Expansion Coefficient of Methoxybenzylidene Butylaniline through the Liquid-Crystal Phase Transition

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The density of methoxybenzylidene butylaniline has been measured for a 10 °C temperature range about the nematic-isotropic transition temperature. The coefficient of expansion has been fitted to an equation of the form $\beta = \beta_0 + Z|T - T_c|^{-G}$ both above and below the transition point. The values of T_c found from above and below are interpreted as virtual transition temperatures. The power law is taken as evidence that fluctuations play a measurable role in determining the expansion coefficients.

INTRODUCTION

One of the most important features of the liquid-crystal system is that it is condensed. The increase in density on ordering of the molecules corresponds to an increase in the molecular attraction. This is possibly the main driving force for liquid-crystal ordering. It therefore seemed reasonable to want an accurate determination of the density and the coefficient of volume expansion of a liquid crystal about its transition temperature. This was done for the nematic room-temperature liquid-crystal methoxybenzylidene butylaniline (MBBA) with a clearing point of $44.65 \pm 0.15°C$. Pretransitional phenomena were found both above and below T_c, which could be fitted with powers of $(T - T_c)$.

Maier and Saupe[1] have given density data for p-azoxyanisole (PAA), from which they have deduced a qualitative indication of pretransitional phenomena. However, as will be discussed below, the accuracy of these data is not sufficient to determine the mathematical nature of these effects.

EXPERIMENTAL METHOD

The MBBA was obtained from Varilight Corporation[2] and was used as received without further purification. The density of the material was 1.049 g/cm^3 at 22 °C. The measurements were done using Archimedes principle; namely, a submerged object appears to be lighter by the weight of the liquid displaced. The apparatus is as shown in Fig. 1.

A Cahn Ventron electrobalance, No. 2500 RH, was used to measure the apparent weight of a plumb bob (a cylindrical piece of glass) submerged in the sample contained in the inner chamber of a double-chambered density cell. The bob was attached to the scale pan by means of a 0.001-in. tungsten wire. This was used to minimize the effect of surface tension on the weight reading as well as to minimize the change in buoyancy as the

liquid level changes (the level changes slightly owing to thermal expansion of the liquid). The stated sensitivity of the balance is 2 μg, which, with a bob volume of 1.5 cm^3, should make it possible to detect changes in the density of 1 ppm.

The temperature was controlled by passing water through the outer jacket of the density cell. The temperature of the water was controlled to a few tenths of a millidegree centigrade. This was achieved by using a well-stirred 45-gal drum of water as a constant-temperature heat reservoir. The temperature of the large drum was changed linearly with time by means of a second smaller water bath (about 3 liters) in which the temperature was controlled and swept either up or down at approximately 2 °C/day (sweep rates from 0 to ± 25 °C/day were possible by changing the rate of rotation of a Leeds & Northrup K2 potentiometer which was used to control the temperature). The short-term stability of the small bath was about 10 m°C. Water from the smaller bath then circulated in a heat exchanger placed in the 45-gal drum. All water pipes, as well as the drum and the density cell, were encased by foam insulation to minimize the effect of room-temperature fluctuations. The room temperature varied slowly and by no more than ± 0.5 °C.

In order to measure the coefficient of expansion the temperature of the water flowing to the density cell was cycled by applying a modulated heat input with a pair of ordinary immersion heaters. The second heater was placed in the outflow from the density cell and the power alternated with the first so that the total heat added to the water system was constant. The temperature was cycled with an approximate square wave with a period of 8 min and an amplitude of 0.1 °C, as shown in Fig. 2. Several levels of heat were used to "square up" the response. The long period was to allow thermal equilibrium to be established. The problem of equilibrium is likely the greatest source of data scatter. The temperature was measured with a

Hewlett Packard quartz thermometer, No. 2801A, with a sensitivity of 0.1 m°C for a 10 sec scanning period.

The outputs from the quartz thermometer and the Cahn electrobalance (capacitively averaged for 10 sec) were punched on paper tape and then analyzed with a computer.

METHOD OF ANALYSIS

At the end of each half cycle of temperature five values for the weight and the temperature were taken over a period of one minute and averaged. These were used to compute a mean temperature, a mean weight, and an expansion coefficient dm/dT for consecutive half cycles. These values were then further averaged in groups of 10 resulting in a table of values of temperature, change in weight of the liquid from the lowest measured temperature, and the expansion coefficient.

The dependence of the mean weight on the mean temperature for a typical run in which the sweep rate was $-2\,°C/day$ is shown in Fig. 3. Very similar data were obtained when the sweep rate was positive.

The first-order transition occurs over a temperature interval of 0.3 °C. This is likely the result of impurities, as discussed below. The data as presented in Fig. 3 show a slightly broader transition because of the 0.1 °C amplitude of the temperature cycling, since passing through the transition
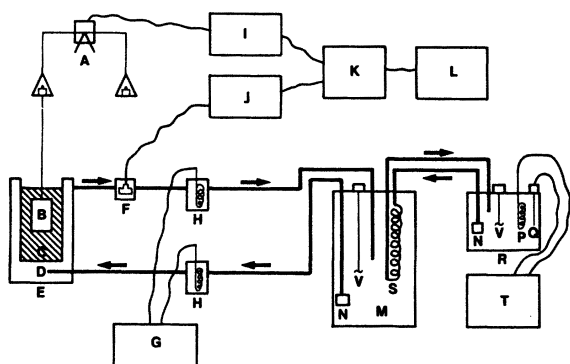

FIG. 1. Block diagram of the apparatus used to determine the coefficient of expansion, consisting of: A, Cahn electrobalance; B, plumb bob; C, liquid-crystal sample; D, water jacket; E, density cell; F, quartz thermometer; G, temperature cycling controller; H, immersion heaters; I, balance control unit; J, quartz thermometer control unit; K, digital voltmeter and scanner; L, teletype; M, 45-gal (Imp.) water bath; N, pumps; P, immersion heater; Q, platinum thermometer; R, 3-liter water bath; S, heat exchanger; T, Leed & Northrup K2 potentiometer and associated electronics to control and linearly sweep the temperature; V, stirrer. The large arrows show the direction of water flow.

results in a discontinuity in the density. The data can be treated to show directly the 0.3 °C transition range. The transition temperatures were reproducible to better than 0.01 °C in four runs.

A solution for the volume expansion coefficient

$$\beta = \frac{1}{v}\frac{dV}{dT} = \frac{1}{m}\frac{dm}{dT} \tag{1}$$

was then assumed of the form

$$\beta = \beta_0 + Z|T - T_c|^{-G}. \tag{2}$$

The temperature T obtained is an average of two temperatures differing by 0.2 °C. Thus the data for the coefficient of thermal expansion was actually curve-fitted to an equation of the form

$$\bar{\beta} = \frac{1}{V_0}\frac{V(T+0.1) - V(T-0.1)}{0.2}, \tag{3a}$$

$$\bar{\beta} = \beta_0 + Z[|T - T_c + 0.1|^{(1-G)} - |T - T_c - 0.1|^{(1-G)}]/0.2(1 - G). \tag{3b}$$

This was especially important close to the clearing point since here $T - T_c$ is a small number and the difference between Eq. (2) and Eq. (3b) is significant.

This equation has the four parameters β_0, Z, T_c, and G. A least-squares fit was then made to this equation for the data above and below the transition point. It was possible to fit the data for the expansion coefficient with curves that resulted in an rms error of about 0.25%

The data were analyzed in the following way. Values for T_c and G were picked and then a least-squares fit was performed to determine the best values of β_0 and Z to fit the data. For this set of four values the mean-square error was determined. In Figs. 4 and 5 are shown the results of this type of analysis. What is shown is the mean-square error s plotted against the exponent G, with
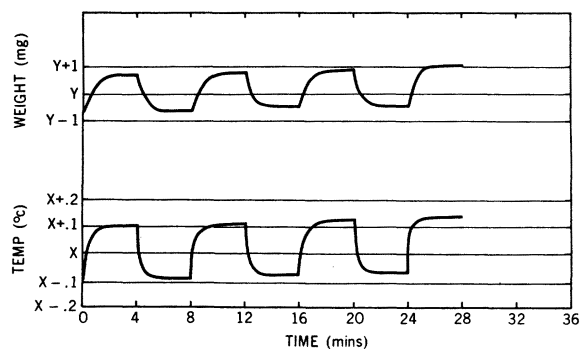

FIG. 2. Schematic showing the cycling of the temperature and weight as a function of time. They consist of an approximate square wave with a period of 8 min. superimposed on a linear ramp of 2 °C/day.

the transition temperature T_c as a parameter. Figure 4 is the analysis of the data for $T < T_c$, while Fig. 5 is concerned with $T > T_c$.

The values obtained would give as an equation for the expansion coefficient below the clearing point

$$\beta = (694 + 435(44.82 - T)^{-0.56}) \times 10^{-6}/°C, \qquad (4)$$

while above the clearing point the equation obtained is

$$\beta = (626 + 192(T - 44.61)^{-0.21}) \times 10^{-6}/°C. \qquad (5)$$

The values in these equations were used in Eq. (3b) to generate the solid lines shown in Fig. 6 along with the original data points. Also shown in Fig. 6, on an expanded scale, is the scatter of the experimental points about the derived curves.

A peculiar deviation in the data of about 2% from a smooth curve was observed about 1 °C below the transition. This appeared repeatedly when the temperature was swept negatively. Its explanation is unknown, possibly some surface-orienting effect of the liquid crystal on the plumb bob. The worst points were omitted from the curve fitting.

The question arises as to the uncertainty in the values picked for the parameters obtained. We have arbitrarily decided to pick an increase of 10% in the mean-square error. Using this criterion we obtain

$$T_c^N = 44.82^{+0.11}_{-0.08},$$
$$G^N = 0.56^{+0.11}_{-0.09} \qquad (6)$$

for the data below the clearing point. Above the clearing point we obtain

$$T_c^I = 44.61^{+0.08}_{-0.12},$$
$$G^I = 0.21^{-0.12}_{+0.16}. \qquad (7)$$

We have attempted to apply the same analysis to the data obtained by Maier and Saupe.[1] The problem with their data is the large uncertainty in their results, especially close to the transition temperature. As stated above we have found that the transition has a finite width. One must therefore be careful about the data obtained near the transition. We found that for Maier and Saupe's data the solution obtained changes drastically as the number of points used in the analysis is changed. We have
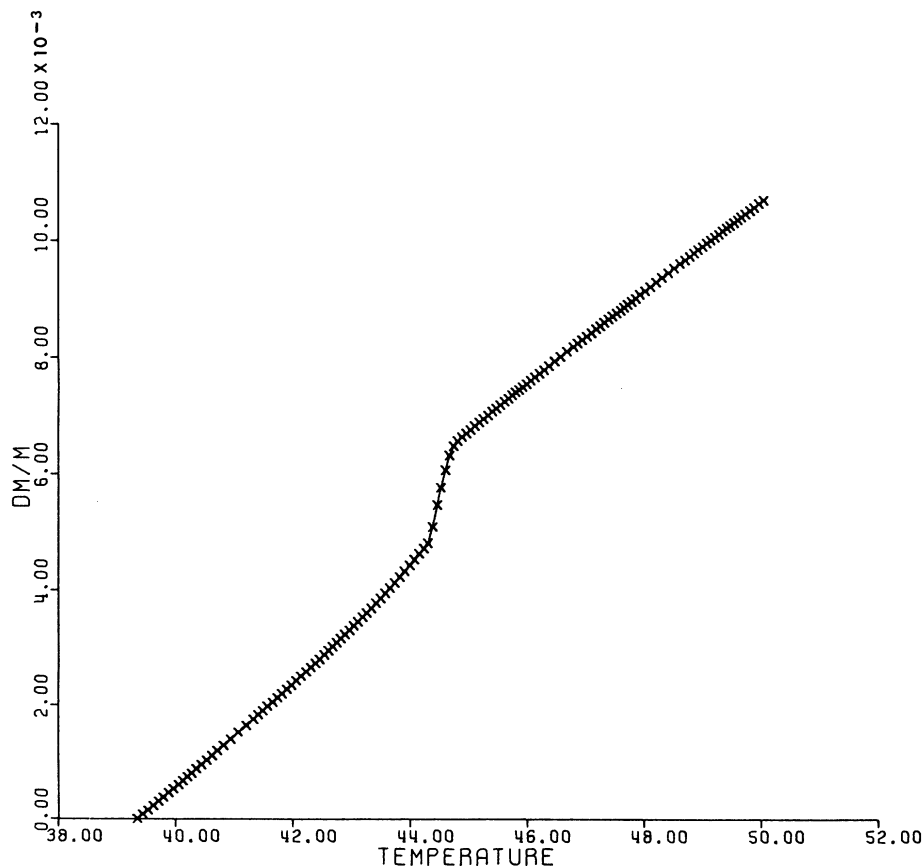

FIG. 3. The relative change in mass of a constant volume of MBBA as a function of temperature.
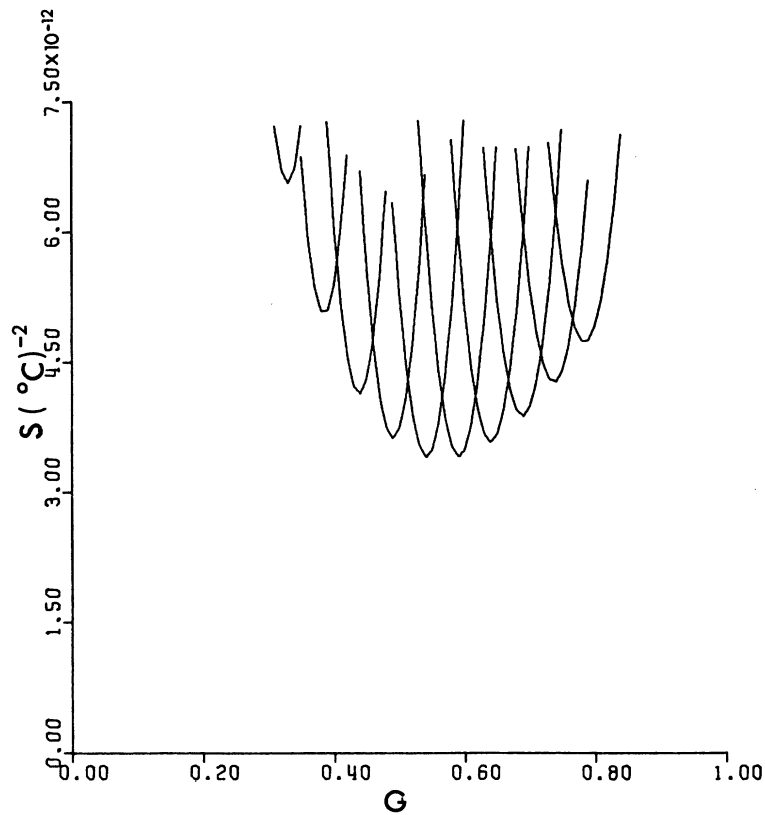
FIG. 4. The mean square error S in the experimental values of the coefficient of thermal expansion below the transition point as calculated from Eq. (3) as a function of G with T_c as a parameter. T_c varies from 44.60 to 45.05 °C in steps of 0.05 °C from left to right. The minimum is for $G = 0.56$, $T_c = 44.82$ °C.
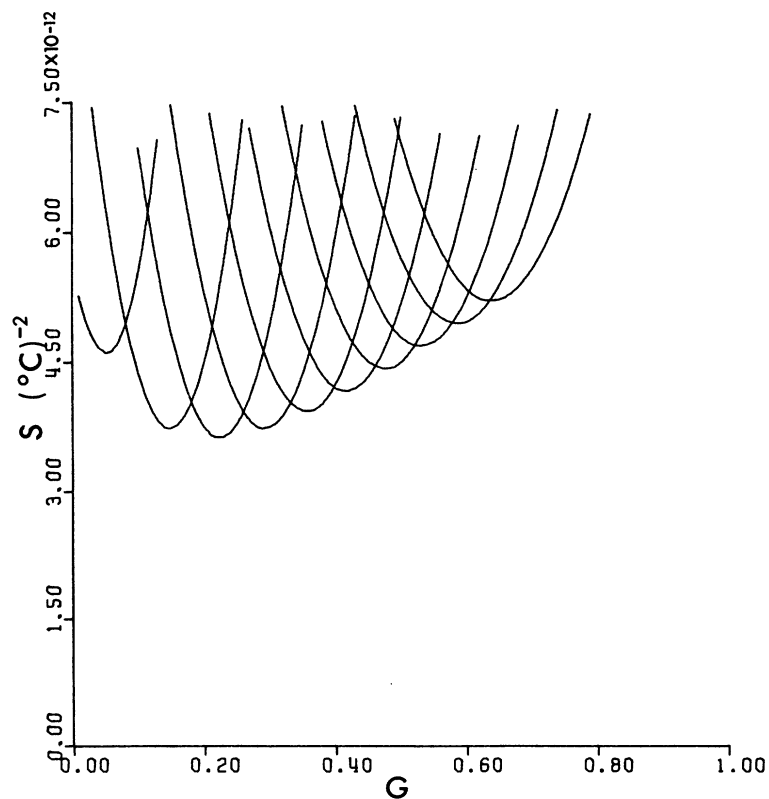

FIG. 5. As in Fig. 4 but for data above the transition point. T_c varies from 44.70 to 44.25 °C in steps of 0.05 °C from left to right. The minimum is for $G = 0.21$, $T_c = 44.61$ °C.

therefore not been able to obtain a consistent mathematical fit to Maier and Saupe's data for PAA.

DISCUSSION

The primary justification for the use of Eq. (2) is that this form is suggested by the many results, both theoretical and experimental, for many properties near a critical temperature. The liquid-crystal transition is intrinsically first order because of the asymmetry in the dependence of the free energy on the order parameter. (The quadrupolar order parameters goes from 1 to $-\frac{1}{2}$.) But when formulated in terms of the Landau theory of phase change the liquid-crystal transition can be thought of as an interrupted second-order phase

change. Thus fluctuation phenomena will occur, but the regions of singularity are never reached in equilibrium. As far as we know there is no theory that connects the volume expansion directly to this order parameter. Nevertheless, one can assume the existence of an order parameter and expand the volume in a power series

$$V = f(s) = V_0(T) + a(T)S + b(T)S^2 + \cdots, \qquad (8)$$

and similarly for the energy

$$E = g(S) = E_0(T) + c(T)S + d(T)S^2 + \cdots. \qquad (9)$$

As long as a critical point is not obtained such analytic expansions should be valid. It would then follow that if the major temperature dependence is in the order parameter and S is small,
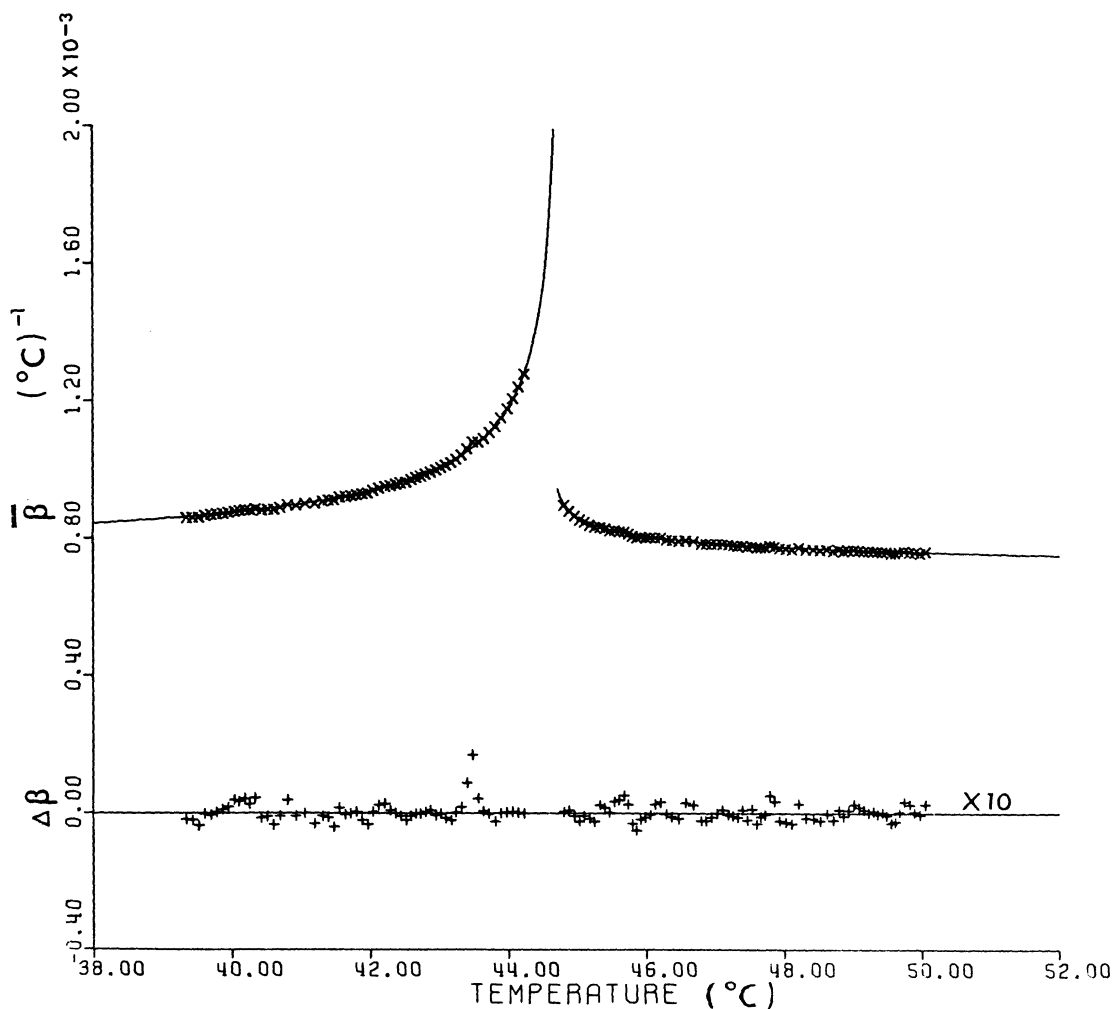

FIG. 6. Comparison of experimental results with Eqs. (4) and (5). The mean coefficient of expansion $\bar{\beta}$ is calculated from the data using Eq. (3a) and compared with the expression (3b) using the numbers given in Eqs. (6) and (7). The upper curve shows $\bar{\beta}$ calculated from the data as x's and the results of Eq. (3b) as a solid line. The differences of the x's and the solid line are shown at the bottom on a scale expanded 10 times. The two points in the unexplained peak at 43.5 °C were eliminated in the analysis.

$$\beta \propto \frac{dE}{dT} = C_p, \qquad (10)$$

where C_p is the specific heat of the system. With this connection one can then appeal to the widely used[3] expression for the specific heat near a critical point,

$$C_p = A(T - T_c)^{-\alpha} + C_0. \qquad (11)$$

Such behavior has been found in the specific heat of PAA as shown by Arnold.[4]

This argument should have some validity above the transition temperature where for S we must take a short-range order parameter. Above T_c we find $G = 0.21$. This is consistent with the general finding that α is a number small compared with unity. Below the transition the connection between β and long-range order parameter Q is more tenuous.

The schematic behavior of the free energy[5] as a function of long-range order parameter is illustrated in Fig. 7. Note that for a liquid crystal in the ordered state the virtual critical temperature T_c^N corresponds to a finite order parameter. Thus we might expect that

$$Q = Q_N + A_1(T_c^N - T)^{\beta'}, \qquad (12)$$

where Q_N is the order at the inflection point on the free-energy curve for $T = T_c^N$. If we postulate that the density change is proportional to Q then

$$\left(\frac{1}{V}\frac{dV}{dT} - \beta_0\right) \propto \left(-\frac{dQ}{dT}\right) = A_1\beta'(T_c^N - T)^{\beta'-1}. \qquad (13)$$

From Eq. (2)

$$\frac{1}{V}\frac{dV}{dT} - \beta_0 = Z(T_c^N - T)^{-G} \qquad (14)$$

and one is tempted to compare G and $1 - \beta'$. From magnetism (and lattice gases) one obtains values of β' between $\frac{1}{3}$ and $\frac{1}{2}$. Thus the values of $1 - \beta'$ lie between $\frac{2}{3}$ and $\frac{1}{2}$. The value we obtain for G is 0.56. In view of the significant difference between the quadrupolar order parameter of nematic liquid crystals and the dipolar order parameter of magnetism (and lattice gases) it is likely that the close comparison between $1 - \beta'$ and G is only fortuitous.

VOLUME DISCONTINUITY ACROSS THE TRANSITION

There are several volume changes which can be assigned to the first-order transition. One of these might be the difference between the beginning and the end of the transition region. The form of our solutions implies, however, that the pre-transitional regions both below and above the transition point are infinite in extent. This is not surprising since the density change is itself a mani-

festation of changes in local ordering.

Another value for a volume change across the transition can be obtained by integrating Eq. (4) and (5) to an estimated clearing point of 44.65 °C and determining the volume difference obtained. Using this method we find $\Delta V/V = 0.11\%$ across the transition.

A third method, that suggested by Maier and Saupe[1] of extending the data above the transition point to a sufficiently high temperature so that the short-range order is negligible, has proved to be unfeasible. The reason for this is as explained above; namely, the term in $(T - T_c)^{-G}$ is such a slowly decreasing function for G small. For example, with $G = 0.21$, when $T - T_c$ is 5 °C this term contributes 17% to the expansion coefficient; at $T - T_c = 100$ °C the singular term's contribution is still 12%. Thus in trying to estimate the volume change across the transition with the short-range order removed all we can do is make a minimum estimate of $\Delta V/V = 0.13\%$.

COMPARISON OF CRITICAL TEMPERATURE IN NEMATIC AND ISOTROPIC STATES

From the Landau theory of phase changes applied to nematic liquid crystals it is possible to distinguish three temperatures. In Fig. 7 we show the dependence of the free energy on the order parameter for a range of temperatures.[5] T_F is the first-order transition temperature. T_c^I is the virtual critical temperature as observed in the disordered state, and T_c^N is the virtual critical temperature as observed in the ordered state. We obtain from our curve-fitting procedure
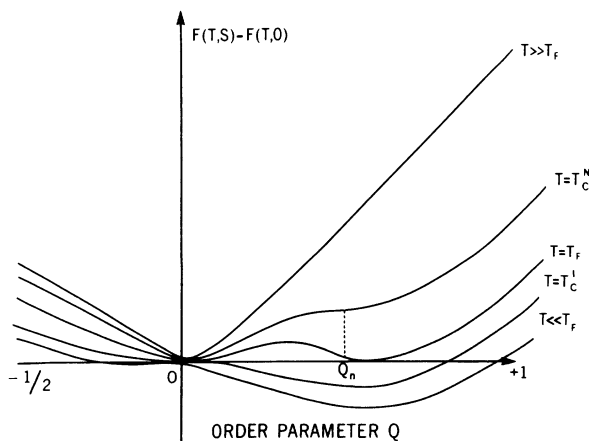

FIG. 7. Temperature dependence of the dependence of the free energy upon long-range order parameter Q for the nematic liquid crystal. The horizontal inflection point occurs at the origin for T_c^I and at a finite order parameter for T_c^N. At T_F the two phases coexist.

$T_c^N \doteq 44.82\,°C$ and $T_c^I = 44.61\,°C$.

The existence of a 0.3 °C transition region rather than an abrupt transition as expected from Fig. 7 clouds the question of what to take for T_F. As the density varies linearly with temperature in this region we deem it reasonable to take the middle of this region. This yields the value $T_F = 44.65 \pm 0.01\,°C$. This indicates that if it were not for the 0.3 °C two-phase-transition region one could come quite close to T_c^I on decreasing temperature. We believe that this 0.3 °C two-phase region is not intrinsic and could possibly be eliminated by proper sample preparation.

INFLUENCES OF IMPURITIES

The most likely impurities in MBBA are water and the hydrolysis products of MBBA itself. The present experiments were carried out in a closed system in which a dessicant was maintained at room temperature. The system was closed for the six month duration of these measurements. The start and stop temperatures of the 0.3 °C two-phase-transition region were reproducible during this time to within ±0.01 °C. By deliberately increasing the dew point of the atmosphere in the balance system we were able to increase the two-phase-transition region to 8 °C with the upper temperature reduced to 39 °C. Ideally we would like to go the other way and narrow the transition region to 0.01 °C or less. Either our dessicant has not completely removed the water or there are other impurities present. Our transition temperature appears typical of those reported for MBBA by other workers. Yet slightly higher transition temperatures have been reported when additional purifications have been carried out.[6] It appears worthwhile to pursue this question further. For if the two-phase region could be eliminated one should be able to approach very close the virtual transition temperature from above.

CONCLUSION

We have presented what we believe to be the most accurate determination of the density of a nematic liquid crystal for a 10 °C temperature range about the first-order phase transition using the liquid-crystal MBBA. We have obtained evidence of pre-transitional phenomena both above and below the clearing point as well as evidence for two virtual critical temperatures.

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