Anomalous heat capacity for nematic MBBA near clearing point

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Abstract. The pretransition properties of the heat capacity on the both sides of the nematic – isotropic phase transition for the liquid crystal MBBA (n-methoxybenzylidene-n –butylaniline) are discussed on the basis of the Landau-de Gennes theory. Agreement between theory and experiment allows to obtain the critical exponents gamma and beta.

1. Introduction
Experimental and theoretical investigation of the statistical properties of heat capacity in nematic liquid crystals, especially near the phase transition to isotropic phase, is important both for the physics of phase transition and for nematic liquid crystal themselves. The analysis of the temperature dependence of the specific heat showed that the fluctuations of the OP are not small near phase transition point. Experiments on heat capacity are usually interpreted from the point of view of fluctuations of the modulus order parameter (OP), which are the principal cause of anomalously temperature dependence near phase transition point. But in addition to these modulus OP fluctuations there are the fluctuations of the orientation and biaxial fluctuations that disturb the uniaxiality of the OP.

Critical phenomena in phase transitions in liquid crystals, accompanied by the vanishing of long-rang orientational order of the long axes of the molecules, have been sufficiently studied. The existing experimental data [1] indicate that, as the nematic-isotropic transition point is approached the specific heat increases. This characteristic anomalies in the temperature are connected with the spatially-inhomogeneous fluctuations of the complex order parameter of nematic.

In this work we have attempted to carry out quantitative analysis of the possibility of the application of the Landau-de Gennes theory for the description of critical anomalies both above and below the nematic-isotropic (NI) phase transition.

2. Landau-de Gennes theory and fluctuations
In the phenomenological Landau-de Gennes theory [2] the free energy associated with the long-wavelength part of the tensor OP $Q_{\alpha\beta} = Q(n_\alpha n_\beta - 1/3 \cdot \delta_{\alpha\beta})$ fluctuations for a uniaxial nematic in the neighborhood of the phase transition ($\hat{n}$ is a unit vector, director) in the one constant approximation, is given by
\[
F = V \left( \frac{1}{2} AQ^2 - \frac{1}{3} BQ^3 + \frac{1}{4} CQ^4 \right) + \frac{1}{2} \int d\mathbf{r} \left[ \nabla \cdot (A - 2BQ + 3CQ^2) \mathbf{P}_2^0 \mathbf{P}_2^0 + L \nabla \mathbf{P}_2^0 \nabla \mathbf{P}_2^0 \right] + 2 \left( A - BQ + CQ^2 \right) \mathbf{P}_2^1 \mathbf{P}_2^{-1} + 2L \nabla \mathbf{P}_2^1 \nabla \mathbf{P}_2^{-1} + 2 \left( A + 2BQ + CQ^2 \right) \mathbf{P}_2^2 \mathbf{P}_2^{-2} + 2L \nabla \mathbf{P}_2^2 \nabla \mathbf{P}_2^{-2} \right]
\]

where \( A = a(T - T^*) \) and \( B, C \) are temperature independent constants, \( Q \) is a module of \( \mathbf{P} \), \( T^* \) - the lowest possible temperature for isotropic phase, \( L \) is an elastic constant. The first part of \( F \) is the Landau expansion in terms of the scalar \( \mathbf{P} \). \( Q = 0 \) corresponds to the isotropic phase, while in the nematic phase:

\[
Q_N = B \cdot \left( 1 + \tau^{1/2} \right) / 2C, \quad \tau = \left( T^{**} - T \right) \left( T^{**} - T^* \right)^{-1}.
\]

Here \( T^{**} = T^* + B^2 / 4ac \) is the upper limit of stability for the nematic phase. From the first part of expression (1) we can easily find the temperature and latent heat of the transition:

\[
T_c = T^* + \frac{2}{9} \frac{B^2}{aC}, \quad H = \frac{1}{2} \frac{aB^2}{C^2} T_c
\]

as well as the susceptibility and heat capacity above and below the transition point:

\[
\chi^{-1} = \begin{cases} 
\frac{a(T - T^*)}{2}, & T > T_c, \\
\frac{2a(T^{**} - T)(\tau + \sqrt{\tau})}{T_c}, & T < T_c \end{cases}, \quad C_p = \begin{cases} 
0, & T > T_c, \\
\frac{a^2(1 + \tau^{-1/2}) \cdot (2c)^{-1}}{T}, & T < T_c
\end{cases}
\]

The susceptibility in the isotropic phase shows the linear divergence. At the same time the susceptibility in the nematic phase has a linear plus a square-root divergence, i.e. a deviation from the Curie-Weiss law in the mean field approximation and \( \gamma \) exponent is less than one [3].

Let us consider nematic as a continuous homogeneous medium. Characteristic lengths of considerable change of \( \langle P_{2m} \rangle \) must be greater than the distance between molecules, i.e. \( \left| \mathbf{k} \right| < k_{\text{max}} \).

Now we use the equipartition theorem to find the thermal averages of the fluctuations of the longitudinal, transverse and biaxial modes. In the isotropic phase one can find

\[
\langle P_{2m} P_{2m} \rangle = \langle P_{2m}^1 P_{2m}^{-1} \rangle = \langle P_{2m}^2 P_{2m}^{-2} \rangle = k_B T \left( \chi^{-1} + Lk^2 \right)^{-1}
\]

While in the nematic phase we obtain

\[
\langle P_{2m}^0 P_{2m}^0 \rangle = k_B T \chi^{-1} + Lk^2, \quad \langle P_{2m}^1 P_{2m}^{-1} \rangle = k_B T Lk^2, \quad \langle P_{2m}^2 P_{2m}^{-2} \rangle = k_B T \left( 3BQ + Lk^2 \right)
\]

Here \( \chi^{-1} \) is determined by the expression (3), and

\[
3BQ = 6a(T^{**} - T^*) (1 + \sqrt{\tau})
\]

In the isotropic phase the fluctuations of all the five modes are degenerate. They increase in the long-wave limit \( (k \to 0) \) as \( T \to T^* \) according to the Curie-Weiss law.

In the nematic phase the fluctuations spectrum splits. \( \langle P_{2m}^0 P_{2m}^0 \rangle \) is the OP longitudinal fluctuations. \( \langle P_{2m}^1 P_{2m}^{-1} \rangle \) is the transverse fluctuations (director), which are not critical and represent Goldstone modes.
in the symmetry-broken phase. \( \langle P_z^2 P_{-z}^2 \rangle \) determine biaxial fluctuations, where the biaxial susceptibility \( (3BQ)^{-1} \), contrary to the longitudinal \( \chi^{-1} \), tends to a finite value at \( T = T^* \) \( (\tau = 0) \).

In the isotropic phase the excess specific heat capacity per unit volume due to OP fluctuations is given by

\[
\Delta C_\rho = \frac{5k_BT^2}{8\pi^2} \left( \frac{\partial \chi^{-1}}{\partial T} \right)^2 \left( \chi^{-1} L^3 \right)^{-1/2} \left( \frac{\arctg(x)}{1+x^2} \right),
\]  

(7)

where \( x = k_m^0 \xi \), \( \xi = \xi_0 \left( \frac{T^*}{T-T^*} \right)^{1/2} \) and \( \xi_0 = \left( \frac{L}{aT} \right)^{1/2} \) is the bare OP correlating length.

Here \( k_m \) is the upper limit of integration with respect to the wave vector of fluctuation modes. The continuous model we are used assumes averaging over a small but macroscopic volume. Therefore all our expressions are correct up to wave vector \( k_m \).

To compare the expression (7) with the experimental data, it is convenient to rewrite it in the form

\[
C_\rho = \Delta C_{\rho_0} + \frac{BT^2}{\sqrt{T - T^*}} \arctg \frac{A}{\sqrt{T - T^*}} + \frac{ABT^2}{T - T^* + A^2},
\]  

(8)

\[
A = \frac{k_m L^{1/2}}{a^{1/2}} = k_m^0 \xi_0 \sqrt{T^*}, \quad B = \frac{5}{8\pi^2} \frac{k_m a^{3/2}}{L^{1/2}} \frac{M}{\rho},
\]

Because direct experimental observation of \( T^* \) is not possible, it have to be treated as adjustable parameter (together with \( A \) and \( B \)) in the fits. Furthermore, no data points in the range \( T - T^* < 1 \) was covered in the fits. We consider the Gaussian approximation only that is correct not to close to the transition point. The best agreement with experiment was obtained for the parameter values \( A = 22.12, \quad T^* = 317.97 \text{ K}, \quad \Delta C_{\rho_0} = 499.11 \text{ J \cdot (mol \cdot K)^{-1}}, \quad B = 1.24 \cdot 10^{-4} \). The fitting of experimental data [4] result is presented at figure 1. The fitting parameters \( A \) and \( B \) are connected with each other through the equation (8), which immediately allows to get \( (k_m)^{-1} = 5.5 \text{ Å}, \xi_0 = 6.82 \text{ Å}. \) Our value of \( \xi_0 \) is close to the value obtained in [5]. For density and the molecular weight of MBBA we used \( \rho = 1.049 \text{ g \cdot cm}^{-3}, \quad M = 267.37 \text{ g \cdot mol}^{-1}. \)

The treatment of the fluctuation part of the specific heat at the nematic phase is more complex. The entropy density associated with fluctuations is obtained by differentiating (1) with respect to the temperature. The subsequent ensemble average gives the entropy change due to fluctuations. The final expression for the fluctuation induced heat capacity has the form

\[
\Delta C_\rho = \frac{T}{2} \frac{\partial^2 \chi^{-1}}{\partial T^2} \sum_k \left( \langle |P_z^0|^2 \rangle \right)^2 + T \frac{\partial^2 (3BQ)}{\partial T^2} \sum_k \langle P_z^2 P_{-z}^2 \rangle
\]

\[
= - \frac{T}{2} \left( \frac{\partial \chi^{-1}}{\partial T} \right)^2 \sum_k \langle |P_z^0|^2 \rangle^2 - T \left( \frac{\partial^2 (3BQ)}{\partial T^2} \right) \sum_k \langle P_z^2 P_{-z}^2 \rangle^2
\]  

(9)
Figure 1. Specific heat above the transition temperature. Solid line show theoretical data and circles show the experimental data of Anisimov [4].

Note that in (9) there are present components which are proportional to the second derivative with respect to reverse susceptibilities. It is caused by the fact that the longitudinal susceptibility in nematics does not obey Curie-Weiss law, and the reverse biaxial susceptibility is directly proportional to OP. The formula (9) can be used to describe the experimental data [4].

The results of the experimental research of the heat capacity, OP and susceptibility demonstrate that the use of expressions (2), (3) and (6) have the difficulties of describing the data in the nematic phase.

Changing to some other temperature scale $T_1 > T^{**}$ we can approximate the expression (2) in the corresponding temperature range to get the following formula:

$$Q_N = \frac{B}{2C} \frac{T_{1}^{T^{**}-T_{i}}}{\beta} t^\beta, \quad (10)$$

where $t = (T_{1} - T_{1})^T_{1}^{-1}$. $\beta$ and $T_{1}$ are fitting parameters. The equation (10) has the form of widely used the Haller relation [6]. The reverse of the longitudinal and biaxial susceptibilities in this case have the following forms $\chi^{-1} = \chi_0^{-1} t^\gamma$, $\chi_0 = (2aT)^{-1}$, $3BQ = 3\chi_0^{-1} t^\beta$.

Using these definitions, we find the expression for heat capacity in the nematic phase:
\[ C_p = \Delta C_{p_0} + C_{\text{Landau}} + \Delta \varepsilon_p \Delta C_{p_0} + 2 \kappa^2 H \beta \frac{T}{T_c - T_1} t^{2\beta - 1} + \]
\[ + \frac{k_B T^2}{2} \frac{1}{2\pi^2} \frac{2^{1/2}}{\xi_0 T_1} \frac{3^{3/4}}{t^{1/2}} \left[ \arctg \left( \frac{x_0}{1 + x_0^2} \right) \right]^{\gamma} - \gamma (\gamma - 1) \left[ \frac{1}{x_0 - \arctg (\frac{x_0}{1 + x_0^2})} \right] \right] \]
\[ + \frac{k_B T^2}{2} \frac{1}{2\pi^2} \frac{6^{1/2}}{\xi_0 T_1} \frac{3^{3/4}}{t^{1/2}} \left[ \arctg \left( \frac{x_2}{1 + x_2^2} \right) \right]^{\beta^2 - 2\beta (\beta - 1) \left[ \frac{1}{x_2 - \arctg (\frac{x_2}{1 + x_2^2})} \right] \right] \]

Here \( T \) is the transition latent heat and for the nematic MBBA its experimental value is \( H = 0.78 \text{ J} \cdot \text{g}^{-1} \) [1]. \( L_N \) is the elastic constant in nematic phase which is not equal to one in isotropic phase. The second term in equation (11) is the heat capacity obtained in the Landau theory. In order to determine quantitative agreement of (11) with experimental data we treat variable parameters \( T_1, \xi_0, \Delta C_{p_0} \) and make a fitting in temperature range \( T < T_c - 1^\circ \), because of the approximation used. After that we get following parameter values that give the best fit: \( T_1 = 320.97^\circ \), \( \xi_0 = 9.08 \text{ Å} \), \( \Delta C_{p_0} = 489.5 \text{ J} \cdot (\text{mol} \cdot \text{K})^{-1} \) (see the figure 2), as well as the critical exponents \( \beta = 0.2 \) [7] and \( \gamma = 0.68 \) [8].

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**Figure 2.** Specific heat above and below the transition temperature. Solid lines show theoretical data and circles and triangles show the experimental data [4].
The agreement of theoretical formula (11) with experiment shows us that the use of empirical approximation procedure of Haller for OP and similar procedure for the longitudinal susceptibility in the Landau-de Gennes model gives a satisfactory description of heat capacity experiments in nematic phase. The critical exponent $\beta$ of order parameter is in good agreement with the experimental data for MBBA [9]. The regular part of the heat capacity $\Delta C_p$ in nematic phase is a bit less than the corresponding value in the area higher than the transition point, and it coincides with experiment.

3. Conclusions
In this paper we have presented the analysis of the specific heat anomaly near the NI transition. Experiments show a complex behavior in which Gaussian and non-Gaussian fluctuations cannot be neglected [2]. The absence of the divergence at the NI transition point allows us to expect of using the Gaussian approximation or weakly interacted fluctuation limit. The existence of the cubic invariant in (1) is probably the main reason for the failure of the mean-field description in the vicinity of the NI transition. From the analysis due to Landau-de Gennes model we obtained for the critical exponents $\gamma = 0.68$, $\beta = 0.2$, which are in qualitative agreement with those obtained for MBBA from different sources. The temperature dependence of the heat capacity in the nematic phase is connected with the change in the degree of nematic order and with the increase of the longitudinal and biaxial fluctuations. In the isotropic phase the fluctuation contribution is the only one.

It is interesting to note that from the renormalization group study [10] it follows that the critical anomalies can be connected either with the presence of the fixed point, which described the transition near the isolated singular point, or with the two fixed points which are due to the specific character of the fluctuations in the nematic. The last of them are a saddle and a stable focus. In the neighbourhood of a first-order transition line of the phase diagram of the renormalization group equations the transition is controlled by saddle fixed point, in the vicinity of which $\gamma = 0.58$, $\beta = 0.23$.

4. References
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