Theory of the anomalous critical behavior for the smectic-A–hexatic transition

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We propose a theoretical explanation for the long-standing problem of the anomalous critical behavior of the heat capacity near the smectic-A–hexatic phase transition. Experiments find a large specific heat critical exponent $\alpha = 0.5$–$0.7$, which is inconsistent with a small negative value $\alpha \approx -0.01$ expected for the three-dimensional $XY$ universality class. We show that most of the observed features can be explained by treating simultaneously fluctuations of the hexatic orientational and translational (positional) order parameters. Assuming that the translational correlation length $\xi_t$ is much larger than the hexatic correlation length $\xi_h$, we calculate the temperature dependence of the heat capacity in the critical region near the smectic-A–hexatic phase transition. Our results are in quantitative agreement with the calorimetric experimental data.

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1. INTRODUCTION

Smectic liquid crystals are remarkable layered phases exhibiting an astonishingly rich variety of structures. The simplest smectic phase is the smectic-A liquid crystal. It consists of a stack of liquid layers, which are positionally ordered in the transverse direction. Another smectic phase, the smectic C, shows, in addition, a nematic orientational order within the layers. In the late 1970s, some smectic phases were identified to possessing a hexagonal orientational order inside the layers, first as a theoretical suggestion [1,2] and later from the direct experimental observation [3–6]. These phases are termed as hexatic smectics or hexatics. Let us emphasize that the long-range orientational order in the hexatic layers is not accompanied by a long-range positional (translational) order. It is worth noting that the hexatic phases are not merely peculiar states of a few liquid-crystalline materials. They also appear in biological systems [7,8] and even in the planetary or astrophysical science as a form of dust plasma [9]. Investigation of the hexatics is a multidisciplinary area including many fundamental physical problems and involving various questions of chemistry and biology. However, even after some decades of investigations of the hexatics, a complete description of this liquid-crystalline state is still not available, and a number of phenomena remain to be clarified.

In this work we examine properties of a liquid crystal near the continuous smectic-A–hexatic phase transition. Such transitions are observed in a variety of materials [3,4,6,10–18]. We use the Landau approach introducing phenomenologically the hexatic orientational order parameter [19]. A similar approach is widely used for the phase transition from an isotropic liquid to the nematic phase, which is characterized by a second-order symmetric traceless tensor $Q_{ik}$ [20]. In the nematic phase the average value of the order parameter $Q_{ij}$ is nonzero and the complete rotational symmetry of the isotropic liquid is reduced to the quadrupolar symmetry of the nematic.

A “nematiclike” orientational order parameter can be also introduced for the smectic-C phases. The order parameter is again a second-order symmetric traceless tensor. However, the tensor is determined inside smectic layers; hence, the order parameter is a $2 \times 2$ tensor, unlike the $3 \times 3$ tensor of the three-dimensional nematic phase. A nonzero average value of the order parameter means a reduction of the uniaxial rotational symmetry $D_{\infty h}$ of the layers of the smectic-A phase to the biaxial rotational symmetry $D_{2h}$ in the smectic-C phase. In other words, layers in the smectic C are invariant with respect to the twofold rotations, whereas layers are isotropic in the smectic A.

Similarly to the smectic-A–smectic-C phase transition, the smectic-A–hexatic transition leads to a reduction of the rotational symmetry in smectic layers. The corresponding symmetry in the hexatic state is $D_{h}h$ instead of $D_{3h}$ in the smectic C. The hexatic order parameter is a six-rank symmetric irreducible tensor $Q_{ijklm}$ having only components within layers. The irreducibility means that $Q_{ijklm}=0$. In the smectic-A phase the average value of the tensor $Q_{ijklm}$ is zero and layers are isotropic. In the hexatic phase this average value becomes nonzero; as a result, layers of the hexatic phase are invariant under sixfold rotations about the orthogonal axis. The irreducibility implies that the tensor $Q_{ijklm}$ has only two independent components [21]. Smectic layers are almost parallel. If we direct the $Z$ axis perpendicular to the layers, then these two independent components of the tensor can be chosen as $Q_{xxxxxx}$ and $Q_{xxxxxy}$. It is convenient to introduce a scalar complex field $\Psi$ instead of the tensor $Q_{ijklm}$:

$$\Psi = Q_{xxxxxx} + iQ_{xxxxxy}.$$  

At the rotation by the angle $\chi$ around the $Z$ axis the field $\Psi$ is transformed as

$$\Psi \rightarrow \exp(6i\chi)\Psi.$$  

The field $\Psi$ is equivalent to the traditional hexatic order parameter introduced in [1,2] in terms of the molecular bond orientations (see also the textbooks [19,20]).

With the order parameter in hand, at the next step one has to derive the Landau energy functional for the smectic-A–hexatic transition. The energy remains invariant under global rotations of the phase of the order parameter $\Psi$. Therefore, the
Landau functional $\mathcal{F}_{\text{LD}}$ contains only even terms in $\Psi$. This means that the smectic-$A$–hexatic transition must be a second-order phase transition; see the textbooks [19,22–24]. Since the hexatic order parameter has two independent components, the phase transition belongs to the same $XY$ universality class as the superfluid transition in helium. Hence, the heat capacity exponent $\alpha$ for the smectic-$A$–hexatic phase transition has to be small and negative, $\alpha \approx -0.01$ (see the experimental data and Monte Carlo simulation results discussed in [24–26]). Note that the second-order $\epsilon$ expansion [27] gives a small positive $\alpha \approx 0.01$. Contrary to these expectations, all known calorimetric data for the smectic-$A$–hexatic phase transition [10–18] give relatively large values $\alpha = 0.5–0.7$. Thus, there is an obvious problem and the main goal of this work is to explain the existing controversy.

Two alternative explanations for this discrepancy were suggested before. Using the fact that $\alpha$ is close to 0.5, it was assumed that the smectic-$A$–hexatic transition occurs in the vicinity of a tricritical point [28]. In this case a kind of crossover behavior can be observed, similar to the situation near the nematic–smectic-$A$ tricritical point (see details in the works [29,30]). However, it is hard to believe that all known hexatic liquid-crystalline materials, irrespective of the width of the hexatic phase stability region, which ranges from a few to 50 K [15], are always near the tricritical point and, in addition, are always on the continuous transition side.

Another suggestion [31–33] is based on the observation that the measured critical exponents for the hexatic–smectic-$A$ phase transition are close to values predicted for the $q$-state Potts models [34] with $q = 3$ or $q = 4$ in two or three dimensions. It remains largely unclear how and why the Potts model is related to the physics of the phase transition with the two-component order parameter. In our opinion, this approach is not consistent with the entire massif of the experimental data.

We propose another way to reconcile the concept of the phase transition universality with the experimental data for the smectic-$A$–hexatic phase transition. Recent progress in the x-ray scattering techniques [6] reveals an unusual feature of the hexatic liquid crystals. Namely, very narrow peaks are observed in the x-ray scattering data in the hexatic phase. The correlation length $\xi_r$, of the positional order parameter $\delta \rho$, extracted from the x-ray data [6] for 3(10)OBC, is anomalously large in the hexatic phase; it changes from about 3 nm in the vicinity of the transition point up to 20 nm deeply in the hexatic phase. In the phenomenological approach this means that the hexatic phase is very close to crystallization. In the framework of our macroscopic approach we cannot explain why $\xi_r$, in the hexatic smectics is so large. It must be a topic of a separate microscopic investigation.

In the situation when $\xi_r$ is large, it is necessary to take into account a coupling between the hexatic order parameter and positional order parameter. Due to this coupling the critical behavior, characteristic for the superfluid helium universality class, should be observed at the condition $\xi_0 \gg \xi_r$, where $\xi_0$ is the correlation length of the hexatic order parameter. In the opposite limit, at $\xi_0 \ll \xi_r$, it is necessary to take into account the self-interaction of the hexatic order parameter mediated via the fluctuations of the translational order parameter. This interaction is effectively nonlocal and it can lead to a nonstandard critical behavior. In the following, we examine this possibility.

Of course, the standard critical behavior must be observed at the condition $\xi_h \gg \xi_r$. However, this condition is fulfilled only in a narrow vicinity of the phase transition point. Unfortunately, it is impossible to estimate the width of this region from the available experimental data. The standard theory [19,22] suggests only that $\xi_h \sim \xi_0 |T – T_h| / T_h^{-1}$, where $\xi_0$ is the bare correlation length, $T_h$ is the smectic-$A$–hexatic transition temperature, and $\nu = 0.76$ is the critical exponent of the correlation length of the order parameter in three-dimensional space. Assuming $\xi_0 \approx 0.1$ nm, we find that $\xi_h$ is a few times larger than $\xi_r \approx 3$ nm in the vicinity of the transition point $\Delta T / T_h \lesssim 10^{-3}$. Beyond this region the intermediate asymptotic behavior caused by the interaction of the hexatic order parameter $\Psi$ with the fluctuations of translational order parameter $\delta \rho$ takes place. The main goal of this work is to develop a theoretical description for this case and to compare the obtained predictions with the known calorimetric data.

In Sec. II we introduce the model and present its theoretical investigation. In Sec. III we examine the fluctuation effects in the framework of our model. In Sec. IV we compare our theoretical results and calorimetric experimental data. Our main statements are summarized in the Conclusion, Sec. V.

II. MODEL

Our model is based on the consideration of two strongly fluctuating fields: the hexatic order parameter $\Psi$ and the short-range density modulation $\delta \rho$, which is the order parameter for the crystallization phase transition. We consider a vicinity of the smectic-$A$–hexatic phase transition where fluctuations of $\Psi$ are strong and the standard critical behavior with universal critical exponents characteristic for a two-component order parameter is expected. As was noted before, the observed singularity of the heat capacity near the smectic-$A$–hexatic phase transition does not agree with the standard behavior. We believe that this unusual behavior is a result of interaction of the order parameter $\Psi$ with fluctuations of the short-range density modulations $\delta \rho$. This interaction is also relevant in the hexatic phase outside of the critical region, where effects related to the nonzero mean value of the order parameter $\Psi$ must be taken into account. We defer investigation of corresponding effects for future work.

The main assumptions of our model are based on the experimental x-ray scattering patterns. It is well known that the x-ray scattering is produced by the short-range electron density fluctuations which are proportional to the mass density fluctuations $\delta \rho$. The scattering intensity is determined by the pair correlation function of $\delta \rho$. The Fourier transform of the correlation function is known as the structure factor $S(q)$:

$$S(q) = \int d^3r \exp(-i\mathbf{q}\cdot\mathbf{r})(\delta \rho(r_1)\delta \rho(r_2)).$$

For the smectic phases, the structure factor $S(q)$ has quasi-Bragg peaks at $q_x, q_y = 0$, $q_z = 2\pi / l$ (where $l$ is the thickness of the smectic layers) and also maxima at $q_x = q_0$, $q_x^2 + q_y^2 = q_0^2$, where $q_0^2$ is of the order of a characteristic intermolecular distance in the smectic layers. As was
experimentally established for hexatics [6], the structure factor \( S(q) \) is almost independent of \( q \), near the cylinder \( q_\perp = q_0 \) (more precisely, one should consider the quasimomentum defined within the first Brillouin zone in the \( Z \) direction). In terms of the positional order parameter \( \delta \rho \), this weak dependence of the structure factor on \( q_\perp \) means that the relevant fluctuations of \( \delta \rho \) are strongly confined in the central part of the smectic layers.

The x-ray scattering data provide the information on the temperature dependence of the structure factor \( S(q) \) near the smectic-\( A \)–hexatic phase transition (see [6] and references therein). In the smectic-\( A \) phase the pattern is a bright diffuse ring (cylinder in the three-dimensional reciprocal space) parallel to the smectic layers with the radius \( q_\perp = q_0 \). In the hexatic phase the ring splits into six spots, according to the sixfold rotational symmetry of the phase. The angular dependence of the structure function \( S(q) \) is related to a nonzero average value of the order parameter \( \Psi \) in the hexatic phase. Each spot is narrow in the radial direction (along \( q_\perp \)) and elongated in the angular direction. The radial behavior of the structure function is characterized by the correlation length \( \xi_{\|} \). As we already noted, for 3(10)OBC the correlation length \( \xi_{\|} \) changes from about 3 nm in the vicinity of the transition point up to 20 nm in the hexatic phase. Thus, the correlation length significantly exceeds the characteristic molecular size.

We analyze the critical behavior of a liquid crystal near the smectic-\( A \)–hexatic phase transition where fluctuations of the hexatic order parameter \( \Psi \) are strong. In this region the angular dependence of the structure function in the hexatic phase is weak and therefore it is neglected below. We are interested in the temperature region where the condition

\[
\xi_{\|} > \xi_h
\]  

(4)

is valid; as above, \( \xi_h \) is the correlation length of the hexatic order parameter. As was explained in the Introduction, the inequality (4) is violated only in the narrow vicinity of the smectic-\( A \)–hexatic transition temperature, where the critical behavior characteristic for the superfluid phase transition is restored. Beyond this narrow region, that is, in the region where the inequality (4) is valid, a special theoretical analysis of the critical behavior is needed, which is the subject of our work.

As a rule, crystalization of an ordinary liquid or a liquid crystal is a strong first-order transition. In particular, the latent heat per molecule is of the order of \( k_B T_m \), where \( k_B \) is the Boltzmann constant and \( T_m \) is the crystallization temperature. In such a situation it is natural to expect that the positional correlation length \( \xi_{\|} \) is of the order of the molecular scale \( q_0^{-1} \). Since the experimental data [6] suggest \( \xi_{\|} \gg q_0^{-1} \), we believe that the crystallization of hexatics is a weak first-order phase transition. Therefore, the weak crystallization theory [35] is a natural tool to describe the positional fluctuations near the phase transition in both the hexatic and the smectic-\( A \) phases. In this theory the characteristic value of the short-range mass density \( \delta \rho \) (positional order parameter) is much smaller than the average uniform mass density. Thus, according to the Landau approach, the energy can be expanded into a series over \( \delta \rho \). The expansion, known as the Landau functional determines the correlation functions of \( \delta \rho \), e.g., the structure factor (3).

The second-order term in the Landau functional is written as

\[
\mathcal{F}_{(2)} = \int \frac{d^3q}{(2\pi)^3} \left[ \frac{a}{2} |\delta \rho(q)|^2 + \frac{b}{2} (q_\perp - q_0)^2 |\delta \rho(q)|^2 \right]. 
\]  

(5)

Here \( \delta \rho(q) \) is the Fourier transform of \( \delta \rho(r) \) and \( a, b \) are Landau expansion coefficients. The coefficient \( a \) diminishes as the temperature decreases. As usual, in the Landau approach we assume that \( a \propto (T - T_c) \), where \( T_c \) is the bare crystallization temperature, i.e., the stability limit of the hexatic state in the mean-field approximation. The coefficient of \( |\delta \rho(q)|^2 \) in Eq. (5) has a minimum at \( q_\perp = q_0 \). It corresponds to the maximum of the structure function (3) at \( q_\perp = q_0 \). The dependence on \( q_\perp \) in the expression (5) was omitted because the experimental observations [6] show no dependence of the structure function on \( q_\perp \).

The fourth-order term of the Landau expansion over \( \delta \rho \) can be written as

\[
\mathcal{F}_{(4)} = \int \frac{d^3q_1 d^3q_2 d^3q_3 d^3q_4}{(2\pi)^9} \delta(q_1 + q_2 + q_3 + q_4)
\times \frac{j}{24} \delta \rho(q_1) \delta \rho(q_2) \delta \rho(q_3) \delta \rho(q_4). 
\]  

(6)

The contribution (6) describes the self-interaction of the short-range density fluctuations. Generally, the factor \( j \) depends on the wave vectors \( q_1 \sim q_4 \). Below, for the sake of simplicity, we suggest that \( j = \text{const} \). Note that since the positional order parameter \( \delta \rho \) is a scalar quantity, a third-order term over \( \delta \rho \) in the Landau functional is allowed by the symmetry. Below we neglect the third-order term because the experiment demonstrates the large value of the positional correlation length \( \xi_{\parallel} \). Indeed, if the third-order term is not small, then the crystallization of the hexatic phase would be a strong first-order transition and \( \xi_{\parallel} \) would be of the order of the molecular size.

The average value of the short-range density modulation \( \delta \rho \) is zero in both smectic-\( A \) and hexatic phases. In other words, there is no long-range positional order in the smectic layers. Note that we are interested in the mass density with the wave vectors near the circle \( q_\perp = q_0 \) (besides the standard for all smectics quasi-Bragg peaks at \( q_\perp = 2\pi/\lambda, q_\parallel = 0 \), reflecting the density modulation in the direction perpendicular to the layers). Near the smectic-\( A \)–hexatic phase transition, above and below the transition temperature \( T_h \), the short-range density modulation \( \delta \rho \) is a strongly fluctuating quantity, which agrees with the fact that the correlation length \( \xi_{\|} \) is large. Therefore, to find the structure function (3) one has to calculate fluctuation corrections to the bare value determined by the second-order term (5). A theoretical framework of the corresponding analysis can be found in our survey [35]; here we adopt the method for a smectic phase near the smectic-\( A \)–hexatic phase transition.

The interaction between the orientational order parameter and the density fluctuations is described by a cross-term of the Landau functional depending on the both fields \( \delta \rho \) and \( \Psi \). The main interaction term in the Landau functional can be written as

\[
\mathcal{F}_{\text{int}} = -\frac{1}{2q_0^6} \Re \int dV \Psi \{ \partial_{\|} - i \partial_\perp \} \delta \rho \times |\delta \rho|^2, 
\]  

(7)
where distortions of the smectic layers were neglected. Note that the transformation law (2) demonstrates explicitly the rotational invariance of the interaction term (7). This interaction produces, in particular, the hexagonal angular dependence of the density correlations in the hexatic phase, where the mean value of $\Psi$ is nonzero. Note that fixing the coefficient in Eq. (7) (that is equal to unity), we define the normalization of the orientational order parameter $\Psi$.

### III. FLUCTUATION EFFECTS

To determine the correlation functions of the order parameters $\Psi$ and $\delta \rho$, one has to take into account a self-interaction of the fields and their coupling. The self-interaction of the hexatic order parameter $\Psi$ leads to a universal scaling behavior characterized by a set of critical exponents [19,23,24,36]. The self-interaction of the parameter $\delta \rho$ produces effects that can be examined in the weak crystallization theory; see Ref. [35]. In addition, it is necessary to take into account the coupling between the order parameters $\Psi$ and $\delta \rho$. We consider this coupling in the framework of the perturbation theory, which is possible if the coupling is small (see below).

An analysis of the fluctuational effects shows that in the smectic-$A$ phase the structure function (3) can be written as

$$S(q) = \frac{T}{\Delta + b(q_\perp - q_0)^2},$$  \hspace{1cm} (8)

where $b$ is the same coefficient as in the Landau functional (5). Below, the parameter $\Delta$ is called gap. As it follows from the expression (8), the translational correlation length is $\xi_{\text{tr}} = \sqrt{b/\Delta}$. The expression (8) is valid in the smectic-$A$ phase; in the hexatic phase the structure function acquires the hexagonal angular dependence. However, in the vicinity of the smectic-$A$–hexatic phase transition, which we consider in this work, the angular dependence is weak and it will be ignored in our analysis. Thus, we use the expression (8) both for the smectic-$A$ and the hexatic phases. The expression (8) is justified by the inequality $q_0 \xi_{\text{tr}} \gg 1$, which is the main applicability condition of our theory.

The gap $\Delta$ depends strongly on the temperature. The bare value of the gap is $a$ [see Eq. (5)]; the value is renormalized due to the self-interaction of the density fluctuations. The main fluctuation contribution to $\Delta$ is determined by the one-loop term depicted by the Feynman diagram

$$\Delta = a + \frac{T q_0 \lambda}{4 \sqrt{b \Delta}},$$  \hspace{1cm} (10)

in a close analogy to the weak crystallization theory of three-dimensional liquids; see details in the survey [35]. Note, that Eq. (10) has a solution for both positive and negative $a$. This implies that the hexatic phase remains metastable below the crystallization temperature.

Next we should take into account the interaction between the orientational order parameter $\Psi$ and the positional order parameter $\delta \rho$, determined by the term (7) in the Landau functional. The interaction between the orientational and positional order parameters modifies the correlation functions of both fluctuating quantities $\Psi$ and $\delta \rho$. We examine this effect using the perturbation theory; that is, we take into account only the first corrections to the correlation functions related to the interaction (7). The applicability condition of the perturbative approach is formulated at the end of this section.

Let us examine contributions to the gap $\Delta$ caused by the interaction. Contributions to $\Delta$ related to the interaction term (7) can be represented by the Feynman diagrams

\[ F(r_1, r_2) = \langle \Psi(r_1) \Psi^*(r_2) \rangle. \]  \hspace{1cm} (13)

According to the second-order phase transitions theory [19,23,24,36], the Fourier transform of the correlation function (13) has the form

$$F(q) = \frac{1}{q^{2-\eta}} f(q \xi_b),$$  \hspace{1cm} (14)

where $\eta$ is the so-called anomalous critical exponent. For the superfluid universality class $\eta \approx 0.02$, see Refs. [24–26]. The scaling function $f$ in Eq. (14) provides that $F$ depends solely on $|T - T_a|$ if $q \xi_b \ll 1$ and solely on $q$ in the opposite limit $q \xi_b \gg 1$; see Refs. [19,23,24,36].

In the smectic-$A$ phase the contribution (11) is zero. Indeed, the closed loop in the diagram (11) corresponds to the single point average $\langle (i \partial_t - i \lambda) \delta \rho \rangle^2$; see Eq. (7). Such average is zero due to isotropy of the smectic-$A$ layers. This contribution is also negligible in the hexatic phase in the vicinity of the phase transition. Thus, one should take into account solely the term (12) that gives the contribution to the gap $\Delta$

$$\delta \Delta = -\frac{1}{2T} \int \frac{d^3q}{(2\pi)^3} F(q) S(k + q),$$  \hspace{1cm} (15)

where $k$ is the wave vector of the density fluctuation. Here the wave vector $k$ lies near the ring (cylinder) $k_\perp = q_0$, whereas the wave vector $q$ can be estimated as $q \sim \xi_b^{-1}$. Thus, the inequalities $k \gg q$ and $\Delta \ll bq^2$ are valid. The first inequality is related to the condition that $\xi_b q_0 \gg 1$, which is valid near the phase transition point. The second inequality is equivalent to the condition (4). Using these inequalities, one obtains

$$\delta \Delta = -\frac{1}{8\pi^2 \sqrt{b \Delta}} \int dq_z dq_\perp F(q),$$  \hspace{1cm} (16)

where we used the expression (8) at the derivation of (16). Finally, we obtain an equation for $\Delta$,

$$\Delta = a + \frac{T q_0 \lambda}{4 \sqrt{b \Delta}} + \delta \Delta,$$  \hspace{1cm} (17)
instead of Eq. (10). Equation (17) determines the temperature dependence of the gap \( \Delta \) in the critical region.

In the region \( q\delta_h \gg 1 \), the pair correlation function \( F(q) \propto q^{1-\nu} \) [19,23,24,36]. Therefore, there is an ultraviolet contribution to the integral \( \int dq d\eta F \) to be included into a redefinition of the factor \( \lambda \), entering Eq. (17). Besides, as follows from Eq. (14), there is a negative critical contribution to the integral \( \int dq d\eta F \) that behaves like \( \propto |T - T_0|^\nu \). We are interested just in this term which produces a singular contribution to the gap \( \Delta \). Taking derivative of Eq. (17) and keeping in mind that \( \Delta \) remains finite at the transition point, we find

\[
\frac{\partial}{\partial T} \Delta \propto |T - T_0|^\nu - 1. \tag{18}
\]

The singularity is integrable due to \( \eta, \nu > 0 \). Therefore, the gap \( \Delta \) remains finite at the transition point, which justifies our approach.

Now we can formulate the applicability condition of our perturbation approach. For this purpose it is necessary to compare the contribution presented by the one-loop diagram (12) with the higher-order contributions, determined by many-loop diagrams. An example of two-loop diagram is presented in the figure

\[
\text{(19)}
\]

Straightforward estimation shows that one can neglect diagram (19) in comparison with diagram (12) if

\[
\delta \Delta \ll \Delta, \tag{20}
\]

where \( \delta \Delta \) is determined by Eq. (16). If the inequality (20) is not valid, summation of an infinite series of terms is needed. Such analysis is beyond the scope of this work.

Our theory yields the additional contributions to the heat capacity related to the positional degree of freedom \( \delta \rho \). The main contribution is associated with the \( T \) dependence of the coefficient \( a \) in Eq. (5). Namely, we find for the \( a \)-dependent part of the free energy

\[
\frac{\partial F_a}{\partial T} = \frac{V}{2} \frac{\partial a}{\partial T} (\delta \rho)^2 = \frac{\partial a}{\partial T} \frac{T V q_0}{4l b^4 \Delta} \tag{21}
\]

where the thickness of the smectic layer \( l \) appears due to integration over \( q_0 \) within the first Brillouin zone. Evaluating the derivative of the expression (21) over the temperature, we find the following critical contribution to the heat capacity:

\[
-T \frac{\partial^2 F_a}{\partial T^2} = \frac{V}{8} \frac{\partial a}{\partial T} \frac{T^2 q_0}{b^4 \Delta} \frac{\Delta}{\partial T}. \tag{22}
\]

One can easily find from Eq. (18) that the contribution (22) diverges near the phase transition with the exponent \( 1 - \nu \eta \), close to unity.

The additional contribution to the heat capacity (22) is crucial for our approach. The main message of the work (see details in the next section) is that a sum of two critical contributions to the heat capacity, with the “small” exponent \( \alpha \) and with the “large” exponent \( 1 - \nu \eta \), enables one to describe quantitatively the known experimental data.

### IV. Comparison with Experiment

Unfortunately, the experimental x-ray scattering data are very scarce for the critical region of the smectic-\( A \)-hexatic phase transition. In such a situation it is useless to estimate the three unknown parameters in the gap equation by fitting a small number of experimental points. In contrast, the calorimetric data in the critical region are quite informative. Thus, we focus on the measurable specific heat behavior and take a pragmatic approach to understand calorimetric features of the smectic-\( A \)-hexatic smectic phase transition and provide relationships between different physical properties.

The calorimetric data for 65OBC liquid-crystalline material known from the literature [10–18] show that the smectic-\( A \)-hexatic transition is the second-order transition with a strong nearly symmetric singularity of the heat capacity. The value of the critical exponent \( \alpha \) is extracted in the works from the fitting of a single power law dependence to the experimental data in the temperature range \( |T - T_0| > 0.1 \text{ K} \). For 65OBC the obtained critical exponent is \( \alpha \approx 0.64 \), and the critical amplitude ratio is \( A^+ / A^- \approx 0.84 \). Note that the critical exponent of heat capacity \( \alpha \) depends on the material. Results presented in [12] give the values ranging from 0.48 to 0.67 for eight different substances. This difference cannot be attributed only to yet immature sample preparation, some external noise, etc.

Our theory states that the singular part of the heat capacity in the intermediate critical region is a sum of two terms: the first term with the standard small critical exponent \( \alpha \) characteristic for the theory of the two-component order parameter universality class and the second term with the exponent \( 1 - \nu \eta \approx 0.985 \); see Eq. (22). The second contribution originates from the interaction of the order parameters \( \Psi \) and \( \delta \rho \). Thus, to fit the experimental data we utilize an expression for the heat capacity,

\[
C = \frac{p_1}{x^{0.015}} + \frac{p_3}{x^0} + p_5, \quad \text{if } x < 0, \tag{23}
\]

\[
C = \frac{p_2}{x^{0.013}} + \frac{p_4}{x} + p_5, \quad \text{if } x > 0,
\]

where \( C = (T - T_h )/T_h \) is the reduced temperature, and we used the value of the exponent \( \alpha = -0.013 \) from the standard data for the two-component order parameter in three dimensions presented in [24–26]. The obtained values giving the best fitting are \( T_h = 341.11 \text{ K} \), \( p_1 = -48.09599 \), \( p_2 = -48.19495 \), \( p_3 = 0.0008 \), \( p_4 = 0.0064 \), and \( p_5 = 91.60242 \). Although the determined parameters \( p_3 \) and \( p_4 \) are much smaller than \( p_1 \) and \( p_2 \), they are still larger than the fitting accuracy. Physically, the smallness of \( p_3 \) and \( p_4 \) confirms the above assumption of a weak coupling term (7).

Figure 1 presents results of the specific heat computation in our model [see Eqs. (22) and (23)] and the experimental data [17] (which almost coincide, up to a regular shift of the sample-dependent transition temperature, with the data presented in Refs. [10] and [16]). We see a reasonable agreement of the experimental data and the results of calculation valid in the temperature range about 0.6 K–1 K around \( T_h \). The exponent \( \alpha \) found in [10,16,17] is based on the single power-law fitting of the experimental data in the temperature range 0.005 \( < |T - T_h|/T_h < 1.5 \). In this more broad temperature region we expect...
a crossover behavior which can be approximated by a single, but not universal, power law. Understanding all the limitations, we are confident that our model captures the essential features of the smectic-A–hexatic phase transition in the intermediate critical region with two strongly fluctuating and coupled order parameters.

V. CONCLUSION

The main result of our work is the formulation of the model which provides quantitative description of the calorimetric data for the smectic-A–hexatic transition. We also explain the large value of the heat capacity critical exponent. In order to avoid any confusion, let us emphasize that we do not try to overthrow the fundamental concept of universality for the second-order phase transitions. There is no doubt that in the immediate vicinity of the smectic-A–hexatic transition temperature, the universal behavior of the heat capacity must be observed. Outside this region the critical behavior does not correspond to the standard universality, and its description calls for additional ingredients that are presented in our work.

Our model involves the interaction between the strongly fluctuating orientational (hexatic) order and positional degrees of freedom, \( \Psi \) and \( \delta \rho \). It offers a new nontrivial scenario for the temperature dependencies of the specific heat and x-ray scattering patterns near the smectic-A–hexatic phase transition. The approach allows one to reconcile the phase transition universality concept and the calorimetric experimental data for the smectic-A–hexatic phase transition. Thus, our work resolves the old discrepancy related to the large value of the heat capacity exponent for this phase transition.

In this paper we study the behavior of the system in the critical region near the transition point, i.e., in the region of strong fluctuations of the hexatic order parameter \( \Psi \). However, the model can be applied also to the hexatic phase outside the critical region. In this region one has to take into account fluctuations of both \( \Psi \) and \( \delta \rho \). These fluctuations in the hexatic phase are different from those in the critical region due to nonzero mean value of the order parameter \( \Psi \). A description of the region is a subject for future investigations.

One should keep in mind that our scheme implies the weakness of the interaction between the orientational and the positional degrees of freedom. That is why we restrict ourselves to the first corrections over this interaction. The consideration of the behavior in the case when the coupling is not small is beyond the scope of our consideration.

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