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Theory of Melting of Molecular Crystals: The Liquid Crystalline Phase

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Abstract—The theory of melting of molecular crystals developed by Pople and Karasz, which takes into account order-disorder processes in both the positions and orientations of the molecules, is discussed in a slightly modified form. The theory is an extension of the two-lattice model of Lennard-Jones and Devonshire so as to allow the molecules to take up two orientations on any site. It is assumed in this paper that the energy required for a molecule to diffuse to an interstitial site varies as V^{-4} , as in the original formulation, but that the orientational barrier varies as V^{-3} , in conformity with recent calculations of the orientational potential energy in nematic liquid crystals. The thermodynamic properties of the disordered system are evaluated relative to those of the perfectly ordered one using the Bragg-Williams approximation. For small orientational barriers, the theory predicts two transitions, a solid state rotational transition followed by a melting transition. For larger orientational barriers, the two transitions coalesce and there is a corresponding increase in the entropy of fusion. For even larger orientational barriers, the positional melting precedes the rotational melting and there occurs an intermediate phase, similar to the nematic mesophase, that has orientational order but no positional order. The predicted entropies of transition from the liquid crystal to the isotropic phase for a certain range of orientational barriers are comparable to those observed in nematic compounds. Theoretical curves are drawn for the degree of orientational order, the anomalous specific heat and thermal expansion as functions of temperature in the liquid crystalline range, and for the variation of the transition temperatures with pressure. The curves reproduce the trends in the physical properties of nematic liquid crystals.

1. Introduction

X-ray studies of the crystal structures of typical nematogenic compounds, such as *p*-azoxyanisole, *p*-azoxyphenetole and anisaladiazine, show that the long, narrow molecules are parallel or nearly parallel and interleave one another to form an imbricated arrangement.⁽¹⁻³⁾ The transition from the crystalline to the nematic phase

is accompanied by the breakdown of the positional order of the molecules, but not of the orientational order. The mesophase is fluid because of the facility with which the molecules slide over one another whilst still retaining their parallelism. The breakdown of the orientational order occurs at a higher temperature when the liquid crystal transforms into the isotropic liquid. The solid-nematic and the nematic-isotropic transitions are both attended by changes of entropy and volume, which are about 10–50 times larger for the former transition. The degree of orientational order of the molecules is defined by the long range order parameter

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

where θ is the angle which the long axis of the molecule makes with the uniaxial direction of the medium. The limits of s are 1 for a perfectly ordered crystalline arrangement and 0 for the completely disordered isotropic liquid. Experiments reveal that s decreases suddenly at the solid-nematic transition point, and then falls gradually with rise of temperature in the liquid crystalline range. At the second transition point T_c , there is again a discontinuous change and s drops catastrophically to 0. Properties associated with orientational order, as for example the specific heat of the liquid crystal, exhibit an anomalous increase in the neighbourhood of T_c .

Various types of models have been put forward to characterize the basic difference between the solid and liquid states of matter and to evaluate the thermodynamic changes involved, but it would be fair to say that no theory has yet been constructed that is able to give a satisfactory quantitative description of the melting process. (For a review of the theories and a critical discussion of the problem, see Ubbelohde.⁽⁴⁾) The most successful treatment of the melting of inert gas crystals is that of Lennard-Jones and Devonshire,^(5,6) who regarded the mechanism of fusion as a positional order-disorder phenomenon. They postulated that the molecules may occupy sites on one of two interpenetrating lattices, referred to as A-sites and B-sites. The lowest energy configuration is that in which all molecules occupy the same kind of sites, say the A-sites. With increasing temperature, the number of molecules in the interstitial B-sites increases till a critical stage is reached when there is complete collapse of the long range order and both kinds of sites become

equally populated. The system in which there is an equal number of occupied and unoccupied A-sites corresponds to a liquid, for, under such circumstances, migration from one site to another becomes easily possible. By assuming that the energy of interaction between molecules in adjacent A- and B-sites is dependent on volume, Lennard-Jones and Devonshire derived a statistical theory of the thermodynamics of the melting process whose predictions agree with the data for a number of spherical or nearly spherical molecules.

However, the theory fails for anisotropic molecules where the effect of orientational disorder becomes important. The thermodynamic data suggest that there are two classes of molecular crystals: those which undergo phase transitions associated with rotational motions at temperatures below the melting point and those for which the rotational and melting transitions coalesce. The former have entropies of fusion lower than the inert gas crystals, whereas the latter have much higher entropies of fusion (see Ubbelohde⁽⁴⁾).

Pople and Karasz^(7,8) proposed a simple extension of the two-lattice model of Lennard-Jones and Devonshire by means of which it is possible to give a reasonable quantitative interpretation of the variations in the thermodynamic properties of melting of molecular crystals. They assumed that the molecule may take up one of two orientations on any site, so that it now has four possibilities, A_1 , A_2 , B_1 , B_2 . The perfectly ordered system (which corresponds to the solid at zero temperature) may then be regarded as one in which all molecules occupy the same configuration, A_1 or A_2 or B_1 or B_2 , and the completely disordered system (or the liquid phase) as one having the four configurations equally populated. Clearly, there can also be systems with positional order and no orientational order and vice versa.

When a molecule is turned into an unfavorable orientation, local strains are set up and consequently there is an increased tendency for the molecules in the vicinity to move to interstitial sites. To allow for this, Pople and Karasz made the simple assumption that the orientational component of the AB interactions is negligible as compared with that of the AA or BB interactions, so that the B-sites near a misorientation in an A-lattice (and similarly the A-sites near a misorientation in a B-lattice) are favored. Accordingly, the

energy required for a molecule to diffuse to an interstitial B-site in an A-lattice (or an interstitial A-site in a B-lattice) is determined only by the AB interactions regardless of orientation, and the energy required for a molecule to assume an A_2 -orientation in an A_1 -lattice (or a B_2 -orientation in a B_1 -lattice) is determined by the A_1A_2 (or B_1B_2) interactions only. They assumed that both these energies are repulsive in origin and vary as V^{-4} . For small orientational barriers, the model predicts two transitions, a rotational transition followed by a melting transition. For larger orientational barriers the two transitions coalesce and there is a single transition with a much larger entropy of fusion. The maximum entropy of fusion predicted by the model is about 6 cal/mole deg, whereas, in fact, much higher values are often observed. Despite this limitation, which arises mainly from the restriction of two possible orientations per site, the model does provide a logical basis for interpreting the effects of hindered rotation on the thermodynamics of fusion.

For even larger orientational barriers, the model predicts that the positional melting should precede the rotational melting, so that there should occur an intermediate phase, similar to the nematic liquid crystalline phase, which has orientational order but no positional order. However, Pople and Karasz have not investigated this range of orientational barriers. We have found that the model in its present form leads to very large entropies for the nematic-isotropic transition and also fails to reproduce any of the distinctive properties of the nematic phase, such as the rapid variation of the degree of orientational order with temperature, the anomalous specific heat, etc.

Recent theoretical studies⁽⁹⁾ have shown that the orientational potential energy of the molecule in a nematic assembly is determined mainly by dispersion and repulsion interactions which vary approximately as V^{-2} and V^{-4} respectively. Based on an inter-molecular potential function involving these two types of interactions and assuming an average volume dependence of V^{-3} , a statistical theory of long range orientational order in nematic liquid crystals has been developed which leads to a consistent quantitative explanation of the properties of *p*-azoxyanisole.⁽¹⁰⁾ In the light of this evidence, it would seem more realistic to suppose that the orientational barrier in the model varies as V^{-3} rather than as V^{-4} , especially since, according to the approximations discussed earlier, we are here con-

cerned with interactions between molecules on the *normal* lattice sites (i.e. the A_1A_2 or B_1B_2 interactions) and not between molecules on adjacent A- and B-sites. We shall therefore introduce this modification in the theory and discuss its applications to liquid crystalline transitions. It turns out that the theory at once gives results which are in agreement with observed trends in the properties of nematic liquid crystals.

2. The Statistical Model

We define the degree of positional order as $q = 2Q - 1$, where Q is the fraction of molecules occupying the A-sites; and the degree of orientational order as $s = 2S - 1$, where S is the fraction of molecules occupying the 1-orientations. Let there be z B-sites adjacent to each A-site and z' A-sites closest to each A-site. (This implies, of course, that there are also z A-sites adjacent to each B-site and z' B-sites closest to each B-site.) Let W be the repulsive energy of an AB interaction and W' the orientational potential energy of an A_1A_2 or B_1B_2 interaction.

Using the Bragg-Williams approximation, the partition function for disorder is given by⁽⁷⁾

$$\begin{aligned} N^{-1} \log \Omega = & -(1+q) \log \left(\frac{1+q}{2} \right) - (1-q) \log \left(\frac{1-q}{2} \right) - \frac{1+s}{2} \log \left(\frac{1+s}{2} \right) \\ & - \left(\frac{1-s}{2} \right) \log \left(\frac{1-s}{2} \right) - \frac{zW}{kT} \left(\frac{1-q^2}{4} \right) \\ & - \frac{z'W'}{kT} \left(\frac{1-s^2}{4} \right) \left(\frac{1+q^2}{2} \right). \end{aligned} \quad (1)$$

Applying the conditions of equilibrium of the system,⁽⁷⁾ and putting $W = W_0(V_0/V)^4$ and $W' = W'_0(V_0/V)^3$, we obtain

$$\log \frac{1+q}{1-q} = \frac{zW}{kT} \left[\frac{1}{2} - \frac{V}{V_0} \nu \left(\frac{1-s^2}{4} \right) \right] q, \quad (2)$$

$$\log \frac{1+s}{1-s} = \frac{zW}{kT} \frac{V}{V_0} \nu \left(\frac{1+q^2}{2} \right) s, \quad (3)$$

where $\nu = z'W'_0/zW_0$ is a measure of the relative barriers for the rotation of a molecule and for its diffusion to an interstitial.

The component of the Helmholtz free energy due to disorder $F'' = -kT \log \Omega$ and the pressure due to disorder $p'' = -(\partial F''/\partial V)_T$. Hence from (1)

$$\frac{p'' V_0}{NkT} = \frac{zW}{kT} \frac{V_0}{V} \left[(1 - q^2) + \frac{3}{8} \frac{V}{V_0} \nu (1 - s^2) (1 + q^2) \right], \quad (4)$$

where q and s are now the equilibrium values determined by (2) and (3). If p' denotes the contribution of the ordered system to the pressure, the total pressure $p = p' + p''$. The complete isotherm was evaluated in the manner described by Pople and Karasz,⁽⁷⁾ except that the equilibrium values of q and s had to be re-determined for every different kT/ϵ , so that the calculations were much more involved. Here ϵ is the minimum energy of interaction of a pair of particles given by the 6-12 intermolecular potential.

Hereafter, q and s will be understood to refer to those values that minimize the free energy.

3. The Thermodynamics of the Phase Transitions

For low zW/kT , $q = s = 0$ is the only solution that minimizes the free energy for any given kT/ϵ , while for very large zW/kT , $q = s = 1$ is the only solution. The behavior for intermediate zW/kT depends critically on the strength of the orientational barrier. Figure 1 illustrates the variation of q and s with zW/kT for three typical values of ν . For small ν , q leaves 0 at a lower zW/kT than s (Fig. 1a). As ν increases, the separation between the q and s curves decreases till a stage is reached when q and s rise suddenly from 0 at the same zW/kT (Fig. 1b). For large ν , the situation is reversed and s departs from 0 at a smaller zW/kT (Fig. 1c).

For ν less than about 0.3 the theory predicts two transitions, a solid state rotational transition followed by a melting transition. For ν between 0.3 and 0.8, the two transitions coalesce and there occurs a single transition with a much greater entropy of fusion. These results are in qualitative agreement with those discussed by Pople and Karasz. There are, of course, some quantitative differences, but we shall not discuss them in this paper. We shall here consider only the liquid crystalline transitions in detail.

When ν is greater than 0.8, there are again two transitions. The

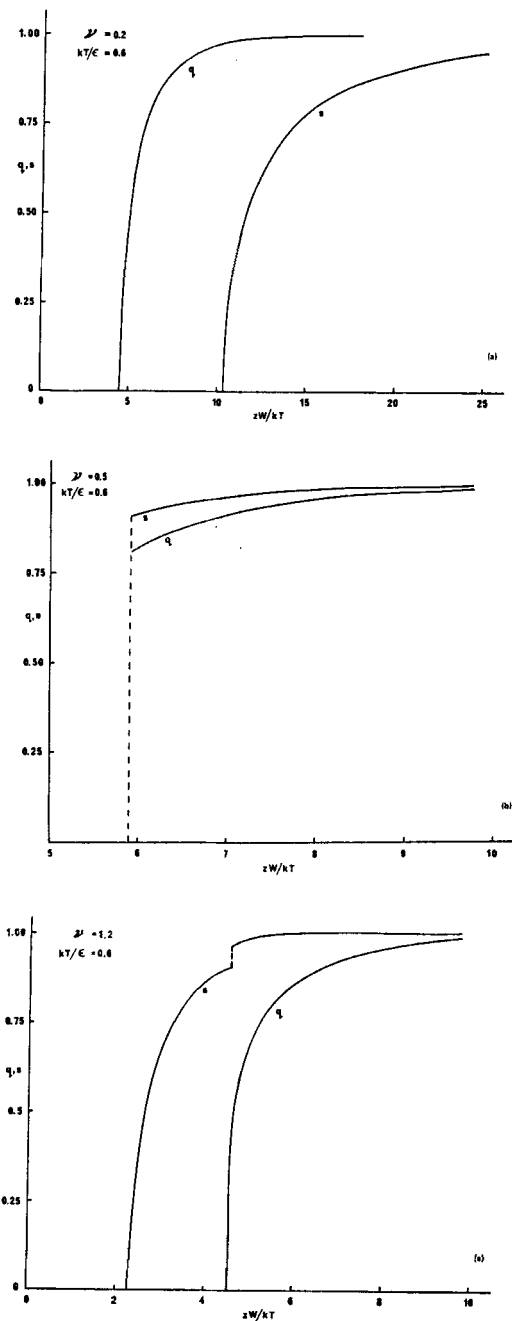


Figure 1. Variation of equilibrium values of q and s with zW/kT , (a) $\nu = 0.2$, (b) $\nu = 0.6$, (c) $\nu = 1.2$.

theoretical isotherm for the first transition temperature is shown in Fig. 2 for $\nu = 1.3$. The sigmoid portions of the curve correspond to phase transitions, i.e. the two phases will be in equilibrium at a given pressure when the areas enclosed by the curve above and below the pressure line are equal. For example, the points A and B in Fig. 2

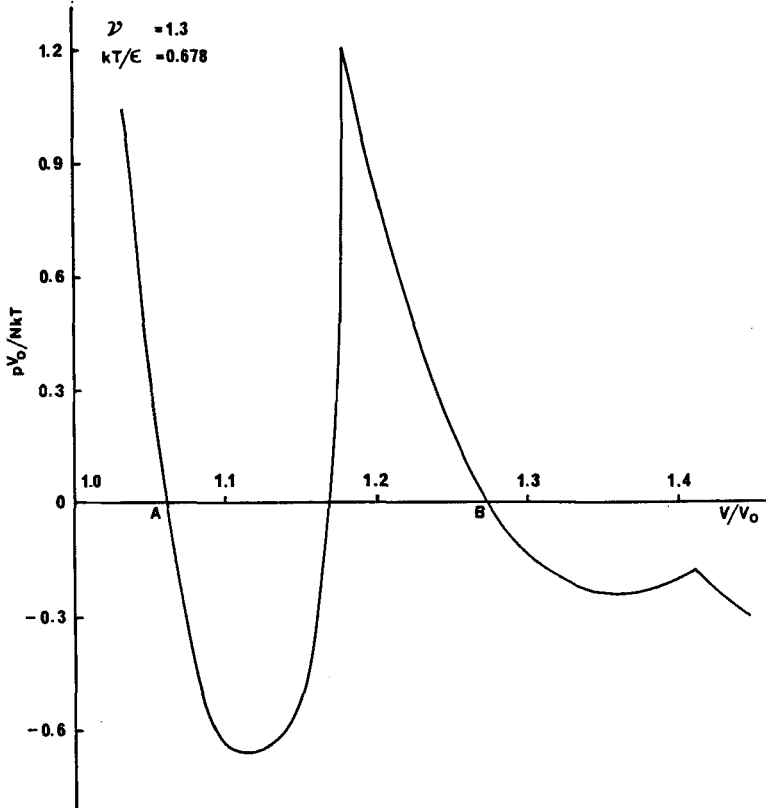


Figure 2. Theoretical isotherm for the solid-nematic transition temperature.

represent two such states in equilibrium at zero pressure, A corresponding to a solid ($q = 0.915$, $s = 1.0$) and B to an intermediate phase with $q = 0$, $s = 0.796$. Evidently, for a higher temperature there will be a second transition which is characterized by the breakdown of the orientational order. The intermediate phase is therefore similar to the nematic mesophase which has orientational order but no translational order. (The smectic and cholesteric types of liquid

crystal cannot be compared with the intermediate phase predicted by this simple model.)

The sigmoid shape of the isotherm in Fig. 2 signifies a first-order transition accompanied by changes of entropy and volume. As ν decreases, the kink in the isotherm associated with the nematic-isotropic transition becomes less pronounced, with the result that ΔS and ΔV decrease steadily. When ν is less than about 1.1 (but greater than 0.8), the isotherm loses its sigmoid shape and exhibits only a change of slope at the transition as shown in Fig. 3. Thermodynamically, this represents a second-order transition with no change of volume or entropy. As far as we are aware, no case has yet been observed of a second-order nematic-isotropic transition. The positional melting, on the other hand, remains a first-order transition for all values of ν .

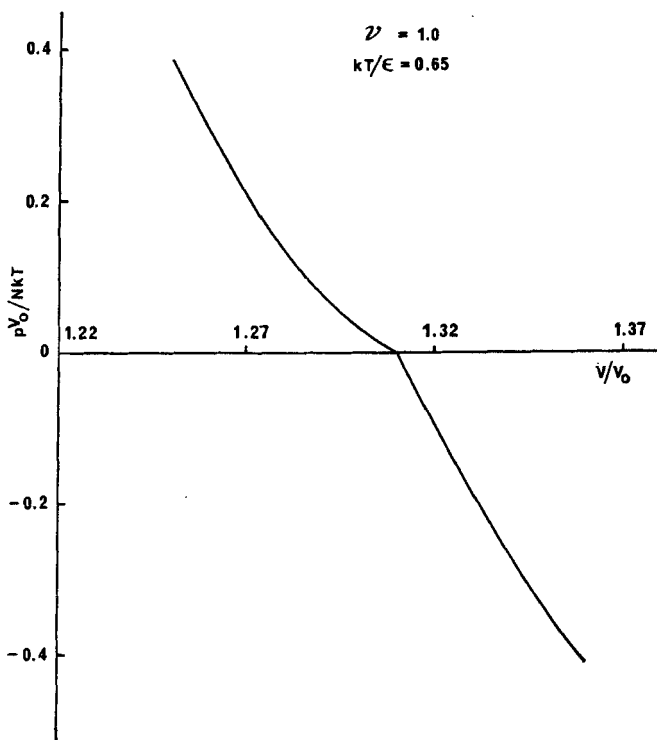


Figure 3. Theoretical isotherm showing second-order nematic-isotropic transition.

The entropy of the system due to disorder

$$\begin{aligned}
 S'' &= - \left(\frac{\partial F''}{\partial T} \right)_v \\
 &= -Nk \left[(1+q) \log \left(\frac{1+q}{2} \right) + (1-q) \log \left(\frac{1-q}{2} \right) + \left(\frac{1+s}{2} \right) \log \left(\frac{1+s}{2} \right) \right. \\
 &\quad \left. + \left(\frac{1-s}{2} \right) \log \left(\frac{1-s}{2} \right) \right]. \tag{5}
 \end{aligned}$$

Hence the entropy of transition $\Delta S = \Delta S' + \Delta S''$ can be found by calculating the entropies of the two phases in equilibrium using (5) and the tabulated values of S' for the ordered system.⁽¹¹⁾ The theoretical results for a few ν are given in Table I along with the available data for some compounds.^(12-15,22) For comparison, we also give the values derived from the Pople and Karasz theory.

As far as the solid-nematic transition is concerned, both theories give very nearly the same $\Delta S/R$ and $\Delta V/V$, but the values are significantly lower than the observed data. This limitation of the theory was also noted by Pople and Karasz. A simple model of this type cannot be expected to give an adequate description of the diverse kinds of molecular motion that can take place in such structures and to account for their contributions to the entropy of transition. For the nematic-isotropic transition, there is a striking difference between the results of the two theories. $\Delta S/R$ and $\Delta V/V$ given by the present theory for this transition is only a small fraction of the corresponding values for the solid-nematic transition. This is indeed a distinctive feature of nematic transitions in general.⁽¹⁶⁾ Furthermore, the theoretical s at the two transition temperatures compare very favourably with the experimental data.^(17,22)

In contrast, the Pople and Karasz equations lead to large $\Delta S/R$ and $\Delta V/V$ for the nematic-isotropic transition, and an s which hardly changes between the two transitions. We have also verified that the specific heat and thermal expansion calculated from their equations are practically independent of temperature in the liquid crystalline range. In point of fact, these quantities are strongly temperature dependent in nematic compounds, as we shall see in the next section.

TABLE I

Present theory		Solid-nematic transition		Pople and Karasz		Experimental	
ν	$\Delta S/R$	$\Delta V/V$	ν	$\Delta S/R$	$\Delta V/V$	x	$(CH_2)_xHOC_6H_4NONC_6H_4OH(CH_2)_x$ $\Delta S/R$ $\Delta V/V$
1.15	2.74	0.22	<1.925	no mesophase		1	9.29
1.18	2.67	0.21	1.95	2.24	0.19	2	8.02 0.084
1.20	2.62	0.21	2.10	2.15	0.18	3	8.45
1.30	2.48	0.20	2.30	2.10	0.18	4	6.72
						5	5.04
Nematic-isotropic transition							
<1.1	2nd ord. trans.		<1.925	no mesophase		1	0.203 0.0035
1.15	0.12	0.01	1.95	1.17	0.15	2	0.410 0.0060
1.18	0.19	0.02	2.10	1.40	0.20	3	0.285
1.20	0.24	0.03	2.30	1.57	0.23	4	0.385
1.30	0.53	0.06				5	0.328
s (nematic) at the transition temperatures T_1 and T_c							
s (present theory)		s (Pople and Karasz)		s (experimental)			
ν	T_1	T_c	ν	T_1	T_c	T_1	T_c
1.15	0.643	0.308	1.95	0.892	0.879	0.51	0.34
1.18	0.684	0.403	2.10	0.922	0.912	0.69	0.47
1.20	0.719	0.450	2.30	0.956	0.940	0.68	0.38
						0.70	0.38
						0.67	0.35

4. The Properties of the Liquid Crystalline Phase

By drawing isotherms for different temperatures and noting their intersections with the zero pressure line, s and V/V_0 can be determined as a function of kT/ϵ . From the slopes of the curve for V/V_0 versus kT/ϵ , a quantity proportional to the coefficient of thermal expansion can also be found. The results are presented in Figs 4, 6 and 8, as functions of T/T_c , where T_c is the nematic-isotropic transition temperature.

The contribution of the disorder to the specific heat at constant volume can be evaluated from the general thermodynamic relation

$$C_v = k \left[T^2 \left(\frac{\partial^2 \log \Omega}{\partial T^2} \right)_V + 2T \left(\frac{\partial \log \Omega}{\partial T} \right)_V \right]. \quad (6)$$

$$\begin{aligned} N^{-1} \left(\frac{\partial \log \Omega}{\partial T} \right)_V = & \left[-\log \left(\frac{1+q}{2} \right) + \log \left(\frac{1-q}{2} \right) + \frac{zWq}{2kT} - \frac{z'W'}{kT} \left(\frac{1-s^2}{4} \right) q \right] \\ & \cdot \left(\frac{\partial q}{\partial T} \right)_V + \left[-\frac{1}{2} \log \left(\frac{1+s}{2} \right) + \frac{1}{2} \log \left(\frac{1-s}{2} \right) + \frac{z'W'}{kT} \right. \\ & \cdot \left. \left(\frac{1+q^2}{4} \right) s \right] \left(\frac{\partial s}{\partial T} \right)_V + \frac{zW}{kT^2} \left(\frac{1-q^2}{4} \right) + \frac{z'W'}{kT^2} \\ & \cdot \left(\frac{1-s^2}{4} \right) \left(\frac{1+q^2}{2} \right). \end{aligned} \quad (7)$$

The coefficients of $(\partial q/\partial T)_V$ and $(\partial s/\partial T)_V$ in (7) vanish because of the equilibrium conditions (2) and (3). Therefore,

$$\begin{aligned} N^{-1} \left(\frac{\partial^2 \log \Omega}{\partial T^2} \right)_V = & \left[-\frac{zWq}{kT^2} + \frac{z'W'}{kT^2} \left(\frac{1-s^2}{4} \right) q \right] \left(\frac{\partial q}{\partial T} \right)_V - \frac{z'W'}{kT^2} \left(\frac{1+q^2}{4} \right) s \\ & \cdot \left(\frac{\partial s}{\partial T} \right)_V - \frac{zW}{kT^3} \left(\frac{1-q^2}{2} \right) - \frac{z'W'}{kT^3} \left(\frac{1+q^2}{4} \right) (1-s^2). \end{aligned} \quad (8)$$

Putting $q = 0$ in the nematic phase, we have from (6), (7) and (8)

$$\begin{aligned} \frac{C_v}{R} = & -\frac{z'W'}{4k} s \left(\frac{\partial s}{\partial T} \right)_V = -\frac{zW_0}{4\epsilon} \left(\frac{V_0}{V} \right)^3 \nu s \left[\frac{\partial s}{\partial(kT/\epsilon)} \right]_V \\ = & -1.4655 \left(\frac{V_0}{V} \right)^3 \nu s \left[\frac{\partial s}{\partial(kT/\epsilon)} \right]. \end{aligned} \quad (9)$$

We have already seen that the intersection of the isotherm with the zero pressure line gives s and V/V_0 of the liquid crystal at that temperature and pressure. The value of s at the same V/V_0 but at a

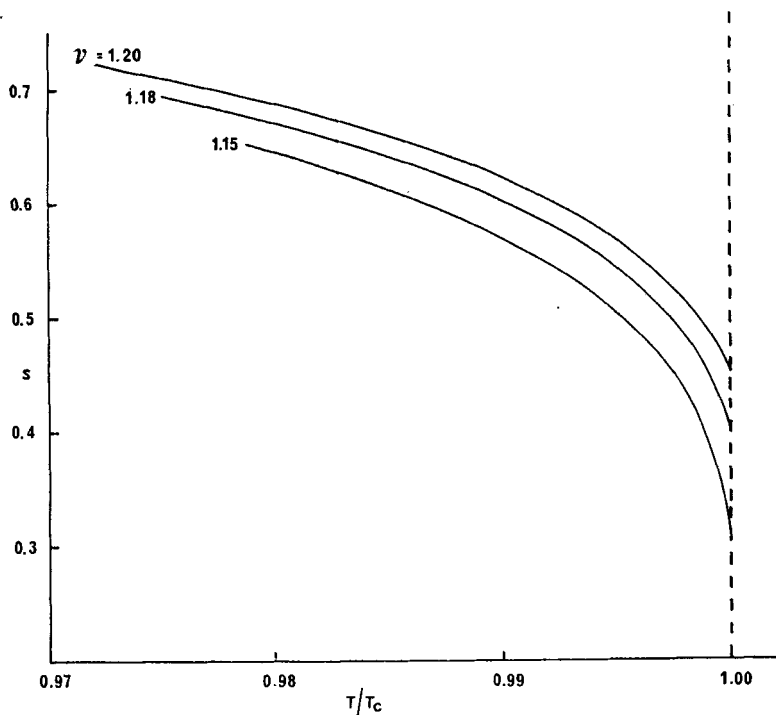


Figure 4. Theoretical variation of the degree of orientational order with temperature in the liquid crystal (at zero pressure) for $\nu = 1.2, 1.18$ and 1.15 .

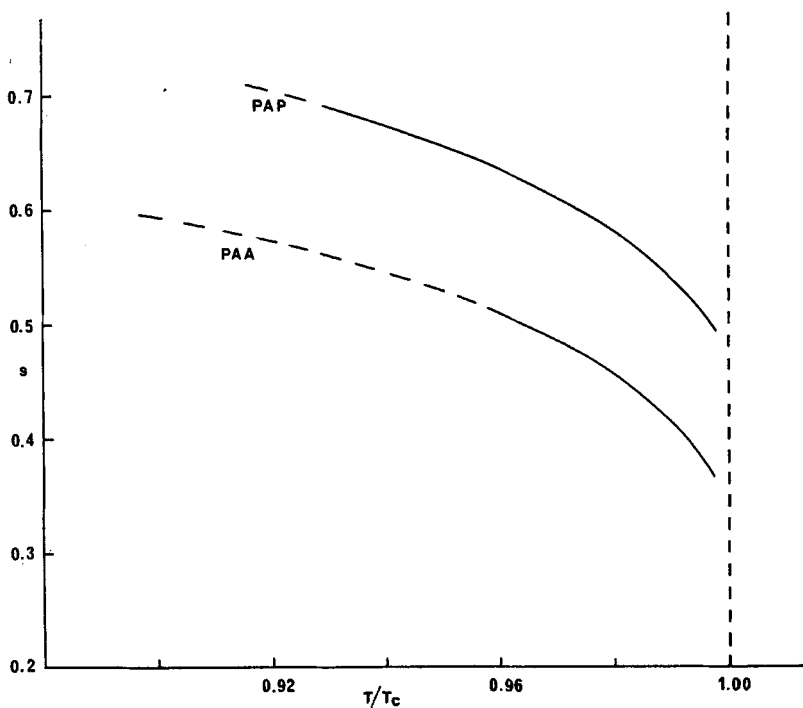


Figure 5. Degree of orientational order in *p*-azoxyanisole (PAA) and *p*-azoxyphenetole (PAP) in the nematic phase. The dashed portions of the curves represent the supercooled regions (Chandrasekhar and Madhusudana⁽¹³⁾).

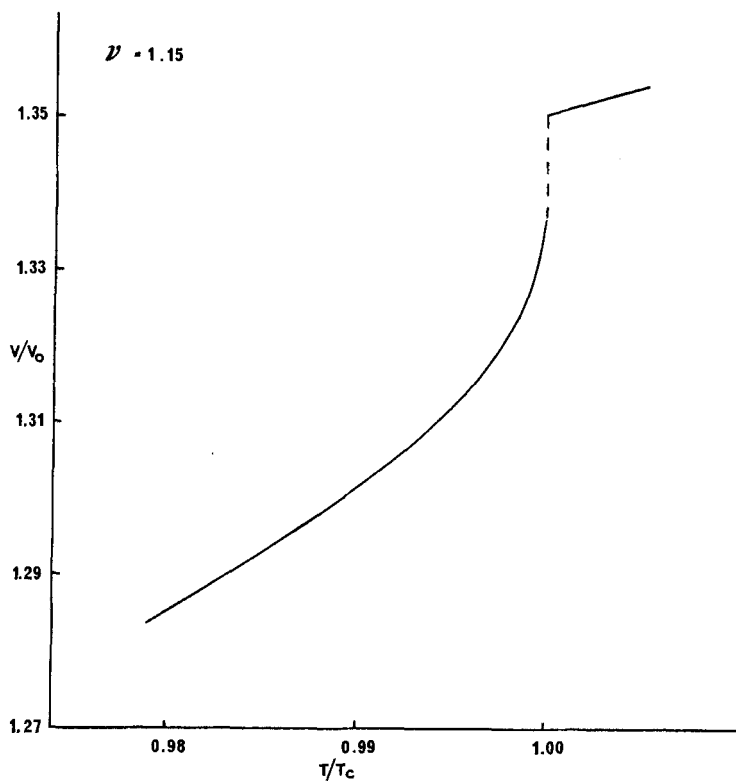


Figure 6. Theoretical variation of volume in nematic and isotropic phases (at zero pressure).

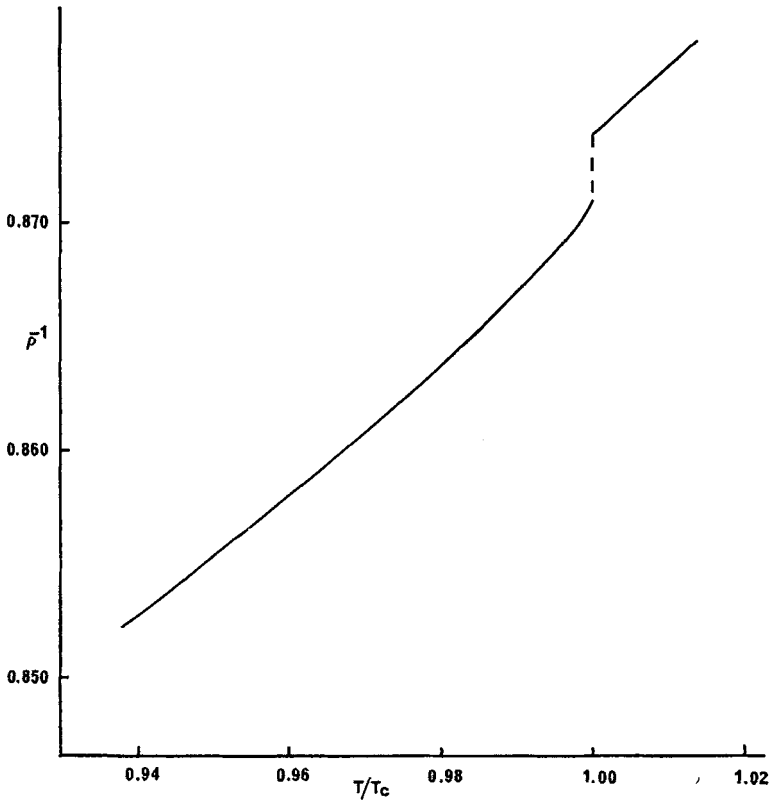


Figure 7. Variation of specific volume of *p*-azoxyanisole in nematic and isotropic phases (Maier and Saupe⁽¹⁵⁾).

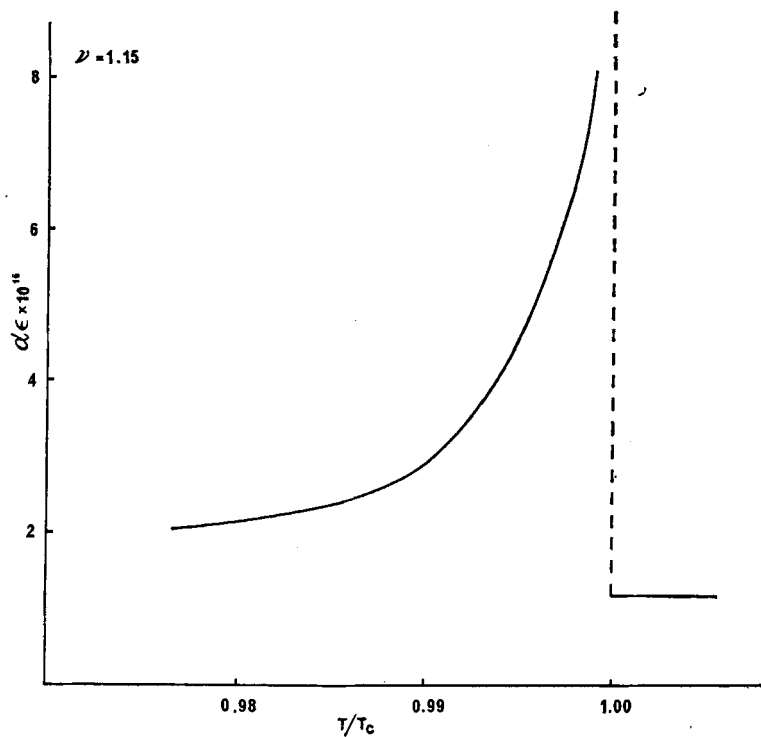


Figure 8. Theoretical coefficient of thermal expansion in nematic and isotropic phases (derived from Fig. 6).

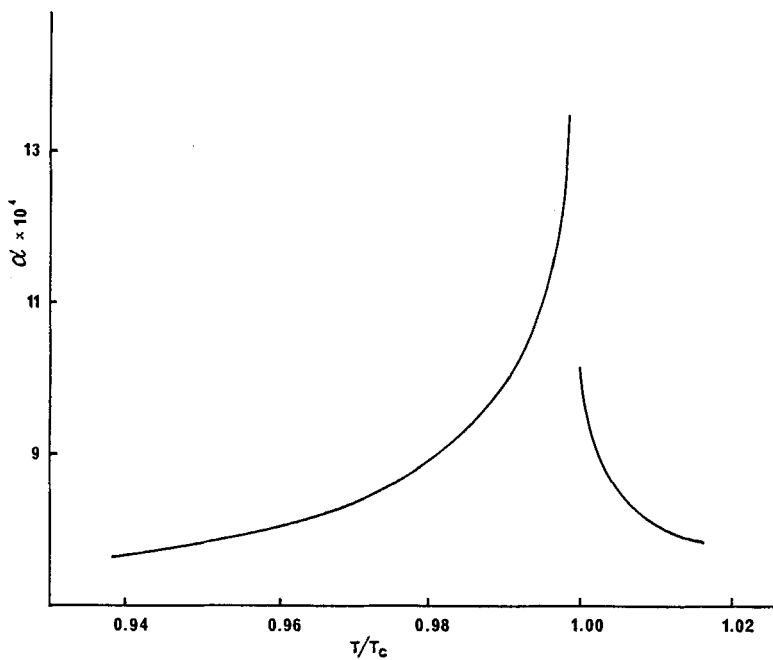


Figure 9. Coefficient of thermal expansion of *p*-azoxyanisole in nematic and isotropic phases (Maier and Saupe⁽¹⁵⁾).

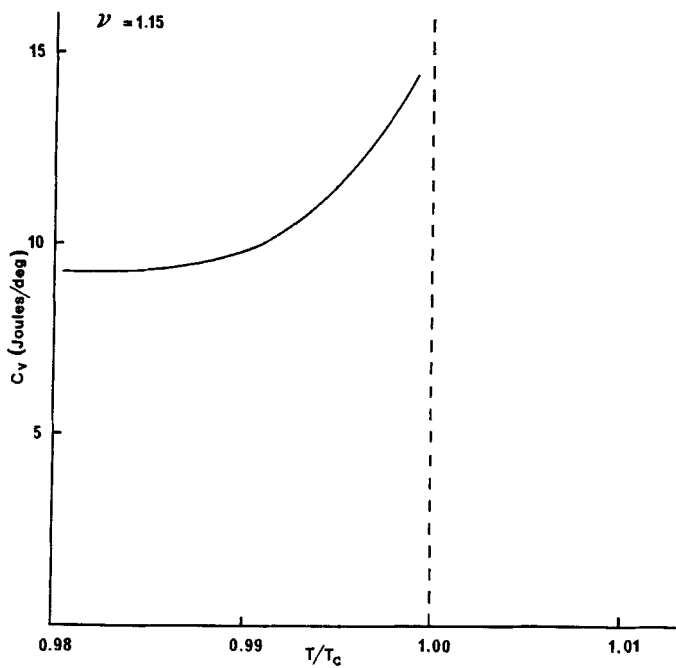


Figure 10. Theoretical contribution of orientational disorder to the specific heat at constant volume in the nematic phase.

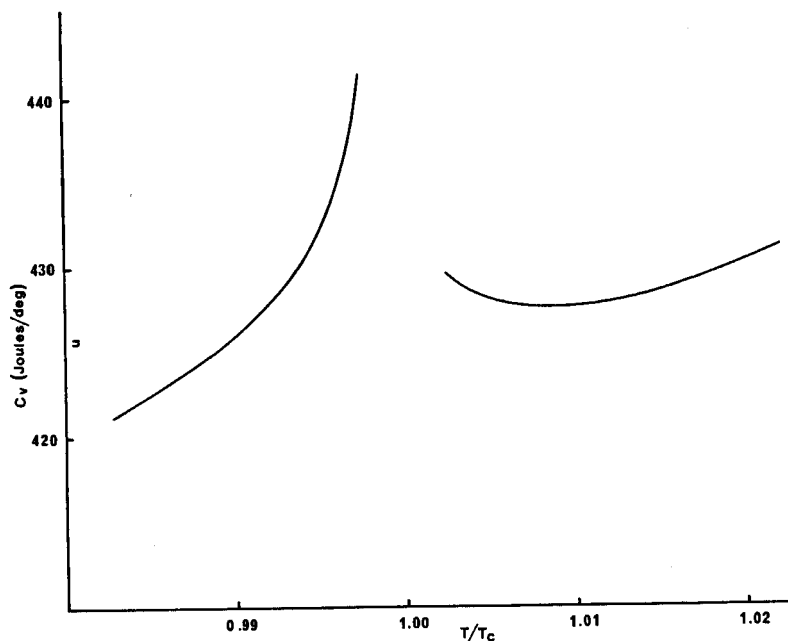


Figure 11. Specific heat at constant volume of *p*-azoxyanisole in nematic and isotropic phases (derived from experimental values of $C_p^{(12)}$ and $\beta_{is}^{(21)}$).

different kT/ϵ , and hence $[\partial s/\partial(kT/\epsilon)]_V$, can be obtained from an isotherm for a slightly different kT/ϵ . The specific heat derived in this manner as a function of T/T_c is shown in Fig. 10.

The trends exhibited by the theoretical curves can be seen to be quite similar to those observed experimentally (Figs. 4–11); there is even a fair measure of quantitative agreement.

5. Effect of Pressure on the Temperatures of Transition

Using the isotherms drawn for a range of temperatures and applying the principle of equal areas, the equilibrium pressures for the transitions can be determined as a function of kT/ϵ . Figure 12 shows the results for $\nu = 1.15$.

The increase of the transition temperatures of *p*-azoxyanisole with pressure has been studied experimentally by Hulett,⁽¹⁸⁾ by Puschin and Grebenschtschikow⁽¹⁹⁾ and by Robberecht⁽²⁰⁾. The data of Robberecht, which agree almost exactly with those of Hulett, are

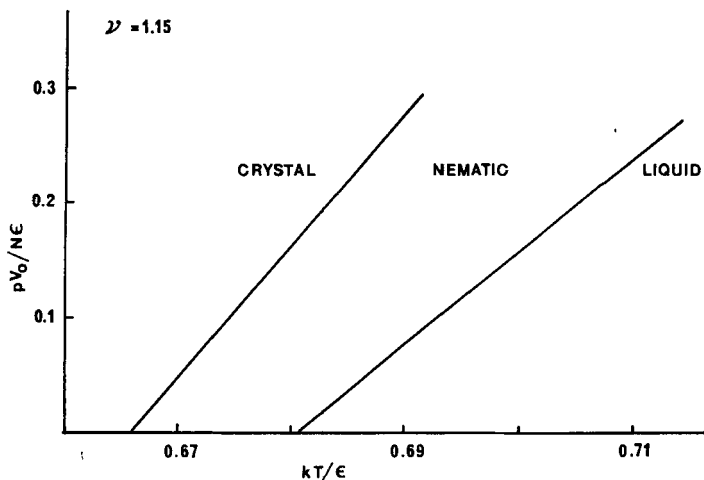


Figure 12. Theoretical variation of the transition temperatures with pressure.

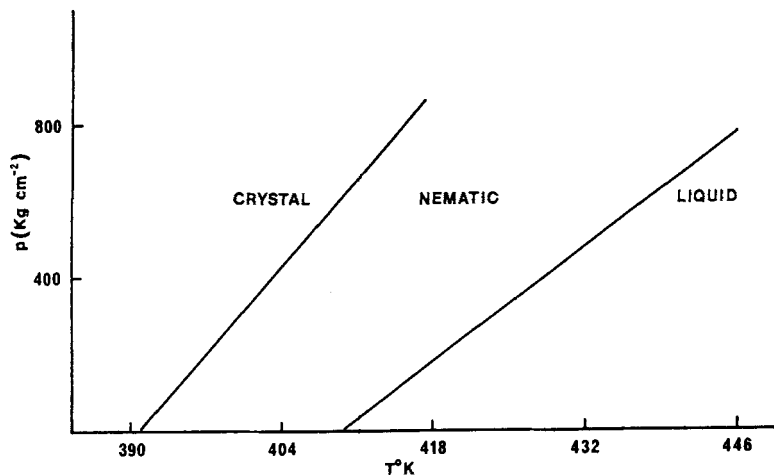


Figure 13. Experimental variation of the transition temperatures of *p*-azoxyanisole with pressure (Robberecht⁽²⁰⁾).

shown in Fig. 13. Qualitatively, the agreement can be seen to be satisfactory. In particular, the prediction that dT/dp should be slightly greater for the second transition than for the first one is borne out by experiment.

As emphasized earlier, a simple model of the type considered here

cannot be expected to be applicable in detail to any particular substance, but the over-all qualitative agreement confirms that the theory does serve to explain broadly the mechanism of formation of the liquid crystalline phase and to elucidate some of its important physical properties.

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REFERENCES

1. Bernal, J. D. and Crowfoot, D., *Trans. Faraday Soc.* **29**, 1032 (1933).
2. Galigne, J. L. and Falgueirettes, J., *Acta Cryst.* **B24**, 1523 (1968).
3. Chistyakov, I. G., *Kristallografiya* **8**, 859 (1963).
4. Ubbelohde, A. R., *Melting and Crystal Structure* (Clarendon Press, Oxford, 1965).
5. Lennard-Jones, J. E. and Devonshire, A. F., *Proc. Roy. Soc.* **A169**, 317 (1939).
6. Lennard-Jones, J. E. and Devonshire, A. F., *Proc. Roy. Soc.* **A170**, 464 (1939).
7. Pople, J. A. and Karasz, F. E., *J. Phys. Chem. Solids* **18**, 28 (1961).
8. Karasz, F. E. and Pople, J. A., *J. Phys. Chem. Solids* **20**, 294 (1961).
9. Chandrasekhar, S., Krishnamurti, D., and Madhusudana, N. V., *Mol. Cryst. and Liq. Cryst.* **8**, 45 (1969).
10. Chandrasekhar, S. and Madhusudana, N. V., *Mol. Cryst. and Liq. Cryst.* (to be published).
11. Wentorf, R. H., Buehler, R. J., Hirschfelder, J. O. and Curtiss, C. F., *J. Chem. Phys.* **18**, 1484 (1950).
12. Arnold, H., *Z. Physik. Chem. (Leipzig)* **226**, 146 (1964).
13. Chandrasekhar, S. and Madhusudana, N. V., "Colloque sur les Cristaux Liquides, Montpellier, June 1969, *J. de Physique* **C4**, **30**, 24 (1969).
14. Bauer, E. and Bernamont, J., *J. Phys. Radium* **7**, 19 (1936).
15. Maier, W. and Saupe, A., *Z. Naturforsch.* **159**, 287 (1960).
16. Porter, R. S., Barrall, E. M. and Johnson, J. F., *Accounts Chem. Res.* **2**(2), 53 (1969).
17. Saupe, A., *Angew. Chem. Internat. Edit.* **7**, 97 (1968).
18. Hulett, G. A., *Z. Physik. Chem.* **28**, 629 (1899).
19. Puschin, N. A. and Grebenschtschikow, I. W., *Z. Physik. Chem. (Leipzig)* **124**, 270 (1926).
20. Robberecht, J., *Bull. Soc. chim. belges* **47**, 597 (1938).
21. Kapustin, A. P. and Bykova, N. T., *Soviet Physics-Crystallography* **11**, 297 (1966).
22. Maier, W. and Markau, K., *Z. Physik Chem.*, **28**, 190 (1961).