CAN UNIAXIAL MODELS PRODUCE BIAXIAL ORDER?

S. Romano,
Istituto Nazionale per la Fisica della Materia e
Dipartimento di Fisica ”A. Volta”, Università di Pavia,
via A. Bassi 6,
I-27100 Pavia (ITALY)
`telephone` +39 − 0382 − 987487
`fax` +39 − 0382 − 987563
e-mail: `Silvano.Romano@pv.infn.it`

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Abstract

We have recently studied various mesogenic lattice models, involving classical uniaxial particles, possessing $D_{\infty h}$ symmetry, whose centres of mass are associated with a two-dimensional (square) lattice; interactions are restricted to nearest neighbours and involve both mutual orientations between the two particles and their orientations with respect to the intermolecular vectors; in $2-d$, the anisotropic character of these potential models does not preclude the existence of orientational order at finite temperature.

The models were studied by means of Mean Field (MF) theory and Monte Carlo simulations; in some cases, they were found to produce a low-temperature phase possessing biaxial order. MF predictions and simulation results appear to agree qualitatively, but in quantitative terms the MF prediction for the biaxial to uniaxial transition temperature is some 50% too high.

In some other cases, both MF and simulation results show homeotropic anchoring, and a weaker uniaxial orientational order, now surviving up to temperatures higher than the transition temperature of the $3-$dimensional counterpart, possibly at all finite temperatures.

Keywords: liquid crystals,nematics, lattice models, anchoring, monolayers.

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In addition the bulk properties of Liquid Crystals, their surfaces and interfaces, and their behaviour in restricted geometries (e.g. polymer-dispersed drops, thin layers, mesogens in porous media) are of great interest in fundamental as well as applicative terms, and have been extensively studied, both experimentally and theoretically; in comparison with the bulk, profound modifications may result from the restricted environment; for example, experiments on nematic thin layers show that, depending on mesogen and substrate, the Nematic to Isotropic transiton may survive, or disappear, or change to continuous, and its transition temperature may both decrease or (more seldom) increase.

In some theoretical studies one considers the extreme case where particles' centres of mass are associated with a $2-$dimensional space; the effect of dimensionality can be gauged by comparisons with potential models defined by the same interaction law, but where particles' centers of mass belong to a $3-$dimensional space (the $3-d$ counterparts, or $3-d$ versions, for short). A number of such models have been discussed in the Literature both in the case where particles' centres of mass are associated with a lattice, and in the continuum one where they sweep the plane R^2; existence or absence of an ordering transition taking place at finite temperature have been proven rigorously in some simple cases.

We are considering here $n-$component unit vectors (usually $n = 3$), associated with the nodes of a $d-$dimensional lattice Z^d ($d = 2, 3$); let $\mathbf{x}_k$ denote the coordinate vectors of lattice sites, let $\mathbf{u}_k$ denote the unit vectors, and let $u_{k,\alpha}$ denote their Cartesian components with respect to an orthonormal basis $E = \{\mathbf{e}_\alpha,\ \alpha = 1, 2, 3\}$, (partly) defined by lattice axes. To fix the notation, when $d = 2$, $\mathbf{e}_3$ (the $z-$axis) shall be taken to be orthogonal to the lattice plane, and $\mathbf{e}_1,\ \mathbf{e}_2$ shall be referred to as lattice axes; the unit vectors $\mathbf{u}_k$ can also be parameterized by usual polar angles $\{\theta_k,\ \phi_k\}$; all interactions are restricted to nearest neighbours.

According to the quantum theory of intermolecular forces the dipolar contribution to the dispersion energy between two identical, neutral and centrosymmetric linear molecules has the general form

$$D_{jk} = \frac{1}{r^6}[g_0 + g_1(a_j^2 + a_k^2) + g_2 a_j a_k b_{jk} + g_3 b_{jk}^2 + g_4(a_j a_k)^2], \tag{1}$$

$$\mathbf{r} = \mathbf{x}_j - \mathbf{x}_k,\ r = |\mathbf{r}|,\ \mathbf{s} = \mathbf{r}/r,\ a_j = \mathbf{u}_j \cdot \mathbf{s},\ a_k = \mathbf{u}_k \cdot \mathbf{s},\ b_{jk} = \mathbf{u}_j \cdot \mathbf{u}_k. \tag{2}$$

Under additional simplifications, Eq. (1) leads to the expression proposed by London, Heller and de Boer (LHB) in the $1930's$, i.e.

$$\tilde{D}_{jk} = \frac{\epsilon}{r^6}[(\gamma^2 - \gamma)S_{jk} - \frac{3}{2}\gamma^2 h_{jk} + \gamma^2 - 1],\ \epsilon = \frac{3}{4}\overline{E}\overline{\alpha}^2, \tag{3}$$

where

$$h_{jk} = (3a_j a_k - b_{jk})^2,\ S_{jk} = P_2(a_j) + P_2(a_k),\ \overline{\alpha} = \frac{1}{3}(\alpha_\parallel + 2\alpha_\perp),\ \gamma = \frac{\alpha_\parallel - \alpha_\perp}{3\overline{\alpha}}. \tag{4}$$

Here $\alpha_\parallel, \alpha_\perp$ are the eigenvalues of the molecular polarizability tensor, γ denotes its relative anisotropy, and $\overline{E}$ is a mean excitation energy; the extreme case $\gamma = -(1/2)$ corresponds to no polarizability along the molecular symmetry axis, whereas in the other extreme $\gamma = +1$ there is polarizability along the molecular axis only. In the following, let Δ_{jk} denote the restriction of $\tilde{D}_{jk}$ to nearest neighbours, i.e.

$$\Delta_{jk} = \epsilon[(\gamma^2 - \gamma) S_{jk} + \gamma^2(-\frac{3}{2} h_{jk} + 1)], \tag{5}$$

where the purely positional term appearing in Eq. (3) has been dropped.

Lattice models based on Eq. (3) have been investigated by simulation in $3-d$; the nearest-neighbour model Δ_{jk} produces a nematic-like ordering transition; in contrast, inclusion of next-nearest neighbours produces a ground state structure with sub-lattice order but no net orientational order.

Another related mesogenic potential model was proposed by Nehring and Saupe (NS) over 25 years ago, and has the form

$$\Phi_{jk} = -\frac{\epsilon}{r^6} h_{jk}; \tag{6}$$

it has often been used for approximate calculations of elastic properties its restriction to nearest neighbours, defined by

$$\Psi_{jk} = \epsilon(-\frac{3}{2} h_{jk} + 1), \tag{7}$$

has later been studied by simulation in $3-d$. Comparison between the relevant equations (Eq. (3) and (7)), shows that NS corresponds to the limiting case $\gamma = +1$ in the LHB model. Moreover, on a saturated cubic lattice and under periodic boundary conditions, the two models Δ_{jk} and Ψ_{jk} become equivalent (see below).

For the present model the configuration where the two molecules are parallel to each other and to the intermolecular vector (i.e. $a_j = a_k = b_{jk} = \pm 1$) has an energy $-\epsilon(2\gamma + 3\gamma^2)$; in contrast, when both molecules are parallel to each other and perpendicular to the intermolecular vector, the energy is $\epsilon[\gamma - (3/2)\gamma^2]$; both configurations correspond to minima in the dispersion potential.

For a periodically repeated sample on a lattice Z^d, each particle interacts with $(2d)$ nearest neighbours, and the possible orientations of the intermolecular vector $\mathbf{s}$ are $\pm\mathbf{e}_\alpha,\ \alpha = 1, \ldots d$; moreover, for any unit vector $\mathbf{u}_k$ and for any lattice site $\mathbf{x}_k$,

$$\mathbf{u}_k \cdot \mathbf{u}_k = \sum_{\alpha=1}^{3} (\mathbf{e}_\alpha \cdot \mathbf{u}_k)^2; \tag{8}$$

when $d = 3$, this identity entails that, upon summing over all interacting pairs, the terms in the pair potential containing S_{jk} cancel out [1,2]; thus $\Delta_{jk} = \gamma^2 \Psi_{jk}$, and any (non-zero) value of γ can be scaled away. On the other hand, when $d = 2$,

$$\sum_{\alpha=1}^{2} P_2(\mathbf{u}_k \cdot \mathbf{e}_\alpha) = -P_2(\mathbf{u}_k \cdot \mathbf{e}_3); \tag{9}$$

upon summing over all interacting pairs, the named terms in the pair potential now result in a single-site quantity, tending to orient particles along $\mathbf{e}_3$ (homeotropic anchoring) when $\gamma < 0$, or to keep them in the lattice plane for $\gamma > 0$ (planar anchoring).

For $d = 3$ the ground-state configuration of the dispersion model Δ_{jk} corresponds to all particles pointing along a lattice axis, with an energy $W_0^* = -6\gamma^2$ per site, where the asterisk means scaling by ϵ. On the other hand, in $2-d$ the sign of γ plays a major role, i.e. one finds

$$\begin{cases} W_0^* = +2\gamma - 3\gamma^2, & \gamma < 0, \quad \mathbf{u}_j \parallel \mathbf{e}_3, \ \forall j \\ W_0^* = -[\gamma + (9/2)\gamma^2], & \gamma > 0, \quad \mathbf{u}_j \parallel \mathbf{e}_1, \ \mathit{or}\ \mathbf{u}_j \parallel \mathbf{e}_2, \ , \ \forall j \end{cases}; \tag{10}$$

in the cases considerered here, $W_0^*(\gamma = +1) = -11/2$, $W_0^*(\gamma = +1/2) = -1.625$; $W_0^*(\gamma = -1/2) = -1.75$.

An important chapter of Liquid Crystal continuum theory involves the calculation of director patterns by minimizing the total elastic free energy for assigned values of the elastic constants and under specific boundary conditions; a few analytical solutions are known although, in general, numerical methods have been implemented, usually involving appropriate discretization schemes. In some cases, these configurations have been obtained by numerical procedures where the elastic free energy density plays the same role as the overall potential energy in a standard Metropolis Monte Carlo simulation. The interaction energies or potentials used in these studies are short-ranged but, in general, not pairwise additive, unless the three elastic constants are set to a common value, thus reducing the potential model to the well-known Lebwohl-Lasher model (LL). In this context, a few years ago, it has been noticed that one can construct, in different ways, a lattice model with pairwise additive interactions, approximately reproducing the elastic free-energy density, where the parameters defining the pair potential are expressed in terms of of elastic constants; for example, a potential model of this kind, originally proposed by Gruhn and Hess, has been investigated by Monte Carlo simulation, using a simple-cubic lattice and periodic boundary conditions; more recently, the named potential model has been used for studying the Fréedericksz transition and the Schadt-Helfrich cell by simulation. The potential parameters are given by linear combinations of elastic constants (see also below): strictly speaking the pair potential does not depend on temperature (nor on density), whereas the elastic constants do, and the additional arbitrariness in the choice is another aspect of the approximate nature of the correspondence. Another approximate correspondence was defined and investigated by simulation in $3-d$. we also present here the Mean Field (MF) and Monte Carlo (MC) simulation study of a $2-d$ lattice system based on the latter "elastic models", with the same parameterization as used for their $3-d$ counterparts.

We recall definitions of the two "elastic models"; model M1 [3,4] has the form

$$\Phi = \Phi_{jk} = \lambda S_{jk} + \mu(a_j a_k b_{jk} - \frac{1}{9}) + \nu P_2(b_{jk}) + \rho S_{jk} P_2(b_{jk}). \tag{11}$$

By the argument outlined in the original paper, the four strength parameters $\lambda,\ \mu,\ \nu,\ \rho$ are defined by the following combinations of elastic constants, including a factor Λ, with dimension of a length, for dimensional consistency:

$$\begin{cases} \lambda &= \frac{1}{3}\Lambda(2K_1 - 3K_2 + K_3) \\ \mu &= +3\Lambda(K_2 - K_1) \\ \nu &= \frac{1}{3}\Lambda(K_1 - 3K_2 - K_3) \\ \rho &= \frac{1}{3}\Lambda(K_1 - K_3). \end{cases} . \tag{12}$$

The model involves three elastic constants and four linearly dependent potential parameters, connected by the condition

$$\mu + 3(\lambda + \rho) = 0. \tag{13}$$

Another possible correspondence had been studied, leading to the form M2:

$$\begin{cases} \lambda &= +\frac{2}{3}\Lambda(K_1 - K_2) \\ \nu &= -\frac{2}{3}\Lambda K_2 \\ \mu &= \Lambda(-K_1 + 2K_2 - K_3) \\ \rho &= 0 \end{cases} , \tag{14}$$

now involving only three linearly independent parameters; thus

$$\Psi = \Psi_{jk} = \lambda S_{jk} + \mu(a_j a_k b_{jk} - \frac{1}{9}) + \nu P_2(b_{jk}). \tag{15}$$

In Refs. [4,5], the chosen parameters were taken from the elastic constants of the comparatively simple and extensively studied nematogen 4,4'-dimethoxyazoxybenzene (para-azoxyanisole, PAA) at 120 ^0C, which corresponds to a reduced temperature, T/T_{NI}, of 0.963, as reported in the book by de Gennes and Prost, i.e.

$$K_1 = 7 \times 10^{-12}\ N,\ K_2 = 4.3 \times 10^{-12}\ N,\ K_3 = 17 \times 10^{-12}\ N. \tag{16}$$

The calculated coefficients $\lambda,\ \mu,\ \nu,\ \rho$ were rescaled by dividing by $|\nu|$; thus potential model $M1$ becomes

$$\Phi = \epsilon \left[\lambda S_{jk} + \mu(a_j a_k b_{jk} - \frac{1}{9}) + \nu P_2(b_{jk}) + \rho S_{jk} P_2(b_{jk}) \right], \tag{17}$$

$$\lambda = 0.79039,\ \mu = -1.0611,\ \nu = -1,\ \rho = -0.43668. \tag{18}$$

A similar treatment had been applied to Eq. (15), so that the resulting pair potential $M2$ had the form

$$\Psi = \epsilon \left[\lambda S_{jk} + \mu(a_j a_k b_{jk} - \frac{1}{9}) + \nu P_2(b_{jk}) \right], \tag{19}$$

$$\lambda = 0.62791,\ \mu = -5.3721,\ \nu = -1. \tag{20}$$

Notice that in both cases $\lambda > 0$, so that the effective single-site term tends to favour homeotropic anchoring. Moreover, let $\mathbf{v}$ denote an arbitrary unit vector; the configuration $\mathbf{u}_k = \pm\mathbf{v}$, $\forall k$, defines the ground-state for the Gruhn-Hess model (Eqs. (11) and (12)), whose energy is $-(2/3)\Lambda(K_1 + K_2 + K_3)$ (or $-2.4716\ \epsilon$/particle with the present parameterization, Eq. (18)); the value is independent of the orientation of $\mathbf{v}$ with respect to lattice axes, and, as noted in Refs. [6], this degeneracy reflects the condition in Eq. (13). On the other hand, at low but finite temperature, one may expect thermal fluctuations to select some range of orientations (ordering from disorder, [7,8]); in the present case, this means $\mathbf{v} = \mathbf{e}_3$ (homeotropic anchoring); the result was obtained by means of an approximate harmonic (spin-wave) treatment, and is confirmed by simulation.

Let now $\mathbf{v}$ denote an arbitrary unit vector belonging to the lattice plane, i.e.

$$\mathbf{v} = \cos\chi \mathbf{e}_1 + \sin\chi \mathbf{e}_2 \tag{21}$$

the configuration $\mathbf{u}_k = \pm\mathbf{v}$, $\forall k$, defines the ground-state for the present model $M2$ (planar anchoring), whose potential energy per particle is $-(1/9)\Lambda(K_1 + 4K_2 + 7K_3)$, or $U_0^* = -5.5504$ with the present parameterization (Eq. (18)); the value is independent of χ, i.e. of the orientation of $\mathbf{v}$ with respect to two lattice axes. Here also, at low but finite temperature, one may expect thermal fluctuations to select some range of orientations; in the present case, this means $\chi = 0, \ \mathbf{v} = \mathbf{e}_1$; the result was obtained by means of an approximate harmonic (spin-wave) treatment carried out along the lines of Ref. [8], and is essentially confirmed by simulation. Notice also that, in this case, the μ term is stronger than and prevails against the λ term.

In $3-d$ there are recognizable but not dramatic quantitative differences between LL, NS, and the elastic models; in contrast, in $2-d$, the anisotropic interaction models may allow the existence of orientational order at finite temperature, and produce different anchorings.

TABLES

TABLE I. Transitional properties for different simulated models in 3−d; for LL the ratio Θ_{MC}/Θ_{MF} is 0.850.

Potential model	Θ_{MC}	ΔU^{*}_{NI}	$\Delta S_{NI}/R$	$\overline{P}_2^{NI}$	$\overline{P}_4^{NI}$	Θ_{MC}/Θ_{MF}
$M1$	1.368 ± 0.002	0.066 ± 0.005	0.048 ± 0.004	0.26 ± 0.01	0.045 ± 0.002	0.837
$M2$	2.380 ± 0.002	0.079 ± 0.006	0.033 ± 0.003	0.25 ± 0.01	0.041 ± 0.002	0.821
NS	2.238 ± 0.001	0.29 ± 0.02	0.13 ± 0.02	0.30 ± 0.01	0.09 ± 0.002	0.847

A MF treatment can be worked out and leads to the following expressions for the free energy and its gradients

$$A^*_{MF} = (g_0 X^2 + g_2 Y^2) - T^* \log \Xi, \tag{22}$$

$$\frac{\partial A^*_{MF}}{\partial X} = 2g_0 X - g_6 \frac{\int \mathcal{F}_0 d\omega}{\Xi},\ \ \frac{\partial A^*_{MF}}{\partial Y} = 2g_2 Y - g_8 \frac{\int \mathcal{F}_2 d\omega}{\Xi}, \tag{23}$$

where

$$\Xi = \int \exp[+\beta\Omega] d\omega,\ \ \Omega = (g_4 + g_6 X)\mathcal{F}_0 + g_8 \mathcal{F}_2,\ \ \beta = 1/T^*, \tag{24}$$

$$\mathcal{F}_0 = C_{2,0}(\theta,\phi) = P_2(\cos\theta),\ \ \mathcal{F}_2 = Re[C_{2,2}(\theta,\phi)] = (1/4)\sqrt{6}\sin^2\theta\cos(2\phi) \tag{25}$$

$$\int \ldots d\omega = (1/4\pi)\int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} \ldots d\phi, \tag{26}$$

and

$$g_0 = +3\gamma^2,\ \ g_2 = +10\gamma^2,\ \ g_4 = -2\gamma,\ \ g_6 = +6\gamma^2,\ \ g_8 = +20\gamma^2. \tag{27}$$

Here $C_{2,m}(\theta,\phi)$ denote modified spherical harmonics; X and Y are the two variational parameters, to be determined at each temperature by minimizing A^*_{MF}; the consistency equations are obtained by setting its gradients to zero. In contrast to other more common cases, uniaxial symmetry of the resulting ordered phase has *not* been assumed here, i.e. the present general treatment deals with a uniaxial $D_{\infty h}$ particle in a possibly biaxial phase; notice also that only the g_4 term actually depends on the sign of γ.

For each temperature over a fine grid, the free energy was minimized by numerical routines using both the function and its gradients; the resulting variational parameters were then used to calculate the energy

$$U^*_{MF} = \frac{\partial(\beta A^*_{MF})}{\partial\beta} = -(g_0 X^2 + g_2 Y^2) - 2g_0 \frac{g_4}{g_6} X, \tag{28}$$

where the consistency equations were allowed for in the right-hand expression; the specific heat was calculated from U^*_{MF} by numerical differentiation. Based on the variational parameters, we also calculated the quantities

$$\overline{\eta}_\alpha = \langle P_2(\mathbf{u} \cdot \mathbf{e}_\alpha) \rangle; \tag{29}$$

by the underlying symmetry, the second-rank ordering tensor is diagonal in the $E-$frame, and the above quantities $\overline{\eta}_\alpha$ are its eigenvalues; these quantities were suitably recombined to give second-rank order parameters (see below).

A major difference between the two models emerged in the MF treatment, as could partly be anticipated from the ground states, i.e. when $\gamma = -1/2$, we found $X > 0,\ Y = 0$ at all temperatures, hence cylindrical symmetry around $\mathbf{e}_3$; on the other hand, when $\gamma = +1/2$, we found a low-temperature region where $Y > 0$, i.e. biaxial behaviour.

$M1$ and $DM(\gamma = -1/2)$

Simulation results obtained for different observables showed practically no sample-size dependence, so that only results obtained with the largest sample-size $q = 120$ were plotted in most Figures; moreover the various quantities exhibit a smooth temperature dependence, and show a rather good agreement between MF and simulation.

Simulation results for configurational heat capacity are plotted in Figs. (1). Simulation results and MF predictions for $\overline{P}_2$, $\overline{P}_4$ are plotted in Fig. (2); another comparison of predictions for the structural properties can be obtained by plotting $\overline{P}_4$ versus $\overline{P}_2$, thus eliminating the explicit temperature dependences of the order parameters, as we have done in Fig. (3), showing an even better agreement between MF and MC.

The $SODF$, calculated at $T^* = 0.875$ for $q = 100$, is plotted in Fig. (4), and shows the expected maximum when $\cos\theta$ is unity. To check the quantitative aspects of this, the first four order parameters were calculated by convoluting the appropriate Legendre polynomials with this distribution function, and found to be

$\overline{P}_2 = 0.383 \ \pm 0.002$,

$\overline{P}_4 = 0.096 \ \pm 0.001$,

$\overline{P}_6 = 0.018 \ \pm 0.0001$.

$\overline{P}_8 = 0.0025 \pm 0.0001$.

These results for $\overline{P}_2$ to $\overline{P}_8$ were used to construct a truncated expansion of the singlet orientational distribution function, including terms up to $\overline{P}_8$. An alternative route to $f(\theta)$ is via the maximum entropy approach i.e. via the quantities

$$f_{ME,2}(\theta) \propto \exp[c_2' P_2(\cos\theta)], \tag{30}$$

$$f_{ME,4}(\theta) \propto \exp[c_2'' P_2(\cos\theta) + c_4'' P_4(\cos\theta)]; \tag{31}$$

Here the c parameters were determined by appropriate consistency constraints. We found

$c_2' = 1.724$

$c_2'' = 1.721,\ c_4'' = +0.0053,\ c_4''/c_2'' = +0.003.$

Results of this fitting process are reported in Fig. (4), where $\log f(\theta)$ is plotted versus $\cos^2\theta$: simulation data, maximum-entropy estimates, and polynomial approximant, all come to coincide to the resolution of the figure. The $SODF$ of the $3-d$ (NS) counterpart was calculated at $T^* = 2.225$ [1], where we found $\overline{P}_2 = 0.423\ \pm 0.003$, $\overline{P}_4 = 0.136\ \pm 0.001$, and a maximum-entropy analysis gave the result $c_4''/c_2'' = +0.086$.

To summarize, in this case the potential model produces homeotropic anchoring, and its behaviour is similar to the elastic potential model M1; the agreement between MF and simulation is better here than there, possibly because of the role of thermal fluctuations, producing "order from disorder" in that case.

A weak surface ordering surviving above the bulk Nematic-Isotropic transition temperature has been observed experimentally for monolayers of $5CB$ (pentylcyanobiphenyl) in a suitable porous matrix [13].

$\underline{M2,\ DM(\gamma = +1/2),\ DM(\gamma = +1)}$

MF predicts the potential energy to evolve continuosly with temperature, with a discontinuous change of slope (a jump in C_V) taking place at $\Theta_{MF} = 0.710$; moreover, for $T^* \geq \Theta_{MF}$ the minimization procedure returns $Y = 0$, $\overline{\eta}_1 = \overline{\eta}_2$, $\overline{\zeta}_3 = \overline{\eta}_3 < 0$, i.e. uniaxial orientational order with negative order parameter and director orthogonal to the lattice plane; for $T^* \leq \Theta_{chs} = 0.699$ MF yielded $\overline{\zeta}_3 = \overline{\eta}_1 > 0$, $R_{22} > 0$, i.e. biaxial order with director along $\mathbf{e}_1$ and positive order parameter; between Θ_{chs} and Θ_{MF} the three $\overline{\eta}_\alpha$ were all different, and $\overline{\zeta}_3 = \overline{\eta}_3 < 0$; MF predicts a discontinuous change of order parameters across Θ_{chs} (although with a rather weak discontinuity for $\overline{P}_4$), but a continuous one across Θ_{MF}.

Results for configurational heat capacity are plotted in Fig. (5); they show a rather weak sample-size dependence, and a maximum, possibly a cusp, at $T^* \approx 0.47$.

Simulation results and MF predictions for second- and fourth-rank ordering quantities are compared in Figs. (6), (7), and Fig. (8), where sample-size effects are examined.

These Figures show a low-temperature régime ($T^* \lesssim 0.46$) where simulation results are insensitive to sample size, $\overline{\zeta}_3 = \overline{\eta}_1 > \overline{\eta}_2$, $\overline{R}_{22} > 0$, i.e. system is biaxial with a positive order parameter, and the main director is aligned along a lattice axis.

At higher temperatures, η_1 and η_2 start switching roles, ζ_3 and its macrostep averages fluctuate between positive and negative values; these fluctuations rather quickly reduce $\overline{R}_{22}$ to zero, whereas $\overline{\zeta}_3 \neq \overline{\eta}_3$, and the change of $\overline{P}_2$ from positive to negative values takes place more slowly; on the other hand, $\overline{\eta}_3$ appears to evolve with temperature in a continuous and monotonic fashion. At even higher temperatures ($T^* \gtrsim 0.49$ for $q = 120$), $\overline{\zeta}_3 = \overline{\eta}_3$, $\overline{\eta}_1 = \overline{\eta}_2$, i.e. the system becomes uniaxial with negative order parameter and director orthogonal to the lattice plane. Notice that $\overline{P}_2$ first decreases with increasing temperature, reaches a negative minimum, and then slowly increases (decreasing in magnitude). Fig. (8) shows that the transition region where $\overline{P}_2$ changes from $\overline{\eta}_1$ to $\overline{\eta}_3$ recognizably shrinks upon increasing sample size; a weaker sample-size dependence of simulation results in the transition region (not reported here) has been observed for $\overline{P}_4$.

Simulation evidence suggests a second-order transition, taking place between two differently ordered phases, both exhibiting planar anchoring; the transition temperature is estimated to be $\Theta_{MC} = 0.471 \pm 0.002$, based on the behaviour of the specific heat; its uncertainty is conservatively taken to be twice the temperature step used in the simulation.

MF predictions and simulation results appear to agree qualitatively, but in quantitative terms, MF overestimates the transition temperature by some 50%.

The presence of different anchorings of the ordered phase, depending on the sign of γ, has also been noted in Ref. [2] (Figs. (4c) and (5c)).

Let us conclude by summarizing similarities and differences between various recently investigated nematogenic lattice models [9–12] associated with a $2-d$ lattice and with nearest-neighbour interactions. On the one hand, both the DM defined by $\gamma = -1/2$ and the "elastic " model $M1$ exhibit a rather similar behaviour, producing homeotropic anchoring, with no evidence of a phase transition, and uniaxial order probably surviving at all finite temperatures; moreover, MF predictions agree rather well with simulation results. On the other hand, $M2$ exhibits a recognizable similarity with the DM's defined by $\gamma = 1/2$ and $\gamma = 1$ (NS); here MF agrees qualitatively with simulation, but, un quantitative terms, it significantly overestimates the transition temperature, roughly by the same amount (50%) in the three cases.

The mild quantitative differences one observes in $3-d$ between $M1$, $M2$, NS and LL become far more pronounced qualitative ones in $2-d$, now involving existence or absence of an ordered phase, as well as types of anchoring.

TABLE II. Biaxial to uniaxial transition temperatures for for different simulated models in 2−d.

Potential model	Θ_{chs}	Θ_{MF}	Θ_{MC}
$DM(\gamma = +1/2)$	0.699	0.710	0.471 ± 0.002
$DM(\gamma = +1)$	2.573	2.592	1.780 ± 0.004
$M2$	2.6553	2.6618	1.71 ± 0.01

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FIGURES

FIG. 1. $\gamma = -1/2$, configurational specific heat: MF prediction (continuous curve), and simulation results obtained with different sample sizes: circles: $q = 40$; squares: $q = 60$; triangles $q = 80$; diamonds: $q = 100$; crosses: $q = 120$; the associated statistical errors, not shown here, range between 1 and 5 %.

FIG. 2. $\gamma = -1/2$, results for long-range order parameters. Discrete symbols are are used for simulation results, obtained with $q = 120$: $\overline{P}_2$ (circles); $\overline{P}_4$ (squares). Continuous line: MF prediction for $\overline{P}_2$; dashed line: MF prediction for $\overline{P}_4$.

FIG. 3. $\gamma = -1/2$, plot of $\overline{P}_4$ versus $\overline{P}_2$: simulation results (circles, $q = 120$), and MF prediction (continuous curve); simulation results were taken between $T^* = 0.4$ and $T^* = 1.2$; vertical dotted lines mark on the MF curve the points corresponding to the following temperatures, right to left: 0.4, 0.45, 1.2, 1.3.

FIG. 4. $\gamma = -1/2$, simulation results for the $SODF$ at $T^* = 0.875$; relative statistical errors on $f(\theta)$ range up to 0.2%; second-order and fourth-order maximum-entropy estimates of the $SODF$, as well as its eighth-order polynomial approximant (see text) are indistinguishable from simulation results to the resolution of the figure.

FIG. 5. $\gamma = +1/2$, configurational specific heat: MF prediction (continuous curve), and simulation results obtained with different sample sizes: circles: $q = 40$; squares: $q = 60$; triangles $q = 80$; diamonds: $q = 100$; crosses: $q = 120$; the associated statistical errors, not shown here, range between 1 and 5 %.

FIG. 6. $\gamma = +1/2$, eigenvalues of the second-rank ordering tensor. Discrete symbols are are used for simulation results, obtained with sample size $q = 120$: circles: $\overline{\eta}_1$; squares: $\overline{\eta}_2$; triangles: $\overline{\eta}_3$. Other curves are the corresponding MF predictions: continuous line: $\overline{\eta}_1$; dashed line: $\overline{\eta}_2$, dotted line: $\overline{\eta}_3$. The vertical dashed-dotted line marks the temperature $\Theta_{chs} = 0.699$ where MF predicts the eigenvalue with the largest magnitude to change from positive to negative sign; see also the text.

FIG. 7. $\gamma = +1/2$, second and fourth-rank order parameters. Discrete symbols are are used for simulation results, obtained with sample size $q = 120$: circles: $\overline{P}_2$; squares: $\overline{R}_{22}$; triangles: $\overline{P}_4$. The other curves are the corresponding MF predictions: continuous line: $\overline{P}_2$; dashed line: $\overline{R}_{22}$; dotted line: $\overline{P}_4$; the vertical dashed-dotted line has the same meaning as in the previous Figure.

FIG. 8. $\gamma = +1/2$, results for second-rank order parameters in the transition region. Discrete symbols are are used for simulation results, obtained with different sample sizes: crosses: $\overline{P}_2$ for $q = 40$; stars: $\overline{R}_{22}$ for $q = 40$; circles: $\overline{P}_2$ for $q = 80$; squares: $\overline{R}_{22}$ for $q = 80$; triangles: $\overline{P}_2$ for $q = 120$; diamonds: $\overline{R}_{22}$ for $q = 120$. The other curves are the corresponding MF predictions: continuous line: $\overline{P}_2$; dashed line: $\overline{R}_{22}$.