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Lattice melting at the clearing point in frustrated systems

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This communication was stimulated by a meeting of the Sonderforschungsbereich 335, 'Anisotrope Fluide' at the Technische Universität Berlin, in December 1994. At this conference we realized that there are some very strong similarities between the melting processes of blue phases, twist grain boundary phases, and cubic D phases to the isotropic, amorphous liquid. In all three cases the melting appears to be a two stage process with a sharp melting enthalpy followed by a broad diffuse endotherm as the disorganized liquid is formed. In this article we wish to draw attention to similarities in the nature of these melting processes, to suggest a general descriptive model for the breakdown in molecular ordering, and to stimulate a theoretical debate in order to gain an understanding of the role of frustration phenomena in melting processes.

1. Introduction

At a recent meeting of the Sonderforschungsbereich 335, 'Anisotrope Fluide' at the Technische Universität Berlin concerning *Chirality in Liquid Crystals*, we recognized that there were considerable similarities between the related melting processes of blue phase III, the TGB A* phase, and the cubic D phase to the isotropic liquid. In all three cases the melting process starts with a sharp enthalpy and is followed by a broad diffuse endotherm. Thus, the melting processes appear to take place in two stages. In this article we describe the experimental results obtained for each melting process and suggest related models in each case to describe the breakdown in molecular ordering. We hope by bringing these issues forward, and suggesting that there is a common physical cause for these processes, we will stimulate theoretical interest in this topic.

2. Results

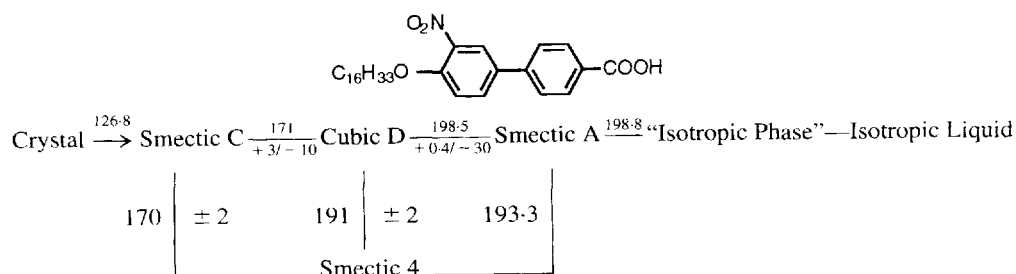
2.1. The cubic D to isotropic liquid transition

Gray [1] originally noted that when the cubic D phases of the homologous 4-*n*-hexadecyloxy- and 4-*n*-octa-

decyloxy-3-nitrobiphenyl-4-carboxylic acids melted to the isotropic liquid they were accompanied by another melting event that seemed to take place in the liquid phase itself. The temperatures for the various *phase transformations* for the hexadecyloxy compound were quoted as follows by Gray [1] and Demus *et al.* [2] (see scheme). Gray reported that the octadecyloxy compound behaves similarly, except that it has a direct transformation from the D phase to the isotropic liquid, missing out the transition to a smectic A phase. At the clearing point a broad diffuse 'hump' was however seen by differential scanning calorimetry for both compounds, which suggests that another 'phase transformation' occurs within the temperature range of the liquid (i.e. a so-called 'isotropic' to isotropic liquid conversion). In the microscope, using a waveplate in conjunction with crossed polarizer, a honeycomb texture was seen which indicated the presence of a biphasic region.

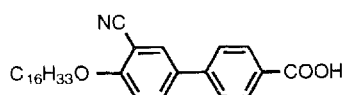
No temperatures were given for the isotropic liquid to isotropic liquid interconversion by Gray; however, it was noted [1] that 7°C above the 'isotropic liquid' transformation, X-ray diffraction showed that some ordering of the molecules was still present for the hexadecyloxy compound. A broad ring with a mean *d* value of 44 Å was

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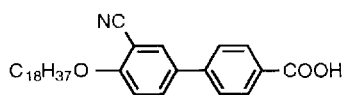


detected while the material was in its first so-called 'isotropic liquid' state. This diffuse ring was found to remain on cooling into the smectic A phase, even though the molecular length of the hydrogen-bonded dimer of the hexadecyloxy compound was determined to be about 65.6 Å. Gray suggested this result implies that the aliphatic chains are appreciably melted.

The analogous cyano-substituted equivalent acids were also examined and shown to exhibit similar broad diffuse 'humps' by scanning calorimetry [1]. The transformation temperatures for the hexadecyloxy and octadecyloxy compounds are shown together below.



Crystal $\xrightarrow{131}$ Smectic C $\xrightarrow{166}$ (144–153 on cooling) Cubic D $\xrightarrow{201}$
 "Isotropic Phase"—Isotropic Liquid



Crystal $\xrightarrow{131}$ Smectic C $\xrightarrow{156}$ (138 on cooling) Cubic D $\xrightarrow{201}$
 "Isotropic Phase"—Isotropic Liquid

Subsequently Kutsumizu, Yamada and Yano [3] went on to prepare other homologues (C_{11} to C_{22}) of the series of nitro compounds reported by Gray. Figure 1 (after Kutsumizu, Yamada and Yano [2]) shows the melting thermograms for all of the compounds reported. It can be seen from this figure that the melting process for the D to liquid phase is characterized first by a sharp melting endotherm and followed by a broad diffuse peak. This phenomenon possibly starts with the tetradecyloxy or pentadecyloxy homologues where the diffuse peak is almost amalgamated with the sharp endotherm. However, for the higher homologues, the presence of diffuse peaks in the thermograms is clear.

2.2. The TGB A* to isotropic liquid transition

The transition from the smectic A* phase to the isotropic liquid in 'highly' chiral liquid crystals was examined in detail by Goodby *et al.* [4, 5]. It was found for a family of chiral substituted phenyl propiolates that, as the alkoxy chain was lengthened, the smectic A* to isotropic

liquid transformation becomes mediated via conversions to and from a frustrated phase, called the twist grain boundary (TGB A*) phase. In the layered smectic A* phases of these materials, the molecules actually prefer to form a helical macrostructure perpendicular to the long axes of the molecules; however, this desire is suppressed by the fact that the molecules are organized in layers. When the 'molecular chirality' is strong and/or the layers are weak enough, the inclination to produce a twisted structure overcomes the layer ordering, and a helical structuring is produced perpendicular to the molecular long axes and parallel to the layers. The helical ordering is a result of the frustration between molecular chirality and layer ordering and is unusual in the fact that the twist

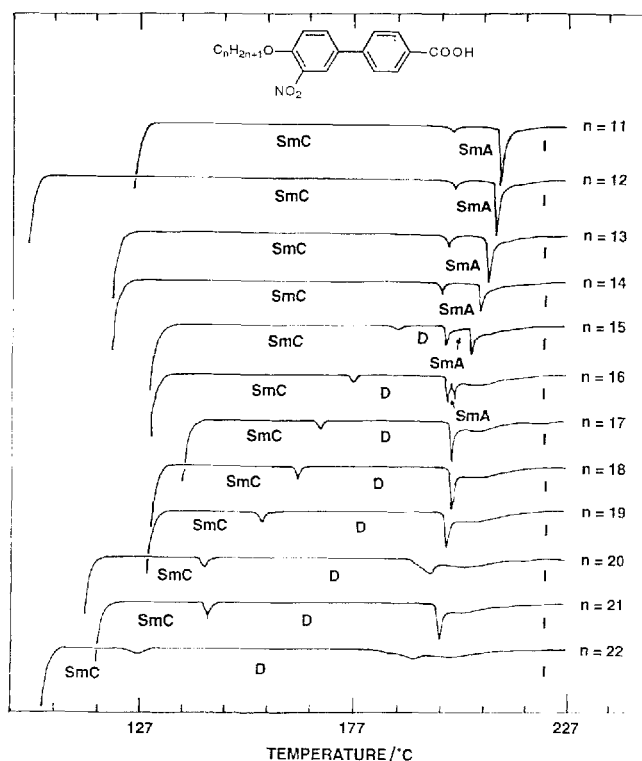
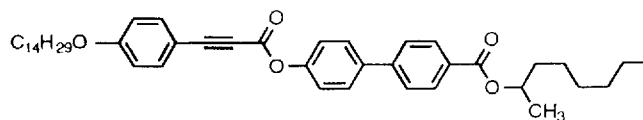


Figure 1. Differential scanning calorimetry thermograms shown as a function of increasing alkoxy chain length for the 4'-*n*-alkoxyoxy-3-nitrophenyl-4-carboxylic acids (after Kutsumizu, Yamada and Yano [2]).



14P1M7

<i>R</i> and <i>S</i> Isomers	Crystal ⁷⁸ Smectic C* ^{89.7} TGB A* ^{93.8} "Isotropic Phase"—Isotropic Liquid
Enthalpy ΔH	Crystal 7.1 Smectic C* 0.04 TGB A* 0.3 "Isotropic Phase"—Isotropic Liquid
Racemate (\pm)	Crystal ^{68.5} Smectic C ^{90.3} Smectic A ^{97.7} Isotropic Liquid
Enthalpy ΔH	Crystal 6.9 Smectic C 0.05 Smectic A 1.24 Isotropic Liquid

(Enthalpy values in cal g⁻¹)

is manifested by a regular array of screw dislocations. Sheets or blocks of the smectic A* phase are rotated through a small angle, relative to one another, by rows of screw dislocations—hence the name twist grain boundary phase.

It was shown that the presence of twist grain boundary phases is dependent on the optical purity of the material and the stereochemical parameters which define the chiral structure of the compound. In addition, the melting thermograms of these compounds showed a sharp melting endotherm for the transformation from the liquid crystalline state to the isotropic liquid accompanied by a broad peak in the temperature range of the liquid, i.e. similar to the conversions seen in the cubic D phase materials. In addition, it was shown that both the liquid crystal to liquid transformation temperature and the accompanying enthalpy associated with the sharp peak were depressed for the chiral compound over its racemic modification. No broad peak was detected for the racemate, and interestingly the enthalpy value for the smectic A to liquid transition for the racemate was found to be approximately equal to the sum of the broad peak and the sharp melting endotherm of the chiral enantiomer. These related phase behaviours are shown above for 1-methylheptyl 4'-(4-*n*-tetradecyloxyphenylpropioloyloxy)biphenyl-4-carboxylate (14P1M7).

Figure 2 (after Nishiyama [6]) shows a typical trend for the differential scanning thermograms of a series of compounds that exhibit TGB A* phases [6]. At short alkoxy chain lengths, the clearing transition is marked by a single sharp endotherm, but as the chain length is increased, starting with the dodecyl homologue, a broad enthalpy appears in the region of the liquid phase. The broad peak, as in the case of the D phase, starts at a point where one phase (in both cases the smectic A phase) is eclipsed as the chain length is extended.

X-ray diffraction in the liquid phase, just above the transformation from the liquid crystalline state, shows a broad diffuse peak, as shown in figure 3 (after Goodby, Waugh, Stein, Chin, Pindak and Patel) for (*S*) or

(*R*)-1-methylheptyl 4'-(4-*n*-tetradecyloxyphenylpropioloyloxy)biphenyl-4-carboxylate (14P1M7). Clearly the diffuse diffraction peak shows that there is some remnant ordering of the molecules in the isotropic liquid. It was suggested that, as the TGB A* phase is analogous to the Abrikosov phase found in Type II superconductors [7],

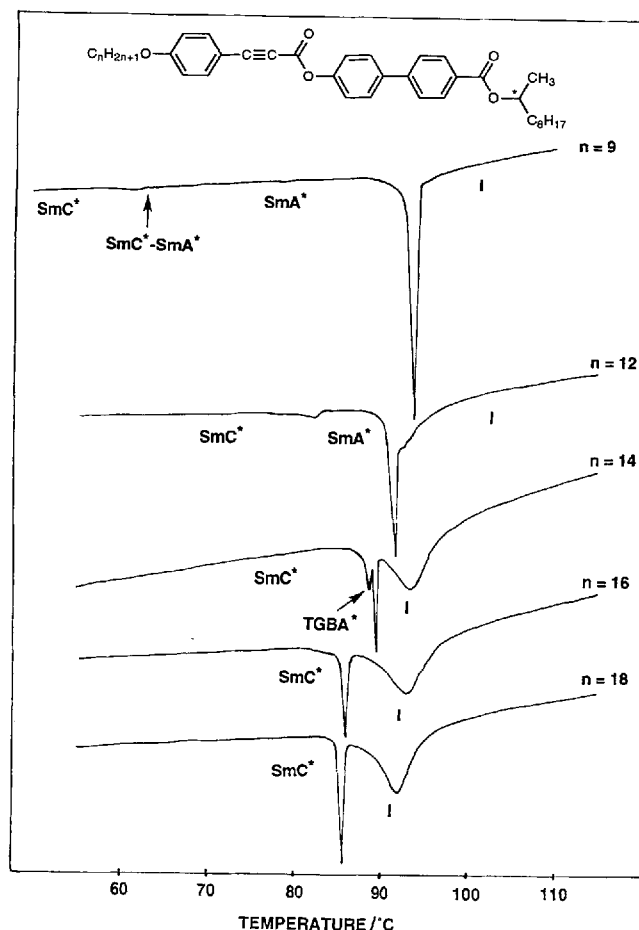


Figure 2. Differential scanning calorimetry thermograms shown as a function of increasing *n*-alkoxy chain length for the (*S*)-1-methylnonyl 4'-(4-*n*-alkoxyphenylpropioloyloxy)biphenyl-4-carboxylates (after Nishiyama [5]).

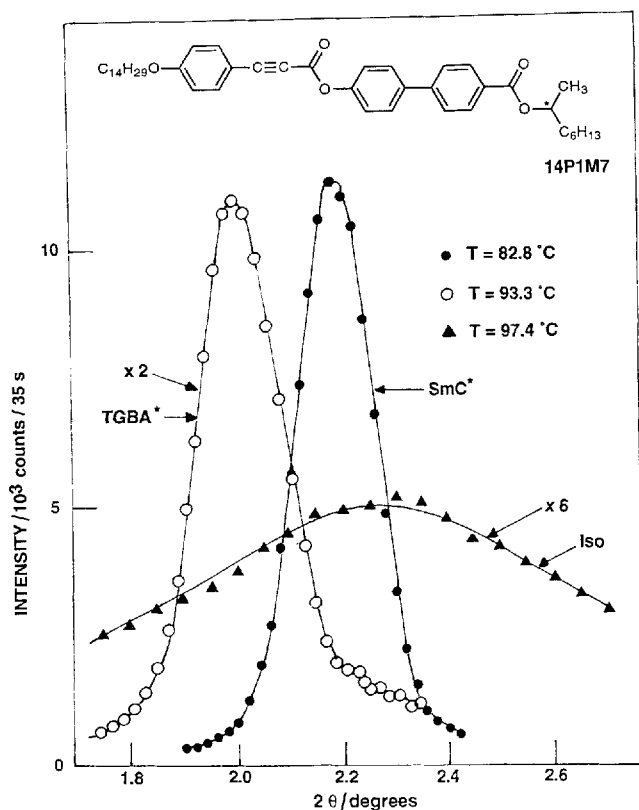


Figure 3. X-ray diffraction scattering profiles in the smectic C^* , TGB A^* and liquid states of (*S*)-1-methylheptyl 4'-(4-*n*-tetradecyloxyphenylpropiolyloxy)biphenyl-4-carboxylate (14P1M7) (after Goodby, Waugh, Stein, Chin, Pindak and Patel [3]).

then this phenomenon could be related to entangled and disentangled flux liquid phases found in superconductors [8]. The proposed flux liquids in TGB related systems could take a form where either the screw dislocations or the smectic A^* sheets melt first at the conversion to the liquid leaving an entangled or disentangled 'fog-type' phase [9].

Similarly, the tilted equivalent of the TGB A^* phase, the TGB C^* analogue, also exhibits a diffuse peak in the isotropic phase as determined by differential scanning calorimetry [10]. However, it is less clear in this case what the structure of the TGB C^* phase is, as there are two possible variants, one where the inter-layer twist of the tilt ordering is expelled (TGB C) and one where it still exists (TGB C^*).

2.3. The blue phase to isotropic liquid transition

Blue phases have been known for a number of years [11], but their structures are as yet not completely understood [12]. Probably the least well-understood of the blue phases is blue phase III or the blue 'fog' phase as it is sometimes called. The 'fog' phase has been suggested

to be the melted version of the cubic blue phases [13], or it could involve random double twist cylinders [14], or have icosahedral, quasi-crystalline order [15], or it possesses bond orientational order [16].

As a result of the many systems that have been investigated, it has been suggested that the blue phase III to isotropic liquid transition is discontinuous [17]. However, recently Kutnjak, Garland, Passmore and Collings [18] have shown for (*S,S*)-4-(2-methylbutyl)phenyl 4-(2-methylbutyl)biphenyl-4'-carboxylate (SSMBBPC), see below, that there is strong evidence that the BP_{III} to isotropic liquid transition is supercritical. This implies that the BP_{III} and isotropic liquid phases have the same macroscopic symmetries and in this compound convert from one to the other continuously.



Heat capacity and static light scattering studies on SSMBBPC indicate that there is a continuous evolution of blue phase III into the amorphous, isotropic liquid. In addition, the dynamic light scattering investigations showed that there are no critical fluctuations. Figure 4 (after Kutnjak, Garland, Passmore and Collings [18])

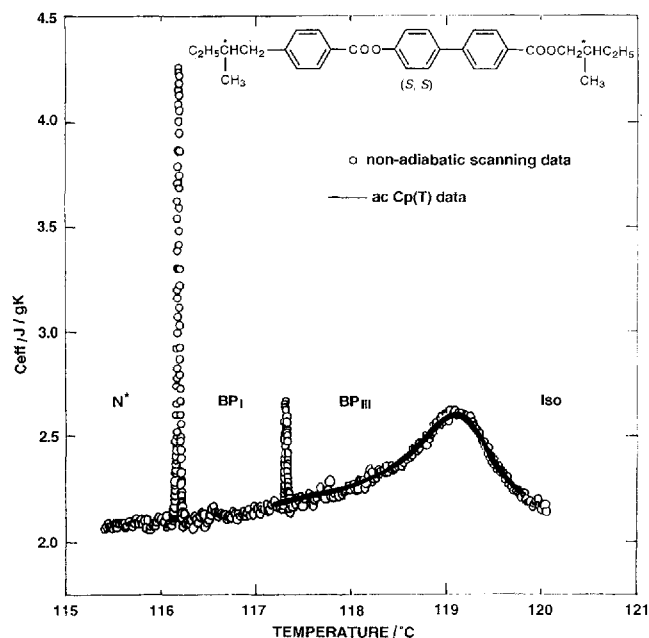


Figure 4. The specific heat capacity variation in the N^* -BP_I-BP_{III}-isotropic liquid transition region for (*S,S*)-4-(2-methylbutyl)phenyl 4'-(2-methylbutyl)biphenyl-4-carboxylate (SSMBBPC).

shows heat capacity measurements for SSMBBPC using a high-resolution calorimeter. No latent heat peak is found when BP_{III} converts to the isotropic liquid, which is in contrast to the situation when the compound has a lower optical purity (i.e. 'molecular chirality') and for some mixtures of SSMBBPC and its racemate.

The existence of a critical point for the BP_{III} to I transition indicates that the structure of BP_{III} must necessarily have isotropic symmetry, i.e. it must have a structure which is similar to that of a liquid. However, the presence of optical activity and optical reflection suggests that the structure of blue phase III cannot be totally isotropic.

3. Discussion

In the original articles published on the discovery of the TGB phase, speculations were made about the nature of the phenomenon which occurred in the liquid state just above the clearing point transition [4, 5, 8]. It was suggested that the ordering found in the amorphous liquid could be due to the formation of structures related to the entangled or disentangled flux liquids found in Type II superconductors [8]. Certainly, the structures near to, and within, the screw dislocations (equivalent to the normal phase) which punctuate the smectic A* phase (equivalent of the superconducting phase) are of considerable interest and speculation. As the smectic A* layers approach a screw dislocation the layers must twist out of the plane as they move into the spiral defect. The molecules can remain either perpendicular to the layers, in which case they probably bend into the defect, or if they remain parallel to the helical axis of the defect they essentially become tilted with respect to the layer planes, i.e. the phase must change its structure from being smectic A*-like at the edge of the defect to being smectic C*-like. As the centre of the defect is approached, the molecules become increasingly tilted with respect to the layers, and indeed the layers will eventually become meaningless and the molecules will effectively have a nematic-like ordering near the core of the defect. This effect is similar to that seen for spiral staircases; the handrail supports are effectively tilted with respect to the handrail, but a layer ordering is still maintained. However, closer to the axis of the spiral staircase the handrail becomes extended and the supports becomes much more tilted with respect to the rail as shown in figure 5.

We might consider, therefore, that the cores of the screw dislocations are nematic-like and will have a different clearing temperature with respect to the bulk phase. As the materials do not exhibit chiral nematic phases we could assume that the temperature at which the cores of the defects melt is, therefore, lower than that of the surrounding bulk phase. It is possible that as the TGB A* phase melts, the defects melt first, thus breaking the lattice-like

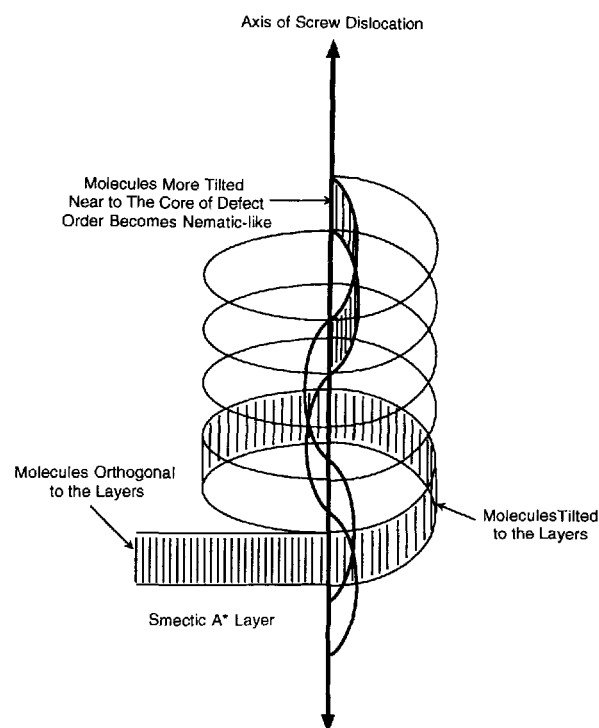


Figure 5. A schematic representation of the local ordering in a screw dislocation in the TGB A* phase.

ordering. The energy evolved at this transition will correspond to a sharp enthalpy typically obtained for a lattice melting. The phase will then have a bulk smectic A* layer structure punctured with puddles of liquid, i.e. corresponding to the formation of a disentangled phase. As the temperature is increased, the unstructured smectic A* phase will melt in a biphasic way to the liquid, i.e. in cybotactic clusters. Thus, a broad diffuse enthalpy might be expected for this process. The clearing transition from the liquid crystalline state to the amorphous liquid might then be characterized by two events, a lattice melting and a gradual continuous melting of the remaining phase to the liquid which corresponds to a sharp peak followed by a broad enthalpy.

The fact that the clearing point temperature for the racemic form (smectic A to isotropic liquid) is approximately the same as the temperature of the maximum heat flow change for the broad peak seen for the enantiomers provides circumstantial evidence that supports this model, i.e. both conversions correspond to the melting of the smectic A (or A*) phase to the liquid. X-ray diffraction supports the view that there is some remnant ordering of the smectic A* phase in the amorphous liquid after melting [4] (between the sharp peak and the broad peak). In addition, CD analysis shows that similar effects also occur for the TGB C* to isotropic liquid phase change [19]. A schematic representation of the structural changes

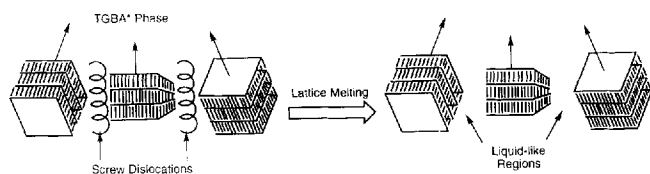


Figure 6. The melting process of the TGB A* phase to the amorphous liquid.

occurring at the TGB A* to liquid transmutation is depicted in figure 6.

A similar description can be used to explain the melting of blue phase III to the liquid. At the clearing transformation, the lattice of defects melts giving a sharp enthalpy peak seen in the specific heat data. This leaves remnants of a double twist structure filled with liquid-like regions, i.e. an entangled phase. Further heating produces a slow melting of the remaining double twist structure to the liquid. The cartoon shown in figure 7 attempts to depict this phenomenon for a blue phase with O^5 symmetry (the O^5 structure is used for simplicity, but a similar model will apply for the other blue phase structures).

Recently, Lubensky and Stark have developed a new theoretical model which can be used to describe the cholesteric/nematic to isotropic phase change [20]. In their model, a scalar order parameter is introduced in addition to the usual orientational order parameter (which is allowed in chiral phases). A Hamiltonian is developed which describes structures at length scales above a critical length. This Hamiltonian is described by Lubensky and Stark as a 'coarse grained Hamiltonian'. Using these order parameters two phases are obtained where the average value for the orientational order parameter is zero. The new order parameter is non-zero in both of these cases, and hence the system belongs to the same Ising universality class as the liquid-gas transition. Hence a critical point in the coexistence line between these phases is predicted, and it is suggested that this corresponds to the BP_{III} to I conversion.

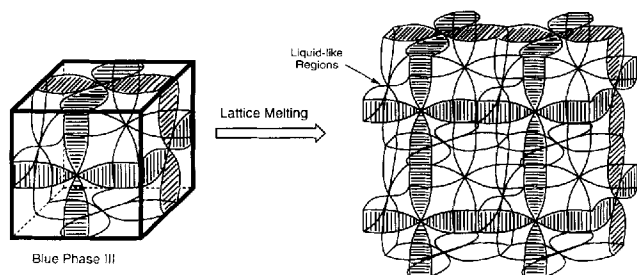


Figure 7. The melting process of a blue phase to the amorphous liquid. (A blue phase with O^5 symmetry was selected for this drawing simply because it is the simplest blue phase structure to draw using double twist structures that include the positions of the molecules.)

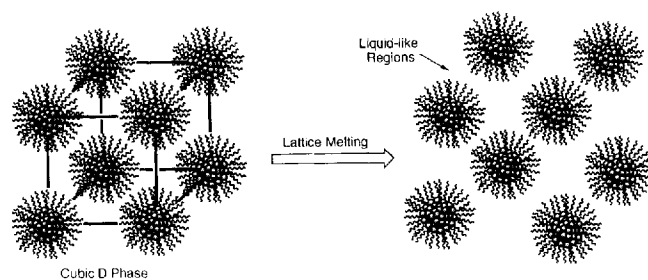


Figure 8. The melting process of the D phase to the amorphous liquid.

Turning now to the D phase, again a lattice is present, but this time not necessarily a lattice composed of defects. However, the structure is made up of molecular clusters that have been created via a form of molecular frustration, which involves polar interactions between the nitro or cyano groups and hydrogen bonding interactions between the carboxylic acid moieties. This form of frustration is therefore slightly different from the ones experienced in the TGB and blue phases, which are a result of the competition between molecular chirality and mesophase ordering.

In the D phase, the cubic lattice probably melts first, resulting in the formation of a sharp peak in the DSC trace. Once the lattice is broken, the liquid will contain clusters of the preceding phase floating in liquid-like regions of melted aliphatic chains, i.e. the structure could almost appear as micellar. Thus, there is an analogy with the TGB and blue phase melting processes—a lattice melting leaving cybotactic-like remnants/clusters of the preceding phase which slowly melt on further heating to give free molecular species in the amorphous liquid. Figure 8 shows a cartoon of the melting process for the cubic D phase. Of course, the cooling process from the amorphous liquid back to the liquid crystal state is perceived to be the reverse procedure.

4. Conclusions

In this article we have attempted to draw attention to the similarities between the melting behaviours of TGB phases, blue phases and cubic D phases in the hope that this will stimulate theoretical discussion as to the true nature and universality of these processes. Indeed it is possible that this phenomenon is not restricted to the phases discussed, but may also be applicable to the melting of nematic phases [21], Q phases [22] and antiferroelectric phases [23].

We wish to thank Professors Gray and Garland and Drs Pindak, Patel and Ungar for stimulating discussions.

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