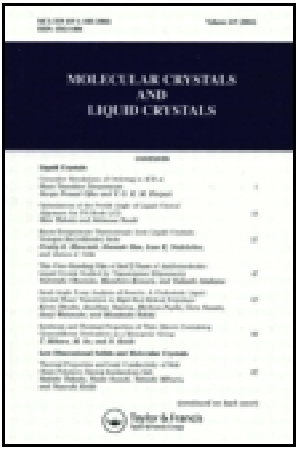

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# Discontinuity in the Properties of p-azoxyanisole at the Nematic-Isotropic Melt Phase Transition

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# Discontinuity in the Properties of *p*-azoxyanisole at the Nematic–Isotropic Melt Phase Transition

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The purpose of this communication is to present a discussion on the structural description of the nematic and the isotropic melt phases respectively of *p*-azoxyanisole based on the physical properties data available in the literature. Theories such as the " swarm ", " continuum " and " molecular statistics " for describing the nematic structure are discussed in great details in the literature.(1,2,5) Experimental data on " $\mu$ " viscosity,(2,5) " $\chi$ " magnetic susceptibility,(2) " $\epsilon$ " dielectric constant,(2,7) " $k$ " thermal conductivity(3,9,11) etc., are also reported. All these properties show a sharp discontinuity at the nematic–isotropic melt phase transition temperature $T_c$.(1)

In the nematic range, any anisotropic property $\phi_{ij}$ of the long symmetric molecules (with transverse isotropy) can be written as follows:(3)

$$\phi_{ij} = \delta_{ij}\phi_{\perp} + (\phi_{\parallel} - \phi_{\perp})\langle n_i n_j \rangle \tag{1}$$

where " $\|$ " and " $\perp$ " indicate respectively the principal directions parallel and perpendicular to the nematic alignment axis; $n_i$ is the $i$ component of the " director "; $\delta_{ij}$ is the Kronecker Delta and $\langle\ \rangle$ is the ensemble average over a distribution of orientation. Rewriting,

$$\phi_{ij} = \delta_{ij}\phi_0{}^* + (\phi_{\parallel} - \phi_{\perp})\left\langle n_i n_j - \frac{\delta_{ij}}{3}\right\rangle \tag{2}$$

where $\phi_0{}^*$ is the isotropic property of the randomly oriented nematic; $\langle n_i n_j - \delta_{ij}/3\rangle$ is termed as the " anisotropy tensor " $A_{ij}$.(4)

For random orientation, $A_{ij}$ is zero.

$$\phi_{ij} = \delta_{ij}\phi_0^* = \delta_{ij}(\phi_\parallel + 2\phi_\perp)/3 \tag{3}$$

In the isotropic melt phase, it is known that

$$\phi_\parallel \equiv \phi_\perp = \phi_0 \tag{4}$$

Recently, the validity of Eq. (3) in the nematic range was confirmed by making independent measurements of the self-diffusion coefficients $D_\parallel$, $D_\perp$, $D_0^*$ and $D_0$ for *p*-azoxyanisole at different temperatures(10). Some typical values of various properties are given in table 1. $\phi_0^*$ values are calculated from Eq. (3) using $\phi_\parallel$ and $\phi_\perp$ data where an independent measurement of $\phi_0^*$ is not available. $\phi_0$ is the value obtained by extrapolation of data from the isotropic melt phase to the nematic range. $\phi_0^*$ and $\phi_0$ are significantly different in the entire nematic range up to the transition temperature $T_c$.

TABLE 1 Experimental Data for *p*-azoxyanisole at 126 °C (Values inside brackets are at the nematic–isotropic transition $T_c$ = 135 °C)

| Ref. | $\phi$ | $\phi_\parallel$ | $\phi_\perp$ | $\phi_0^*$ | $\phi_0$[a] |
|---|---|---|---|---|---|
| 3, 9, 12 | $k(10^{-4}$ cal/cm sec °C) | 2.52 (- - - -)[b] | 3.60 (- - - -) | 3.24 (3.11) | 3.79 (3.76) |
| 7 | $\epsilon$ | 5.6 (5.63) | 5.77 (5.7) | 5.71 (5.68)[b] | 5.81 (5.71) |
| 2 | $\chi(10^{-7})$ | 4.67 (4.88) | 5.83 (5.69) | 5.43 (5.42)[b] | 5.39 (5.39) |
| 10 | $D(10^{-5}$ cm$^2$/sec) | 2.05 (1.79) | 1.13 (1.37) | 1.44 (1.51) | 1.54 (1.7) |

[a] extrapolated from isotropic melt state.
[b] calculated from Equation 3.

The existing theories of the nematic–isotropic melt phase transition show that the two phases differ mainly in the degree of molecular alignment, with the isotropic melt phase having random molecular orientations due to thermal motions. The degree of molecular order is perfect near the crystalline–nematic phase transition with increasing disorder with rise in temperature. The degree of molecular orientational order can be controlled externally by applying electric, magnetic field etc.(5)

Both the thermal conductivity and self-diffusion data confirm the validity of Eq. (3) to nematic *p*-azoxyanisole. Ultrasonic attenuation studies on some nematics also support this.(9a) $\phi_0^*$ data in both cases were obtained without the application of external fields. This indicates that the nematic phase in its free state is *randomly* oriented due to rotational Brownian motions. If the orientation is random in both nematic and isotropic phases, a discontinuity in $\phi_0$ is not to be expected at $T_c$. But, $\phi_0^*$ and $\phi_0$ are different at the transition point as seen in table 1. This raises a question as to the exact difference between the randomly oriented nematic phase and the random isotropic melt state. The idea of random orientation in the free nematic due to Brownian motion comes from " swarm " theory which is generally not favoured in comparison with the " continuum " theory.

It is clear from the preceding discussion that the two phases differ in the " scale " at which randomness exists. In the isotropic melt phase, the orientation correlation or coherence distance is extremely small even if one considers the " cybotactics " or " microswarms " in the melt.(4) But, in the nematic phase, the corresponding correlation distance is at a " swarm " or macromolecular scale. The size of these swarms or clusters or pacquets is of the order of a micron containing about $10^5$ molecules,(5,6,8,13) as determined by X-ray and light scattering techniques. The rodlike molecules are less orderly aligned in the microswarms as compared with the almost perfect alignment in the nematic swarm.(4) With increasing temperature, the nematic swarms decrease in size accompanied by an increasing disorder in the molecular alignment due to weakening intermolecular forces.

In summary, experimental data on the physical properties of *p*-azoxyanisole seem to favour the ideas of " swarm " theory, which gives a probable explanation for the discontinuity at the nematic–isotropic melt phase transition. Further experimental information on similar data on different nematic mesophases are required to confirm the above points. Thermal conductivity data is being obtained by the authors to be published at a later date.

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