ORDERED STATES OF A NEMATIC LIQUID

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The interaction employed in the Maier-Saupe theory of the nematic state is generalized in a manner consistent with the asymmetry of the molecules that exhibit such a phase. In the molecular field approximation such an interaction then yields a first-order transition from the isotropic to a uniaxial state followed, at lower temperatures, by a second-order transition to a biaxial state.

Organic molecules that exhibit a nematic liquid crystalline state characteristically have molecules which are elongated and flat.[1] Insofar as most observed properties of these liquids are concerned, the nematic state has uniaxial symmetry, that is, while the long axes of the molecules are aligned parallel to each other, the orientational distribution function is independent of the rotational angle of the molecules about their long axes. There does exist one observation of optical activity[2] which may show this to be an inadequate picture.

It has recently been shown that there is a smectic phase which is biaxial[3] and one might inquire as to whether there can exist a biaxial nematic phase. The existing molecular field theory of nematic liquids[4] starts from an interaction of the form $P_2(\cos\theta_{ij})$ between two molecules, derived from the lowest order London interaction, where θ_{ij} is the angle between the long molecular axes. With such an interaction the molecules are, in effect, entities with axial symmetry. The theory predicts a first-order transition from an isotropic to a uniaxial nematic state. We shall show that the simplest generalization of this interaction leads to just such a first-order transition followed, at lower temperature, by a second-order transition to a biaxial state. Such a second transition might account for an anomaly observed in the specific heat of p-azoxyanisole (PAA) in the nematic state.[5]

The energy of interaction between two asymmetrical molecules can be expanded in a series of terms which are functions of the orientations of the molecules and of the line joining their centers of gravity. London forces are probably dominant, but other forces may also play an important role. We can proceed without prejudice on this point because it is only the angular form of the interaction which will be relevant. An effective orientational interaction is obtained if we average over the relative positions of an interacting pair of fixed orientation. Our use of such an averaging process presupposes a two-particle distribution function which is factorable into a spherically symmetric radial and an orientational part, which while not strictly valid, as is transparently the case in the smectic type of order, should give qualitatively reasonable results for nematic and cholesteric liquids.

Such a procedure yields an effective pair interaction which is a sum (over l) of contributions of the form

$$\sum_{m\,m'm''} (-1)^m D_{m'm}^{(l)}(\alpha_1,\beta_1,\gamma_1) D_{m''-m}^{(l)}(\alpha_2,\beta_2,\gamma_2) Q_{lm'} Q_{lm''}, \tag{1}$$

where the $D_{m'm}^{(l)}$ are the elements of the transformation matrices of the spherical harmonics, Y_{lm}, under rotation, and $\alpha_i,\beta_i,\gamma_i$ are the Euler angles of axes attached to molecule i relative to a fixed set of axes.[6] The Q_{lm} are molecular parameters which transform under rotation as the Y_{lm}. For $l=2$ and symmetric molecules such that Q_{2m} is zero unless $m=0$, (1) reduces to the P_2 interaction of Maier and Saupe.

The qualitative success of the Maier-Saupe theory leads one to expect that the $l=2$ is the most important. We therefore investigate in the molecular field approximation the consequences of an interaction in which each molecule interacts with z nearest neighbors (z being an effective coordination number) with an energy

$$w_{ij} = -\sum_{m\,m'm''} (-1)^m D_{m'm}^{(2)}(R_i) D_{m''-m}^{(2)}(R_j) Q_{2m'} Q_{2m''}, \tag{2}$$

where R_i denotes the rotation with Euler angles $\alpha_i,\beta_i,\gamma_i$. The molecular axes can always be chosen so that $Q_{2,\pm1}=0$, and $Q_{2,2}=Q_{2,-2}$ is real. Thus (2) depends on only two molecular parameters, Q_{20} and Q_{22}.

The ground state of a system with such pairwise interactions is one in which all of the molecules

have the same orientation. This is easily seen if one uses for the Q_{2m} a Cartesian representation in which this effective "quadrupole" is a real symmetric matrix of zero trace. Then (2) can be written

$$w_{ij} = -\text{Tr}(R^{-1}QRQ),$$

where R is the orthogonal matrix for the rotation of the axes of molecule i into those of molecule j. The Schwartz inequality then yields

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

with equality holding when R is the identity. Thus $|w_{ij}|^2$ attains its absolute maximum when the molecules have identical orientations, and w_{ij} then attains its absolute minimum value.

With the neglect of correlation and the assumption of the same orientational distribution function for each molecule one obtains for the free energy per molecule

$$F/N = \tfrac{1}{2}z\sum_m(-1)^m\overline{Q}_{2,-m}\overline{Q}_{2,m} - kT\ln Z, \tag{3}$$

where

$$\overline{Q}_{2,m} = \frac{1}{Z}\int dR\, Q_{2m}(R)\exp\left\{\beta z\sum_{nn'}(-1)^n D_{n'n}(R)Q_{2,n'}\overline{Q}_{2,-n}\right\}, \tag{4}$$

$$Z = \int dR\exp\left\{\beta z\sum_{mm'}(-1)^m D_{m'm}(R)Q_{2m'}\overline{Q}_{2,-m}\right\}, \tag{5}$$

and $\beta = 1/kT$. The free energy is a function of the set of order parameters $\overline{Q}_{2m}$, and the condition of self-consistency (4) is just the condition for the extremalization of F/N with respect to the $\overline{Q}_{2m}$.

The isotropic state, with $\overline{Q}_{2m} = 0$ for all m, is always an extremum of F/N. In order to examine the symmetry of the solutions of (4), we first note that for any solution that describes an ordered state it is always possible to choose the frame of reference so that $\overline{Q}_{2,\pm1} = 0$ and $\overline{Q}_{22} = \overline{Q}_{2,-2}$ is real. It can be proved that a power series expansion of Z must have the form

$$Z = \sum_n(1/n!)(\beta z)^n\sum_p c_p^{(n)}F_p^{(n)}(Q)F_p^{(n)}(\overline{Q}), \tag{6}$$

where $F_p^{(n)}(Q)$ is a rotational-invariant function of Q, homogeneous of nth degree in the components of Q. The index p is necessary since for $n \geq 6$ there is more than one rotational invariant.

Now for a second rank spherical tensor there are two fundamental invariants which, for the way in which we have chosen our axes in this case, are $Q_{20}^2 + 2Q_{22}^2$ and $Q_{20}(Q_{20}^2 - 6Q_{22}^2)$. (These are, except for a constant factor, the trace of the square of Q and the determinant of Q in a Cartesian representation.) All invariants of higher degree are just polynomials of these two. This observation permits the evaluation by simple means of the coefficients $c^{(n)}$ in (6) for terms up through $n = 5$ as there is just one invariant for each of these terms. The $c^{(n)}$ can then be found by reduction to the axially symmetric case for which $Q_{2,2}$ and $\overline{Q}_{2,2}$ are zero. Equation (6) also shows that Z, and hence F/N, are even functions of $\overline{Q}_{22}$. Thus F/N as a function of $\overline{Q}_{22}$ always has an extremum at $\overline{Q}_{22} = 0$, i.e., for the uniaxial state.

We have seen, however, that the ground state is not uniaxial. Thus if the highest temperature transition is from the isotropic to a uniaxial state, then a second transition to a state of lower symmetry must occur. There remains the question as to whether the transition is directly to the biaxial state, or if the uniaxial state occurs first as the temperature is lowered. This question we cannot answer rigorously but must rely on the terms available in the power series expansion of F/N. In this connection it is convenient to use polar coordinates in the order-parameter space, by defining

$$\overline{Q}_{20} = r\cos\theta, \quad \overline{Q}_{22} = 2^{-1/2}r\sin\theta, \tag{7}$$

so that

$$\overline{Q}_{20}^2 + 2\overline{Q}_{22}^2 = r^2, \quad \overline{Q}_{20}(\overline{Q}_{20}^2 - 6\overline{Q}_{22}^2) = r^3\cos3\theta \tag{8}$$

with similar relations between Q_{20}, Q_{22}, and polar coordinates R, Θ. Then one obtains

$$\frac{F}{N} + \ln 8\pi^2 = \frac{1}{\beta}\left\{\left[(2\beta zR^2)^{-1} - \frac{1}{10}\right](\beta zRr)^2 - \frac{1}{105}(\beta zRr)^3\cos3\Theta\cos3\theta + \frac{(\beta zRr)^4}{700} + \frac{(\beta zRr)^5\cos3\Theta\cos3\theta}{1925} + \cdots\right\}. \tag{9}$$

If one puts $\Theta = \theta = 0$ and $r/R = S$, the free energy reduces to that of Maier and Saupe for the axially

symmetric case where $S = \langle P_2(\cos\beta) \rangle$ is their order parameter. The adequacy of the expansion (9) in this case can be judged from the comparison between the Maier-Saupe accurate determination of the clearpoint temperature, T_K, and the order parameter at the transition, S_K, and the corresponding values obtained from the terms in (9). In our notation, the accurate values are $T_K = 1.101(zR^2/5k)$ and $r_K/R = 0.4292$. From (9) in the uniaxial limit one obtains $T_K = 1.095(zR^2/5k)$ and $r_K/R = 0.377$. The accuracy seems adequate to a determination of the sequence of the transitions, if not of the temperature at which a second transition should take place.

We can, without loss of generality, assume Q_{20} and Q_{22} positive. We can further take $Q_{20} \geq 6^{1/2}Q_{22}$, which can always be assured by appropriate choice of the molecular z axis. Then at $\theta = 0$ the free energy given by (9) has a positive second derivative with respect to θ for all $r < r_K$ and all temperatures greater than T_K for the uniaxial state. Thus there is a transition from the isotropic to the uniaxial state. At some lower value of T and greater value of r the curvature at the minimum in the $\theta = 0$ plane becomes zero and at this point a second-order transition to the biaxial state will occur.

Such a sequence of transitions is consistent with the asymmetry of the molecules in real nematic liquids and should therefore occur. However, crystallization of the medium or the onset of a smectic phase may intervene. In PAA however, which has a nematic range of 116-135°C, there has been observed an anomaly in the specific heat at 128°C which may be associated with such a symmetry change as we predict.[5] Optical observation may permit a determination as to whether this is the case. There is another complicating feature, however. Nematic liquids are strongly surface active. In thin films the interface with a substrate can play a dominant role. The observation of the symmetry change below the clearpoint may best be carried out in a film spread across an orifice.[7]

With regard to interactions of the form (1), we remark that if a small term with odd l is included in the interaction, then the ordered state will exhibit optical activity, even if the molecules possess a plane of symmetry.

[1]G. W. Gray, *Molecular Structure and Properties of Liquid Crystals* (Academic, New York, 1962).

[2]R. Williams, J. Chem. Phys. 50, 1324 (1969).

[3]T. R. Taylor, J. L. Fergason, and S. L. Arora, Phys. Rev. Letters 24, 359 (1970).

[4]W. Maier and A. Saupe, Z. Naturforsch. 14a, 882 (1959).

[5]E. M. Barrall, II, R. S. Porter, and J. F. Johnson, J. Phys. Chem. 71, 895 (1967).

[6]The definitions of the Euler angles and of the phases of the spherical harmonics and the $D_{m'm}^{(l)}$ are those of A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton Univ., Princeton, N. J., 1957).

[7]Williams (Ref. 2) observed the optical activity of PAA in a film in which surface effects (except those intrinsic to the material due to the anisotropy of the surface tension) were eliminated or reduced and he does not remark on any change in his observations at 128°C. The role of an applied magnetic field, as used by Williams, in stabilizing one ordered phase relative to the other has yet to be examined.