Tricritical behavior of nematic crystals near the transition to an isotropic liquid

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The tricritical behavior of nematic liquid crystals near the transition to an isotropic liquid has been discovered as a result of very precise measurements of the heat capacity. The assumption of the closeness of this transition to the tricritical point offers the best possibility of consistently explaining existing experiments on the heat capacity, light scattering, order parameter, and it eliminates the question of long-range action in liquid crystals.

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Previously[1] we reported on the results of an experimental study of the heat capacity of two nematic liquid crystals: MBBA (*p*-methoxybenzylidene-*p*-*n*-butylaniline) and BMOAB (*p*-*n*-butyl-*p'*-methoxy-azoxybenzol) in the vicinity of the phase transition between isotropic liquid and the liquid-crystal state ($N \rightleftarrows I$).

The $N \rightleftarrows I$ phase transition is traditionally described, starting from the expansion of the thermodynamic potential in powers of the tensor order parameter Q (Landau-de Gennes theory[2])

$$\phi - \phi_0 = \frac{1}{2} a\tau Q^2 - \frac{1}{3} b Q^3 + \frac{1}{4} c Q^4, \tag{1}$$

where $\tau = (T - T_c)/T_c$ (T_c is the susceptibility divergence temperature.)

The smallness[1,3] of the constant $b \approx 0.06$ leads to the fact that the jump in entropy is small and the transition is close to a transition of the second kind ($b = 0$). The constant c also turned out to be unexpectedly small; this raised the question of the possible nearness of the transition $N \rightleftarrows I$ to the tricritical point ($c = 0$).[1] Since such an assumption requires an examination of the of the traditional concepts of the reasons for the closeness of the $N \rightleftarrows I$ transition to a transition of the second kind and of the nature of the pre-transition (fluctuational) phenomena in this case, we have made

more precise and detailed measurements of the heat capacity of these same substances. The measurements were made by means of an improved adiabatic calorimeter with agitation of the sample. Regulation of the power, delivered during the movement of the magnetic stirrer, made it possible to achieve an average random error of 0.05% for a calorimetric step width of ~0.1 K. This is nearly an order of magnitude better than in Ref. 1. Measurements with regulated agitations made it possible to use all the measured values in the analysis up to the transition temperature.

The constants of the approximation formulas and their confidence intervals for a confidence coefficient of 0.68 as well as the degree of adequacy of the description were determined by means of a nonlinear regression analysis of the data by means of the program package described in Ref. 4. First of all we attempted to approximate the data with a power dependence

$$\frac{C_p}{R} = \frac{T}{T_c} A_0 |\tau|^{-\alpha} + C_0(\tau), \tag{2}$$

where the "regular" part $C_0(\tau) = A_1 + A_2\tau + A_3\tau^2$, the constants α, T_c and A_i are variable parameters. The values obtained for the exponents α^- for the nematic and α^+ for the isotropic phase are listed in the first row of Table I. These values are not entered in any of the theoretical schemes. The heat capacity curve, following from the Landau-de Gennes theory and calculated from the formulas given in Ref. 1, is represented by the solid line in Fig. 1. It is characterized by the sudden jump $\Delta C_p = a^2/2c$ in the heat capacity. The experimental curve is fundamentally different from the theoretical by virtue of the absence of the jump in the regular parts and the large value of the anomaly in the isotropic phase.

TABLE I. Critical exponents near $N \rightleftarrows I$ transition.

Critical exponent	α^+	α^-	γ	ν	β
Experiment	0.18 ±0.06	0.35 ±0.03	1 [3]	0.5 [8]	0.18–0.20[10]
Experiment with corrections taken into account	0.5	0.5	–	–	0.25 [11]
Landau-de Gennes theory	"jump"		1	0.5	0.5
Isolated point, ϵ-expansion, terms $\sim\epsilon$ taken into account[6]	−0.04	−0.04	1.3	0.64	0.37
Tricritical point	0.5	0.5	1	0.5	0.25

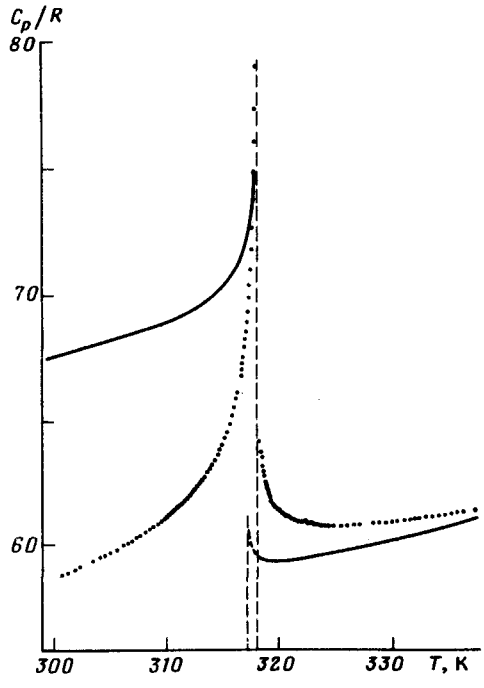

FIG. 1. Experimental heat capacity values of MBBA and results of Landau-de Gennes theory with the fluctuational corrections in the Ornstein-Zernicke approximation taken into account (solid line).

On the other hand, the intermediate nature of the values of the critical exponents in the table (between $\alpha = 0.5$ for the tricritical point[5] and $\alpha = 0$ for the isolated critical point[6]) suggests (first stated in Ref. 1) the fact that the experimental interval of temperatures ($10^{-1} > |\tau| > 10^{-3}$) lies in the transition region from tricritical behavior to critical. In a qualitative comparison of the temperature dependences of the heat capacity near the $N \rightleftarrows I$ transition and near the critical point of NH_4Br the thing that is striking is their remarkable similarity.[7] At the same time an attempt to describe the temperature dependence of the heat capacity by Eq. (2) with a fixed exponent $\alpha^+ = \alpha^- = 0.5$ (as at the tricritical point) leads to inadequacy in the model. This result can be explained, first of all, by the transition, as mentioned above, from tricritical behavior to critical ("crossover") and, secondly, by the need to take account of the logarithmic factors.[5] Therefore the heat capacity data for MBBA and BMOAB were analyzed in accordance with the simplest interpolation model

$$\frac{C_p}{R} = \frac{1}{B_1 |\tau|^{0.5} + B_2 |\tau|^{\alpha}} + C_0(\tau). \tag{3}$$

The best agreement with experiment is achieved for $\alpha = 0.1$. In this case the model (3) adequately describes the data in both phases. In all cases the constant B_2 is 15–30 times smaller than B_1; therefore the second term in the denominator of (3) is

comparable to the first only for $|\tau| < 10^{-3}$. Consequently, the tricritical behavior is the determining factor within the entire experimental interval of temperatures both in the nematic and in the isotropic phase. Insofar as the logarithmic factors are concerned, they can be ignored against the background of the "crossover" given the existing accuracy of the calorimetric experiment.

The proposed interpretation of the $N \rightleftarrows I$ transition makes it possible to explain consistently the entire set of experimental data: the "classical" value of the exponents γ and ν for the susceptibility and correlation radius,[3,8] the value of the exponent $\beta \approx 1/4$ for the temperature dependence of the order parameter, first mentioned by Keyes[9]; the question of the need to introduce "long-range action"[2] is removed.

The short-range character of the intermolecular forces in a liquid crystal was directly verified by us by measuring the heat capacity of a BMOAB-isooctane mixture near the critical point of liquid-liquid equilibrium. It was found that the critical exponent is $\alpha = 0.114 \pm 0.011$ and the ratio $A_0^-/A_0^+ = 1.97 \pm 0.40$. These values of α and A_0^-/A_0^+ are universal for all liquids and liquid mixtures with a short-range intermolecular potential. Of course, the assumption of tricritical behavior of nematic liquid crystals is very powerful. The tricritical point arises as a result of the interaction of two different order parameters. The situation with regard to this is not completely clear for liquid crystals and requires further experimental and theoretical studies.

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