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Dipolar and dispersion interactions in nematogens
A computer simulation study

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A classical system, consisting of identical cylindrically symmetric particles, with centres fixed on a simple-cubic lattice, may or may not support nematic-like orientational order depending on the interaction potential. For example, a Lebwohl–Lasher potential model produces orientational order, as does an anisotropic London–de Boer dispersion potential restricted to nearest neighbours, although increasing its range destroys the orientational order and brings about a staggered configuration of the system. In consequence, a Maier–Saupe molecular field treatment is appropriate in the first two cases, but not in the last. On the other hand, according to computer simulation results, a purely dipolar interaction produces a low temperature antiferroelectric phase which can be regarded as an extreme case of a nematogen. We carried out Monte Carlo simulations on a potential model defined by a linear combination of dipolar and full ranged London–de Boer dispersion terms, in order to study their competition. To save computer time and yet monitor the physically relevant changes, we have varied their relative weights, while keeping fixed both the temperature and the anisotropy parameter in the dispersion potential. Simulation results show that in energetic terms the two interactions are cooperative, whereas in structural terms their interplay brings about first a weak but recognizable increase of nematic ordering, and then its collapse with the onset of the staggered configuration.

1. Introduction

At present, realistic pair potentials at various levels of sophistication have been obtained for some simple molecules such as the inert gases, water, methane, nitrogen, oxygen and benzene, by combining a number of properties and techniques [1, 2], both experimental and theoretical; they have also been used for computer simulation studies. The molecular complexity of nematogens has so far mostly prevented the determination of their potentials of comparable quality (and their subsequent use in simulation experiments) [2, 3].

Computer simulations of liquid crystals have been carried out on various potential models [4–24], mostly drastically simplified, yet producing long range orientational (nematic) ordering. As an addititional simplification, the lattice model approximation has often been used; its practical advantages and conceptual limitations are discussed elsewhere [25]. Simulation of hard elongated particles has proved rather fruitful [14–16], and the anisotropic overlap model proposed by Gay and Berne also seems appropriate [23, 24]. The models adopted in the first computer simulation studies of liquid crystals consisted of cylindrically symmetric particles whose centres were restricted to a simple cubic lattice and interacting via a nearest neighbour pair potential given by

$$W_{jk} = -\varepsilon P_2(\mathbf{u}_j \cdot \mathbf{u}_k), \quad \varepsilon > 0. \tag{1}$$

Here $\{\mathbf{u}_k\}$ are the unit vectors defining the molecular orientations, and $P_2(\mathbf{u}_j \cdot \mathbf{u}_k)$ is the second Legendre polynomial [4–12]. This potential is known to produce an ordered phase stable at low temperature [26], and the resulting disordering transition has been extensively investigated theoretically [27–32]. The corresponding $P_4(\mathbf{u}_j \cdot \mathbf{u}_k)$ lattice model has also been studied via simulation [13], and been found to support an ordered phase.

The functional form of the pair potential defined by equation (1) is unrealistic in various ways, for it assumes the interaction energy to be independent of the orientation with respect to the intermolecular vector. In order to overcome this limitation, we have simulated the behaviour [21] of a system of cylindrically symmetric particles on a simple cubic lattice, interacting via an anisotropic London–de Boer dispersion potential [33, 34] restricted to nearest neighbours. This pair potential is of particular interest because it was used in the original derivation of the Maier–Saupe molecular field treatment of nematic ordering [35]. The simulation results again showed the existence of a low temperature ordered phase, a broad qualitative agreement with the simpler functional form (1), and reasonable success for the molecular field approximation. Later an attempt was made to increase the range of the dispersion potential [36], and it turned out that inclusion of interactions with next nearest neighbours does destroy the (overall) orientational order, and further increase of the potential range does not alter the result.

Real nematogens usually possess appreciable multipole moments, mostly neglected in simulated models; the optimal mutual orientation of two linear point quadrupoles is a T-shaped geometry, so that we can expect this interaction to hinder nematic ordering. On the other hand, it is known that dipolar interactions are not essential for nematic behaviour, as can be seen from the existence of such a phase for *p*-quinquephenyl, but they can play a significant role in some specific cases, for example, the alkyl- and alkyloxycyanobiphenyls [37]. Moreover, both theoretical and simulation results indicate cases where they enhance the stability of a nematic phase [36, 38].

In our previous work [39, 40], a simple cubic dipolar lattice was simulated and found to support an antiferroelectric phase at low temperature, i.e. orientational order (as measured by a nematic or even rank order parameter) without spontaneous polarization. A qualitatively similar result was also obtained by simulating a two-dimensional array of purely dipolar plane rotators, with centres fixed on a square lattice [41]. Thus, both potential models can be regarded as extreme cases of model nematogens (extreme, because nematogenic molecules are not point-dipoles) [39–41].

The present paper aims at studying the competition between these two interactions, and reports Monte Carlo calculations on a classical system, consisting of cylindrically symmetric particles whose centres of mass are fixed on a simple cubic lattice and whose interaction potential is a combination of a dipolar and an anisotropic London–de Boer dispersion term [33, 34]. The pair potentials are

$$W_{jk} = U_{jk} + V_{jk}, \tag{2}$$

where

$$U_{jk} = \Lambda(-3a_j a_k + b_{jk})/R^3, \tag{3}$$

$$\begin{aligned} V_{jk} = {} & \eta\{\gamma[1 - (3/2)(a_j^2 + a_k^2)] \\ & + (3/2)\gamma^2[a_j^2 + a_k^2 - 9a_j^2 a_k^2 + 6a_j b_{jk} a_k - b_{jk}^2]\}/R^6; \end{aligned} \tag{4}$$

$$\mathbf{R} = \mathbf{x}_j - \mathbf{x}_k, \quad R = |\mathbf{R}|, \quad b_{jk} = \mathbf{u}_j \cdot \mathbf{u}_k, \tag{5}$$

$$a_j = (\mathbf{u}_j \cdot \mathbf{R})/R, \quad a_k = (\mathbf{u}_k \cdot \mathbf{R})/R, \tag{6}$$

and

$$\Lambda = p^2/(4\pi\varepsilon_0\sigma^3). \tag{7}$$

Here σ is the nearest neighbour separation, $\{\mathbf{x}_j\}$ are the dimensionless centre-of-mass coordinates and p is the value of the dipole moment; γ is the relative anisotropy in the polarizability tensor

$$\gamma = (\alpha_\parallel - \alpha_\perp)/(\alpha_\parallel + 2\alpha_\perp), \tag{8}$$

and $\eta > 0$ is the scalar component of the dispersion interaction [22]. In order to vary the relative weights of the two terms, we define

$$\eta = \Lambda\xi. \tag{9}$$

Calculations were carried out for different values of ξ, while keeping both temperature and γ fixed; this was done in order to save computer time while still monitoring the physically relevant changes of the system.

2. The ground states

In this section we obtain some information about the ground states for the two separate potentials U and V and for this combination. The ground state of the purely dipolar system is not known in general, but can be calculated after assuming a certain unit cell (or periodicity) and using a treatment due originally to Luttinger and Tisza [42] and then developed by other authors [43–48]. This reduces the problem to calculating the eigenvalues and eigenvectors of an appropriate hermitian matrix whose dimension is $3N$, where N is the number of dipoles in the unit cell [see the Appendix]. After carrying out these calculations for eight dipoles, the lowest eigenvalue was found to have an energy

$$U_0^* = -2{\cdot}676\Lambda/\text{particle}, \tag{10}$$

associated with the continuously degenerate configuration $D(\psi, \varphi)$ [42, 48]

$$\left.\begin{aligned} \mathbf{x} &= h\mathbf{e}_1 + k\mathbf{e}_2 + l\mathbf{e}_3, \quad \forall(h, k, l) \in Z^3, \\ \mathbf{u} &= \mathbf{u}(h, k, l) = (-1)^{k+1}\sin\psi\cos\varphi\mathbf{e}_1 + (-1)^{h+1}\sin\psi\sin\varphi\mathbf{e}_2 \\ &\quad + (-1)^{h+k}\cos\psi\mathbf{e}_3. \end{aligned}\right\} \tag{11}$$

Here $\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$ are the orthogonal unit vectors of the cubic lattice, and the angles ψ and φ can be restricted to $0 \leqslant \psi \leqslant \pi/2$ and $0 \leqslant \varphi \leqslant \pi/4$ [48]. (For arbitrary values of ψ and φ, $D(\psi, \varphi)$ can be reduced to the set of vectors $\mathbf{x}$ and $\mathbf{u}$ obtained from equation (11) for $h, k, l = 0, 1$.)

The various isoenergetic configurations $D(\psi, \varphi)$ possible can be quite different in terms of their orientational order. This can be easily seen by calculating their nematic ordering tensor $Q_{\lambda\mu}(\psi, \varphi)$, given by

$$\begin{aligned} Q_{\lambda\mu}(\psi, \varphi) &= (3\langle u_\lambda u_\mu\rangle - \delta_{\lambda\mu})/2, \\ &= q_\lambda\delta_{\lambda\mu}, \end{aligned} \tag{12}$$

where

$$\left.\begin{aligned} q_1 &= (3\cos^2\varphi\,\sin^2\psi - 1)/2, \\ q_2 &= (3\sin^2\varphi\,\sin^2\psi - 1)/2, \\ q_3 &= (3\cos^2\psi - 1)/2. \end{aligned}\right\} \qquad (13)$$

The eigenvalue with the largest magnitude (to be denoted by $\bar{q}$) ranges between $-\frac{1}{2}$ and $+1$. We also define some specific configurations [48], i.e.

$$\left.\begin{aligned} D_1 &= D(0, \varphi), \quad \forall\varphi, & &\text{where } \bar{q} = 1, \\ D_2 &= D(\pi/2, \pi/4), & &\text{where } \bar{q} = -1/2, \\ D_3 &= D(a\cos(1/\surd 3), \pi/4), & &\text{where } \bar{q} = 0. \end{aligned}\right\} \qquad (14)$$

D_1 is an antiferroelectric structure, with all the dipoles pointing along the $\pm z$ axis; D_2, or, in more general terms, $D(\pi/2, \varphi)$, is a layered structure where all the dipoles lie in the (x, y) lattice plane and form two interpenetrating antiferroelectric sublattices, whose directions make an angle 2φ. The configuration D_3 consists of four orientationally ordered sublattices, whose dipoles point along the tetrahedral directions $(1, 1, 1)$, $(1, -1, -1)$, $(-1, 1, -1)$, $(-1, -1, 1)$, giving no net dipole moment of the cell and no overall (nematic) orientational order. We could try using the Luttinger–Tisza treatment [42] on a larger unit cell, but then the problem quickly becomes computationally intractable, while the sample size is still small in comparison with those used in simulation; moreover, $D(\psi, \varphi)$ does not necessarily support overall nematic orientational order.

We have performed Monte Carlo calculations on the pure dipolar model, at low temperature ($T^* = 0{\cdot}2$ and $T^* = 0{\cdot}45$, where $T^* = kT/\Lambda$), using different sample sizes ($N = 1000$ and $N = 1728$) and different initial configurations (D_1, D_2 and D_3). After equilibration, we found the same mean values within statistical uncertainty, and a rather large value of the order parameter, irrespective of the sample size and the initial configuration (see the following results and [39, 40]). Thus, at low temperature, the continuous degeneracy is effectively reduced, and D_1 can be taken as the ground state for the pure dipolar model, or, to put it in a different way, typical low temperature configurations can still be described by equation (11), but now ψ is close to zero and both ψ and φ are probably spatially modulated [41].

As for the pure dispersion potential, when the two molecules are parallel to each other and to the intermolecular vector, their energy has a minimum $-\eta(2\gamma + 3\gamma^2)$; in contrast, when the two molecules are parallel to each other but perpendicular to the intermolecular vector, their energy is $\eta(\gamma - 3/2\eta^2)$, and this corresponds to a saddle point in the energy hypersurface [36].

We report in table 1 absolute values of the dispersion energies, for different lattice configurations and for different ranges of the potential; all the energies are negative, and the units are $\eta\gamma^2$/particle, since terms linear with respect to γ in equation (4) cancel by cubic symmetry. On the basis of table 1 and of simulation results [21, 36] we can conclude that, for a pure nearest neighbour dispersion potential, D_1 is the ground state, whereas both D_2 and D_3 are too high in energy; for a pure full ranged dispersion potential, D_3 is the ground state, but D_1 and D_2 are now much closer to it in energy. Thus, for the ground state of the combined potential we expect a transition from D_1 to D_3 occurring at some value of ξ.

Table 1. Absolute values of the dispersion energy, for different lattice configurations and different ranges of the potential: $r - 1$, nearest neighbours; $r - 2$, next nearest neighbours; and $r - 3$, infinite range. All of the quantities have a negative and the units are $\eta\gamma^2$/particle.

Configuration	$r - 1$	$r - 2$	$r - 3$
D_1	6·000	5·813	5·817
D_2	5·250	5·859	5·879
D_3	5·000	5·875	5·900 (±0·0005)

3. Computational aspects

Periodic boundary conditions were used in the simulation [9, 25] and the long range character of the dipolar interaction was accounted for by using the Ewald–Kornfeld algorithm for lattice summations [49–53]. Calculations were carried out on samples consisting of $N = 10^3$ dipoles, the reduced temperature was fixed to $T^* = 0{\cdot}2$ and the anisotropy parameter was set to $\gamma = 0{\cdot}8$. Dimensionless reduced temperatures and energies are given by

$$T^* = k_B T/\Lambda, \quad W^* = \langle W \rangle/(N\Lambda), \tag{15}$$

where $\langle W \rangle$ is the mean sample energy and W^* is the mean energy per particle.

Calculations were carried out for increasing ξ, i.e. the equilibrated configuration produced at one value of ξ was used to start both the production run at the same value of ξ and the equilibration run at the next higher one; the pure dispersion case is formally reported as $\xi = 1$. As an additional check, we carried out some calculations for decreasing ξ, i.e. we took the equilibrated configuration at $\xi = 0{\cdot}125$, changed ξ to 0·05 and re-equilibrated, obtaining the same average results within statistical uncertainty. Equilibration runs took between 1000 and 2500 cycles (moves per particle) and production runs took between 2500 and 5000 cycles. Sub-averages for evaluating statistical errors were calculated over macrosteps consisting of 100 cycles; particles underwent random rotations according to the algorithm proposed by Barker and Watts [54].

The thermodynamic quantities calculated include the total potential energy W^* and its components U^* and V^*, and the configurational specific heat C_v^* as the fluctuational quantity

$$C_v^* = (1/N)[\langle W^2 \rangle - \langle W \rangle^2]/(kT)^2. \tag{16}$$

The structural quantities calculated include the mean dipole moment per particle, orientational correlation functions, Kirkwood g factors and order parameters. The mean dipole moment per particle is given by

$$\mathbf{M} = (1/N)\left\langle \sum_{k=1}^{N} \mathbf{u}_k \right\rangle, \tag{17}$$

and for all values of ξ its components were found to be zero within the statistical error (±0·003), i.e. no spontaneous polarization developed, as expected. Orientational correlation functions were defined by [55]

$$G_L(n) = \langle P_L(\mathbf{u}_j \cdot \mathbf{u}_k) \rangle \tag{18}$$

as a function of $n = |\mathbf{x}_j - \mathbf{x}_k|^2$, where $P_L(\mathbf{u}_j \cdot \mathbf{u}_k)$ are Legendre polynomials, and $L = 1, 2, 3, 4$. The Kirkwood g factors are defined by [56]

$$g_L = \{2/[N(N-1)]\} \left\langle \sum_{j<k} P_L(\mathbf{u}_j \cdot \mathbf{u}_k) \right\rangle, \quad L = 2, 4. \tag{19}$$

In keeping with nematics, we define the order parameters by the mean values

$$\bar{P}_L = (1/N) \left\langle \sum_{k=1}^{N} P_L(\mathbf{u}_k \cdot \mathbf{v}) \right\rangle, \quad L = 2, 4, \tag{20}$$

where the unit vector $\mathbf{v}$ defines the director. Since its orientation is not, in general, known in advance and can change in the course of simulation, we had to follow a more elaborate procedure. We have calculated for each macrostep [8, 25] both the second rank ordering tensor

$$Q_{\lambda\mu} = (3\langle u_\lambda u_\mu \rangle - \delta_{\lambda\mu})/2, \tag{21}$$

and its fourth rank equivalent

$$\begin{aligned} S_{\lambda\mu\nu\varrho} = {} & [35\langle u_\lambda u_\mu u_\nu u_\varrho \rangle - 5(\delta_{\nu\varrho}\langle u_\lambda u_\mu \rangle + \delta_{\mu\varrho}\langle u_\lambda u_\nu \rangle \\ & + \delta_{\mu\nu}\langle u_\lambda u_\varrho \rangle + \delta_{\lambda\varrho}\langle u_\mu u_\nu \rangle + \delta_{\lambda\nu}\langle u_\mu u_\varrho \rangle + \delta_{\lambda\mu}\langle u_\nu u_\varrho \rangle) \\ & + (\delta_{\lambda\mu}\delta_{\nu\varrho} + \delta_{\lambda\nu}\delta_{\mu\varrho} + \delta_{\lambda\varrho}\delta_{\mu\nu})]/8. \end{aligned} \tag{22}$$

$Q_{\lambda\mu}$ is then diagonalized to obtain its eigenvalues $\{q_1, q_2, q_3\}$ and eigenvectors $\{\boldsymbol{\tau}_1, \boldsymbol{\tau}_2, \boldsymbol{\tau}_3\}$. The eigenvector associated with the eigenvalue with the largest magnitude gives the director orientation in the laboratory frame; additional checks indicate it to be stable over the macrostep length used here [25]. In order to compensate for director fluctuations over several macrosteps, we reordered the eigenvalues first, and then averaged them; this can be achieved by different schemes [39]:

(*a*) by the even permutation producing the numbers $\{r_j | j = 1, 2, 3\}$ such that $r_1 \leqslant r_3$ and $r_2 \leqslant r_3$;
(*b*) by the even permutation producing the numbers $\{s_k\}$ such that $|s_1| \leqslant |s_3|$ and $|s_2| \leqslant |s_3|$;
(*c*) by the even permutation producing the numbers $\{t_k\}$ such that $|t_1| \geqslant |t_3|$ and $|t_2| \geqslant |t_3|$.

Let $\{\bar{r}_k\}$ be their averages over all macrosteps; we found for all ξ values $\bar{r}_3 \geqslant |\bar{s}_3| \geqslant 2|\bar{t}_3|$; moreover, in the ordered region, we have $\bar{r}_j = \bar{s}_j$, $\bar{s}_3 > 0$ and $\bar{r}_1 = \bar{r}_2$ within statistical error; in the disordered region the order parameter should be zero apart from sample size effects: here we found $\bar{r}_3 > \bar{s}_3$ and $\bar{s}_3 \approx 2\bar{t}_3$ within the combined statistical errors. The quantity $\bar{r}_3$ is expected to overestimate the amount of orientational order, whereas $2|\bar{t}_3|$, if anything, is expected to underestimate it; this quantity has been proposed as an appropriate order parameter in the disordered region [14]. Thus, also in the present case [39], the choice of $\bar{s}_3$ as the relevant order parameter is found to be consistent for all values of ξ.

The eigenvectors $\{\boldsymbol{\tau}_k\}$ define the column vectors of an orthogonal matrix $\mathbf{A}$ such that

$$\sum_{j=1}^{3} \sum_{k=1}^{3} A_{\lambda j} A_{\mu k} Q_{jk} = q_\lambda \delta_{\lambda\mu}, \tag{23}$$

which, in turn induces an orthogonal transformation of S

$$S'_{\lambda\mu\nu\varrho} = \sum_{i=1}^{3}\sum_{j=1}^{3}\sum_{k=1}^{3}\sum_{l=1}^{3} A_{\lambda i}A_{\mu j}A_{\nu k}A_{\varrho l}S_{ijkl}; \qquad (24)$$

reordering the eigenvalues of $Q_{\lambda\mu}$ also induces a corresponding reordering of indices of $S'_{\lambda\mu\nu\varrho}$ to produce $S''_{\lambda\mu\nu\varrho}$.

Alternatively and equivalently, we can take $\{\tau'_k\}$ to be the suitably reordered eigenvectors defining the orthogonal matrix **B** and the transformation

$$S''_{\lambda\mu\nu\varrho} = \sum_{i=1}^{3}\sum_{j=1}^{3}\sum_{k=1}^{3}\sum_{l=1}^{3} B_{\lambda i}B_{\mu j}B_{\nu k}B_{\varrho l}S_{ijkl}. \qquad (25)$$

We define [8]

$$\bar{P}_4 = \bar{S}''_{3333}, \qquad (26)$$

where the bar denotes an average over all macrosteps.

4. Results and discussion

The results for the potential energy are shown in table 2, they indicate a regular decrease of both U^* and V^* with increasing ξ. Thus in energetic terms, the two interactions are cooperative. The configurational specific heat was found to range between 1·0 and 1·1, with a statistical uncertainty of the order of 5 per cent for all examined values of ξ, so we can take the common value of 1·05 ± 0·05. For the structural properties, the order parameters are shown in figure 1 and the Kirkwood g factors are shown in figure 2; the orientational correlation functions for some selected values of ξ are shown in figures 3 to 6. In the ordered region, both $\bar{P}_2$ and $\bar{P}_4$ agree with the long-range limit of the correponding correlation functions, according to [25]

$$\bar{P}_L^2 = \lim_{n\to\infty} G_L(n), \quad L = 2, 4. \qquad (27)$$

In structural terms, at the temperature considered, the system exhibits a rather high degree of sub-lattice ordering, as indicated by the pronounced oscillations of the correlation functions; moreover, the interplay of dipolar and dispersion interactions brings about first a small but recognizable increase of the overall long range nematic

Table 2. Energy results, in units Λ/particle at the temperature $T^* = 0{\cdot}2$; the statistical error is usually within 0·25 per cent.

ξ	$-U^*$	$-V^*$	$-W^*$
0	2·476	–	2·476
0·025	2·499	0·067	2·566
0·05	2·516	0·141	2·657
0·075	2·531	0·219	2·750
0·0875	2·536	0·265	2·801
0·1	2·541	0·306	2·847
0·125	2·551	0·390	2·912
0·15	2·560	0·476	3·036
0·175	2·568	0·563	3·131
0·2	2·575	0·650	3·225
1	–	3·570	3·570

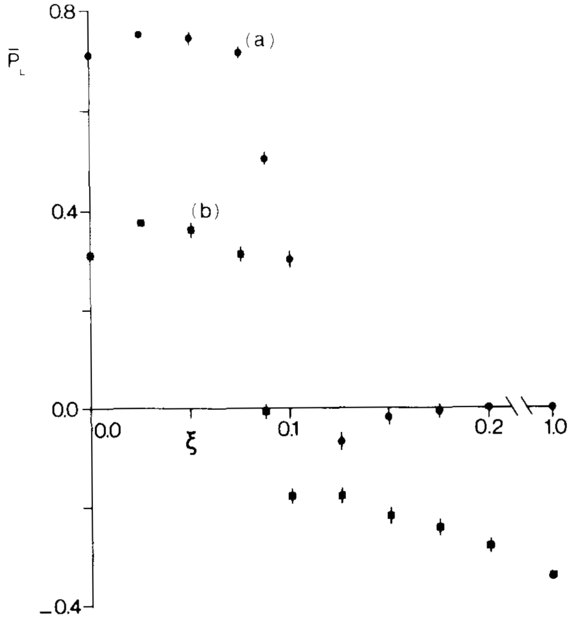

Figure 1. Plots of the order parameters (*a*) $\bar{P}_2$, (*b*) $\bar{P}_4$, versus ξ.

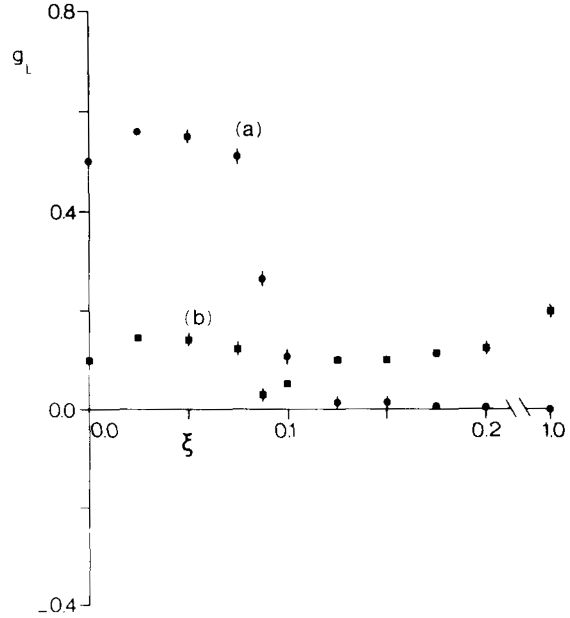

Figure 2. Plots of the Kirkwood *g* factors (*a*) g_2, (*b*) g_4, versus ξ.

ordering, then its decrease and breakdown, followed by the ultimate onset of a D_3-like configuration. This can be seen most clearly by comparing the correlation functions for $\xi = 0{\cdot}15$ with those for $\xi = 1$ (cf. figures 3 to 6), and can be rationalized in terms of relative stabilities of the (ground-state) configurations D_1 and D_3.

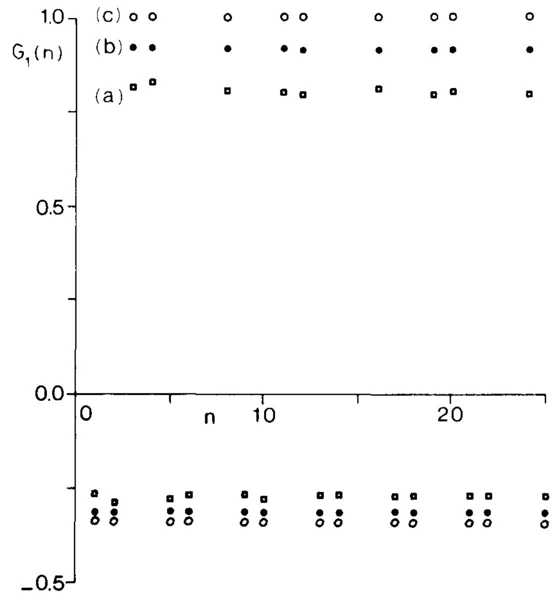

Figure 3. Plots of $G_1(n)$ for different values of ξ and different configurations; (*a*) $\xi = 0$; (*b*) $\xi = 0{\cdot}15$; (*c*) D_1, D_2, and D_3.

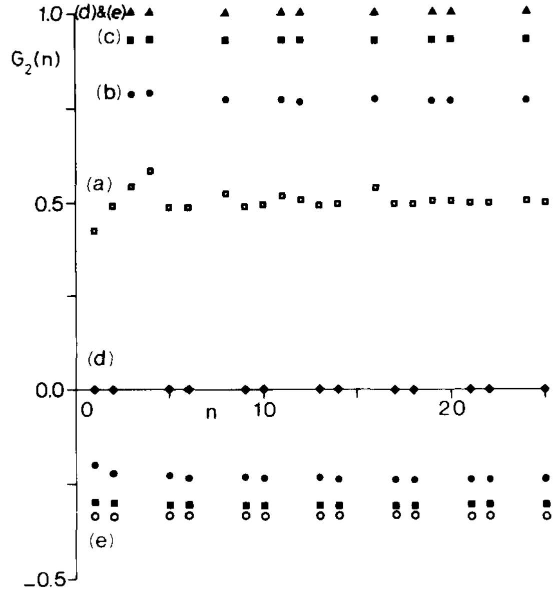

Figure 4. Plots of $G_2(n)$ for different values of ξ and different configurations: (*a*) $\xi = 0$; (*b*) $\xi = 0{\cdot}15$; (*c*) $\xi = 1$; (*d*) D_2; (*e*) D_3.

The present results show that the anisotropic de Boer–London dispersion potential alone cannot possibly be responsible for nematic behaviour, or at least not for this lattice model. Such a result may seem to conflict with the well-known molecular field result obtained by Maier and Saupe [35], but it should be noticed that, upon using the molecular field averaging procedure, different (even radically different) potentials are reduced to the same pseudopotential. In order to make this point more perspicuous,

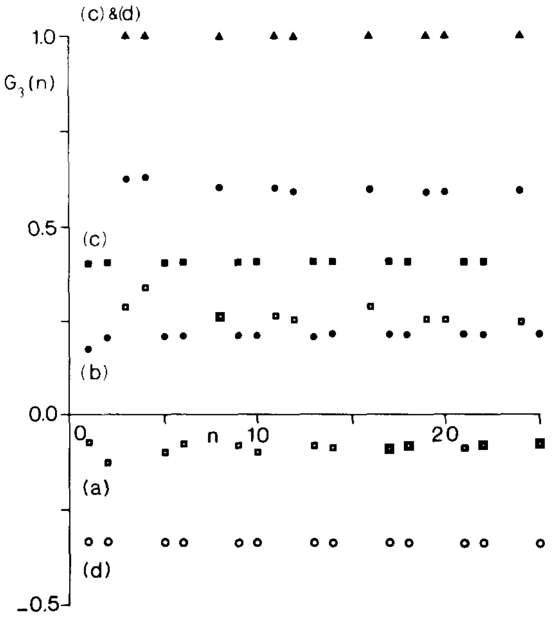

Figure 5. Plots of $G_3(n)$ for different values of ξ and different configurations: (*a*) $\xi = 0$; (*b*) $\xi = 0{\cdot}15$; (*c*) D_3; (*d*) D_1 and D_2.

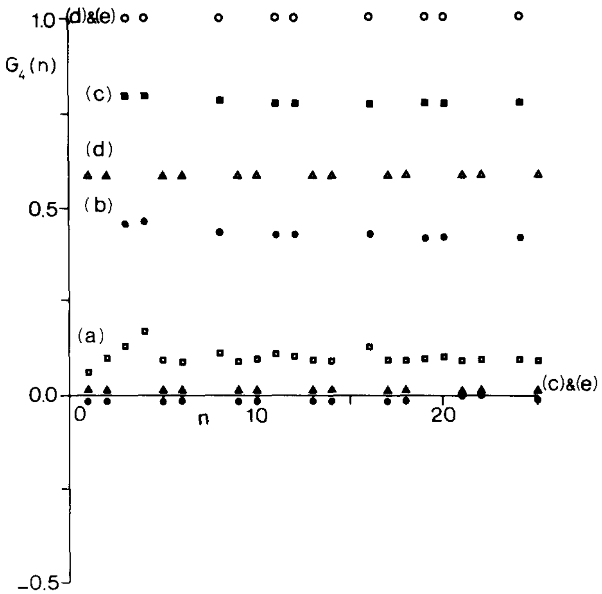

Figure 6. Plots of $G_4(n)$ for different values of ξ and different configurations: (*a*) $\xi = 0$; (*b*) $\xi = 0{\cdot}15$; (*c*) $\xi = 1$; (*d*) D_2; (*e*) D_3.

let us reconsider the molecular field averaging procedure for the dispersion potential on a simple cubic lattice [21]. When the potential is restricted to nearest neighbours, it does sustain orientational order and its molecular field averaging gives a pseudopotential

$$\tilde{V}(\beta) = -12\eta\gamma^2 P_2(\cos\beta), \tag{28}$$

where β is the angle between the molecular symmetry axis and the director; the molecular field treatment is, in this case, a reasonable approximation. Inclusion of next nearest neighbours destroys the long range orientational order (see also table 1), yet molecular field averaging of the resulting potential can be repeated along the lines of [21] and yields

$$\tilde{V}(\beta) = -(93/8)\eta\gamma^2 P_2(\cos\beta), \tag{29}$$

with the same meaning of symbols. Equations (28) and (29) define the same functional form (apart from a scaling factor), but now this kind of molecular field approach is physically meaningless. The existence of a director has been assumed in both cases: it makes sense in the former but not in the latter.

In a recent paper by Sadreev [57], the absence of long-range orientational order for a purely dipolar lattice is proved. On the other hand, both analytical and numerical results for other cases [18, 58] point to the conclusion that the absence of order in the thermodynamic limit need not exclude its existence for a macroscopically large sample. For example, it is sometimes possible to prove [58] that the relevant quantity (order parameter or transition temperature) vanishes in the thermodynamic limit like $O(1/\ln N)$.

The present calculations were carried out using, amongst other machines, a VAX VMS 11/780 computer, partly supported by funds from the Italian Ministry of Education (fondi 40% del Ministero della Pubblica Istruzione); computer time on a CRAY machine was allocated by the Italian CNR. The author wished to thank Professor G. R. Luckhurst (Department of Chemistry, The University, Southampton) for helpful discussion and suggestions.

Appendix

Here we give an outline of the Luttinger–Tisza treatment [42–48]. The dipolar potential (cf. equation (3)) can be written as

$$U_{jk} = \Lambda \sum_{\alpha=1}^{3} \sum_{\beta=1}^{3} u_{j\alpha}\theta(j\alpha, k\beta)u_{k\beta}, \tag{A 1}$$

where the subscripts α and β refer to cartesian components and the dipolar interaction tensor is defined by

$$\theta(j\alpha, k\beta) = (-3R_\alpha R_\beta + R^2\delta_{\alpha\beta})/R^5. \tag{A 2}$$

Let the cubic unit cell of the system contain $N = v^3$ dipoles, and let $E = \{u_{j\alpha} | j = 1, 2, \ldots, N; \alpha = 1, 2, 3\}$ define an arbitrary configuration of it, whose corresponding energy per dipole is given by

$$U/\Lambda = (1/2N) \sum_{j,\alpha} u_{j\alpha} \sum_{k,\beta}{}' \theta(j\alpha, k\beta)u_{k\beta}. \tag{A 3}$$

Here the subscript j runs over all particles in the unit cell, whereas the subscript k runs over all particles in the unit cells and all their lattice images. Taking periodicity into account, this expression can be rewritten as

$$U/\Lambda = (1/2N) \sum_{j,\alpha} \sum_{k,\beta} u_{j\alpha}\, \Theta(j\alpha, k\beta)u_{k\beta}, \tag{A 4}$$

where

$$\Theta(j\alpha, k\beta) = {\sum_{L\in Z^3}}' (-3s_\alpha s_\beta + s^2\delta_{\alpha\beta})/s^5. \tag{A 5}$$

$$\mathbf{s} = (\mathbf{x}_j - \mathbf{x}_k) + \nu\mathbf{L}, \tag{A 6}$$

and both j and k now run over all particles in the unit cell. The sums appearing in equations (A 3) and (A 5) exclude the case $j = k$ and $L = 0$, as indicated by the primes.

The tensor Θ possesses the symmetry properties

$$\Theta(j\alpha, k\beta) = \Theta(k\beta, j\alpha), \quad \Theta(j\alpha, j\beta) = \delta_{\alpha\beta}\Theta(j\alpha, j\alpha), \tag{A 7}$$

where $\Theta(j\alpha, j\alpha)$ is independent of j and α. The configuration E defines an element in a real vector space F whose dimension is $3N$; on the other hand, let $\zeta = \{\zeta_{j\alpha} | j = 1, 2, \ldots, N; \alpha = 1, 2, 3\}$ be an arbitrary non-null element of F which, without loss of generality, can be assumed to (or be redefined so as to) have norm N, i.e.

$$\sum_{j=1}^{N}\sum_{\alpha=1}^{3} \zeta_{j\alpha}^2 = N. \tag{A 8}$$

The element ζ thus defines a configuration of the unit cell if and only if its components satisfy the condition

$$\sum_{\alpha=1}^{3} \zeta_{j\alpha}^2 = 1, \quad \forall j. \tag{A 9}$$

The stronger condition (A 9) implies the weaker one but not the converse. Equations (A 3) and (A 5) for the energy of a configuration can be rewritten

$$U/\Lambda = (1/2N) \sum_{a=1}^{3N}\sum_{b=1}^{3N} u_a\Theta_{ab}u_b, \tag{A 10}$$

so that it is now a quadratic form in F space. Let ϱ_a indicate the eigenvalues of the tensor, and $P_a = (p_{j\alpha}^a)$ indicate its eigenvectors, constituting an orthonormal basis of F, normalized according to equation (A 8). Owing to completeness, each vector of F can be expanded

$$\zeta = \sum_{a=1}^{3N} c_a P_a \tag{A 11}$$

so that equations (A 8), (A 9) and (A 10) read

$$U/\Lambda = (1/2N) \sum_{a=1}^{3N} c_a^2\varrho_a, \tag{A 12}$$

$$\sum_{a=1}^{3N} c_a^2 = 1, \tag{A 13}$$

$$\sum_{\alpha=1}^{3}\sum_{a=1}^{3N} [c_a p_\alpha^a]^2 = 1, \quad \forall j. \tag{A 14}$$

The standard procedure for determining the extrema of equation (A 12) under the constraints (A 13) and (A 14) is the use of lagrangian multipliers, which proves rather cumbersome [42]. It turns out to be easier and quicker first to minimize the energy under the weak constraint alone, and then to check by inspection whether the strong one is satisfied. We carried out calculations for $N = 8$, and found triply degenerate eigenvalues (owing to the underlying lattice symmetry), with eigenvectors satisfying the strong constraint.

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