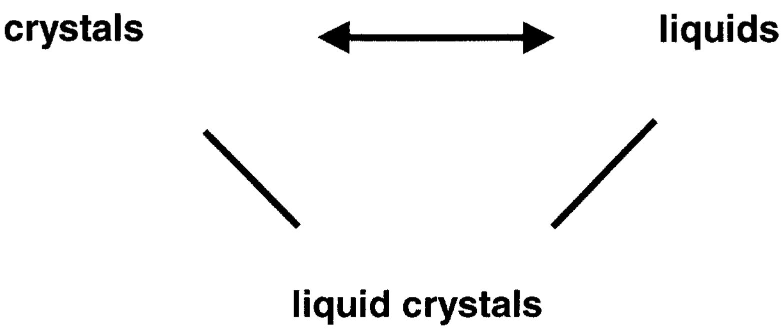
Vorlesung "Flüssigkristalle" (12.04.2006)
Sommersemester 2006
Prof.Dr.F.Kremer

Content

- Liquid crystals: A state of matter between that of crystals and liquids Physical origin and its description.
- Order parameters: How to describe different states of order?
- The Landau-de Gennes approach to describe the nematic/isotropic phase transition.
- Dynamics in Liquid Crystals.
- The principle of LC-displays (with experiments).



Crystals are characterised by a long-range positional and orientational order; **liquids** (and glasses) lack any long-range order, instead they have a short range positional correlation, with a certain decay-length.In an X-ray experiment for instance crystals deliver diffraction patterns while for glasses an "amorphous halo" is obtained.

Liquid crystals form a special state of matter; they do have a long range orientational order in (typically) **one** or **two** dimensions while their positional order is short-ranged. How is this achieved? Liquid crystals are molecules with a strong form-anisotropy; their shape can be rod-like, disc-like or sandinic.

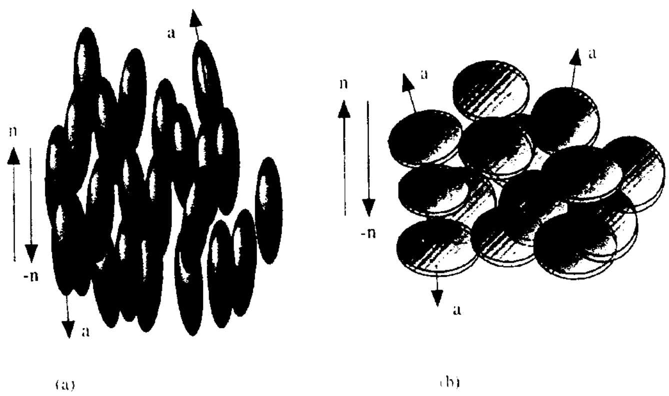


Figure 2.20. Uniaxial (a) calamitic and (b) discotic nematics can be viewed as a system of elongated rods or disks with axes **a** oriented preferentially along a common director **n**. Directions **n** and −**n** are equivalent even if the molecular axis **a** is a true vector. The units in the picture represent either individual molecules in the case of thermotropic nematics or micelles in the case of lyotropic nematics.

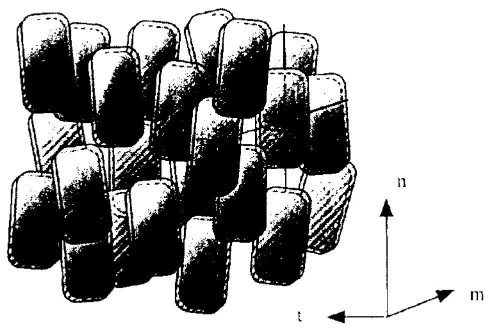
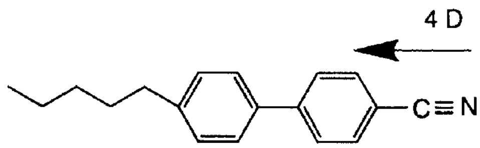
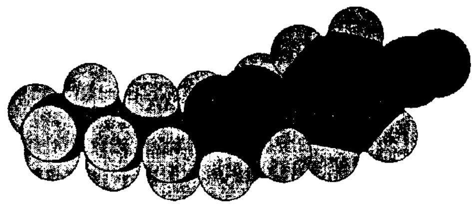


Figure 2.21. Biaxial nematic phase.

Typical molecular structures are for instance p-Pentyl-p'-Cyanobiphenyl (5CB)



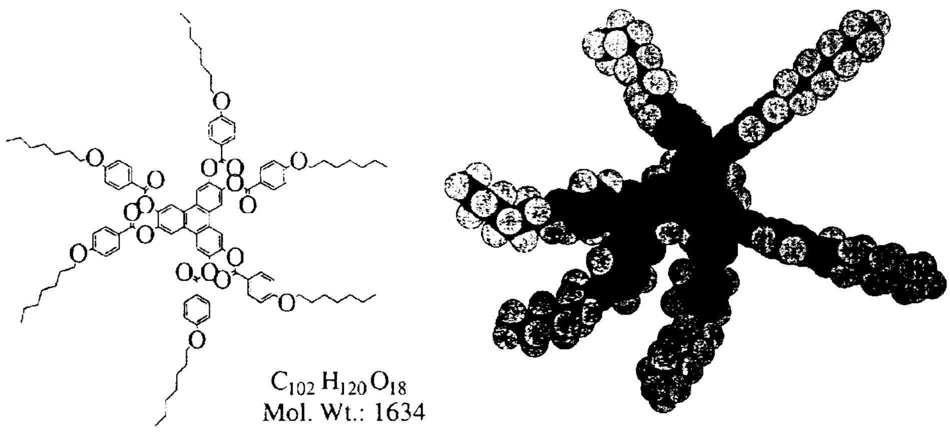
$C_{18}H_{19}N$
Mol. Wt.: 249



solid $\xleftrightarrow{22.5^oC}$ nematic $\xleftrightarrow{35^oC}$ isotropic

Figure 2.12. Chemical formula, molecular structure, and phase diagram of 5CB. Note that the benzene rings are located in different planes.

which has a nematic mesophase, or Hexa-n-hexyloxybenzoate-triphenylene



solid $\xleftrightarrow{168^oC}$ discotic nematic $\xleftrightarrow{253^oC}$ isotropic

Figure 2.16. Hexa-n-hexyloxybenzoate-triphenylene: chemical structure, phase diagram, and one of the possible molecular configurations; note that the chains are not necessarily parallel to the central disk group. See N.H. Tinh, H. Gasparoux, and C. Destrade, Mol. Cryst. Liq. Cryst. **68**, 101 (1981).

which forms a discotic nematic mesophase.

The **physical origin** of the L.C. phase is the chemical and structural combination of stiff, form-anisotropic molecular building blocks with amorphous, highly flexible structure elements (e.g. the aliphatic CH_2-"tails").

Liquid crystalline mesophases can have a manifold of different molecular orders; the lowest symmetry has the nematic phase:

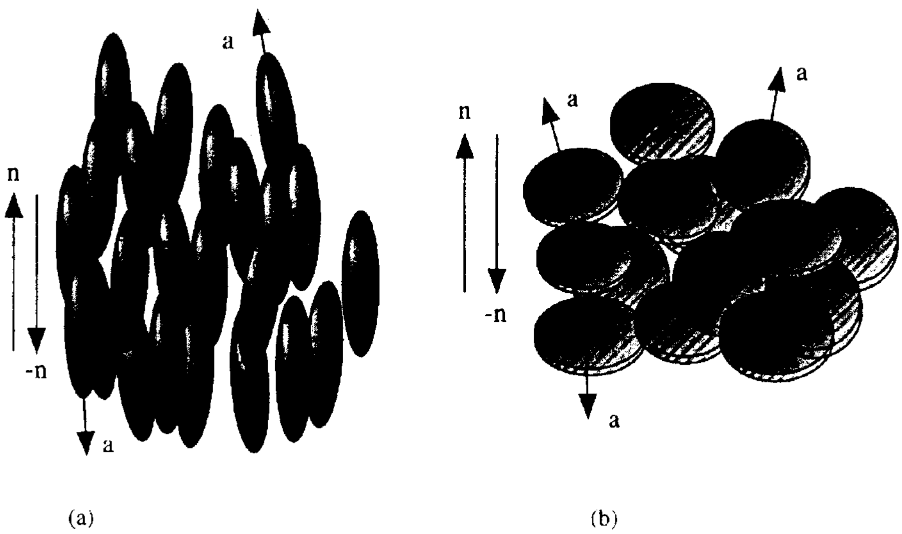


Figure 2.20. Uniaxial (a) calamitic and (b) discotic nematics can be viewed as a system of elongated rods or disks with axes **a** oriented preferentially along a common director **n**. Directions **n** and **−n** are equivalent even if the molecular axis **a** is a true vector. The units in the picture represent either individual molecules in the case of thermotropic nematics or micelles in the case of lyotropic nematics.

It is an uniaxial phase, noted as N; the unit vector **n** along the optical axis is called the **director**. On average a centro-symmetric order is established, thus **n** and – **n** are equivalent notations **n** ≡ **-n**. The director is an axis of continuous rotational symmetry with the point group of a homogeneous circular cylinder $D_\infty h$. The director is experimentally defined by the optical axis, the difficulty remains to describe the *distribution of the orientational order* of the individual molecules. Concerning their positional order the molecules behave like a glass.

As rare example biaxial nematics exist, N_B.

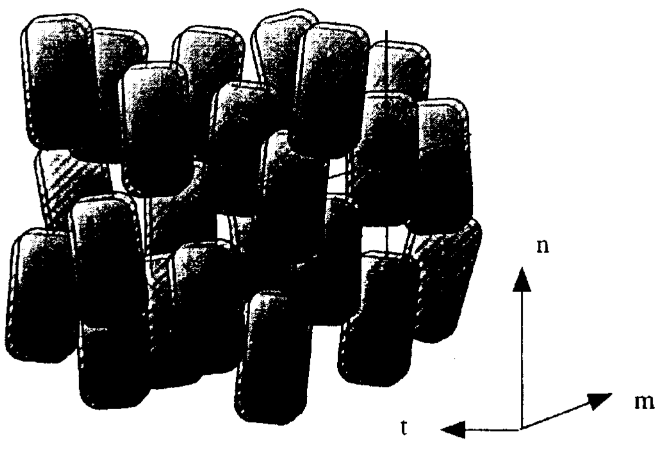


Figure 2.21. Biaxial nematic phase.

A biaxial phase is characterised by three directors **n**, **t** and **m=n** × **t** with **n** ≡ **-n**, **t** ≡ **-t** and **m** ≡ **-m;** when the L.C.-molecule or part of it are chiral, i.e. not equal to its mirror image the nematic phase may show a twist with a helical pitch p; this is called a cholesteric phase N*.

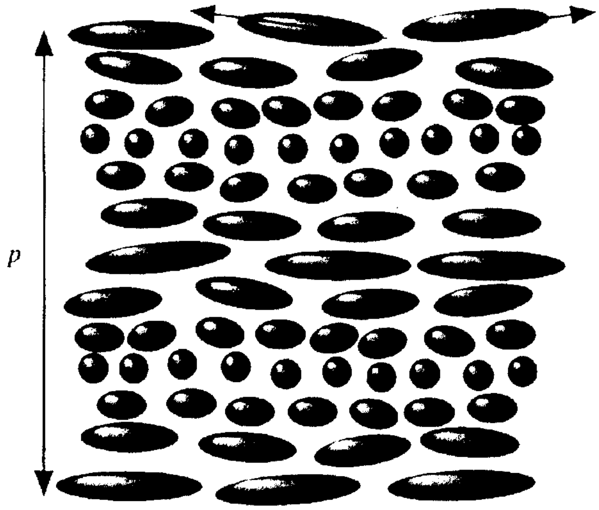
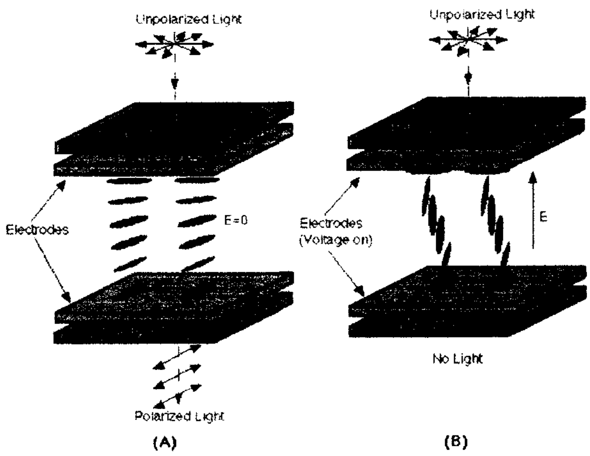


Figure 2.22. Cholesteric phase: a twisted nematic.

A cholesteric phase is characterised by three directors **n** "along" the local molecular axis, **c** along the axis of helicity (which is also the optical axis if the pitch is much smaller than the light wavelength) and **m** = **n** x **c**. These three directors form a trihedron of directions (**n** = -**n**, **c** = -**c**, **m** = -**m**) that rotates with the cholesteric pitch.

Funktionsweise einer Schadt-Helfrich Anzeige (Twisted Nematic (TN) Zelle)



Bei feldfreien Zustand durchsichtig.
Feld an ==>Dunkel !

Smectic Phases

Smectics are layered phases with quasi-long range *1D translational* order. Within the layers the molecules show *fluid-like* arrangement.

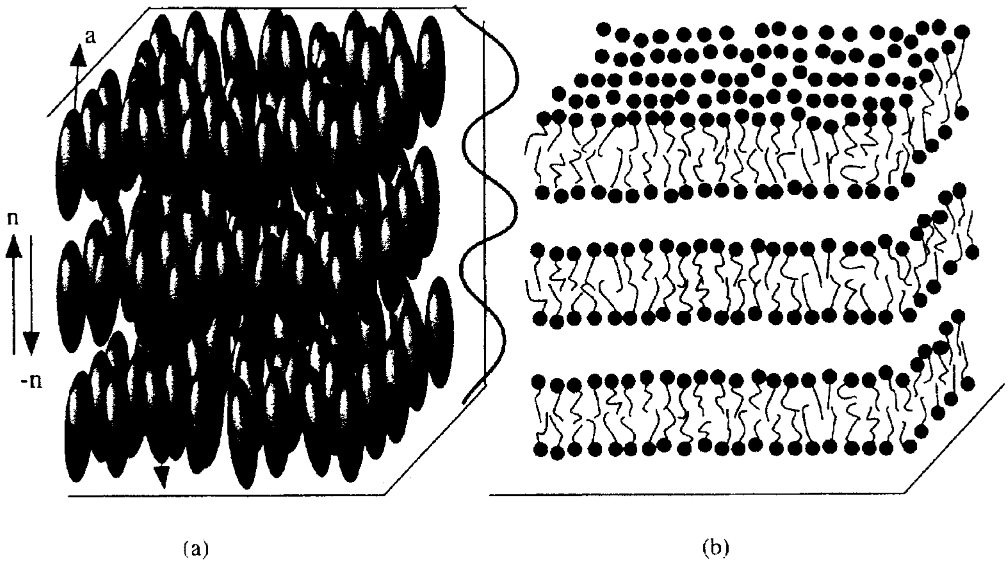


Figure 2.23. (a) Thermotropic smectic A phase with periodic modulation of density; (b) lyotropic L_α phase with surfactant bilayers separated by water; the layer of water might be much thicker than the surfactant bilayer.

The smectic A (Sm-A) is a uniaxial phase with the optical axis perpendicular to the layers.

The smectic C (Sm-C) is a biaxial phase because the molecules are tilted with respect to the layer normal t.

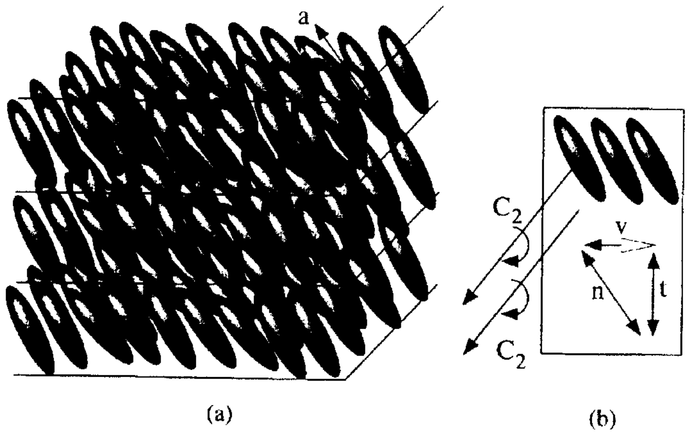


Figure 2.24. Smectic C phase (achiral): (a) general structure; (b) elements of symmetry; see text.

For chiral molecules in Sm-C phases a helical superstructure is obtained as well.

Order parameters: How describe different states of order in a molecular system?

The phase transition ferromagnetic/paramagnetic is a second order phase transition. As characterising parameter the *intensive* variable magnetisation per unit volume can be used.

In the ferromagnetic state the spins interact and align parallel; with increasing temperature this interaction weakens and averages to 0 at the Curie-temperature T_c.

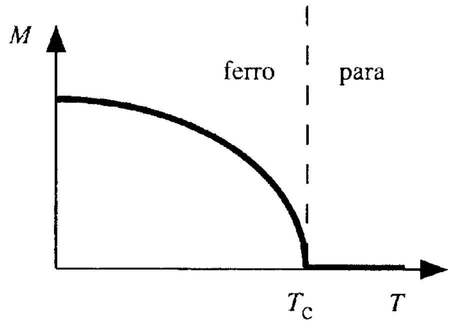


Figure 3.2. The magnetization amplitude M as a function of temperature T; T_C is the temperature of the second-order phase transition between the ferromagnetic and the paramagnetic states.

The description of the order in a nematic phase.

The director **n** bears no information about the degree of orientational order. If the Z-axis is chosen to be parallel to **n** a function

$$f(\vartheta,\varphi)\,d\Omega \tag{1}$$

describes the probability of finding a molecular axis $\vec{a}$ within a solid angle $d\Omega = \sin\vartheta\, d\vartheta\, d\varphi$ about the direction (ϑ, e). Because $+\vec{a}$ and $-\vec{a}$ are equivalent in the nematic bulk

$$f(\vartheta,\varphi) \equiv f(\pi-\vartheta,\varphi) \tag{2}$$

Because of the axial symmetry holds

$$\frac{\partial f(\vartheta,\varphi)}{\partial\varphi} = 0 \tag{3}$$

Hence every molecule is certainly oriented in the interval $0 \le \vartheta < \pi$ with

$$f(\vartheta,\varphi) = f(\vartheta) \tag{4}$$

Normalisation:

$$\iint f(\vartheta,\varphi)\, d\Omega = 2\pi\int_0^\pi f(\vartheta)\sin\vartheta\, d\vartheta = 1 \tag{5}$$

T_0 describe the orientational order the order parameter s was (first) introduced by Tsvetkov (1942).

$$s = 2\pi\int_0^\pi \underbrace{\frac{1}{2}\left(3\cos^2\vartheta - 1\right)}_{P_2(\cos\vartheta)} f(\vartheta)\sin\vartheta\, d\vartheta \tag{6}$$

Legendre polynomial of second rank.

In the **isotropic phase**, all orientations are equally probable, hence

$$f(\vartheta, e) = \frac{1}{4\pi} \qquad (7)$$

Inserting into (6) delivers: $s = 0$

In the *most ordered state*, all molecules have the orientation $\vartheta = 0$, hence

$$f(\vartheta) = \frac{1}{4\pi}\delta(\vartheta)$$

$\delta(\vartheta)$ is the Dirac-δ-function.

This results in $s = 1$

Qualitatively one obtains:

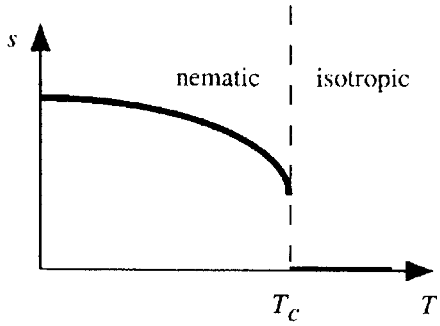


Figure 3.5. Behavior of the scalar order parameter in the nematic phase at the first-order N-I transition.

Landau-de Gennes approach

The free energy is expanded due to the phase transition temperature in terms of the order parameter s

$$F = F(V,T,s) = F_0 + V(Ks + \frac{1}{2}As^2 + \frac{1}{3}Bs^3 + \frac{1}{4}Cs^4 ...) \qquad (1)$$

Stability conditions:

Extremum: $\frac{\partial F}{\partial s} = 0$ Minimum: $\frac{\partial^2 F}{\partial^2 s} > 0$ (2)

- The absolute value of F has no physical meaning:

$$\Rightarrow F_0 = 0 \qquad (3)$$

- Restriction to order < 4; $\Rightarrow$ D, E ... = 0
- The isotropic liquid with s = 0 must be a solution: $\Rightarrow$ K = 0

because $\frac{\partial F}{\partial s} = 0 \quad \Rightarrow \quad V\left(K + As + Bs^2 + Cs^3\right) = 0$ (4)

- Assumption: Linear temperature dependence of

$$A = a\left(T - T^*\right) \qquad B_0 \text{ and } C_0 \text{ are constant} \qquad (5)$$

$$F = \frac{1}{2}a\left(T - T^*\right)s^2 + \frac{1}{3}B_0 s^3 + \frac{1}{4}C_0 s^4 \qquad (6)$$

I: $$\frac{\partial F}{\partial s} = a\left(T - T^*\right)s + B_0 s^2 + C_0 s^3 = 0 \qquad (7)$$

II: $$\frac{\partial^2 F}{\partial s^2} = a\left(T - T^*\right) + 2B_0 s + 3C_0 s2 > 0 \qquad (8)$$

from I: $s = 0$ is solution (9)

$$s^2 + \frac{B_0}{C_0}s + \frac{a\left(T - T^*\right)}{C_0} = 0 \qquad (10)$$

$$s_{\frac{1}{2}} = -\frac{B_0}{C_0^2} \pm \frac{1}{2C_0}\sqrt{B_0^2 - 4aC_0\left(T - T^*\right)} \qquad (11)$$

Two cases:

1.) $$a\left(T - T^*\right) > \frac{B_0^2}{4C_0} \qquad (12)$$

$s = 0$ is the only stable solution

2.) $$a\left(T - T^*\right) < \frac{B_0^2}{4C_0} \qquad (13)$$

$$s_{\frac{1}{2}} = -\frac{B_0}{2C_0} \pm \frac{1}{2C_0}\sqrt{B_0^2 - 4aC_0\left(T - T^*\right)} \quad ; s=0 \qquad (14)$$

two solutions for s

At the critical temperature T_c: $F_N = F_I$

$$F - F_0 = s_c^{\ 2}\left[\frac{1}{2}a\left(T_c - T^*\right) + \frac{1}{3}B_0 s_c + \frac{1}{4}C_0 s_c^{\ 2}\right] = 0 \qquad (15)$$

I: $$s_c^{\ 2} - \frac{4B_0}{3C_0}s_c + 2\frac{a(T_c - T^*)}{C_0} = 0 \qquad (16)$$

And additionally also at T_c:

$$\frac{\partial F}{\partial s} = a\left(T_c - T^*\right)s_c + B_0 s_c^{\ 2} + C_0 s_c^{\ 3} = 0 \qquad (17)$$

II: $$s_c^{\ 2} - \frac{B_0}{C_0}s_c + \frac{a(T_c - T^*)}{C_0} = 0 \qquad (18)$$

2*II-I: $$s_c^{\,2}+\frac{2B_0}{3C_0}s_c=0 \qquad (19)$$

$$s_c=-\frac{2B_0}{3C_0} \qquad (20)$$

hence at T_c: $s = 0$ or $s=-\dfrac{2B}{3C}$

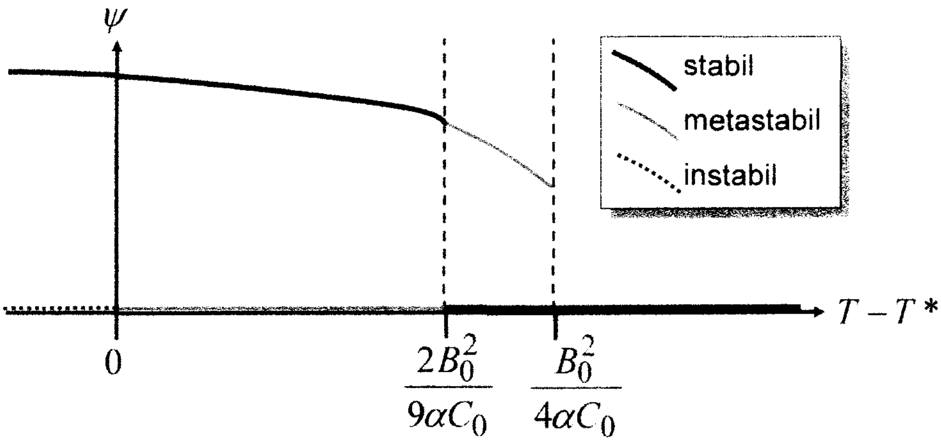
for $s > 0$ follows with $C > 0$: $B< 0$.

Inserting (20) into (15) for $T = T_c$:

$$F-F_0=\left[-\frac{2B}{3C}\right]^2\left[\frac{1}{2}a\left(T-T^*\right)+\frac{1}{3}B\left(-\frac{2B}{3C}\right)+\frac{1}{4}C\left(-\frac{2B}{3C}\right)^2\right]=0$$

$$a\left(T_c-T^*\right)=\frac{2}{9}\frac{B^2}{aC}>T^*$$

$$\Rightarrow \quad T_c=T^*+\frac{2}{9}\frac{B^2}{aC}>T^* \qquad (21)$$



- Sprung im Ordungsparameter
- Überhitzung/Unterkühlung

$$T_{klär}=T^*+\frac{2B_0^2}{9\alpha C_0}$$

Landau – de Gennes approach

The free energy is expanded close to the phase transition temperature in terms of the order parameters

$$F = F(V, T, s) = F_0 + V\left(Ks + \frac{1}{2}As^2 + \frac{1}{3}Bs^3 + \frac{1}{4}Cs^4 + \dots\right.$$

Stability conditions: (1

Extremum: $\frac{\partial F}{\partial s} = 0$ Minimum $\frac{\partial^2 F}{\partial s^2} > 0$ (2

- The absolute value of F has no physical meaning:

$$\Rightarrow F_0 = 0$$ (3

- Restriction to order < 4; ⇒ D, E ... = 0

- The isotropic liquid with s = 0 must be a solution: ⇒ K = 0 !

because $\frac{\partial F}{\partial x} = 0 \Rightarrow V(K + As + Bs^2 + Cs^3) = 0$ (4

• Assumption: Linear temperature dependence of $A = a(T-T^*)$ (5)

B_0 and C_0 are constant.

$$F = \frac{1}{2} a(T-T^*) s^2 + \frac{1}{3} B_0 s^3 + \frac{1}{4} C_0 s^4 \quad (6)$$

$$\text{I:} \quad \frac{\partial F}{\partial s} = a(T-T^*) s + B_0 s^2 + C_0 s^3 \overset{!}{=} 0 \quad (7)$$

$$\text{II:} \quad \frac{\partial^2 F}{\partial s^2} = a(T-T^*) + 2B_0 s + 3C_0 s^2 \overset{!}{>} 0 \quad (8)$$

From I: $s = 0$ is solution (9)

$$s^2 + \frac{B_0}{C_0} s + \frac{a(T-T^*)}{C_0} = 0 \quad (10)$$

$$s_{1/2} = -\frac{B_0}{C_0 2} \pm \frac{1}{2C_0} \sqrt{B_0^2 - 4 a C_0 (T-T^*)} \quad (11)$$

Two cases: 1.) $a(T-T^*) > \frac{B_0^2}{4C_0}$ (12)

$S=0$ is the only stable solution

2.) $a(T-T^*) < 0$ (13)

$$S_{1/2} = -\frac{B_0}{2C_0} \pm \frac{1}{2C_0}\sqrt{B_0^2 - 4a\,C_0\,(T-T^*)}$$ (14)

Two solutions for S

At the critical temperature T_c : $F_N = F_I$

$$F - F_0 = S^2\left[\frac{1}{2}a(T-T^*) + \frac{1}{3}BS + \frac{1}{4}CS^2\right] = 0$$ (15

$$\Rightarrow S = \frac{-2B \pm \sqrt{4B^2 - 18a(T-T^*)\,C}}{3C}$$ (16)

Close to T_c the term $18a(T-T^*)\cdot C$ becomes small hence

$$S = -\frac{4B}{3C}$$ (17)

Hence at T_c : $S = 0$ or $S = -\frac{4B}{3C}$

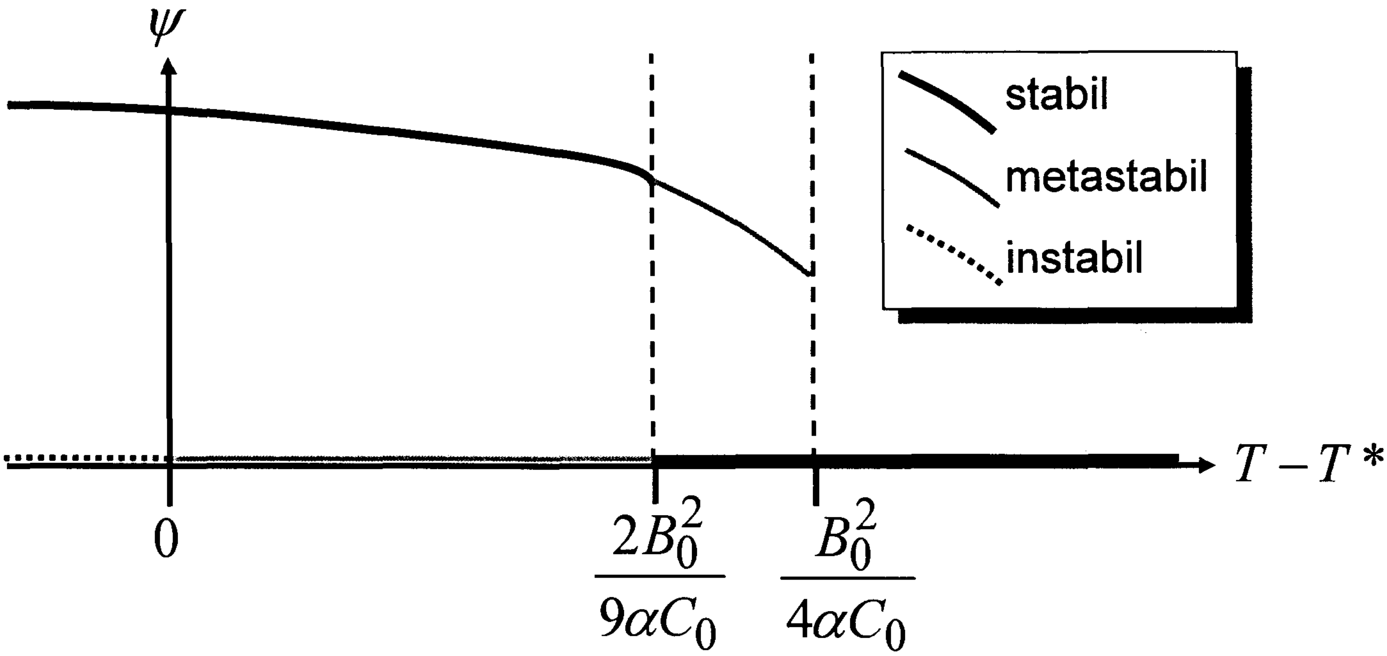
for $S > 0$ follows with $C > 0$
$B < 0$.

Inserting (*) into (1) for $T = T_c$:

$$F - F_0 = \left[-\frac{4B}{3C}\right]^2 \left[\frac{1}{2}a(T-T^*) + \frac{1}{3}B\left(\frac{-4B}{3C}\right) + \frac{1}{4}C\left(-\frac{2B}{3C}\right)^2\right) = 0$$

$$\Rightarrow a(T_c - T^*) = \frac{2}{9}\frac{B^2}{C}$$

$$T_c = T^* + \frac{2}{9}\frac{B^2}{aC} > T^*$$



- Sprung im Ordungsparameter
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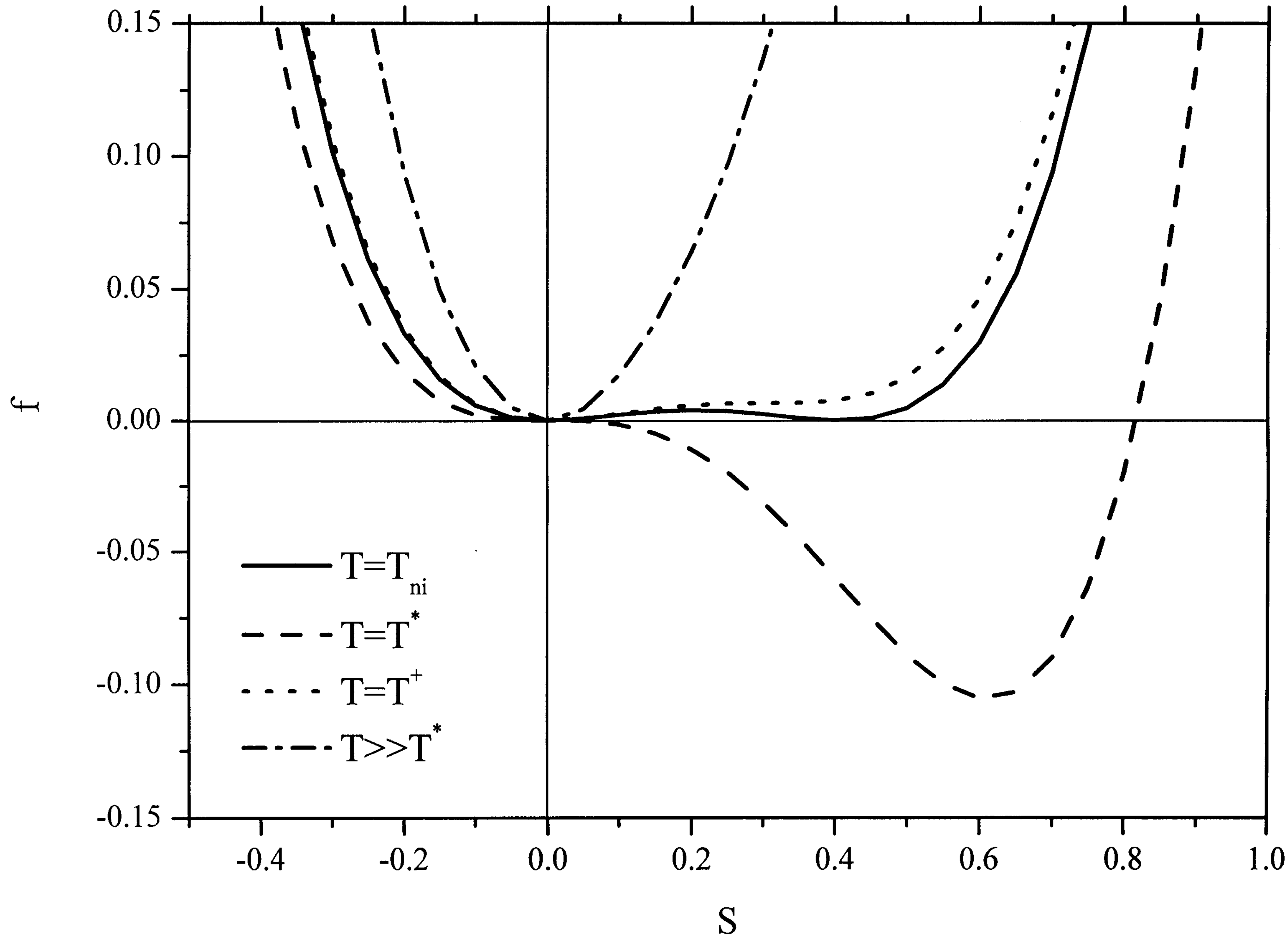
$$T_{klär} = T^* + \frac{2B_0^2}{9\alpha C_0}$$



0.15
0.10
0.05
0.00
-0.05
-0.10
-0.15
f
-0.4
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
S
T=T_ni
T=T*
T=T+
T>>T*

Summary

- Liquid crystals form a special state of matter – between that of crystals and liquids. Typically in 1 or 2 dimensions one has crystalline and in the other glassy "order".
- The degree of ordering is described by an "order parameter"
- An expansion of the free energy with respect to the order parameters at the phase transition enables one to describe phenomenologically the phase transition (Landau-de Gennes approach).
- The dynamics of L.C. is characterised by molecular fluctuations but as well (in case of chiral L.C.) by collective modes (soft- and Goldstone mode).
- L.C. displays are based on the anchoring of L.C. molecules due to surface interactions and by "switching" their orientation with external electric fields.