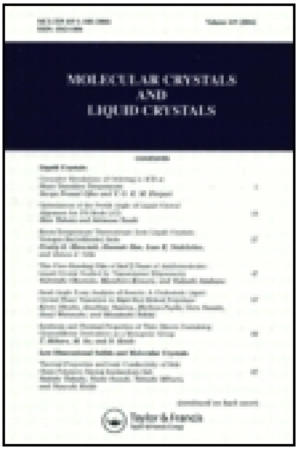

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Lattice Gas of Axially Symmetric Ellipsoids

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Lattice Gas of Axially Symmetric Ellipsoids

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We propose a lattice gas model of axially symmetric ellipsoids as a suitable model for an assembly of molecules which exhibits orientational phase transitions. In the case of nematic compounds, for example, with decreasing temperature the system has two successive transitions according to the scheme: gas → isotropic liquid → nematic liquid, if certain conditions are satisfied. For an isotropic interaction between very long ellipsoids the system exhibits only one transition from gas to nematic state. A rank two tensorial interaction leads quantitatively to similar results. In these two cases the molecular axes can be freely chosen. We also give an exhaustive study of a rank four tensorial interaction, which features some special properties.

Nous proposons un modèle du type "lattice gas" d'ellipsoides de révolution qui permet de décrire divers types de transitions orientationelles. Dans le cas, par exemple d'un composé nématique on peut observer, lorsque la temperature décroit, deux transitions successives: gaz → liquide isotrope → nématique si certaines conditions sont satisfaites. Pour une interaction isotrope on a démontré que si les ellipsoides sont suffisamment longs, seule une transition subsiste: gaz → nématique. Une interaction tensorielle de rang deux conduit qualitativement aux mêmes résultats. Dans les deux cas les axes des molecules ont une direction quelconque. Nous avons aussi étudié de façon détaillée le cas d'une interaction tensorielle de rang quatre, qui présente certaines particularités nouvelles.

I INTRODUCTION

In this article we propose a lattice gas model[1] of axially symmetric ellipsoids, which can describe various phase transitions of the first order. We have studied our model in the molecular field approximation, which gives correctly all the qualitative features of the phase transitions. The transition point is determined from the coexistence condition of the two phases in equilibrium.

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We shall establish some relations among the interaction constants and relate the shape of the phase diagram to the parameters of the model.

We discuss the application of this model to some specific problems. The first one is the description of phase transitions in liquid crystals.[2] Several statistical treatments of inflexible rods or rigid spherocylinders have appeared in the literature. For example the treatment of M. Cotter and D. Martire[3] and G. Lasher,[4] the Monte Carlo studies of G. Lasher,[5,6] and other studies.[7–9] Our theory applied in liquid crystals does not include the process of crystal melting studied recently.[10–12] In Reference (12) a theory of phase transitions is presented using the expandable lattice theory[13] to the system of rod-like molecules.

Our model could also be used to describe phase transitions in molecular crystals like solid hydrogen which exhibit orientational ordering.[14–20]

II DESCRIPTION OF THE MODEL

If we use the Einstein summation convention the Hamiltonian of the system may be written in the following general form:

$$\mathscr{H} = -\frac{1}{2}\sum_{\substack{ij\\(n.n.)}} J^{ij}_{\alpha\beta\gamma\delta}(\sigma^i Q^i_{\alpha\beta})(\sigma^j Q^j_{\gamma\delta}) - \mu\sum_i \sigma^i \tag{2.1}$$

where

a) $J^{ij}_{\alpha\beta\gamma\delta} Q^i_{\alpha\beta} Q^i_{\gamma\delta}$ is a rank four tensorial interaction (T_4 interaction) between ellipsoids i and j of neighbouring sites. (If we consider the simple cubic lattice the number of such nearest neighbours is 6).

b) μ is the chemical potential.

c) $\sigma^i = \begin{cases} +1 \text{ means that the site } i \text{ is occupied} \\ 0 \text{ means that the site } i \text{ is empty.} \end{cases}$

In fact, $\langle\sigma\rangle = \rho$ is the density of ellipsoids.

We shall begin our study taking into consideration the particular cases:

$$J_{\alpha\beta\gamma\delta} = J\delta_{\alpha\gamma}\delta_{\beta\delta} \tag{2.2}$$

which will be called the isotropic interaction or I-interaction, and

$$J_{\alpha\beta\gamma\delta} = J_{\alpha\gamma}\delta_{\beta\delta} \tag{2.3}$$

which will be called the rank two tensorial interaction or T_2-interaction.

III I-INTERACTION

1) $\rho = 1$.

The Hamiltonian of an assembly of N ellipsoids *occupying all lattice points*, with nearest neighbour interactions, is given by:

$$\mathscr{H} = -\frac{J}{2} \sum_{\substack{ij \\ (n.n.)}} Q^i_{\alpha\beta} Q^j_{\alpha\beta} \tag{3.1}$$

with $J > 0$.

To treat this Hamiltonian in the molecular field approximation, we have to consider a Hamiltonian $\mathscr{H}_0$ representing the interaction of ellipsoids with an external tensorial local field $E^i_{\alpha\beta}$:

$$\mathscr{H}_0 = -\sum_i E^i_{\alpha\beta} Q^i_{\alpha\beta} \tag{3.2}$$

Since the ellipsoids are axially symmetric in the coordinate system of their eigenvectors, they can be represented by the matrix:

$$\mathbf{Q} = \begin{pmatrix} Q & 0 & 0 \\ 0 & Q & 0 \\ Q & 0 & 1-2Q \end{pmatrix}.$$

Assuming that the states derived from this interaction have axial symmetry, we have

$$\mathbf{E} = \begin{pmatrix} E_1 & 0 & 0 \\ 0 & E_1 & 0 \\ 0 & 0 & E_2 \end{pmatrix}.$$

Then (3.2) referred to the principal axes of the molecular field is:

$$\mathscr{H} = -E_{\alpha\alpha} \sum_i Q^i_{\alpha\alpha} \tag{3.3}$$

The main problem is to evaluate the partition function Z_0 defined by:

$$Z_0 = (z_Q)^\nu = [\text{Trace} \exp(-\beta h_0)]^\nu = \left[\int e^{-\beta h_0}\, \mathrm{d}\Omega\right]^\nu \tag{3.4}$$

where $\beta = 1/kT$, $\nu = N$ sites number, and $h_0 = -E_{\alpha\alpha} Q_{\alpha\alpha}$.

The $Q_{\alpha\beta}$'s are parameters which characterize the molecule (the ellipsoid). When referred to a coordinate system fixed in the ellipsoids, they are constant parameters (Q, Q, $1 - 2Q$), equal for all ellipsoids in the system. When referred to a coordinate system fixed in space (axes of the molecular field), they depend on the orientation of the molecule. If (Θ, φ, ψ) are the Euler angles of the rotation that carries the molecular axes onto the space-fixed axes we find:

$$E_{\alpha\alpha}Q_{\alpha\alpha} = (2E_1 + E_2)\left[Q + \frac{(1-3Q)(1-\varepsilon)}{2} + \frac{(1-3Q)(3\varepsilon-1)}{2}\cos^2\varphi\right] \tag{3.5}$$

with

$$\varepsilon = \frac{E_2}{2E_1 + E_2}$$

The function z_Q, in the molecular field approximation, is then:

$$z_Q = 8\pi^2 \exp\left[\frac{2E_1 + E_2}{3kT} - \frac{A}{3}\right] I(A) \tag{3.6}$$

with

$$A = \frac{(2E_1 + E_2)(3\varepsilon - 1)(1 - 3Q)}{2kT}$$

and

$$I(A) = \int_0^1 e^{Ax^2}\,\mathrm{d}x.$$

The thermodynamic potential is given by

$$F_E = F_0 + \langle \mathscr{H} - \mathscr{H}_0 \rangle_0 \tag{3.7}$$

consequently the potential per molecule (per site) is

$$f_E = f_0 - 3J \sum_\alpha \langle Q_{\alpha\alpha}\rangle^2 + E_{\alpha\alpha}\langle Q_{\alpha\alpha}\rangle. \tag{3.8}$$

Minimizing (3.8) with respect to the $E_{\alpha\alpha}$'s, we find

$$E_{\alpha\alpha} = 6J\langle Q_{\alpha\alpha}\rangle = 6J\eta_\alpha. \tag{3.9}$$

So that:

$$2E_1 + E_2 = 6J$$

$$\varepsilon = \frac{E_2}{2E_1 + E_2} = \langle Q_{zz}\rangle = \eta_z$$

$$\langle Q_{xx}\rangle = \eta_x = \langle Q_{yy}\rangle = \eta_y = \frac{1 - \eta_z}{2}$$

The self-consistency condition can be written as:

$$\eta_z = Q + (1 - 3Q)B(A) = -\frac{\partial f_0}{\partial E_{xx}}$$

with

$$B(A) = \frac{1}{2A}\left[\frac{e^A}{\int_0^1 e^{Ax^2}\,\mathrm{d}x} - 1\right]$$

or

$$s = \frac{\tau A}{1 - 3Q} = (1 - 3Q)[3B(A) - 1] \tag{3.10}$$

where $s = 3\eta_z - 1$ is the order parameter and $\tau = kT/3J$.

The potential per ellipsoid is now:

$$\frac{f}{3J} = \tau\left[\frac{A}{3} - \ln 8\pi^2 I(A)\right] + \tfrac{1}{6}(s^2 + 2). \tag{3.11}$$

First of all, we note that (3.10) will, at all temperatures, admit the trivial solution, corresponding to the isotropic state:

$$s = 0 \qquad (\text{or} \quad \eta_x = \eta_y = \eta_z = \tfrac{1}{3}).$$

The other solution describes a nematic phase. Thus for higher temperatures the isotropic fluid is stable, then there is a first order transition at:

$$\frac{\tau_Q}{(1 - 3Q)^2} = \frac{1}{3{,}4061}; \qquad s_Q = 0.86(1 - 3Q) \tag{3.12}$$

If we want to define the order parameter according to Maier and Saupe,[21] then:

$$s_{\mathrm{MS}} = \frac{s}{2(1 - 3Q)}$$

and the value of the order parameter just below τ_Q is:

$$s^0_{\mathrm{MS}} = \frac{s_Q}{2(1 - 3Q)} = 0.43$$

which is in good agreement with many experiments.[22-26]

2) ρ variable.

The Hamiltonian of the lattice gas of ellipsoids is given by:

$$\mathscr{H} = -\frac{J}{2}\sum_{\substack{ij\\(n.n.)}} (\sigma^i Q^i_{\alpha\beta})(\sigma^j Q^j_{\alpha\beta}) - \mu \sum_i \sigma^i. \tag{3.13}$$

In the molecular field approximation it will be replaced by:

$$\mathscr{H}_0 = -\sum_i E^i_{\alpha\beta} Q^i_{\alpha\beta} - H \sum_i \sigma^i = \mathscr{H}_Q + \mathscr{H}_{LG} \tag{3.14}$$

so that

$$Z_0 = \operatorname{Tr} e^{-\beta\mathscr{H}_0} = [\operatorname{Tr} e^{-\beta h_0} e^{\beta H\sigma}]^{\nu} = (z_Q z_{LG}) \tag{3.15}$$

with

$$z_{LG} = 1 + e^{\beta H}.$$

In our case (simple cubic lattice) the thermodynamic potential per site (per unit volume) is:

$$f_{E,H} = f_Q + f_{LG} - 3J\rho^2(\eta_\alpha \eta_\alpha) + E_{\alpha\alpha}\eta_\alpha + (H - \mu)\rho \tag{3.16}$$

where

$$\rho = \langle \sigma \rangle = \frac{e^{\beta H}}{1 + e^{\beta H}}$$

The solution minimizes the potential $f_{E,H}$:

$$\frac{\partial f_{E,H}}{\partial E_{\alpha\alpha}} = (E_{\gamma\gamma} - 6J\rho^2\eta_\gamma)\frac{\partial \eta_\gamma}{\partial E_{\alpha\alpha}} = 0$$

$$\frac{\partial f_{E,H}}{\partial H} = [H - \mu - 6J\rho(\eta_\alpha \eta_\alpha)]\frac{\partial \rho}{\partial H} = 0$$

or

$$\begin{aligned} E_{\gamma\gamma} &= 6J\rho^2\eta_\gamma \\ H &= \mu + 6J\rho \sum_\alpha \eta_\alpha^2. \end{aligned} \tag{3.17}$$

The self-consistency condition is now:

$$s = \frac{A\tau}{\rho^2(1 - 3Q)} = (1 - 3Q)[3B(A) - 1] \tag{3.18}$$

the thermodynamic and the chemical potentials are given by:

$$\begin{aligned} \frac{f}{3J} &= \tau\left[\frac{A}{3} + \ln\frac{1-\rho}{8\pi^2 I(A)}\right] + \frac{\rho^2}{6}(3s^2 + 2) \\ \frac{\mu}{3J} &= \tau \ln\frac{\rho}{1-\rho} - \frac{\rho}{3}(s^2 + 2). \end{aligned} \tag{3.19}$$

The isotropic phase is defined by:

$$\begin{aligned} \frac{\mu_I}{3J} &= \tau \ln \frac{\rho_I}{1 - \rho_I} - 2\frac{\rho_I}{3} \\ \frac{f_I}{3J} &= \tau \ln \frac{(1 - \rho_I)}{8\pi^2} + \frac{\rho_I^2}{3}. \end{aligned} \tag{3.20}$$

The solution of problem is obtained by equating the thermodynamic and chemical potentials ((3.19) and (3.20)) of the two phases at the same temperature:

$$f(A) = f_I(\rho_I)$$
$$\mu(A) = \mu_I(\rho_I).$$

These equations with the help of computer calculations (A.P.L./360) give us the curve $\mu(\tau)$, for the order-disorder phase transition (Figures 1a, 1b and 2a). We have found that if $\mu \to +\infty$ $\tau \to \tau_Q$ $(\rho = 1)$. For $\tau \to 0$

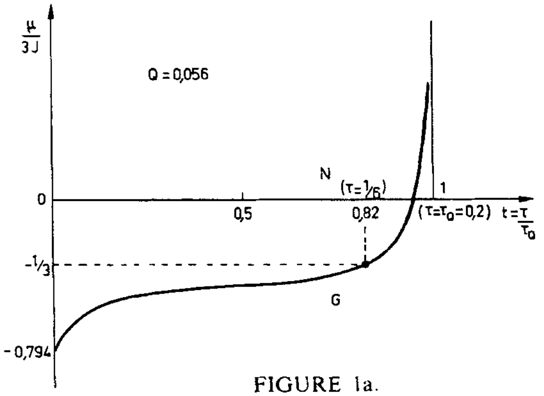

FIGURE 1a.

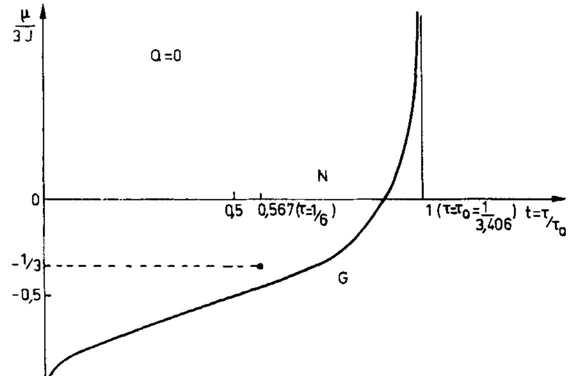

FIGURE 1b.

($T \to 0$ K) $\mu \to$ a finite value. There is a problem with $\tau \to 0$, because $\mathrm{d}\mu/\mathrm{d}T \to +\infty$ or $\mathrm{d}p/\mathrm{d}T \to k \ln 8\pi^2$. In fact, it results from the classical nature of the model.

Since the ground state of our system is an ordered state there appear to be two possibilities:

1) the lattice gas first undergoes a transition to the isotropic–liquid state (at $\mu = \frac{1}{3}$) and then at lower temperature will make the transition to the nematic phase. The condensation curve intersects the isotropic–nematic transition curve in a triple point. At temperatures below the triple point, there exists only the transition curve gas-nematic, therefore the condensation curve has been represented by a dotted line (Figure 2a).

2) With decreasing temperature the system goes directly from the gas phase to the nematic state if $Q \leq Q_t = 0.056$. (Figures 1a, 1b).

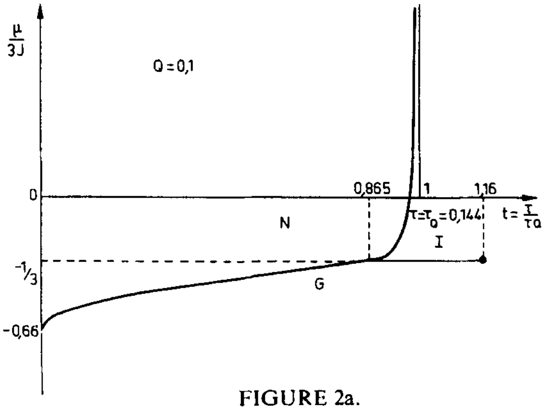

FIGURE 2a.

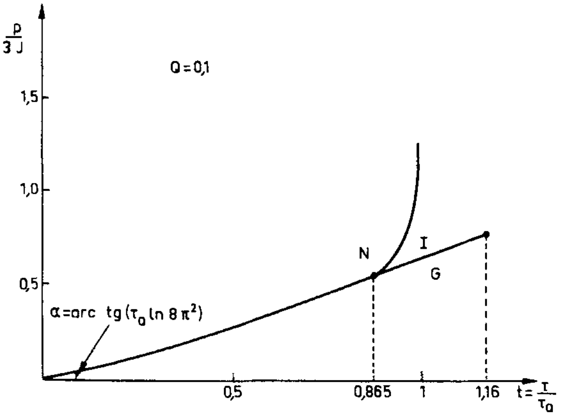

FIGURE 2b.

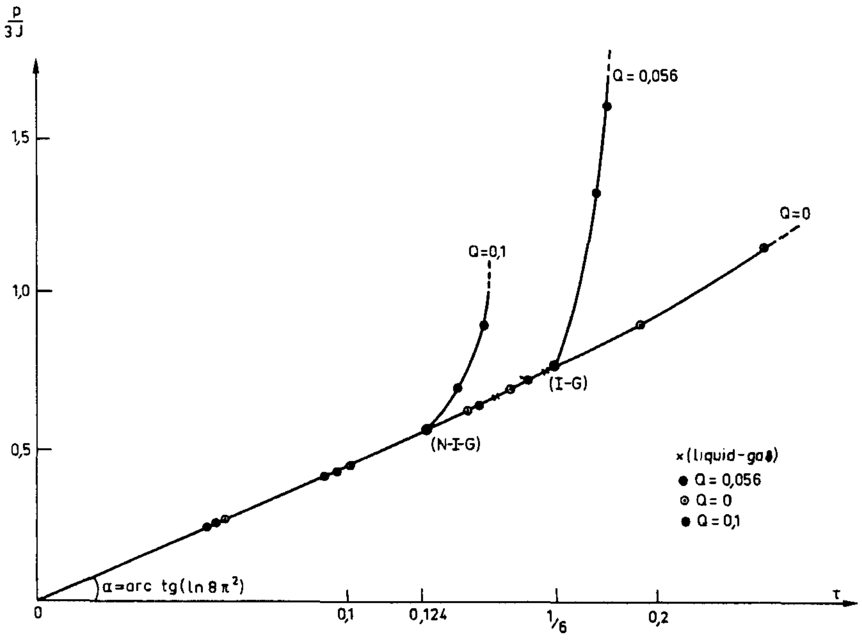

FIGURE 2c.

Measuring the volume in suitable units, we have

$$p = -\frac{1}{V}(U - TS - \mu N) = -f \tag{3.21}$$

from which we may derive the $p - T$ phase diagrams (Figures 2b, 2c), where the break in slope of the gas–liquid phase boundary is numerically very small and consequently not clearly visible.

IV T_2-INTERACTION

The Hamiltonian is given by:

$$\mathcal{H} = -\frac{1}{2}\sum_{\substack{ij\\(n.n.)}} J^{ij}_{\alpha\gamma}(\sigma^i Q^i_{\alpha\beta})(\sigma^j Q^j_{\gamma\beta}) - \mu\sum_i \sigma^i. \tag{4.1}$$

If we take into account the symmetry properties of the energy of two interacting ellipsoids (if the centers of the two ellipsoids are on the Oz axis the energy is unaltered by a rotation around Oz) there are 2 nonvanishing constants J_1 and J_2, and the tensor is given by

$$\mathbf{J} = \begin{pmatrix} J_1 & 0 & 0 \\ 0 & J_1 & 0 \\ 0 & 0 & J_2 \end{pmatrix}.$$

The molecular field approximation gives the result of Section III with

$$6J = 2(2J_1 + J_2) \tag{4.2}$$

This model will lead to a possible arrangement of the long-range nematic order if

$$J_1 > 0 \qquad J_2 < 0 \quad \text{and} \quad J_1 + J_2 > 0 \tag{4.3}$$

V T_4-INTERACTION

1) Symmetry properties.

$J_{\alpha\beta\gamma\delta}$ is a tensor of rank four, which has in general $3^4 = 81$ components. If we take into account the symmetry properties we find that there are very few independent interaction constants.

The tensors $Q_{\alpha\beta}$ and $Q_{\gamma\delta}$ are symmetric with respect to the interchange of two indices, from which it follows that the product $Q_{\alpha\beta}Q_{\gamma\delta}$ is symmetric with respect to the interchange of α and β, γ and δ or $\alpha\beta$ and $\gamma\delta$. Consequently we have:

$$J_{\alpha\beta\gamma\delta} = J_{\beta\alpha\gamma\delta} = J_{\alpha\beta\delta\gamma} = J_{\gamma\delta\alpha\beta}.$$

Let us consider the interaction between two ellipsoids as shown in Figure 3. We first take into account the symmetry with respect to a plane, for example, the yz plane. We make change of axes $x = -x$, $y = y$, $z = z$. The matrix

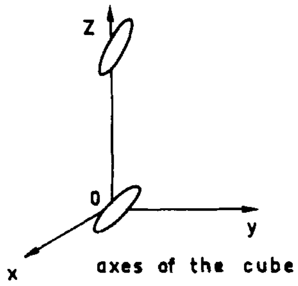

FIGURE 3

describing this transformation is

$$P = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

In a cartesian system there is no distinction between covariant and contravariant tensors so that in such a system of coordinates:

$$J_{xyyy} = P^{\alpha}_{x} P^{\beta}_{y} P^{\gamma}_{y} P^{\delta}_{y} J_{\alpha\beta\gamma\delta} = -J_{xyyy}$$

or $J_{xyyy} = 0$.

By precisely similar arguments we can show that the nonvanishing components are $J_{\alpha\alpha\beta\beta}$ or $J_{\alpha\beta\alpha\beta}$.

Of course, our system possesses cylindrical symmetry. It is unaltered by a rotation about the z-axis:

$$R = \begin{pmatrix} \cos\Theta & \sin\Theta & 0 \\ -\sin\Theta & \cos\Theta & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

where Θ is any angle.

Repeating the calculations for this transformation (similar to those used above for the reflection) we find 5 nonvanishing independent coupling constants:

$$\begin{aligned} J_{xxxx} &= J_{yyyy} = J_1 \\ J_{zzzz} &= J_2 \\ J_{xxzz} &= J_{yyzz} = J_3 \\ J_{xxyy} &= J_4 \\ J_{xzxz} &= J_{yzyz} = J_5 \\ J_{xyxy} &= \tfrac{1}{2}[J_1 - J_4] \end{aligned} \tag{5.1}$$

2) $\rho = 1$.

In this case the Hamiltonian is given by

$$\mathscr{H} = -\frac{1}{2} \sum_{\substack{ij \\ (n.n.)}} J^{ij}_{\alpha\beta\gamma\delta} Q^{i}_{\alpha\beta} Q^{j}_{\gamma\delta} \tag{5.2}$$

From (5.1) we can write:

$$\begin{aligned} \frac{\langle\mathscr{H}\rangle_0}{N} = {} & -(2J_1 + J_2)(\langle Q^c_{xx}\rangle^2 + \langle Q^c_{yy}\rangle^2 + \langle Q^c_{zz}\rangle^2) \\ & - 2(2J_3 + J_4)(\langle Q^c_{xx}\rangle\langle Q^c_{yy}\rangle + \langle Q^c_{yy}\rangle\langle Q^c_{zz}\rangle + \langle Q^c_{zz}\rangle\langle Q^c_{xx}\rangle) \\ & - 4(2J_5 + J_6)(\langle Q^c_{xy}\rangle^2 + \langle Q^c_{yz}\rangle^2 + \langle Q^c_{zx}\rangle^2). \end{aligned} \tag{5.3}$$

referred to axes of the cube (of the simple cubic lattice). When referred to a coordinate system fixed in space (concretely to proper axis of the molecular field) we find:

$$\mathbf{Q}^{c} = R_1 \mathbf{Q}^{\mathrm{M.F}} R_1^{-1}$$

where $R_1(\alpha_1, \beta_1, \gamma_1)$ is the matrix of the rotation that transforms the molecular field axes into the cube-axes. Therefore (5.3) which is a scalar can be written as:

$$\frac{\langle \mathscr{H} \rangle_0}{N} = (D\Phi + C)(\eta_1 - \eta_3)^2 - B(\eta_1^2 + 2\eta_1\eta_3) \tag{5.4}$$

where

$$\begin{aligned} \Phi(\alpha_1, \beta_1) &= \sin^2\alpha_1 \cos^2\alpha_1 \sin^4\beta_1 + \sin^2\beta_1 \cos^2\beta_1 \\ D &= -2(2J_1 + J_2) + 2(2J_3 + J_4) + 4(2J_5 + J_6) \\ B &= 2J_1 + J_2 + 2(2J_3 + J_4) \\ C &= 2J_1 + J_2 \end{aligned}$$

Minimizing the thermodynamic potential we obtain:

$$\begin{aligned} E_1 &= E_2 = (D\Phi + C)(\eta_1 - \eta_3) + B(\eta_1 + \eta_3) \\ E_3 &= -2(D\Phi + C)(\eta_1 - \eta_3) + 2B\eta_1 \end{aligned} \tag{5.5}$$

The physically stable solution minimizes the potential as a function of the Euler angles $(\alpha_1, \beta_1, \gamma_1)$. So that we have calculated the extremum points which are tabulated in Table I.

Inspection of Table I suggests:

$$\begin{aligned} E_1 &= E_2 = 6J\eta_1 + J' \\ E_3 &= 6J\eta_3 + J' \end{aligned} \tag{5.6}$$

with:

I. for the direction [111]: $D > 0$ or $2J_1 + J_2 < 2J_3 + J_4 + 2(2J_5 + J_6)$

$$\begin{aligned} 6J &= 4(2J_5 + J_6) \\ J' &= \tfrac{2}{3}[(2J_1 + J_2) + 2(2J_3 + J_4) - 2(2J_5 + J_6)] \end{aligned} \tag{5.7}$$

II. for the direction [001]: $D < 0$ or $2J_1 + J_2 > 2J_3 + J_4 + 2(2J_5 + J_6)$

$$\begin{aligned} 6J &= 2(2J_1 + J_2 - 2J_3 - J_4) \\ J' &= 2(2J_3 + J_4) \end{aligned} \tag{5.8}$$

III. for an arbitrary direction: $D = 0$ or $2J_1 + J_2 = 2J_3 + J_4 + 2(2J_5 + J_6)$

$$\begin{aligned} 6J &= 2(2J_1 + J_2 - 2J_3 - J_4) \\ J' &= 2(2J_3 + J_4) \end{aligned} \tag{5.9}$$

TABLE I

	[001]		[111]
	$\beta_1 = K\pi$	$\beta_1 = (2K+1)\frac{\pi}{4}$	$\beta_1 = \text{arc sin} \pm \sqrt{\frac{2}{3}}$
	$\alpha_1 = \alpha_1$	$\alpha_1 = 2K\pi$	$\alpha_1 = (2K+1)\frac{\pi}{4}$
$\frac{\partial\Phi}{\partial\alpha_1}, \frac{\partial\Phi}{\partial\beta_1}, \frac{\partial^2\Phi}{\partial\alpha_1\partial\beta_1}$	0	0	0
$\frac{\partial^2\Phi}{\partial\alpha_1^2}$	0	$\frac{1}{2}$	$-\frac{8}{9}$
$\frac{\partial^2\Phi}{\partial\beta_1^2}$	2	-2	$-\frac{4}{3}$
$Det = \begin{vmatrix} \frac{\partial^2 f}{\partial\alpha_1^2} & \frac{\partial^2 f}{\partial\alpha_1\partial\beta_1} \\ \frac{\partial^2 f}{\partial\alpha_1\partial\beta_1} & \frac{\partial^2 f}{\partial\beta_1^2} \end{vmatrix} \sim$	0	$-D^2$	$\frac{32}{27}D^2$
$\text{Trace} = \left(\frac{\partial^2 f}{\partial\alpha_1^2} + \frac{\partial^2 f}{\partial\beta_1^2}\right) \sim$	$-2D$	$+\frac{3}{2}D$	$+\frac{16}{9}D$
Φ	0	$\frac{1}{4}$	$\frac{1}{3}$
extremum	min $D < 0$	saddle point	min $D > 0$

From these we may deduce, as previously in Section III.1, the same self-consistency condition and an expression of the potential $f/3J$, where a complementary term $-J'/6J$ is present.

By considering the nematic arrangement of the ellipsoids we similarly obtain the following relations among the coupling constants:

$$\begin{gathered} J_1 > J_4 > J_3 > J_2 \\ 2J_3 < J_1 + J_2(2J_1 + J_2 > 2J_3 + J_4) \end{gathered} \tag{5.10}$$

3) ρ-variable.

The Hamiltonian of the system is (2.1). By the same procedure it is not difficult to draw conclusions from our approximate model calculations.

There are a complementary term $(J'/6J)\rho^2$ for the potential $f/3J$ and another one $-2\rho(J'/6J)$ for the chemical potential $\mu/3J$.

TABLE II

Direction	[111]			[001]		any direction	
J_1	1	1	1	1	1	1	1
J_2	-0.1 (> -0.2)	-0.1 (> -0.2)	-0.1 (> -0.2)	-0.1 (> -0.2)	-0.02 (> -1.82)	-0.1 (> -0.2)	-0.02 (> -1.82)
J_3	0.4	0.4	0.4	0.4	0.05	0.4	0.05
J_4	0.8	0.8	0.8	0.8	0.08	0.8	0.08
J_5	0.05 $(> +1/40)$	0.1 $(> +1/40)$	1.35 $(> +1/40)$	$< +1/40$	<0.22	$= +1/40$	$=0.22$
J_6	0.1	0.1	0.1	0.1	0.46	0.1	0.46
$J'/6J$	3.92	2.50	-0.03	5.83	0.1	5.83	0.1
Q_l	—	—	0.048	—	0.042	—	0.042

The same computer method can be generalized in this case. In Table II we have given some limit values of Q_l.

In general for

$$\left[\frac{1}{6}\left(1 + \frac{J'}{6J}\right)\middle/\frac{(1-3Q)^2}{3.4061}\right] > 1$$

or

$$\frac{J'}{6J} > \frac{1}{0.567} - 1 \sim 0.763$$

there is no Q_l.

VI CONCLUSION

Our model can be used to describe phase transitions in nematics. The new and interesting feature is the existence of a critical ratio between the axes of the ellipsoid ($Q_l/(1 - 2Q_l) = 0.063$) beyond which there is no more isotropic liquid–nematic transition. This has not been observed until now probably because the molecules which could exhibit such a feature are broken as temperature increase, before the nematic–gas transition could be observed. This critical ratio could be observed by the study of solutions of long organic molecules in isotropic liquids at various concentrations.

This model could be used to describe phase transitions in some molecular crystals as the ortho-hydrogen and the para-deuterium. These compounds at low temperature undergo transitions to orientationally ordered structures with molecules parallels to specific crystal axes.[14–18] This cooperative ordering seems to be largely determined by the quadrupole–quadrupole molecule interactions.[17,19,20] To explain the existence of several sublattices it would probably be necessary to take into account interactions between second neighbours.

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Appendix

Assuming that molecules at 0 K can be oriented only along the three orthogonal directions (the x, y and z-axis) and using a simple cubic lattice model, we obtain four relative configurations of two neighbouring molecules (ellipsoids) as shown in Figure 4.

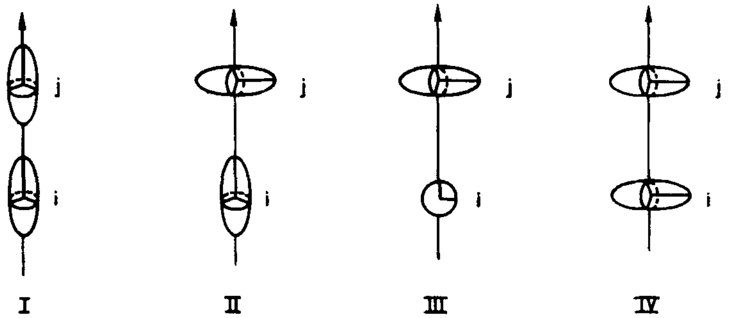

FIGURE 4.

1) I-interaction.

The energies for four relative configurations drawn in Figure 4 are:

$$E_{\mathrm{I}} = -J[2Q^2 + (1 - 2Q)^2] = E_{\mathrm{IV}}$$
$$E_{\mathrm{II}} = -J[Q^2 + 2Q(1 - 2Q)] = E_{\mathrm{III}}$$

For $J > 0$; ($E_{\mathrm{I}} = E_{\mathrm{IV}} < E_{\mathrm{II}} = E_{\mathrm{III}}$) and only the nematic arrangement is possible.

2) T_2-interaction.

From the expression:

$$J^{ij}_{\alpha\gamma} Q^i_{\alpha\beta} Q^j_{\gamma\beta} = J_1[Q^i_{xx}Q^j_{xx} + Q^i_{xy}Q^j_{xy} + Q^i_{xz}Q^j_{xz} + Q^i_{yx}Q^j_{yx} + Q^i_{yy}Q^j_{yy} + Q^i_{yz}Q^j_{yz}]$$
$$+ J_2[Q^i_{zz}Q^j_{zz} + Q^i_{zy}Q^j_{zy} + Q^i_{zx}Q^j_{zx}]$$

we deduce:

$$E_{\mathrm{I}} = -[2J_1Q^2 + J_2(1 - 2Q)^2]$$
$$E_{\mathrm{II}} = -[J_1Q^2 + (J_1 + J_2)Q(1 - 2Q)]$$
$$E_{\mathrm{III}} = -[2J_1Q(1 - 2Q) + J_2Q^2]$$
$$E_{\mathrm{IV}} = -[J_1(1 - 2Q)^2 + (J_1 + J_2)Q^2]$$

Assuming that in the limit $Q = 0$ (very long ellipsoids) the configuration I (Figure 4) is less preferable than II, III, IV and the fourth most favorable, we have:

$$J_1 > 0 \quad \text{and} \quad J_2 < 0$$

(for $Q = 0$, $E_{\mathrm{II}} = E_{\mathrm{III}} = 0$, $E_{\mathrm{I}} = -J_2$ and $E_{\mathrm{IV}} = -J_1$).

We have demonstrated that in this case the inequality:

$$E_{\mathrm{IV}} < E_{\mathrm{III}} < E_{\mathrm{II}} < E_{\mathrm{I}}$$

holds for all $Q \in [0, 1/3]$.

Comparing the total energies of every ellipsoid for other configurations we obtain the nematic case as a favorable one when:

$$J_1 + J_2 > 0$$

from which:

$$2J_1 + J_2 > 0$$

3) T_4-interaction.

From the expression:

$$\begin{aligned} J_{\alpha\beta\gamma\delta}Q^i_{\alpha\beta}Q^j_{\gamma\delta} = {} & J_1(Q^2_{xx} + Q^2_{yy}) + J_2Q^2_{zz} \\ & + J_3(Q^i_{xx}Q^j_{zz} + Q^i_{zz}Q^j_{xx} + Q^i_{yy}Q^j_{zz} + Q^i_{zz}Q^j_{yy}) \\ & + J_4(Q^i_{xx}Q^j_{yy} + Q^i_{yy}Q^j_{xx}) + 4J_5(Q^2_{xz} + Q^2_{yz}) + 4J_6Q^2_{xy} \end{aligned}$$

we find:

$$\begin{aligned} E_{\mathrm{I}} = {} & -[2J_1Q^2 + J_2(1 - 2Q)^2 + 4J_3Q(1 - 2Q) + 2J_4Q^2] \\ E_{\mathrm{II}} = {} & -\{J_1[Q^2 + Q(1 - 2Q)] + J_2Q(1 - 2Q) \\ & + J_3[2Q^2 + Q(1 - 2Q) + (1 - 2Q)^2] + J_4[Q(1 - 2Q) + Q^2]\} \\ E_{\mathrm{III}} = {} & -\{J_12Q(1 - 2Q) + J_2Q^2 + 2J_3[Q^2 + Q(1 - 2Q)] \\ & + J_4[Q(1 - 2Q)^2 + Q^2]\} \\ E_{\mathrm{IV}} = {} & -\{J_1[Q^2 + (1 - 2Q)^2] + J_2Q^2 + 2J_3[Q^2 + Q(1 - 2Q)] \\ & + 2J_4Q(1 - 2Q)\} \end{aligned}$$

In a precisely similar way we obtain that our coupling constants obey the conditions:

$$J_1 > J_4 > J_3 > J_2$$

The nematic case is favorable if:

$$J_1 + J_2 > 2J_3$$

$$(2J_1 + J_2 > 2J_3 + J_4)$$

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