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Statistical Theory of Orientational Order in Nematic Liquid Crystals

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Abstract—Assuming a model based on dispersion and repulsion interactions, it is shown that the orientational potential energy of a molecule in a nematic liquid crystal is expressible as

$$U_i = -(u_0 + u_2 \cos^2 \theta_i + u_4 \cos^4 \theta_i + u_6 \cos^6 \theta_i + \dots),$$

$$\text{where } u_0 = w_{00} + w_{02} \overline{\cos^2 \theta} + w_{04} \overline{\cos^4 \theta} + \dots$$

$$u_2 = w_{20} + w_{22} \overline{\cos^2 \theta} + w_{24} \overline{\cos^4 \theta} + \dots,$$

etc., $w_{mn} = w_{nm}$, and θ is the angle which the long axis of the molecule makes with the uniaxial direction of the medium. Using a slightly simplified form of this function, a statistical theory of long range orientational order in the nematic state is developed. The thermodynamic properties of the ordered system are evaluated relative to those of the completely disordered one, and the conditions of equilibrium are discussed. The constants of the potential function are determined for *p*-azoxyanisole that lead to a theoretical curve for the degree of orientational order and a volume change at the nematic-isotropic transition point in good agreement with observations. However, the predicted latent heat of the nematic-isotropic transition is significantly higher than the experimental value suggesting that a certain degree of short range order persists in the liquid phase. The calculated latent heat of transition as well as the specific heat and the compressibility of the liquid crystal fit the experimental data when a correction factor is included in the theory to allow for the effect of short range order. The magnetic birefringence of the liquid phase gives an independent estimate of the short range order which confirms the previous calculations.

1. Introduction

The properties of nematic liquid crystals indicate a high degree of orientational order of the molecules but no translational order.

The degree of orientational order has been investigated experimentally by a number of techniques in recent years. The measurements yield a long range order parameter, first introduced by Zwetkoff,¹ viz.,

$$s = \frac{1}{2}(3 \overline{\cos^2 \theta} - 1)$$

where θ is the angle which the long axis of the molecule makes with the uniaxial direction of the liquid crystal. According to this definition, the limits of s are 1 for the perfectly ordered crystalline arrangement and 0 for the completely disordered isotropic liquid. Experiments reveal that s in the liquid crystalline phase has an intermediate value which falls gradually as the temperature rises up to the nematic-isotropic transition point T_c . At T_c , a first-order transition takes place and s drops abruptly to 0.

A theory of the orientational order of the molecules in nematic liquid crystals was developed by Maier and Saupe²⁻⁵ assuming an orientational potential energy function based on dispersion forces. The theory leads to a universal curve for s as a function of $TV^2/T_c V_c^2$, where T and V are the temperature and molar volume in the nematic phase, T_c and V_c the corresponding values at the nematic-isotropic transition point. Although the predicted variation of s agrees with the experimental data for some compounds, significant deviations from the common curve have been observed in many cases.⁶ Chen, James and Luckhurst⁷ measured the degree of order of a paramagnetic probe, vanadyl acetylacetate, in eight nematic liquid crystals using the electron resonance technique and found that the potential function of the form suggested by Maier and Saupe, when applied to describe the solvent-solvent and solvent-solute interactions, fails to account for the data satisfactorily. Similar conclusions have been drawn by the present writers⁸ from precise determinations of s in *p*-azoxyanisole and *p*-azoxyphenetole from optical data. A new and simple formula proposed by Vuks⁹ for the polarization field associated with strongly anisotropic molecules was applied to the refractive index measurements of Chatelain and Germain¹⁰ and found to yield accurate and internally consistent results.

Contrary to the prediction of the theory, separate curves were obtained for the two compounds, s being considerably lower for *p*-azoxyanisole than for *p*-azoxyphenetole throughout the nematic range. It is clear therefore that the theory in its present form does not allow a satisfactory quantitative description of the nematic state, a conclusion that had in fact been arrived at earlier by Saupe.⁶

The part played by permanent electric dipoles in determining liquid crystalline behaviour has been the subject of many detailed studies. The early experiments to detect free charges on the surface of the liquid crystal,^{11,12} carried out with a view to testing Born's dipole theory^{13,14} (see also Ref. 22), yielded negative results. The existence of the hysteresis loop and of polarized domains have been reported recently,¹⁵⁻¹⁹ but the question of ferroelectricity in nematic liquid crystals has not yet been settled unequivocally. Whether polarized domains do exist or not, evidence appears to be fairly conclusive that dipole-dipole interactions do not contribute much to the orientational potential energy. In particular, the extensive studies of Gray^{20,21} on mesomorphic behaviour and chemical constitution have established that substituents of widely varying polarities produce only minor changes in the thermodynamic properties of the nematic phase.

In a recent paper²² an expression was derived for the intermolecular potential energy arising from dispersion, dipole-dipole, induction and repulsion forces and a theory was developed of the birefringence of the nematic medium in terms of the Boltzmann distribution of the oriented molecules. The theory explains the observed result that the temperature coefficient of the extraordinary index is large and negative whereas that of the ordinary index is comparatively small and positive. Analysis of the experimental data on *p*-azoxyanisole and *p*-azoxyphenetole indicated that dispersion and repulsion forces play a predominant role in determining orientational order. This result is in conformity with the observations of Gray, referred to earlier, regarding the relative contribution of the polar groups to nematic stability.

In the light of this evidence, we shall assume in this paper that permanent dipole-dipole and induction effects are negligible and derive the expression for the orientational potential energy in a form that can be conveniently used for working out a statistical theory of long range orientational order in the nematic state. We shall then apply the theory in detail to evaluate the properties of *p*-azoxyanisole.

2. Orientational Potential Energy in the Nematic State

It was shown in a previous paper²² that the dipole-dipole contribution to the average dispersion energy of interaction per pair of molecules making angles θ_i , θ_j with the uniaxial direction of the nematic medium is

$$\begin{aligned}
 U_{ij}^{\text{disp}} = & -\frac{g}{r_{ij}^6} \left[\left(\frac{3\overline{\gamma_{rij}^2} - 2}{2} + \frac{9}{2}\overline{\alpha_{rij}^4} + \frac{9}{2}\overline{\alpha_{rij}^2\beta_{rij}^2} \right) \right. \\
 & \times (1 - \cos^2 \theta_i - \cos^2 \theta_j + \cos^2 \theta_i \cos^2 \theta_j) \\
 & + 9\overline{\alpha_{rij}^2\gamma_{rij}^2} (\cos^2 \theta_i + \cos^2 \theta_j) \\
 & \left. + (1 - 6\overline{\gamma_{rij}^2} - 18\overline{\alpha_{rij}^2\gamma_{rij}^2} + 9\overline{\gamma_{rij}^4}) \cos^2 \theta_i \cos^2 \theta_j \right], \quad (1)
 \end{aligned}$$

where α_{rij} , β_{rij} , γ_{rij} are the direction cosines of the intermolecular radius vector \mathbf{r}_{ij} with respect to the space fixed coordinate system, the *Z* axis being the optic axis of the medium; *g* is a molecular parameter involving the electronic charge and mass, the oscillator strength and the polarizability. The molecular distribution function is assumed to be cylindrically symmetric, as has been confirmed by X-ray studies.^{23,24} To evaluate the repulsive potential energy between a pair of identical linear molecules as a function of their relative orientations, each molecule was replaced by three centres of repulsion, two near its ends and one at its centre. The average repulsion energy per pair of molecules was shown to be expressible as²²

$$\begin{aligned}
 U_{ij}^{\text{rep}} &= (R_0 + R'_0 \cos^2 \theta_i + R''_0 \cos^4 \theta_i + \cdots) + \cos^2 \theta_j \\
 &\quad \times (R_2 + R'_2 \cos^2 \theta_i + \cdots) \\
 &\quad + \cos^4 \theta_j (R_4 + R'_4 \cos^2 \theta_i + \cdots) + \cdots \\
 &= R_{0i} + R_{2i} \cos^2 \theta_j + R_{4i} \cos^4 \theta_j + \cdots.
 \end{aligned} \tag{2}$$

The energy is symmetrical in θ_i and θ_j so that $R'_0 = R_2$, $R''_0 = R_4$, etc. We shall assume that the repulsion terms vary as V^{-4} .

From (1) and (2) the energy of interaction per pair of molecules due to dispersion and repulsion forces is

$$\begin{aligned}
 U_{ij} &= - \left[\frac{g}{r_{ij}^6} \left\{ \left(\frac{3\overline{\gamma_{rij}^2} - 2}{2} + \frac{9}{2} \overline{\alpha_{rij}^4} + \frac{9}{2} \overline{\alpha_{rij}^2 \beta_{rij}^2} \right) (1 - \cos^2 \theta_i) \right. \right. \\
 &\quad \left. \left. + 9 \overline{\alpha_{rij}^2 \gamma_{rij}^2} \cos^2 \theta_i \right\} - R_{0i} \right] \\
 &\quad - \left[\frac{g}{r_{ij}^6} \left\{ \left(\frac{3\overline{\gamma_{rij}^2} - 2}{2} + \frac{9}{2} \overline{\alpha_{rij}^4} + \frac{9}{2} \overline{\alpha_{rij}^2 \beta_{rij}^2} \right) (\cos^2 \theta_i - 1) \right. \right. \\
 &\quad \left. \left. + 9 \overline{\alpha_{rij}^2 \gamma_{rij}^2} + (1 - 6\overline{\gamma_{rij}^2} - 18\overline{\alpha_{rij}^2 \gamma_{rij}^2} + 9\overline{\gamma_{rij}^4}) \cos^2 \theta_i \right\} \right. \\
 &\quad \left. - R_{2i} \right] \cos^2 \theta_j + R_{4i} \cos^4 \theta_j + \cdots \\
 &= - (l_i + m_i \cos^2 \theta_j + n_i \cos^4 \theta_j + \cdots),
 \end{aligned}$$

say, where l_i , m_i , n_i , etc. each consist of a sum of terms involving even powers of $\cos \theta_i$. Hence the total interaction energy of a molecule i with all its neighbours j is

$$U_i = - \sum_j (l_i + m_i \cos^2 \theta_j + n_i \cos^4 \theta_j + \cdots). \tag{3}$$

We shall make the approximation that U_i has an average volume dependence of V^{-3} , and that the summations are expressible in terms of the mean values $\overline{\cos^2 \theta}$, $\overline{\cos^4 \theta}$, etc., so that (3) may be written in the form

$$U_i = - V^{-3} [L_i + M_i \overline{\cos^2 \theta} + N_i \overline{\cos^4 \theta} + \cdots]. \tag{4}$$

Clearly, (4) may also be expressed as

$$U_i = -(u_0 + u_2 \cos^2 \theta_i + u_4 \cos^4 \theta_i + \dots), \quad (5)$$

where $u_0 = w_{00} + w_{02} \overline{\cos^2 \theta} + w_{04} \overline{\cos^4 \theta} + \dots$

$$u_2 = w_{20} + w_{22} \overline{\cos^2 \theta} + w_{24} \overline{\cos^4 \theta} + \dots$$

$$u_4 = w_{40} + w_{42} \overline{\cos^2 \theta} + w_{44} \overline{\cos^4 \theta} + \dots$$

etc., where $w_{02} = w_{20}$, $w_{04} = w_{40}$, etc., or in general $w_{mn} = w_{nm}$.

For the convenience of developing a statistical theory of the nematic state we shall write the orientation-dependent part of the potential energy function (5) in the form

$$\begin{aligned} U_i = -V^{-3} & \left[A \left(\frac{3 \overline{\cos^2 \theta} - 1}{2} + \frac{3 \cos^2 \theta_i - 1}{2} \right) + B \left(\frac{3 \overline{\cos^2 \theta} - 1}{2} \right. \right. \\ & \cdot \left. \frac{3 \cos^2 \theta_i - 1}{2} \right) + C \left(\frac{5 \overline{\cos^4 \theta} - 1}{4} + \frac{5 \cos^4 \theta_i - 1}{4} \right) \\ & + D \left(\frac{3 \overline{\cos^2 \theta} - 1}{2} \cdot \frac{5 \cos^4 \theta_i - 1}{4} + \frac{3 \cos^2 \theta_i - 1}{2} \right. \\ & \cdot \left. \left. \frac{5 \overline{\cos^4 \theta} - 1}{4} \right) + E \left(\frac{7 \overline{\cos^6 \theta} - 1}{6} + \frac{7 \cos^6 \theta_i - 1}{6} \right) \right] \quad (6) \end{aligned}$$

neglecting higher terms. We shall suppose that A, B, \dots, E are independent of volume and temperature and thus disregard effects due to variations in the molecular distribution function. To this approximation, A, B, \dots, E may be taken to have the same values in the liquid crystalline and liquid phases. In the isotropic liquid

$$\frac{3 \overline{\cos^2 \theta} - 1}{2} = \frac{5 \overline{\cos^4 \theta} - 1}{4} = \frac{7 \overline{\cos^6 \theta} - 1}{6} = 0.$$

Therefore, in order that U_i given by (6) may vanish in the liquid phase, we shall take $A = C = E = 0$. The potential energy may then be written as

$$\begin{aligned} U_i &= -V^{-3} \left[B s_1 \frac{3x_i^2 - 1}{2} + D \left(s_1 \frac{5x_i^4 - 1}{4} + s_2 \frac{3x_i^2 - 1}{2} \right) \right] \\ &= -V^{-3} (a' x_i^4 + b' x_i^2 + c'), \text{ say,} \quad (7) \end{aligned}$$

where

$$x = \cos \theta,$$

$$x_i = \cos \theta_i,$$

$$s_1 = \frac{3\overline{x^2} - 1}{2},$$

$$s_2 = \frac{5\overline{x^4} - 1}{4},$$

$$a' = \frac{5}{4} D s_1,$$

$$b' = \frac{3}{2} (B s_1 + D s_2)$$

and

$$c' = -\frac{1}{4} [2B s_1 + D(s_1 + 2s_2)].$$

The new order parameter s_2 that we have introduced, like s_1 , varies from 1 to 0 over the range from perfect ordering to complete disorder. The experimental methods used so far lead to an estimate of s_1 only and not of s_2 .

3. Thermodynamic Properties of the Ordered System

We shall now derive expressions for the thermodynamic properties of the ordered system *relative* to those of the completely disordered one on the basis of (7).

3.1. ENTROPY AND FREE ENERGY

The average values of x_i^2 and x_i^4 are

$$\begin{aligned} \overline{x_i^2} &= \int_0^1 x_i^2 \exp(-U_i/kT) dx_i / \int_0^1 \exp(-U_i/kT) dx_i \\ &= \int_0^1 x_i^2 \exp(ax_i^4 + bx_i^2) dx_i / \int_0^1 \exp(ax_i^4 + bx_i^2) dx_i, \end{aligned} \quad (8)$$

$$\text{and } \overline{x_i^4} = \int_0^1 x_i^4 \exp(ax_i^4 + bx_i^2) dx_i / \int_0^1 \exp(ax_i^4 + bx_i^2) dx_i, \quad (9)$$

where $a = a'/kTV^3$, $b = b'/kTV^3$ and $c = c'/kTV^3$; c cancels out in the numerator and denominator of (8) and (9).

Since (7) represents the *mutual* energy of interaction of a molecule with its neighbours, the internal energy per mole due to orientational order is evidently

$$\begin{aligned} U_s &= \frac{1}{2}N\overline{U}_i = -\frac{1}{2}NkT \frac{\int_0^1 (ax_i^4 + bx_i^2 + c) \exp(ax_i^4 + bx_i^2) dx_i}{\int_0^1 \exp(ax_i^4 + bx_i^2) dx_i} \\ &= -\frac{1}{2}NkT(\overline{ax_i^4} + \overline{bx_i^2} + c), \end{aligned} \quad (10)$$

where N is the Avogadro number. The partition function for a single molecule

$$f_i = \int_0^1 \exp(ax_i^4 + bx_i^2 + c) dx_i,$$

so that the contribution of the orientational order to the entropy is given by

$$\begin{aligned} S_s &= -Nk \left[\frac{\int_0^1 (ax_i^4 + bx_i^2 + c) \exp(ax_i^4 + bx_i^2) dx_i}{\int_0^1 \exp(ax_i^4 + bx_i^2) dx_i} \right. \\ &\quad \left. - \log \int_0^1 \exp(ax_i^4 + bx_i^2 + c) dx_i \right] \\ &= -Nk[(\overline{ax_i^4} + \overline{bx_i^2}) - \log \int_0^1 \exp(ax_i^4 + bx_i^2) dx_i]. \end{aligned} \quad (11)$$

The component of the Helmholtz free energy due to order

$$\begin{aligned} F_s &= U_s - TS_s \\ &= NkT \left[\frac{1}{2}(\overline{ax_i^4} + \overline{bx_i^2}) - c - \log \int_0^1 \exp(ax_i^4 + bx_i^2) dx_i \right]. \end{aligned} \quad (12)$$

3.2 THE EQUILIBRIUM CONDITIONS

The thermodynamic condition for the equilibrium of the ordered phase is

$$\left(\frac{\partial F_s}{\partial s_1} \right)_{V,T} = \left(\frac{\partial F_s}{\partial s_2} \right)_{V,T} = 0.$$

$$\begin{aligned}
\left(\frac{\partial F_s}{\partial s_1}\right)_{V,T} = NkT & \left[\frac{1}{2} a \overline{x_i^4} \left(\frac{1}{s_1} + \frac{1}{\overline{x_i^4}} \frac{\partial \overline{x_i^4}}{\partial s_1} \right) \right. \\
& + \frac{1}{2} b \overline{x_i^2} \left\{ \frac{B + D(\partial s_2 / \partial s_1)}{Bs_1 + Ds_2} + \frac{1}{\overline{x_i^2}} \frac{\partial \overline{x_i^2}}{\partial s_1} \right\} \\
& - \frac{c}{2} \left\{ \frac{B + D(\frac{1}{2} + \partial s_2 / \partial s_1)}{Bs_1 + D(\frac{1}{2}s_1 + s_2)} \right\} \\
& - \frac{\int_0^1 \exp(ax_i^4 + bx_i^2) \left\{ \frac{ax_i^4}{s_1} + bx_i^2 \frac{B + D(\partial s_2 / \partial s_1)}{Bs_1 + Ds_2} \right\} dx_i}{\int_0^1 \exp(ax_i^4 + bx_i^2) dx_i} \Bigg]_{V,T} \\
= \frac{N}{V^3} & \left[\frac{B}{4} \left(3s_1 \frac{\partial \overline{x_i^2}}{\partial s_1} - 3\overline{x_i^2} + 1 \right) + \frac{D}{4} \left(3s_2 \frac{\partial \overline{x_i^2}}{\partial s_1} - \frac{5}{2} \overline{x_i^4} + \frac{1}{2} \right) \right. \\
& \left. + \frac{D}{4} \left(\frac{5}{2} s_1 \frac{\partial \overline{x_i^4}}{\partial s_1} - 3\overline{x_i^2} \frac{\partial s_2}{\partial s_1} + \frac{\partial s_2}{\partial s_1} \right) \right]_{V,T}. \quad (13)
\end{aligned}$$

Clearly (13) vanishes when

$$\overline{x_i^2} = \frac{2s_1 + 1}{3} = \overline{x^2} \quad (14)$$

and

$$\overline{x_i^4} = \frac{4s_2 + 1}{5} = \overline{x^4}. \quad (15)$$

Similarly, it can be proved that $(\partial F_s / \partial s_2)_{V,T}$ vanishes under the same circumstances. Therefore, (14) and (15) represent the two conditions of equilibrium of the ordered system. Hereafter the suffix i in $\overline{x_i^2}$, $\overline{x_i^4}$, etc. will be omitted.

3.3 VOLUME CHANGE AND LATENT HEAT OF TRANSITION

The Gibbs free energy of the nematic phase at T_c may be written as

$$G_n = F_l(V_1, T_c) + F_s(V_1, T_c) + P_c V_1,$$

where F_l is the component of the Helmholtz free energy due to the isotropic liquid (or the completely disordered system) and

F_s , the component due to order, and V_1 the molar volume of the liquid crystal at T_c . For the isotropic liquid we have similarly

$$G_l = F_l(V_2, T_c) + P_c V_2,$$

where V_2 is the molar volume of the liquid at T_c . Therefore,

$$G_n - G_l = F_l(V_1, T_c) - F_l(V_2, T_c) + F_s(V_1, T_c) - P_c \Delta V, \quad (16)$$

where $\Delta V = V_2 - V_1$ is the change of volume at T_c . Further

$$F_l(V_1, T_c) - F_l(V_2, T_c) = - \int_{V_1}^{V_2} \left(\frac{\partial F_l}{\partial V} \right)_{T_c} dV = \int_{V_1}^{V_2} P_l dV.$$

Noting that the pressure of the liquid at (T_c, V_2) is P_c , we may put

$$P_l(V, T_c) = P_c + \left(\frac{\partial P_l}{\partial V} \right)_{T_c} (V - V_2).$$

Since $(\partial P_l / \partial V)_{T_c} \simeq -1/\beta V_2$, where β is the isothermal compressibility of the liquid at T_c ,

$$\begin{aligned} \int_{V_1}^{V_2} P_l dV &= \int_{V_1}^{V_2} \left(P_c - \frac{V - V_2}{\beta V_2} \right) dV \\ &= P_c \Delta V + \frac{(\Delta V)^2}{2\beta V_2} \\ &= P_c \Delta V - \frac{1}{2} \Delta P \cdot \Delta V, \end{aligned} \quad (17)$$

where $\Delta P = P_c - P_l(V_1, T_c)$.

But we know that for the nematic phase

$$P_c = P_l(V_1, T_c) + P_s(V_1, T_c), \quad (18)$$

where P_s is the contribution of the orientational order to the pressure, so that from (16), (17) and (18),

$$G_n - G_l = F_s + \left(\frac{\partial F_s}{\partial V} \right)_{T_c} \frac{\Delta V}{2}.$$

Since the Gibbs free energy does not change at the transition,

$$G_n - G_l = 0 \text{ and } \Delta V = -2F_s/(\partial F_s/\partial V)_{T_s}. \quad (19)$$

$$\left(\frac{\partial F_s}{\partial V}\right)_T = \left(\frac{\partial F_s}{\partial V}\right)_{s,T} + \left(\frac{\partial F_s}{\partial s_1}\right)_{V,T} \left(\frac{\partial s_1}{\partial V}\right)_T + \left(\frac{\partial F_s}{\partial s_2}\right)_{V,T} \left(\frac{\partial s_2}{\partial V}\right)_T,$$

where s stands for the orientational order. As we have seen earlier, the equilibrium of the phase requires that

$$\left(\frac{\partial F_s}{\partial s_1}\right)_{V,T} = \left(\frac{\partial F_s}{\partial s_2}\right)_{V,T} = 0.$$

Hence, from (12)

$$\left(\frac{\partial F_s}{\partial V}\right)_{s,T} = \left(\frac{\partial U_s}{\partial V}\right)_{s,T} - T \left(\frac{\partial S_s}{\partial V}\right)_{s,T}.$$

But, it is easily shown from (11) that

$$\left(\frac{\partial S_s}{\partial V}\right)_{s,T} = 0.$$

Therefore, from (10)

$$\left(\frac{\partial F_s}{\partial V}\right)_T = \frac{3}{2} NkT \left(\frac{a\bar{x}^4 + b\bar{x}^2 + c}{V} \right). \quad (20)$$

Substituting in (19)

$$\frac{\Delta V}{V} = \frac{2 \log \int_0^1 \exp(ax^4 + bx^2) dx - \{\frac{1}{5}a(5\bar{x}^4 + 1) + \frac{1}{3}b(3\bar{x}^2 + 1)\}}{\frac{3}{2}\{\frac{1}{5}a(5\bar{x}^4 - 1) + \frac{1}{3}b(3\bar{x}^2 - 1)\}}. \quad (21)$$

The heat of transition from the nematic to the liquid phase is given by

$$\begin{aligned} H &= T_c[S_l(V_2, T_c) - S_n(V_1, T_c)] \\ &= T_c[S_l(V_2, T_c) - S_l(V_1, T_c) + S_l(V_1, T_c) - S_n(V_1, T_c)] \\ &= T_c \left[\int_{V_1}^{V_2} \left(\frac{\partial S_l}{\partial V}\right)_{T_c} dV - S_s(V_1, T_c) \right]. \end{aligned}$$

$$\left(\frac{\partial S_l}{\partial V}\right)_{T_c} = \left(\frac{\partial P_l}{\partial T}\right)_V = - \frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T} = \frac{\alpha}{\beta}$$

where α is the coefficient of thermal expansion and β the isothermal compressibility of the liquid at T_c . Therefore

$$H = T_c \left[\frac{\alpha}{\beta} \Delta V - S_s(V_1, T_c) \right] \quad (22)$$

assuming that α/β is sensibly constant over the range ΔV . Both α and β are known to exhibit a very slight increase with increase of volume (see, for example, Bridgman²⁵) but as we are concerned here with volume changes of the order of a fraction of a per cent, we may justifiably neglect the variation of α/β .

3.4 SPECIFIC HEAT AND COMPRESSIBILITY

The specific heat at constant volume of the nematic phase may be written as

$$C_{v_n}(T) = C_{v_i}(T) + C_{v_s}(T)$$

where $C_{v_s}(T)$ is the contribution due to order and C_{v_i} that due to the completely disordered system.

$$C_{v_s}(T) = \left(\frac{\partial U_s}{\partial T} \right)_v = -NkT \left[\frac{2}{3}b \frac{\partial s_1}{\partial T} + \frac{4}{5}a \frac{\partial s_2}{\partial T} \right]_v \quad (23)$$

from (10). The specific heat at constant pressure of the nematic phase is

$$C_{p_n} = C_{v_n} + \left(\frac{\alpha^2 VT}{\beta} \right)_n,$$

where β is the isothermal compressibility. Using a similar expression for the liquid phase

$$C_{p_n}(T) = C_{p_i}(T) + C_{v_s}(T) + T \left[\left(\frac{\alpha^2 V}{\beta} \right)_n - \left(\frac{\alpha^2 V}{\beta} \right)_i \right] \quad (24)$$

In order to evaluate β theoretically, we assume that the pressures due to order and disorder are additive, so that to a good approximation

$$\left(\frac{1}{\beta} \right)_n = \left(\frac{1}{\beta} \right)_i + \left(\frac{1}{\beta} \right)_s. \quad (25)$$

Since

$$\left(\frac{1}{\beta}\right)_s = -V \left(\frac{\partial P_s}{\partial V}\right)_T = -V \frac{\partial}{\partial V} \left(-\frac{\partial F_s}{\partial V}\right)_T,$$

we obtain from (20),

$$\left(\frac{1}{\beta}\right)_s = 3NkT \left[\frac{2}{3}b \left\{ \left(\frac{\partial s_1}{\partial V}\right)_T - \frac{2s_1}{V} \right\} + \frac{4}{5}a \left\{ \left(\frac{\partial s_2}{\partial V}\right)_T - \frac{2s_2}{V} \right\} \right]. \quad (26)$$

Differentiating (8) and (9) with respect to volume it can be shown that

$$\begin{aligned} \left(\frac{\partial s_1}{\partial V}\right)_T & \left[\frac{2}{3} - \frac{a}{s_1} (\overline{x^6} - \overline{x^4} \cdot \overline{x^2}) - \frac{bB}{Bs_1 + Ds_2} \{ \overline{x^4} - (\overline{x^2})^2 \} \right] \\ & + \left(\frac{\partial s_2}{\partial V}\right)_T \left[-\frac{bD}{Bs_1 + Ds_2} \{ \overline{x^4} - (\overline{x^2})^2 \} \right] \\ & = -\frac{3}{V} \left[a(\overline{x^6} - \overline{x^4} \cdot \overline{x^2}) + b\{ \overline{x^4} - (\overline{x^2})^2 \} \right] \end{aligned} \quad (27)$$

$$\begin{aligned} \text{and } \left(\frac{\partial s_1}{\partial V}\right)_T & \left[-\frac{a}{s_1} \{ \overline{x^6} - (\overline{x^4})^2 \} - \frac{bB}{Bs_1 + Ds_2} (\overline{x^6} - \overline{x^4} \cdot \overline{x^2}) \right] \\ & + \left(\frac{\partial s_2}{\partial V}\right)_T \left[\frac{4}{5} - \frac{bD}{Bs_1 + Ds_2} (\overline{x^6} - \overline{x^4} \cdot \overline{x^2}) \right] \\ & = -\frac{3}{V} \left[a\{ \overline{x^6} - (\overline{x^4})^2 \} + b(\overline{x^6} - \overline{x^4} \cdot \overline{x^2}) \right]. \end{aligned} \quad (28)$$

These equations can be solved for $(\partial s_1/\partial V)_T$ and $(\partial s_2/\partial V)_T$. By differentiating (8) and (9) with respect to temperature, we get a similar pair of equations from which $(\partial s_1/\partial T)_V$ and $(\partial s_2/\partial T)_V$ can be evaluated. Substituting these quantities in (23), (26) and using (24) and (25) the specific heat at constant pressure and the isothermal compressibility of the nematic phase can be evaluated theoretically provided the contributions due to disorder are known.

4. Application of the Theory to *p*-azoxyanisole

Para-azoxyanisole is undoubtedly the most extensively studied of the nematic compounds. Its molecular orientation parameter

s_1 has been determined over a wide temperature range by several methods: from birefringence,^{6,8} nuclear magnetic resonance,⁵ electron spin resonance,²⁶ infrared,²⁷ ultraviolet²⁸ and diamagnetic anisotropy^{29,5} studies. Measurements have also been made of its latent heat³⁰⁻³³ and volume change⁴ at the nematic isotropic transition point, and of its density,⁴ specific heat^{30,31} and ultrasonic velocity³⁴⁻³⁶ in the liquid crystalline and liquid phases. We shall now apply the theory in detail to this compound, evaluate its thermodynamic properties and compare them with the experimental data.

The following integrals were necessary for the theoretical calculations:

$$\int_0^1 x^{2n} \exp(ax^4 + bx^2) dx, \quad n = 0, 1, 2, 3, 4.$$

Applying Simpson's method, the five integrals were evaluated numerically with the aid of a computer for ranges of values of a and b in steps of 0.1. A suitable interpolation procedure was employed for intermediate values when required. The appropriate values of a and b were chosen that gave the correct magnitude for $\Delta V/V$ according to (21) and also led to a satisfactory curve for s_1 as a function of temperature. Precise density determinations at different temperatures in the liquid crystalline and liquid phases of *p*-azoxyanisole have been made by Maier and Saupe,⁴ who have also reported a value of $\Delta V/V = 0.0035$. Using the density measurements (and the empirical formula for the density as a function of temperature proposed in a previous paper²² for interpolation and extrapolation wherever necessary) the theoretical curve for s_1 was calculated using the equilibrium conditions (14) and (15). The constants of the potential function for *p*-azoxyanisole which give a value of $\Delta V/V = 0.0035$ and a good fit for the s_1 curve were found to be

$$\begin{aligned} B &= 4.5448 \times 10^{-6} \text{ erg cm}^9, \\ D &= -1.0460 \times 10^{-6} \text{ erg cm}^9. \end{aligned}$$

The theoretical curve for s_1 along with recent experimental

values is shown in Fig. 1 and it can be seen that the fit is satisfactory. The broken curve represents the variation predicted by the theory of Maier and Saupe.

To evaluate the heat of transition from (22) we require the coefficient of thermal expansion α of the liquid, which has been measured by Maier and Saupe,⁴ and the isothermal compressibility β which has been evaluated by Kapustin and Bykova^{3a} from their ultrasonic velocity measurements. Both α and β

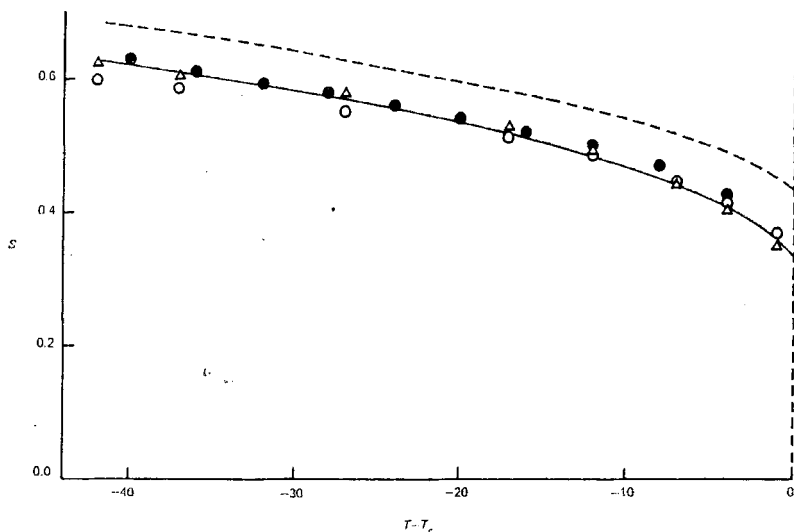


Figure 1. The long range orientational order parameter s_1 as a function of temperature in *p*-azoxyanisole. ——— present theory; - - - - - theory of Maier and Saupe; ● experimental data of Glarum and Marshall²⁶ (from ESR measurements); △ data of Saupe⁶ (from optical measurements); ○ data of Chandrasekhar and Madhusudana⁸ (from optical measurements).

exhibit anomalous behaviour in the liquid phase just above the transition point. The values decrease rapidly at first as the temperature rises, and then gradually become linear functions of temperature as in normal liquids. A reasonable extrapolation of these quantities to lower temperatures from the linear region is possible. The extrapolated values correspond to the

contributions of the completely disordered system in our theory. Using the extrapolated values of $\alpha = 7.52 \times 10^{-4}$ per degree and $\beta = 65.7 \times 10^{-12}$ cm²/dyne at T_c and substitution in (22) gives $H = 1230$ joules/mol. The experimental values reported by the different authors for the latent heat required to convert the liquid crystal into the normal liquid are set out below :

Arnold ³⁰	690 joules/mol.
Barrall <i>et al.</i> ³¹	740 joules/mol.
Sakevich ³²	780 joules/mol.
Chow and Martire ³³	760 joules/mol.

Although the different determinations do not agree well, it is clear that the theoretical value is significantly higher.

The specific heat at constant pressure and the isothermal compressibility of the liquid crystal have been evaluated for one temperature from (23), (24), (25) and (26). The contribution of C_p due to disorder was obtained by extrapolating Arnold's linear relation for the normal liquid. At $T_c - 1$, the calculated C_p and β are 574.1 joules/mol deg and 135.3×10^{-12} cm²/dyne as compared with the experimental values of 606.2 joules/mol deg¹⁸ and 88.2×10^{-12} cm²/dyne²⁴ respectively. The specific heat is in fair agreement, but the compressibility is considerably higher than the observed data.

The reason for the discrepancy between theory and experiment is readily understood. We have worked out the orientational potential energy of a single molecule in the field due to its surrounding medium disregarding entirely the correlations between neighbouring molecules, which undoubtedly exist not only in the liquid crystal but also in the liquid. As far as the "excess" properties associated with long-range order are concerned, a simple though not rigorous method of taking into account the influence of local ordering is to reduce the effective number of independent molecular entities, i.e., to replace the Avogadro number N by N/n , where n is a correction factor. It is seen from (8), (14), (15) and (21) that this does not affect the calculations of s_1 and $\Delta V/V$, but it does alter the latent heat of transition, specific

heat and compressibility given by (22), (23) and (26) respectively. The results for H are set out below:

	Theoretical				Experimental
	$n = 1$	$n = 2$	$n = 3$	$n = 4$	
H	1230	798	655	583	690, 740, 780, 760 joules/mol.

The agreement is much better for $n = 2$ and 3 than for $n = 1$ and 4. The theoretical curves for the specific heat and the compressibility are shown in Figs. 2 and 3 for $n = 2$ and 3. The dashed lines are the contributions due to disorder obtained by extrapolating the values for the normal liquid. H and β are rather sensitive to n , but not C_p . This is because an increase of n decreases C_v as well as β , so that C_p changes only slightly. Owing to the scatter in the experimental data it is not possible to estimate n precisely, but a value slightly less than 3 appears

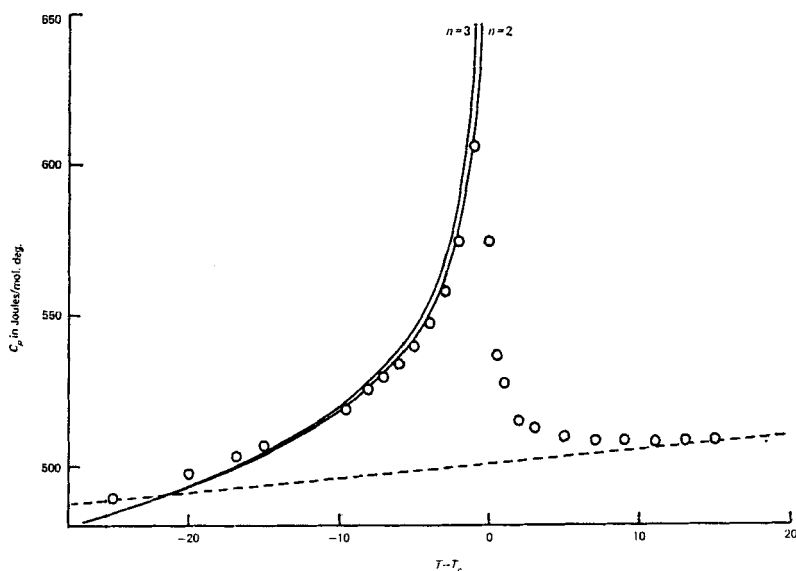


Figure 2. Specific heat at constant pressure of *p*-azoxyanisole in nematic phase as a function of temperature. ——— theoretical variation; - - - - - contribution due to disorder extrapolated from the data for normal liquid; ○ experimental values of Arnold.³⁰

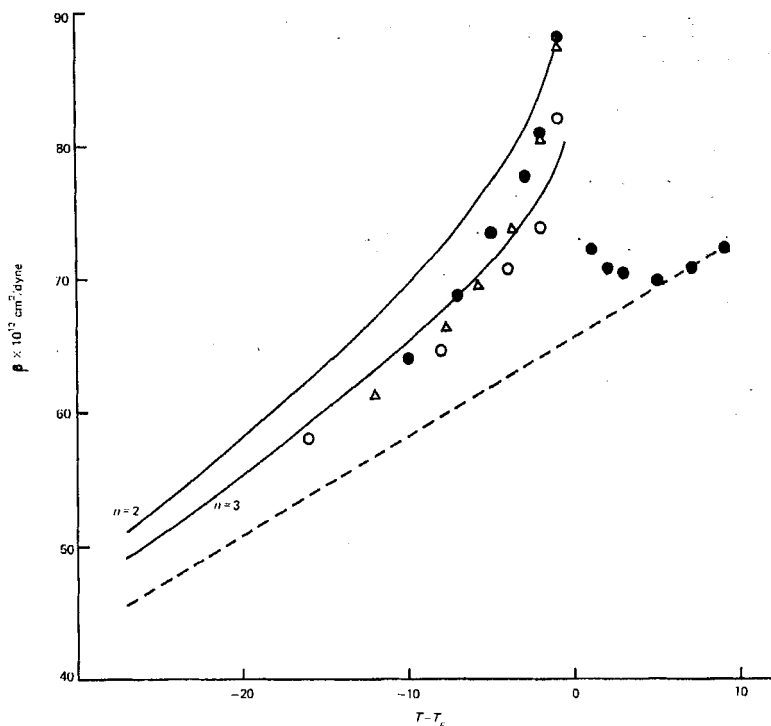


Figure 3. Isothermal compressibility of *p*-azoxyanisole in the nematic phase as a function of temperature. ——— theoretical variation; - - - - - contribution due to disorder extrapolated from the data for the normal liquid; ○ experimental data of Gabrielli and Verdini³⁴; △ data of Hoyer and Nolle³⁵; ● data of Kapustin and Bykova.³⁶

to give the best over-all fit. The observed variation of β with temperature is somewhat faster than given by theory. Recalling that β involves the second differential of the energy with respect to volume, the slight difference in the rate of variation is at least partly due to the approximation made that the potential energy has an average V^{-3} dependence.

5. The Magnetic Birefringence in the Liquid Phase

The factor n may be interpreted crudely as the effective number of *perfectly aligned* molecules in a cluster. The magnetic bire-

fringe in the liquid phase provides a means of estimating n approximately. If χ_{\parallel} and χ_{\perp} are the principal diamagnetic susceptibilities of the molecule and α_{\parallel} and α_{\perp} its principal optical polarizabilities, the corresponding values for the cluster may be taken to be $n\chi_{\parallel}$, $n\chi_{\perp}$ and $n\alpha_{\parallel}$, $n\alpha_{\perp}$. Applying the standard theory (see, for example, Beams³⁷), it is readily shown that the Cotton-Mouton constant

$$C = \frac{4\mu}{\lambda H^2} = \frac{2\pi\nu n}{15kT\mu\lambda} \left(\frac{\mu^2 + 2}{3} \right)^2 (\chi_{\parallel} - \chi_{\perp})(\alpha_{\parallel} - \alpha_{\perp}), \quad (29)$$

where ν is the number of molecules/cc and μ the refractive index of the liquid in the absence of the magnetic field.

The magnetic birefringence of *p*-azoxyanisole in the liquid phase has been measured at different temperatures relative to that of nitrobenzene by Zadoc-Kahn.³⁸ At the highest temperature ($T_c + 52^\circ$), where the magnetic behaviour is that of a normal liquid, C is 2.7 times the value for nitrobenzene for $\lambda 5780$. The principal diamagnetic susceptibilities of the crystal, which have been determined by Foex,²⁹ give $(\chi_{\parallel} - \chi_{\perp}) = 10.4 \times 10^{-30}$ cc. (The degree of orientational order in *p*-azoxyanisole in the nematic phase derived from Foex's data is about 10% higher than that obtained by other methods,⁵ suggesting that his value of the diamagnetic anisotropy may be a little low. The value of n calculated below may thus be a slight over-estimate). Substituting C for nitrobenzene = 235×10^{-14} , $\alpha_{\parallel} - \alpha_{\perp} = 35.4 \times 10^{-24}$ (see reference 8), $\mu = 1.620$ and the density $\rho = 1.102$ (μ and ρ being obtained by extrapolating the values at lower temperatures), n turns out to be 4.0.

It is gratifying to note that n is of the same order as that estimated from the thermodynamic theory.

To summarize: starting from an intermolecular potential function of the form

$$U_i = -V^{-3} \left[B \left(\frac{3 \overline{\cos^2 \theta} - 1}{2} \cdot \frac{3 \cos^2 \theta_i - 1}{2} \right) + D \left(\frac{3 \overline{\cos^2 \theta} - 1}{2} \cdot \frac{5 \cos^4 \theta_i - 1}{4} + \frac{5 \overline{\cos^4 \theta} - 1}{4} \cdot \frac{3 \cos^2 \theta_i - 1}{2} \right) \right]$$

based on dispersion and repulsion forces, a theory is developed of the nematic liquid crystalline phase. Putting $B = 4.5448 \times 10^{-6}$, $D = -1.0460 \times 10^{-6}$ and $n \sim 3$, where n is a numerical factor to allow for the effect of short-range order, the following physical properties have been derived theoretically for *p*-azoxyanisole which are in good quantitative agreement with the experimental data:

- (i) the long-range orientational order parameter $s_1 = \frac{1}{2}(3 \overline{\cos^2 \theta} - 1)$ and its variation with temperature;
- (ii) the volume change at the nematic-liquid transition point;
- (iii) the latent heat of transition to the liquid phase;
- (iv) the specific heat at constant pressure and its variation with temperature;
- (v) the isothermal compressibility and its variation with temperature.

The magnetic birefringence of *p*-azoxyanisole in the liquid phase confirms the existence of short-range order.

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