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Monte Carlo simulations of phase transitions in liquid crystals

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Abstract

The nematic to isotropic phase transition in a liquid crystal is investigated using Monte Carlo simulations. Effects of the rate of heating/cooling and aligning fields are studied. New parameters based on the divergence of the molecular axes are suggested to obtain information about the order in the system.

1. Introduction

Liquid crystals are technologically important materials and are studied intensively both experimentally and theoretically. These materials exist in a number of phases such as smectic, nematic, cholesteric, isotropic etc. The Monte Carlo technique has been applied by a number of workers [1–7] to study the transitions between different phases. Molecules are generally assumed to be rod-like so that their internal structure is ignored, except for the existence of a long axis. In continuum lattice models, the molecules are allowed to assume any orientation (and position) in space, whereas, in discrete lattice models, they can assume only some predefined discrete orientations. Chick and Viney [8,9] have made detailed comparisons of the continuum versus discrete models while studying the nematic to isotropic phase transition on the basis of a hard-core repulsive force and have concluded that continuum models have some distinct advantages over the discrete models. In the pioneering work by Lasher [1], the molecules were allowed to take one of the 12 predefined directions and a first order nematic to isotropic transition was established. Lebwohl and Lasher [2], hereafter denoted by LL, studied the same system in the continuum model. More recently, Nandi et al. [7] used an approach similar to that taken by LL but allowed the interaction energy to depend on the separation between the molecules and attempted to obtain a smectic to nematic phase transition.

The purpose of this communication is to draw attention to certain cautions that must be exercised in such simulations. In particular, the role of the rate of heating/cooling, suitability of the parameter $\eta_z = \langle P_2(\cos\theta)\rangle$ defined with respect to an arbitrary z-axis and effects of an applied field are examined. We confine the simulation to a $10 \times 10 \times 10$ cubic lattice of molecules and look for the nematic to isotropic phase transition.

2. The basic method

The interaction energy of a pair of molecules is assumed to be [10]

$$U_{ij} = -\epsilon P_2(\cos\theta_{ij}),$$

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where θ_{ij} is the angle between the molecules, $P_2(x)$ is the Legendre polynomial of the second order and ϵ is a strength parameter, assumed to be constant in this investigation. Only nearest-neighbour interactions are taken into account. The orientation of a molecule is represented by the spherical coordinates (θ, ϕ) defined with respect to the axes along the edges of the cubic lattice.

From a given configuration of the molecules, a new configuration is evolved using the prescription of Metropolis et al. [11]. Each molecule is allowed to make an attempt to change its orientation randomly. If the total interaction energy decreases ($\Delta E < 0$), this change is accepted. Otherwise, the change is accepted with a probability $\exp(-\Delta E/kT)$. A large number of repetitions of this process (several thousand passes) equilibrates the system, i.e., its energy becomes constant. We calculate the average energy over 100 consecutive passes and look for the constancy of this average to decide on equilibration.

2.1. Initial configuration

The initial configuration is quite important in such simulations. In their investigations, LL observed that it is computationally advantageous to start with a completely random configuration for a temperature above the transition, and with a completely ordered configuration for a temperature below the transition. Nandi et al. [7] have taken the final configuration at a lower temperature as the initial configuration for the next higher temperature. Apart from considerations of the computational speed, these choices have important physical significance. A completely random configuration corresponds to a very high temperature and subjecting it to Metropolis algorithm at a lower temperature would essentially mean sudden cooling. Similarly, a completely ordered configuration subjected to a high temperature would imply a sudden heating. It is known that quenching a system from high temperatures allows it to retain some structure of the high-temperature phase. Rochev et al. [12] have investigated the effect of sudden cooling of liquid crystals using Mössbauer spectroscopy and radiothermoluminescence and found that the phase of a liquid crystal at a given temperature depends strongly on its thermal history. Similarly, the structure obtained on sudden heating may be biased by the low-temperature phase.

Taking the final configuration at a temperature as the initial configuration for the next higher temperature would mean slow heating.

2.2. Order parameter

The nematic order in a liquid crystal is represented by the matrix

$$T_{ij} = \langle \nu_i \nu_j - \tfrac{1}{3}\delta_{ij} \rangle,$$

where ν_i $(i = 1, 2, 3)$ denote the Cartesian coordinates of the unit vector along a molecular axis and the averaging is performed over all the molecules. The eigenvalues of this matrix are $\frac{2}{3}\eta$, $\frac{1}{3}\eta$, $-\frac{1}{3}\eta$ where the quantity η is known as the order parameter and can be written as

$$\eta = \tfrac{1}{2}\langle 3\cos^2\theta - 1 \rangle.$$

Here θ represents the angle between the molecular axis and the director (the preferred direction for orientation). In several of the Monte Carlo simulations on liquid crystals reported in the literature [1,7], the order parameter is evaluated from this last expression where θ is measured from an arbitarily chosen z-axis. We call this quantity η_z. Such a choice may lead to computational difficulties and/or misleading results as this expression is not invariant under the rotation of the crystal. LL have reported such computational difficulties and suggested a remedy in choosing the proper initial configuration. Nandi et al. [7] have worked with the initial configuration completely oriented along the z-axis and hoped that the director will remain along the same direction as simulations proceed at higher temperatures. However, this may not always be true because the Metropolis algorithm decides the configuration on the basis of the change in energy and all configurations corresponding to a given energy are in principle reached if the number of trials is sufficiently large. As one can have the director along any axis with the same energy, a change in the director during the simulation is not unlikely and hence η_z calculated with respect to a chosen fixed z-axis may not reflect the true order.

To investigate these difficulties we have calculated the order parameter η by evaluating the eigen-

values of the matrix T_{ij}. Also, we suggest below some alternative parameters to reflect the order in a nematic crystal.

2.3. Alternative parameters to measure order

2.3.1. Angular divergence of the long axes

In an aligned liquid crystal, the angles θ_{ij} between the long axes are small. The average and the dispersion of the angles between the neighbouring molecules will carry information about the order. For a perfectly aligned state, θ_{ij} has zero mean and zero dispersion. In a perfectly random configuration, θ_{ij} is distributed about a mean value of 57.3° with a standard deviation of $\Delta\theta = 21.5°$. This can be seen as follows,

$$\langle \theta_{ij} \rangle = \frac{\int_0^{\pi/2} \theta \sin\theta \, d\theta}{\int_0^{\pi/2} \sin\theta \, d\theta} = 57.3°,$$

$$(\Delta\theta)^2 = \frac{\int_0^{\pi/2} \left(\theta - \langle \theta_{ij} \rangle\right)^2 \sin\theta \, d\theta}{\int_0^{\pi/2} \sin\theta \, d\theta}$$

giving $\Delta\theta = 21.5°$.

So $\langle \theta_{ij} \rangle$ and $\Delta\theta$ may be used to indicate the nematic order.

2.3.2. Dispersion in the average energy per molecule

It is wellknown that the fluctuation in the simulated energy is much larger near the transition than at temperatures away from the transition. We calculate the standard deviation of the average energy per molecule in equilibrium and show that this quantity U_σ can be used to detect the phase transition.

We now report the results of our investigations of phase transitions – nematic to isotropic and vice versa – with slow heating/cooling of the system. The energy is reported in the units of ϵ and the temperature in ϵ/k.

3. Phase transition on slow heating / cooling

Equilibrium configurations were generated at different temperatures by slowly heating or cooling the system. For the cooling cycle, we started with a random configuration at $T = 2.0$. The equilibrated configuration at this temperature was taken as the starting configuration for the next lower temperature $T = 1.9$. Similarly equilibrium configurations were generated at other temperatures. The simulation parameters namely, energy/molecule U, order parameter η, divergence parameters $\langle \theta_{ij} \rangle$ and $\Delta\theta$ were

Table 1
Parameters in equilibrium configurations reached from completely random configuration by slowly cooling the system

T [ϵ/k]	U [ϵ]	U_σ [ϵ]	η	$\langle \theta_{ij} \rangle$ [deg]	$\Delta\theta$ [deg]
2.0	−0.315	0.0042	0.039	52.3	22.5
1.9	−0.335	0.0047	0.040	52.0	22.5
1.8	−0.360	0.0050	0.042	51.6	22.5
1.7	−0.387	0.0052	0.043	51.2	22.6
1.6	−0.422	0.0066	0.049	50.6	22.6
1.5	−0.460	0.0062	0.053	50.0	22.6
1.4	−0.512	0.0076	0.057	49.2	22.7
1.3	−0.578	0.0110	0.070	48.2	22.7
1.2	−0.685	0.0200	0.100	46.4	22.7
1.1	−1.180	0.050	0.456	38.8	21.2
1.0	−1.580	0.030	0.624	32.3	18.4
0.9	−1.840	0.018	0.708	28.5	16.2
0.8	−2.030	0.016	0.759	25.5	14.3
0.7	−2.185	0.014	0.800	23.1	12.7

U = average energy per molecule, U_σ = standard deviation of U. η = order parameter obtained from the matrix T_{ij}.

Table 2
Parameters in equilibrium configurations reached from the completely ordered configuration by slowly heating the system

T [ϵ/k]	U [ϵ]	U_σ [ϵ]	η	$\langle\theta_{ij}\rangle$ [deg]	$\Delta\theta$ [deg]	η_z
0.1	−2.898	0.0026	0.976	7.6	4.0	0.973
0.2	−2.795	0.0042	0.952	11.0	5.8	0.927
0.3	−2.685	0.0065	0.925	13.7	7.3	0.749
0.4	−2.571	0.0084	0.898	16.1	8.6	0.881
0.5	−2.451	0.0090	0.869	18.4	9.9	0.838
0.6	−2.328	0.0096	0.837	20.6	11.2	0.733
0.7	−2.182	0.012	0.802	23.0	12.7	0.621
0.8	−2.019	0.014	0.756	25.7	14.4	0.063
0.9	−1.831	0.018	0.701	28.6	16.3	0.030
1.0	−1.577	0.032	0.624	32.6	18.6	−0.096
1.1	−1.186	0.062	0.462	38.6	21.2	0.092
1.2	−0.677	0.015	0.091	46.6	22.7	0.009
1.3	−0.576	0.010	0.067	48.2	22.7	0.0
1.4	−0.510	0.006	0.057	49.2	22.7	0.001

averaged over 100 successive trials. Such averages were calculated for several thousand trials. From this the mean values and the standard deviations of the parameters were obtained. The results are shown in Table 1.

For the heating cycle, we started with all the molecules pointing towards the z-axis and subjected the system to the temperature $T = 0.1$ which is much smaller than the transition temperature. The final equilibrium configuration at this temperature was taken as the starting configuration for $T = 0.2$ and so on. Table 2 gives the parameters at different temperatures in this heating cycle.

In the starting configuration at $T = 0.1$, all the molecules are along the z-axis which is therefore the director. The order parameter η in this configuration is therefore equal to $\eta_z = \langle P_2(\cos\theta)\rangle$ where θ is the angle of the molecular axis with the z-axis. However, as the simulation proceeds at a higher temperature the director may itself change the direction. To see how well η_z represents order at higher temperatures, we have calculated η_z at each temperature. Table 2 includes these values.

Here are some observations from these simulations.

(a) Fig. 1 shows the correlation of $\langle\theta_{ij}\rangle$ and $\Delta\theta$ with the order parameter η obtained by diagonalizing the matrix T_{ij}. The nice correlation shows that $\langle\theta_{ij}\rangle$, $\Delta\theta$ may be used to measure the order in the system. Polynomial fittings to the data show that these quantities may be quite well represented as functions of η by the following expressions:

$$\langle\theta_{ij}\rangle = 56.3 - 148.6\eta + 676.4\eta^2 - 1513.8\eta^3 + 1488\eta^4 - 554.1\eta^5,$$

$$\Delta\theta = 22.6 + 0.532\eta + 3.13\eta^2 - 23.6\eta^3.$$

On the other hand, η_z does not correlate with η.

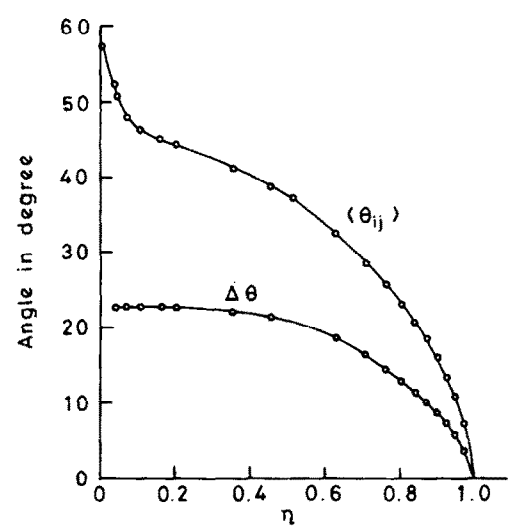

Fig. 1. Correlation of the divergence parameters $\langle\theta_{ij}\rangle$ and $\Delta\theta$ with the order parameter η.

(b) The equilibrium was achieved in about 3000 to 5000 passes in most of the cases though about 15 000 passes were given at each temperature. There was no difficulty in going to temperatures below the transition temperature in the cooling cycle or to temperatures above the transition temperature in the heating cycle. Thus the difficulty pointed out by LL does not occur in our approach.

(c) The values of U, U_σ, $\langle \theta_{ij} \rangle$, $\Delta\theta$, η at a particular temperature from the cooling cycle and from the heating cycle match very well.

(d) In the cooling cycle (Table 1), we started with a completely random configuration (at the highest temperature) and hence there is no preferred direction. Thus η_z gave only indirect information about the transition. It remained close to zero for temperatures $T > 1.1$ and fluctuated at $T \leqslant 1.1$ indicating a transition between $T = 1.1$ and 1.2. On the other hand, the order parameter η obtained from the matrix T_{ij} is stable at each temperature. Also, the divergence parameters $\langle \theta_{ij} \rangle$ and $\Delta\theta$ change more rapidly in the range 1.2–1.0 indicating the onset of transition. Similar observations were made from the heating cycle. Fig. 2 shows the variations of $\langle \theta_{ij} \rangle$ and $\Delta\theta$ versus T which clearly indicate a transition at around $T = 1.12$. To monitor the region near the transition more sensitively, we simulated configurations between $T = 1.0$ and 1.2 in steps of $\Delta T = 0.02$ in the heating as well as in the cooling cycle. The figures include these data.

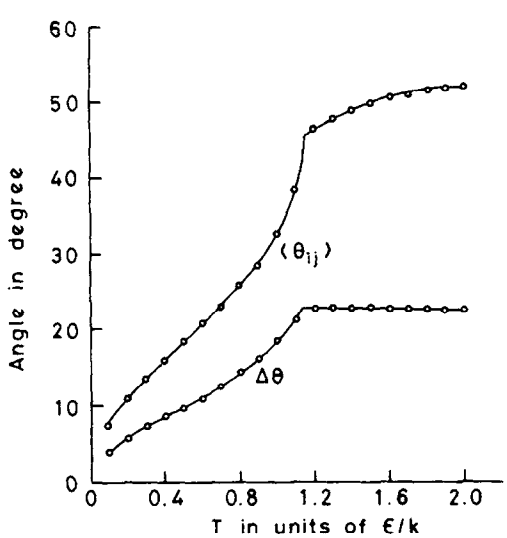

Fig. 2. The divergence parameters $\langle \theta_{ij} \rangle$ and $\Delta\theta$ as a function of temperature. Average values are used where data were available from the heating as well as the cooling cycle. The discontinuity in the slopes indicate a phase transition at $T = 1.12$.

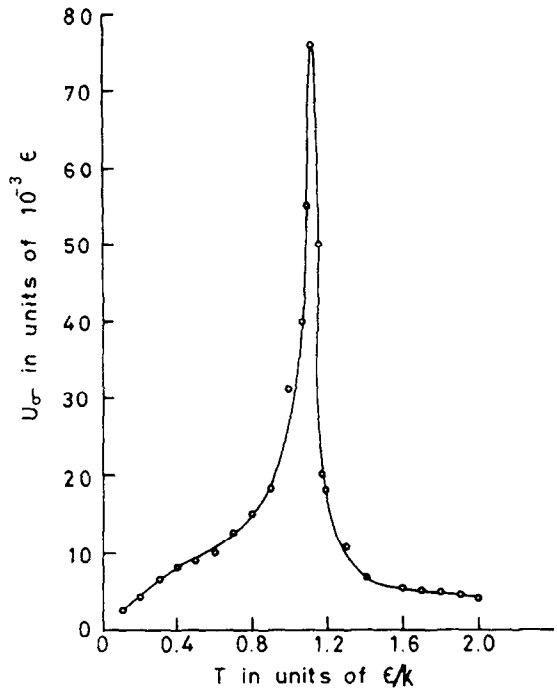

Fig. 3. Standard deviation of the average energy per molecule as a function of temperature.

(e) As the temperature is increased slowly in the heating cycle (Table 2), η_z decreases and abruptly drops at $T = 0.8$. This may give an impression that the transition to the isotropic phase has taken place at this temperature. But this is incorrect as shown by the values of η, U_σ, $\langle \theta_{ij} \rangle$ and $\Delta\theta$. It is a known fact that if a liquid crystal in a nematic phase, not too far away from the transition temperature, is left without any aligning field, the long range order disappears in due course of time. Order may still persist but the mobility of the molecules keeps on changing the direction of the order at the local level. The parameter η_z, not being invariant under rotation, is therefore not a good indicator of the transition even if one starts with a perfectly ordered system at some low temperature making the z-direction the director at this temperature. LL have used the specific heat

capacity to identify the transition temperature which is certainly a much more reliable parameter. Nandi et al. [7] appear to have worked with the parameter η_z only, which needs critical examination.

(f) The standard deviation U_σ of the average energy per molecule is plotted in Fig. 3 as a function of temperature. It peaks at $T = 1.12$ indicating the phase transition.

(g) The change $\Delta\eta$ in the order parameter is about 0.35 which agrees well with the calculations of the mean field theory.

4. Specific heat capacity and latent heat of transition

From the tabulated values of the energy U, we calculated the specific heat capacity $(1/N)\,\mathrm{d}U/\mathrm{d}T$. Fig. 4 shows its variation with temperature. The transition temperature as given by this figure is $T = 1.12$ in excellent agreement with LL and with our earlier conclusion based on η, U_σ, $\langle\theta_{ij}\rangle$ and $\Delta\theta$.

The latent heat of transition can also be estimated from Fig. 1. We can extrapolate the segments of the curve for $T < 1.0$ and $T > 1.2$ to meet at a point. The difference between the area under the actual $(1/N)\,\mathrm{d}U/\mathrm{d}T$ versus T curve and under the extrapolated curve should approximate the latent heat. This exercise gives a latent heat of 0.50ϵ per molecule, a value close to 0.522ϵ obtained in the mean field approximation of Maier and Saupe [10]. The latent heat of transition obtained by LL is 1.09ϵ. The reason for this high value may lie in the rapid heating/cooling. If we obtain the configuration at a temperature just above T_0 by suddenly cooling the system from a very high temperature, we may lock in more energy than required. Similarly, the configuration obtained just below T_0 by suddenly heating the system from a very low temperature may have less energy than expected at this temperature. The difference would then be large leading to a large latent heat.

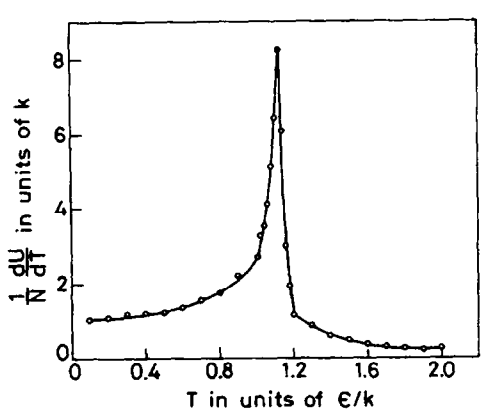

Fig. 4. The specific heat capacity as a function of temperature. The discontinuity at $T = 1.12$ a indicates phase transition at this temperature. The latent heat calculated from this curve is 0.50ϵ per molecule.

5. Application of an aligning field

A magnetic field $\boldsymbol{B}$ is often applied to align a liquid crystal in the nematic phase. In the simplest model the energy of a molecule in the presence of such a field is given by

$$U = -\boldsymbol{\mu}\cdot\boldsymbol{B} = -\mu B\cos\theta = -\epsilon'\cos\theta.$$

We include this energy in our model to simulate the effects of an aligning field. We take equilibrated configurations at temperatures $T = 1.3, 1.2, \ldots, 0.7$ from the cooling cycle where the z-axis was not the preferred direction as indicated by the values of η_z. We apply the field in the z-direction with $\epsilon' = 0.1\epsilon$ to these configurations. We evaluated η_z to see the effect of the field in aligning the crystal along the field. We found that for $T = 1.3$ and 1.2, η_z remained close to zero even after 2×10^4 passes, whereas, for temperatures below $T = 1.1$, η_z took high values in roughly 10^4 passes. At $T = 1.1$ it fluctuated between 0 and 0.4. So the field aligns the system below the transition temperature but not above it.

6. Conclusions

We have investigated the nematic to isotropic phase transition in a liquid crystal using Monte Carlo simulations. It is pointed out that the rate of heating/cooling has an appreciable effect on the final configuration. The order parameter η_z defined with respect to an arbitrary z-axis is shown to be a misleading parameter in identifying phases under

certain conditions. The order parameter η is obtained by diagonalizing the order parameter matrix T_{ij}. New parameters based on the divergence of the molecular axes are suggested to elucidate the transition. The transition temperature obtained from our simulations is in excellent agreement with the earlier works. The latent heat of transition obtained from our simulations is in good agreement with the values calculated using the mean field approximation. The discontinuity in the order parameter at the transition is also in agreement with the mean field theory. An aligning field is included in the simulation and the results are found to be along the expected lines.

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