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Translated by J. G. Adashko

Temperature dependence of the heat capacity of the nematic liquid crystal MBBA on going into the isotropic phase

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 (Submitted February 5, 1976)
 Zh. Eksp. Teor. Fiz. 71, 692-699 (August 1976)

Results are given of the measurement of the heat capacity and latent heat of transition to the isotropic phase for the liquid crystal MBBA (*n*-methoxybenzylidene-*n*'-butylaniline). Values of the critical exponents a and a' are obtained. The anomaly of the heat capacity is found to be pronounced in a narrow temperature range $|T-T_d| > 1^\circ\text{C}$ in the vicinity of the phase transition. The experimental data are discussed on the basis of the Landau phenomenological theory with allowance for spatially inhomogeneous fluctuations of the characteristic transition parameter. It is shown that the theory cannot describe the anomaly of the heat capacity in the isotropic phase in the case $|T-T_d| < 1^\circ\text{C}$.

PACS numbers: 61.30.+w, 65.40.Hq, 64.70.Ew

INTRODUCTION

Critical phenomena in phase transitions in liquid crystals, accompanied by the vanishing of long-range orientation order in the locations of the long axes of the molecules, have been insufficiently studied to date. The existing experimental data^[1,2] indicate that, as the isotropic-nematic phase transition point is approached, the light scattering intensity increases, and the magnetic double refraction, which plays a role of a generalized susceptibility, becomes larger. There are also indications of the presence of characteristic anomalies in the temperature dependence of the heat capacity,^[3,4] which can be connected with the spatially-inhomogeneous fluctuations of the characteristic parameter of the phase transition. In the Landau theory, the effect of correlation of the fluctuations is taken into account by the introduction of small corrections to the thermodynamic potential.^[5,6] A similar approach has been fruitful in the case of ferroelectrics^[7]; however, there are practically no experimental data which could be used for quantitative estimates in liquid crystals.

In the present work, we have attempted to carry out quantitative analysis of the possibility of the application of the Landau theory for the description of critical anomalies in the region of the phase transition from the nematic to the isotropic phase. This analysis is carried out on the basis of accurate measurements of the

heat capacity of the liquid crystal MBBA (*n*-methoxyl benzylidene *n*'-butylaniline).

METHODOLOGY AND EXPERIMENTAL RESULTS

The heat capacity C_p and the latent heat of transition $\Delta q(T_c)$ of the liquid crystal MBBA were measured in an adiabatic calorimeter of the Strelkov construction.^[8] The liquid crystal of MBBA, synthesized according to the usual method, was subjected to systematic purification: vacuum distillation, recrystallization from absolute ethanol, and drying in a vacuum desiccator in the presence of P_2O_5 . The temperature of transition to the isotropic phase amounted to 42.49°C , according to our measurements of the heat capacity.

The calorimetric cell consisted of a cylindrical thin-walled (wall thickness ≈ 0.5 mm) glass ampoule with a copper-silver coating and an axial opening for the insertion of a thermometer and a heater. The liquid crystal, whose mass amounted to ~ 6 g, was placed in a cylindrical gap of thickness 3 mm. After the liquid crystal was put in the calorimetric cell, the latter was sealed shut. During the entire time of the experiment (6 months), the temperature of the phase transition, which corresponds to the maximum in the heat capacity, did not change. The temperature was measured by a platinum resistance thermometer TSPN-1 (100 ohm) with an accuracy to within 0.001°C (in the proper scale

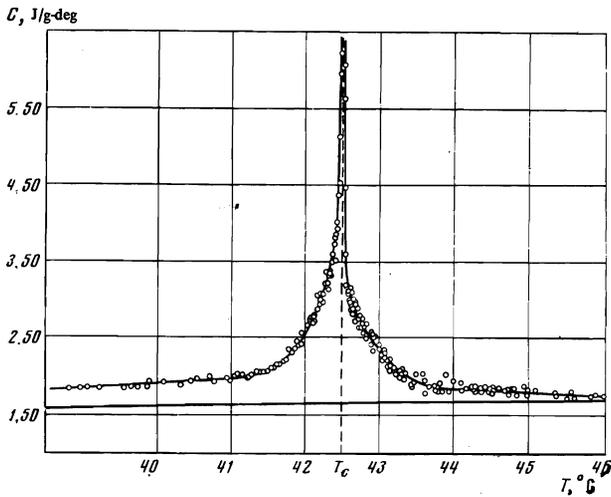


FIG. 1. Temperature dependence of the heat capacity of MBBA, $T_c = 42.49^\circ\text{C}$.

of the thermometer). The set of screens that were employed and the electronic circuit for regulation of the adiabatic conditions^[9] allowed us to carry out the measurements of the heat capacity at temperature variations of the order of 10^{-4} – 10^{-5} deg/min.

The error in the measurement of the heat capacity depends on the value of the calorimetric interval ΔT and amounts to 1–2% at $\Delta T > 0.1^\circ$ (at the wings of the anomalies), increasing to 10% at $\Delta T \approx 0.02$ – 0.03° . For points that are far from the temperature of the maximum (by $\sim 0.1^\circ$), the error in the determination of the heat capacity amounted to 3–5%.

Figure 1 shows the temperature dependence of the heat capacity of MBBA in the vicinity of the phase transition. Attention is called to the fact that the anomaly is expressed in a narrow range of temperatures $|T - T_c| < 1^\circ$. The central part can be separated from the anomalous portion of the heat capacity corresponding to a δ -divergence and due, as it turns out, to the release of the latent heat $\Delta q(T_c)$.

For the determination of the form of the temperature dependence of the heat capacity on both sides of the transition, we made use of the following procedure. We separated the regular part of the heat capacity, which is not connected with the phase transition, by extrapolation of the high-temperature ($T > 50^\circ\text{C}$) branch of the heat capacity to the region of the phase transition

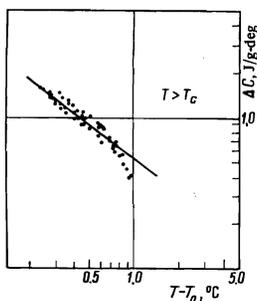


FIG. 2. Anomalous part ΔC_p of the heat capacity of MBBA in the isotropic phase near the transition temperature; log-log scale, $T_0 = 42.30^\circ\text{C}$, $T_c = 42.49^\circ\text{C}$.

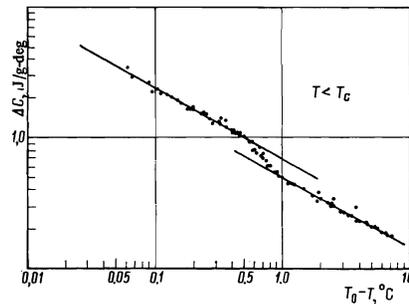


FIG. 3. Anomalous part ΔC_p of the heat capacity of MBBA in the nematic phase; log-log scale, $T_0 = 42.51^\circ\text{C}$, $T_c = 42.49^\circ\text{C}$.

$$C_p = C_p^0 + \Delta C_p,$$

where C_p^0 changes weakly with temperature and amounts to ≈ 1.65 J/g-deg at $T = 43^\circ\text{C}$. The anomalous parts ΔC_p of the heat capacity were approximated by formulas of the type

$$\Delta C_p = A(T - T_0)^{-a}. \quad (1)$$

The constants A , T_0 , a were determined by the method of least squares on the computer "Mir-2" with account of possible deviations of the value of C_p^0 .

The results of the calculation are the following:

1. $T > T_c$.

The dependence of the form (1) was obtained in the temperature range

$$\Delta C_p = 0.54(T - 42.30)^{-0.73 \pm 0.04}, \quad T - T_c < 0.6^\circ. \quad (2a)$$

2. $T < T_c$,

$$\Delta C_p = 0.70(42.51 - T)^{-0.53 \pm 0.03}, \quad T_c - T < 0.7^\circ; \quad (2b)$$

$$\Delta C_p = 0.51(42.51 - T)^{-0.52 \pm 0.03}, \quad T_c - T > 1^\circ. \quad (2c)$$

These dependences are shown as log-log plots in Figs. 2 and 3.

The sufficiently sharp peak of the heat capacity allows us to determine the particular transition temperature $T_c = (42.49 \pm 0.03)^\circ\text{C}$, with which one can connect the release of the latent heat of the transition $\Delta q(T_c)$ and the jump in the volume ΔV . The analytic expressions for ΔC_p obtained above and below the transition show that the difference $T_c - T_0$ for Eq. (2a) amounts to $\approx 0.2^\circ$ and appreciably exceeds the uncertainty in the location of T_c . The excess (anomalous) heat capacity ΔC_p is connected with the value of the total thermal effect of the transition Δq_{tot} by the expression

$$\Delta q_{\text{tot}} = \int_{T_1}^{T_2} \Delta C_p dT, \quad (3)$$

where T_1 and T_2 correspond to the initial and final temperature of the anomalous behavior of ΔC_p in correspondence with Fig. 1:

$$\Delta q_{\text{tot}} = \Delta q(T < T_c) + \Delta q(T_c) + \Delta q(T > T_c). \quad (4)$$

The calculation yields

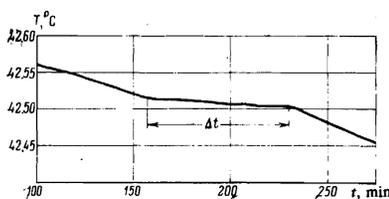


FIG. 4. Cooling of MBBA near the transition temperature. Rate of temperature change $dT/dt = 0.0014$ deg/min; Δt is the duration of the temperature pause.

$$\Delta q(T < T_c) \approx 1.20 \text{ J/g}, \Delta q(T > T_c) \approx 0.88 \text{ J/g}.$$

Graphical integration of $\Delta C_p = \Delta C_p(T)$ does not allow us to determine the value of $\Delta q(T_c)$, since it corresponds to a δ -divergence of the heat capacity.

For the determination of the value of the latent heat of the transition we have made use of the method of quasistatic thermograms.^[10] In the presence of a small stable linear temperature variation of the calorimeter, the release of the latent heat was determined at some temperature in this method from the presence of a plateau in the coordinates temperature-time. We recorded 3 thermograms of heating and 4 thermograms of cooling.

The rate of change of the temperature amounted to 0.0011–0.0015 deg/min. Figure 4 shows the portions of the thermogram of cooling near the transition temperature. The temperature change was recorded by a continuous method with the use of the automatic recorder N 373-1.

The value of the latent heat of transition $\Delta q(T_c)$ was determined by starting from the relation

$$\Delta q(T_c) = \left(\frac{dT}{dt} \right) C_p \Delta t, \quad (5)$$

where dT/dt is the rate of change of the temperature of the calorimeter near the transition temperature T_c ; C_p is the value of the heat capacity in the corresponding temperature interval, and Δt is the time required to establish the temperature. The basic error (up to 20%) in the determination of the latent heat of the transition was provided by the inaccuracy in the determination of this quantity connected with the conditions of operation of the experiment. The value of $\Delta q(T_c)$ calculated on the basis of these data amounted to (0.5 ± 0.1) J/g. The release of the latent heat took place at temperatures lying in the range 42.23–42.60 °C. The mean transition temperature, obtained by the method specified, amounted to $T_c = (42.50 \pm 0.05)$ °C. We note that by the quantity $\Delta q(T_c)$ we mean the lower limit of the latent heat of transition, since the different distortion factors can lead to a smearing out of the δ -shaped divergence of the specific heat, thus decreasing the value of $\Delta q(T_c)$. In correspondence with the results, the ratio $\Delta q(T_c)/\Delta q_{\text{tot}} \approx 0.2$.

In the work of Hirakawa and Kai,^[3] the results were given of the measurement of the heat capacity of the liquid crystal MBBA, and the presence of two peaks in

the heat capacity is indicated in the region of isotropic-nematic phase transition. Our measurements did not confirm this conclusion. In a narrow temperature range $|T - T_c| \approx 0.20^\circ$ in the vicinity of the phase transition, we encountered the same difficulties in the measurement of the heat capacity as in the investigation of the critical flows of liquids.^[10] The experimental scatter in this interval, if we do not take special measures, greatly exceeds the accuracy with which the measurements are carried out. In our opinion, the most important reason for this is the loss of homogeneity of the system, owing to the presence of the calorimetric step ΔT . The different times of establishment of equilibrium in samples with different degrees of nematic order also leads to the appearance of non-stationary temperature gradients. The nonstationary temperature gradients in the calorimeter upset the adiabatic regime of the calorimeter before the establishment of equilibrium in the system. The scatter of the experimental points in the interval considered can amount to 5–6% in the case of a prolonged expectation value of the establishment of equilibrium in the system (3–4 hours from point to point), whereas the adiabatic regime of operation of the calorimeter was established about one hour after heating. We note that questions of the state of equilibrium of the measured thermodynamic parameters of the liquid crystals near their transition temperature are important for the correct interpretation of the results and require experimental and theoretical treatment.

DISCUSSION OF THE RESULTS

The temperature dependences of the heat capacity $C_p = C_p(T)$ and the thermal effect of the transition at $T < T_c$ and $T > T_c$ are connected, respectively, with the change in the degree of nematic order Q_{ij} and with the increase in the fluctuations of the quantity $Q_{ij}(r)$ in the isotropic phase upon approach to $T = T_c$. We compare the conclusions of the phenomenological theory with the experimental data obtained. The phenomenological theory, developed in the spirit of the Landau theory, set forth by De Gennes^[11] for the description of the phase transition from the nematic to the isotropic phase, starts out from the following expansion of the thermodynamic potential $F = F(P; T; Q_{ij})$ in the tensor parameter Q_{ij} of the transition in the neighborhood of the phase transition:

$$F = F_0 + \frac{1}{2} A Q_{ij} Q_{ij} - \frac{1}{3} B Q_{ij} Q_{jk} Q_{ki} + \frac{1}{4} C Q_{ij} Q_{jk} Q_{kl} Q_{li} + \frac{1}{2} L \left(\frac{\partial Q_{ij}}{\partial X_i} \right)^2, \quad (6)$$

where $Q_{ij} = \frac{1}{2} Q (3n_i n_j - \delta_{ij})$ is the tensor order parameter, n_i and n_j are the components of the director, Q is the scalar order parameter: $-\frac{1}{2} \leq Q \leq 1$, δ_{ij} is the Kronecker delta. The last term in Eq. (6) describes the additional energy associated with the correlations of the spatially-inhomogeneous fluctuations $\Delta Q_{ij}(r)$. The coefficient L is equal to $L \approx K/2Q^2$ in order of magnitude (K is the elastic constant of the liquid crystal), 10^{-6} dynes.

In the isotropic phase of a nematic liquid crystal there should be two correlation lengths r_{c1} and r_{c2} and, correspondingly, two different coefficients L_1 and L_2 in the expansion (6).^[12] This is important for the description

of the location of the long axes of the molecules on the boundary of the isotropic and nematic phases, but does not affect our results, since $L_1 \approx L_2$ and the form of the correlation energy for L_1 and L_2 is functionally the same. The thermodynamic potential, written in the form (6), contains an invariant of third order and, consequently, only one isolated point of discontinuity of the phase transition can exist,^[13] where $A(P, T) = 0$ and $B(P, T) = 0$.

The equation $A(P, T) = 0$ describes the line of first-order phase transitions with a finite jump in the order parameter. For given P , we have $A = A'(T - T')$. We note that if we are situated on the lines of phase transitions near the point of discontinuous phase transition, then it is no longer possible to neglect the temperature dependence of the coefficient $B = B(T)$ and the thermodynamic system changes. We do not know of any experimental data confirming this possibility; therefore, in the following, we shall assume that the temperature dependences of the thermodynamic quantities are determined by the coefficients $A = A'(T - T^*)$. The temperature T^* corresponds to the lower limit of existence of the isotropic liquid.^[12]

The thermodynamic potential F can be written as a function of the scalar order parameter Q , whence we can obtain expressions for the quantities of interest to us in the usual way, in particular, $Q = Q(T)$, $\Delta q(T_c)$ ^[14] and so on:

$$Q = \frac{B}{6C} \left[1 + \left(1 - \frac{8}{9} \frac{T - T^*}{T_c - T^*} \right)^{1/2} \right], \quad T < T_c, \quad (7)$$

$$Q = 0, \quad T > T_c, \quad (8)$$

$$\Delta q(T_c) = A'B^2T_c/27C^2, \quad (8)$$

$$T_c - T^* = B^2/27A'C. \quad (9)$$

For the value of the energy barrier ΔF separating the isotropic and nematic phases we have

$$\Delta F = \frac{\Delta q(T_c)}{16} \frac{T_c - T^*}{T_c} \quad (10)$$

The experimental data obtained by us allow us to estimate several quantities: starting out from $\Delta q(T_c) \approx 0.5$ J/g, $\Delta q(T < T_c) \approx 1.20$ J/g and $T_c - T^* \approx 0.20^\circ$ which, as we shall see below, follows from a comparison of the temperature at which the expression (2a) diverges with $T_c = 42.49^\circ\text{C}$, we obtain

$$\frac{Q_{\max}^2}{Q^2(T_c)} = \frac{\Delta q(T < T_c) + \Delta q(T_c)}{\Delta q(T_c)},$$

where $Q(T_c)$ is the jump in the order parameter in the phase transition from the nematic to the isotropic phase, and Q_{\max} is the maximum value of the order parameter in the nematic phase. At $Q(T_c) = 0.3 - 0.4$, $Q_{\max} = 0.55 - 0.75$, we have

$$A' = 0.017 \text{ J/g-deg} \approx 0.2 \text{ J/cm}^3\text{-deg}, \quad C = 0.038 \text{ J/g}.$$

$$B = 0.065 \text{ J/g}, \quad \Delta F = 2 \times 10^{-5} \text{ J/g}.$$

For the temperatures T^{**} which determine the upper limit of existence of the superheated nematic phase, we find

$$T^{**} = T^* + B^2/24A'C = T_c + 1/6(T_c - T^*) = T_c + 0.02^\circ\text{C}.$$

Thus, the interval $T^{**} - T^*$ in which the nematic and the isotropic phases can co-exist amounts at most to $\approx 0.22^\circ\text{C}$, which, together with the small value of ΔF , also explains why it is so difficult to discern the temperature hysteresis in the given phase transition.

The temperature dependence of the heat capacity in the isotropic phase can be obtained by the standard method developed by Levanyuk^[5] for the region in which the fluctuations of the order parameter are small:

$$\frac{1}{V} \int \langle Q_{ij}^2(r) \rangle dV \ll Q^2(T_c).$$

We take into account approximately the tensor character of the order parameter, $\langle Q_{ij}^2(k) \rangle \sim n \langle Q^2(k) \rangle$, where $Q(k)$ are the Fourier components of the quantity $Q(t)$ and $n \approx 10$. In accord with Levanyuk,^[5] we have

$$C_p = C_p^0 + \frac{k_B T_c^2 n}{16\pi} \left(\frac{A'}{L} \right)^{1/2} (T - T^*)^{-1/2}. \quad (11)$$

Setting $A' = 0.02 - 0.04$ J/cm³-deg and $L \approx 10^{-6}$ dyne, we obtain for the coefficient in the case of the singular term a quantity of the order of $0.02 - 0.06$ J/g-deg^{1/2}. At the same time, a larger (≈ 0.05) value of this coefficient follows at once from experiment for $T = T_c < 0.6^\circ$, and the value of the critical exponent is 0.73 ± 0.04 . It is seen from Fig. 1 that we can describe the experimental data by Eq. (11) only at $T - T_c > 1^\circ$, i. e., in the range of temperatures in which the coefficient in the case of $T = T^*$ actually becomes small.

Thus, we reach the conclusion that in the isotropic phase it is not possible to use the approximation which leads to Eq. (11) in the vicinity of the phase transition $T - T_c < 1^\circ$. In this range of temperatures, evidently, the correlation effects can no longer be considered as small, and the critical exponents determined from experiment are the true ones satisfying the relations of similarity theory.

The significant divergence of the heat capacity in this region can be connected with the closeness of the investigated first-order transition to the isolated point of discontinuous phase transition. Here, as shown by Vigman, Larkin and Filev,^[15] it is impossible to expect a universal dependence of the thermodynamic quantities on the temperature, since the boundary between the similarity region and the Landau region occurs at distances of the order of degrees from the phase transition line. Along with this, there is no possibility of observing a distortion, of the dependence of the heat capacity near the temperature transition, a distortion due to the smearing out of the δ divergence of the specific heat, for example, because of the presence of impurities in the sample.

At $T < T_c$, the heat-capacity anomaly can be connected basically with the change in the degree of nematic (orientation) order Q in correspondence with Eq. (7):

$$C_p = C_0 \left\{ 1 + 3 \left[1 + 8 \frac{T_c - T}{T_c - T^*} \right]^{-1/2} \right\}; \quad (12)$$

$$C_0 = \frac{1}{54} \frac{A'B^2T}{C^2(T_c - T^*)} = \frac{\Delta q(T_c)}{2(T_c - T^*)}.$$

Substituting the values for $\Delta q(T_c)$ and $T_c - T^*$ which are known from experiment, we obtain $C_0 \approx 1.25$ J/g-deg, which is somewhat lower than the experimental value $C_0 \approx 1.65$ J/g-deg at $T = 43^\circ\text{C}$. However, it should be taken into account that the value $\Delta q(T_c) = 0.5$ J/g is much more likely to be undervalued; at $\Delta q(T_c) = 0.65$ J-g, the value of $C_0 \approx 1.65$ J/g-deg. It follows from (12) that

$$\begin{aligned} T=T^*, \quad C_p &= 2C_0 \approx 3.2 \text{ J/g-deg} \\ T=T_c, \quad C_p &= 4C_0 \approx 6 \text{ J/g-deg.} \end{aligned}$$

The values obtained agree satisfactorily with the data of Fig. 1, where $T^* \approx 42.30^\circ\text{C}$, $T_c \approx 42.49^\circ\text{C}$. Setting $C_0 = 1.50$ J/g-deg and $T_c - T^* \approx 0.2$, and neglecting units in the expression under the square root, we have for the heat capacity C_p

$$C_p = 1.50 + 0.70 (T_c - T)^{-0.5},$$

which agrees well with the result obtained from experiment for $T_c - T < 0.7^\circ\text{C}$.

Thus, Eq. (12) gives the correct asymptotic behavior of the heat capacity at $T < T_c$ over a wide range of temperatures. However, taking into account the results obtained for the isotropic phase, we cannot neglect the possibility of random coincidence of the experimentally obtained critical exponent with the value which follows from the phenomenological theory in the immediate vicinity of T_c . The fact that the temperature dependence of the heat capacity at $T < T_c$ cannot be described with a single coefficient in the case of a singular term, over the entire temperature range, argues in support of this proposition (see Fig. 3, and Eqs. (2b), (2c)).

In this connection, it should be noted that the problem of the region of applicability of the phenomenological theory to phase transitions in liquid crystals requires special consideration, since the dispersion (van der Waals) forces of interaction of the molecules, which are responsible for the orientation ordering in nematic liquid crystals, have an effective radius of interaction r_0 that is approximately equal to the intermolecular dis-

tance. The existence of a region of applicability of the phenomenological theory can be connected with the increase in the effective radius of interaction due to the existing anisotropic form of the molecules which form the nematic liquid crystals (the ratio of the length of the molecule to its diameter is of the order of 4-5). Such a possibility was discussed earlier by de Gennes.^[16]

The authors thank K. V. Avilov for help in the calculations on the computer, E. V. Generalova and N. B. Titova for preparation and purification of the material and A. Z. Rabinovich for valued discussions.

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Translated by R. T. Beyer