two layers at once, adjacent for convenience, such as layers n and $n + 1$ in Figure 6. The first step is to segregate the two sublattices as shown in the Figure. This is accomplished very rapidly on the DAP, by parallel merge statements:

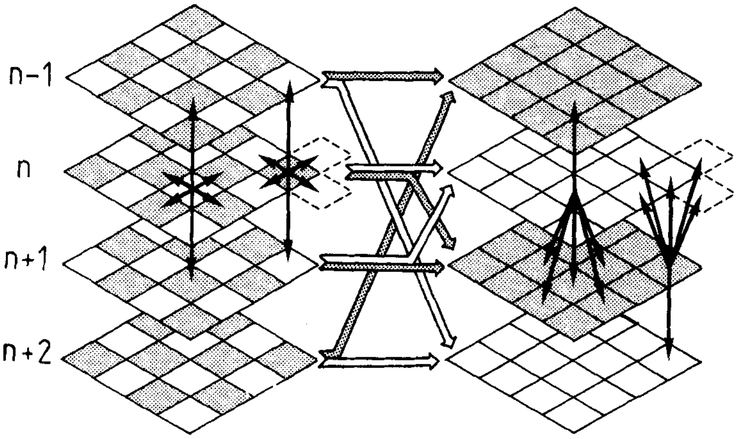

Figure 6 The checkerboard colouring of sublattices, and the data transformation used in the Monte Carlo program. For clarity we depict a 4 × 4 DAP, and show four successive layers. Nearest-neighbour interactions are shown as black arrows. Dashed squares represent periodic images. On the left we show the original system, and on the right the transformed system. Monte Carlo moves are applied successively to the central black and white sublattices, and the transformation is then reversed.

```
BLACKS = MERGE ( S( , ,N), S( , ,N + 1), MASK )
WHITES = MERGE ( S( , ,N + 1), S( , ,N), MASK )
```

where the `LOGICAL MATRIX` variable `MASK` contains `TRUE` and `FALSE` values in a checkerboard pattern. The `MERGE` function selects values from its first argument wherever `MASK` is `TRUE`, and values from its second argument wherever `MASK` is `FALSE`. It is also useful to carry out this procedure on the neighbouring layers $n - 1$ and $n + 2$, as shown in the Figure:

```
MORE–BLACKS = MERGE ( S( , ,N + 2), S( , ,N - 1), MASK )
MORE–WHITES = MERGE ( S( , ,N - 1), S( , ,N + 2), MASK )
```

The way nearest-neighbour interactions are mapped by this transformation is shown in Figure 6. First, an attempt is made to move all the molecules in the `BLACKS` variables to new trial orientations `TRIALS`, the changes in interactions with neighbours being rapidly evaluated using the DAP built-in shifting operations, in the following way:

```
DELTA–E  =  TRIALS * WHITES (-, ) - BLACKS * WHITES(-, )
+         + TRIALS * WHITES(+, ) - BLACKS * WHITES(+, )
+         + TRIALS * WHITES( ,-) - BLACKS • WHITES( ,-)
+         + TRIALS * WHITES( ,+) - BLACKS * WHITES( ,+)
+         + TRIALS * WHITES ( , ) - BLACKS * WHITES ( , )
+ + TRIALS * MORE–WHITES( , ) - BLACKS * MORE–WHITES( , )
```

We have simplified this statement for clarity: in reality, the interactions involve the three components of the molecular axis vectors, and are quadratic, not linear, in the product `BLACKS*WHITES`. The (±, ±) notation signifies shifting by one lattice spacing in each of the transverse directions; note that periodic boundary conditions in these directions are built in to the DAP hardware. After accepting or rejecting these moves in the normal way, all the molecules in the `WHITES` variables are treated similarly. Finally, the transformation of Figure 6 is reversed, again at little cost in time, by statements of the form

```
        S (MASK,N)  =  BLACKS
    S (.NOT.MASK,N)  =  WHITES
     S (MASK,N + 1)  =  WHITES
S (.NOT.MASK,N + 1)  =  BLACKS
```

The whole of the above procedure is enclosed in a loop over layers, two at a time. The top and bottom surface layers are handled in a straightforward manner. Although it is most convenient to use an even number of layers in our work, and to treat pairs of layers in sequence, this is not essential. Also, it is a simple matter to modify the program to treat other transverse dimensions such as 16 × 16 or 64 × 64, without losing efficiency. As written, the program runs at a rate of about 55000 attempted MC moves per second.

References

[1] D. Frenkel, "Computer simulation of hard-core models for liquid crystals", *Molecular Physics*, **60**, 1 (1987).

[2] M.P. Allen, D. Frenkel, and J. Talbot, "Molecular dynamics simulation using hard particles", *Computer Physics Reports*, to appear.

[3] M.P. Allen and D. Frenkel, "Observation of dynamical precursors of the isotropic-nematic transition by computer simulation", *Physical Review Letters*, **58**, 1748 (1987); M.P. Allen and D. Frenkel, "Calculation of liquid-crystal Frank constants by computer simulation", *Physical Review*, **A37**, 1813 (1988); M.P. Allen, "Molecular graphics and the computer simulation of liquid crystals", *Molecular Simulation*, **2**, 301 (1989).

[4] D.J. Adams, G.R. Luckhurst, and R.W. Phippen, "Computer simulation studies of anisotropic systems. XVI. The Gay-Berne model nematogen", *Molecular Physics*, **61**, 1575 (1987).

[5] D.A. Dunmur and M.R. Wilson, "Structure-property relationships in liquid crystals: can modelling do better than empiricism?", *Molecular Simulation*, these proceedings.

[6] K. Binder and D. P. Landau, "Wetting and layering in the nearest-neighbor simple-cubic Ising lattice: a Monte Carlo investigation", *Physical Review*, **B37**, 1745 (1988).

[7] D.B. Nicolaides and R. Evans, "Monte Carlo study of phase transitions in a confined lattice gas", *Physical Review*, **B**, to appear.

[8] J.H. Sikkenk, J.O. Indekeu, J.M.J. van Leeuwen, and E.O. Vossnack, "Molecular dynamics simulation of wetting and drying at solid-fluid interfaces", *Physical Review Letters*, **59**, 98 (1987).

[9] K. Binder, "Monte Carlo study of thin magnetic Ising films", *Thin Solid Films*, **20**, 367 (1974).

[10] K. Binder and P.C. Hohenberg, "Surface effects on magnetic phase transitions", *Physical Review*, **B9**, 2194 (1974).

[11] D.P. Landau, "Finite size behaviour of the simple cubic Ising lattice", *Physical Review*, **B14**, 255 (1976).

[12] D.P. Landau, "Applications in surface physics", in *Monte Carlo methods in Statistical Physics*, (Topics in Current Physics 7,) K. Binder ed., Chapter 9 (Springer, 1986).

[13] see T.J. Sluckin and A. Poniewierski, "Orientational wetting transitions and related phenomena in nematics", in *Fluid Interfacial Phenomena*, C.R. Croxton, ed (Wiley 1985), and references therein.

[14] M.P. Allen, "A computer simulation study of the surface properties of a liquid crystal film" in preparation.

[15] P.A. Lebwohl and G. Lasher, "Nematic liquid crystal order – a Monte Carlo calculation", *Physical Review*, **A6**, 426 (1972); erratum *ibid.*, **A7**, 2222 (1973).

[16] U. Fabbri and C. Zannoni, "A Monte Carlo investigation of the Lebwohl-Lasher lattice model in the vicinity of its orientational phase transition", *Molecular Physics*, **58**, 763 (1986).

[17] G.R. Luckhurst, T.J. Sluckin, and H.B. Zewdie, "Computer simulation studies of anisotropic systems. XV. The surface properties of the Lebwohl-Lasher model nematogen", *Molecular Physics*, **59**, 657 (1986).

[18] N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.H. Teller, and E. Teller, "Equation of state calculations by fast computing machines" *Journal of Chemical Physics*, **21**, 1087 (1953).

[19] M.N. Barber, "Finite-size scaling", in *Phase transitions and critical phenomena*, C. Domb and J.L. Lebowitz, eds, **8**, chapter 2 (Wiley 1983).

[20] D. Mermin and H. Wagner, "Absence of ferromagnetism or antiferromagnetism in one- or two-dimensional isotropic Heisenberg magnets", *Physical Review Letters*, **17**, 1133 (1966).

[21] H.E. Stanley and T.A. Kaplan, "Possibility of a phase transition for the two-dimensional Heisenberg model", *Physical Review Letters*, **17**, 913 (1966).

[22] R.E. Watson, M. Blume, and G.H. Vineyard, "Classical Heisenberg magnet in two dimensions", *Physical Review*, **B2**, 684 (1970).

[23] D.S. Ritchie and M.E. Fisher, "Finite-size and surface effects in Heisenberg films", *Physical Review*, **B7**, 480 (1973).

[24] C. Kawabata and A.R. Bishop, "Monte Carlo evidence for inhomogeneous states in the two-dimensional classical Heisenberg model", *Solid State Communications*, **33**, 453 (1980).

[25] M.E. Fisher, "The theory of critical point singularities", in *Critical Phenomena*, (Proceedings of the International School of Physics "Enrico Fermi", **51**,), M.S. Green ed., p1 (Academic, 1971).

[26] M.E. Fisher and A.E. Ferdinand, "Interfacial, boundary, and size effects at critical points", *Physical Review Letters*, **19**, 169 (1967).

[27] M.S.S. Challa, D.P. Landau, and K. Binder, "Finite-size effects at temperature-driven first-order transitions", *Physical Review*, **B34**, 1841 (1986).

[28] D. Fincham, "Parallel computers and molecular simulation", *Molecular simulation*, **1**, 1 (1987).

[29] J.A. Barker and R.O. Watts, "Structure of water: a Monte Carlo calculation", *Chemical Physics Letters*, **3**, 144 (1969).

[30] R. Friedberg and J.E. Cameron, "Test of the Monte Carlo method: fast simulation of a small Ising lattice", *Journal of Chemical Physics*, **52**, 6049 (1970).

[31] see K. Binder, "Recent trends in the development and application of the Monte Carlo method", in *Monte Carlo methods in Statistical Physics*, (Topics in Current Physics 7,) K. Binder ed., Chapter 10 (Springer, 1986), and references therein.

[32] D.P. Landau and R.H. Swendsen, "Tricritical universality in two dimensions", *Physical Review Letters*, **46**, 1437 (1981).

[33] M.E. Mann, C.H. Marshall, and A.D.J. Haymet, "Nematic liquid crystals. A Monte Carlo simulation study in higher dimensions", *Molecular Physics*, **66**, 493 (1989).