Theory of Melting of Molecular Crystals III: The Effect of Short Range Orientational Order on Liquid Crystalline Transitions

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Abstract—The theory of melting of molecular crystals developed in Parts I and II is extended to include short range orientational order. The thermodynamic properties are evaluated by the quasi-chemical method, which is mathematically equivalent to Bethe's treatment, and the theory is applied to liquid crystalline transitions. The interesting result is obtained that the nematic–isotropic transition is always first order, and that although the long range orientational order disappears suddenly at this transition point, a certain degree of short range orientational order persists in the isotropic phase. The specific heat exhibits both pre- and post-transition anomalies, in conformity with observations. The thermal expansion and isothermal compressibility show pre-transition anomalies but, contrary to experimental facts, no post-transition anomalies, indicating that even the quasi-chemical approach is not quite adequate for explaining all the properties.

1. Introduction

Though the long range orientational order of the molecules disappears abruptly at the nematic–isotropic transition point, the post-transition anomalies in the specific heat, magnetic birefringence, etc., reveal that an appreciable degree of short range orientational order persists in the liquid phase. Theoretical calculations[1,2] of the entropy of transition also show conclusively that short range order is present even at temperatures well above the transition point. In the light of this evidence, we shall reformulate the theory of melting of molecular crystals discussed in Parts I[3] and II[4] so as to include the effect of short range order. The theory was developed previously by the use of the Bragg–Williams or zeroth approximation;

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we shall now adopt the quasi-chemical approach or the first approximation.[5]

2. The Model

As before, we consider a two-lattice model consisting of N A-sites and N B-sites. A molecule can take up one of two orientations on any site so that it has four possibilities, A_1, A_2, B_1 and B_2. The energy required for a molecule to diffuse to an interstitial site depends on the AB interactions and the orientational barrier is determined by the A_1A_2 or B_1B_2 interactions. Let Q be the fraction of the molecules occupying A-sites and S the fraction occupying 1-orientations. There are then

$$NQS \text{ molecules in } A_1 \text{ positions}$$

$$NQ(1 - S) \text{ molecules in } A_2 \text{ positions}$$

$$N(1 - Q)S \text{ molecules in } B_1 \text{ positions}$$

$$N(1 - Q)(1 - S) \text{ molecules in } B_2 \text{ positions.}$$

To take into account the short range orientational order, we write out the number of AA (or BB) pairs on neighbouring sites occupied in four possible ways. For this purpose it is convenient to regard the A-lattice as consisting of 2 sublattices, each of $N/2$ sites, designated by A' and A''. Let there be

$$\tfrac{1}{2}z'NQ^2X \qquad\qquad\qquad A_1'A_1'' \text{ pairs,}$$

where z' is the number of A-sites closest to any A-site. This determines the number of $A'A''$ pairs occupied in three other ways as given below :

$$\tfrac{1}{2}z'NQ^2(S - X) \qquad\qquad A_1'A_2'' \text{ pairs,}$$

$$\tfrac{1}{2}z'NQ^2(S - X) \qquad\qquad A_2'A_1'' \text{ pairs,}$$

$$\tfrac{1}{2}z'NQ^2(1 - 2S + X) \qquad A_2'A_2'' \text{ pairs.}$$

Similarly, there are

$$\tfrac{1}{2}z'N(1 - Q)^2X \qquad\qquad B_1'B_1'' \text{ pairs,}$$

$$\tfrac{1}{2}z'N(1 - Q)^2(S - X) \qquad B_1'B_2'' \text{ pairs,}$$

$$\tfrac{1}{2}z'N(1 - Q)^2(S - X) \qquad B_2'B_1'' \text{ pairs,}$$

$$\tfrac{1}{2}z'N(1 - Q)^2(1 - 2S + X) \qquad B_2'B_2'' \text{ pairs.}$$

We ignore short range positional order. The partition function for disorder is therefore

$$\Omega = \gamma(Q, S, X)\exp[-\{zNWQ(1-Q) + z'NW'(S-X)(1-2Q+2Q^2)\}/kT],$$

(1)

where W is the repulsive energy of an AB interaction, W' the orientational potential energy of an A_1A_2 or B_1B_2 interaction, and z the number of A-sites adjacent to each B-site.

$$\gamma(Q, S, X)$$

$$= \left\{\frac{[\tfrac{1}{2}N]!}{[\tfrac{1}{2}NQ]![\tfrac{1}{2}N(1-Q)]!}\right\}^4 \left\{\frac{[\tfrac{1}{2}NQ]!}{[\tfrac{1}{2}NQS]![\tfrac{1}{2}NQ(1-S)]!}\right\}^2$$

$$\cdot \frac{[\tfrac{1}{2}z'NQ^2X_0]!\{[\tfrac{1}{2}z'NQ^2(S-X_0)]!\}^2[\tfrac{1}{2}z'NQ^2(1-2S+X_0)]!}{[\tfrac{1}{2}z'NQ^2X]!\ \{[\tfrac{1}{2}z'NQ^2(S-X)]!\}^2\ [\tfrac{1}{2}z'NQ^2(1-2S+X)]!}$$

$$\cdot \left\{\frac{[\tfrac{1}{2}N(1-Q)]!}{[\tfrac{1}{2}N(1-Q)S]![\tfrac{1}{2}N(1-Q)(1-S)]!}\right\}^2$$

$$\cdot \frac{[\tfrac{1}{2}z'N(1-Q)^2X_0]!\{[\tfrac{1}{2}z'N(1-Q)^2(S-X_0)]!\}^2[\tfrac{1}{2}z'N(1-Q)^2(1-2S+X_0)]!}{[\tfrac{1}{2}z'N(1-Q)^2X]!\ \{[\tfrac{1}{2}z'N(1-Q)^2(S-X)]!\}^2\ [\tfrac{1}{2}z'N(1-Q)^2(1-2S+X)]!}$$

$$\simeq \left\{\frac{N!}{[NQ]![N(1-Q)]!}\right\}^2 \frac{[NQ]!}{[NQS]![NQ(1-S)]!}$$

$$\cdot \frac{[\tfrac{1}{2}z'NQ^2X_0]!\{[\tfrac{1}{2}z'NQ^2(S-X_0)]!\}^2[\tfrac{1}{2}z'NQ^2(1-2S+X_0)]!}{[\tfrac{1}{2}z'NQ^2X]!\ \{[\tfrac{1}{2}z'NQ^2(S-X)]!\}^2\ [\tfrac{1}{2}z'NQ^2(1-2S+X)]!}$$

$$\cdot \frac{[N(1-Q)]!}{[N(1-Q)S]![N(1-Q)(1-S)]!}$$

$$\cdot \frac{[\tfrac{1}{2}z'N(1-Q)^2X_0]!\{[\tfrac{1}{2}z'N(1-Q)^2(S-X_0)]!\}^2[\tfrac{1}{2}z'N(1-Q)^2(1-2S+X_0)]!}{[\tfrac{1}{2}z'N(1-Q)^2X]!\ \{[\tfrac{1}{2}z'N(1-Q)^2(S-X)]!\}^2\ [\tfrac{1}{2}z'N(1-Q)^2(1-2S+X)]!}$$

for large N, where $X_0 = S^2$ is the value of X corresponding to complete randomness (see Ref. 5). Maximizing (1) with respect to X leads to the relation

$$\frac{X(1-2S+X)}{(S-X)^2} = \exp(2W'/kT),$$

which could also have been arrived at by Bethe's method.[5,6] Hence

$$X = \frac{(2\alpha S + 1) - [1 + 4\alpha S(1-S)]^{\frac{1}{2}}}{2\alpha},$$

(2)

where

$$\alpha = [\exp(2W'/kT) - 1].$$

The other two conditions of equilibrium are

$$\frac{\partial \log \Omega}{\partial Q} = \frac{\partial \log \Omega}{\partial S} = 0,$$

which yield the following equations:

$$\log \frac{Q}{1-Q} = \left[\frac{z'}{2}\{S^2 \log S^2 + 2(S - S^2) \log (S - S^2) + (1 - 2S + S^2) \log (1 - 2S + S^2)\right.$$

$$- X \log X - 2(S - X) \log (S - X) - (1 - 2S + X) \log (1 - 2S + X)\}$$

$$\left. + \frac{zW}{2kT} - \frac{z'W'}{kT}(S - X)\right] (2Q - 1),\qquad($$

$$\log \frac{S}{1-S} = \left[z'\{S \log S^2 + (1 - 2S) \log (S - S^2) + (S - 1) \log (1 - 2S + S^2)\}\right.$$

$$- \frac{z'}{2}\left\{\frac{\partial X}{\partial S} \log X + 2\left(1 - \frac{\partial X}{\partial S}\right) \log (S - X) + \left(\frac{\partial X}{\partial S} - 2\right) \log (1 - 2S + X)\right\}$$

$$\left. - \frac{z'W'}{kT}\left(1 - \frac{\partial X}{\partial S}\right)\right] (1 - 2Q + 2Q^2).\qquad(-$$

We put

$$W = W_0(V_0/V)^4,$$

$$W' = W_0'(V_0/V)^3,$$

and introduce the parameter

$$\nu = z'W_0'/zW,$$

which is a measure of the relative barriers for the rotation of a molecule and for its diffusion to an interstitial site. For the purpose of numerical calculations, we assume the model to be two inter-penetrating face-centred cubic lattices, so that $z = 6$ and $z' = 12$.

The variation of the equilibrium values of Q, S and X with zW/kT are shown in Fig. 1 for $\nu = 1.35$ and $kT/\epsilon = 0.665$. For the convenience of representing all three quantities in the same diagram, $X^{\frac{1}{2}}$ has been plotted rather than X. It is interesting to observe that $X^{\frac{1}{2}}$ does not drop to 0.5 along with S, showing that short range order is appreciable even for low zW/kT. Hereafter Q, S and X will be understood to refer to the equilibrium values determined by (2), (3) and (4).

3. Evaluation of the Thermodynamic Properties

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

$$\frac{p'' V_0}{NkT} = \frac{zW}{kT} \frac{V_0}{V} \left[4Q(1-Q) + 3\nu \frac{V}{V_0} (1 - 2Q + 2Q^2)(S - X) \right].$$

The entropy of the system due to disorder

$$S'' = -Nk \left[2Q \log Q + 2(1-Q) \log (1-Q) + S \log S + (1-S) \log (1-S) \right.$$

$$- \frac{z'}{2} (1 - 2Q + 2Q^2)\{ X_0 \log X_0 + 2(S - X_0) \log (S - X_0)$$

$$+ (1 - 2S + X_0) \log (1 - 2S + X_0) - X \log X - 2(S - X) \log (S - X)$$

$$\left. - (1 - 2S + X) \log (1 - 2S + X)\} \right].$$
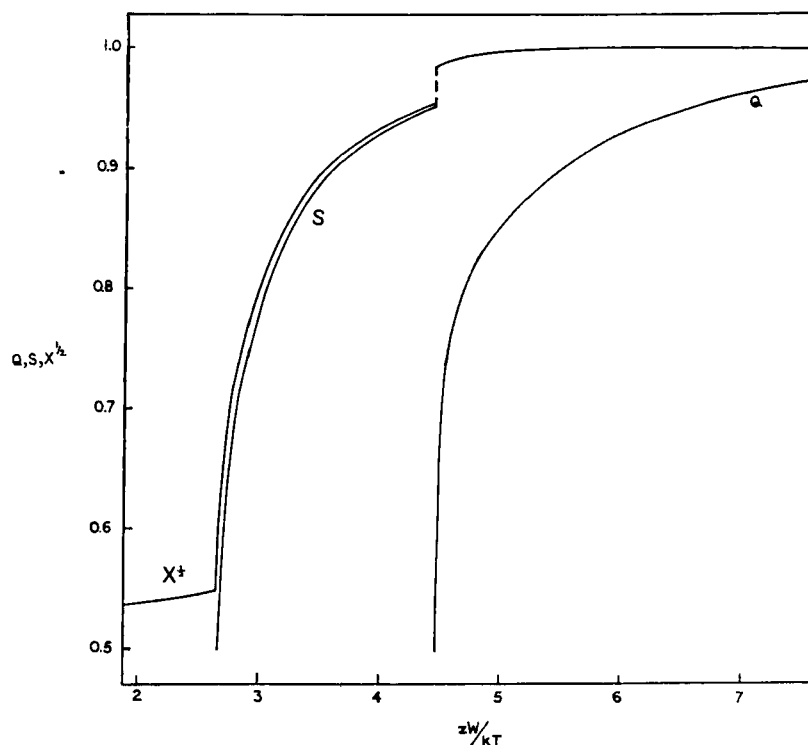

Figure 1.   Variation of equilibrium values of Q, S and $X^{\frac{1}{2}}$ with zW/kT ($\nu = 1.35$, $kT/\epsilon = 0.665$).

The complete isotherm and the entropy of transition were evaluated in the manner described in Part I. For $\nu < 1.3$, there is a single transition in which both the long range positional and orientational order parameters collapse simultaneously. For $\nu > 1.3$, the positional melting precedes the rotational melting, both transitions being attended by changes of entropy and volume. The second order nematic–isotropic transition predicted by the zeroth approximation for a certain range of ν does not occur in this case. The important new result that the nematic–isotropic transition should always be first order is in accord with the observed facts.

The entropy and volume change associated with the solid–nematic transition is practically the same as given by the zeroth approximation, but the corresponding values for the nematic–isotropic transition are significantly different. $\Delta S/R$ and $\Delta V/V$ for the nematic–isotropic transition for a few values of ν are presented in Table 1. From a comparison with Table 1 of Part I,[3] it will be seen that for a given ν the present theory gives an entropy of transition much less than that predicted by the zeroth approximation. This is evidently due to the presence of short range orientational order in the liquid phase.

TABLE 1   Nematic–isotropic Transition

ν	$\dfrac{\Delta S}{R}$	$\dfrac{\Delta V}{V}$
1.32	0.14	0.01
1.35	0.20	0.02
1.40	0.32	0.03
1.50	0.53	0.06

Using Eq. (6) of Part I[3] and proceeding along similar lines, the contribution of the orientational disorder to the specific heat of the nematic and isotropic phases turns out to be

$$\frac{C_v}{R} = 2.931 \left(\frac{V_0}{V}\right)^3 \nu \left[\frac{\partial(S-X)}{\partial(kT/\epsilon)}\right]_V . \tag{5}$$

The isothermal compressibility due to disorder can be evaluated from the general thermodynamic relation

$$\frac{1}{\beta} = -kTV\left(\frac{\partial^2 \log \Omega}{\partial V^2}\right)_T .$$

$$J^{-1}\left(\frac{\partial \log \Omega}{\partial V}\right)_T = \left(\frac{\partial Q}{\partial V}\right)_T \left[-2\log \frac{Q}{1-Q} + z'\{S^2 \log S^2 + 2(S - S^2)\log(S - S^2)\right.$$

$$+ (1 - 2S + S^2)\log(1 - 2S + S^2) - X\log X - 2(S - X)\log(S - X)$$

$$\left. - (1 - 2S + X)\log(1 - 2S + X)\}(2Q - 1) + \left\{\frac{zW}{kT} - \frac{z'W'}{kT}2(S - X)\right\}(2Q - 1)\right]$$

$$+ \left(\frac{\partial S}{\partial V}\right)_T \left[-\log \frac{S}{1-S} + z'(1 - 2Q + 2Q^2)\{S\log S^2 + (1 - 2S)\log(S - S^2)\right.$$

$$+ (S - 1)\log(1 - 2S + S^2)\} - \frac{z'}{2}(1 - 2Q + 2Q^2)\left\{\frac{\partial X}{\partial S}\log X\right.$$

$$\left. + 2\left(1 - \frac{\partial X}{\partial S}\right)\log(S - X) + \left(\frac{\partial X}{\partial S} - 2\right)\log(1 - 2S + X)\right\}$$

$$\left. - \frac{z'W'}{kT}(1 - 2Q + 2Q^2)\left(1 - \frac{\partial X}{\partial S}\right)\right] + \frac{zW}{kTV}4Q(1 - Q)$$

$$+ \frac{3z'W'}{kTV}(1 - 2Q + 2Q^2)(S - X).$$

The coefficients of $(\partial Q/\partial V)_T$ and $(\partial S/\partial V)_T$ vanish because of the maximizing conditions (3) and (4). Therefore

$$N^{-1}\left(\frac{\partial^2 \log \Omega}{\partial V^2}\right)_T = \frac{zW}{kT}\left[(2Q - 1)\left(\frac{\partial Q}{\partial V}\right)_T\left\{\frac{6\nu}{V_0}(S - X) - 4V\right\}\right.$$

$$- \frac{20Q(1 - Q)}{V^2} - \frac{12\nu}{VV_0}(1 - 2Q + 2Q^2)(S - X)$$

$$\left. + \frac{3\nu}{V_0}(1 - 2Q + 2Q^2)\left\{\frac{\partial(S - X)}{\partial V}\right\}_T\right].$$

Putting $Q = \frac{1}{2}$ in the nematic and isotropic phases

$$\frac{1}{\beta} = NzW\left[\frac{5}{V} + \frac{6\nu}{V_0}(S - X) - \frac{3\nu}{2}\frac{V}{V_0}\left\{\frac{\partial(S - X)}{\partial V}\right\}_T\right]$$

$$= 5.862\left(\frac{N\epsilon}{V_0}\right)\left(\frac{V_0}{V}\right)^4\left[5\frac{V_0}{V} + 6\nu(S - X) - \frac{3\nu}{2}\left(\frac{V}{V_0}\right)\left\{\frac{\partial(S - X)}{\partial(V/V_0)}\right\}_T\right]. \quad (6)$$

The intersection of an isotherm with the zero pressure line determines S, X and V/V_0 for that temperature and pressure. $(S - X)$ at the same kT/ϵ but a slightly different V/V_0, and hence $[\partial(S - X)/\partial(V/V_0)]_T$ in (6), can be derived from the same isotherm ; $(S - X)$ at the same (V/V_0) but at a different (kT/ϵ), and hence $[\partial(S - X)/\partial(kT/\epsilon)]_V$ in (5), can be obtained from an isotherm for a slightly different kT/ϵ. The long range order parameter $s = (2S - 1)$, the specific heat, thermal expansion and isothermal compressibility evaluated in this manner are shown in Figs. 2–5. The specific heat exhibits a slight post-transition anomaly (Fig. 3), whereas according to the zeroth approximation C_v/R should vanish in the liquid phase. However, contrary to experimental facts, the thermal expansion and isothermal compressibility curves do not show such an anomaly (Figs. 4 and 5), indicating that even the first approximation is not quite adequate for explaining all the properties.
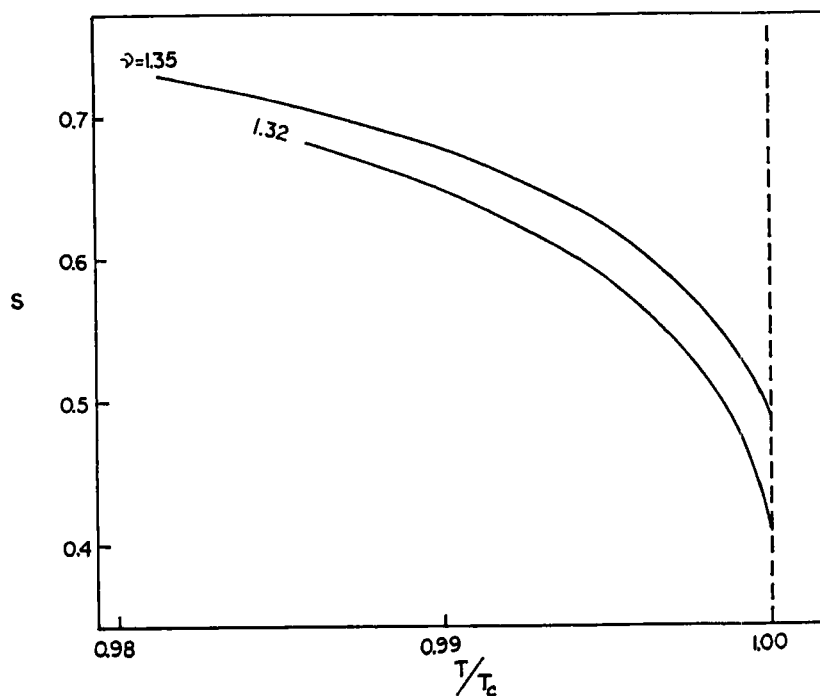

Figure 2.   Long range orientational order parameter $s = (2S - 1)$ in the nematic phase (at zero pressure) for $\nu = 1.32$ and 1.35.
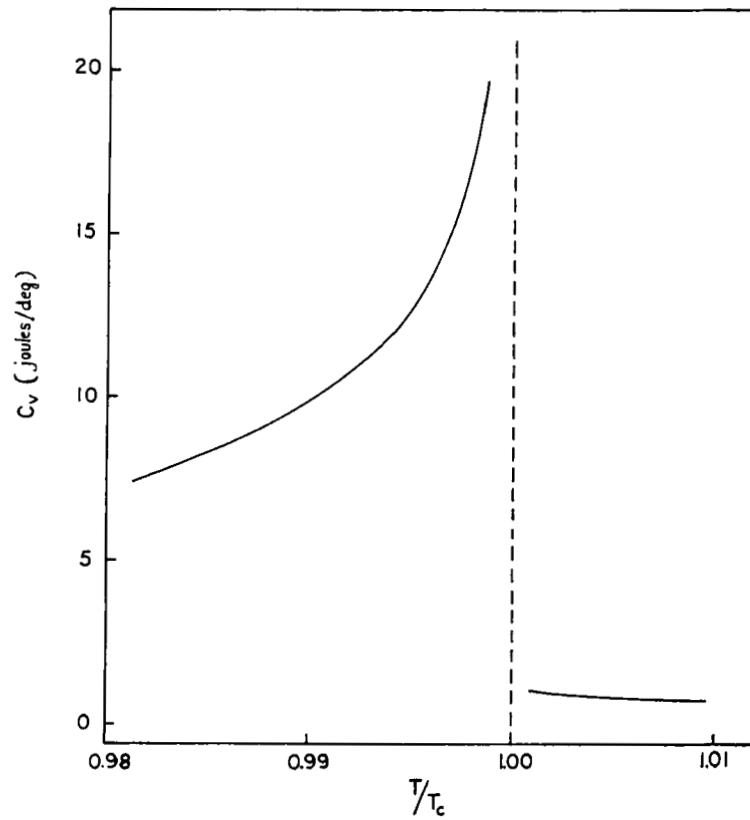
Fig. 3.   Contribution of orientational disorder to the specific heat at constant volume in nematic and isotropic phases ($\nu = 1.35$).
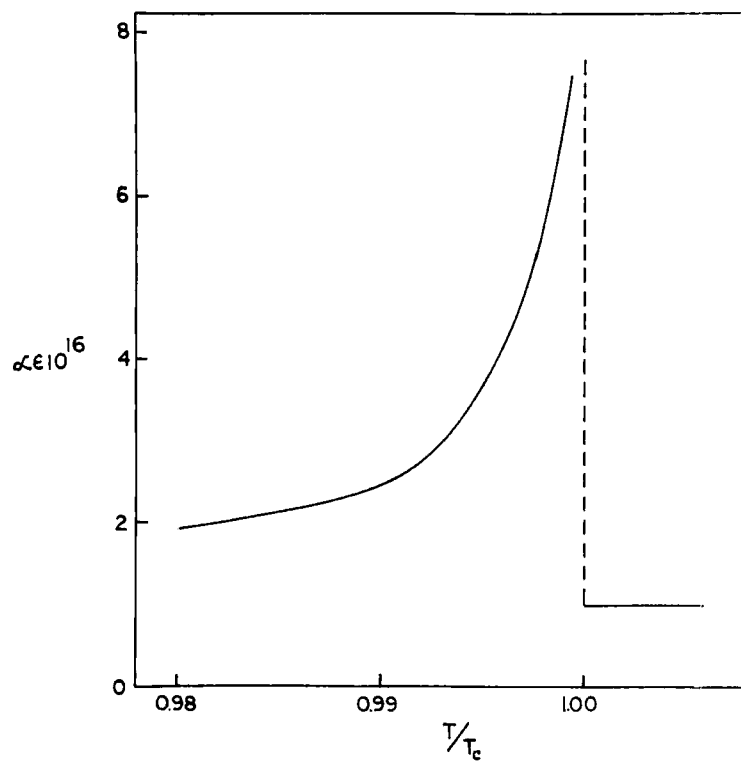
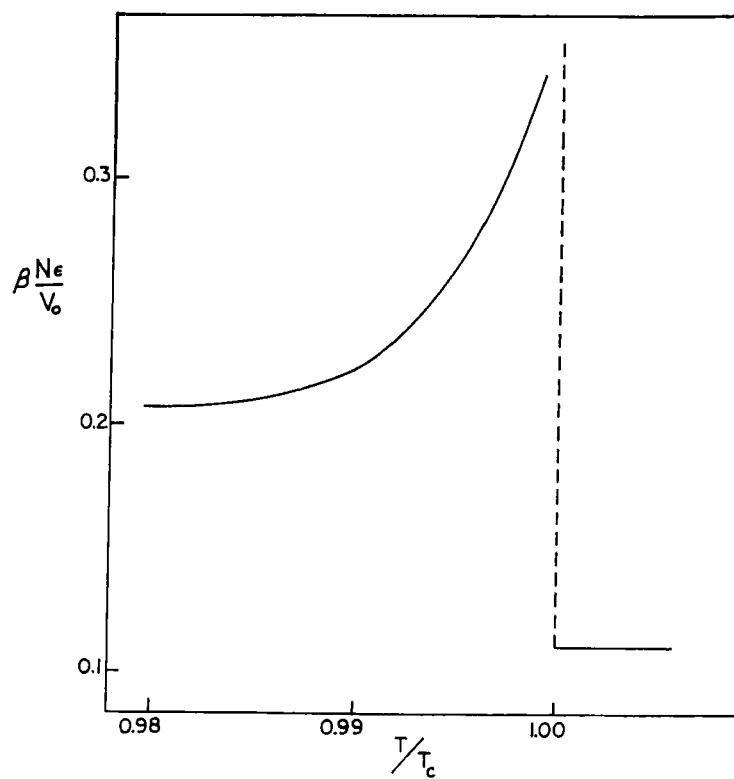Figure 4.   Coefficient of thermal expansion in nematic and isotropic phases
(ν = 1.35).

Figure 5.   Isothermal compressibility due to disorder in nematic and isotropic phases ($\nu = 1.35$).

4. Acknowledgement

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