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Successive Transitions in a Nematic Liquid

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Successive Transitions in a Nematic Liquid†

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Abstract—The general form of the energy of interaction between two asymmetric molecules is considered. This leads to a generalization of the Maier–Saupe model of a nematic liquid. The exact state of minimum internal energy of the system is found to be biaxial. In the molecular field approximation the consistency relations yield two distinct ordered states, a uniaxial state and a biaxial state. It is shown that with decreasing temperature the fluid will have two successive transitions according to the scheme: isotropic→uniaxial order→biaxial order.

Introduction

The prevailing picture of a nematic liquid is that of an optically uniaxial fluid. The corresponding one-particle orientational distribution function is then axially symmetric. The structures of the individual molecules are far from possessing axial symmetry and are often lath-like.(1) It would therefore seem that nematic liquid might possess a biaxial state. Such a structure has been hypothesized by Williams(2) to account for his observations of optical activity in PAA. The ordered states of nematic liquid may therefore be richer in possible symmetries than had been imagined.

The fullest existing statistical mechanical theory of the nematic state, a molecular field treatment by Maier and Saupe,(3) gives a description of the uniaxial state. In their work the orientational interaction between two molecules is taken proportional to $P_2(\cos\theta)$ where θ is the angle between the long axes of the molecules, and P_2 is the Legendre polynomial of second degree. This is the form of the

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interaction between two axially symmetric quadrupoles. The states derived from this interaction necessarily have axial symmetry.

In the following we shall discuss the possible forms of the orientational interaction between two asymmetric molecules and shall then specialize it to the simplest generalization of the P_2 interaction, namely, a more general quadrupole–quadrupole type of coupling, which we then treat in the molecular field approximation. It will be shown that the orientational ground state is one in which all of the molecules have identical orientations, and is therefore biaxial. The clearpoint is nonetheless associated with a first-order transition between the isotropic state and a uniaxial state. At some temperature below the clearpoint the liquid, if it remains liquid, will undergo a second transition to the biaxial state.

The Orientational Interaction Energy

We shall assume that the orientational interaction energy of the liquid is a sum of pair-wise interactions among the molecules. We shall further assume that an effective pair interaction between the molecules can be obtained by averaging the energy of two molecules of fixed orientation over all directions of the intermolecular vector, $\mathbf{r}_{ij}$. This latter assumption, which is the same as that used by Maier and Saupe, is a severe limitation. One is treating the two-particle distribution function as if it were separable into a spherically symmetric radial part and an orientationally dependent part. This is transparently not true in the smectic type of order but is a more suitable approximation for nematic and cholesteric states and should give qualitatively reasonable results.

No assumption will be made concerning the physical origin of the inter-molecular potential. Whether the liquid crystal state arises because of the hard-core repulsive forces or the longer range dispersion forces is a matter of indifference in the following since it is only the angular form of the interaction that will play a role.†

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† Maier and Saupe$^{(3)}$ derived the orientational interaction from the lowest order dispersion force. Their intermolecular potential therefore has a v^{-2} dependence where v is the specific volume. This, however, cannot be taken literally. For a first-order transition one can derive the thermodynamic relation

$$(\mathrm{d}/\mathrm{d}T_k)\ln v = \alpha - \beta\, \mathrm{d}p/\mathrm{d}T$$

We shall expand the intermolecular potential in a complete set of functions of the Euler angles which specify the orientations of the molecules with respect to a fixed set of axes, and functions of the direction of the vector joining the centers of gravity of the two molecules, $\mathbf{r}_{ij}$. This expansion introduces coefficients which are, in their transformation properties under rotation, analogs of the multipole moments of a charge distribution. They are parameters that characterize the molecule. When referred to a coordinate system fixed in the molecule, they are constant parameters, the same for all molecules in the system. When referred to a coordinate system fixed in space, they depend on the orientation of the molecule. In a spherical representation these quasi-multipole moments will be denoted by $Q_{lm}(\alpha, \beta, \gamma)$ where α, β, γ are the Euler angles of the rotation that carries the space-fixed axes into the molecular axes.⁽⁵⁾ In a cartesian representation the parameters are denoted $Q_{ij \ldots k}(\alpha, \beta, \gamma)$ where $i, j, \cdots k$ take the values 1, 2, 3 (or x, y, z). The Q_{lm} transform under rotations of the molecule just as do the spherical harmonics. Thus if Q_{lm}, without specification of an angular argument, denotes the parameters referred to axes fixed in the molecule, then:

$$Q_{lm}(\alpha, \beta, \gamma) = \sum_{m'} D^{(l)}_{m'm}(\alpha, \beta, \gamma)\, Q_{lm'}. \tag{1}$$

The $D^{(l)}_{m'm}$ are the elements of the representations of the rotation group. Their properties are discussed in Ref. 5, and are briefly summarized in the Appendix.

The most general orientational interaction between molecules i and j is:

$$\sum_{l_1 l_2 l_3} a_{l_1 l_2 l_3} \sum_{m_1 m_2 m_3} \begin{pmatrix} l_1 l_2 l_3 \\ m_1 m_2 m_3 \end{pmatrix} Q_{l_1 m_1}(\alpha_i, \beta_i, \gamma_i)\, Q_{l_2 m_2}(\alpha_j, \beta_j, \gamma_j)\, Y_{l_3 m_3}(\theta, \phi), \tag{2}$$

where θ, ϕ are the polar and azimuthal angles of $\mathbf{r}_{ij}$, and the first factor in the sum on m_1, m_2, m_3 is a $3j$-symbol. The coefficients

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where T_k is the transition temperature, $\mathrm{d}p/\mathrm{d}T$ is the slope of the coexistence curve, and α, β, v are respectively the limiting values of the thermal expansion coefficient, the isothermal compressibility and the specific volume of one of the two phases at the transition. If the interaction has the form $v^{-n} f(\theta_{ij})$, then $(\mathrm{d}/\mathrm{d}T_k) \ln v = -1/nT_k$. Available data for PAA yield a value of $n \approx 13$ (see Ref. 4).

$a_{l_1 l_2 l_3}$ are functions of the magnitude $\mathbf{r}_{ij}$. The transformation properties of the Q_{lm} and Y_{lm} ensure that such a sum is invariant to rotations of the spatial frame of reference. Dipole–dipole forces are given by terms with $(l_1, l_2, l_3) = (1, 1, 2)$, whereas induced dipole-induced dipole dispersion forces (as well as quadrupole–quadrupole forces) are given by a combination of terms with $l_1 = 2$, $l_2 = 2$, and $l_3 = 0, 2, 4$. Terms with odd values of l_1 and l_2 would rigorously be zero for centrosymmetric molecules. Such odd-parity terms can occur in the cholesteric state, and if Williams's(2) hypothesis is correct they may also be present in PAA.

If Eq. (2) is averaged over all orientations of $\mathbf{r}_{ij}$, then all terms vanish except those with $l_3 = m_3 = 0$. The $3j$-symbols in the surviving terms of the sum are:

$$\begin{pmatrix} l_1 & l_2 & 0 \\ m_1 & m_2 & 0 \end{pmatrix} = \delta_{l_1 l_2}\, \delta_{m_1 m_2} (-1)^{l_1 - m_1} (2l_1 + 1)^{-1/2}, \tag{3}$$

and so Eq. (2) becomes:

$$\sum_l a_l \sum_m (-1)^{-m} Q_{lm}(\alpha_i, \beta_i, \gamma_i)\, Q_{l-m}(\alpha_j, \beta_j, \gamma_j). \tag{4}$$

This is the effective orientational interaction between two molecules in the fluid. With the use of Eq. (1) this can be written:

$$\sum_l a_l \sum_{mm'm''} (-1)^m D^{(l)}_{m'm}(R_i)\, D^{(l)}_{m''-m}(R_j)\, Q_{lm'}\, Q_{lm''}, \tag{5}$$

where R has been used to denote the rotation (α, β, γ) that carries the space axes into the molecular axes. An alternative form of Eq. (5) is:

$$\sum_l a_l \sum_{m'm''} (-1)^{m'} D^{(l)}_{m''-m'}(R_{ij})\, Q_{lm'}\, Q_{lm''}, \tag{6}$$

where $R_{ij} = R_i R_j^{-1}$. This form makes explicit the fact that the energy depends only on the relative orientations of the two molecules, and hence is clearly invariant to rotations of the space axes.

Which terms in Eq. (6) will play a significant role in nematic liquids? It is plausible that terms will decrease in importance with increasing l if only because orientational oscillations will tend to wash out terms of higher values of l. Thus we will restrict our attention to the first few terms in Eq. (6). Furthermore, since nematic liquids do exist which are made up of centrosymmetric molecules,(1) the odd-parity terms do not play an essential role in the existence of the nematic state. We shall therefore restrict attention to terms with $l = 2$ and, indeed, the qualitative success of the Maier–Saupe theory does indicate that these are the most important terms. Terms with $l = 1$ can be introduced as a perturbation in order to obtain the kind of state pictured by Williams or a cholesteric state. We shall therefore assume an effective interaction energy between molecules i and j given by:

$$w_{ij} = -\sum_{mm'm''} (-1)^m D^{(2)}_{m'm}(R_i)\, D^{(2)}_{m''m}(R_j)\, Q_{2m'}\, Q_{2m''}. \tag{7}$$

The sign has been chosen so as to yield a stable state of parallel orientation, as will be seen shortly.

Nothing has been said thus far about the range of the interaction. If our assumed interaction is the anisotropic part of the London interaction, then it falls off at least as fast as $1/r^6$ at large separations. The repulsive forces are of much shorter range. The material is, however, a liquid and the diffusion of the molecules through the liquid will increase the effective range of the interaction. Each molecule will then have the same interaction with a large number of other molecules. For each molecule, therefore, we shall take Eq. (7) as its interaction with each of z neighbors, z being an effective coordination number in the liquid. We shall, for convenience, drop the index $l = 2$ henceforth.

For axially symmetric molecules, the interaction (7) reduces to the P_2 interaction of Maier and Saupe. With such symmetry the only nonzero quadrupole tensor component is Q_{20} (denoted simply Q_0 in the following), so that:

$$Q_m = Q_0\, \delta_{m0}. \tag{8}$$

Then, with

$$D^{(2)}_{0m}(\alpha, \beta, \gamma) = (4\pi/2l+1)^{1/2}\, Y_{2m}(\beta, \gamma), \tag{9}$$

we find:

$$\begin{aligned} w_{ij} &= -(4\pi/2l+1)\, Q_0^2 \sum_m (-1)^m\, Y_{2m}(\beta_i, \gamma_i)\, Y_{2-m}(\beta_j, \gamma_j) \\ &= -Q_0^2\, P_2(\cos\beta_{ij}) \end{aligned} \tag{10}$$

from the addition theorem for spherical harmonics. (Alternatively (6) can be used to get the same result.)

In a cartesian representation Eq. (7) is:

$$w_{ij} = -\mathrm{Trace}\,(\mathbf{R}^{-1}\,\mathbf{QRQ}) \tag{11}$$

where **R** is the orthogonal matrix for the rotation of the axes of molecule i into those of molecule j, and **Q** is the quasi-quadrupole tensor. Its components form a real symmetric matrix with zero trace. Thus, one can choose the molecular axes so that **Q** is diagonal. These diagonal elements are real and their sum is zero, and so only two can be independent. In terms of the spherical components of the tensor, this means that $Q_{\pm 1} = 0$ and $Q_{+2} = Q_{-2}$ is real. We shall choose as the molecular z-axis that axis for which the magnitude of the corresponding diagonal element of **Q** is largest. The relation between the spherical and cartesian representation of **Q** is given by:

$$Q_{xx} = -(2/3)^{1/2} Q_0 + 2Q_2, \qquad Q_{yy} = -(2/3)^{1/2} Q_0 - 2Q_2,$$
$$Q_{zz} = 2(2/3)^{1/2} Q_0. \tag{12}$$

We shall in the following denote these spherical components by:

$$Q_0 = Q, \qquad Q_2 = q. \tag{13}$$

Our choice of the molecular z-axis means that:

$$|Q| \geqslant 6^{1/2} |q|. \tag{14}$$

For a molecular orientation R relative to the space axes, each $Q_m(R)$ is a two-parameter linear combination of the $D_{m'm}(R)$. Thus, from Eq. (1) and the symmetry properties of the D's given in the Appendix:

$$\begin{aligned} Q_2(R) &= Q\, D_{02}(R) + q[D_{22}(R) + D_{-22}(R)] \\ &= Q^*_{-2}(R). \end{aligned} \tag{15a}$$

$$\begin{aligned} Q_0(R) &= Q\, D_{00}(R) + q[D_{20}(R) + D_{-20}(R)] \\ &= Q^*_0(R). \end{aligned} \tag{15b}$$

The State of Minimum Orientational Energy

The state of minimum orientational energy for the assumed interaction is easily obtained through the use of the form in Eq. (11). The Schwartz inequality yields immediately

$$|w_{ij}|^2 \leqslant [\mathrm{Tr}\,(R^{-1}\, QR)^2]\, [\mathrm{Tr}\, Q^2]$$

with equality holding when R is the identity. The invariance of the trace to a similarity transformation then yields:

$$|w_{ij}|^2 \leqslant [\mathrm{Tr}\, Q^2]^2. \tag{16}$$

Thus $|w_{ij}|$ attains its absolute maximum when the molecules have identical orientations, and w_{ij} then attains its absolute minimum value. The state of minimum energy of this system is therefore optically biaxial.

Molecular Field Approximation

We assume an orientational distribution function,

$$f(R) = f(\alpha, \beta, \gamma), \tag{17}$$

where

$$\int \mathrm{d}R\, f(R) = \int_0^{2\pi} \mathrm{d}\alpha \int_0^{\pi} \mathrm{d}\beta \sin\beta \int_0^{2\pi} \mathrm{d}\gamma\, f(\alpha, \beta, \gamma) = 1. \tag{18}$$

The expectation value of any function of α, β, γ will be denoted by a bar, as for example:

$$\bar{D}_{m'm} = \int \mathrm{d}R\, D_{m'm}(R) f(R), \tag{19}$$

$$\begin{aligned} \bar{Q}_m &= \int \mathrm{d}R\, Q_m(R) f(R) \\ &= \sum_{m'} \bar{D}_{m'm}\, Q_{m'}. \end{aligned} \tag{20}$$

It is readily seen that the barred quantities obey the relations:

$$\bar{D}_{-m'-m} = (-1)^{m'+m}\, \bar{D}^*_{m'm}, \tag{21a}$$

$$\bar{Q}_{-m} = (-1)^m\, \bar{Q}^*_m. \tag{21b}$$

The energy of interaction of a molecule with its z neighbors, averaged over the orientations of the neighbors, is then:

$$\bar{W}_i(R_i) = -z \sum_{mm'm''} (-1)^m D_{m'm}(R_i)\, \bar{D}_{m''-m}\, Q_{m'}\, Q_{m''}, \tag{22a}$$

$$= -z \sum_{mm'} (-1)^m D_{m'm}(R_i)\, \bar{Q}_{-m}\, Q_{m'}. \tag{22b}$$

The orientational distribution function, in the molecular field approximation, is then:

$$f(R) = \frac{1}{Z} \cdot \exp\{-\beta\, \bar{W}_i(R)\}, \tag{23}$$

where:

$$Z = \int \mathrm{d}R \exp\{-\beta\, \bar{W}_i(R)\}. \tag{24}$$

The self-consistency of the approximation is assured by the requirement that the $\bar{Q}_m$ satisfy:

$$\bar{Q}_m = \frac{1}{Z}\sum_{m'} Q_{m'} \int \mathrm{d}R\, D_{m'm}{}^{(R)} \exp\left\{\beta z \sum_{n'n} (-1)^n D_{n'n}(R)\, \bar{Q}_{-n} Q_{n'}\right\}. \quad (25)$$

The self-consistency condition can also be written as:

$$\bar{Q}_m = \frac{1}{\beta z} (-1)^m \frac{\partial}{\partial \bar{Q}_{-m}} \ln Z. \quad (26)$$

There may, in general, be more than one solution of Eq. (25). The physically stable solution is the one that minimizes the free energy. With the assumed distribution function, the internal energy and the entropy are, respectively:

$$U = -\frac{Nz}{2}\sum_m (-1)^m \bar{Q}_{-m} \bar{Q}_m, \quad (27)$$

$$\begin{aligned} S &= -Nk \int \mathrm{d}R\, f(R) \ln f(R) \\ &= -Nk\, \beta z \sum_m (-1)^m \bar{Q}_{-m} \bar{Q}_n + Nk \ln Z, \end{aligned} \quad (28)$$

so that the free energy per molecule is:

$$F/N = +\frac{z}{2}\sum_m (-1)^m \bar{Q}_{-m} \bar{Q}_m - \frac{1}{\beta} \ln Z. \quad (29)$$

It can be seen that the consistency equations (26) are the conditions for the free energy to be an extremum with respect to the order parameters, $\bar{Q}_m$.

Because we have chosen to work within a spherical representation, one feature of the consistency conditions (25) is obscured, that is, that every solution, by means of an appropriate choice of the laboratory frame of reference, will have the form:

$$\bar{Q}_{\pm 1} = 0; \qquad \bar{Q}_0, \bar{Q}_{+2} = \bar{Q}_{-2}, \text{ real}. \quad (30)$$

Had we worked with a cartesian representation, it would have been evident that $\bar{\mathbf{Q}}$ for any solution would be a real, symmetric matrix, hence diagonalizable by proper choice of the frame of reference. If it is then expressed in spherical representation, its components would obey (30). In seeking solutions of (25), we can therefore limit ourselves to those satisfying (30). Therefore all indices m, m', etc., in the consistency equation can be taken to assume even values only.

On the Solutions of the Consistency Conditions

In this section we shall show that with decreasing temperature the system undergoes a first-order transition to a state possessing axial symmetry. At some lower temperature, however, another ordered state will arise having a lower symmetry, consistent with the biaxial symmetry of the ground state.

We first note that (25) will, at all temperatures, admit the trivial solution, corresponding to the isotropic state,

$$\bar{Q}_m = 0. \tag{31}$$

For this isotropic state,

$$Z_I = 8\pi^2. \tag{32}$$

$$(F/N)_I = -\frac{1}{\beta}\ln 8\pi^2. \tag{33}$$

We next consider the existence of an axially symmetric solution of (25), that is, a solution of the form:

$$\bar{Q}_m = \delta_{m0}\,\bar{Q}_0\,. \tag{34}$$

With this assumption (25) becomes:

$$\delta_{m0}\,\bar{Q}_0 = \frac{1}{Z}\sum_{m'} Q_{m'} \int \mathrm{d}R\, D_{m'm}(R)\exp\left\{\beta z\bar{Q}_0 \sum_{n'} D_{n'0}(R)\, Q_{n'}\right\}. \tag{35}$$

The exponential is then a function of the Euler angles α, β, but not of γ. Hence the integration over γ in (33) yields zero unless the $D_{m'm}(R)$ factor is also independent of γ, that is, $m = 0$. The equation then reduces to that of Maier and Saupe for axially symmetric molecules, and a self-consistent solution exists.

In order to see what changes are introduced by the more general interaction, we first sketch the results of the Maier–Saupe theory. Figure 1 shows the free energy as a function of the order parameter $S = \bar{Q}_0/Q$. (In the case of nematic liquids we are concerned only with positive values of S). Above a temperature T^*, the only extremum occurs at the origin, $S = 0$. When $T \leqslant T^*$ a pair of extrema at finite values of S develop in the curve, coalescing when $T = T^*$. The local minimum is unstable relative to the isotropic state until $T = T_k$. For $T < T_k$ the local minimum becomes the

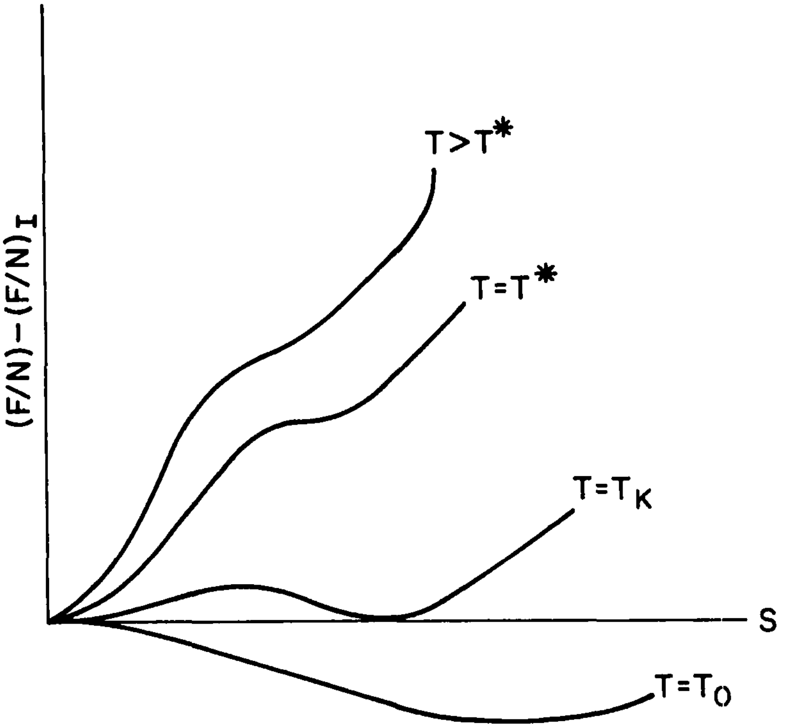

Figure 1. Free energy in the Maier–Saupe theory as a function of the order parameter S at the clearpoint, T_K, and at temperatures above and below T_K.

stable solution. At a still lower temperature, T_0, the local maximum coalesces with the extremum at the origin. The values S_k and T_k/T_0 are independent of the strength of the interaction and are consequences of its form alone. Maier and Saupe obtain the accurate values:

$$T_k/T_0 = 1.101, \qquad S_k = .4292. \tag{36}$$

In the axially symmetric case there is only a single angular variable and in fact the integral in the expression for Z can be evaluated in terms of a tabulated function, Dawson's integral.(8) Here we shall rely on an expansion of the integrand, which does not seem encouraging in view of the fact that the order parameter at the transition has so large a value. In order to gauge the feasibility of using such an expression, we consider the axially symmetric case.

With $q = 0$, $\bar{Q}_{\pm 2} = 0$, and the free energy given by (29), we obtain:

$$\begin{aligned}\Delta(F/N) &= F/N - (F/N)_I \\ &= \frac{1}{\beta}\left\{\left(\frac{1}{2\beta z Q^2} - \frac{1}{10}\right)(\beta z Q^2 S)^2 - \frac{1}{105}(\beta z Q^2 S)^3\right. \\ &\qquad \left. + \frac{1}{700}(\beta z Q^2 S)^4 + \frac{1}{1925}(\beta z Q^2 S)^5 + \cdots\right\}. \qquad (37)\end{aligned}$$

If only the first two terms are retained, one gets a second-order transition at a temperature T_0 given by:

$$\frac{1}{\beta_0 z Q^2} = \frac{kT_0}{zQ^2} = \frac{1}{5}. \qquad (38)$$

With retention of the fourth degree term there is a first-order transition (determined by $\Delta(F/N) = 0$ and $\partial(\Delta F/N)/\partial S = 0$) at a temperature T_k, with order parameter S_k where:

$$\frac{T_k}{T_0} = 1.16, \qquad S_k = .77, \qquad (39)$$

which do not compare well with (36). If terms through S^5 are kept, then for the first-order transition one obtains:

$$\frac{T_k}{T_0} = 1.095, \qquad S_k = .377, \qquad (40)$$

in fair agreement with (36). We therefore expect that terms up to fifth degree in the order parameter are adequate for obtaining the essential results of a more detailed calculation of the molecular field free energy.

Returning to the more general case expressed by (22) and (24), by expansion one obtains:

$$\begin{aligned}Z = \int \mathrm{d}r \left\{1 + \beta z \sum_{mm'} (-1)^m D_{m'm}(R)\, \bar{Q}_{-m} Q_{m'}\right. \\ \left. + \cdots + \frac{1}{n!}(\beta z)^n \left[\sum_{mm'} (-1)^m D_{m'm}(R)\, \bar{Q}_{-m} Q_{m'}\right]^n + \cdots\right\}. \qquad (41)\end{aligned}$$

The first few terms in (41) are easily evaluated with the use of

$$\int \mathrm{d}R = 8\pi^2 \qquad (42a)$$

$$\int \mathrm{d}R\, D_{m'm}(R) = 0, \tag{42b}$$

$$\int \mathrm{d}R\, D_{m'_1 m_1}(R)\, D_{m'_2 m_2}(R) = \frac{8\pi^2}{5}\, \delta_{m_1, m_2}\, \delta_{m'_1, -m'_2} (-1)^{m_1 + m'_1} \tag{42c}$$

so that:

$$Z = 8\pi^2 \left\{ 1 + \frac{(\beta z)^2}{10} \left(\sum_m (-1)^m Q_{-m} Q_m \right) \left(\sum_m (-1)^m \bar{Q}_{-m} \bar{Q}_m \right) + \cdots \right\}. \tag{43}$$

We note that the second degree term is the product of a rotationally invariant function of the Q_m and the same rotationally invariant function of the $\bar{Q}_m$, with a numerical coefficient. A simple physical argument proves that every term in the expansion (41) must have such a structure. Since there are no external fields in the problem, the laboratory axes, with respect to which the $\bar{Q}_m$ are defined, can be chosen freely. Similarly the molecular axes can be freely chosen. (We had earlier made a specific choice for the sake of algebraic simplicity, but (41) is quite general and in no way dependent on that choice.) The free energy, and therefore Z, must consequently be invariant to rotations of the laboratory axes as well as to rotations of the molecular axes. Thus Z must be a sum of products of invariants. Furthermore, the symmetry of (41) with respect to Q_m and $\bar{Q}_m$ means that each term is a product of the same invariant for the $\bar{Q}_m$ as for the Q_m. (The result can be obtained by a more formal mathematical argument based on the transformation properties of the Q_m, $\bar{Q}_m$, and $D_{m'm}$.) Thus the general term in (41) has the form:

$$\frac{1}{n!} (\beta z)^n \sum_p c_p^{(n)} F_p^{(n)} (Q_m) F_p^{(n)} (\bar{Q}_m), \tag{44}$$

where $F_p^{(n)}$ is a rotationally invariant function of nth degree and $c_p^{(n)}$ is a numerical coefficient. For $n \geqslant 6$ there will be more than one invariant, and so the index p is necessary for the general term.

Now all of the invariants of a second rank spherical tensor can be decomposed into a product of powers of two fundamental invariants, namely:

$$F_\alpha(Q_m) = \sum_{m_1 m_2} \begin{pmatrix} 2 & 2 & 0 \\ m_1 & m_2 & 0 \end{pmatrix} Q_{m_1} Q_{m_2}, \tag{45a}$$

$$F_\beta(Q_m) = \sum_{m_1 m_2 m_3} \begin{pmatrix} 2 & 2 & 2 \\ m_1 & m_2 & m_3 \end{pmatrix} Q_{m_1} Q_{m_2} Q_{m_3}. \tag{45b}$$

In a cartesian representation these are proportional to the trace of the square of **Q** and the determinant of **Q**, respectively.⁽⁷⁾ In the case of interest, with the axes chosen so as to make $Q_{\pm 1} = 0$, these are:

$$F_\alpha(Q_m) = \frac{1}{\sqrt{5}}(Q^2 + 2q^2), \tag{46a}$$

$$F_\beta(Q_m) = -\sqrt{\frac{2}{35}}\, Q\,(Q^2 - 6q^2). \tag{46b}$$

It is clear now that there is just one invariant of **Q** of degree 2, 3, 4, and 5, namely, F_α, F_β, F_α^2, $F_\alpha F_\beta$, respectively. There are however two independent invariants of degree 6, F_α^3 and F_β^2. So long as there is only one invariant, the coefficient in (44) can be found easily. These coefficients are independent of the Q_m and $\bar{Q}_m$. Consequently, if we put q and $\bar{Q}_2$ equal to zero, thereby reducing the problem to that of Maier and Saupe, then the c_p can be found by comparison of (44) with the corresponding terms in the easily evaluated expansion of:

$$\int \mathrm{d}R \exp\,[\beta z\, Q\, \bar{Q}_0\, P_2(\cos\theta)]. \tag{47}$$

Thus, the terms up to the fifth degree in the expansion of the free energy in the present case can be obtained from the expansion (37) which gives:

$$\begin{aligned} \Delta(F/N) = \frac{1}{\beta}\{&[(2\beta z(Q^2+2q^2)^{-1} - 1/10](\beta z)^2(Q^2+2q^2)(\bar{Q}_0^2+2\bar{Q}_2^2)\\ &-(1/105)(\beta z)^3 Q(Q^2-6q^2)\bar{Q}_0(\bar{Q}_0^2-6\bar{Q}_2^2)\\ &+(1/700)(\beta z)^4(Q^2+2q^2)^2(\bar{Q}_0^2+2\bar{Q}_2^2)^2\\ &+(1/1925)(\beta z)^5 Q(Q^2-6q^2)(Q^2+6q^2)\cdot\bar{Q}_0(\bar{Q}_0^2-6\bar{Q}_2^2)\\ &\cdot(\bar{Q}_0^2+2\bar{Q}_2^2)\cdots\}. \end{aligned} \tag{48}$$

To determine where the free energy has its minimum, it is convenient to introduce polar coordinates in the parameter space of $\bar{Q}_0$, $\bar{Q}_2$. Thus we put:

$$\begin{aligned} \bar{Q}_0 &= r\cos\theta, & \bar{Q}_2 &= 2^{-1/2}\, r\sin\theta\\ \bar{Q}_0^2+2\bar{Q}_2^2 &= r^2, & \bar{Q}_0(\bar{Q}_0^2-6\bar{Q}_2^2) &= r^3\cos 3\,\theta. \end{aligned} \tag{49}$$

and also:

$$\begin{aligned} Q &= R\cos\Theta, & q &= 2^{-1/2}\, R\sin\Theta\\ Q^2+2q^2 &= R^2, & Q(Q^2-6q^2) &= R^3\cos 3\,\Theta. \end{aligned} \tag{50}$$

Equation (48) then becomes:

$$\Delta(F/N) = \frac{1}{\beta}\{[(2\beta zR^2)^{-1} - 1/10](\beta zRr)^2 + (\beta zRr)^4/700 - (\beta zRr)^3[55/3 - (\beta zRr)^2] \cos 3\,\Theta \cos 3\,\theta(1/7 \cdot 11 \cdot 25) + \cdots\}. \tag{51}$$

We can, without loss of generality, assume Q and q positive. Then condition (14) implies that $-\pi/6 \leqslant \Theta \leqslant \pi/6$. The spatial frame of reference can be chosen so that $\bar{Q}_0$ and $\bar{Q}_2$ satisfy condition (14), that is $|\bar{Q}_0| \geqslant 6^{1/2}|\bar{Q}_2|$. There are then two physically distinct regions for θ, namely $-\pi/6 \leqslant \theta \leqslant \pi/6$ and $5\pi/6 \leqslant \theta \leqslant 7\pi/6$. The second region, with $\bar{Q}_0 = 0$, corresponds to a state in which the molecular z-axes lie in the spatial x, y-plane. In the axially symmetric case of Maier and Saupe such a state is never stable relative to the isotropic state. This is also true for the free energy given by Eq. (51), at least for values of the order parameter for which the approximation is valid. We need consider, therefore, only the first region in order to discuss the transition from the isotropic state to an ordered state.

Since the ground state of the system is a biaxial state, there appear to be two possibilities: (1) with decreasing temperature the system makes a transition directly from the isotropic to the biaxial state; (2) the system first undergoes a transition to the uniaxial state and then at lower temperature will make the transition to the biaxial state. Examination of Eq. (51) shows that this depends on the sign of $[55/3 - (\beta zRr)^2]$. If this quantity is positive for given values of $1/kT$ and r, then the free energy as a function of θ has its minimum at $\theta = 0$; if it is negative, then the minimum of the free energy occurs for $\theta \neq 0$. Now, at the Maier–Saupe clearpoint, we have from Eq. (36), in our notation,

$$\frac{\beta_0 zR^2}{\beta_K zR^2} = \frac{T_K}{T_0} = 1.101, \quad \frac{r_K}{R} = S_K = .4292.$$

Then

$$[55/3 - (\beta_K z r_K R)^2] = [55/3 - 25(T_0/T_K)S_K] = 6.31 > 0,$$

and the system will therefore go from the isotropic to the uniaxial state. The transition is of first order and, since $\bar{Q}_2$ remains zero and q plays no role, the transition is identical with that of the Maier–Saupe theory.

As the temperature is lowered further, the free energy minimum as a function of r moves out to higher values of r and becomes deeper, as is indicated in Fig. 1. As a function of θ, however, the free energy minimum becomes shallower with increasing r and β, and eventually $\theta = 0$ becomes a maximum with respect to θ with minima developing at either side of the $\theta = 0$ axis, as shown schematically in Fig. 2. This change in the curvature of the free energy surface occurs as the coefficient of cos 3 θ in Eq. (51) becomes less positive, and eventually becomes negative. When the curvature changes sign, that is when the point for the minimum free energy of the uniaxial state becomes a saddle point, there then occurs a second order transition to the biaxial state which has the symmetry of the ground state.

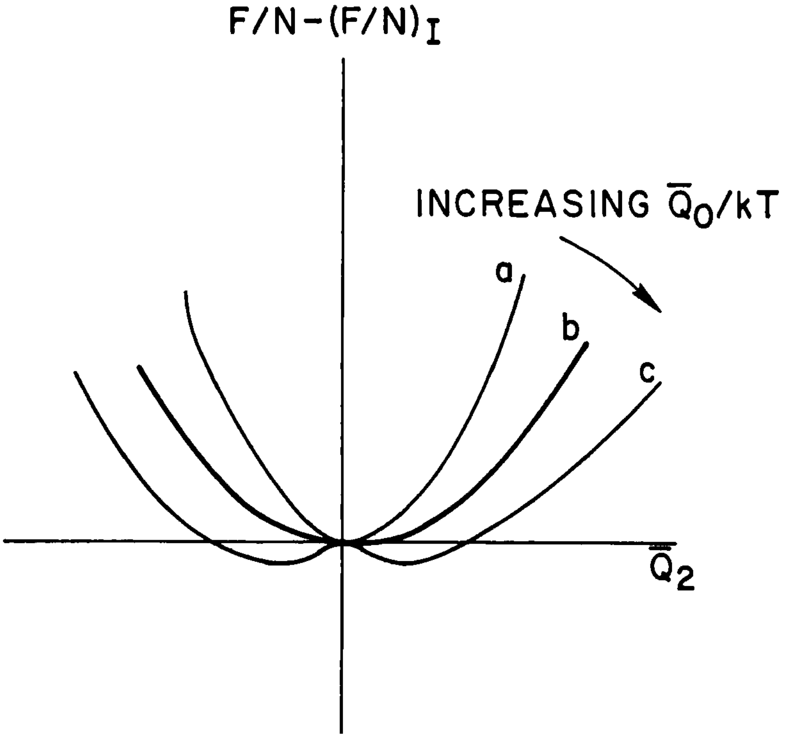

Figure 2. Free energy as a function of the order parameter $\bar{Q}_2$ in the neighborhood of the free energy minimum for the uniaxial state. Curve b shows the cross-section of the surface at the temperature at which a second order transition from the uniaxial to the biaxial state occurs; curves a and c show the sections at somewhat higher and lower temperatures, respectively.

There is an alternative possibility. At some temperature between T'_K and the temperature at which the free energy develops a saddle point at the uniaxial state, there may develop a minimum off the $\theta = 0$ axis, that is, for finite values of $\bar{Q}_2$. There would then occur a first order transition to the biaxial state. The expansion yielding Eq. (51) is inadequate to rule out this possibility.

Discussion

We have shown that by allowing an interaction of more general angular form than that employed by Maier and Saupe, and which is consistent with the pronounced asymmetric form of nematogenic molecules, the application of the molecular field approximation yields a prediction of a sequence of transitions according to the scheme isotropic → uniaxial order → biaxial order. It is possible that the onset of crystallization, or of a smectic phase, would preclude the observation of the second transition in many nematic materials. If such a transition does occur, it should be manifested in the specific heat and in the optical properties of the material. We shall discuss the available evidence on these two points for PAA.

In PAA, which has a nematic range of 116–135 °C, an anomaly in the specific heat has been observed at 128 °C which may be associated with the symmetry change that we predict.(8–10) The anomaly is quite small but the authors of Reference 9 remark, " The portion of the nematic specific heat between 128° and 134.4° appears to be reproducible and stable." They go on to say of this anomaly that, " The only other evidence for existence other than the present work is given by Martin and Müller. Arnold observed a change in his values but discounted the data. Since this minor anomaly has been observed by at least three independent workers, it is apparently not a calorimetric artifact." They also note that no such anomaly was apparent in specific volume, viscosity, and surface tension measurements.

A particular difficulty arising in the optical observation of a biaxial phase is due to surface forces. If a thin film of nematic liquid is placed between solid substrates, the " accidental " orientation of the molecules on wetting the substrates could produce a mixture of small biaxial domains having only a single principal axis in common. With ordinary microscope resolution such a polycrystalline sample would appear to be uniaxial. In Williams's⁽²⁾ observations an attempt was made to avoid such effects. In his case one surface of the film was free and the other surface was in contact with a substrate which had been treated so as to minimize surface interactions. Williams interpreted his observations in terms of a biaxial structure but he did not remark on any abrupt change at 128 °C, the temperature at which the specific heat anomaly was seen to occur. It has been proposed⁽¹¹⁾ that deformation of the free surface accompanied by orientational distortion below the surface was responsible for the effects seen by Williams. However, Williams's published curve of optical rotary power vs wavelength of the light shows a $1/\lambda^2$ dependence which is consistent with a molecular mechanism and the kind of structure proposed by Williams. The significance of Williams's experiment would therefore appear to be open to question.

Appendix

Some properties of the $D^{(l)}_{m'm}(\alpha, \beta, \gamma)$ (Taken from Ref. 5.).

The matrices $D^{(l)}(R) = D^{(l)}(\alpha, \beta, \gamma)$, with elements $D^{(l)}_{m'm}(R)$, form an irreducible representation of the rotation group in three dimensions. The matrix elements obey the following symmetry relations:

$$D^{(l)}_{m'm}(\alpha, \beta, \gamma) = D^{(l)}_{mm'}(-\gamma, -\beta, -\alpha)^*, \tag{A.1}$$

$$D^{(l)*}_{m'm}(\alpha, \beta, \gamma) = (-1)^{m'-m} D^{(l)}_{-m'-m}(\alpha, \beta, \gamma), \tag{A.2}$$

$$D^{(l)}_{m'm}(\alpha, \beta, \gamma) = (-1)^{l+m'} D^{(l)}_{-m'm}(-\alpha, \beta+\pi, \gamma). \tag{A.3}$$

Since $-\gamma$, $-\beta$, $-\alpha$ are the Euler angles of the rotation inverse to $R(\alpha, \beta, \gamma)$, Eq. (A.1) is merely a statement of the unitary property of $D^{(l)}(R)$. The group property of the $D^{(l)}(R)$ means that:

$$D^{(l)}_{m'm}(RS) = \sum_{m''} D^{(l)}_{m'm''}(R)\, D^{(l)}_{m''m}(S). \tag{A.4}$$

The central row and column of $D^{(l)}(R)$ has a particularly simple form, that is:

$$D^{(l)}_{m0}(\alpha, \beta, \gamma) = (-1)^m (4\pi/2l+1)^{1/2}\, Y_{lm}(\beta, \alpha), \tag{A.5}$$

$$D^{(l)}_{0m}(\alpha, \beta, \gamma) = (4\pi/2l+1)^{1/2}\, Y_{lm}(\beta, \gamma). \tag{A.6}$$

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