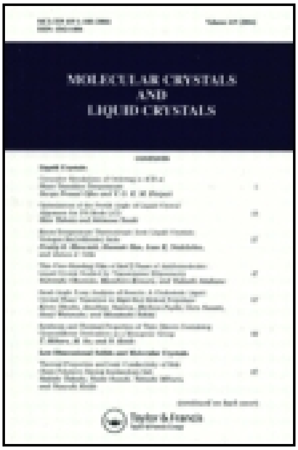

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The Mesophase-Isotropic Phase Transition for a Thermotropic Liquid Crystal: The Effect of Shear Flow

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The Mesophase-Isotropic Phase Transition for a Thermotropic Liquid Crystal: The Effect of Shear Flow

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Recent developments in the theory of melting are discussed, particularly those concerning the contribution of defects and the bifurcation of the on-site potential in the liquid. It is proposed that the configurational entropy for a nematic-isotropic transition is of the order of (1/3) $R \ln 2$. It is also proposed that a study of the mesophase-isotropic transition temperature, under conditions of steady flow, could provide a way of assessing the contribution of defects to the melting process.

I INTRODUCTION

One theory of melting suggests that dislocation proliferation in a crystalline solid might be the path by which a crystal is transformed to a liquid. The onset of dislocation formation has recently been shown, by molecular dynamics calculations, to be associated with bifurcation of the on-site potential at the melting point.[1] It was argued that this bifurcation might be the origin of the volume-indepedent entropy of melting, $R \ln 2$, discussed previously.[2] The purpose of the present communication is to extend these ideas to the more complicated liquid crystal domain and to investigate whether bifurcation also plays a role in transitions of mesophase systems.

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For polyatomic molecules, the situation is obviously more complex than for the monatomic case. Here, the melting process will lead to an additional entropy increase due to hindered modes of internal rotation, which become thermally populated in the liquid state. For a flexible chain molecule, such as polymethylene, the contribution due to internal modes, ΔS_i, is given approximately by

$$\Delta S_i = (N - 3)R \ln [1 + 2 \exp(-\varepsilon/kT)] \qquad (1)$$

where N is the number of carbon atoms in the chain, and ε is the energy difference between the trans and gauche states. Experimentally, one finds[3] a linear dependence between ΔS and N, in agreement with Eq. (1),

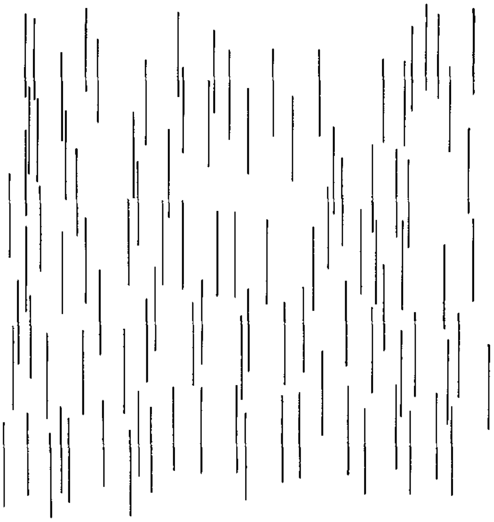
$$\Delta S = R[1.10 + 1.18\, N] \qquad (2)$$

On a molar basis, both the volume change[4] and the entropy increase due to the contribution of internal modes, as predicted by Eq. (1), are known to increase linearly with N. However, less than one-quarter of the coefficient is attributable to the volume change.[5] It should be noted that for $N \equiv 0$, a residual entropy change equal to 1.1 R remains, and that this quantity is about 160 % of $R \ln 2$.

Consider a hypothetical nematic liquid crystal that is perfectly aligned, with an order parameter, $\langle P_2 \rangle$, of unity given by

$$\langle P_2 \rangle = \frac{3\langle \cos^2 \theta \rangle - 1}{2} \qquad (3)$$

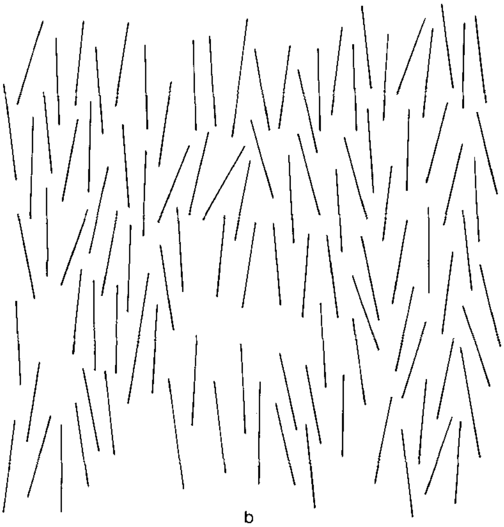
θ being the angle between the vector describing the individual rod-like molecules and the director. This is a situation which is schematically shown in Figure 1a, in which all molecules are absolutely parallel to the director, i.e. a perfect nematic displaying total orientational order *only* with respect to the coordinate θ. *We postulate that for such a perfect nematic, the entropy of melting, corrected for the contribution of internal modes and volume change, would be* $(1/3)\, R \ln 2 = 0.458$ *cal mol*$^{-1}$ *K*$^{-1}$. For all physically realizable situations, however, $\langle P_2 \rangle$ will be of the order of 0.4 ± 0.1 at the melting point, as schematically depicted in Figure 1b. The individual molecules will not be completely ordered with respect to the director. *For such physically realizable systems, we postulate that the entropy of melting, corrected for the contribution of internal modes and volume change would be* $\alpha(1/3)\, R \ln 2$, *with* $0 < \alpha < 1$. The physical interpretation of α is that it is a parameter which takes into account the familiar decrease in the order parameter (partial melting) reflecting an increase in the configurational entropy as the nematic-isotropic transition is approached.[6]



a

$P_2 = 1$

FIGURE 1a A schematic representation of perfect one-dimensional crystal, i.e. a nematic liquid crystal having an order parameter of 1.



b

$0 < P_2 < 1$

FIGURE 1b A schematic representation of a nematic liquid crystal having an order parameter of 0.6.

The configurational entropy of melting for a hard-rod mean field approximation of a nematic-isotropic transition is given by[7]

$$\Delta S = \frac{1/2\, Nv}{T_m} \langle P_2 \rangle^2_{T_m} \tag{4}$$

with $\langle P_2 \rangle_{T_m}$ being a universal constant equal to 0.4289, at the universal value of the melting point $T_m = 0.22019\, v/k$. This gives $\Delta S = 0.83$ cal mol^{-1} K^{-1}. Here N is Avogadro's number, k is Boltzmann's constant, and v a material parameter. This is in good agreement with the two postulates, being 180% of (1/3) R ln 2.

In this paper data have been assembled from the literature for liquid crystalline materials for which both the volume change and entropy values are available for the nematic-isotropic transition. This enables one to ascertain the experimental value of the configurational entropy, free of the complicating factor of volume change, thus permitting the above postulate to be evaluated. In addition, calculations have been made which seek to clarify the possible contribution of mechanically introduced defects to the depression of the melting point. This is seen as a way of evaluating the correctness of the hypothesis that defects do indeed mediate the crystal-liquid transition.

II EXPERIMENTAL DATA

Table I shows data for eleven compounds for which both the volume change and entropy are available for the nematic-isotropic phase transition. The chemical structures are indicated in Figure 2. Since the reported discrepancy in the transition temperature of several degrees gives a corresponding error in the entropy of 1%, only an average transition temperature is given in the table. ΔS is calculated from the ratio $\Delta H/T_{n-i}$. The small volume changes associated with this transition, a few tenths of a percent, render these measurements difficult and the data are accordingly sparse. These data are plotted in Figure 3. The average of all points gives an entropy change of 0.416 cal mol^{-1} K^{-1}, while the linear extrapolation gives 0.258 cal mol^{-1} K^{-1}. The linear regression line has a correlation coefficient of 0.362. The scatter in the data is therefore large, but this is to be expected because:

1) both the volume and enthalpy changes are small and are therefore accompanied by considerable experimental uncertainty,[8]

2) the demarcation of the transition is not clearly defined, since the calorimetric data often show evidence of pre-transitional effects. This is complicated by the fact that the data are obtained by different investigators in different laboratories,

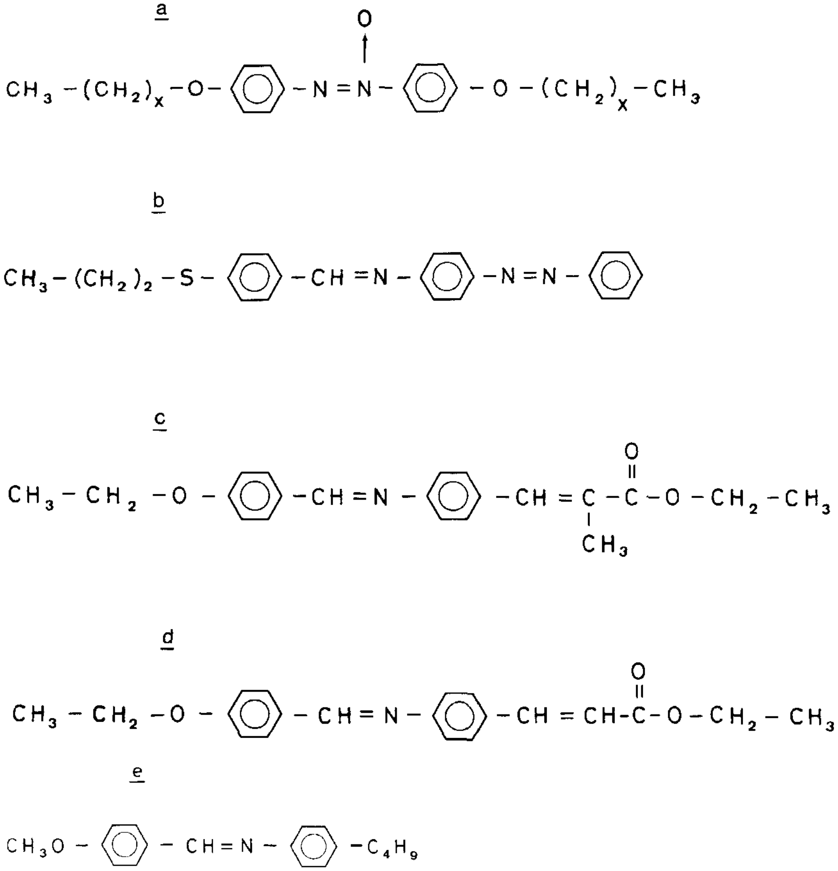


FIGURE 2 Structural formulas for the compounds described in Table I.

3) $\langle P_2 \rangle$ at the melting point is not in fact a universal constant[6] with the entropy of the transition varying as the second power of $\langle P_2 \rangle_{T_m}$. In addition, when considering the scatter in the data relative to that for the melting of metals,[2] one must bear in mind that these compounds are very different in their chemical composition, and in some cases are further complicated by the so-called odd-even effect.

It is to be noted that the average value from Figure 3 of 0.416 cal mol^{-1} K^{-1} is 91% of (1/3)R ln 2 (= 0.458 cal mol^{-1} K^{-1}) as predicted, i.e. very close to, though slightly less than, (1/3)R ln 2.

This very close agreement is probably fortuitous. An extrapolation of the entropy data to zero volume change would be preferable. Although this is

TABLE I

Thermodynamic data for some selected compounds at the nematic-isotropic transition

Compound Designation	Chemical name	Possibility of internal modes	T_{n-i}	ΔH	ΔS	$\Delta V/V$
-	-	-	^{o}K	$\frac{cal}{mole}$	$\frac{cal}{mole \cdot {}^{o}K}$	-
1, Fig. 2a,x=o	4-4'-dimethoxy-azoxy-benzene	-	407.2[9-12]	137.3[10] 176.[11-12]	.337 .432	.0035[9] .0036[13]
2, Fig. 2a,x=1	4-4'-diethoxy-azoxy-benzene	-	439.8[9-10]	326.3[9]	.742	.0060[9,14]
3, Fig. 2a,x=2	4-4'-di-n-propoxy-azoxy-benzene	-	395.9[9-10]	160.8[9]	.406	.0029[9]
4, Fig. 2a,x=3	4-4'-di-n-butoxy-azoxy-benzene	~3	409.4[9-10]	247.0[9]	.603	.003[9]
5, Fig. 2a,x=4	4-4'-di-n-pentoxy-azoxy-benzene	~3[2]	395.7[9-10]	172.7[9]	.436	.002[9]

6, Fig. 2a,x=5	4-4'-di-n-hexoxy-azoxy-benzene	$\sim 3^{3}$	402.4^{9-10}	249.9^{9}	.621	$.003^{9}$
7, Fig. 2a,x=6	4-4'-di-n-heptoxy azoxy-benzene	$\sim 3^{4}$	397.2^{9-10}	243.2^{9}	.612	$.003^{9}$
8, Fig. 2b	4-(4-n-propylmercapto-benzalamino)-azobenzene	-	387.0^{15}	88^{15}	.227	$.00085^{15}$
9, Fig. 2c	4-(4-ethoxybenzalamino)-α-methyl-ethylcinnamate	-	396.7^{15}	48^{15}	.121	$.0019^{9}$ $.00307^{15}$
10, Fig. 2d	4-(4-ethoxybenzalamino)-ethylcinnamate	-	433.4^{15}	120^{15}	.277	$.00448^{15}$
11, Fig. 2e	4-Methoxybenzilidene-4'-butylaniline	~ 3	$317.4^{16,17}$	-	$.469^{16}$	$.0013^{17}$

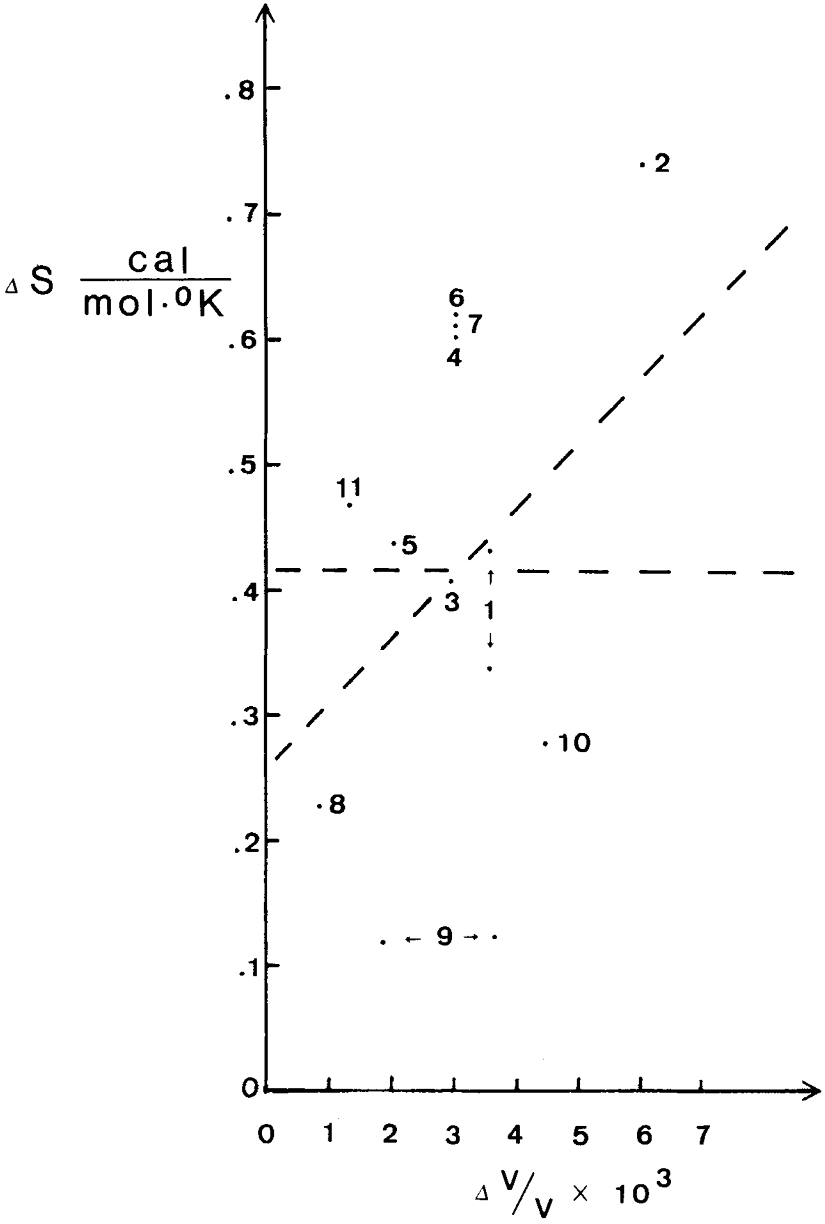


FIGURE 3 A plot of the entropy of the nematic-isotropic transition as a function of the volume change for some selected compounds as indicated in Table I. The horizontal line is the mean value while the sloped line is the result of a linear regression of the data points.

difficult, owing to the large experimental scatter, a value of $\Delta S = 0.258$ cal $\text{mol}^{-1}\ \text{K}^{-1}$ can nevertheless be obtained, i.e. 56% of $(1/3)R \ln 2$. There is therefore an intrinsic configurational entropy change at the transition, over and above the volume-related component, which is often attributed to density changes related to the difference between the ordered and disordered states. This agreement with our postulate would appear to be more than coincidence, and we believe therefore that the postulate thus merits further study. It is also interesting to note that those compounds which are capable of exhibiting internal modes (e.g. 4, 5, 6, 7) do not segregate themselves to any appreciable extent from the rest of the data, as could be expected in light of Eqs. (1) and (2). This is interpreted as indicating that the alkyl side chains are already freely rotating in the nematic phase, and that melting to the isotropic liquid does not alter their conformational distribution. This view is in good agreement with deuterium nuclear magnetic resonance quadrupolar splitting experiments performed to determine the local order parameter of alkyl side chains in liquid crystals.[18]

III THE EFFECT OF EXTERNAL FORCES

In a melting experiment, performed on a sample not subject to external forces, the energy required to cause bifurcation, and hence to form dislocations, is provided by a heat bath in the form of the thermal motion of the atoms as the temperature is raised to the melting point. This picture implies that if dislocations could be formed by alternative means, less thermal energy would be required and hence melting would occur at a lower temperature. The extent of dislocation formation resulting from radiation damage in a crystal,[19] for example, would not be expected to give an experimentally detectable effect sufficient to test this hypothesis. It is proposed here that one investigate the effect of mechanical energy input, e.g. shear flow, on the clearing temperature for a mesophase-isotropic transition in a thermotropic liquid crystal.

It has been demonstrated for example that the effect of shear flow on a monodomain smectic sample is to introduce a massive concentration of defects.[20] It is also well known that, under certain circumstances, the mechanical energy contribution of a system subject to stress can be significant relative to the background thermal energy, kT. The transition behavior can thus be influenced.[21,22] It is therefore proposed to investigate the transition temperature of the mesophase-isotropic transition under conditions of shear flow. This type of experiment will give an indication as to the correctness of the view that defect formation is a mechanistic precursor to melting.

The free energy change associated with the transition from mesophase to isotropic liquid, in the unperturbed state, is given by

$$\Delta G_0 = \Delta H_0 - T_0 \Delta S_0 = 0 \tag{5}$$

The mesophase system is then mechanically sheared so that work is done on it. We assume that all this work goes into the production of defects, thus increasing the free energy of the system. The combined energy from thermal and mechanical sources required to produce the transition under shear will then be equal to the latent heat of the transition in the unperturbed state

$$\Delta H_0 = T_1(\Delta S_1 + \Delta S_2) \tag{6}$$

where T_1 is the melting point under shear, $T_1 \Delta S_1$ is the thermal contribution to the latent heat, and $T_1 \Delta S_2$ is the steady-state mechanical energy input which goes into defect production. To calculate $T_1 \Delta S_2$ consider E, the energy flux per unit volume given by

$$E = \sigma \dot{\gamma} \tag{7}$$

σ being the shear stress and $\dot{\gamma}$ the shear rate.

The stress can be obtained via the viscosity, η, from

$$\sigma(\dot{\gamma}) = \eta(\dot{\gamma})\dot{\gamma} \tag{8}$$

Smectic liquid crystals are known to be highly non-Newtonian such that[22]

$$\eta \propto \dot{\gamma}^{-1} \tag{9}$$

implying

$$\sigma(\dot{\gamma}) \sim \text{constant} \tag{10}$$

Smectics would be the logical candidate for such an experiment since they are known to have a high viscosity. More mechanical energy can thus be injected into the system, with a corresponding enhancement of the effect. Representative data for thermotropic smectics indicate that[23]

1) $\sigma(\dot{\gamma}) \sim 10^2$ dyne cm^{-2},
2) relaxation times are of the order of 1 s,
3) shear rates of 10–100 s^{-1} are obtainable,
4) E therefore will be of the order of 10^4 erg s^{-1} cm^{-3},
5) $T_1 \Delta S_2 \sim 10^4$ erg cm^{-3} $= 2.4 \times 10^{-4}$ cal cm^{-3},
6) with a density of 1 g cm^{-3}, $T_1 \Delta S_2 \sim 2.4 \times 10^{-4}\, M$ cal mol^{-1}, M being the molecular weight.

Substituting in Eq. (5), one has

$$T_1 = \frac{T_0 \Delta S_0 - 2.4 \times 10^{-4} \cdot M}{\Delta S_1} \tag{11}$$

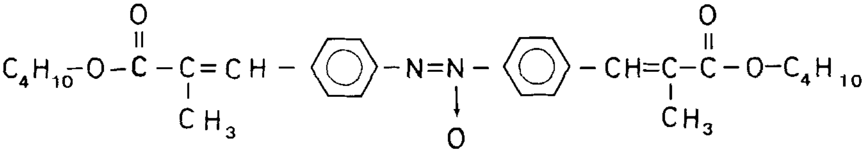


FIGURE 4 The chemical structure of di-*n*-butyl-*p*-azoxy-α-methyl-cinnamate.

for $\Delta S_1 \sim \Delta S_0$

$$T_0 - T_1 = \Delta T = \frac{2.4 \times 10^{-4} \cdot M}{\Delta S_0} \tag{12}$$

To optimize the melting point depression due to shearing as given in Eq. (12) one desires a compound with high molecular weight, high viscosity, and a minimal transition entropy. A favorable example, from a non-exhaustive survey of the literature, is given by: di-*n*-butyl-*p*-azoxy-α-methyl cinnamate,[24] the structure of which is shown in Figure 4. For this compound $M = 488$, $\Delta S = 1.8$ cal K^{-1}, and $T_0 = 103$°C. Substitution into Eq. (12) gives a melting point depression of 0.06°C, a small but detectable decrease.

The detection of such a transition could be accomplished, for example, by the dramatic change in light scattering properties upon passage into the isotropic phase. The utilization of a laser beam would facilitate the focusing of the beam on to the sample such that the experiment could be performed while the viscometer was in operation. The discovery of numerous polymeric materials having thermotropic liquid crystalline properties could make samples available for which this effect was substantially enhanced.[25]

CONCLUSION

It is shown that for a nematic-isotropic transition the configurational entropy is approximately $(1/3)R \ln 2$. This is consistent with the concept that melting is accompanied by a bifurcation of the potential at the transition temperature for these one-dimensional crystals, as has been shown previously for metals and simple molecular solids. From the entropy data it can be seen that the alkyl side chains are already freely rotating in the liquid crystalline state.

It is shown from preliminary calculations that the effect of shear flow on the transition temperature for the mesophase-isotropic transition can give an evaluation of the defect contribution to the melting process. For a chosen example, a melting point depression of 0.06°C could be expected.

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