

Landau weak crystallization theory and its application to phase transitions in membranes.

E.I. Kats¹

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

1. Collaboration with V.Lebedev.

INTRODUCTION on WEAK CRYSTALLIZATION.

Prehistory of Weak Crystallization.

Situation when 3D crystallization is close to 2-d order phase transition is not impossible. However because it requires to satisfy certain conditions it is very rare in nature.

- Soon after Van der Waals presented his thesis (1873), he suggested that solid-liquid transitions might behave in a similar manner ;
- in 1882 (Wied. Ann., **15**, 446) M.Planck tried to predict a critical point of water-ice transition (later on it was one of the motivation for high-pressure researches which lead to the discovery of many new solid phases, but no solid-liquid end points were found) ;
- F.Lindemann (1910) introduced crystallization criterion which works also for 2-d order transition (it was the 1-st citation of famous Einstein paper (1907) on crystal vibrations)
- Landau (1937) has applied his theory of continuous phase transitions to crystallization.
- BKT (1970/1971 B, 1972/1973 KT) melting in 2d (similar theory was proposed by R.Feynman in 1972 but never published).

Weak Crystallization.

- The order parameter

$$\Psi = \frac{\rho_{short}}{\rho}$$

where ρ is long-wavelength component of density, and Ψ contains only components of the order of inverse molecular scale.

- In liquid phase $\langle \Psi \rangle = 0$, and in a crystal $\langle \Psi \rangle \neq 0$. In conventional ("strong") crystallization $\langle \Psi \rangle \simeq 1$, whereas for a weak crystallization $\langle \Psi \rangle \ll 1$.

$$\begin{aligned} \frac{F}{V} = & \sum_q \frac{\omega(q)}{2} \Psi(q) \Psi(-q) - \sum_q \frac{\mu(q_1, q_2, q_3)}{6} \Psi(q_1) \Psi(q_2) \Psi(q_3) \\ & + \sum_q \frac{\lambda(q_1, q_2, q_3, q_4)}{24} \Psi(q_1) \Psi(q_2) \Psi(q_3) \Psi(q_4) \end{aligned}$$

where V is system volume ; $q_1 + q_2 + q_3 = 0$ and $q_1 + q_2 + q_3 + q_4 = 0$ since F is real. Linear over Ψ term is absent because Ψ by its definition (short-wavelength field) does not include zero harmonic.

- Because Ψ is a short-wavelength field, q -dependence of the coefficients is essential issue.

Landau weak crystallization free energy.

- $$\omega(q) = \tau + b(q - q_0)^2$$

if $|q - q_0| \ll q_0$, then

$$(q - q_0)^2 \simeq \frac{(q^2 - q_0^2)^2}{4q_0^2}$$

- $$F_{har} = \int d^3r \left[\frac{\tau}{2} \psi^2 + \frac{b}{8q_0^2} ((\nabla^2 + q_0^2)\psi)^2 \right]$$

- Then μ can be considered as a constant, since the only possibility to have $q_1 + q_2 + q_3 = 0$ and $|q_i| = q_0$ is a perfect triangle, for which no any degree of freedom. If $\lambda = const$ (this is not granted by a symmetry), then

$$F_{int} = \int d^3r \left[-\frac{\mu}{6} \psi^3 + \frac{\lambda}{24} \psi^4 \right]$$

- Weak crystallization holds in the vicinity of an isolated point in the $P - T$ plane : $\tau = 0$ and $\mu = 0$ (in this sense similar to a critical point with its position also defined by two conditions).

Mean field theory I

- τ changes its sign in the vicinity of transition point, i.e., $\tau = \alpha(T - T_*)$.
- Generally speaking $\langle \Psi \rangle$ contains infinite number of Fourier harmonics. However if $\Psi \ll 1$ is granted, only a finite set of main harmonics (with amplitudes $|c_j^{main}| \gg |c_j^{other}|$) can be selected

$$\langle \Psi \rangle = 2\text{Re} \sum_j c_j \exp(iq_j r)$$

- $|q_j| = q_0$ (can not strongly deviate for $\Psi \ll 1$). If the low-temperature phase has a certain symmetry $\langle \Psi \rangle$ must be invariant under this symmetry operations, i.e., the set of q_j does not change and c_j are transformed into each other, and $|c_j| = \text{const}$.
- If there is only a single vector : smectic A (SA)

$$\langle \Psi \rangle = 2\sqrt{A} \cos(\phi + q_0 z)$$

where A and ϕ are amplitude and phase of density modulation Ψ , and z axis is along density modulation direction.

- 3 vectors : 2D hexagonal crystal of liquid columns (discotic, D_h).
- 6 vectors (diagonals of a cube) - BCC crystal.

Mean field theory II.

- To analyze all (infinite) sets of possible crystalline and quasi-crystalline structures is not feasible even with modern computers. Thus one has to rely on semi-quantitative heuristic arguments.
- Let us consider only 2-d and 4-th order terms in the Landau free energy, and assume $\lambda = \text{const}$.

$$\frac{F}{V} = \tau NA + \frac{\lambda}{2}(N^2 - (N/2))A^2$$

where N is a number of main harmonics.

- Minimization over A at $\tau < 0$ gives

$$\frac{F}{V} = -\frac{\tau^2 N}{\lambda(2N - 1)}$$

thus $N = 1$, i.e. at large enough (negative) τ , only SA phase is realized.

- At "intermediate" value of τ , cubic vertex μ favoring to triangles of q_j has to be taken into account, and competition of both tendencies yields to the following cascade of phase transitions :

$$SA - D_h - BCC - I$$

Phase diagram at $\lambda = \text{const}$ and $\mu = \text{const}$

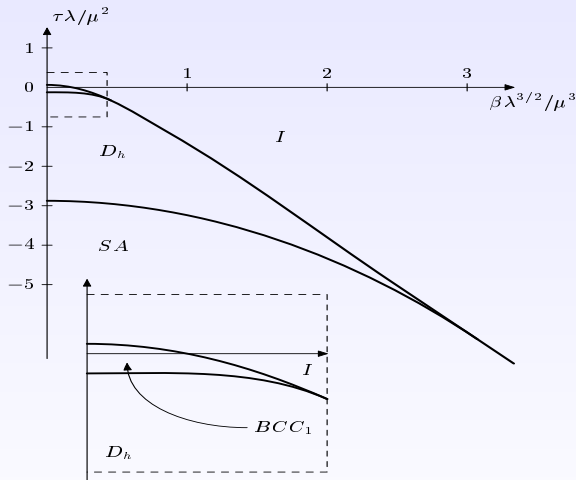


FIGURE: $\beta \equiv \lambda T q_0^2 / (4\pi b^{1/2})$.

Fluctuations I.

- For weak crystallization theory fluctuations are small but their effect is not weak!
- Fluctuations of the order parameter can be characterized by their correlation functions. In the weak crystallization theory, the pair correlation function of Ψ is characterized by the “gap” Δ entering the expression for the Fourier transform (having in mind a single membrane, in what follows only 2D)

$$\langle \Psi(\mathbf{r})\Psi(0) \rangle = \int \frac{d^2q}{(2\pi)^2} \exp(i\mathbf{q}\mathbf{r}) F(\mathbf{q})$$

$$F(\mathbf{q}) = \frac{T}{\Delta + b(q - q_0)^2},$$

The expression is correct in a narrow vicinity of the circle $q = q_0$ in the reciprocal space.

Fluctuations II.

- The one-loop equation for the gap Δ

$$\Delta = \tau + \frac{\lambda}{2} \langle \Psi^2 \rangle = \tau + \frac{T\lambda q_0}{4\sqrt{\Delta b}}$$

- Where we substituted

$$\langle \Psi^2 \rangle = \int \frac{d^2 q}{(2\pi)^2} \frac{T}{\Delta + b(q - q_0)^2} = \frac{Tq_0}{2\sqrt{\Delta b}}.$$

This is dominant contribution to the average $\langle \Psi^2 \rangle$ provided the applicability condition of the weak crystallization theory $\Delta \ll bq_0^2$ is satisfied.

MAIN PHASE TRANSITION in MEMBRANES.

One of the most disputed but still not completely understood fundamental issue.

Biological membranes.

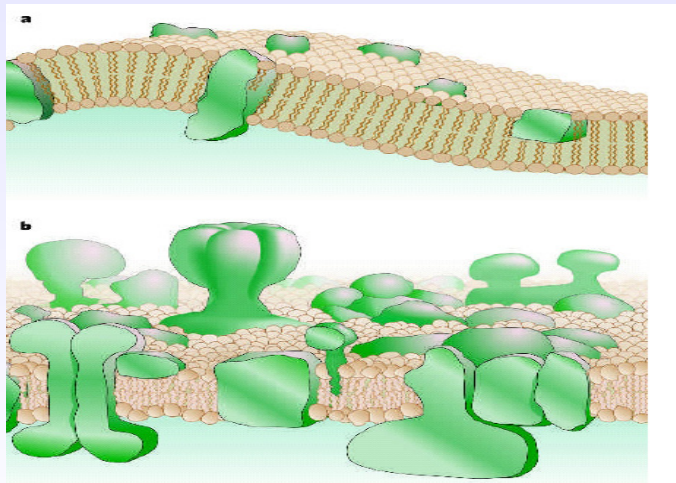
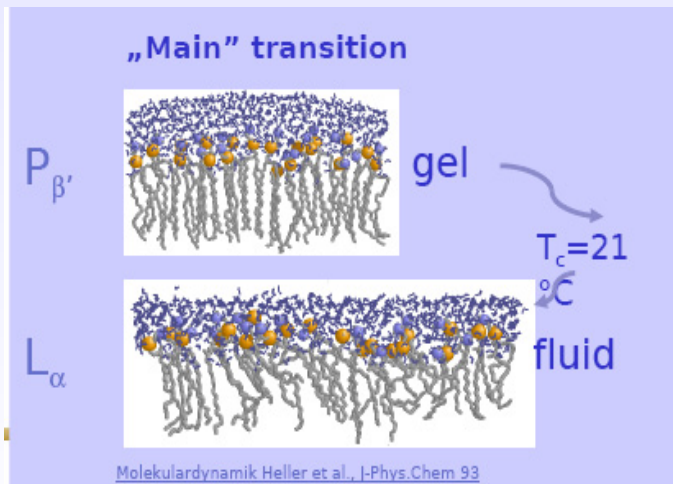


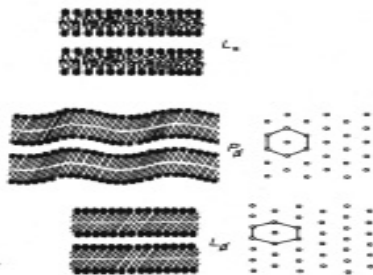
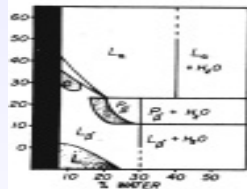
FIGURE: Total membrane area in a human body is about 200 km^2 .

Main phase transition in membranes.



Membrane phase diagram.

Lipid/Water Phase Diagram

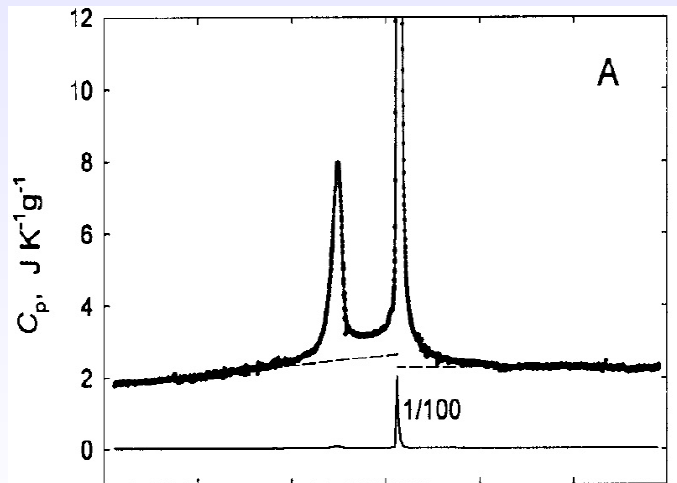


Parameters: temperature + hydration

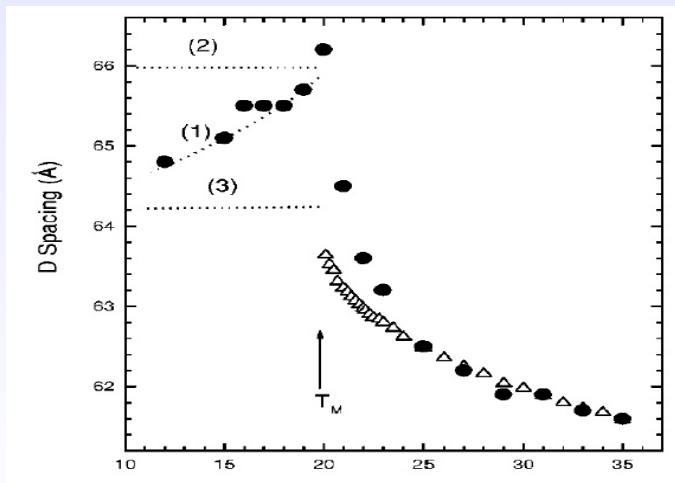
Our aim and hope.

- Experimental data indicate that the first order nature of the phase transition is accompanied by critical behaviors (with unusually large exponents) of various quantities in the high-temperature (liquid) phase, which are seemingly contradictory features.
- We propose a theoretical scheme enabling to explain such unusual behavior.

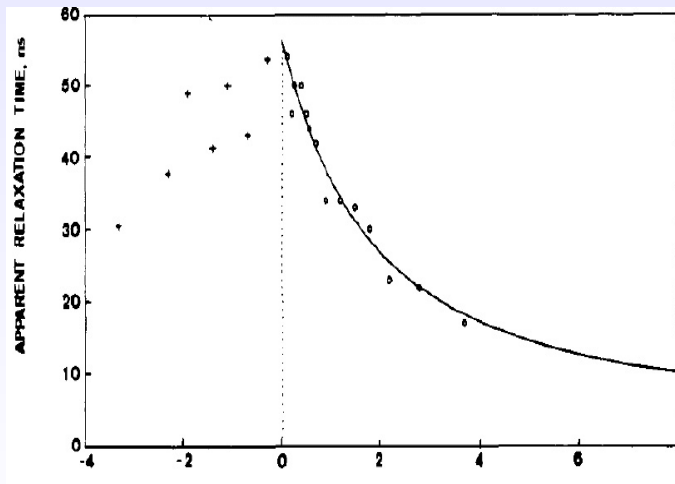
Specific heat.



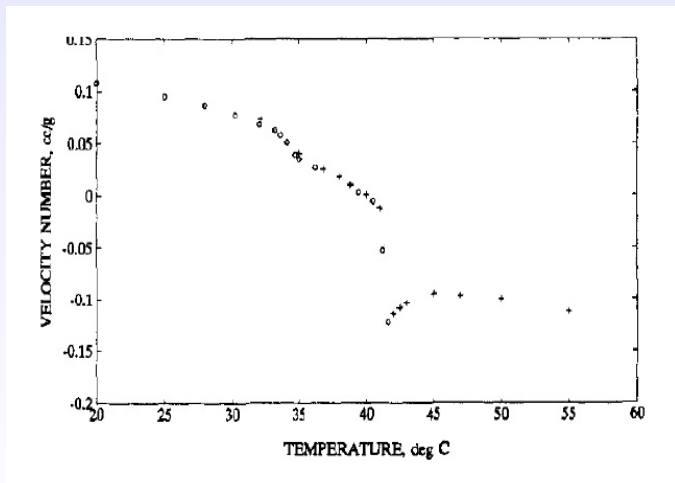
Repeat distance.



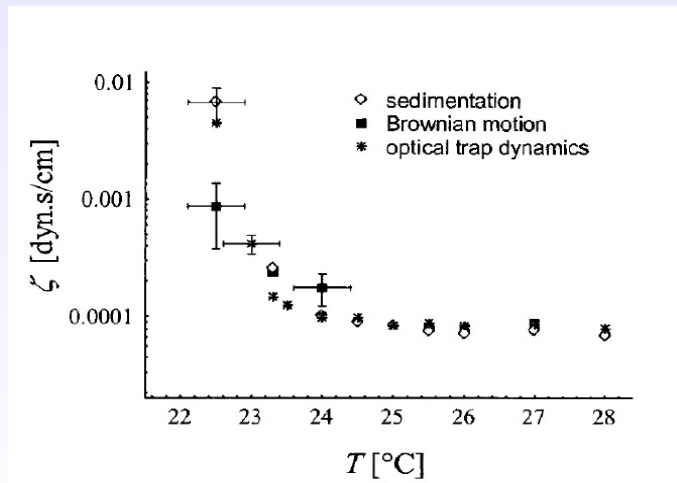
Relaxation time



Sound velocity.



Membrane viscosity.



A sort of summary :

- the lamellar repeat distance d exhibits at $T \rightarrow T_m$ a scaling behavior, which can be fitted by an exponent $\simeq 1$;
- an anomalous part of the specific heat follows at $T \rightarrow T_m$ a scaling behavior with an unusually large exponent ;
- the membrane internal viscosity (friction) scales with an exponent $\simeq 3/2$;
- the membrane bending modulus κ decreases essentially in the same temperature range.

Our model and theory I

- In the ripple phase, the membrane is deformed and the order parameter Ψ , describes fluctuations of the membrane curvature and then the average $\langle \Psi \rangle$ is the membrane spontaneous curvature.
- In the ripple phase the average $\langle \Psi \rangle$ is a periodic function of coordinates. Such periodic averages are examined in the framework of the weak crystallization theory. For a single membrane stretched along the $X - Y$ plane

$$F = \int dx dy \left\{ \frac{1}{2} \tau \Psi^2 + \frac{b}{8q_0^2} [(\nabla^2 + q_0^2)\Psi]^2 + \frac{\lambda}{24} \Psi^4 \right\}$$

Since the fluctuations are deviations from the symmetric membrane, there are only even in Ψ terms. As usual $\tau \propto T - T_*$, where T_* is close to the transition temperature T_m .

- However, the functional does not describe the liquid-gel phase transition. To obtain the transition, one should take into consideration coupling between the order parameter Ψ and other membrane degrees of freedom, e.g., membrane density or, bilayer thickness, φ .
- Because of the symmetry $\Psi \rightarrow -\Psi$ the order parameter is coupled quadratically to the scalar quantity φ .

Our model and theory II

$$F = \int dx dy \left\{ \frac{1}{2}(\tau + \varphi)\Psi^2 + \frac{b}{8q_0^2} [(\nabla^2 + q_0^2)\Psi]^2 + \frac{\lambda}{24}\Psi^4 + f(\varphi) \right\} .$$

One could arbitrary normalize φ , thus to choose the coefficient in front of φ . Since the parameter φ characterizes a deviation of the membrane thickness from its high-temperature value, the function f has to have a minimum at $\varphi = 0$.

- One may get a first order phase transition related to a jump in φ , note, however, that the average value $\langle \Psi \rangle$ is equal to zero in the both phases (high-temperature (liquid) phase and in the the low-temperature (gel) phase).
- Even though fluctuations of Ψ are weak in the high-temperature (liquid) phase they are of crucial importance for stabilization of the low-temperature (gel) phase. Another important feature of the low-temperature phase is its slow relaxation !

Our model and theory III

- Additional effects due to the coupling of the order parameter Ψ to the membrane thickness φ should be taken into account.
- The one-loop equation for the gap Δ

$$\Delta = \tau + \varphi + \frac{\lambda}{2} \langle \psi^2 \rangle = \tau + \varphi + \frac{T\lambda q_0}{4\sqrt{\Delta b}}$$

- The expression is correct both for the high-temperature (liquid) and low-temperature (gel) phase which are distinguished by the φ values. To establish a temperature dependence of φ and to calculate the transition temperature one should examine the free energy F of the membrane considered as a function of φ .
-

$$\exp(-F(\varphi)/T) = \int \mathcal{D}\Psi \exp(-F(\Psi, \varphi)/T)$$

- Then one finds

$$\frac{1}{A} \frac{\partial F}{\partial \varphi} = \frac{1}{2} \langle \psi^2 \rangle + \frac{\partial f}{\partial \varphi} = \frac{Tq_0}{4\sqrt{\Delta b}} + \frac{\partial f}{\partial \varphi}$$

$\varphi(T)$ is determined by $\partial F / \partial \varphi = 0$.

Our model and theory IV

- In a vicinity of the transition temperature T_m the equation has two different solutions, corresponding to the liquid and to the gel phases. The transition point is determined by the relation $F_1 - F_2 = 0$.
- To find the energy difference, one can consider formally the free energy F , as a function of arbitrary φ . Then one can calculate the free energy difference between the liquid and the gel phase

$$\frac{F_2 - F_1}{A} = \frac{Tq_0}{2b^{1/2}} \left(\Delta_2^{1/2} - \Delta_1^{1/2} \right) - \frac{T^2 q_0^2 \lambda}{32b} \left(\frac{1}{\Delta_2} - \frac{1}{\Delta_1} \right) + f(\varphi_2) - f(\varphi_1)$$

The expression implies that the liquid and gel phases are isotropic, that is $\langle \psi \rangle$ is zero in the both phases.

Results of the weak crystallization theory applied to phase transitions between two isotropic phases not exhibiting any kind of crystalline order.

- In the limit of weak fluctuations (small q_0) $|\varphi_2| \gg |\varphi_1|$ and $\Delta_1 \gg \Delta_2$ in the vicinity of the liquid-gel transition $\Delta \approx \tau$, and φ_1 is determined

$$\frac{Tq_0}{4\sqrt{\tau b}} + \Lambda\varphi_1 = 0, \quad \Lambda = \frac{\partial^2 f}{\partial \varphi^2}(0)$$

- For the gel phase

$$\tau + \varphi_2 + \frac{T\lambda q_0}{4\sqrt{\Delta_2 b}} = 0.$$

- The condition $\partial F / \partial \varphi_2 = 0$ is

$$\frac{Tq_0}{4\sqrt{\Delta_2 b}} + \frac{\partial f}{\partial \varphi_2} = 0$$

- Combining everything we find τ -dependence of φ_2 :

$$\tau + \varphi_2 = \lambda \frac{\partial f}{\partial \varphi_2}$$

Results II.

- T_m is determined by the relation $F_1 = F_2$:

$$\frac{T^2 q_0^2 \lambda}{32b\Delta_2} = f(\varphi_2) \quad \rightarrow \quad \lambda(\partial f / \partial \varphi_2)^2 = 2f(\varphi_2)$$

- Determining φ_2 from the equation we find the transition point τ_0 . If $\tau_0 > 0$ that is if $T_m > T_*$. Otherwise before the liquid-gel transition the liquid-ripple transition happens.

Results III.

- If λ is small then $f(\varphi_2) = 0$ and $\tau_0 = -\varphi_2$. Therefore the sign of τ_0 depends on the sign of the solution to the equation $f(\varphi_2) = 0$. In this case both, the liquid-gel and the liquid-ripple transitions, are possible.
- If λ is large then $\partial f / \partial \varphi_2 = 0$, (more precisely, $\partial f / \partial \varphi_2 \propto \lambda^{-1/2}$). Then $\tau_0 = \lambda \partial f / \partial \varphi_2 \propto \lambda^{1/2}$. Then since $\partial f / \partial \varphi_2 < 0$, we conclude $\tau_0 < 0$. Therefore at large λ the transition to the ripple phase always occurs.

New/old physical effects I.

- Applying weak crystallization theory we calculate the heat capacity C

$$C \propto \int d^2r_1 d^2r_2 \langle \psi^2(\mathbf{r}_1) \psi^2(\mathbf{r}_2) \rangle \propto \Delta^{-3/2}$$

In the liquid (high-temperature) phase $\Delta \approx \tau \propto T - T_*$ and we obtain the exponent 3/2 for the heat capacity.

- The same correlation function determines a singular contribution $\langle \phi(\mathbf{r}_1) \phi(\mathbf{r}_2) \rangle \propto \langle \psi^2(\mathbf{r}_1) \psi^2(\mathbf{r}_2) \rangle$. Then for $q \ll q_0$, $\int d^2r \exp(iqr) \langle \phi(r) \phi(0) \rangle_{\text{sing}} \propto \Delta^{-3/2}$.
- Theory predicts also singular behavior of the Helfrich (bending) module of the membrane. The symmetry admits a correction to κ , proportional to Ψ^2 :

$$\kappa_{\text{sing}} \propto \langle \Psi^2 \rangle \propto \Delta^{-1/2}$$

- Singular behavior of the shear viscosity μ of the membrane $\mu_{\text{sing}} \propto \Delta^{-3/2}$ ($\mu_{\text{gel}} \gg \mu_{\text{liq}}$, therefore the gel relaxation time can be very large).

New/old physical effects II.

- Structure factor

$$S(\mathbf{q}) \propto \int dx dy \exp(-i\mathbf{q}\mathbf{r})\varphi(\mathbf{r})\varphi(0)\rangle.$$

Theory predicts following (negative !) singular contribution to the structure factor

$$S_{\text{sing}}(\mathbf{q}) \propto \int dk_x dk_y F(\mathbf{k})F(\mathbf{q} + \mathbf{k}).$$

The quantity $|S_{\text{sing}}|$ has maxima at $q = 0$ and $q = 2q_0$.

- A q -dependence of $|S_{\text{sing}}|$ near the maxima reads as

$$S_{\text{sing}}(q) \propto \frac{1}{\Delta\sqrt{4\Delta + bq^2}} \quad q \ll q_0$$

$$S_{\text{sing}}(q) \propto \frac{1}{\Delta} \text{Im} \left(q - 2q_0 - 2i\sqrt{\Delta/b} \right)^{-1/2} \quad 0 < q - 2q_0 \ll q_0,$$

$$S_{\text{sing}}(q) \propto \frac{1}{\Delta} \text{Re} \left(q - 2q_0 - 2i\sqrt{\Delta/b} \right)^{-1/2} \quad 0 < 2q_0 - q \ll q_0$$

OPTIONAL SLIDES.

Smectic A - Smectic C transition.

- Why Gi number is small ?

$$F = \int dx dy dz \left[\frac{K_{\perp}}{2} (\nabla_{\perp} c)^2 + \frac{K_{\parallel}}{2} (\nabla_z c)^2 + \frac{1}{2} \alpha (T - T_m) c^2 + \frac{\lambda}{24} c^4 \right]$$

- Natural estimations $K_{\perp} \simeq \kappa/d$, $K_{\parallel} \simeq \kappa \delta^2/d^3$, $\alpha \simeq \kappa/(T \delta^2 d)$, $\lambda \simeq \kappa/(\delta^2 d)$ (δ - membrane thickness, d - intermembrane distance).
- Then

$$Gi \simeq \frac{T \lambda^2}{\alpha K_{\parallel} K_{\perp}^2} \simeq \left(\frac{T}{\kappa} \right)^2 \left(\frac{d}{\delta} \right)^4$$

and $C_{sing} \propto (d/\delta^4) T^{1/2}/(T - T_m)^{1/2}$ (independent of small parameter T/κ).

Smectic A - Smectic C + Weak crystallization transitions.



$$F = \int dx dy \left[\frac{a}{2} c^2 + \frac{b}{2} (\nabla c)^2 + \frac{\lambda}{24} c^4 + \frac{\eta}{720} c^6 + \frac{\tau}{2} \psi^2 + \frac{b'}{8q_0^2} ((\nabla^2 + q_0^2)\psi)^2 + \frac{\lambda'}{24} \psi^4 - \frac{\gamma}{4} \psi^2 c^2 \right]$$

- Then equations to solve

$$a + \frac{\lambda}{6} c^2 - \frac{\gamma}{2} \langle \psi^2 \rangle = 0$$

and

$$\Delta = \tau - \frac{\gamma}{2} c^2 + \frac{\lambda'}{2} \langle \psi^2 \rangle = 0$$

If a gel phase is a crystalline membrane.

- If $\rho(x, y, z)$ - crystalline membrane mass density, periodic in $x - y$ plane, and localized at $z = 0 \pm \delta$. Then

$$\begin{aligned}\rho(k, q) &= \int dx dy dz \exp(-ikr - iqz) \rho(x, y, z - u) \\ &\equiv \int dx dy \exp(-ikr - iku) \rho(x, y, q)\end{aligned}$$

- Then

$$\begin{aligned}\langle |\rho(k, q)|^2 \rangle &= \int dx_1 dy_1 dx_2 dy_2 \\ &\times \exp[-ik(r_1 - r_2)] \rho(x_1, y_1, q) \rho(x_2, y_2, -q) \langle \exp(-iqu_1 + iqu_2) \rangle\end{aligned}$$

Apparently finite correlation length in a crystalline membrane.

- In the Gaussian approximation

$$\langle |\rho(k, q)|^2 \rangle = A \int dx dy \exp(-ikr) \overline{\rho(x_1, y_1, q) \rho(x_1 + x, y_1 + y, -q)} \\ \times \exp[-(q^2/2) \langle (u_1 - u_2)^2 \rangle]$$

- Because up to $r \simeq d\sqrt{\kappa/T}$ (Helfrich membrane collision distance), $\langle (u_1 - u_2)^2 \rangle \simeq (T/\kappa)r^2$, the last exponent factor is $(T/\kappa)q^2r^2$ and for finite q peaks $q \simeq 2\pi n/d$, then there exists an effective correlation length (even for genuine crystalline membranes) $\xi_c \simeq \sqrt{\kappa/T}d$.

Conventional critical point does not help.

- If there is 2-d order phase transition

$$g = \frac{1}{2}ax^2 + \frac{1}{24}\lambda x^4$$

then $x_0 \propto (T_c - T)^{1/2}$.

- If x couples to a non-critical degree of freedom y as

$$g = \frac{\lambda}{24} (x^2 - x_0^2)^2 + \frac{1}{2\chi}y^2 + \gamma_1 x^2 y + \gamma_2 xy^2$$

- Below T_c

$$y_{\pm} = \frac{\gamma_1 x_0}{(1/\chi) \pm 2\gamma_2 x_0}$$

- Then $\Delta y \equiv y_+ - y_- \propto (T_c - T)^{3/2}$.

Special Ising-like critical point scenario ?

- Main transition latent heat decreases from $Q \simeq 22 \text{ kJ/mol}$ for $n = 14$ to $Q \simeq 5.5 \text{ kJ/mol}$ for $n = 12$ (extrapolating, $Q \simeq 0$ for $n_c \simeq 8$ (however such short chains are soluble in water and do not form membranes)).
- Ising model near n_c (spin up - liquid phase ; spin down -gel phase). Then $n - n_c$ plays a role of temperature, and T plays a role of magnetic field.
- Then one has to recalculate the exponents for $n \rightarrow n_c$ region. E.g. specific heat scales as $1 - (1/\delta)$, where $\delta = 15$ for Ising model.