

COMPUTER SIMULATION STUDIES OF ANISOTROPIC SYSTEMS. XI. SECOND- AND FOURTH-RANK MOLECULAR INTERACTIONS

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Received 18 June 1984

The Maier-Saupe theory for nematic liquid crystals provides a reasonable account of their orientational order and its temperature dependence. The theory is based on second-rank anisotropic interactions and its predictions can be improved by the introduction of higher-rank terms as in the Humphries-James-Luckhurst theory. However comparison with the properties of real nematogens does not allow an unambiguous test of the theory because the form of the pair potential is unknown. This is not the case for computer simulations where the intermolecular potential is defined. We have therefore undertaken a Monte Carlo study of the influence of fourth-rank interactions on nematic behaviour and report the results of our simulations here. The model nematogen used as a reference is that developed by Lebwohl and Lasher in which the particles are confined to the sites of a simple cubic lattice and interact via a second-rank anisotropic potential. The simulation gives the internal energy, the heat capacity at constant volume and the second-rank order parameter as a function of temperature, as well as the nematic-isotropic transition temperature. These results are used to provide the first unambiguous test of the Humphries-James-Luckhurst theory. We also discuss the changes in the transition temperature which are caused by the introduction of the fourth-rank term in the pair potential using thermodynamic perturbation theory for the Helmholtz free energy.

1. Introduction

Computer simulations have contributed a great deal to our present insight of simple fluids [1,2]. The study of liquid crystal phases [3] using simulation techniques is also becoming increasingly important for an understanding of the subtleties of anisotropic systems even though of far more recent development. Calculations aimed at reproducing the experimental results for a specific nematogen are not yet feasible, but several studies of model systems have appeared [4-19]. Apart from a few investigations on systems with translational freedom [16-19], the majority of these simulations

have been concerned with lattice systems. In this kind of work attention is focused on the important orientational properties while translational degrees of freedom are neglected. In practice molecules are assumed to interact according to their orientation, while keeping the centres of mass fixed. The aim is to try and understand the essential characteristics of the order-disorder transition and to investigate how macroscopic orientational properties are related to the intermolecular potential. Another relevant objective is to provide essentially exact solutions for model potentials that have been treated or can be treated with approximate theories. This allows an otherwise impossible test of the effectiveness of the chosen theory. The prototype of these lattice models was first proposed by Lebwohl and Lasher [4] and investigated by several workers

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using the Monte Carlo [4,5,13] and, more recently, the molecular dynamics method [10] as well as a variety of theoretical techniques [19–23]. In this model the cylindrically symmetric particles are restricted to be at the sites of a cubic lattice. They interact through an anisotropic pair potential

$$U_{ij} = -\epsilon_{ij} P_2(\cos \beta_{ij}), \quad (1)$$

where ϵ_{ij} is a positive constant, ϵ , for neighbouring sites i and j and is zero otherwise, $P_2(x)$ is the second Legendre polynomial, while β_{ij} is the angle between the symmetry axes of the two particles. It has been found [4] that this model exhibits an orientational phase transition at a scaled temperature $T_{NI}^* = kT_{NI}/\epsilon = 1.127 \pm 0.003$ [13]. This compares with a molecular field result of $(T_{NI}^*)_{MF} = 1.321$ [7]. In other words, the molecular field theory leads to an overestimation of the transition temperature analogous to the behaviour found for spin systems [24]. In contrast, the behaviour of the second-rank order parameter \bar{P}_2 versus the reduced temperature $T^* = T/T_{NI}$ is found to be in rather satisfactory agreement with the molecular field predictions [13]. Here \bar{P}_2 is the ensemble average of $P_2(\cos \beta)$, where β is the angle made by the molecular symmetry axis with the director. In fact it is common practice to plot experimental order parameters \bar{P}_2 against reduced temperature because this provides a way of comparing results for a variety of different nematogens and to see if the universal curve predicted by the Maier–Saupe molecular field theory is obtained. It is found that, even though a general qualitative agreement with this universal curve exists, there are a number of cases where significant deviations occur [25]. Attempts to generalize the pair potential for dispersion forces originally used by Maier and Saupe [19] to account for these deviations have included the application of the molecular field procedure to a potential written as a general Popl e series expansion [25]. It has been shown by Humphries et al. [26] that a Maier–Saupe-like potential of mean torque is obtained as the first term for axially symmetric interactions, whatever the nature of the underlying intermolecular forces. Since the orientational order and indeed any average property at a certain reduced temperature is determined essen-

tially by the functional form of the potential of mean torque, the relative success of the simple Maier–Saupe theory can be understood. It is more dictated by general symmetry arguments than by the effectiveness of the molecular field procedure itself and the validity of the starting anisotropic pair potential. The generalized version of the molecular field theory showed, however, how to improve upon the Maier–Saupe approach by making the pair potential more realistic. Retaining the constraint of molecular rigidity, this can be achieved by either allowing for deviations from cylindrical symmetry [27] or by keeping terms of rank higher than two in the potential of mean torque [26,28] or both.

We concern ourselves here with the second possibility namely the addition of a fourth-rank Legendre polynomial term to the pair potential in eq. (1). It has been known from some time [26] that this modification improves agreement with the experimental order parameter, although this is to be expected because an additional parameter has been added. It is important therefore to see if the trend and magnitude of the observed variations in, for example, the order parameter versus temperature curve are to be attributed to the changes effected in the pair interaction or rather to an artefact of the molecular field prescription. To test this point the Monte Carlo method is particularly useful and in this paper we set out to consider the anisotropic pair potential

$$U_{ij} = -\epsilon_{ij} [P_2(\cos \beta_{ij}) + \lambda P_4(\cos \beta_{ij})], \quad (2)$$

where the parameter λ gives the strength of the fourth-rank interaction relative to the second. As for the potential in eq. (1), the interaction constant is positive and equal to ϵ if particles i and j are first neighbours and is zero otherwise. The behaviour of a system interacting through such a pair potential has been predicted using the molecular field approximation [26] and two site cluster methods [20,21]. The influence of the fourth-rank term on the transition temperature can be investigated using thermodynamic perturbation theory and we give such an analysis in the following section. The Monte Carlo simulations are described briefly in section 3 and the results of these simulations are

presented in section 4. The transitional properties and the temperature dependence of the internal energy, heat capacity at constant volume and the second-rank order parameter are compared with the predictions of the molecular field theory in section 5. Our conclusions are in section 6.

2. Perturbation theory

A general qualitative understanding of the effect of adding a small term λU_1 to a given reference potential U_0 ,

$$U = U_0 + \lambda U_1, \quad (3)$$

can be obtained using thermodynamic perturbation theory [1,2,29]. The Helmholtz free energy for the perturbed system can be written as

$$A = A_0 + \lambda \langle U_1 \rangle_0 - (\lambda^2/2kT) \langle (U_1')^2 \rangle_0 + \dots, \quad (4)$$

where A_0 is the free energy of the Maier-Saupe-like reference system ($\lambda = 0$), k is the Boltzmann constant, T the absolute temperature and where the averages $\langle \dots \rangle_0$ are taken with respect to the unperturbed distribution. Here $U_1' = U_1 - \langle U_1 \rangle_0$. The expansion in eq. (4) is certainly valid when the perturbation energy is small compared to kT . Thermodynamic perturbation theory has, however, met with considerable success in describing the behaviour of simple fluids even beyond this limit [30] and some recent theoretical results [31] seem to imply that its validity may actually be more extensive. In any event eq. (4) can be useful to draw qualitative conclusions about the relative stabilization of a phase when a term is added to the reference potential. To do this we consider the free energy at the transition temperature of the unperturbed system both for the ordered and for the isotropic phase. From eq. (4) the free energy of the isotropic phase is

$$A^I = A_0^I + \lambda \langle U_1 \rangle_0^I - (\lambda^2/2kT) \langle (U_1')^2 \rangle_0^I + \dots, \quad (5)$$

where the superscript I refers to the disordered phase; a similar expression obtains for the nematic phase with N replacing I. The difference in the Helmholtz free energy between the ordered and

disordered phase is then

$$\Delta A = \lambda \Delta \langle U_1 \rangle_0 - (\lambda^2/2kT) \Delta \langle (U_1')^2 \rangle_0 + \dots, \quad (6)$$

where $\Delta f \equiv f^N - f^I$ and we have used the fact that A_0^N equals A_0^I at the transition for the reference system. Eq. (6) shows that if $\langle U_1 \rangle_0 = 0$ the ordered phase will be stabilized in second order by the perturbation whatever the sign of λ provided the mean square average value of U_1' is larger in the ordered phase, as it should be. Consider, for example, a system of particles exhibiting a small deviation from cylindrical symmetry. In this case the perturbation would be the non-uniaxial part of the total pair potential, namely,

$$U_1(r_{12}, \omega_1, \omega_2) = \sum u_{LL'J}^{kk'}(r_{12}) S_{LL'J}^{kk'}(\Omega), \quad (7)$$

$k, k' \neq 0,$

where $u_{LL'J}^{kk'}(r_{12})$ are interaction coefficients and $S_{LL'J}^{kk'}(\Omega)$ are rotational invariants, with Ω giving collectively the orientation of molecules 1 and 2, i.e. ω_1, ω_2 and of the intermolecular vector [32]. The superscripts k, k' refer to molecule-fixed components and must be zero when the molecules have cylindrical symmetry. Since eq. (7) contains only terms resulting from deviations from cylindrical symmetry $k, k' \neq 0$ averaging over the distribution function of the reference system of rod-like particles for which

$$U_0(r_{12}, \omega_1, \omega_2) = \sum u_{LL'J}^{00}(r_{12}) S_{LL'J}^{00}(\Omega), \quad (8)$$

gives $\langle U_1 \rangle_0 = 0$. In consequence the ordered phase should be stabilized because $\langle (U_1')^2 \rangle_0$ need not vanish and so the transition temperature should be larger than that in the reference system. This prediction is in accord with the results for a molecular field theory [27] and a Monte Carlo simulation [9,33] of a system of biaxial particles. Similar arguments hold for the effect of dipolar forces or indeed of any interaction whose average over a uniaxial reference system vanishes by symmetry.

It has been proposed [34] that the change in the transition temperature caused by the addition of a perturbation to the intermolecular potential for the reference system is given by

$$T_{NI} - T_{NI}^0 = \Delta A / \Delta S_0, \quad (9)$$

where ΔA is evaluated at the transition temperature T_{NI} of the perturbed system. Here T_{NI}^0 is the transition temperature and ΔS_0 is the entropy difference of the nematic and isotropic phases for the reference system. The derivation of this simple result requires the ratio $\Delta U_0/\Delta S_0$ to be independent of temperature and equal to T_{NI}^0 ; in addition ΔS_0 is assumed to be insensitive to temperature variations. It is possible to test the likely validity of these assumptions for a reference system of rod-like particles by using the Maier-Saupe theory to estimate the temperature dependence of ΔU_0 and ΔS_0 . These calculations reveal that although the ratio $\Delta U_0/\Delta S_0$ is insensitive to temperature the entropy difference varies markedly with temperature in the vicinity of the nematic-isotropic transition. In consequence we are unable to employ eq. (9) to determine the perturbation-induced shift in the transition temperature with any certainty.

The situation is rather more complicated if the average of $\langle U_1 \rangle_0$ is non-zero. Thus the evaluation of $\langle U_1 \rangle_0$ requires a knowledge of just the pair distribution in the reference system when the potential is approximated as a sum of pair interactions. In marked contrast the evaluation of $\langle (U_1)^2 \rangle_0$ requires in addition three- and four-body distributions. To simplify the discussion we shall therefore make explicit reference to our lattice model and attempt to approximate the relevant terms. We divide the potential of eq. (2) into a reference part

$$U_0 = -\epsilon \sum_{\langle ij \rangle} P_2(\cos \beta_{ij}), \quad (10)$$

and a perturbation, cf. eq. (3),

$$\lambda U_1 = -\epsilon_4 \sum_{\langle ij \rangle} P_4(\cos \beta_{ij}), \quad (11)$$

where we use the notation $\langle ij \rangle$ to indicate neighbouring sites i, j and $\epsilon_4 = \lambda\epsilon$. Evaluation of the first-order perturbation term is quite straightforward, it is just

$$\lambda \Delta \langle U_1 \rangle_0 = -(\lambda\epsilon zN/2) \Delta \sigma_4^0. \quad (12)$$

Here z is the number of nearest neighbours and we have introduced the definition of the short-range

order parameters [8]

$$\sigma_L = \overline{P_L(\cos \beta_{ij})}, \quad (13)$$

these give the rank L angular correlation at nearest-neighbour distance while the superscript 0 indicates an unperturbed average. The second- and fourth-rank short-range order parameters for the reference state have been evaluated [7] for a system of 1000 particles. In practice at T_{NI}^* we have $(\sigma_2^0)^N \approx 0.39$, $(\sigma_2^0)^I \approx 0.29$, $(\sigma_4^0)^N \approx 0.07$, $(\sigma_4^0)^I \approx 0.04$, $\bar{P}_2 \approx 0.35$ and $\bar{P}_4 \approx 0.08$. This gives an estimate of $-0.09\lambda N\epsilon$ for the right-hand side of eq. (12).

We now consider the second-order perturbation term in eq. (5). If this term is negligible the expected shift in free energy and transition temperature should be essentially symmetric for a change of sign of λ . To estimate the importance of the second-order correction we write down the average mean square perturbation potential as

$$\langle (U_1)^2 \rangle / \epsilon^2 = \sum_{\langle ij \rangle} \sum_{\langle i'j' \rangle} \left[\langle P_4(\cos \beta_{ij}) P_4(\cos \beta_{i'j'}) \rangle_0 - (\sigma_4^0)^2 \right], \quad (14)$$

where the sums are restricted to nearest-neighbour $\langle i, j \rangle$, $\langle i', j' \rangle$ sites. We can divide the contributions to the double sum into three kinds of terms caused by different combinations of the site indices, i.e. terms where the two pairs of sites are the same ($\langle ij \rangle = \langle i'j' \rangle$), terms where there is a site in common (e.g. $\langle ij \rangle$ and $\langle ij' \rangle$) and terms where all four indices are different ($\langle ij \rangle \neq \langle i'j' \rangle$). These different contributions are often written down conveniently in diagrammatic form (cf. e.g. ref. [2]). Counting the number of terms for each type of contribution for our simple cubic lattice we find the right-hand side of eq. (14) to be

$$(zN/2)C_A + z(z-1)NC_B + [zN(zN-4z+2)/4]C_C. \quad (15)$$

Here we have introduced

$$C_A = \langle P_4(\cos \beta_{12}) P_4(\cos \beta_{12}) \rangle_0 - (\sigma_4^0)^2, \quad (16)$$

$$C_B = \langle P_4(\cos \beta_{12}) P_4(\cos \beta_{23}) \rangle_0 - (\sigma_4^0)^2, \quad (17)$$

$$C_C = \langle P_4(\cos \beta_{12}) P_4(\cos \beta_{34}) \rangle_0 - (\sigma_4^0)^2. \quad (18)$$

The term C_A can be evaluated just from a knowledge of the pair distribution for the reference system. By coupling the two rank-four Legendre polynomials $P_4(\cos \beta_{12})$ using the Clebsch-Gordan series we find

$$\begin{aligned} \langle P_4(\cos \beta_{12})^2 \rangle_0 = & (1/9 + 100\sigma_2^0/693 \\ & + 162\sigma_4^0/1001 + 20\sigma_6^0/99 \\ & + 490\sigma_8^0/1287), \end{aligned} \quad (19)$$

and so

$$\begin{aligned} (\lambda^2 \epsilon^2 / 2kT) \Delta C_A \approx & (zN/2) \left[100\Delta\sigma_2^0/693 \right. \\ & \left. + 162\Delta\sigma_4^0/1001 - \Delta(\sigma_4^0)^2 \right] \\ & \times (\lambda^2 \epsilon^2 / 2kT). \end{aligned} \quad (20)$$

At the chosen temperature this contributes to the second-order term on the right-hand side of eq. (6) a quantity $\approx 0.045\lambda^2 N\epsilon$, where we have neglected the small σ_6^0 and σ_8^0 terms.

Evaluation of the contributions C_B and C_C is more complicated. Strictly it involves a knowledge of the three- and four-particle distribution functions for the reference system. Fortunately for our purpose here we are mainly interested in obtaining an approximate estimate for them. To this end we make the rather crude assumption that in evaluating the second-order terms the n -particle distribution for the reference system can be factorized into a product of single-particle distributions. If this is the case it follows immediately that the contribution to eq. (5) of the disconnected term C_C vanishes. The contribution from C_B can be evaluated by first expanding $P_4(\cos \beta_{12})$ using the spherical harmonic addition theorem and employing the cylindrical symmetry of the nematic phase [8] as

$$\begin{aligned} (\lambda \bar{P}_2 \epsilon^2 / 2kT) \Delta C_B \\ \approx Nz(z-1)(\lambda^2 \epsilon^2 / 2kT) \\ \times \left[(1/9 + 100\bar{P}_2/693 + \dots) \bar{P}_4^2 - P_4^2 \right] / (T^*)^2, \end{aligned} \quad (21)$$

which amounts to $\approx 0.026\lambda^2 N\epsilon$. To check our factorization assumption we have recalculated the C_A contribution for various values of λ , $-0.2 < \lambda$

< 0.2 and found that the errors do not exceed 20%. We conclude that the second-order term is significantly smaller than the first although it is not negligible. Since the sign of the second-order contribution is always negative, it stabilizes the anisotropic phase whatever the sign of λ . This means that the shift in transition temperature is not expected to be symmetric in λ . Indeed we expect the stabilization to be greater for positive λ than the destabilization for negative ones. In the following sections we shall see that this is indeed borne out by our computer experiments.

3. The Monte Carlo simulations

We have employed the standard Monte Carlo procedure with periodic boundary conditions, as introduced by Metropolis et al. [35]. The system studied contained 10^3 particles, interacting via the potential in eq. (2), located at the sites of a simple cubic lattice; the orientation of a particle is stored as $\cos \beta$ and α where these are the spherical polar angles of its symmetry axis in the laboratory frame. The variables $\cos \beta$ and α were changed randomly during the simulation for particles chosen at random. The properties calculated by the simulations were the scaled internal energy per particle ($\bar{U}^* \equiv \bar{U}/N\epsilon$, where N is the number of particles) and the heat capacity at constant volume C_V^* . This was determined by numerical differentiation of \bar{U}^* with respect to the scaled temperature ($T^* \equiv kT/\epsilon$) using a cubic spline fitting routine. The second-rank order parameter \bar{P}_2 was determined from the Q tensor [15]

$$Q_{ab} = (3\bar{l}_a \bar{l}_b - \delta_{ab})/2, \quad (22)$$

where l_a is the direction cosine of the molecular symmetry axis with the a laboratory axis. Details of this method as well as other technical aspects of computer simulation studies of liquid crystals have been described by Zannoni [7]. The equilibration stage of a simulation contained typically 5000 cycles, where one cycle is N attempted moves. The production run usually consisted of 10^4 cycles and typically this was divided into 10 equal steps in order to estimate the statistical errors in the quan-

tities calculated. The particles were perfectly aligned in the initial configuration for the lowest temperature. For higher temperatures the starting configuration was taken from a production run at a lower temperature.

4. The results

The simulations were performed for the anisotropic pair potentials with $\lambda = -0.2$ and 0.2 in eq. (2). The simulated results for \bar{U}^* , C_V^* and \bar{P}_2

obtained with the two potentials are plotted against the scaled temperature in figs. 1-3 and are also listed in the appendix.

The scaled heat capacity C_V^* is observed to mimic a divergence for the potential with $\lambda = 0.2$ as expected for a system exhibiting a weak first-order phase transition; from the divergence we are able to estimate the nematic-isotropic transition temperature and this is given in table 1. The temperature dependence of the heat capacity for the potential with $\lambda = -0.2$ exhibits a maximum but not a divergence. However, for temperatures

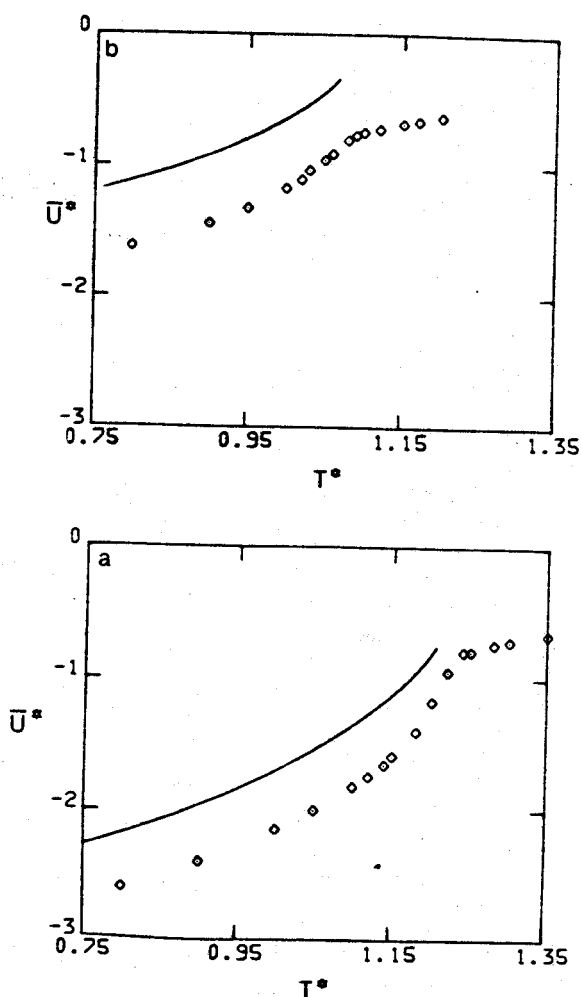


Fig. 1. The dependence of the scaled internal energy \bar{U}^* on the scaled temperature T^* simulated with λ equal to (a) 0.2 and (b) -0.2 . The solid lines show the predictions of the molecular field theory scaled to the transition temperature.

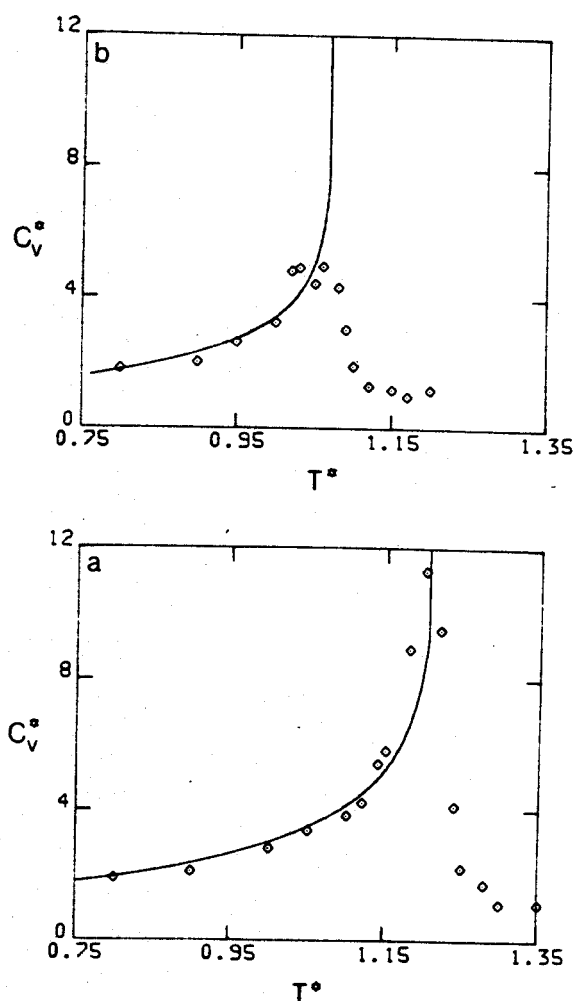


Fig. 2. The temperature dependence of the scaled heat capacity at constant volume determined for the potentials with λ equal to (a) 0.2 and (b) -0.2 . The molecular field predictions scaled to the transition temperatures are shown as the solid lines.

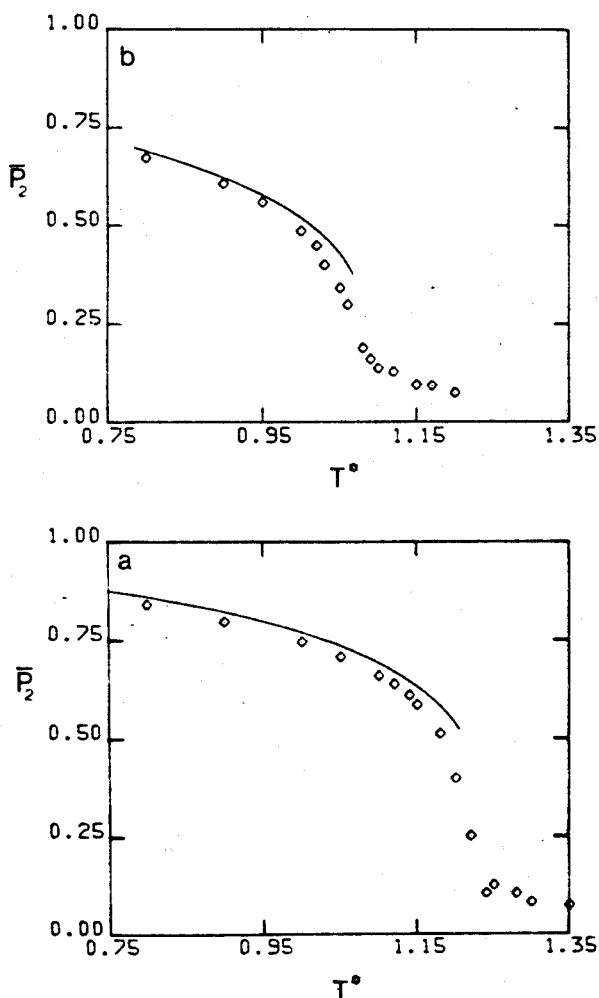


Fig. 3. The dependence of the second-rank order parameter \bar{P}_2 on the scaled temperature simulated for the pair potentials with λ equal to (a) 0.2 and (b) -0.2. The variation of \bar{P}_2 with temperature predicted by the molecular field theory scaled to the transition temperature is shown as the solid lines.

higher than that of the maximum the system is essentially orientationally disordered while for the lower temperature it is ordered. We are able therefore to obtain the temperature for this extremely weak nematic-isotropic transition from the location of the maximum, with the result given in table 1. The rounding of the phase transition exhibited by the heat capacity and indeed the other properties which we have simulated results from the finite sample size; this can also lead to a shift in the transition. In principle such effects may be

allowed for by using scaling arguments developed by Privman and Fisher [36] for first-order phase transitions. However, the finite-size scaling analysis requires simulations for samples of different size and is not straightforward. Fortunately, such an analysis does not seem to be necessary to understand our results, nor to compare them with predictions of the molecular field theory.

The scaled internal energy is essentially a continuous function of temperature, in accord with the weakness of the nematic-isotropic transition found for systems with analogous soft pair potentials [14]. However, a knowledge of the transition temperatures allows us to estimate the entropy of transition, albeit with rather large uncertainty because of the difficult extrapolation of \bar{U}^* to the transition. The results are given in table 1.

The second-rank order parameter \bar{P}_2 is also a continuous function of temperature, for both values of λ , although it does change rapidly with temperature in the vicinity of the phase transition. In addition the order parameter does not vanish completely in the isotropic phase and we attribute this behaviour to the relatively small number of particles used in the simulation [13]. However, we are able to estimate the order parameter at the transition by careful extrapolation of the results found for the nematic phase to the transition temperature. The values so obtained are given in table 1. For comparison we also give in table 1 the analogous quantities determined for the purely second-rank potential, that is with $\lambda = 0$ [13].

The anisotropic pair potentials used in the Monte Carlo simulations are compared with that for the pure second-rank interaction ($\lambda = 0$) in fig. 4. The potential with $\lambda = 0.2$ has a higher barrier to rotation than that for the potential with $\lambda = -0.2$. In addition the attractive well for the $\lambda = 0.2$ potential is steeper than that for the $\lambda = -0.2$ potential. The pure second-rank potential has characteristics which are intermediate between these two. As we have seen from the thermodynamic perturbation theory in section 2 we expect the nematic-isotropic transition to increase or decrease according to the sign of λ . The results of the simulations given in table 1 are in qualitative agreement with this prediction; in addition the shift in T_{N1}^* with respect to the reference system is

Table 1

The transitional properties determined from the Monte Carlo simulations for the pair potential in eq. (2) with $\lambda = \pm 0.2$ together with the predictions of the molecular field theory. The corresponding results are also reported for the system with $\lambda = 0$ [13]; this Monte Carlo simulation used a system of 8000 particles. The numbers in parentheses give the ratio of the observed to the predicted property

λ	T_{NI}^*		\bar{P}_2^{NI}		$\Delta S/R$	
	simulation	molecular field theory	simulation	molecular field theory	simulation	molecular field theory
-0.2	1.067 (0.82)	1.305	0.26 (0.70)	0.372	0.04 (0.12)	0.314
0	1.127 (0.85)	1.322	0.27 (0.63)	0.429	0.06 (0.15)	0.417
0.2	1.205 (0.89)	1.350	0.36 (0.70)	0.516	0.11 (0.18)	0.606

almost but not quite symmetric in λ . Thus the increase in T_{NI}^* is 0.078 for the system with positive λ while the decrease in T_{NI}^* for that with negative λ is 0.060. Such a weak asymmetry indicates that the second-order contribution to the Helmholtz free energy difference at the transition temperature for the unperturbed system is small in comparison with the first-order correction. The other transitional properties also reflect the change in the anisotropy of the pair potential as the contribution of the fourth-rank term varies. For the weaker potential both the entropy of transition and the order parameter at the transition are slightly smaller than those found for the reference system ($\lambda = 0$). However, for the more anisotropic

potential ($\lambda = 0.2$) $\Delta S/R$ and \bar{P}_2^{NI} are significantly larger than those for the reference system ($\lambda = 0$) (cf. table 1). In the following section we shall see how these differences in behaviour compare with the predictions of the molecular field theory developed by Humphries et al. [26].

5. Comparison with molecular field theory

Application of the molecular field approximation to the models which we have studied gives the potential of mean torque as

$$U(\beta) = -z\epsilon \left[\bar{P}_2 P_2(\cos \beta) + \lambda \bar{P}_4 P_4(\cos \beta) \right], \quad (23)$$

where z is the coordination number. The orientational order parameters are obtained from this potential as

$$\begin{aligned} \bar{P}_L = Z^{-1} \int P_L(\cos \beta) \exp\left\{ \left(\frac{z\epsilon}{kT} \right) \right. \\ \left. \times \left[\bar{P}_2 P_2(\cos \beta) + \bar{P}_4 P_4(\cos \beta) \right] \right\} \sin \beta d\beta, \end{aligned} \quad (24)$$

where the orientational partition function is

$$\begin{aligned} Z = \int \exp\left\{ \left(\frac{z\epsilon}{kT} \right) \left[\bar{P}_2 P_2(\cos \beta) \right. \right. \\ \left. \left. + \bar{P}_4 P_4(\cos \beta) \right] \right\} \sin \beta d\beta. \end{aligned} \quad (25)$$

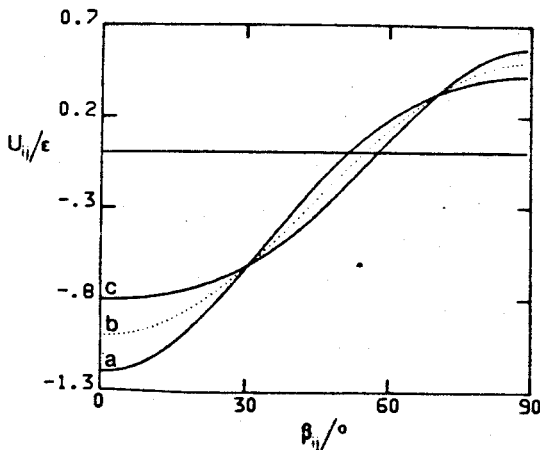


Fig. 4. The anisotropic pair potentials calculated from eq. (2) with λ equal (a) 0.2, (b) 0 and (c) -0.2.

The orientational internal energy per particle is

$$U = -z\epsilon(\bar{P}_2^2 + \lambda\bar{P}_4^2)/2 \quad (26)$$

and the Helmholtz free energy per particle is

$$A = z\epsilon(\bar{P}_2^2 + \lambda\bar{P}_4^2)/2 - kT \ln Z. \quad (27)$$

The transition temperature for a given λ is determined by evaluating the order parameters \bar{P}_2 and \bar{P}_4 from the consistency condition in eq. (24) and using these to evaluate the Helmholtz free energy. The results of such calculations are given in table 1 for $\lambda = \pm 0.2$ as well as for the reference system with $\lambda = 0$, which are the Maier-Saupe results.

The nematic-isotropic transition temperatures predicted for the three systems are found to be greater than those determined by the Monte Carlo simulations. The ratio of the observed to the predicted transition temperature ranges from 0.82 for the least anisotropic pair potential to 0.89 for the most anisotropic; indeed the success of the theory seems to improve with the anisotropy of the pair potential. The failure of the molecular field approximation to predict the transition temperatures is not excessive and may be traced, in large measure, to the inability of the theory to determine the coefficient of the term $\bar{P}_2 P_2(\cos \beta)$ in the potential of mean torque correctly, at least when $\lambda = 0$ [13]. The changes in T_{NI}^* produced by the introduction of the fourth-rank term in the pair potential are found to be much greater than those given by the molecular field theory. Thus the transition temperature is predicted to decrease by 1.2%, for $\lambda = -0.2$ and to increase by 2.1%, for $\lambda = 0.2$ whereas the observed changes are 5.5% and 6.7%, respectively.

The ability of the molecular field theory to predict the second-rank order parameter at the transition is less impressive. The ratio of the observed \bar{P}_2^{NI} to the theoretical value is 0.70 for both potentials containing a fourth-rank contribution. The ratio is 0.63 for the system with $\lambda = 0$ and here the discrepancy has been attributed to the failure of the theory to determine the nematic-isotropic transition temperature correctly [13]. The increase in \bar{P}_2^{NI} on going from the system with $\lambda = -0.2$ to 0.2 is found from the simulation to be $\approx 38\%$, in almost complete agreement with the

prediction of the molecular field theory. In contrast the increases in \bar{P}_2^{NI} on changing λ from -0.2 to 0 and from 0 to 0.2 are not in accord with theory. This discrepancy may obtain because the simulated result for $\lambda = 0$ was determined for a system of 8000 particles [13], which is large in comparison with the 1000 particles used in our simulations and so the results may not be directly comparable.

The molecular field theory is far less successful in its predictions of the entropy of transition; for example with $\lambda = 0$ the ratio of observed to predicted $\Delta S/R$ is only 0.15. Similar discrepancies are found for the pair potentials with fourth-rank contributions and, as for the system with $\lambda = 0$, we attribute these dramatic failures to the gross underestimation of the short-range angular correlations in the isotropic phase. However, the molecular field theory does predict a large increase in the entropy of transition with increasing λ , in qualitative accord with the changes in the simulated values of $\Delta S/R$.

We turn now to a comparison of the observed temperature dependences of C_p^* , \bar{U}^* and \bar{P}_2 for the two systems ($\lambda = \pm 0.2$) with those given by the molecular field theory. In making these comparisons we have changed the value of z employed in the molecular field theory in order to obtain agreement between the observed nematic-isotropic transition temperature and that predicted by the theory. In this way we are able to remove the discrepancy between the temperature dependence obtained from the simulation and that from the theory which comes from the failure of the molecular field theory to predict the transition temperature. The results of these scaled theoretical calculations are shown as the solid lines in figs. 1-3; the vertical parts of the lines in fig. 2 for the heat capacity are a consequence of the jump in the theoretical internal energy at the first-order phase transition. The other theoretical values for C_p^* were obtained by numerical differentiation of the internal energy. Within the nematic phase the agreement between the simulated and the theoretical values of the heat capacity is rather good but the theory fails completely in the isotropic phase where C_p^* is predicted to vanish but clearly does not do so. This marked discrepancy is another

manifestation of the molecular field approximation's failure to account for the short-range angular correlations which it predicts to be absent in the isotropic phase.

The internal energy calculated from the theory is in poor agreement with the results of the simulation for both systems, as we can see from fig. 1. The difference is particularly marked in the isotropic phase where the theoretical \bar{U}^* is zero. For the model used in our simulations the scaled internal energy per particle may be written in terms of the short-range order parameters

$$\bar{U}^* = -z(\sigma_2 + \lambda\sigma_4)/2. \quad (28)$$

The simulations show that the molecular field approximation underestimates this combination which is dominated by the second-rank short-range order parameter. This failure to predict the internal energy contrasts with the apparent success of the theory to give its temperature derivative, the heat capacity. Similarly the difference in the internal energy for the two systems with $\lambda = \pm 0.2$ is well predicted by the molecular field theory, presumably because of a cancellation of errors in estimating the short-range angular correlations.

The temperature dependence of the second-rank order parameter is well accounted for by the theory for both systems, especially at low temperatures (cf. fig. 3). In addition the change in \bar{P}_2 when λ increases from -0.2 to 0.2 predicted by the theory is in good agreement with that obtained from the simulations. Near to the nematic-isotropic transition the order parameter is overestimated by the theory, possibly because the molecular field expression for the Helmholtz free energy is in error and consequently the result for T_{NI} is too low [13]. The simulation experiment overestimates the long-range orientational order in the isotropic phase; this is a result of the relatively small number of particles used in the calculations [14].

6. Conclusions

The results obtained from the Monte Carlo simulation studies of particles interacting via an anisotropic potential containing both second- and

fourth-rank terms have allowed us to make a searching test of the molecular field theory for such nematogens. The theory is found to be relatively successful in predicting the change in behaviour when the sign of the fourth-rank contribution to the pair potential is reversed. The theory is less successful in predicting the nematic-isotropic transition temperature, slightly worse for the second-rank order parameter at the transition and fails completely for the entropy of transition. The temperature dependence of \bar{P}_2 and C_V^* are well predicted by the theory provided allowance is made for its overestimation of T_{NI}^* . The internal energy is consistently underestimated by the theory which results from its inability to predict the short-range angular correlations correctly. Finally we note that the results of our simulation will provide an invaluable test-bed for other approximate theories of liquid crystal formation.

Acknowledgement

We are grateful to the Science and Engineering Research Council for the award of a Studentship to Dr. G.J. Fuller, to NATO for a grant and to Mr. H. Zewdie for performing the molecular field calculations. The computer simulations were carried out on a CDC7600 at the University of Manchester Regional Computing Centre and on a VAX11/780 of the Theoretical Chemistry Group in Bologna. Dr. C. Zannoni thanks C.N.R. and M.P.I. (Rome) for grants toward the cost and maintenance of the VAX11/780.

Appendix

The results of the Monte Carlo simulations for the scaled internal energy per particle \bar{U}^* , the scaled heat capacity at constant volume per particle C_V^* and the second-rank order parameter \bar{P}_2 . Table 2 lists the results obtained for the pair potential in eq. (2) with $\lambda = 0.2$ and table 3 gives those for $\lambda = -0.2$. The error in \bar{P}_2 is estimated to be ± 0.001 while that in \bar{U}^* is between ± 0.001 and ± 0.005 .

Table 2

T	\bar{U}^*	C_T^*	\bar{P}_2
0.80	-2.594	1.9 ± 0.1	0.839
0.90	-2.399	2.1 ± 0.1	0.796
1.00	-2.158	2.8 ± 0.1	0.745
1.05	-2.006	3.3 ± 0.1	0.707
1.10	-1.826	3.8 ± 0.1	0.659
1.12	-1.748	4.2 ± 0.1	0.638
1.14	-1.659	5.4 ± 0.2	0.610
1.15	-1.592	5.8 ± 0.2	0.586
1.18	-1.403	8.9 ± 0.4	0.512
1.20	-1.176	11.3 ± 0.4	0.398
1.22	-0.948	9.5 ± 0.3	0.251
1.24	-0.793	4.1 ± 0.3	0.106
1.25	-0.791	2.2 ± 0.4	0.127
1.28	-0.738	1.7 ± 0.2	0.105
1.30	-0.714	1.1 ± 0.1	0.082
1.35	-0.662	1.1 ± 0.1	0.073

Table 3

T	\bar{U}^*	C_T^*	\bar{P}_2
0.80	-1.622	1.8 ± 0.3	0.673
0.90	-1.447	2.0 ± 0.5	0.607
0.95	-1.330	2.6 ± 0.2	0.558
1.00	-1.180	3.2 ± 0.2	0.484
1.02	-1.113	4.8 ± 0.9	0.447
1.03	-1.042	4.9 ± 0.7	0.398
1.05	-0.964	4.4 ± 0.3	0.340
1.06	-0.915	4.9 ± 0.3	0.298
1.08	-0.811	4.3 ± 0.3	0.189
1.09	-0.775	3.0 ± 0.3	0.161
1.10	-0.751	1.9 ± 0.2	0.138
1.12	-0.727	1.3 ± 0.1	0.129
1.15	-0.683	1.2 ± 0.1	0.095
1.17	-0.664	1.0 ± 0.1	0.093
1.20	-0.631	1.2 ± 0.1	0.075

References

- [1] J.P. Hansen and I.R. McDonald, *Theory of simple liquids* (Academic Press, New York, 1976).
- [2] R. Balescu, *Equilibrium and non-equilibrium statistical mechanics* (Wiley, New York, 1975).
- [3] P.G. de Gennes, *The physics of liquid crystals* (Oxford Univ. Press, London, 1974); S. Chandrasekhar, *Liquid crystals* (Cambridge Univ. Press, London, 1977).
- [4] P.A. Lebowitz and G. Lasher, *Phys. Rev. A* 6 (1972) 426.
- [5] H.J.F. Jansen, G. Vertogen and J.G.J. Ypma, *Mol. Cryst. Liquid Cryst.* 38 (1977) 87.
- [6] H. Meirovitch, *Chem. Phys.* 21 (1976) 251.
- [7] C. Zannoni, in: *The molecular physics of liquid crystals*, eds. G.R. Luckhurst and G.W. Gray (Academic Press, New York, 1979) ch. 9.
- [8] C. Zannoni, in: *The molecular physics of liquid crystals*, eds. G.R. Luckhurst and G.W. Gray (Academic Press, New York, 1979) ch. 3.
- [9] G.R. Luckhurst and S. Romano, *Mol. Phys.* 40 (1980) 129.
- [10] C. Zannoni and M. Guerra, *Mol. Phys.* 44 (1981) 849.
- [11] R.L. Humphries, G.R. Luckhurst and S. Romano, *Mol. Phys.* 42 (1981) 1205.
- [12] R.L. Humphries and G.R. Luckhurst, *Proc. Roy. Soc. A* 382 (1982) 307.
- [13] G.R. Luckhurst and P. Simpson, *Mol. Phys.* 47 (1982) 251.
- [14] G.R. Luckhurst, S. Romano and P. Simpson, *Chem. Phys.* 73 (1982) 337.
- [15] J. Viellard-Barron, *Mol. Phys.* 28 (1974) 809.
- [16] A.L. Tsykalo and A.D. Bagmet, *Mol. Cryst. Liquid Cryst.* 46 (1978) 111.
- [17] G.R. Luckhurst and S. Romano, *Proc. Roy. Soc. A* 373 (1980) 111.
- [18] D. Frenkel and R. Eppenga, *Phys. Rev. Letters* 49 (1982) 1089.
- [19] M. Maier and A. Saupe, *Z. Naturforsch.* 13a (1958) 564; 14a (1959) 882; 15a (1960) 287.
- [20] P. Sheng and P.J. Wojtowicz, *Phys. Rev. A* 14 (1976) 1883.
- [21] N.V. Madhusudana, K.L. Savithramma and S. Chandrasekhar, *Pramana* 8 (1977) 22.
- [22] R. van der Haegen, J. Debruyne, R. Luyckx and H.N.W. Lekkerkerker, *J. Chem. Phys.* 73 (1980) 2469.
- [23] T.E. Faber, *Proc. Roy. Soc. A* 370 (1980) 509.
- [24] K. Binder, in: *Phase transitions and critical phenomena*, Vol. 5B, eds. C. Domb and M.S. Green (Academic Press, New York, 1976).
- [25] G.R. Luckhurst, in: *The molecular physics of liquid crystals*, eds. G.R. Luckhurst and G.W. Gray (Academic Press, New York, 1979) ch. 4.
- [26] R.L. Humphries, P.G. James and G.R. Luckhurst, *J. Chem. Soc. Faraday Trans. II* 68 (1972) 1031.
- [27] G.R. Luckhurst, C. Zannoni, P.L. Nordio and U. Segre, *Mol. Phys.* 30 (1975) 1345.
- [28] C. Zannoni, *Mol. Cryst. Liquid Cryst. Letters* 49 (1979) 247.
- [29] L.D. Landau and E.M. Lifshitz, *Statistical physics* (Pergamon Press, New York, 1970).
- [30] J.A. Barker and D. Henderson, *Rev. Mod. Phys.* 48 (1976) 587.
- [31] G. Stell and O. Penrose, *Phys. Rev. Letters* 51 (1983) 1397.
- [32] A.J. Stone, in: *The molecular physics of liquid crystals*, eds. G.R. Luckhurst and G.W. Gray (Academic Press, New York, 1979) ch. 2.
- [33] R. Hashim, G.R. Luckhurst and S. Romano, to be published.
- [34] W. Helfrich, *Phys. Rev. Letters* 24 (1969) 201; F. Jähnig, *Biophys. Chem.* 4 (1976) 309; H. Trauble, M. Teubner, P. Wolley and H. Eibl, *Biophys. Chem.* 4 (1976) 319.
- [35] N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.H. Teller and E. Teller, *J. Chem. Phys.* 21 (1953) 1087.
- [36] V. Privman and M.E. Fisher, *J. Stat. Phys.* 33 (1983) 385.