

Non-traditional phase transition in liquid crystals.

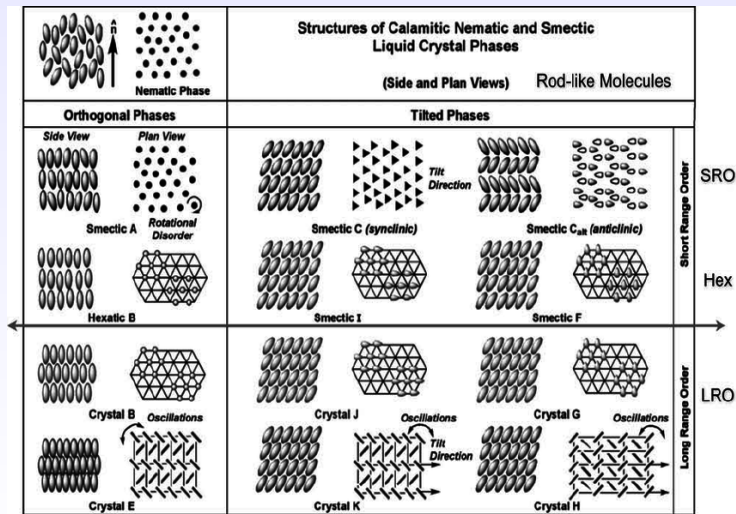
E.I. Kats, V.V. Lebedev, A.R. Muratov

L.D. Landau Institute for Theoretical Physics RAS, Moscow, Russia

Acknowledgments

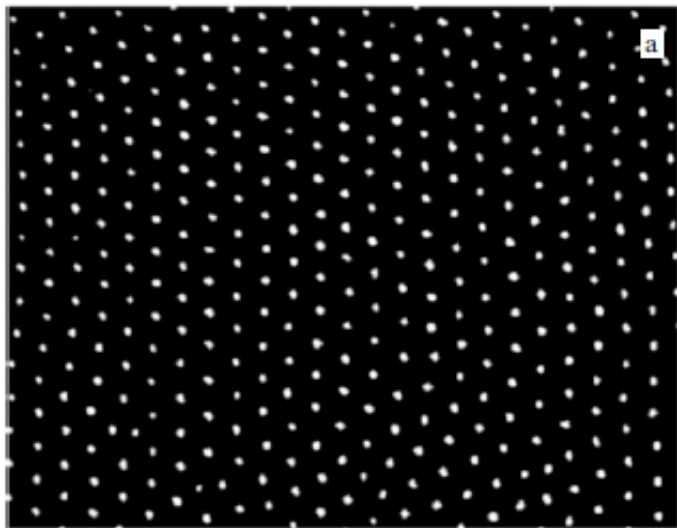
- **Work was funded by the Russian Science Foundation via grant 14-12-00475.**
- **Stimulating discussions with B.I.Ostrovskii, I.A.Vartanyants, and I.A.Zaluzhnyy, inspired this work.**

Topic of this talk : Smectic A - hexatic smectic B phase transition.



Soft-crystals with 3D Lattices

Not only liquid crystals : From Dust plasma to lipid membranes



Background

- All experimental observations suggest a “large” specific heat critical exponent $\alpha = 0.5 \div 0.7$ inconsistent with the universality class for this phase transition predicting the exponent $\alpha \approx -0.01$ (like for the superfluid phase transition).
- Two different suggestions can be found in literature : 1. Since α is near 0.5, it is tempting to assume that the phase transition occurs in a vicinity of a tricritical point. However, it is hard to believe that all known hexatic materials, irrespective to the width of the stability region for the hexatic phase are always near the tricritical point ; 2. Measured experimentally critical exponents are close to those predicted by the 3-state Potts model. However it is not clear how (and why) the Potts model can be mapped to the physics of the hexatics.
- Our approach is based on experimental observations that the crystallization (translational) correlation length ξ_{tr} is larger than the hexatic correlation length ξ_h . It allows us to explain the calorimetric data and is consistent with X-ray scattering measurements.

Experimental data on ξ_{tr} . I

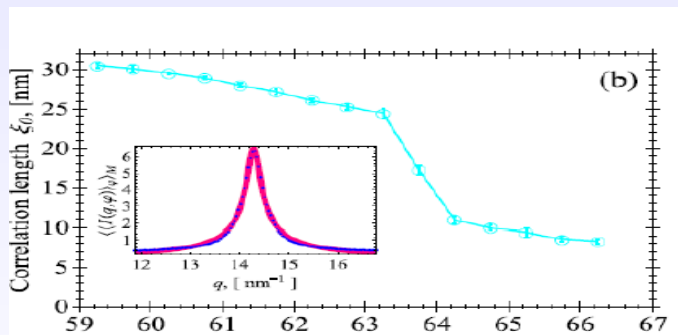


FIGURE : 65OBC sample

Experimental data on ξ_{tr} . II

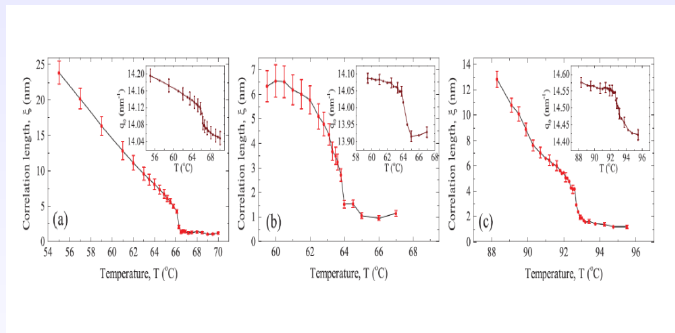


FIGURE : a - 3(10)OBC sample, b - 75OBC sample, c - POL sample ; the insets show the temperature dependence of the diffraction peak maximum.

Hexatic order parameter

- Smectic A – hexatic phase transition means reduction of the rotational symmetry of the smectic layers, from $D_{\infty h}$ in the smectic A state to D_{6h} in hexatics (instead of D_{2h} in smectics C). Hexatic layers are invariant under rotation around the axis of the sixth order. The corresponding order parameter is a six order symmetric irreducible tensor Q_{ijnklm} . Its irreducibility means $Q_{ijklm} = 0$. In the smectic A phase the average value of the tensor is zero (the layers are isotropic) whereas in the hexatic smectic phase the average value of Q_{ijnklm} is non-zero (the smectic layers possess an orientation order). Since the tensor describes the orientation order in the smectic layers, it should be perpendicular to the normal \mathbf{l} to the smectic layers, $l_i Q_{ijnklm} = 0$. Therefore the tensor has only two independent components.

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

where Ψ is equivalent to the traditional hexatic order parameter introduced in the textbooks in terms of the molecular bond orientations.

- At rotation by an angle χ around the Z-axis the order parameter is transformed as

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

Hexatic free energy

- Due to the rotational invariance the Landau functional \mathcal{F}_{La} (determining an energy excess associated with the order parameter Ψ) contains only even in Ψ terms in its expansion. Indeed, just the combinations $\Psi\Psi^*$, $(\Psi\Psi^*)^2$ etc are invariant under the rotation.
- Therefore the smectic A – hexatic phase transition should be of the second order. Since we deal with the two-component order parameter, the phase transition belongs to the same universality class as the superfluid phase transition. Particularly, the heat capacity exponent α for the smectic A – hexatic phase transition should be small and negative $\alpha \approx -0.01$.
- In a dramatic contradiction to this theoretical expectation, all known calorimetric data for the smectic A – hexatic phase transition show large and positive exponent $\alpha = 0.5 \div 0.7$. Thus one encounters an obvious problem, and the main motivation of this work is to find where is a catch.

Positional order fluctuations

The positional order can be described in terms of the short-range density modulation $\delta\rho$ that plays a role of the order parameter for the crystallization phase transition. The short-range density modulation determines X -ray scattering. The pair correlation function of $\delta\rho$ is known as the structure function

$$S(\mathbf{q}) = \int d^3r \exp(-i\mathbf{q}\mathbf{r}) \langle \delta\rho(\mathbf{r}_1) \delta\rho(\mathbf{r}_1 + \mathbf{r}) \rangle.$$

In smectics the structure function has quasi-Bragg peaks in Z -direction at $q_x, q_y = 0$, and maxima at $q_{\perp} = q_0$ where $q_{\perp}^2 = q_x^2 + q_y^2$.

Landau expansion I.



$$\mathcal{F}_{(2)} = \int \frac{d^3 \mathbf{q}}{(2\pi)^3} \left[\frac{a}{2} |\delta\rho(\mathbf{q})|^2 + \frac{b}{2} (q_{\perp} - q_0)^2 |\delta\rho(\mathbf{q})|^2 \right],$$
$$\mathcal{F}_{(4)} = \int dx dy dz \frac{\lambda l}{24} (\delta\rho)^4$$
$$= \int \frac{d^3 q_1 d^3 q_2 d^3 q_3 d^3 q_4}{(2\pi)^9} \delta(\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3 + \mathbf{q}_4)$$
$$\frac{\lambda l}{24} \delta\rho(\mathbf{q}_1) \delta\rho(\mathbf{q}_2) \delta\rho(\mathbf{q}_3) \delta\rho(\mathbf{q}_4),$$

where as usual $a \propto (T - T_*)$

- It is not a traditional Landau expansion (!) :

$$(q_{\perp} - q_0)^2 \delta\rho^2 \rightarrow (q_{\perp}^2 - q_0^2) \delta\rho^2 \rightarrow (\nabla^2 + q_0^2)^2 \delta\rho^2$$

Landau expansion II.

Self-interaction of the translational order parameter $\delta\rho$ renormalizes the bare value of the parameter a . The main fluctuation contribution is determined by the so-called one-loop term



FIGURE : solid line represents the pair correlation function and the bullet represents λ .

Landau expansion III.

- $$S(\mathbf{q}) = \frac{T}{\Delta + b(q_{\perp} - q_0)^2}.$$

- where

$$\Delta = a + \frac{Tq_0\lambda}{4\sqrt{b\Delta}},$$

and

- $$\langle(\delta\rho)^2\rangle = \frac{Tq_0}{2l\sqrt{b\Delta}},$$

where the thickness l of the smectic layer appears due to integration over q_z .

Landau expansion IV.

The crossed over the translational and orientational fluctuations coupling term

$$\mathcal{F}_{\text{int}} = -\frac{1}{2q_0^6} \int dV Q_{ijklmn} \partial_i \partial_j \partial_k \delta \rho \partial_l \partial_m \partial_n \delta \rho.$$

or equivalently

$$\mathcal{F}_{\text{int}} = -\frac{1}{2q_0^6} \text{Re} \int dV \Psi [(\partial_x - i\partial_y)^3 \delta \rho]^2,$$

The cornerstone assumptions

- $$\xi_{tr} \equiv \sqrt{b/\Delta} \gg \xi_h \gg q_0^{-1},$$

- When $\xi_h \gg \xi_{tr}$ one has to recover the standard universal behavior. However, to achieve such large value of ξ_h one has to probe a narrow vicinity of the phase transition point.
- $\xi_h \simeq \xi_0 |(T - T_h)/T_h|^{-\nu}$ where ξ_0 is the bare (microscopic) correlation length, T_h is the second order smectic A – hexatic transition temperature, and $\nu = 0.76$ is the critical exponent of the correlation length.
- Assuming that $\xi_0 \simeq 0.1 \text{ nm}$ we find that ξ_h achieves the value larger than $\xi_{tr} \simeq 3 \text{ nm}$ in the vicinity of the transition point $\Delta T/T_h \lesssim 10^{-3}$. Beyond this region, one has to deal with an interaction of the hexatic order parameter Ψ with the long-correlated translational order parameter $\delta\rho$.
- Analyzing experimental data we conclude that for the standard universal behavior takes place in the vicinity of about 0.1 K around the transition point. Non-standard intermediate critical behavior with strong fluctuations and strong coupling of the orientational and positional order parameters, holds in the region on the order of 1 K around the critical point.

Fluctuation effects I.

- $$F(\mathbf{r}_1, \mathbf{r}_2) = \langle \Psi(\mathbf{r}_1) \Psi^*(\mathbf{r}_2) \rangle,$$

that is invariant under rotations

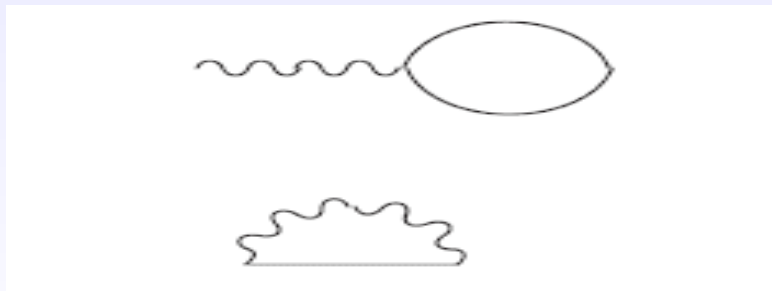


FIGURE : wavy lines correspond to the pair correlation function of the hexatic order parameter.

Fluctuation effects II.

- Fourier transform of the correlation function has the following self-similar form

$$F(\mathbf{q}) = \frac{1}{|(T - T_h)/T_h|^{2-\eta}} f(q\xi_h),$$

where for the superfluid universality class, $\eta \approx 0.02$. F depends solely on $|T - T_h|$ for $q\xi_h \ll 1$ and only on q in the opposite limit.

- In the smectic-A phase the single point average contribution $\langle [(\partial_x - i\partial_y)^3 \delta\rho]^2 \rangle$ is zero (isotropy of the smectic layers). In the vicinity of the phase transition, we are considering, the contribution is also negligible in the hexatic phase. Thus, we have only the term

$$-\frac{1}{2T} \int \frac{d^3q}{(2\pi)^3} F(\mathbf{q}) S(\mathbf{k} + \mathbf{q}),$$

\mathbf{k} is the wave vector of the density fluctuation ($k \gg q$), then

$$\Delta = a + \frac{Tq_0\lambda}{4\sqrt{b\Delta}}$$
$$-\frac{1}{8\pi^2\sqrt{b\Delta}} \int dq_z dq_\perp F(\mathbf{q}) [1 + \Delta/(bq_\perp^2)]^{-1},$$

Fluctuation effects III.

$$\Delta = a + \frac{Tq_0\lambda}{4\sqrt{b\Delta}} + \delta\Delta,$$

where

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

- If $q\xi_h \gg 1$ the pair correlation function $F(\mathbf{q}) \propto q^{\eta-2}$. Therefore there is ultraviolet contribution to the integral $\int dq_z dq_\perp F$ to be included into redefinition of the factor λ , and besides, there is negative critical contribution to the integral $\int dq_z dq_\perp F$ that behaves $\propto |T - T_h|^{\nu\eta}$. Keeping in mind that Δ remains finite at the transition point, we find

$$\frac{\partial}{\partial T} \Delta \propto |T - T_h|^{\nu\eta-1}.$$

The singularity is integrable due to $\eta, \nu > 0$, the gap Δ remains finite at the transition point.

Heat capacity I.

- Additional contributions to the heat capacity related to the positional degree of freedom $\delta\rho$, are associated with the T -dependence of the coefficient a :

$$\frac{\partial F_a}{\partial T} = \frac{V}{2} \frac{\partial a}{\partial T} \langle (\delta\rho)^2 \rangle = \frac{\partial a}{\partial T} \frac{TVq_0}{4l\sqrt{b\Delta}},$$

- Then we find the following critical contribution to the heat capacity

$$-T \frac{\partial^2 F_a}{\partial T^2} = \frac{V}{8} \frac{\partial a}{\partial T} \frac{T^2 q_0}{lb^{1/2} \Delta^{3/2}} \frac{\partial \Delta}{\partial T}.$$

The contribution diverges near the phase transition with the exponent $1 - \nu\eta$, close to unity.

- Our main finding is that a sum of two critical contributions to the heat capacity, with the “small” exponent α and with the “large” exponent $1 - \nu\eta$, enables one to describe quantitatively the experimental data.

Heat capacity II.

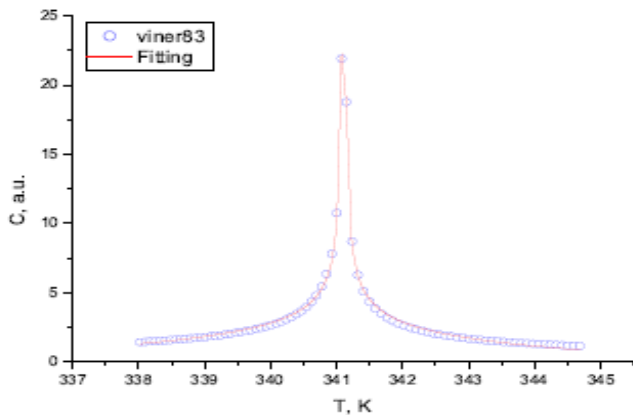
- Namely :

$$C = \frac{p_1}{|x|^{-0.013}} + \frac{p_3}{|x|} + p_5, \quad \text{if } x < 0,$$

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

where $x = (T - T_h)/T_h$ is the reduced temperature, and we borrowed the value of the exponent $\alpha = -0.013$ from the standard data for the two-component order parameter in three dimensions. The obtained values giving the best fitting are $T_h = 341.11K$, $p_1 = -48.09599$, $p_2 = -48.19495$, $p_3 = 0.0008$, $p_4 = 0.00064$ and $p_5 = 91.60242$.

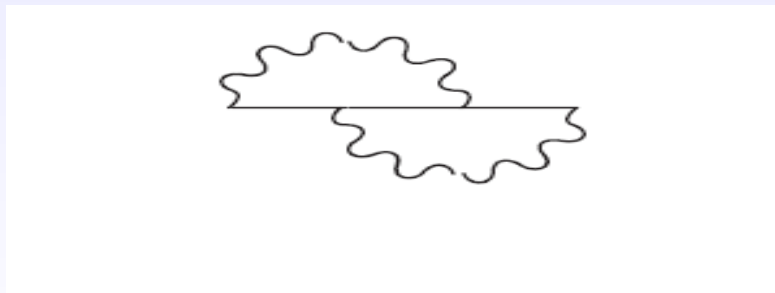
Confronting our theory with calorimetric data for 65OBC



OPTIONAL SLIDES.

Applicability conditions

- First, to get weak first order crystallization transition $\xi_{tr} q_0 \gg 1$ has to be satisfied.
- Second. we should compare the contribution of the one-loop diagram with contributions of higher order, e.g.,



- Straightforward estimation shows that one can neglect the higher loop diagrams if $\delta\Delta \ll \Delta$.