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Compressibility and Thermal Expansion Anomalies in the Isotropic Liquid Crystal Phase

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De Gennes' theory of pretransition effects in the isotropic liquid crystal phase is generalized to include number density and orientational fluctuations. Order fluctuations produce more efficient local packing of rod-shaped molecules with a resulting fluid contraction. This mechanism is proposed to explain the anomalous rise in compressibility and thermal expansivity of liquid crystals above the clearing temperature.

Number density fluctuations which are driven by the order fluctuations are predicted to vary with temperature above the nematic transition as

$$(\Delta\rho)^2 \sim (T - T^*)^{-\gamma}$$

where T is the absolute temperature, T^* is the pseudocritical temperature of nematic ordering, and γ is the exponent determining the growth of the order fluctuations. Light scattering and magnetic birefringence studies have shown γ is very near to one for MBBA. This form for the density deviations implies an incremental compressibility with an exponent equal to one

$$\Delta\kappa_T \sim (T - T^*)^{-1}$$

An additional assumption, that the compressibility anomaly is the sole origin of the expansion anomaly, gives for the incremental expansion above the clearing point

$$\Delta\alpha_p \sim (T - T^*)^{-1}$$

The theory of $\Delta\kappa_T$ is compared to data from sound velocity measurements, though the need for true static measurements is emphasized. The derived form for the expansion coefficient is found to be in good agreement with recent measurements of Gulari and Chu for MBBA.

1 INTRODUCTION

The weak first order nature of the nematic–isotropic phase transition suggests that in important ways the phase change is similar to a critical transition. The key property of a critical system which the pretransitional liquid crystal shares, is a growth of long-range order fluctuations in the high-temperature region before the phase change. De Gennes[1] has made these long-wavelength order fluctuations the basis of a Landau-type[2] theory of the isotropic fluid properties above the clearing point T_k. Though the reason for this theory's success is yet unclear[3,4] (in particular the meaning of the pseudocritical temperature T^* is in dispute[4]), it provides a useful framework to account for the wide variety of short range order effects observed in the transition region.[5]

The Landau model of de Gennes[1] is based on an expansion of the free energy of the fluid in terms of an order parameter and gradients in the order parameter. This is, in essence, the approach used in this article. There are two main differences between de Gennes' theory and the present. The de Gennes' order parameter is macroscopically defined and is a measure of the diamagnetic anisotropy of the system. This choice has its merits and permits an unambiguous empirical determination. In the present theory the order parameter is identified from a spherical harmonic expansion of a pre-averaged molecular probability density. A detailed microscopic theory of correlations in the pretransition region can more easily commence at such a point. Secondly, the present formalism allows for number density fluctuations in addition to orientational ones. In this way anomalies in both the compressibility and thermal expansion can be discussed.[6]

2 ORDER AND DENSITY FLUCTUATIONS

The difference in Helmholtz free energy between the isotropic liquid crystal with local, slowly varying fluctuations in order and density, and the liquid with no fluctuations is taken to be (to second order terms in the fluctuations)

$$A - A_0 = \tfrac{1}{2}kT \iint d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{e}_1\, d\mathbf{e}_2\, C(\mathbf{r}_1, \mathbf{r}_2, \mathbf{e}_1, \mathbf{e}_2) f'(\mathbf{r}_1, \mathbf{e}_1) f'(\mathbf{r}_2, \mathbf{e}_2) \qquad (2.1)$$

where C is proportional to the direct correlation function for a fluid of anisotropic molecules,[7] $f'(\mathbf{r}, \mathbf{e})$ is the fluctuation in the density of molecules at $\mathbf{r}$ in the direction $\mathbf{e}$, kT is Boltzmann's constant times the absolute temperature, and the integrations are taken over the whole volume and over all orientations. The total density is given by

$$f(\mathbf{r}, \mathbf{e}) = \frac{\rho}{4\pi} + f'(\mathbf{r}, \mathbf{e}) \qquad (2.2)$$

where ρ is the average number density in the system. Equation (2.1) is the counterpart in the present theory of the Landau expansion in powers of the order parameter.[8] For simplicity in the present application of the theory, the order parameter s suitable for rod-like molecules is adopted

$$s \equiv \langle \tfrac{1}{2}(3 \cos^2 \theta - 1) \rangle = \langle P_2(\cos \theta) \rangle \tag{2.3}$$

where θ is the angle between the rod axis and a space-fixed z axis, P_2 is the second Legendre polynomial, and the brackets denote Boltzmann-weighted averages. From the definition of f as the probability density, it follows that the local order is

$$s(\mathbf{r}) = \frac{\int d\mathbf{e}\, f(\mathbf{r}, \mathbf{e}) P_2(\cos \theta)}{\int d\mathbf{e}\, f(\mathbf{r}, \mathbf{e})} \tag{2.4}$$

For more general shapes than rod-like, additional order parameters, analogous to (2.3), can be defined so as to include all the second order spherical harmonics.[6] This greater generality is not needed to account for anomalies in the compressibility and expansivity. Axially symmetric fluctuations f' are sufficient. For this reason, the spherical harmonic expansion of $f'(\mathbf{r}, \mathbf{e})$ is approximated by

$$f'(\mathbf{r}, \mathbf{e}) \simeq (4\pi)^{-1}[f_0(\mathbf{r}) + f_2(\mathbf{r}) P_2(\cos \theta)] \tag{2.5}$$

where $f_0(r)$ is the density fluctuation of molecules at $\mathbf{r}$, irrespective of orientation. From (2.4) and (2.5) it also follows that

$$s(\mathbf{r}) = (5\rho)^{-1} f_2(\mathbf{r}) \tag{2.6}$$

so f_2 is proportional to the local order at $\mathbf{r}$.

The quantity which governs pretransition behavior of the fluctuations is $C(\mathbf{r}_1, \mathbf{r}_2, \mathbf{e}_1, \mathbf{e}_2)$ in (2.1). It measures the strength with which fluctuations from the most probable distribution are damped in configuration space, and therefore, determines the correlation length λ of the local order in the isotropic fluid phase. The spherical harmonic expansion of C also reflects the symmetry of the local order regions. The second degree Legendre polynomials are the simplest representation of the fluid anisotropy, and the Maier–Saupe[9] mean-field model of C has the form

$$C(\mathbf{r}_1, \mathbf{r}_2, \mathbf{e}_1, \mathbf{e}_2) = C_{00}(r) + C_{22}(r) P_2(\cos \theta_1) P_2(\cos \theta_2) \tag{2.7}$$

where r is the magnitude of the vector $\mathbf{r}_1 - \mathbf{r}_2$. Equation (2.7) does not predict any direct coupling of density and order deviations. Since the present theory attempts to treat such a coupling explicitly, and assess its thermodynamic consequences, (2.7) is generalized to

$$\begin{aligned} C = C_{00}(r) &+ C_{20}(r)[P_2(\cos \theta_{1r}) + P_2(\cos \theta_{2r})] \\ &+ C_{22}(r) P_2(\cos \theta_1) P_2(\cos \theta_2) \end{aligned} \tag{2.8}$$

where θ_{1_r}, θ_{2_r} are the angles between the local ordering axes and the vector **r** between order regions.[10] When (2.5) and (2.8) are substituted into (2.1) and the angle integrations are performed, the fluctuation free energy becomes

$$\beta(A - A_0) = \tfrac{1}{2}\int d\mathbf{r}_1\, d\mathbf{r}_2\{C_{00} f_0(\mathbf{r}_1)f_0(\mathbf{r}_2) + \tfrac{1}{5}C_{20}[f_0(\mathbf{r}_1)f_2(\mathbf{r}_2) + f_0(\mathbf{r}_2)f_2(\mathbf{r}_1)] + \tfrac{1}{25}C_{22} f_2(\mathbf{r}_1)f_2(\mathbf{r}_2)\} \tag{2.9}$$

where $\beta = (kT)^{-1}$. In terms of the local order $s(r)$, (2.9) is

$$\beta(A - A_0) = \tfrac{1}{2}\iint d\mathbf{r}_1\, d\mathbf{r}_2\{C_{00} f_0(\mathbf{r}_1)f_0(\mathbf{r}_2) + \rho C_{20}[f_0(\mathbf{r}_1)s(\mathbf{r}_2) + f^0(\mathbf{r}_2)s(\mathbf{r}_1)] + \rho^2 C_{22} s(\mathbf{r}_1)s(\mathbf{r}_2)\} \tag{2.10}$$

To proceed further, Fourie series expansions of all quantities in (2.10) are introduced to diagonalize the quadratic (free) energy form. These are given by

$$f_0(r) = M^{-3/2}\sum_{\mathbf{q}} \tilde{f}_0(\mathbf{q})e^{2\pi i\mathbf{q}\cdot\mathbf{r}} \tag{2.11a}$$

$$s(r) = M^{-3/2}\sum_{\mathbf{q}} \tilde{s}(\mathbf{q})e^{2\pi i\mathbf{q}\cdot\mathbf{r}} \tag{2.11b}$$

$$C_{00}(r) = M^{-3}\sum_{\mathbf{q}} \tilde{C}_{00}(\mathbf{q})e^{2\pi i\mathbf{q}\cdot\mathbf{r}} \tag{2.11c}$$

with expressions analogous to (2.11c) for C_{20} and C_{22}. The sums in (2.11) run over all reciprocal lattice vectors **q** defined by

$$\mathbf{q} = q_1\mathbf{i} + q_2\mathbf{j} + q_3\mathbf{k} \qquad q_1, q_2, q_3 = 0, 1, 2, \ldots, M - 1 \tag{2.12}$$

with **i**, **j**, **k** unit basis vectors. The question of the number of Fourier components to use in (2.11) is best discussed in terms of an explicit model for the intermolecular potential, and is deferred to a future article. A rough criterion is $V/M^3 \simeq \lambda^3$ (V = volume of the system, M^3 = the number of Fourier components), i.e. M^3 should be large enough so that the spatial variation of the long-wavelength fluctuations is able to be described. The actual value of M used does not affect the final results.

Introducing (2.11) into (2.10), and using the orthogonality relation

$$\sum_{\mathbf{r}} e^{2\pi i\mathbf{r}\cdot(\mathbf{q}-\mathbf{q}')} = M^3\delta_{\mathbf{q},\mathbf{q}'} \tag{2.12}$$

one obtains

$$\beta(A - A_0) = (\tfrac{1}{2})\sum_{\mathbf{q}} [\tilde{C}_{00}|\tilde{f}_0|^2 + \rho\tilde{C}_{20}(\tilde{f}_0^*\tilde{s} + \tilde{f}_0\tilde{s}^*) + \rho^2\tilde{C}_{22}|\tilde{s}|^2] \tag{2.13}$$

where the **q** dependence of all quantities in the summand is left implicit.

With (2.13) one can compute the magnitude of the fluctuations in density and order. Since the probability of a state of fluctuation at equilibrium is proportional to the reversible work it takes to cause it,[2] the Boltzmann factor $P(\tilde{s}, \tilde{f}_0)$ for the order and density fluctuations is

$$P(\tilde{s}, \tilde{f}_0) = Q^{-1} \exp[-\beta(\tilde{C}_{00}|\tilde{f}_0|^2 + \rho\tilde{C}_{20}(\tilde{f}_0\tilde{s}^* + \tilde{f}_0^*\tilde{s}) + \rho^2 C_{22}|\tilde{s}|^2)] \tag{2.14}$$

where Q is a normalization factor. Using (2.14), one finds

$$\langle|\tilde{f}_0(\mathbf{q})|^2\rangle = 2[\beta\tilde{C}_{00}(1 - R^2)]^{-1} \tag{2.15a}$$

$$\langle|\tilde{s}(\mathbf{q})|^2\rangle = 2[\beta\tilde{C}_{22}(1 - R^2)]^{-1} \tag{2.15b}$$

where R^2 (which measures the coupling between the order and the density), is given by

$$R^2 = \frac{(\tilde{C}_{02})^2}{\tilde{C}_{00}\tilde{C}_{22}} \tag{2.16}$$

De Gennes' result[1] for $\langle|\tilde{s}(\mathbf{q})|^2\rangle$ is recovered if $\tilde{C}_{20} = 0$, for then $R^2 = 0$. The temperature dependence of the order fluctuations is found to be accurately accounted for by assuming[1]

$$\tilde{C}_{22}(q) \simeq a + bq^2 \tag{2.17}$$

with

$$a = a'(T - T^*)^\gamma \tag{2.18}$$

T^* being the pseudocritical temperature (somewhat below the actual transition temperature T_k), and the exponent γ is very nearly one.[1,3] Studies of the angle dependence of the light scattering from isotropic liquid crystals reveal that the second term in (2.17) is small compared to the first.[1,3] It is ignored in the following discussion of the temperature behavior of the density and order fluctuations.

From (2.16) → (2.18) it is apparent that as T approaches T^* from above (assuming $\tilde{C}_{02}$ and $\tilde{C}_{00}$ do not depend much on temperature), R^2 increases resulting in a stronger order-density coupling. From (2.15a)

$$\langle|\tilde{f}_0(\mathbf{q})|^2\rangle \simeq 2[\beta\tilde{C}_{00}(\mathbf{q})]^{-1}[1 + R^2 + \cdots] \tag{2.19}$$

and from the temperature dependence $R^2 \simeq R_0^2(T - T^*)^{-1}$ (from (2.16)–(2.18) and $\gamma \simeq 1$) it follows that as the temperature falls in the neighborhood of the nematic transition the density fluctuations will begin to exhibit an extra contribution of the form

$$\langle|\tilde{f}_0(\mathbf{q})|^2\rangle - \langle|\tilde{f}_0(\mathbf{q})|\rangle_0 \sim A(\mathbf{q}) \cdot (T - T^*)^{-1} \tag{2.20}$$

where $\langle|\tilde{f}_0(\mathbf{q})|^2\rangle_0$ is the magnitude of the fluctuations in the absence of the ordering effect. In particular, the isothermal compressibility of a fluid is proportional to $\langle|\tilde{f}_0(0)|^2\rangle$,[11] so that (2.20) predicts an increment in the compressibility κ_T due to the order–density coupling ($R^2 \neq 0$)

$$\Delta\kappa_T \sim A(0)(T - T^*)^{-1}, \qquad \kappa_T \equiv -\frac{1}{V}\left[\frac{\partial V}{\partial P}\right]_T \tag{2.21}$$

Data on isothermal compressibilities of liquid crystals is not readily available, though such measurements have quite recently been made on supercooled water[12] and a direct test of (2.21) seems possible at present. Lacking static measurements of κ_T, in the next section we compare (2.21) with data gathered from sound velocity studies.[13]

The equation-of-state anomaly in the pretransition region which has received the most experimental scrutiny is the coefficient of thermal expansion.[9,14–17] Unlike the compressibility anomaly discussed above, the expansivity anomaly in the isotropic liquid crystal phase has been discussed theoretically by Imura and Okano.[18] They postulate that the local density increment due to the order ($f_0(\mathbf{r})$ in the present notation) is a quadratic function of the local order (this is to be contrasted to (2.13)). Then, in the spirit of Fixman's calculation of the heat capacity in the critical region,[19] they find the thermal average of the temperature derivative of the density by integrating over the long-wavelength spectrum of the order correlation function. In contrast, the present theory suggests that there is a linear coupling (locally) of order to density. The order fluctuations, which become large near the transition, produce an excess internal pressure and (with the enhanced compressibility) result in a more rapid contraction of the fluid. Our view is that the expansion anomaly is primarily caused by the increase in compressibility as the transition approaches. The general relation between the compressibility and expansivity of a fluid is[20]

$$\alpha_P = \frac{1}{V}\left(\frac{\partial P}{\partial T}\right)_P = \left(\frac{\partial P}{\partial T}\right)_V \kappa_T \tag{2.22}$$

If the expansion anomaly is totally due to the compressibility (i.e., if the thermal pressure coefficient suffers no increment)

$$\Delta\alpha_P \simeq \gamma_V \Delta\kappa_T \tag{2.23}$$

where γ_T is the thermal pressure coefficient $(\partial P/\partial T)_V$. With this approximation and (2.21) for $\Delta\kappa_T$, the expansion anomaly is

$$\Delta\alpha_P \sim B(T - T^*)^{-1} \tag{2.24}$$

where B is assumed constant in the vicinity of the transition.

3 EXPERIMENT

3.1 Compressibility anomaly of PAA

Though the measurements appear entirely feasible at present,[12] data for a direct test of (2.21) does not seem to exist. However, sound dispersion studies on pretransitional liquid crystals have been made and analyzed in terms of an augmented *adiabatic* compressibility,[13,21,22] and through standard thermodynamic relations, an anomaly in the isothermal compressibility has been deduced. The weak link in this argument is, of course, the presumed

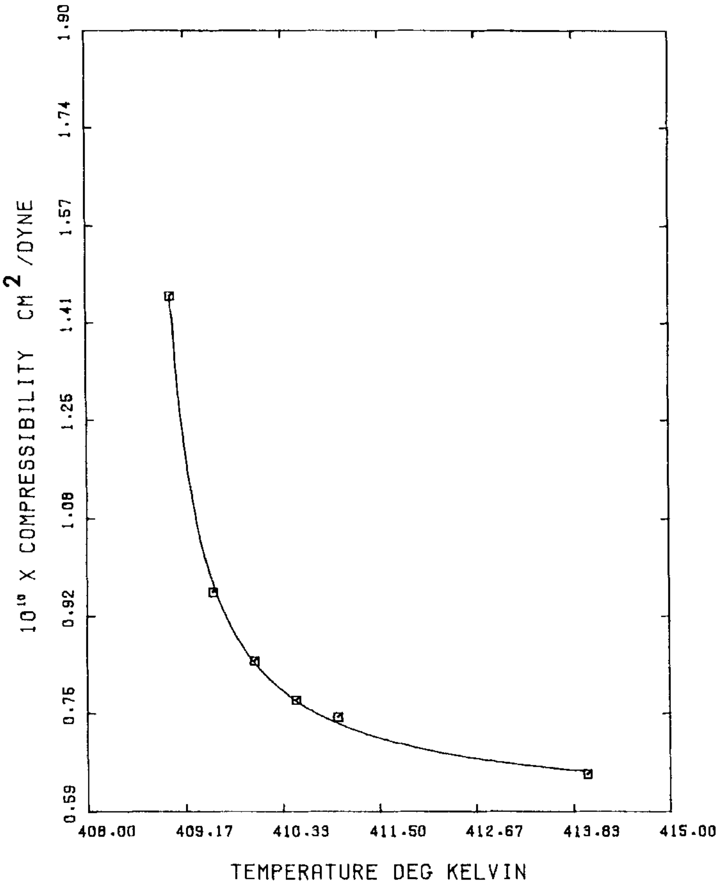

FIGURE 1 Compressibility (isothermal) of *p*-azoxyanisole (PAA) as a function of temperature above the clearing point. Symbols, experimental data from Reference 21; solid curve, present theory (3.2) in text.

relation between the sound velocity and the (static) adiabatic compressibility.[6] Relaxation effects are known to become large near T_k, and it is doubtful that true static properties can be found from dynamic measurements. Mindful of this limitation, we compare the present theory with the published results for p-azoxyanisole (PAA)[13,21,22] in Figure 1. The reported increments in κ_T were fitted to an equation of the form

$$\kappa_T = \kappa_T^0 + A(T - T^*)^{-1} \tag{3.1}$$

on the basis of the analysis presented above and summarized in (2.21). The results for PAA (shown in Figure 1) were well reproduced by

$$\kappa_T^{\mathrm{PAA}} = 5.94 \times 10^{-11} + 3.43 \times 10^{-11}(T - T^*)^{-1} \qquad (\mathrm{cm}^2/\mathrm{dyne})$$
$$T^* = 408.6°\mathrm{K} \tag{3.2}$$

3.2 Thermal expansion anomaly of MBBA

The majority of experimental pretransition studies in recent years are for the room-temperature liquid crystal p-methoxybenzylidene p-butylaniline (MBBA). The present theory (see (2.24)) predicts that in the isotropic phase above the clearing point T_k the coefficient of thermal expansion α_P should have the form

$$\alpha_P = \alpha_P^0 + B(T - T^*)^{-1} \tag{3.3}$$

where α_P^0 is the "normal background" term which is unaffected by the order fluctuations. B is assumed to be independent of temperature. If one considers temperatures very far ($T - T^* > 15°$) from T_k, a linear term should also be included in (3.3) to correct for the temperature dependence of the "background." This refinement is not considered here.

The experimental results for α_P of MBBA just above T_k are conflicting.[9,14-17] All confirm the existence of an anomaly, but differ considerably in the values reported for α_P. As a test of the theoretical form (3.3) we consider two sets of density measurements (Figures 2-3) from the recent work of Gulari and Chu[15] with high-purity MBBA. They report an instrument sensitivity of one part in 10^7. We have numerically differentiated their tabulated densities above T_k. The expansion coefficients $\alpha_P^{GC}(I)$ and $\alpha_P^{GC}(II)$ so obtained are plotted using symbols in Figures 2 and 3. The data was then fitted to (3.3) with the results [in units of $(\mathrm{degK})^{-1}$]

$$\alpha_P^{GC}(I) = 7.773 \times 10^{-4} + 6.694 \times 10^{-5}(T - T^*)^{-1}, \quad T^* = 319.00°\mathrm{K} \tag{3.4}$$

$$\alpha_P^{GC}(II) = 7.725 \times 10^{-4} + 3.015 \times 10^{-5}(T - T^*)^{-1}, \quad T^* = 319.03°\mathrm{K} \tag{3.5}$$

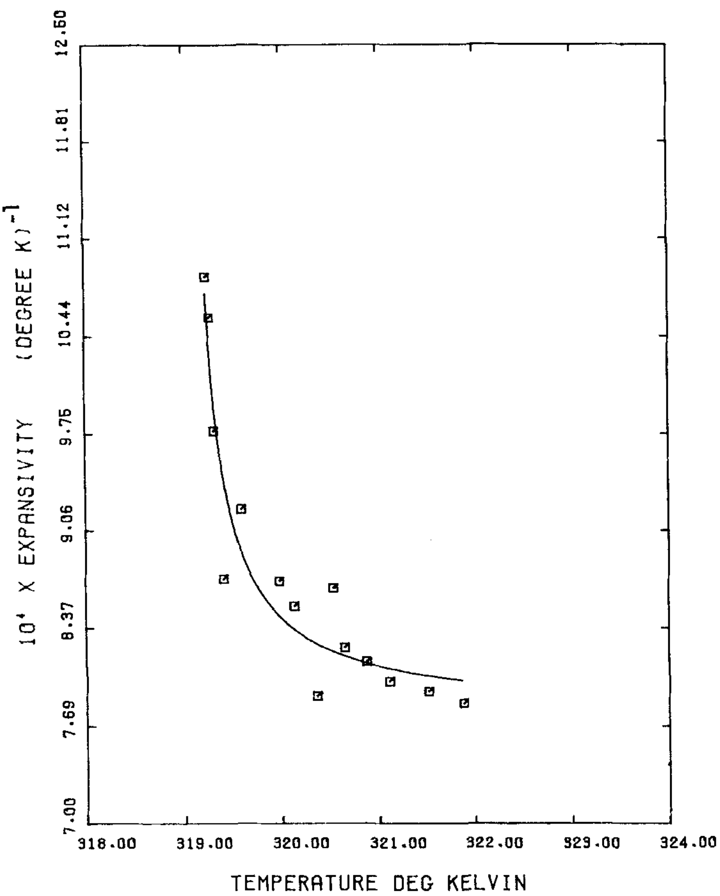

FIGURE 2 Thermal expansion coefficient of MBBA as a function of temperature above the clearing point. Symbols, experimental data from Reference 15; solid curve, present theory, Eqn. (3.4) in text.

The constants in (3.4) and (3.5) were obtained by performing a least squares fit of α_P data to $(T - T^*)^{-1}$, and then varying T^* to give the best fit as determined by the maximum correlation coefficient.

4 CONCLUSIONS

In all cases the fits of the data provided by the theoretical forms (3.1) and (3.3) seem as good as the error in the experimental measurements. For the compressibility data, Alben[13] quotes a likely error of 20%. The expansivity

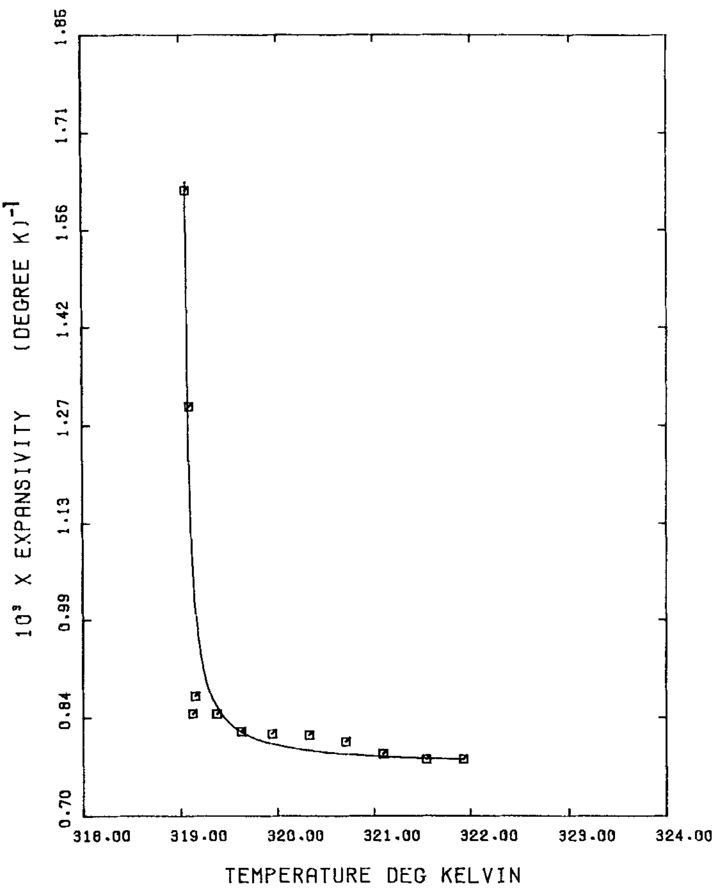

FIGURE 3 Same as Figure 2. Second set of data from Reference 15 plotted using symbols; solid curve = (3.5) of text.

data should be much better than this, yet the stange lack of agreement regarding even the magnitude of the background term,[14–17] κ_T^0, leads one to suspect unforeseen pitfalls in the experiments. Certainly increasing slowness of equilibration is a probable source of error, but since agreement relatively far from the transition is not found, more basic problems with the experimental methods should be considered. Certainly for room-temperature studies calibration of the apparatus with standard substances (i.e., Hg, water) seems highly desirable.

The derivation of the compressibility anomaly (3.1) is taken to be fundamental. In spite of the excellent fit in Figure 1, the data is too crude to provide a good test of this relation. It is hoped that the methods of Reference 12 might be soon employed to confirm or refute (3.1).

The expansion anomaly (3.3) is on less firm theoretical grounds. It requires the approximate validity of (2.23) as well as (3.1). It too must await further experiment, since the discrepancies in the literature are too large to repose confidence in a single measurement technique.

We are aware that considerable opinion[14,15,17,18,23] inclines to the view that the expansivity should diverge with the same exponent as the specific heat, and that the specific heat divergence has an exponent 0.2 → 0.6. The former relation is a consistent consequence of the assumption of Imura and Okano[18] regarding the dependence of the local density on the local order, but we are not convinced of the truth of this assumption (In fact, an alternative (2.15a) has been suggested). Though plausibility arguments, based on static scaling,[24] can be made for a proportionality between the expansion and the specific heat anomalies, this has not been demonstrated for even the simple case of binary mixtures near the critical consolute point.[25,26] Finally, it should be kept in mind that it has not been demonstrated experimentally that the *constant volume* heat capacity has an anomalous part. Experimentally it is C_P, not C_V, which is measured,[9,23] and the difference between them is proportional to the compressibility. An anomaly in the compressibility alone *could* account for an anomaly in C_P. The question of the nature of the anomalies in C_V, C_P, α_P, and κ_T in the isotropic phase of liquid crystals is of great practical interest, and its resolution must await further experimentation.

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