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Molecular Statistical Theory of Nematic Liquid Crystals

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Assuming a model based on permanent dipole–dipole, dispersion, induction and repulsion forces, the potential energy of a molecule in a nematic liquid crystal is derived as a function of its orientation. Analysis of the temperature variation of the degree of orientational order in *p*-azoxyanisole (PAA) and *p*-azoxyphenetole (PAP) indicates that the permanent dipole interactions are relatively unimportant. Making use of a mean field approximation, a statistical theory of long-range orientational order is developed and the thermodynamic properties of the ordered system are derived relative to those of the completely disordered one. Application of the theory to PAA and PAP shows conclusively that a certain degree of short-range orientational order is present in the liquid phase. Using just three parameters for each compound, *viz.* the two constants of the potential function and a numerical factor to allow for short range order, the following physical properties have been evaluated which are in quantitative agreement with the experimental data: the long-range orientational order parameter, specific heat and compressibility as functions of temperature in the liquid crystalline range, the latent heat and volume change at the nematic–isotropic transition point. The magnetic birefringence of the liquid phase affords an independent estimate of the short range order which supports the previous calculations.

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 is conveniently defined by the parameter

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

where θ is the angle which the long axis of the molecule makes with the uniaxial direction of the liquid crystal (Zwetkoff, 1942). 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 decreases gradually with rise of temperature. At the nematic–isotropic point, a first-order transition takes place and s drops catastrophically to 0. Other properties associated with orientational order, such as the specific heat and compressibility, exhibit anomalies in the neighbourhood of the transition.

The part played by permanent electric dipoles in determining liquid crystalline behaviour has been the subject of many investigations. Indeed, the first attempt to give a theory of the optical anisotropy of the liquid crystalline phase was based on permanent dipolar interactions (Born, 1916; Born & Stumpf, 1916). However, the theory predicts that the transition from the isotropic to the liquid-crystalline phase takes place at the critical temperature corresponding to the polarization catastrophe, which, as is well known from the work of Onsager (1936), is not expected to occur. The early experiments to detect free charges on the surface of the liquid crystal, carried out with a view to testing Born's dipole theory, yielded negative results (Szivessy, 1925, 1926) but the existence of the hysteresis loop and of polarized domains has been reported recently (Williams, 1963; Elliot & Gibson, 1965; Kapustin & Vistin, 1965; Heilmeier, 1966). In the light of these observations we attempted a semi-empirical theory of the birefringence of nematic liquid crystals assuming that the interactions are predominantly dipolar (Chandrasekhar & Krishnamurti, 1966). The complete theory, taking into account all types of interactions, which we shall discuss in this paper, proves that this assumption is not valid. Moreover, chemical evidence seems to be quite conclusive that dipoles do not contribute much to the orientational potential energy. In particular, the extensive studies of Gray (1962, 1967) on mesomorphic behaviour and chemical constitution have shown that substituents of widely varying polarities produce only minor changes in the thermodynamic properties of this phase.

Maier & Saupe (1958, 1959, 1960) and Saupe & Maier (1961) developed a statistical theory of orientational order assuming an intermolecular potential function based on dispersion forces, which leads to a universal curve for s as a function of $TV^2/T_cV_c^2$, where T, V are the temperature and molar volume in the nematic phase, T_c, V_c the corresponding values at the nematic–isotropic transition point. Although the predicted variation agrees with the experimental data for some compounds, significant deviations from the common curve have been observed in many cases and it is clear that the theory in its present form cannot be expected to give a satisfactory quantitative description of the nematic state (Saupe, 1968; see also Chen, James & Luckhurst, 1969; Chandrasekhar & Madhusudana, 1969).

In this paper we develop a theory of nematic liquid crystals taking into account permanent dipole–dipole, dispersion, induction and repulsion forces. The theory reduces to that of Maier & Saupe when the potential function is limited to the principal term of the dispersion energy. Some results of the theory have been published earlier (Chandrasekhar, Krishnamurti & Madhusudana, 1969; Chandrasekhar & Madhusudana, 1970) but we give here a more detailed and rigorous treatment, and also discuss its application to two typical nematic compounds, *viz.* *p*-azoxyanisole and *p*-azoxyphenetole.

The orientational potential energy of the molecule

Recent X-ray studies (Chistyakov & Chaikovskii, 1968; Kosterin & Chistyakov, 1968) have established that the (positional) molecular distribution function in nematic liquid crystals is cylindrically symmetric. If α_{rij}, β_{rij}, γ_{rij} are the direction cosines of the intermolecular vector $\mathbf{r}_{ij}$ with respect to a space fixed coordinate system XYZ, Z being the uniaxial direction of the medium, we may write

$$\left.\begin{aligned}
&\overline{\alpha^2_{rij}} + \overline{\beta^2_{rij}} + \overline{\gamma^2_{rij}} = 1\\
&\overline{\alpha^2_{rij}} = \overline{\beta^2_{rij}} \neq \overline{\gamma^2_{rij}}, \text{ or } \overline{\alpha^2_{rij}} = \overline{\beta^2_{rij}} = \tfrac{1}{2}(1-\overline{\gamma^2_{rij}})\\
&\overline{\alpha_{rij}\beta_{rij}} = \overline{\beta_{rij}\gamma_{rij}} = \overline{\gamma_{rij}\alpha_{rij}} = 0\\
&\overline{\alpha^4_{rij}} = \overline{\beta^4_{rij}} \neq \overline{\gamma^4_{rij}}\\
&\overline{\alpha^2_{rij}\beta^2_{rij}} \neq \overline{\beta^2_{rij}\gamma^2_{rij}} = \overline{\gamma^2_{rij}\alpha^2_{rij}}, \textit{ etc.}
\end{aligned}\right\} \quad (1)$$

Permanent dipole–dipole interactions

We shall assume that the dipole moment of the molecule is directed along its long axis. This assumption is justifiable since nuclear magnetic resonance (Lippmann, 1957; see also Maier & Saupe, 1959) indicates that the molecule rotates about its long axis, so that only the component of the dipole moment along this axis is effective.

The interaction energy between two identical dipoles of moment μ is given by

$$U_{ij}^{\text{dip}} = \frac{\mu^2}{r_{ij}^3}(\mathbf{e}_i \,.\, \mathbf{e}_j - 3\mathbf{e}_i \,.\, \mathbf{e}_{rij}\,\mathbf{e}_j \,.\, \mathbf{e}_{rij}),$$

where $\mathbf{e}_i$, $\mathbf{e}_j$ and $\mathbf{e}_{rij}$ are the unit vectors of the dipoles and $\mathbf{r}_{ij}$ respectively. Therefore

$$U_{ij}^{\text{dip}} = \frac{\mu^2}{r_{ij}^3}[(\alpha_i\alpha_j+\beta_i\beta_j+\gamma_i\gamma_j)-3(\alpha_i\alpha_{rij}+\beta_i\beta_{rij}+\gamma_i\gamma_{rij}) \times(\alpha_j\alpha_{rij}+\beta_j\beta_{rij}+\gamma_j\gamma_{rij})],$$

where $\alpha_i\beta_i\gamma_i$, $\alpha_j\beta_j\gamma_j$ and $\alpha_{rij}\beta_{rij}\gamma_{rij}$ are the direction cosines of $\mathbf{e}_i$, $\mathbf{e}_j$ and $\mathbf{e}_{rij}$ respectively. Averaging over $\mathbf{r}_{ij}$, transforming to polar coordinates, *i.e.* $\alpha = \sin\theta \cos\varphi$, $\beta = \sin\theta \sin\varphi$ and $\gamma = \cos\theta$, and averaging over φ, the average potential energy per dipole pair making angles θ_i, θ_j is

$$\begin{aligned}U_{ij}^{\text{dip}} &= -\frac{\mu^2}{r_{ij}^3}(3\overline{\gamma^2_{rij}}-1)\cos\theta_i\cos\theta_j\,,\\ &= -\frac{k_1}{V}\cos\theta_i\cos\theta_j \text{ (say)}\,.\end{aligned} \quad (2)$$

Since the medium as a whole possesses uniaxial symmetry, the same expression is obviously valid even if the dipole moment is inclined to the long axis of the molecule.

For a spherically symmetric molecular distribution function $(3\overline{\gamma^2_{rij}}-1)=0$ and U_{ij}^{dip} vanishes, but if polarized domains exist, this cannot be the case.

Dispersion forces

Van der Merwe (1966*a*) has recently used an oscillator model to derive the expression for the dipole–dipole contribution to the dispersion energy between a pair of anisotropic molecules possessing cylindrical symmetry. Each molecule is associated with three mutually perpendicular dipole oscillators so that the energy involves nine interactions. We adopt this model to evaluate the average dispersion energy between a pair of molecules in the nematic assembly.

The interaction potential energy between two dipole oscillators is given by

$$V_{ij} = \frac{q^2}{r_{ij}^3}(\mathbf{r}_i \,.\, \mathbf{r}_j - 3\mathbf{r}_i \,.\, \mathbf{e}_{rij}\mathbf{r}_j \,.\, \mathbf{e}_{rij}), \quad (3)$$

where q is the charge, $\mathbf{r}_i$ and $\mathbf{r}_j$ are the position vectors of the charges with respect to their equilibrium positions and $\mathbf{e}_{rij}$ is the unit vector of $\mathbf{r}_{ij}$.

Following van der Merwe, we introduce two cartesian coordinate systems, each fixed in one of the pair of molecules, so that the axes are directed along the unit vectors $\mathbf{e}_{1i}$, $\mathbf{e}_{2i}$, $\mathbf{e}_{3i}$ and $\mathbf{e}_{1j}$, $\mathbf{e}_{2j}$, $\mathbf{e}_{3j}$ respectively, the 3-direction in both cases being fixed along the long axis of the molecule.

Hence (3) can be written as

$$V_{ij} = \frac{q^2}{r_{ij}^3}\sum_l \sum_m C_{lm}\,\zeta_{li}\,\zeta_{mj}\,,$$

where $l = 1, 2, 3$, $m = 1, 2, 3$; ζ denotes the component of the displacement vector $\mathbf{r}$ and

$$C_{lm} = \mathbf{e}_{li} \,.\, \mathbf{e}_{mj} - 3\mathbf{e}_{li} \,.\, \mathbf{e}_{rij}\mathbf{e}_{mj} \,.\, \mathbf{e}_{rij}\,.$$

When the molecules are infinitely far apart and in their ground states, their energy corresponding to the unperturbed state is

$$E_{00} = \tfrac{1}{2}h\nu_{\parallel i} + h\nu_{\perp i} + \tfrac{1}{2}h\nu_{\parallel j} + h\nu_{\perp j} = h\nu_{\parallel} + 2h\nu_{\perp}$$

where $\nu_{\parallel}$ and $\nu_{\perp}$ are the frequencies of the oscillators parallel and perpendicular to the length of the molecule. As the molecules approach each other, the system is perturbed owing to the effect of V_{ij}. Since V_{ij} is an odd function of both ζ_{li} and ζ_{mj}, the first order perturbation energy vanishes and the second order perturbation energy, which is the dispersion energy, turns out as

$$U_{ij}^{\rm disp}(d,d)=-\left(\frac{q^2}{r_{ij}^3}\right)^2\sum_{n_i}\sum_{n_j}\frac{\left|\sum_l\sum_m C_{lm}(\zeta_{li}\,\zeta_{mj})_{n_in_j}\right|^2}{(E_{n_in_j}-E_{oo})},$$

where n_i and n_j stand for the triplets of quantum states of the two oscillators. For a linear harmonic oscillator, at most one term survives having a non-zero matrix element $(0|\zeta|1)=(2\xi)^{-1/2}$ connecting its ground state with its first excited state; all other terms $(0|\zeta|n)$ vanish. Here $\xi=\sigma/h\nu$, σ being the stiffness constant.

Using the symbols

$$(\perp,\perp)=(8h\nu_\perp\xi_\perp{}^2)^{-1},$$
$$(\perp,\|)=\{4h(\nu_\perp+\nu_\parallel)\xi_\perp\xi_\parallel\}^{-1},$$
$$(\|,\|)=(8h\nu_\parallel\xi_\parallel{}^2)^{-1},$$

it can be shown that

$$U_{ij}^{\rm disp}(d,d)=-\left(\frac{q^2}{r_{ij}^3}\right)^2[(C_{11}^2+C_{12}^2+C_{21}^2+C_{22}^2)\ (\perp,\perp)$$
$$+(C_{13}^2+C_{23}^2+C_{31}^2+C_{32}^2)(\perp,\|)+C_{33}^2(\|,\|)]\,.$$

Averaging over $\mathbf{r}_{ij}$ as before, introducing polar coordinates and averaging over φ, the average potential energy due to the dipole–dipole contribution to the dispersion interactions per pair of molecules making angles θ_i, θ_j is

$$U_{ij}^{\rm disp}(d,d)=-\frac{g}{r_{ij}^6}\Big[\Big\{\tfrac{9}{2}\,\overline{\alpha_{rij}^4}+\tfrac{9}{2}\overline{\alpha_{rij}^2\beta_{rij}^2}+\tfrac{3}{2}\overline{\gamma_{rij}^2}-1)$$
$$\times(\chi_\parallel^{3/2}+\frac{4\chi_\parallel\chi_\perp}{\chi_\parallel^{1/2}+\chi_\perp^{1/2}}+\chi_\perp^{3/2})+(9\overline{\gamma_{rij}^4}-6\overline{\gamma_{rij}^2}$$
$$+18\overline{\alpha_{rij}^2\gamma_{rij}^2}+1)\chi_\perp^{3/2}+36\overline{\alpha_{rij}^2\gamma_{rij}^2}\frac{\chi_\parallel\chi_\perp}{\chi_\parallel^{1/2}+\chi_\perp^{1/2}}\Big\}$$
$$+(\cos^2\theta_i+\cos^2\theta_j)\Big\{(9\overline{\alpha_{rij}^4}$$
$$+9\overline{\alpha_{rij}^2\beta_{rij}^2}+3\overline{\gamma_{rij}^2}-2)$$
$$\times\left(\frac{\chi_\perp^{3/2}-\chi_\parallel^{3/2}}{2}\right)+(9\overline{\gamma_{rij}^4}-6\overline{\gamma_{rij}^2}+1)$$
$$\times\left(\frac{2\chi_\parallel\chi_\perp}{\chi_\parallel^{1/2}+\chi_\perp^{1/2}}-\chi_\perp^{3/2}\right)+9\overline{\alpha_{rij}^2\gamma_{rij}^2}$$
$$\times\left(\chi_\parallel^{3/2}-\frac{2\chi_\parallel\chi_\perp}{\chi_\parallel^{1/2}+\chi_\perp^{1/2}}\right)\Big\}+\cos^2\theta_i\cos^2\theta_j\,(\tfrac{9}{2}\overline{\alpha_{rij}^4}$$
$$+\tfrac{9}{2}\,\overline{\alpha_{rij}^2\beta_{rij}^2}+9\overline{\gamma_{rij}^4}-\tfrac{9}{2}\overline{\gamma_{rij}^2}-18\overline{\alpha_{rij}^2\gamma_{rij}^2})\Big((\chi_\parallel^{3/2}$$
$$-\frac{4\chi_\parallel\chi_\perp}{\chi_\parallel^{1/2}+\chi_\perp^{1/2}}+\chi_\perp^{3/2}\Big)\Big]=-\frac{1}{V^2}[k_2+k_2'(\cos^2\theta_i$$
$$+\cos^2\theta_j)+k_2''\cos^2\theta_i\cos^2\theta_j]\ (\text{say})\,, \tag{4}$$

where $g=\dfrac{qh}{16\pi}\left(\dfrac{f}{m}\right)^{1/2}$, f is the oscillator strength, m the mass of the electron. We have used the relations $\nu_\parallel=\dfrac{q}{2\pi}\left(\dfrac{f}{m\chi_\parallel}\right)^{1/2}$, *etc.* where χ is the polarizability.

Extending this model, van der Merwe (1966*b*) has also evaluated the dipole–quadrupole contribution to the dispersion energy. Proceeding along the same lines, we have worked out the average energy per pair of molecules in a nematic assembly, but the expression is so lengthy that we shall not present it in detail. We shall merely state that its functional dependence on the orientation is represented by the relation

$$U_{ij}^{\rm disp}(d,q)=-\frac{1}{V^{8/3}}[k_3+k_3'(\cos^2\theta_i+\cos^2\theta_j)$$
$$+k_3''\cos^2\theta_i\cos^2\theta_j+k_3'''(\cos^4\theta_i+\cos^4\theta_j)$$
$$+k_3''''\ (\cos^4\theta_i\cos^2\theta_j+\cos^2\theta_i\cos^4\theta_j)]\,. \tag{5}$$

We neglect the quadrupole–quadrupole contribution.

Induction effect

$$U^{\rm ind}(\mu_i\chi_j)=-\frac{\mu_i^2}{2}[\chi_{\parallel j}(C_{33}^2)+\chi_{\perp j}(C_{32}^2+C_{31}^2)]\ ;$$

similarly,

$$U^{\rm ind}(\mu_j\chi_i)=-\frac{\mu_j^2}{2}[\chi_{\parallel i}(C_{33}^2)+\chi_{\perp i}(C_{23}^2+C_{13}^2)]\,.$$

$$\therefore U_{ij}^{\rm ind}=U^{\rm ind}(\mu_i\chi_j)+U^{\rm ind}(\mu_j\chi_i)$$
$$=-\frac{\mu^2}{2r_{ij}^6}[\{(9\overline{\alpha_{rij}^4}+9\overline{\alpha_{rij}^2\beta_{rij}^2}+3\overline{\gamma_{rij}^2}-2)\ (\chi_\parallel+\chi_\perp)$$
$$+18\overline{\alpha_{rij}^2\gamma_{rij}^2}\chi_\perp\}+(\cos^2\theta_i+\cos^2\theta_j)\{9\overline{\alpha_{rij}^2\gamma_{rij}^2}(\chi_\parallel-\chi_\perp)$$
$$-(9\overline{\alpha_{rij}^4}+9\overline{\alpha_{rij}^2\beta_{rij}^2}+3\overline{\gamma_{rij}^2}-2)\chi_\parallel+(9\overline{\gamma_{rij}^4}-6\overline{\gamma_{rij}^2}+1)\chi_\perp\}$$
$$+\cos^2\theta_i\cos^2\theta_j\{(9\overline{\alpha_{rij}^4}+9\overline{\alpha_{rij}^2\beta_{rij}^2}+3\overline{\gamma_{rij}^2}-2)\ (\chi_\parallel-\chi_\perp)$$
$$+(9\overline{\gamma_{rij}^4}-18\overline{\alpha_{rij}^2\gamma_{rij}^2}-6\overline{\gamma_{rij}^2}+1)\ (\chi_\parallel-2\chi_\perp)\}]$$
$$=-\frac{1}{V^2}[k_4+k_4'(\cos^2\theta_i+\cos^2\theta_j)$$
$$+k_4''\cos^2\theta_i\cos^2\theta_j]\ (\text{say})\,. \tag{6}$$

Repulsion energy

To evaluate the orientation dependent repulsion energy we consider a simplified model consisting of identical linear molecules each of which is replaced by three centres of repulsion, two near the ends of the molecule and one at its centre so that again there will be nine interactions per pair of molecules. Most of the common nematic substances (*e.g.* *p*-azoxyanisole, *p*-azoxyphenetole) have molecules which are very nearly symmetrical about the centre and, therefore, we shall assume that the centres of repulsion near the ends of the molecule are identical but different from that at the middle.

We denote the repulsion centres at the middle of the molecules i and j by C_{1i}, C_{1j} and those at the ends by C_{2i}, C_{3i} and C_{2j}, C_{3j}. Let C_{1i} be chosen as the origin of the coordinate system so that $C_{1i}C_{1j}=\mathbf{r}_{ij}$, and let $C_{1i}C_{2i}=C_{1j}C_{2j}=L$. The coordinates of the six repulsion centres are:

$$C_{1i}(0,0,0);\ C_{2i}(L\alpha_i, L\beta_i, L\gamma_i);$$
$$C_{3i}(-L\alpha_i, -L\beta_i, -L\gamma_i);$$
$$C_{1j}(r_{ij}\alpha_{rij}, r_{ij}\beta_{rij}, r_{ij}\gamma_{rij});$$
$$C_{2j}(r_{ij}\alpha_{rij}+L\alpha_j, r_{ij}\beta_{rij}+L\beta_j, r_{ij}\gamma_{rij}+L\gamma_j)$$

and

$$C_{3j}(r_{ij}\alpha_{rij}-L\alpha_j, r_{ij}\beta_{rij}-L\beta_j, r_{ij}\gamma_{rij}-L\gamma_j)\ .$$

We represent the centre–centre, end–end and centre–end interactions by the interaction constants a_1, b_1; a_2, b_2; and a_3, b_3 respectively. Therefore,

$$U(C_{1i}C_{1j}) = b_1 \exp(-a_1 r_{ij})\ .$$

$$\begin{aligned}U(C_{2i}C_{2j}) &= b_2 \exp(-a_2[r_{ij}^2 + 2L^2 - 2L^2\\ &\quad \times(\alpha_i\alpha_j+\beta_i\beta_j+\gamma_i\gamma_j) + 2Lr_{ij}\,\{\alpha_{rij}(\alpha_j-\alpha_i)\\ &\quad +\beta_{rij}(\beta_j-\beta_i)+\gamma_{rij}(\gamma_j-\gamma_i)\}]^{1/2})\\ &= b_2 \exp\left[-a_2 r_{ij}\left\{1+\frac{2L^2}{r_{ij}^2}-\frac{2L^2}{r_{ij}^2}f_1\right.\right.\\ &\quad \left.\left.+\frac{2L}{r_{ij}}f_2\right\}^{1/2}\right],\\ &= b_2 \exp\left[-a_2 r_{ij}\left\{1+\frac{L}{r_{ij}}f_2+\frac{L^2}{r_{ij}^2}\right.\right.\\ &\quad \times(1-f_1-\tfrac{1}{2}f_2^2+\ldots)+\frac{L^3}{r_{ij}^3}(f_1f_2-f_2+\ldots)\\ &\quad \left.\left.+\frac{L^4}{r_{ij}^4}(-\tfrac{1}{2}+f_1-\tfrac{1}{2}f_1^2+\ldots)\right\}\right],\end{aligned}$$

where $f_1 = \sum_{\alpha\beta\gamma} \alpha_i\alpha_j$ and $f_2 = \sum_{\alpha\beta\gamma} \alpha_{rij}(\alpha_j-\alpha_i)$.

We can similarly work out the other seven terms of the interaction energy. Summing all the nine terms, expanding the exponentials, averaging over $\mathbf{r}_{ij}$ and φ, and rearranging terms, it can be shown that the average repulsion energy per pair of molecules making angles θ_i, θ_j is expressible as

$$\begin{aligned}U_{ij}^{\text{rep}} &= \frac{1}{V^4}[R+R'(\cos^2\theta_i+\cos^2\theta_j)\\ &\quad +R''\cos^2\theta_i\cos^2\theta_j+R'''(\cos^4\theta_i+\cos^4\theta_j)\\ &\quad +R''''(\cos^4\theta_i\cos^2\theta_j+\cos^2\theta_i\cos^4\theta_j)+\ldots]\ .\end{aligned} \tag{7}$$

In general, we may characterize the molecule by $(2n+1)$ centres of repulsion and work out the orientational potential energy in an analogous manner. It is readily shown that the functional dependence on θ_i, θ_j would still remain the same. We have assumed that the average repulsion energy varies as r^{-12}.

The total orientational potential energy

Assuming additivity of pair potentials and neglecting correlation effects, the average interaction energy per pair of molecules due to all types of forces is obtained by adding (2), (4), (5), (6) and (7):

$$\begin{aligned}U_{ij} = -\ &\left[\left(\frac{k_2+k_4}{V^2}+\frac{k_3}{V^{8/3}}-\frac{R}{V^4}\right)+\frac{k_1}{V}\cos\theta_i\cos\theta_j\right.\\ &+\left(\frac{k_2'+k_4'}{V^2}+\frac{k_3'}{V^{8/3}}-\frac{R'}{V^4}\right)(\cos^2\theta_i+\cos^2\theta_j)\\ &+\left(\frac{k_2''+k_4''}{V^2}+\frac{k_3''}{V^{8/3}}-\frac{R''}{V^4}\right)\cos^2\theta_i\cos^2\theta_j\\ &+\left(\frac{k_3'''}{V^{8/3}}-\frac{R'''}{V^4}\right)(\cos^4\theta_i+\cos^4\theta_j)\\ &+\left(\frac{k_3''''}{V^{8/3}}-\frac{R''''}{V^4}\right)(\cos^4\theta_i\cos^2\theta_j+\cos^2\theta_i\cos^4\theta_j)\\ &\left.+\ \ldots\ .\right].\end{aligned} \tag{8}$$

The total interaction energy of the molecule i with all its neighbours j is therefore

$$\begin{aligned}U_i &= \sum_j U_{ij}\\ &= -(U_0+U_1\cos\theta_i+U_2\cos^2\theta_i\\ &\quad +U_4\cos^4\theta_i+\ldots)\ ,\end{aligned} \tag{9}$$

where

$$\begin{aligned}U_0 = &\left[\sum_j\left(\frac{k_2+k_4}{V^2}+\frac{k_3}{V^{8/3}}-\frac{R}{V^4}\right)\right]\\ &+\left[\sum_j\left(\frac{k_2'+k_4'}{V^2}+\frac{k_3'}{V^{8/3}}-\frac{R'}{V^4}\right)\cos^2\theta_j\right]\\ &+\left[\sum_j\left(\frac{k'''}{V^{8/3}}-\frac{R'''}{V^4}\right)\cos^4\theta_j\right]+\ldots,\end{aligned}$$

$$U_1 = \sum_j \frac{k_1}{V}\cos\theta_j\ ,$$

$$\begin{aligned}U_2 = &\left[\sum_j\left(\frac{k_2'+k_4'}{V^2}+\frac{k_3'}{V^{8/3}}-\frac{R'}{V^4}\right)\right]\\ &+\left[\sum_j\left(\frac{k_2''+k_4''}{V^2}+\frac{k_3''}{V^{8/3}}-\frac{R''}{V^4}\right)\cos^2\theta_j\right]\\ &+\left[\sum_j\left(\frac{k_3''''}{V^{8/3}}-\frac{R''''}{V^4}\right)\cos^4\theta_j\right]+\ldots,\end{aligned}$$

etc.

We have already referred to the chemical evidence for the relatively minor role played by the permanent dipoles in determining the stability of the nematic phase. We shall now make an independent estimate of the relative importance of the dipole–dipole term.

Estimate of the permanent dipolar contribution

Let A, B, C be the principal polarizabilities of a molecule referred to its principal axes $X'Y'Z'$. Let XYZ be the fixed coordinate system, Z being so chosen as to coincide with the optic axis of the medium. If E_Z and E_X represent the components of the electric vector of the incident light wave, then the induced moments P_z and P_x are given by

$$\left.\begin{aligned} P_z &= E_Z\,(A\cos^2 ZX' + B\cos^2 ZY' \\ &\quad + C\cos^2 ZZ')\,, \\ P_x &= E_X\,(A\cos^2 XX' + B\cos^2 XY' \\ &\quad + C\cos^2 XZ')\,, \end{aligned}\right\} \qquad (10)$$

where

$$\begin{aligned} \cos^2 ZX' &= \sin^2\theta\cos^2\psi\,, \\ \cos^2 ZY' &= \sin^2\theta\sin^2\psi\,, \\ \cos^2 ZZ' &= \cos^2\theta\,, \\ \cos^2 XX' &= (\cos\psi\cos\varphi\cos\theta - \sin\psi\sin\varphi)^2, \\ \cos^2 XY' &= (-\sin\psi\cos\varphi\cos\theta - \cos\psi\sin\varphi)^2, \\ \cos^2 XZ' &= \sin^2\theta\cos^2\varphi\,, \end{aligned}$$

θ, φ, ψ being the Eulerian angles defining the orientations of $X'Y'Z'$ with respect to XYZ.

To evaluate the polarizabilities χ_z and χ_x, it is necessary to average over all possible orientations taking into account the Boltzmann factor involving the potential energy of the molecule given by (9). Therefore

$$\chi_z = \frac{\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi} P_z \exp\left(-\frac{U}{kT}\right)\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi\,\mathrm{d}\psi}{\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi} E_z \exp\left(-\frac{U}{kT}\right)\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi\,\mathrm{d}\psi}\,.$$

Since the molecules are rotating about their long axes ψ can take all possible values and similarly since the structure is symmetrical about the optic axis, φ can also take all possible values. Integrating over ψ and φ

$$\chi_z = \chi + (\chi_{\parallel} - \chi_{\perp})\left(\frac{2h_1^2}{45} + \frac{4h_2}{45} + \frac{8h_2^2}{945} + \frac{8h_4}{105} + \ldots\right), \qquad (11)$$

where

$$\begin{aligned} \chi_{\perp} &= \frac{A+B}{2}\,, \\ \chi_{\parallel} &= C\,, \\ \chi &= \frac{\chi_{\parallel} + 2\chi_{\perp}}{3}\,, \\ h_1 &= U_1/kT\,, \\ h_2 &= U_2/kT\,,\ \mathit{etc.} \end{aligned}$$

Similarly,

$$\chi_x = \chi - \frac{\chi_{\parallel} - \chi_{\perp}}{2}\left(\frac{2h_1^2}{45} + \frac{4h_2}{45} + \frac{8h_2^2}{945} + \frac{8h_4}{105} + \ldots\right). \qquad (12)$$

The degree of orientational order is given by (Chatelain, 1955)

$$s = \frac{\chi_z - \chi_x}{\chi_{\parallel} - \chi_{\perp}}\,.$$

$$\therefore\ s = \frac{h_1^2}{15} + \frac{2h_2}{15} + \frac{4h_2^2}{315} + \frac{4h_4}{35} + \ldots$$

$$= \frac{1}{V^2k^2T^2}\,\frac{\left(\sum_j k_i' \cos\theta_j\right)^2}{15}$$

$$+ \frac{2}{15kT}\left\{\sum_j\left(\frac{k_2'+k_4'}{V^2} + \frac{k_3'}{V^{8/3}} - \frac{R'}{V^4}\right)\right.$$

$$+ \sum_j\left(\frac{k_2''+k_4''}{V^2} + \frac{k_3''}{V^{8/3}} - \frac{R''}{V^4}\right)\cos^2\theta_j$$

$$\left. + \sum_j\left(\frac{k_3''''}{V^{8/3}} - \frac{R''''}{V^4}\right)\cos^4\theta_j + \ldots\right\} + \ldots$$

$$= \frac{\tau_1}{T^2V^2} + \frac{1}{T}\left(\frac{\tau_2}{V^2} + \frac{\tau_3}{V^{8/3}} + \frac{\tau_4}{V^4}\right)\ (\text{say})\,, \qquad (13)$$

neglecting higher order terms. The τ's involve the molecular distribution function and summations over $\cos\theta_j$ and its powers. The temperature variation of s is determined by the variation of V ($\propto \varrho^{-1}$) and the τ's. A correction could be effected for the variation of V from the thermal expansion measurements. The fractional density change over the entire mesomorphic range is 2–3%, so that we can without appreciable error assume an average correction factor of $(M/\varrho)^3$ for all the terms, M being the molecular weight.

Hence,

$$y = s\,(M/\varrho)^3 \simeq \frac{\tau_1}{T^2} + \frac{\tau_2+\tau_3+\tau_4}{T}$$

or

$$m = \frac{d\ln y}{d\ln T} = \Big[-2\tau_1T^{-2} - (\tau_2+\tau_3+\tau_4)T^{-1}$$

$$+ T^{-1}\frac{\mathrm{d}\tau_1}{\mathrm{d}T} + \frac{\mathrm{d}(\tau_2+\tau_3+\tau_4)}{\mathrm{d}T}\Big]$$

$$\times\,[\tau_1T^{-2} + (\tau_2+\tau_3+\tau_4)T^{-1}]^{-1}\,.$$

$\mathrm{d}\tau_1/\mathrm{d}T$ and $\mathrm{d}(\tau_2+\tau_3+\tau_4)/\mathrm{d}T$, which are negative (since the τ's involve summations over powers of $\cos\theta_j$), may be expected to be small at the lowest temperatures in the nematic range. Clearly, if the permanent dipole term predominates, *i.e.* $(\tau_2+\tau_3+\tau_4)$ is negligible compared with τ_1, the *minimum* value of $|m|$ is 2·0. On the other hand, if τ_1 is negligible compared to the other terms, it is 1·0. The actual value of $|m|$ at the lowest temperatures for which the data are available should give an estimate of the relative importance of the permanent dipole term.

Using the observed s (Chandrasekhar & Madhusudana, 1969) and the density data for p-azoxyanisole (PAA) (Maier & Saupe, 1960) and p-azoxyphenetole (PAP) (Bauer & Bernamont, 1936), we get

PAA	$m = -1{\cdot}04$
PAP	$m = -1{\cdot}10\,.$

The fact that $|m|$ is only slightly greater than 1·0 for both cases shows that dispersion and repulsion forces predominate in both compounds. (The induction energy has the same form as the dipole–dipole part of the dispersion energy, though its contribution may be expected to be small.) The result that the permanent dipole forces do not make an important contribution is in general agreement with the observations of Gray

(1962) and of Maier & Saupe (1959) regarding the stability of the nematic mesophase. Thus

$$U_i \simeq -V^{-3}\,(u_0+u_2\cos^2\theta_i+u_4\cos^4\theta_i+\ldots)\,. \qquad (14)$$

The mean field approximation

For the purpose of developing a theory of long-range orientational order we shall assume a mean field approximation, and express the summations in the coefficients U_0, U_2 *etc.* of (9) in terms of the mean values $\overline{\cos^2\theta}$, $\overline{\cos^4\theta}$ *etc.*; in other words, we shall neglect local variations and short range ordering.

U_{ij} given by (8) is symmetrical in i and j, so that the coefficients u_0, u_2 *etc.*, in (14) can be expressed as

$$\begin{aligned}
u_0 &= w_{00}+w_{02}\,\overline{\cos^2\theta}+w_{04}\,\overline{\cos^4\theta}+\ldots\\
u_2 &= w_{20}+w_{22}\,\overline{\cos^2\theta}+w_{24}\,\overline{\cos^4\theta}+\ldots\\
u_4 &= w_{40}+w_{42}\,\overline{\cos^2\theta}+w_{44}\,\overline{\cos^4\theta}+\ldots\\
&\textit{etc.},
\end{aligned}$$

where $w_{02}=w_{20}$, $w_{04}=w_{40}$, *etc.*, or in general $w_{mn}=w_{nm}$. We may rewrite (14) in the form

$$\begin{aligned}
U_i = -V^{-3}\Bigg[&A\left(\frac{3\,\overline{\cos^2\theta}-1}{2}+\frac{3\cos^2\theta_i-1}{2}\right)\\
&+B\left(\frac{3\,\overline{\cos^2\theta}-1}{2}\cdot\frac{3\cos^2\theta_i-1}{2}\right)\\
&+C\left(\frac{5\,\overline{\cos^4\theta}-1}{4}+\frac{5\cos^4\theta_i-1}{4}\right)\\
&+D\left(\frac{3\,\overline{\cos^2\theta}-1}{2}\cdot\frac{5\cos^4\theta_i-1}{4}\right.\\
&\left.+\frac{3\cos^2\theta_i-1}{2}\cdot\frac{5\,\overline{\cos^4\theta}-1}{4}\right)\\
&+E\left(\frac{7\,\overline{\cos^6\theta}-1}{6}+\frac{7\cos^6\theta_i-1}{6}\right)\Bigg] \qquad (15)
\end{aligned}$$

neglecting an orientation-independent term, as well as terms involving higher powers of cos θ.

We shall now suppose that A, B, …, E are independent of volume and temperature and thus disregard effects due to variations in the molecular distribution function. To this approximation, A,B,. . ., 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 (15) may vanish in the liquid phase, we may conveniently take $A=C=E=0$. The potential energy may then be written as

$$\begin{aligned}
U_i &= -V^{-3}\left[Bs_1\frac{3x_i^2-1}{2}+D\left(s_1\frac{5x_i^4-1}{4}+s_2\frac{3x_i^2-1}{2}\right)\right]\\
&= -V^{-3}(a'x_i^4+b'x_i^2+c')\ \text{(say)}\,, \qquad (16)
\end{aligned}$$

where

$$\begin{aligned}
x &= \cos\theta\,,\\
x_i &= \cos\theta_i\,,\\
s_1 &= \frac{3\overline{x^2}-1}{2}\,,\\
s_2 &= \frac{5\overline{x^4}-1}{4}\,,\\
a' &= \tfrac{5}{4}Ds_1\,,\\
b' &= \tfrac{3}{2}(Bs_1+Ds_2)\\
\text{and}\quad c' &= -\tfrac{1}{4}[2Bs_1+D(s_1+2s_2)]\,.
\end{aligned}$$

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.

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 (16).

Entropy and free energy

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

$$\begin{aligned}
\overline{x_i^2} &= \int_0^1 x_i^2\,\exp(-U_i/kT)\mathrm{d}x_i\Big/\int_0^1\exp(-U_i/kT)\mathrm{d}x_i\\
&= \int_0^1 x_i^2\,\exp(ax_i^4+bx_i^2)\mathrm{d}x_i\Big/\int_0^1\exp(ax_i^4+bx_i^2)\mathrm{d}x_i\,, \qquad (17)
\end{aligned}$$

and

$$\overline{x_i^4} = \int_0^1 x_i^4\,\exp(ax_i^4+bx_i^2)\mathrm{d}x_i\Big/\int_0^1\exp(ax_i^4+bx_i^2)\mathrm{d}x_i\,, \qquad (18)$$

where $a=\dfrac{a'}{kTV^3}$, $b=\dfrac{b'}{kTV^3}$ and $c=\dfrac{c'}{kTV^3}$; c cancels out in the numerator and denominator of (17) and (18).

Since (16) represents the mutual energy of interaction of a molecule with its neighbours, the internal energy per mole due to orientational order is evidently

$$U_s=\tfrac{1}{2}N\overline{U_i}=-\tfrac{1}{2}NkT(a\overline{x_i^4}+b\overline{x_i^2}+c)\,, \qquad (19)$$

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

$$f_i=\int_0^1\exp(ax_i^4+bx_i^2+c)\mathrm{d}x_i\,,$$

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

$$S_s = -Nk\left[\frac{\int_0^1 (ax_i^4+bx_i^2+c)\exp(ax_i^4+bx_i^2)\mathrm{d}x_i}{\int_0^1 \exp(ax_i^4+bx_i^2)\mathrm{d}x_i} - \log\int_0^1 \exp(ax_i^4+bx_i^2+c)\mathrm{d}x_i\right]$$

$$= -Nk\left[(a\overline{x_i^4}+b\overline{x_i^2}) - \log\int_0^1 \exp(ax_i^4+bx_i^2)\mathrm{d}x_i\right]. \tag{20}$$

The component of the Helmholtz free energy due to order

$$F_s = U_s - TS_s$$

$$= NkT\left[\tfrac{1}{2}(a\overline{x_i^4}+b\overline{x_i^2}-c) - \log\int_0^1 \exp(ax_i^4+bx_i^2)\mathrm{d}x_i\right]. \tag{21}$$

The equilibrium conditions

The thermodynamic condition for the equilibrium of the ordered phase is

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

$$\left(\frac{\partial F_s}{\partial s_1}\right)_{V,T} = \frac{N}{V^3}\left[\frac{B}{4}\left(3s_1\frac{\partial\overline{x_i^2}}{\partial s_1} - 3\overline{x_i^2}+1\right) + \frac{D}{4}\left(3s_2\frac{\partial\overline{x_i^2}}{\partial s_1} - \tfrac{5}{2}\,\overline{x_i^4}+\tfrac{1}{2}\right) + \frac{D}{4}\left(\tfrac{5}{2}\,s_1\frac{\partial\overline{x_i^4}}{\partial s_1} - 3\overline{x_i^2}\,\frac{\partial s_2}{\partial s_1} + \frac{\partial s_2}{\partial s_1}\right)\right]_{V,T}. \tag{22}$$

Clearly (22) vanishes when

$$\overline{x_i^2} = \frac{2s_1+1}{3} = \overline{x^2} \tag{23}$$

and

$$\overline{x_i^4} = \frac{4s_2+1}{5} = \overline{x^4}. \tag{24}$$

Similarly, it can be proved that $\left(\frac{\partial F_s}{\partial s_2}\right)_{V,T}$ vanishes under the same circumstances. Therefore, (23) and (24) represent the two conditions of equilibrium of the ordered system. Hereafter the suffix i in x_i^2, x_i^4 *etc.*, will be omitted.

Volume change and latent heat of transition

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

$$G_n = F_l(V_1, T_c) + F_s(V_1, T_c) + P_cV_1,$$

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

$$G_l = F_l(V_2, T_c) + P_cV_2$$

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

$$G_n - G_l = F_l(V_1, T_c) - F_l(V_2, T_c) + F_s(V_1, T_c) - P_c\Delta V, \tag{25}$$

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

Further

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

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

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

Since

$$\left(\frac{\partial P_l}{\partial V}\right)_{Tc} = -\frac{1}{\beta V_2},$$

where β is the isothermal compressibility of the liquid at T_c,

$$\int_{V_1}^{V_2} P_l\mathrm{d}V = \int_{V_1}^{V_2}\left(P_c - \frac{V-V_2}{\beta V_2}\right)\mathrm{d}V$$

$$= P_c\Delta V + \frac{(\Delta V)^2}{2\beta V_2}$$

$$= P_c\Delta V - \tfrac{1}{2}\Delta P\,.\,\Delta V, \tag{26}$$

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

But we know that for the nematic phase

$$P_c = P_l(V_1, T_c) + P_s(V_1, T_c), \tag{27}$$

where P_s is the contribution of the orientational order to the pressure, so that from (25), (26) and (27),

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

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

$$\Delta V = -2F_s\Big/\left(\frac{\partial F_s}{\partial V}\right)_{Tc}. \tag{28}$$

$$\left(\frac{\partial F_s}{\partial V}\right)_T = \left(\frac{\partial F_s}{\partial V}\right)_{s,T} + \left(\frac{\partial F_s}{\partial s_1}\right)_{V,T}\left(\frac{\partial s_1}{\partial V}\right)_T + \left(\frac{\partial F_s}{\partial s_2}\right)_{V,T}\left(\frac{\partial s_2}{\partial V}\right)_T, \tag{29}$$

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 (21)

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

It is easily shown from (20) that

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

Therefore, from (19)

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

Substituting in (28)

$$\frac{\Delta V}{V} = \frac{2\log\int_0^1 \exp(ax^4+bx^2)\mathrm{d}x - \left\{\frac{a}{5}(5\overline{x^4}+1)+\frac{b}{3}(3\overline{x^2}+1)\right\}}{\tfrac{3}{2}\left\{\frac{a}{5}(5\overline{x^4}-1)+\frac{b}{3}(3\overline{x^2}-1)\right\}} \tag{30}$$

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

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

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

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

$$H = T_c\left[\frac{\alpha}{\beta}\Delta V - S_s(V_1, T_c)\right] \tag{31}$$

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, *e.g.*, Bridgman, 1958) 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.

Specific heat and compressibility

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

$$C_{v_n}(T) = C_{v_l}(T) + C_{v_s}(T) ,$$

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

$$C_{v_s}(T) = \left(\frac{\partial U_s}{\partial T}\right)_V = -NkT\left[\tfrac{2}{3}\, b\frac{\partial s_1}{\partial T} + \tfrac{4}{5}\, a\frac{\partial s_2}{\partial T}\right]_V \tag{32}$$

from (19). 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

$$C_{p_n}(T) = C_{p_l}(T) + C_{v_s}(T) + T\left[\left(\frac{\alpha^2 V}{\beta}\right)_n - \left(\frac{\alpha^2 V}{\beta}\right)_l\right] . \tag{33}$$

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

$$\left(\frac{1}{\beta}\right)_n = \left(\frac{1}{\beta}\right)_l + \left(\frac{1}{\beta}\right)_s . \tag{34}$$

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 (29),

$$\begin{aligned} \left(\frac{1}{\beta}\right)_s = 3NkT\Big[&\tfrac{2}{3} b\left\{\left(\frac{\partial s_1}{\partial V}\right)_T - \frac{2s_1}{V}\right\} \\ &+ \tfrac{4}{5} a\left\{\left(\frac{\partial s_2}{\partial V}\right)_T - \frac{2s_2}{V}\right\}\Big] . \end{aligned} \tag{35}$$

Differentiating (17) and (18) with respect to volume it can be shown that

$$\begin{aligned} \left(\frac{\partial s_1}{\partial V}\right)_T &\Big[\tfrac{2}{3} - \frac{a}{s_1}(\overline{x^6} - \overline{x^4}\,.\,\overline{x^2}) - \frac{bB}{Bs_1+Ds_2} \\ &\times\{\overline{x^4} - (\overline{x^2})^2\}\Big] + \left(\frac{\partial s_2}{\partial V}\right)_T \\ &\times\left[-\frac{bD}{Bs_1+Ds_2}\{x^4 - (x^2)^2\}\right] \\ &= -\frac{3}{V}[a(\overline{x^6} - \overline{x^4}\,.\,\overline{x^2}) + b\{\overline{x^4} - (\overline{x^2})^2\}] \end{aligned} \tag{36}$$

and

$$\begin{aligned} \left(\frac{\partial s_1}{\partial V}\right)_T &\left[-\frac{a}{s_1}\{\overline{x^8} - (\overline{x^4})^2\} - \frac{bB}{Bs_1+Ds_2}(\overline{x^6} - \overline{x^4}\,.\,\overline{x^2})\right] \\ &+ \left(\frac{\partial s_2}{\partial V}\right)_T\left[\tfrac{4}{5} - \frac{bD}{Bs_1+Ds_2}(\overline{x^6} - \overline{x^4}\,.\,\overline{x^2})\right] \\ &= -\frac{3}{V}[a\{\overline{x^8} - (\overline{x^4})^2\} + b(\overline{x^6} - \overline{x^4}\,.\,\overline{x^2})]. \end{aligned} \tag{37}$$

These equations can be solved for $(\partial s_1/\partial V)_T$ and $\partial s_2/\partial V)_T$. Differentiating (17) and (18) 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 (32), (35) and using (33) and (34) 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.

Application of the theory to *p*-azoxyanisole and *p*-azoxyphenetole.

PAA and PAP are the only two compounds for which all the relevant experimental data are available for a detailed comparison with the theory, though, even for these two cases, the data reported by different authors do not agree very well. We shall now discuss the application of the theory to these compounds.

The following integrals were necessary for the theoretical calculations:

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

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.

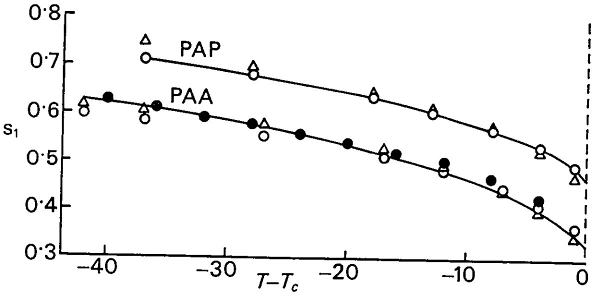

Fig. 1. The long range orientational order parameter s_1 as a function of temperature in *p*-azoxyanisole and *p*-azoxyphenetole. ——— theory; ● experimental data of Glarum & Marshall (1966); △ data of Saupe (1968); ○ data of Chandrasekhar & Madhusudana (1969).

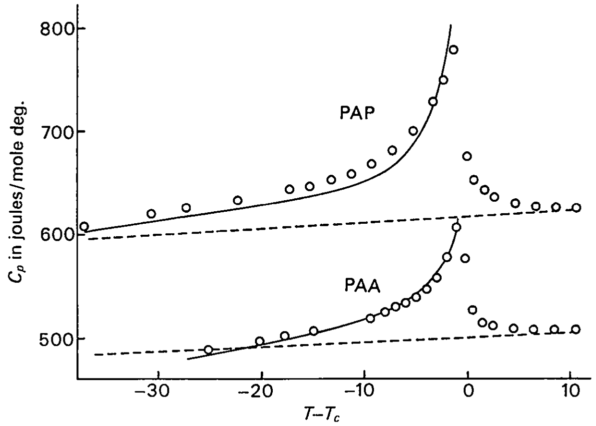

Fig. 2. Specific heat at constant pressure of *p*-azoxyanisole and *p*-azoxyphenetole as a function of temperature. ——— theory; – – – contribution due to disorder extrapolated from the data for normal liquid; ○ data of Arnold (1964).

Using the density data of Maier & Saupe (1960) for PAA, and those of Bauer & Bernamont (1936) for PAP converted to an absolute scale (see Chandrasekhar & Madhusudana, 1969), the theoretical curves for s_1 were calculated using the equilibrium conditions (23) and (24). The constants of the potential function which give good values of $\Delta V/V$ and s_1 (at one temperature) are given below:

	PAA	PAP
$B \times 10^6$ (erg.cm^9)	4·5448	5·2502
$D \times 10^6$ (erg.cm^9)	− 1·0460	0·0675
$\Delta V/V$ (theory)	0·0035	0·0061
$\Delta V/V$ (observed)	0·0035	0·0060

The theoretical curves for s_1 along with recent experimental values are shown in Fig. 1. The agreement can be seen to be satisfactory.

To evaluate H, C_p and β from (31), (33) and (34) we require α, C_p and β of the liquid phase. The latter quantities exhibit anomalous behaviour 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. An 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.

H, C_p and β so calculated are found to differ considerably from the experimental values; in particular H and β are as much as 60–80% 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 method of taking into account the influence of local ordering is to reduce the effective number of independent molecular entities, *i.e.* to replace Avogadro's number N by N/n, where n is a numerical factor. It is seen from (17), (23), (24) and (30) 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 (31), (32) and (35) respectively.

The results for H are set out below.

	n	Theoretical H (joule.mole^{-1})	Experimental H (joule.mole^{-1})
PAA	1	1230	690$^{(i)}$, 740$^{(ii)}$, 780$^{(iii)}$, 760$^{(iv)}$
	2·7	690	
PAP	1	2610	1500$^{(i)}$
	2·3	1580	

(i) Arnold (1964); (ii) Barrall, Porter & Johnson (1967); (iii) Sakevich (1967); (iv) Chow & Martire (1969).

The theoretical curves for the specific heat and compressibility are shown in Figs. 2 and 3. The dashed lines are the contributions due to disorder obtained by extrapolating the values for the normal liquid. The values of n have been chosen to give the best overall fit for H, C_p and β; H and β are very sensitive to n, but not C_p because an increase of n decreases C_v as well as β.

Thus, using just three parameters (B, D and n) for each compound the theory leads to values of s_1, C_p, $\Delta V/V$ and H in good quantitative agreement with observations. The agreement for β is also reasonably satisfactory, but it is evident that 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 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.

The magnetic birefringence of the liquid phase

The factor n may be interpreted as the effective number of *perfectly aligned* molecules in a cluster. The magnetic birefringence of the liquid provides a means of estimating n approximately. If $\eta_\parallel$ and $\eta_\perp$ are the principal diamagnetic susceptibilities of the molecule and $\chi_\parallel$ and $\chi_\perp$ its principal optical polarizabilities, the corresponding values for the cluster may be taken to be $n\eta_\parallel$, $n\eta_\perp$ and $n\chi_\parallel$, $n\chi_\perp$. Applying the standard theory, (see *e.g.*, Beams, 1932) it is readily shown that the Cotton–Mouton constant

$$C=\frac{\Delta\mu}{\lambda H^2}=\frac{2\pi\nu n}{15kT\mu\lambda}\left(\frac{\mu^2+2}{3}\right)^2(\eta_\parallel-\eta_\perp)(\chi_\parallel-\chi_\perp), \tag{38}$$

where ν is the number of molecules/cm^3 and μ the refractive index of the liquid in the absence of the magnetic field.

The magnetic birefringence of PAA in the liquid phase has been measured at different temperatures relative to that of nitrobenzene by Zadoc-Kahn (1936). At the highest temperature ($T_c+52°$), where the magnetic behaviour is that of a normal liquid, C is 2·7 times the value for nitrobenzene for λ_{5780}. The principal diamagnetic susceptibilities of the crystal, which have been determined by Foex (1933), give $(\eta_\parallel-\eta_\perp)=104\times10^{-30}$ cm^3. Substituting C for nitrobenzene $=235\times10^{-14}$ cm^{-1}.gauss^{-2} and using the other relevant data (see Chandrasekhar & Madhusudana, 1969) n turns out to be 4·0.

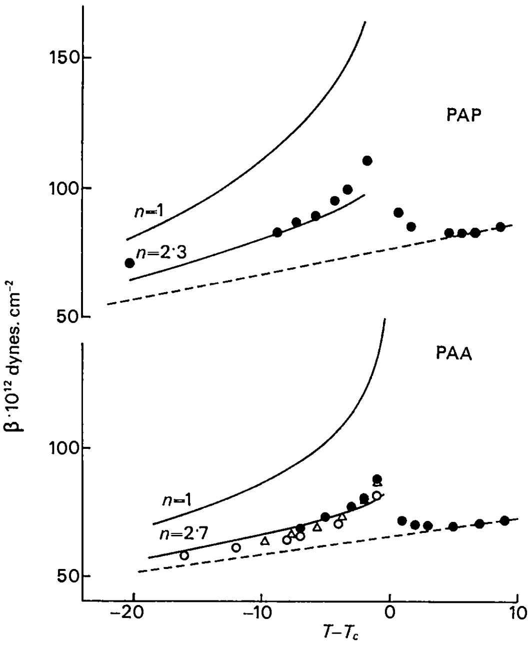

Fig. 3. Isothermal compressibility of *p*-azoxyanisole and *p*-azoxyphenetole. ——— theory; – – – contribution due to disorder extrapolated from the data for the normal liquid; ○ data of Gabrielli & Verdini (1955); △ data of Hoyer & Nolle (1956); ● data of Kapustin & Bykova (1966) and Kapustin (1970).

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

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References

Arnold, H. (1964). *Z. Phys. Chem.* **226**, 146.
Barrall, E. M., Porter, R. S. & Johnson, J. F. (1967). *J. Phys. Chem.* **71**, 895.
Bauer, E. & Bernamont, J. (1936). *J. Phys. Radium,* **7**, 19.
Beams, J. W. (1932). *Rev. Mod. Phys.* **4**, 133.
Born, M. (1916). *S. B. Phys.-math.* **25**, 614.
Born, M. & Stumpf, F. (1916). *S. B. Phys.-math.* **27**, 1043.
Bridgman, P. W. (1958). *The Physics of High Pressure.* London: Bell.
Chandrasekhar, S. & Krishnamurti, D. (1966). *Phys. Letters,* **23**, 459.
Chandrasekhar, S., Krishnamurti, D. & Madhusudana, N. V. (1969). *Mol. Cryst. Liquid Cryst.* **8**, 45.
Chandrasekhar, S. & Madhusudana, N. V. (1969). *J. Phys.* **30**, C4–24.

CHANDRASEKHAR, S. & MADHUSUDANA, N. V. (1970). *Mol. Cryst. Liquid Cryst.* **10**, 151.
CHATELAIN, P. (1955). *Bull. Soc. Franc. Minér. Crist.* **78**, 262.
CHEN, D. R., JAMES, P. G. & LUCKHURST, G. R. (1969). *Mol. Cryst. Liquid Cryst.* **8**, 71.
CHISTYAKOV, I. G. & CHAIKOVSKII, V. M. (1968). *Soviet Phys.-Cryst.* **12**, 770.
CHOW, L. C. & MARTIRE, D. E. (1969). *J. Phys. Chem.* **73**, 1127.
ELLIOT, G. & GIBSON, J. (1965). *Nature, Lond.* **205**, 995.
FOEX, M. G. (1933). *Trans. Faraday Soc.* **29**, 958.
GABRIELLI, I. & VERDINI, L. (1955). *Nuovo Cim.* **II**, 526.
GLARUM, S. H. & MARSHALL, J. H. (1966). *J. Chem. Phys.* **44**, 2884.
GRAY, G. W. (1962). *Molecular Structure and the Properties of Liquid Crystals.* London & New York: Academic Press.
GRAY, G. W. (1967). In *Liquid Crystals.* Edited by G. H. BROWN, G. J. DIENES & M. M. LABES, p. 129. New York & London: Gordon & Breach.
HEILMEIER, G. H. (1966). *J. Chem. Phys.* **44**, 644.
HOYER, W. A. & NOLLE, A. W. (1956). *J. Chem. Phys.* **24**, 803.
KAPUSTIN, A. P. (1970). Private communication.
KAPUSTIN, A. P. & BYKOVA, N. T. (1966). *Soviet Phys.-Cryst.* **11**, 297.
KAPUSTIN, A. P. & VISTIN, L. K. (1965). *Kristallografiya,* **10**, 118.
KOSTERIN, E. A. & CHISTYAKOV, I. G. (1968). *Soviet Phys.-Cryst.* **13**, 229.
LIPPMANN, H. (1957). *Ann Phys. Lpz.* **20**, 265.
MAIER, W. & SAUPE, A. (1958). *Z. Naturforsch.* **13a**, 564.
MAIER, W. & SAUPE, A. (1959). *Z. Naturforsch.* **14a**, 882.
MAIER, W. & SAUPE, A. (1960). *Z. Naturforsch.* **15a**, 287.
MERWE, A. J. VAN DER (1966*a*). *Z. Phys.* **196**, 212.
MERWE, A. J. VAN DER (1966*b*). *Z. Phys.* **196**, 332.
ONSAGER, L. (1936). *J. Amer. Chem. Soc.* **58**, 1486.
SAKEVICH, N. M. (1967). *Izv. Vysshikh Uchebn. Zavedenii, Fiz.* **10**, 52.
SAUPE, A. (1968). *Angew. Chem. Intern. Ed.* **7**, 97.
SAUPE, A. & MAIER, W. (1961). *Z. Naturforsch.* **16a**, 816.
SZIVESSY, G. (1925). *Z. Phys.* **34**, 475.
SZIVESSY, G. (1926). *Z. Phys.* **38**, 159.
WILLIAMS, R. (1963). *J. Chem. Phys.* **39**, 384.
ZADOC-KAHN, J. (1936). *Ann. Phys.* **11**, 455.
ZWETKOFF, V. (1942). *Acta Phys.-chim. URSS.* **16**, 132.

Acta Cryst. (1971). A**27**, 313

The Application of Non-Systematic Many-Beam Dynamic Effects to Structure-Factor Determination

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A method for utilizing non-systematic many-beam dynamic effects for determination of accurate relations between Fourier potentials is described. The effects which are used can be understood and described in terms of three-beam interactions; although quantitative evaluation is based on more interacting beams. The effects are most readily observed in Kikuchi patterns; experimental patterns from silicon are used as an example.

Introduction

It has been shown theoretically and experimentally by Uyeda and coworkers (Uyeda, 1968; Watanabe, Uyeda & Kogiso, 1968), that the contrast of the second-order Kikuchi line may vanish for a particular value of the acceleration voltage. This effect is due to variations in multiple-beam interactions with electron mass, and can be utilized to obtain very accurate relations between structure factors, as shown by Watanabe, Uyeda & Fukuhara (1968). The method does in a very simple way exploit dynamic effects for structure factor determination, but is limited to systematic reflexions and is dependent on high-voltage electron diffraction.

In a previous paper the present authors (Gjønnes & Høier, 1969) have studied enhancement and reduction of Kikuchi-line contrast, with particular emphasis on three-beam interactions. It was shown that a variety of contrast anomalies could be explained in terms of simple rules derived from three-beam considerations, *viz*, if the product $P=U_gU_hU_{g-h}$ of the Fourier potentials involved is positive, a weak beam, g, which is excited simultaneously with a strong beam, h, will be reduced in intensity relative to its two-beam value when the excitation error, ζ_h, of the strong beam is positive, and increased in intensity when ζ_h is negative. When P is negative, the effects are reversed with respect to the sign of ζ_h. Inclusion of more beams in the calculations will not as a rule alter the qualitative features. From this viewpoint the Uyeda–Watanabe effect can be seen as a special case of reduced intensity in a weak beam in a systematic, essentially three beam case, the excitation error of the strong beam being positive and constant along the Kikuchi line $2h$.

It was therefore found desirable to investigate intensity reduction in general, *i.e.* non-systematic, cases in