# Liquid Crystals

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*Liquid Crystal Materials Research Center*
*University of Colorado*

*Liquid crystals are beautiful and mysterious;*
*I am fond of them for both reasons.*

*-Pierre deGennes*

# plan

- overview
  - discovery & early history
- applications
  - displays
  - Other

# *liquid crystal (flussige kristalle)*

*birefringent* ⇨ *“crystalline”*

# birefrinence from Maxwell

$\nabla \times (\nabla \times \vec{E}) = (\varepsilon/c^2)\partial^2\vec{E}/\partial t^2$ with $\vec{E} = \vec{E}_o e^{i(\vec{k}\bullet\vec{r}-\omega t)}$ gives $\vec{k} \times (\vec{k} \times \vec{E}_o) = \varepsilon(\omega^2/c^2)\vec{E}_o$

if $\vec{E}_o \perp \vec{k}$ then $k^2\vec{E}_o = \varepsilon(\omega^2/c^2)\vec{E}_o$. Taking $k_{vac} = \omega/c$, we have $k = k_{vac}n$, for any polarization with $\vec{E}_o \perp \vec{k}$, where $\varepsilon = n^2$.

For anisotropy in the (x,y) plane normal to **k**, with a 2x2 dielectric tensor ε, diagonalized in the x,y frame (x,y are the principal axes of ε):

$\nabla \times (\nabla \times \vec{E}) = (1/c^2)\partial^2/\partial t^2\, \vec{\varepsilon} \bullet \vec{E}$ and $\vec{k} \times (\vec{k} \times \vec{E}) = k^2\vec{E} = (\omega^2/c^2)\vec{\varepsilon} \bullet \vec{E}$,

or $k^2\begin{pmatrix} E_x \\ E_y \end{pmatrix} = (\omega^2/c^2)\begin{pmatrix} \varepsilon_{xx} & 0 \\ 0 & \varepsilon_{yy} \end{pmatrix} \bullet \begin{pmatrix} E_x \\ E_y \end{pmatrix}$.

This leads to the eigenvalue equation

$$0 = \begin{pmatrix} (\omega^2/c^2)\varepsilon_{xx} - k^2 & 0 \\ 0 & (\omega^2/c^2)\varepsilon_{yy} - k^2 \end{pmatrix} \bullet \begin{pmatrix} E_x \\ E_y \end{pmatrix} = [(\omega^2/c^2)\varepsilon_{xx} - k^2]E_x + [(\omega^2/c^2)\varepsilon_{yy} - k^2]E_y$$

and determinant $[(\omega^2/c^2)\varepsilon_{xx} - k^2][(\omega^2/c^2)\varepsilon_{yy} - k^2] = 0$,

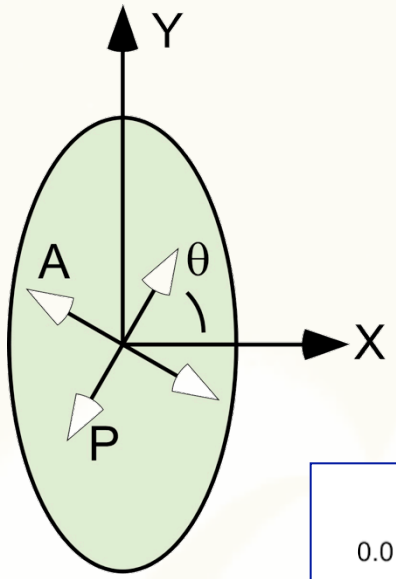
with solutions:

$k = k_{vac}\sqrt{\varepsilon_{xx}} = k_{vac}n_x$ $\qquad E_y = 0$

$k = k_{vac}\sqrt{\varepsilon_{yy}} = k_{vac}n_y$ $\qquad E_x = 0$.

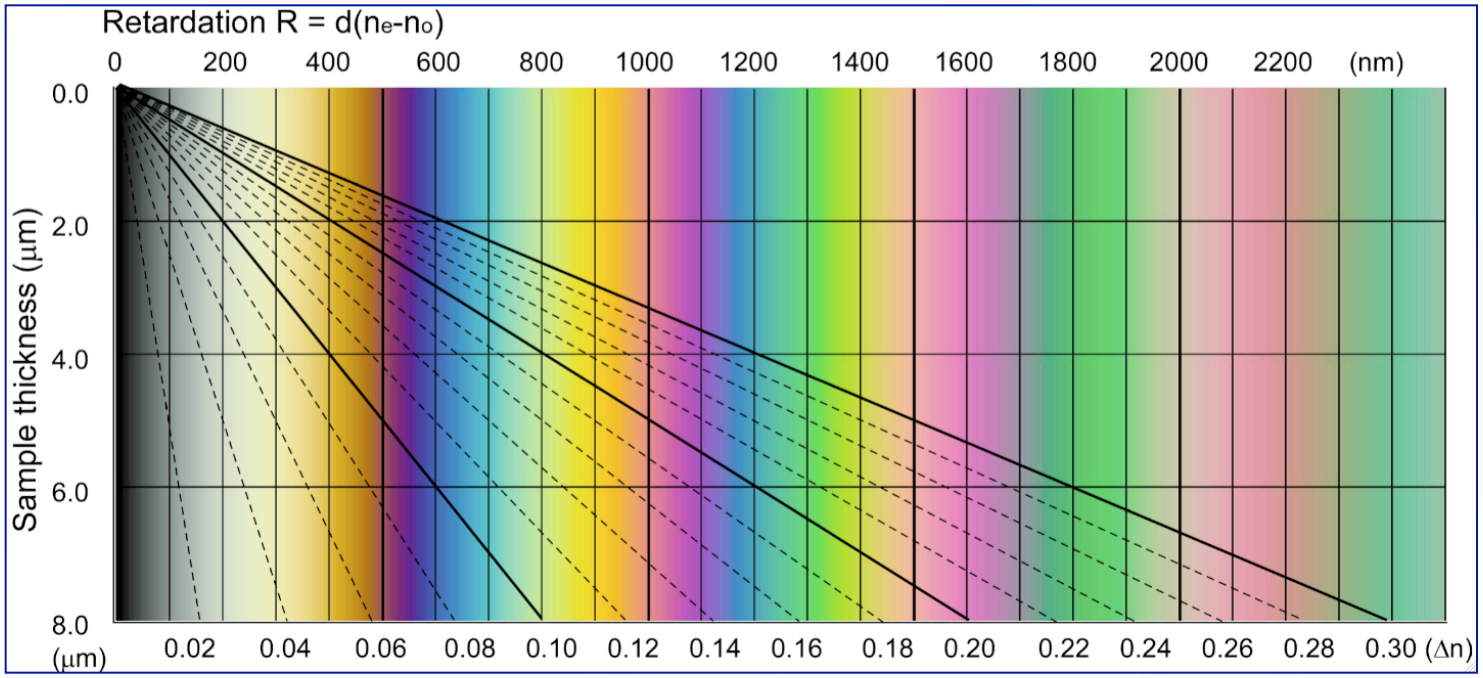
Thus there are two normal modes, one linearly polarized along one principal axis of ε and the other polarized along the other principal axis of ε.

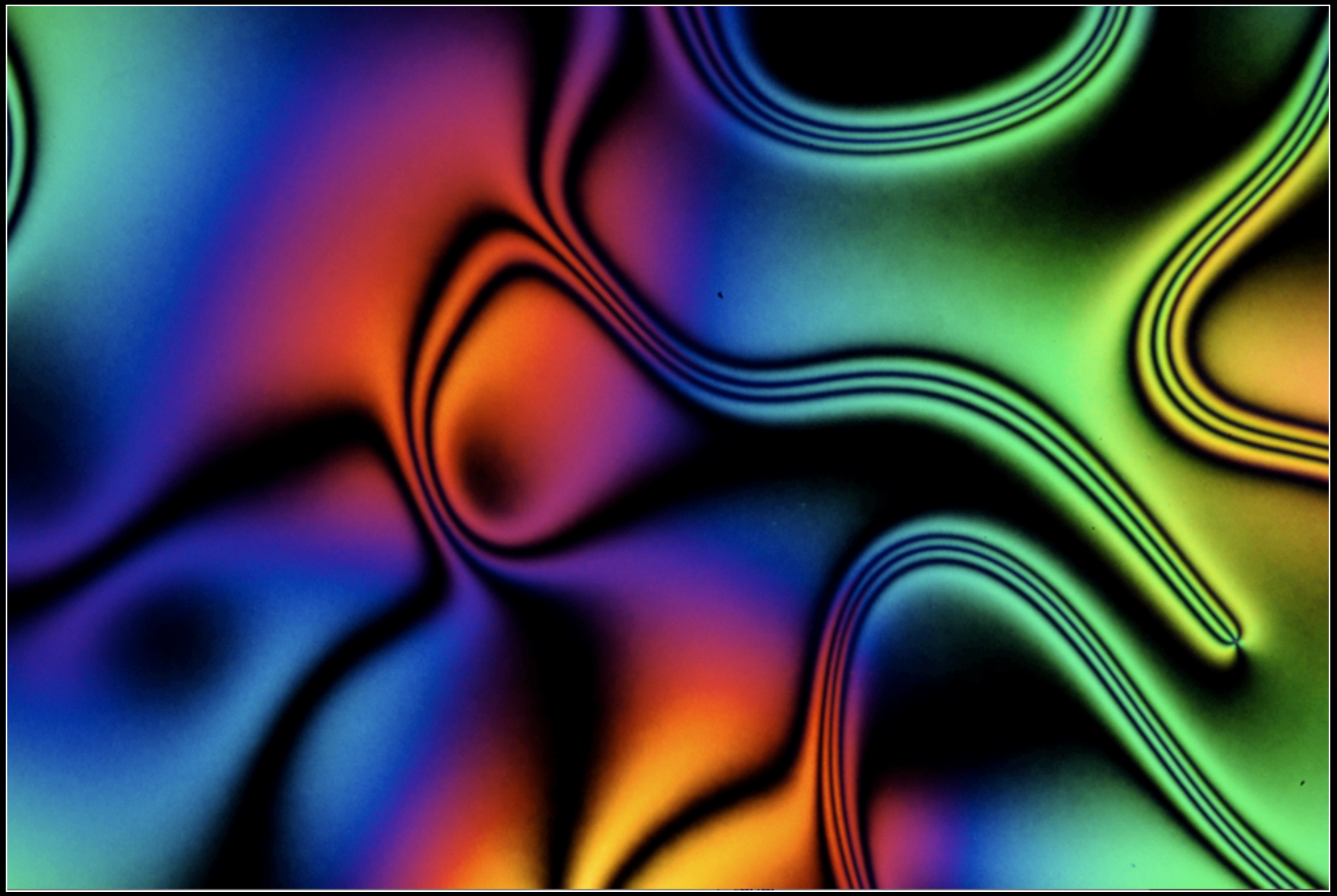
# birefrinence colors

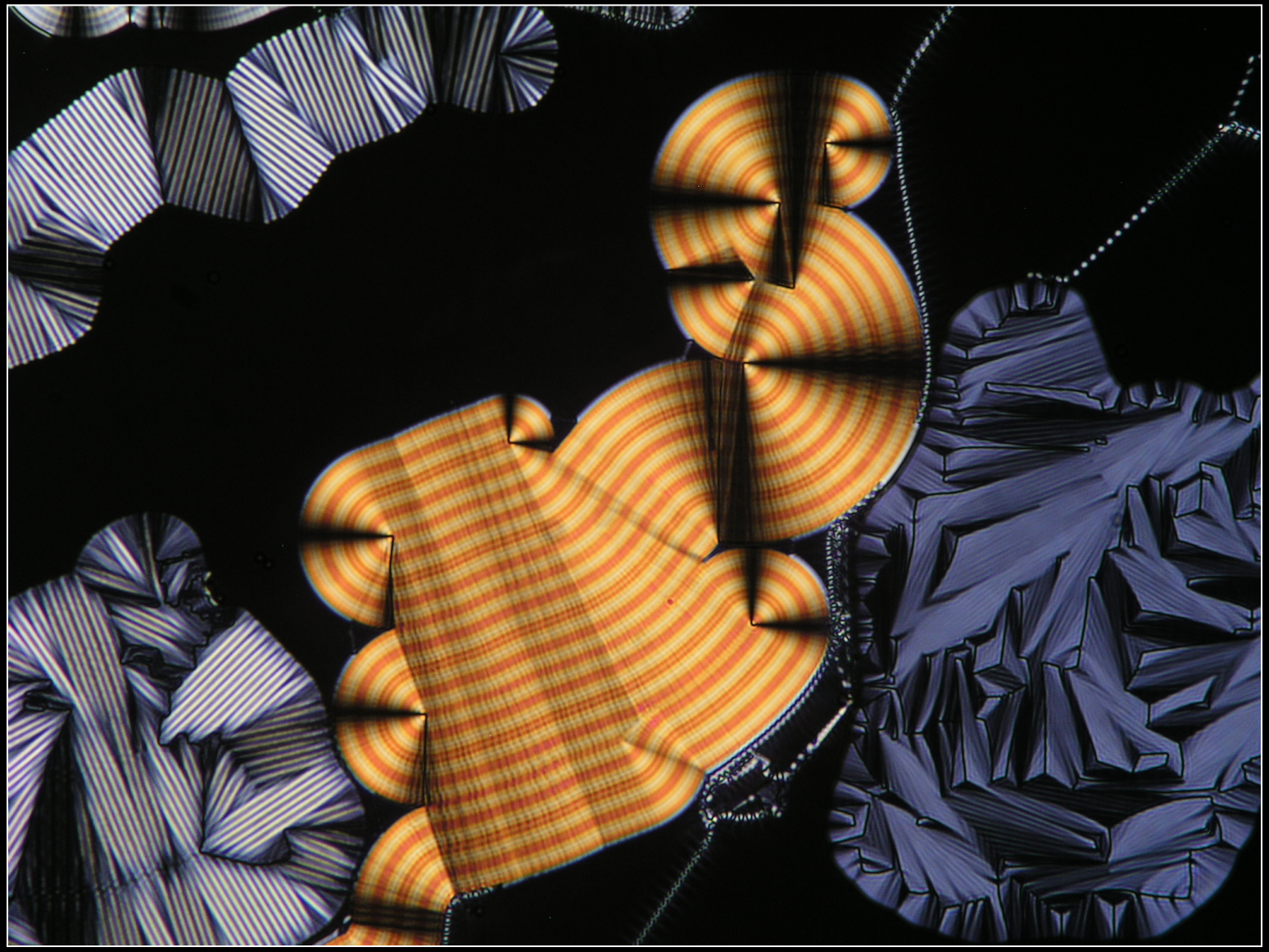


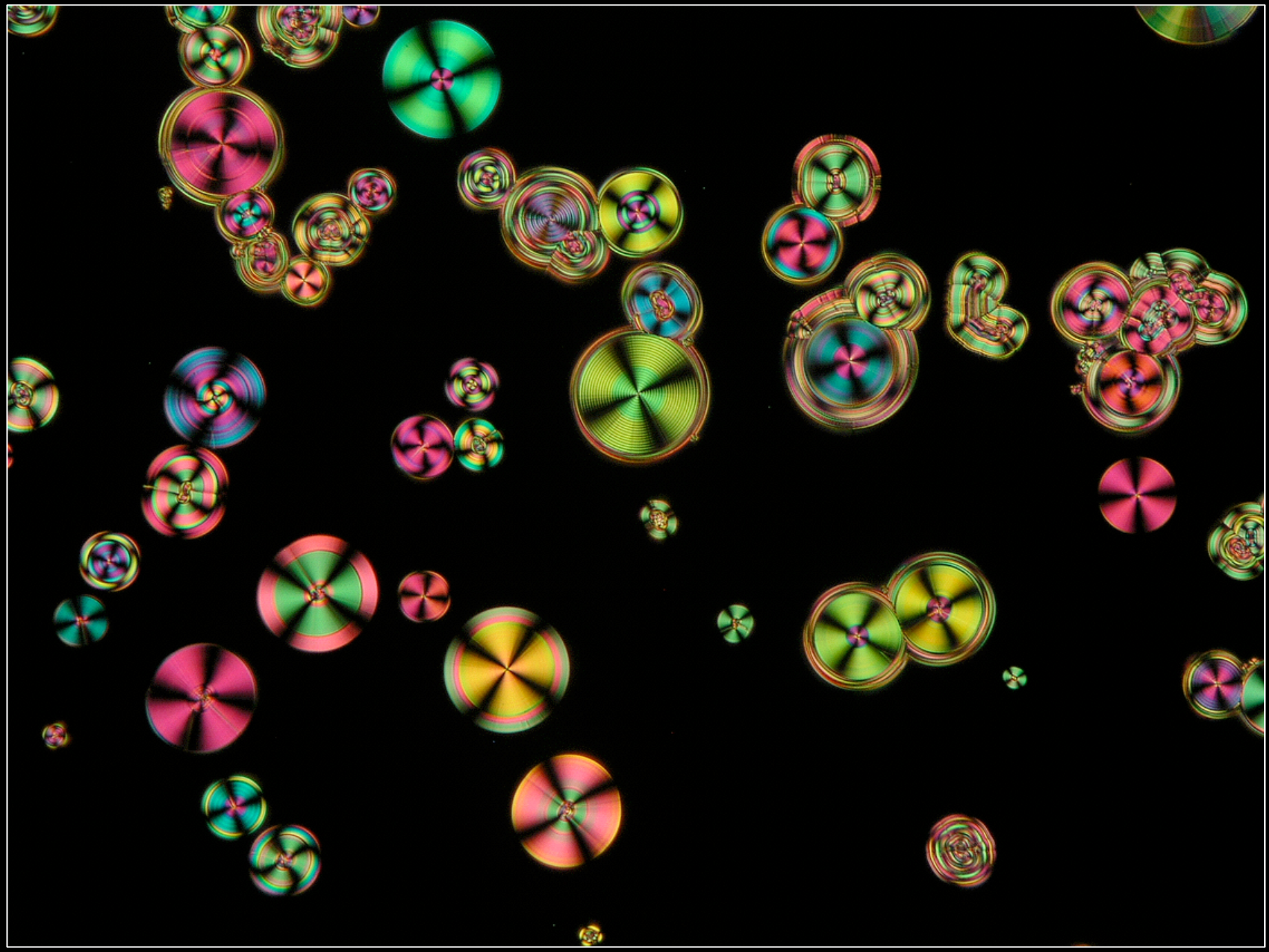

$$I = I_0 \sin^2 2\theta \sin^2 \frac{\pi d \Delta n}{\lambda}$$

- *d = sample thickness*
- *Δn = birefringence*
- *λ = wavelength*

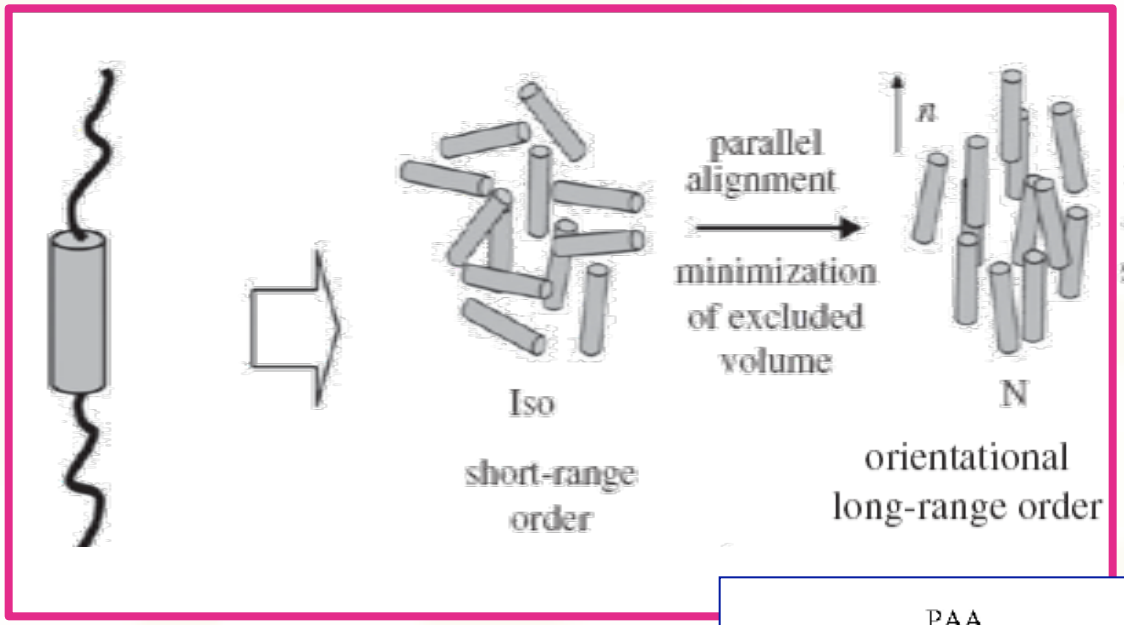






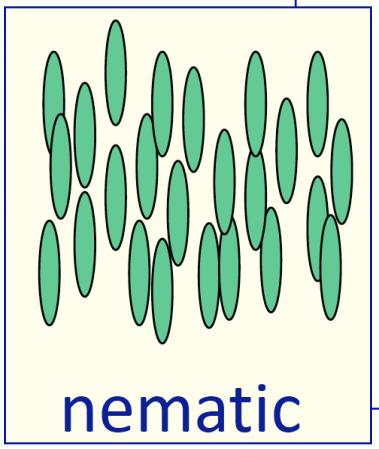


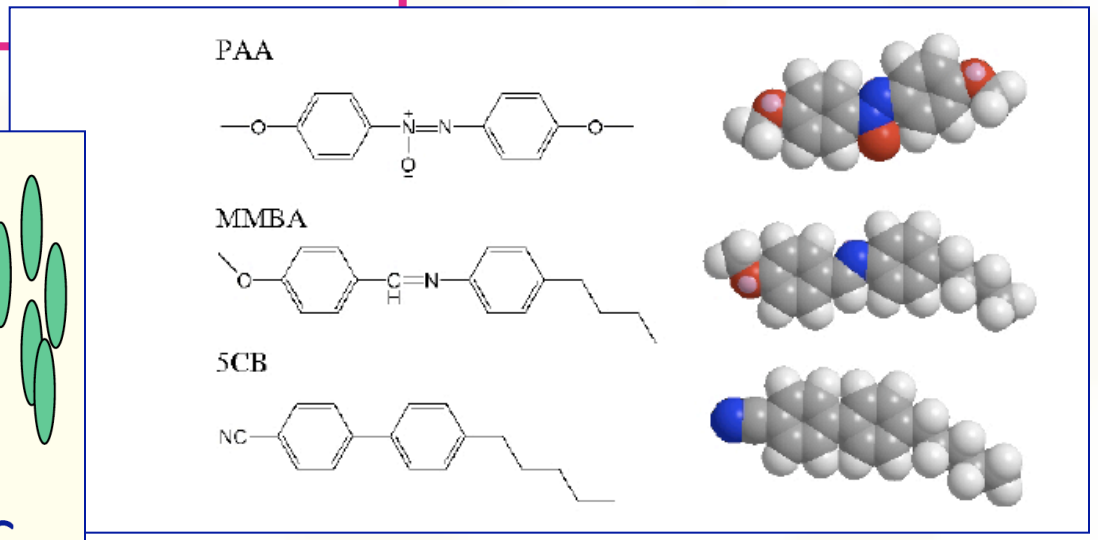
# *pathways to LCs - anisotropy of shape or interaction (orientational ordering)*



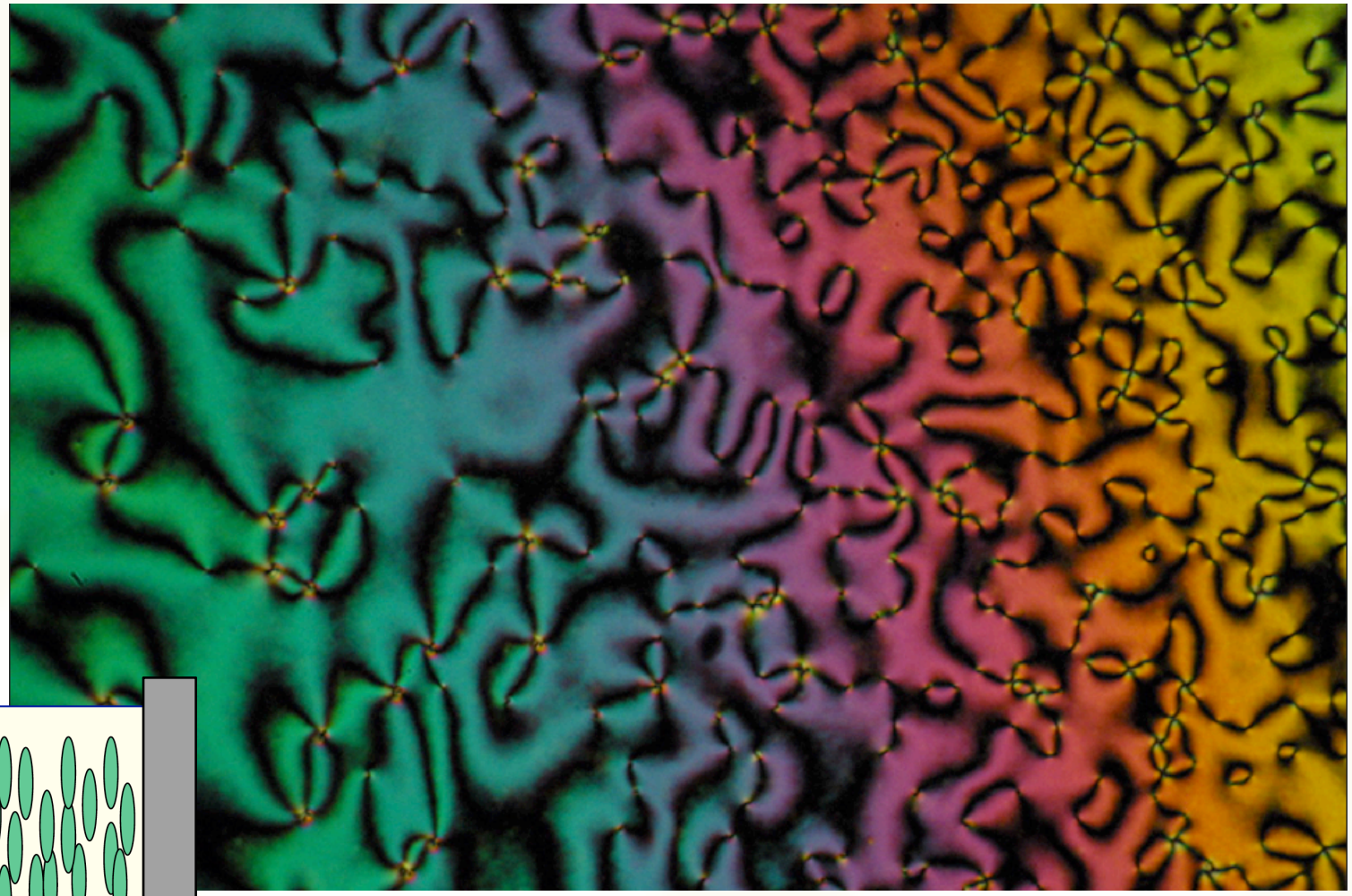

*molecular rods*

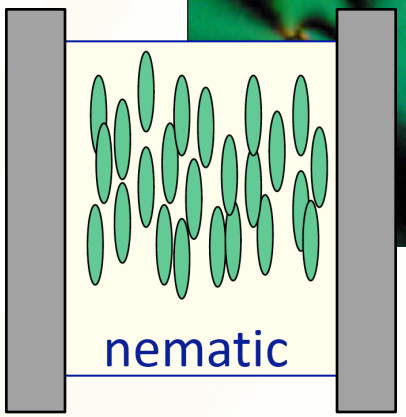
*director n*



# *nematic schlieren texture*

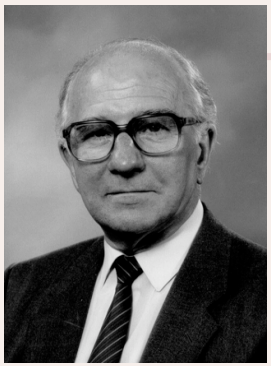





***between clean glass plates***
***(n parallel to the glass, unconstrained in-plane)***

# cyanobiphenyls – George Gray (University of Hull)

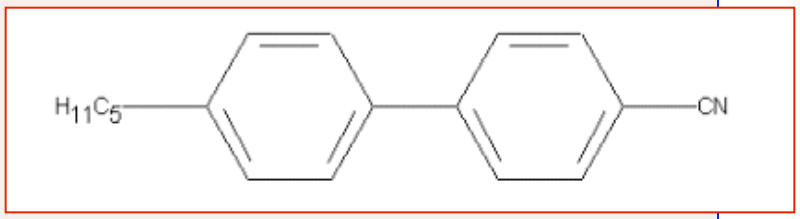
## 5CB – the liquid crystal hydrogen atom



**Advanced Technology** ■

Materials Science and Engineering

*Kyoto Prize citation*




**George William Gray(U.K., 1926-)**

Chemist, Professor Emeritus, University of Hull

A chemist who has made fundamental contributions to research and development of liquid crystal materials, the key component of liquid crystal displays, which have become an indispensable part of today's information-based society. He founded and organized the science of liquid crystal materials, and established practical molecular design methods for the application of these materials.

# discovery

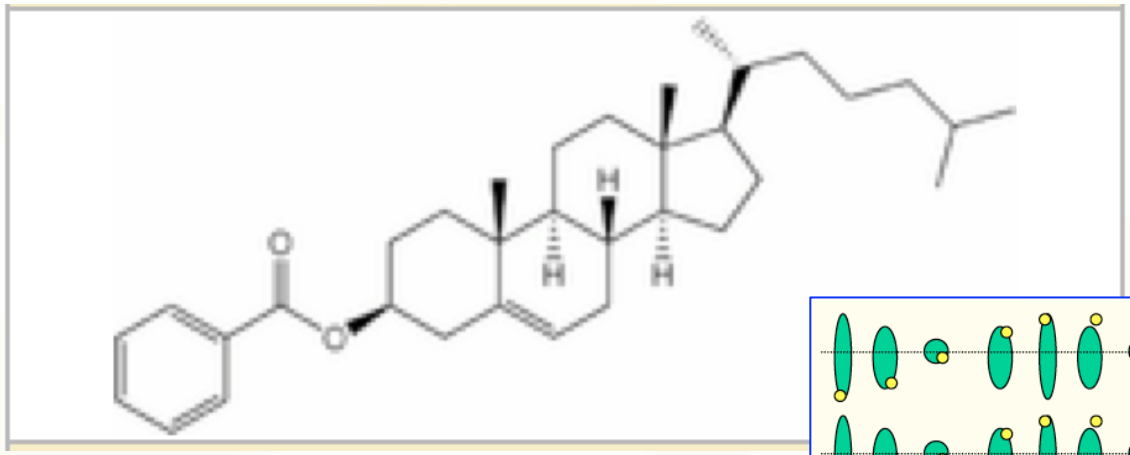
*1888:*

*Austrian botanist*

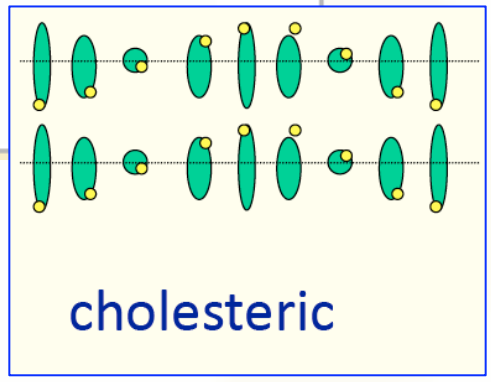
*Friedrich Reinitzer, working in Prague (on carrots)*

***observes 2 'melting points' in cholesterol benzoate:***

| | | | |
|---|---|---|---|
| *solid* | → | *hazy liquid* | *145C* |
| *hazy liquid* | → | *clear liquid* | *178C* |

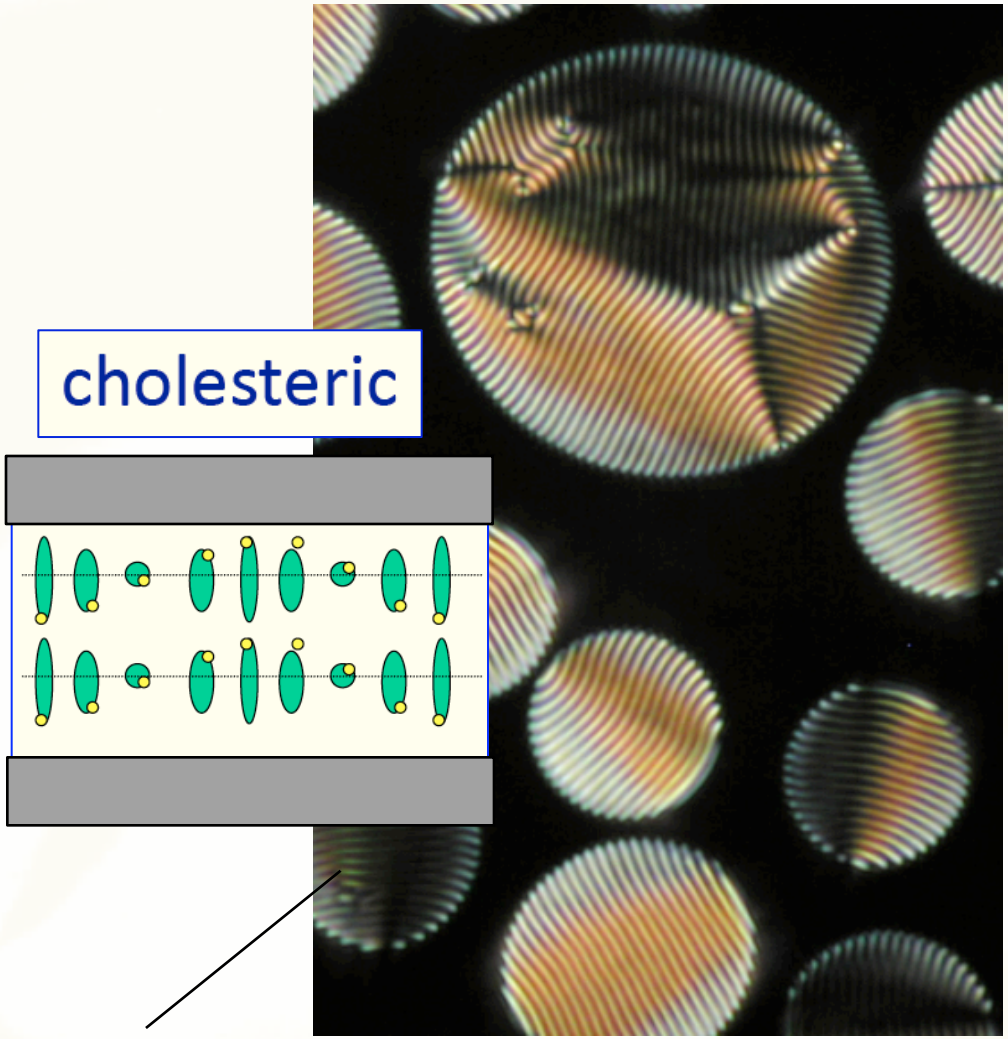


***chirality!***

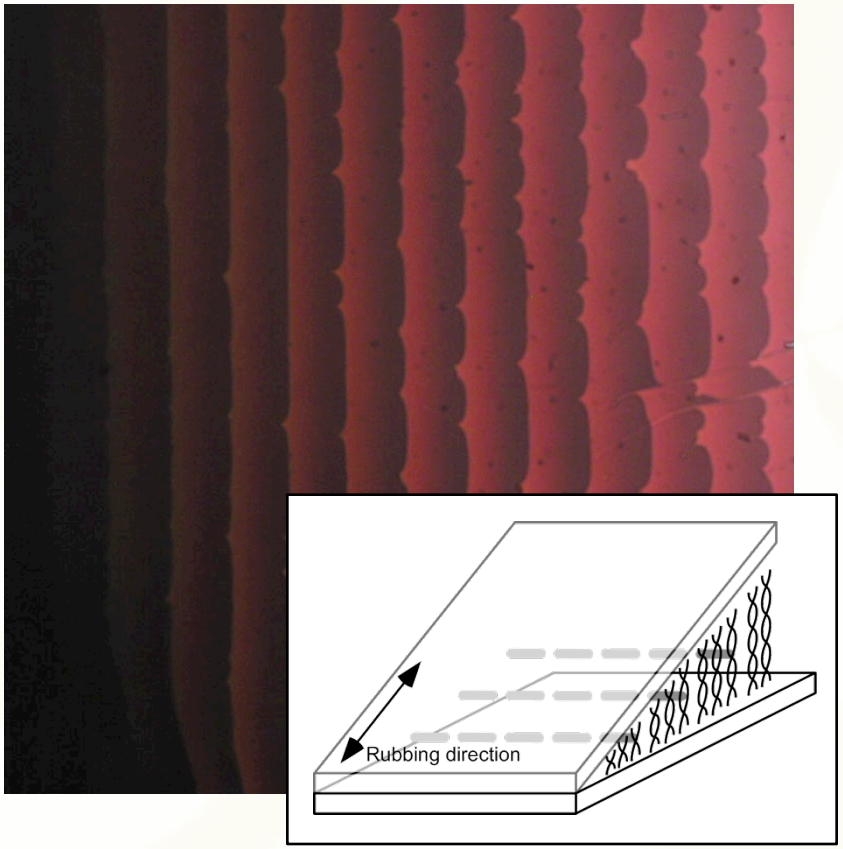



***observations are disruptive, work viewed with skepticism***

# cholesteric (chiral nematic) textures

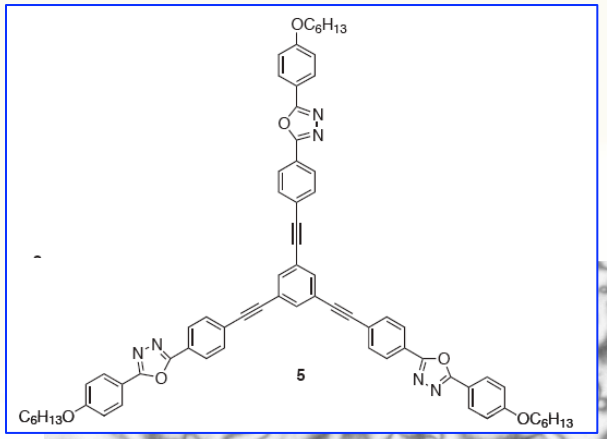


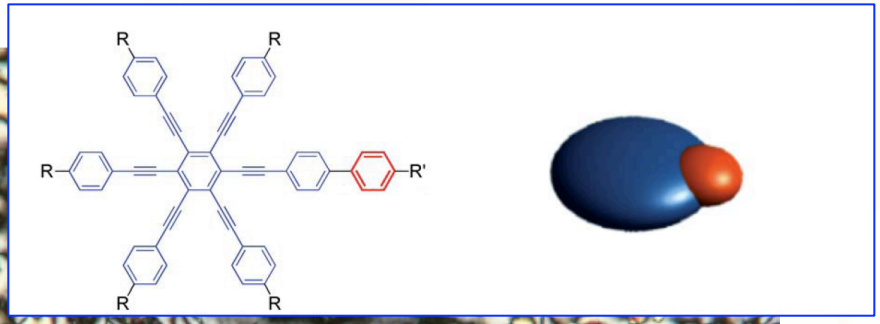

*between treated glass plates (n normal to the glass)*



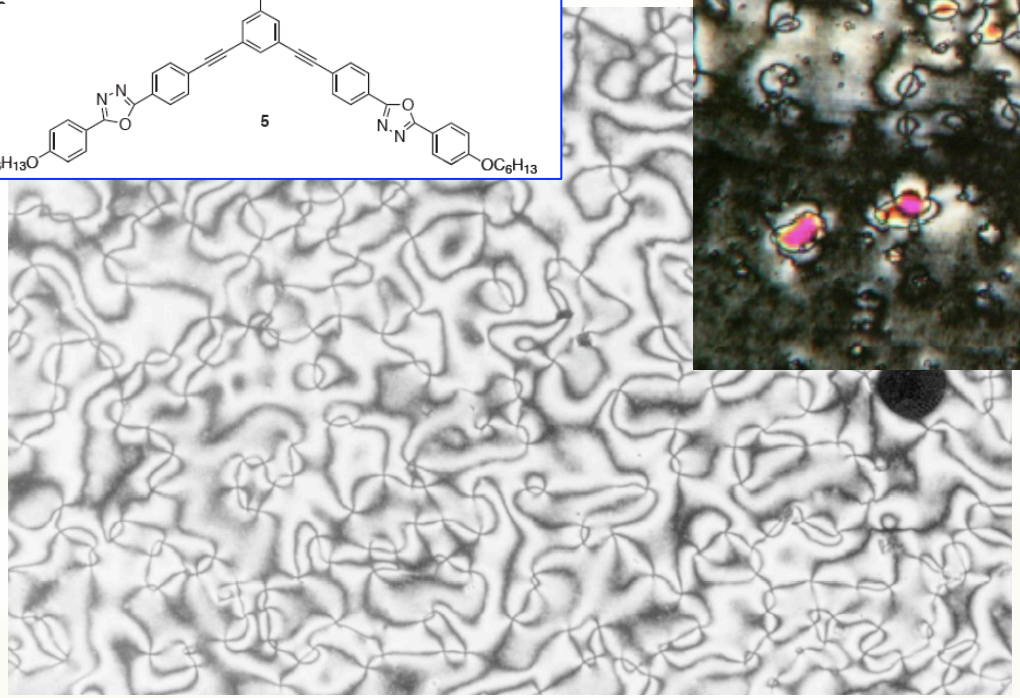

*Grandjean wedge cell texture between treated glass plates (n parallel to the glass, oriented parallel to wedge)*

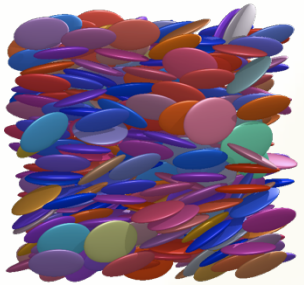
# discotic nematics



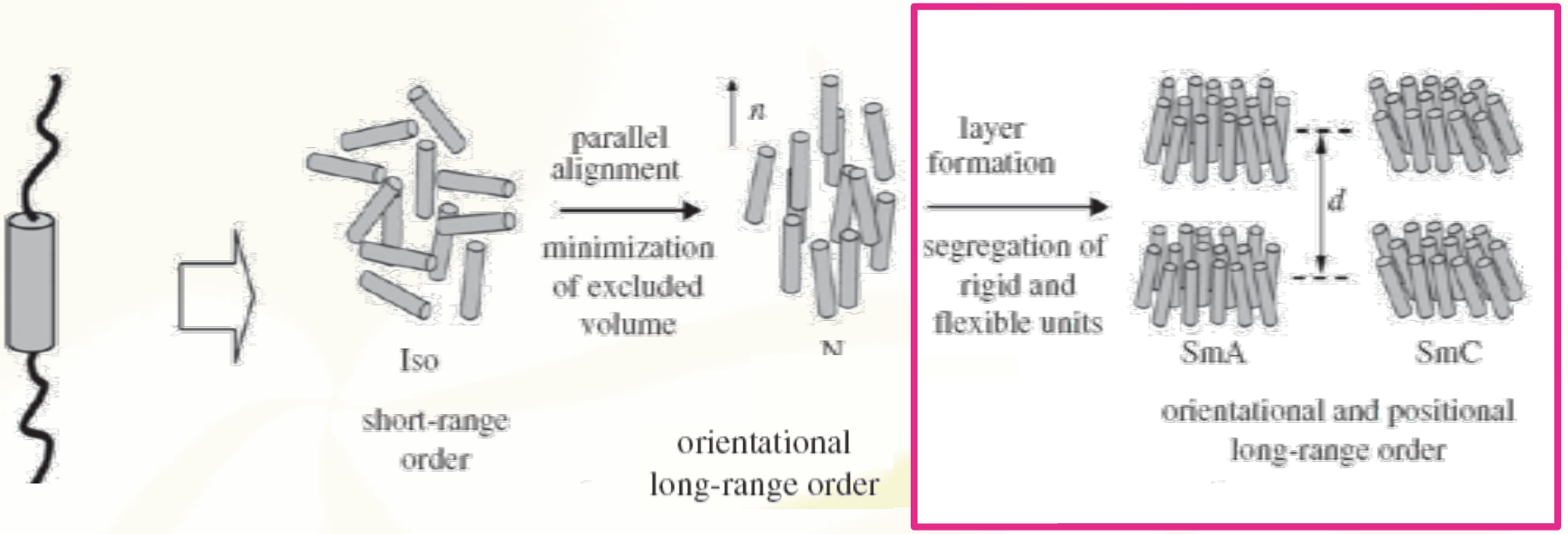


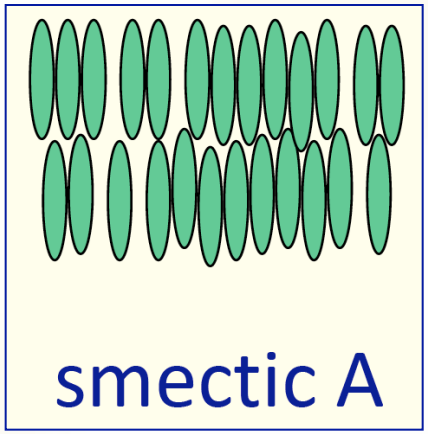



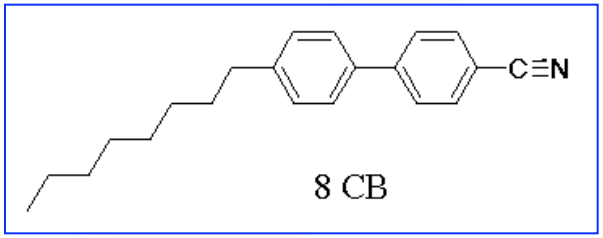


H. Chen, JMC (2012)

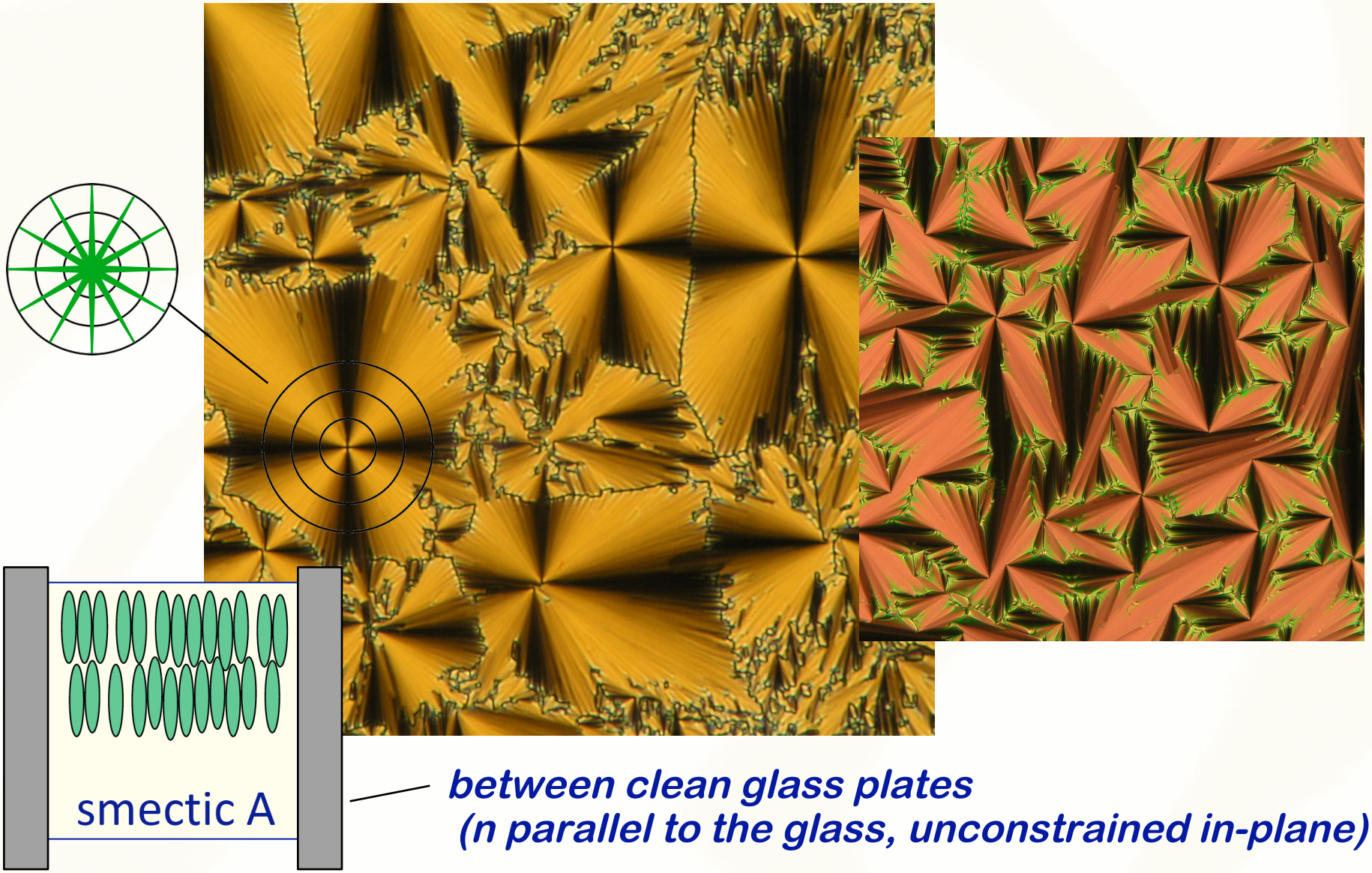
# *pathways to LCs - fluid interfaces (positional ordering)*



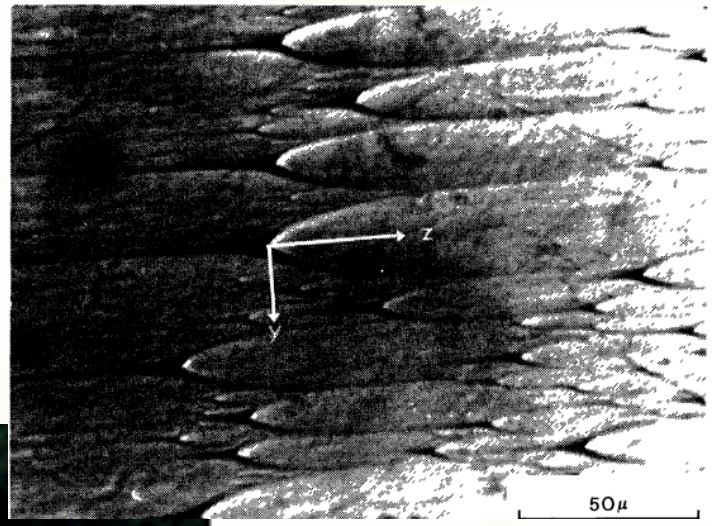
# *smectic A textures*

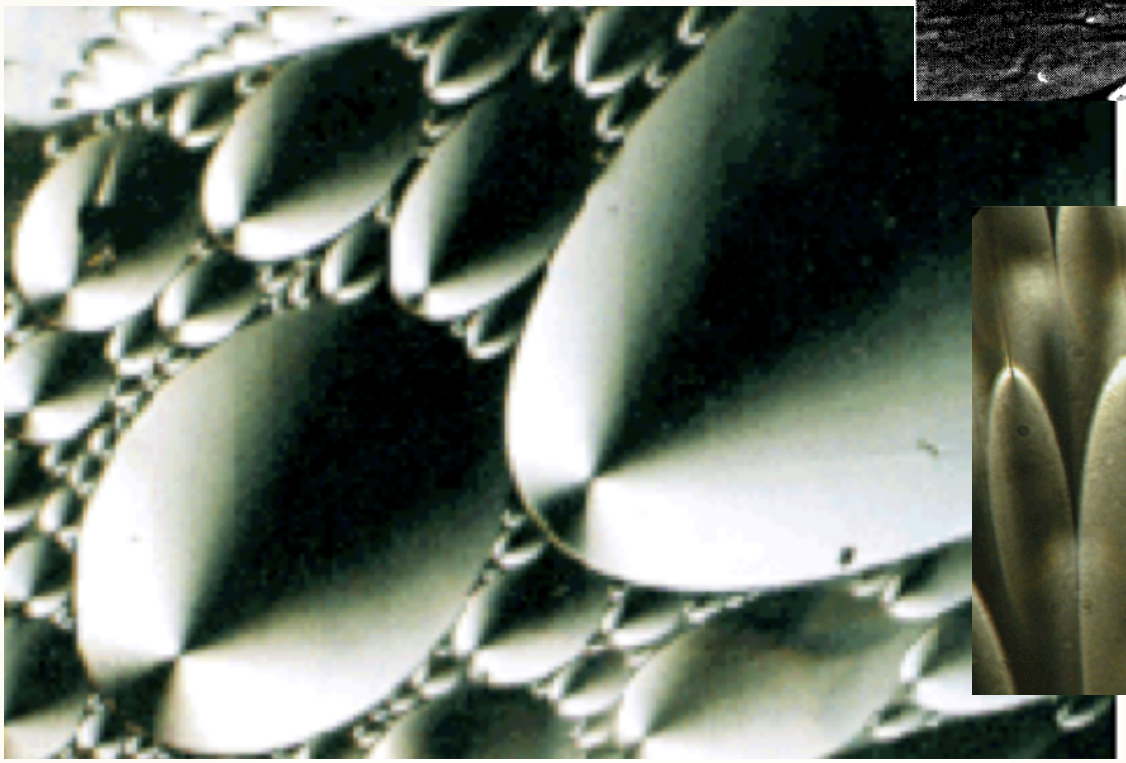


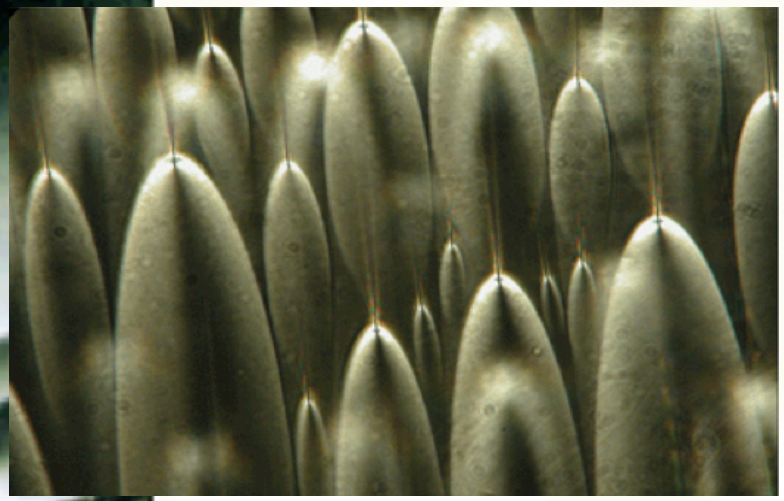

***between clean glass plates***
***(n parallel to the glass, unconstrained in-plane)***

# smectic A focal conic domains

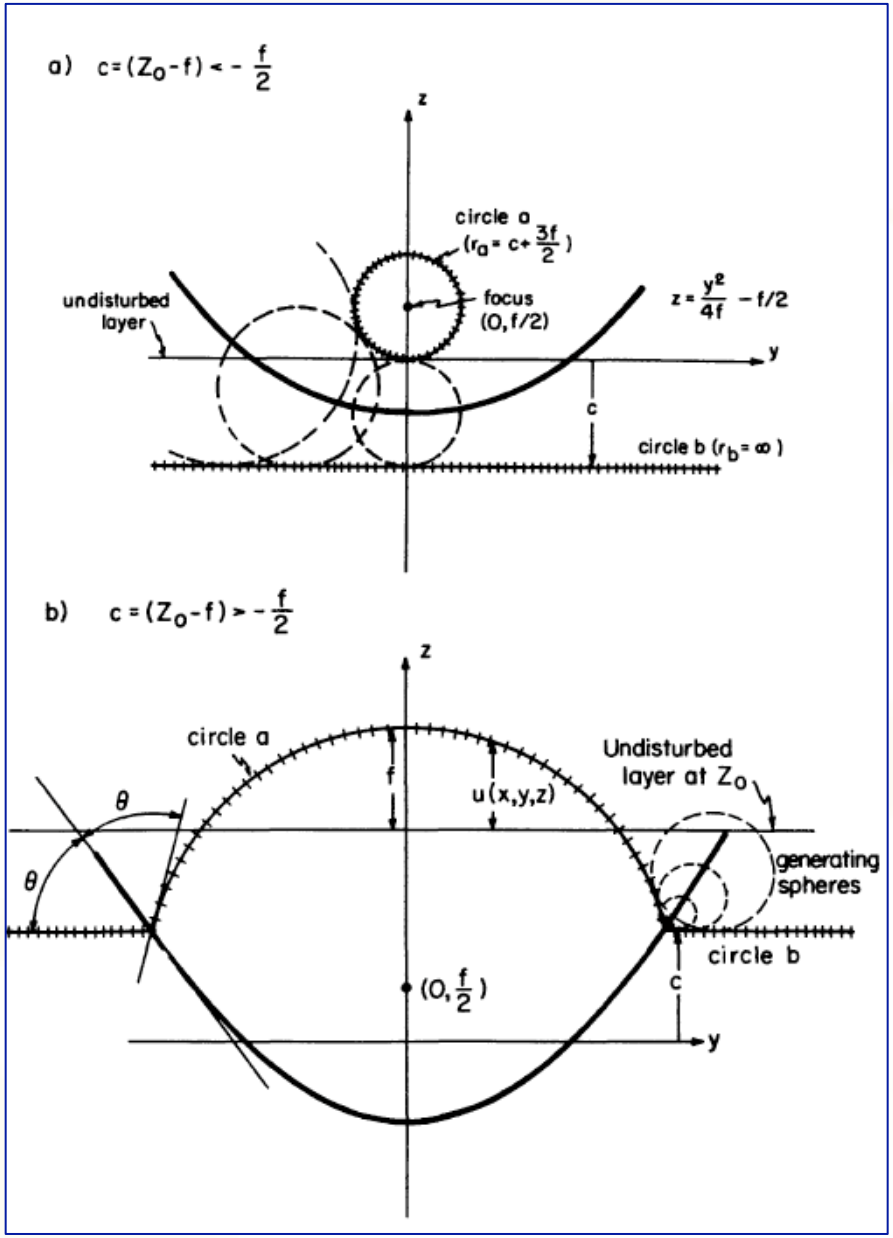
Georges Friedel
1922

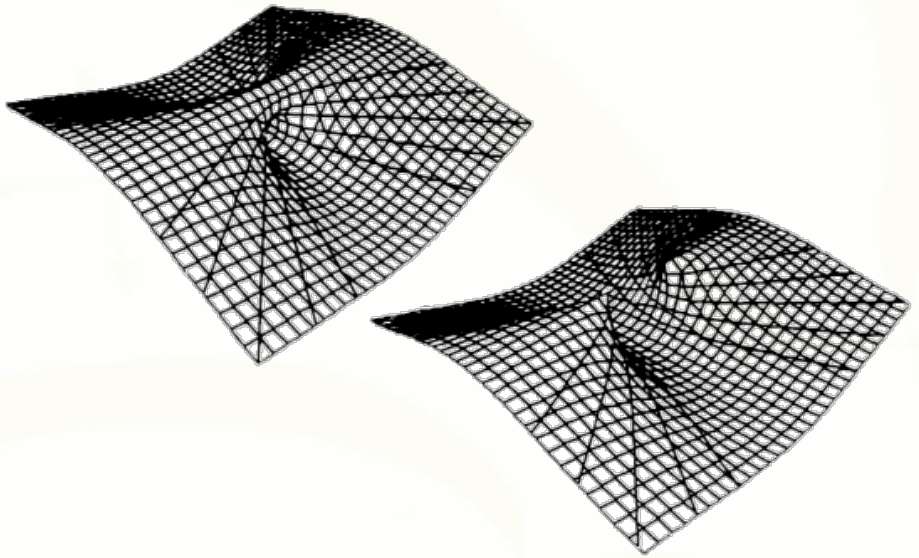


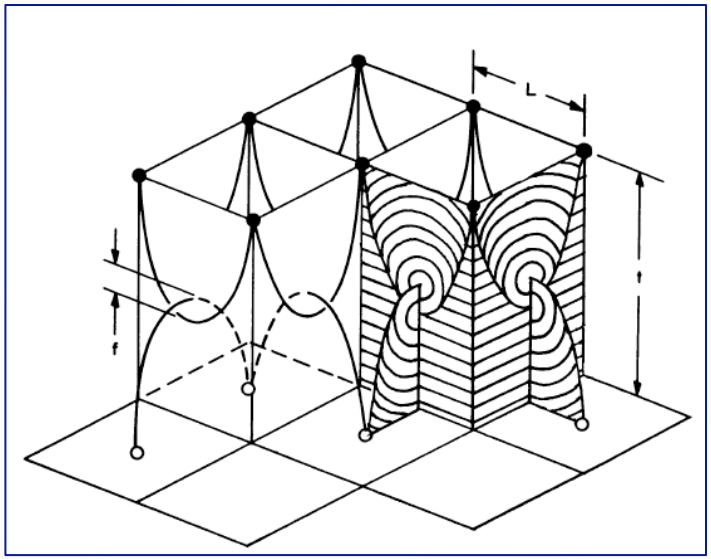





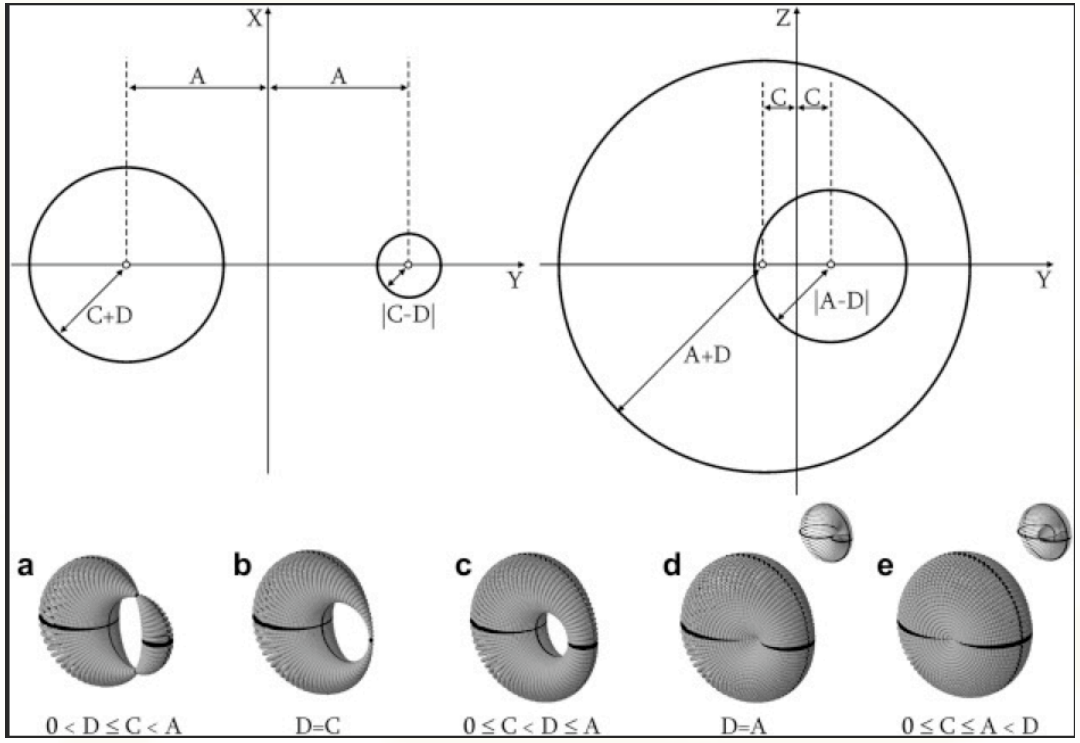
# cyclides of Dupain - parabolic

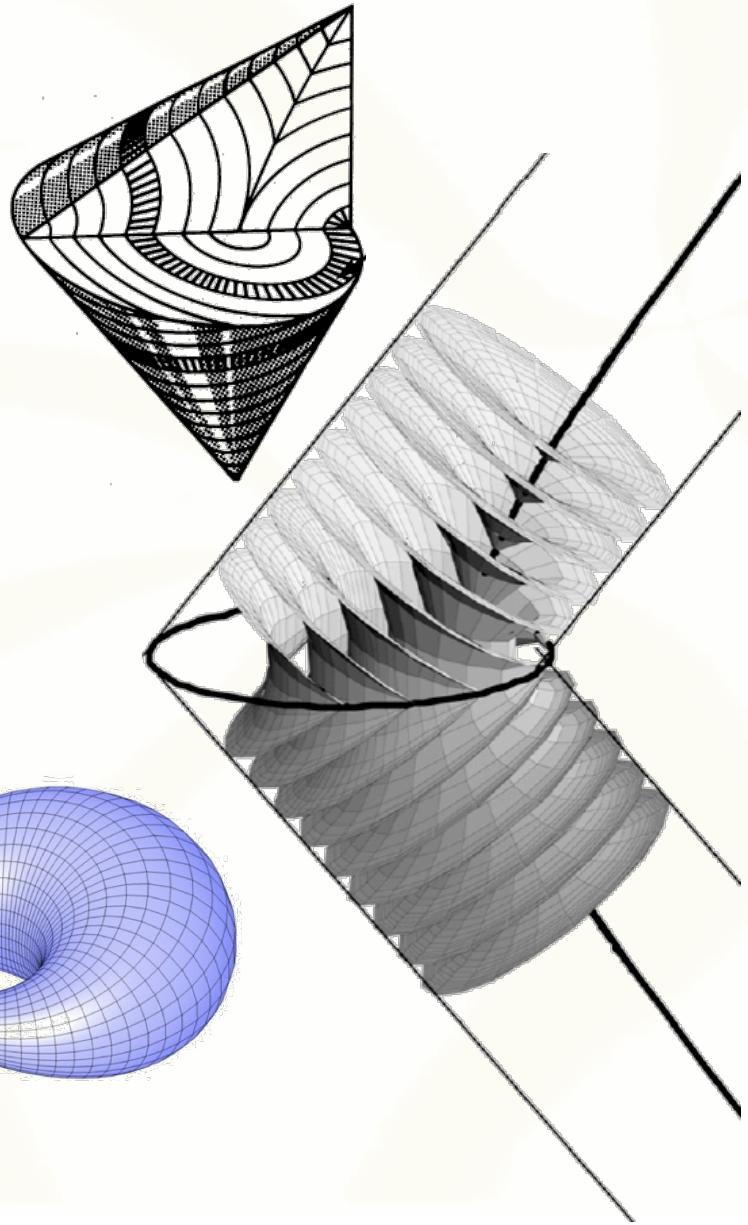


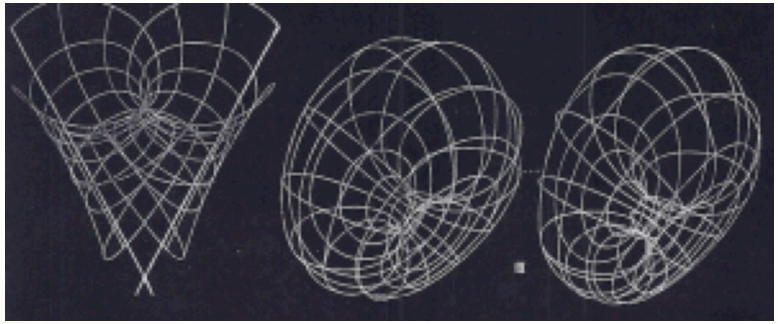





# cyclides of Dupain – ellipse / hyperbola



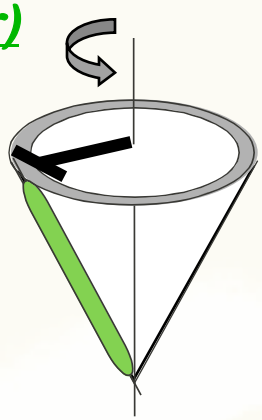


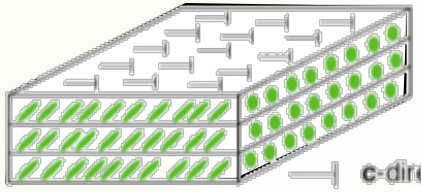


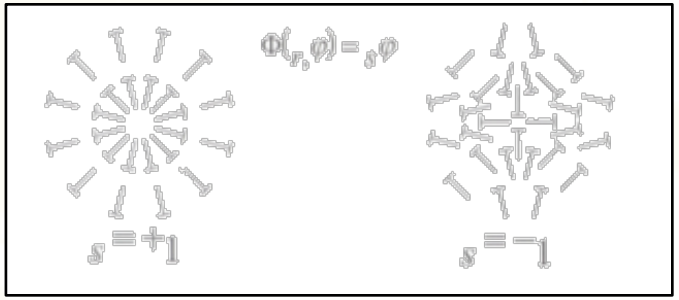
J.C. Maxwell from amazon.com

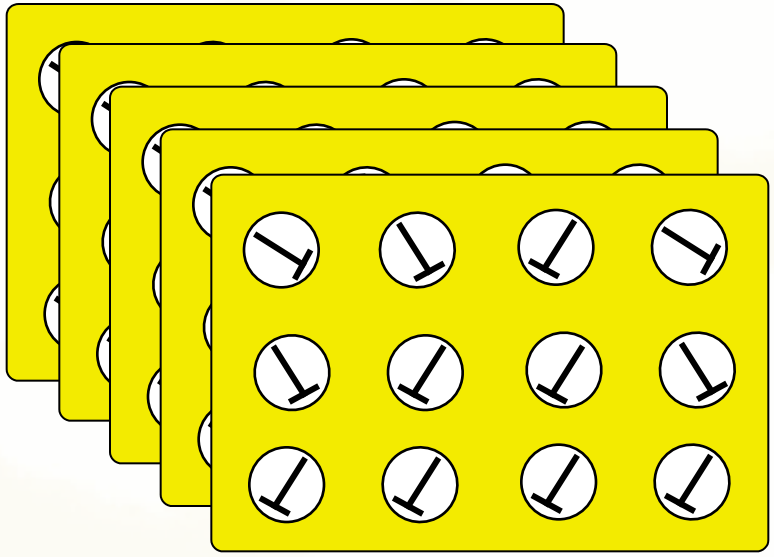
# smectic C

$\phi(r)$



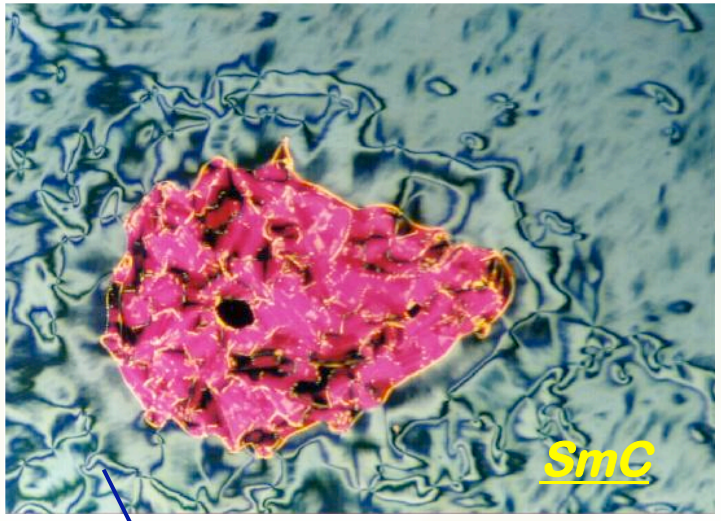


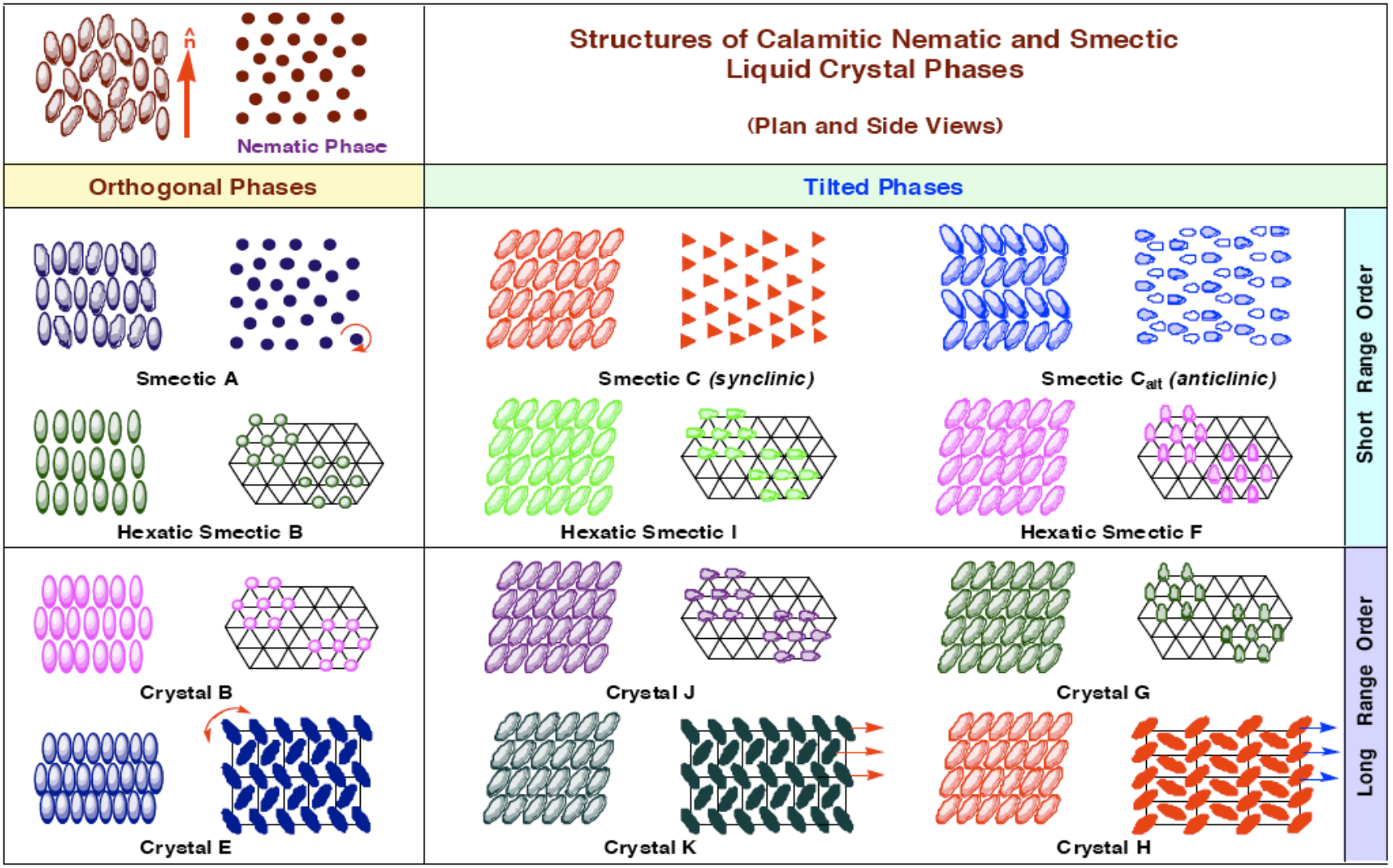
3D XY model

de Gennes (1972)



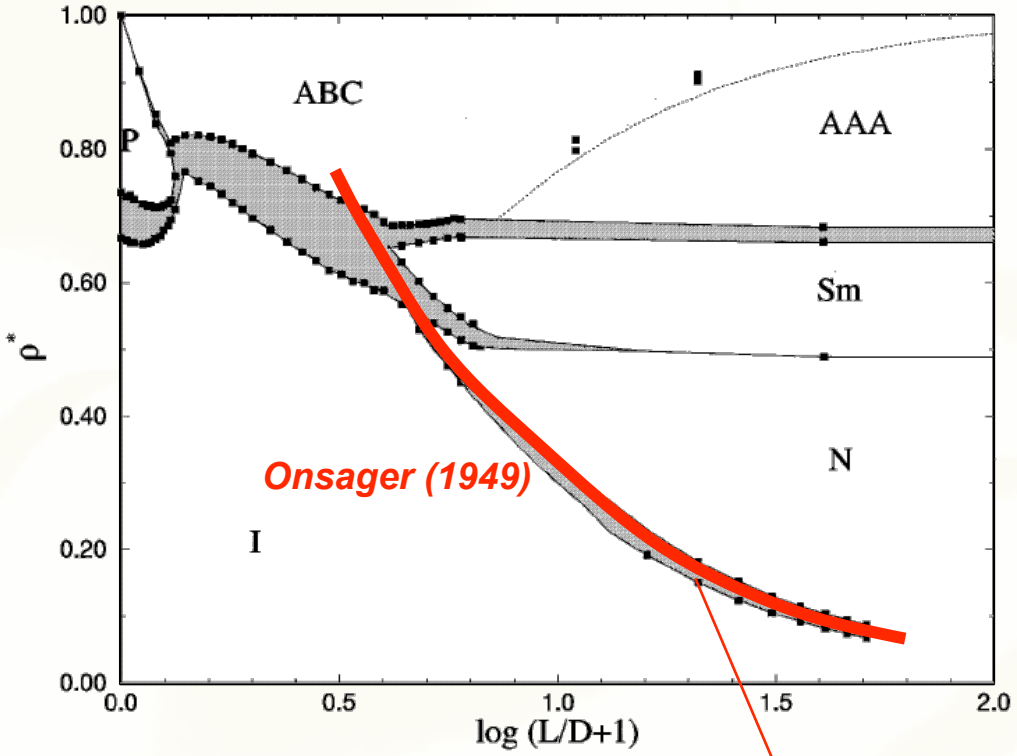

layers parallel to plates

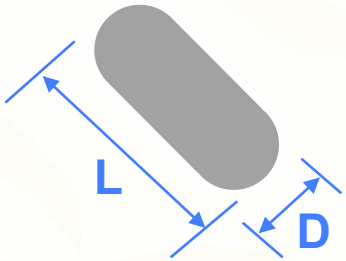
# calamitic liquid crystal phases



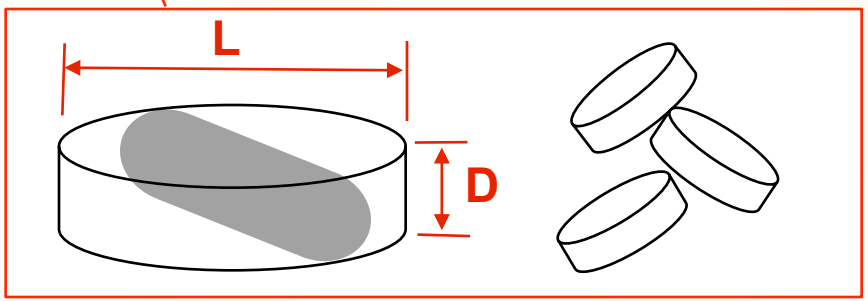
# molecular origins of smectics

## hard spherocylinders

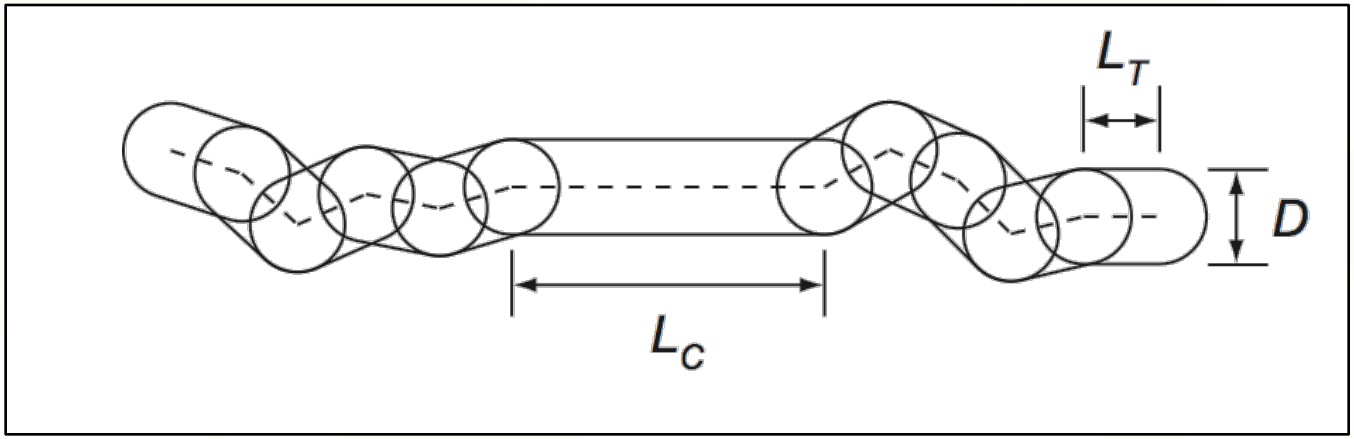


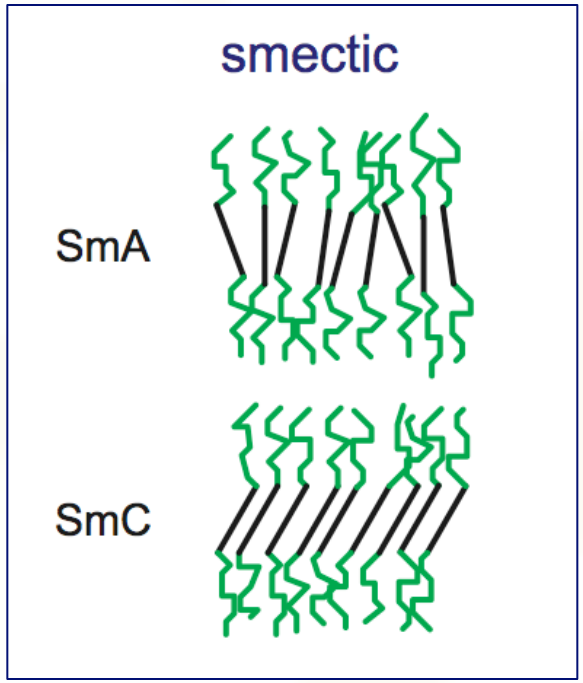

Bolhuis,
Frenkel, JCP (1997)



# *adding flexible tails…*

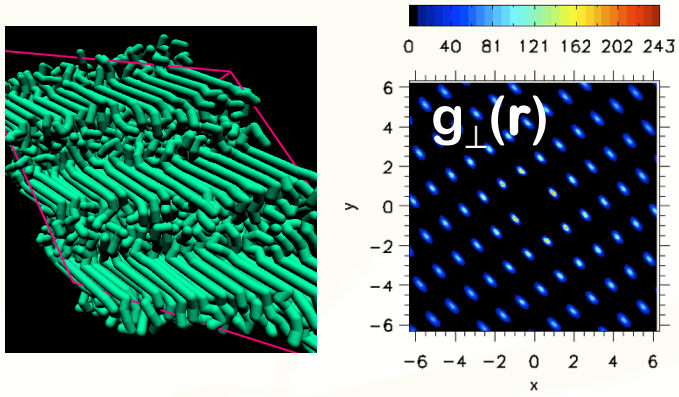



- *soft spherocylinder polymer with rigid core and flexible chains*
- *molecular flexibility controlled by bond angle bending spring constant* $K_{bend}$
- *studied using NPT MD simulation*



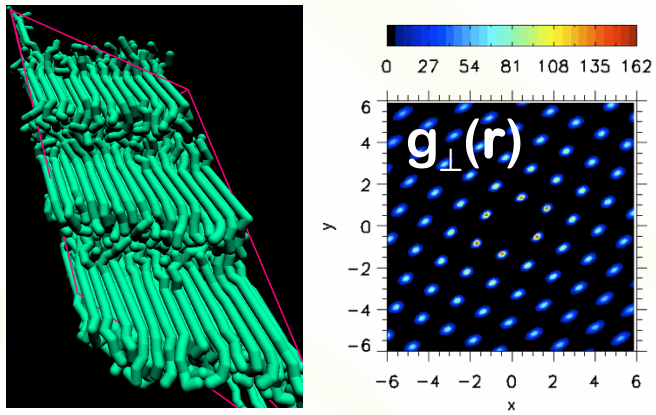
# *gives smectic phases*

## SmF



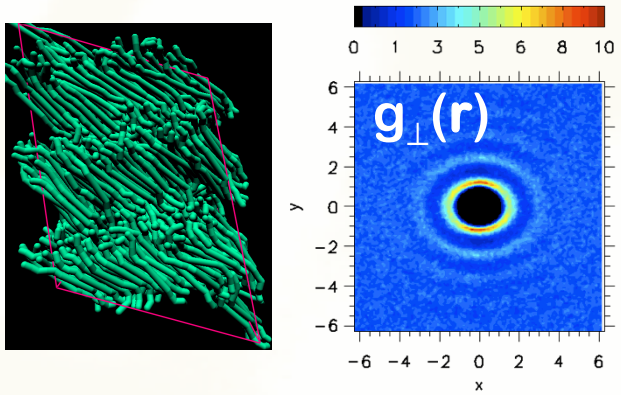

$\beta K_{bend} = 1/4,\ \beta P D^3 = 6$

## SmI



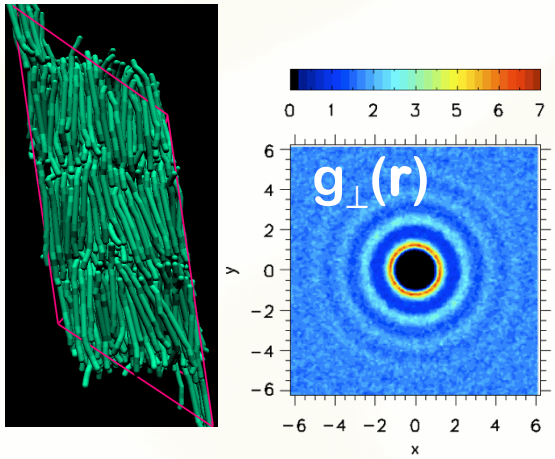

$\beta K_{bend} = 1,\ \beta P D^3 = 5$

## SmC



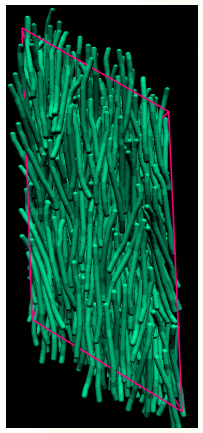

$\beta K_{bend} = 4,\ \beta P D^3 = 1.8$

## SmA



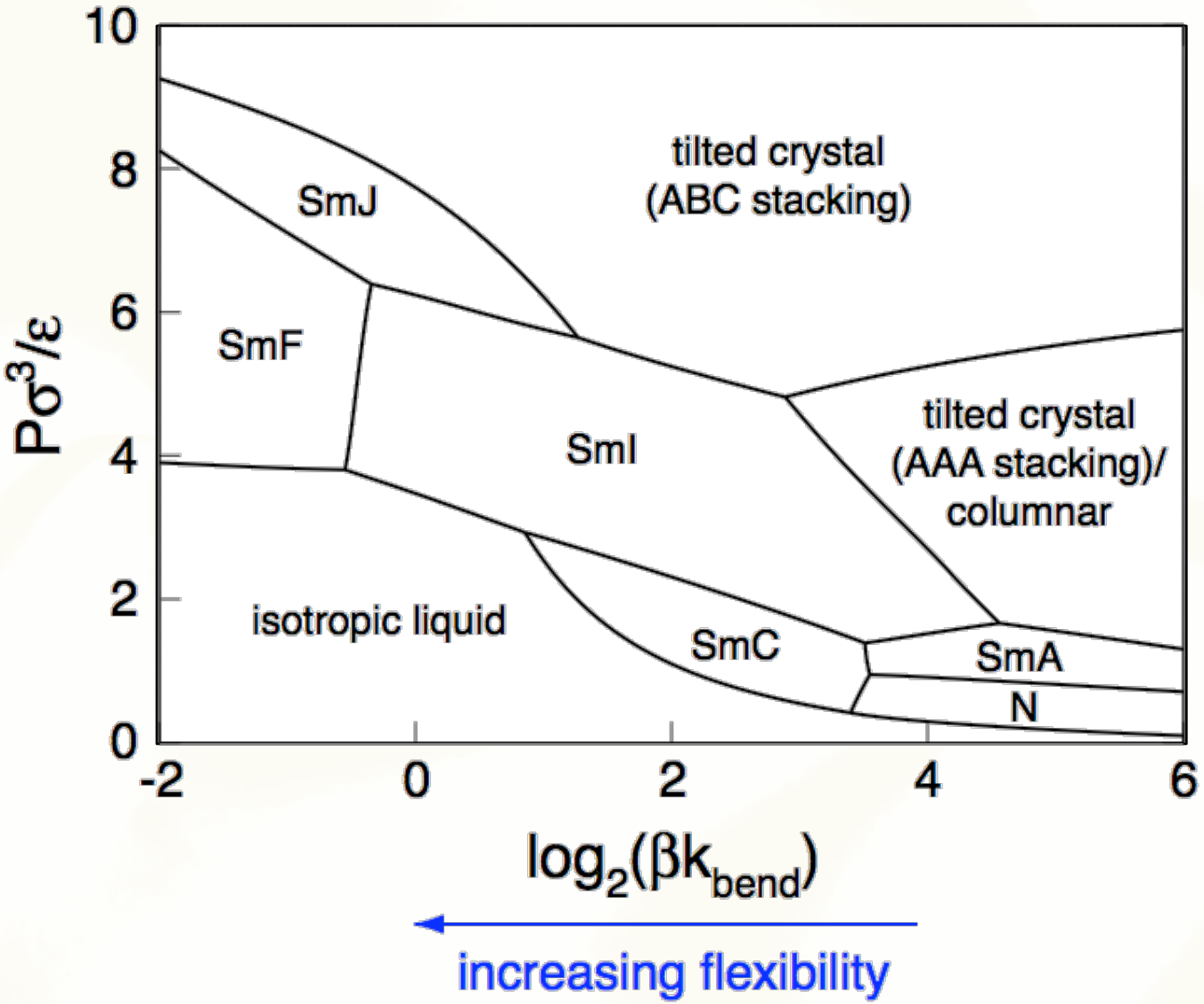

$\beta K_{bend} = 16,\ \beta P D^3 = 1.2$

## N

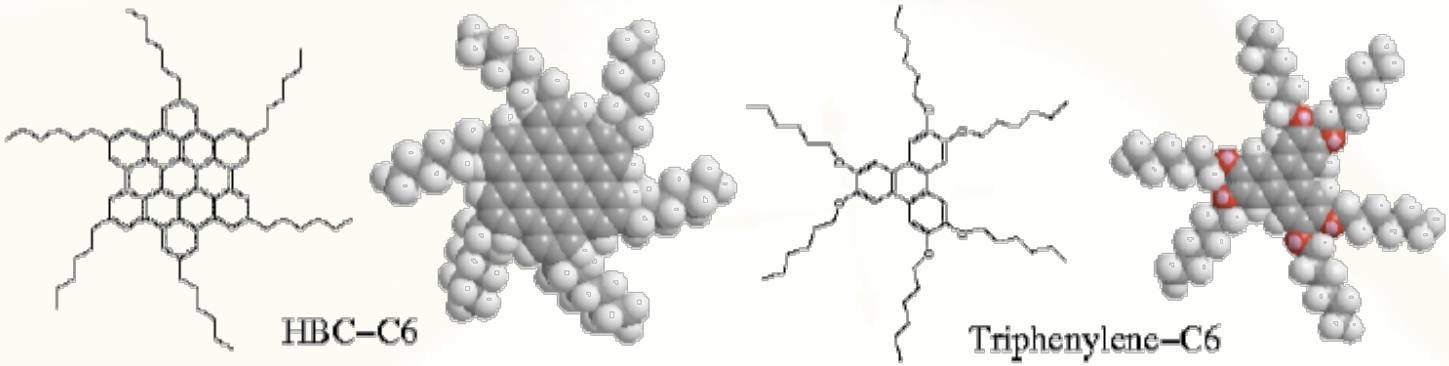


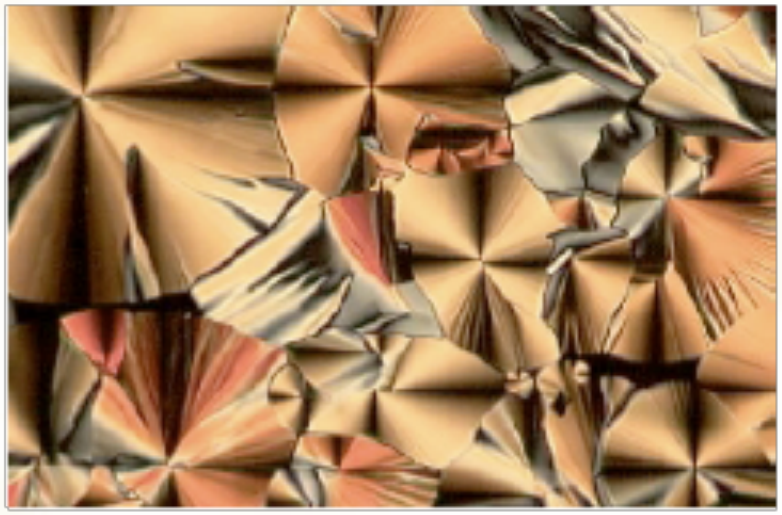
$\beta K_{bend} = 64,\ \beta P D^3 = 0.4$

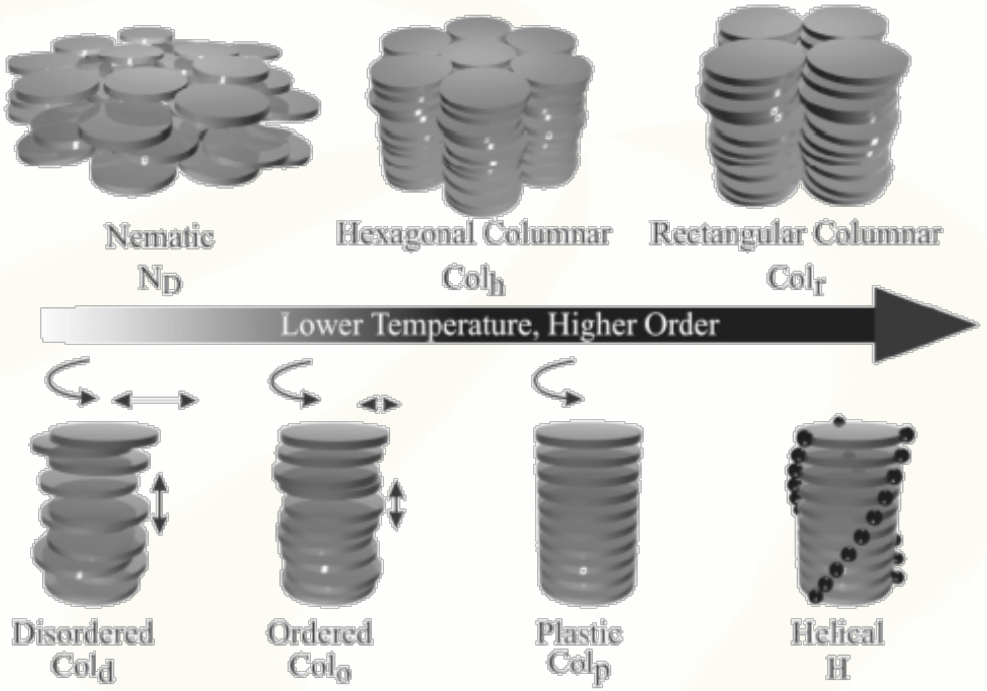
# *phase diagram of flexible-tail spherocylinders*



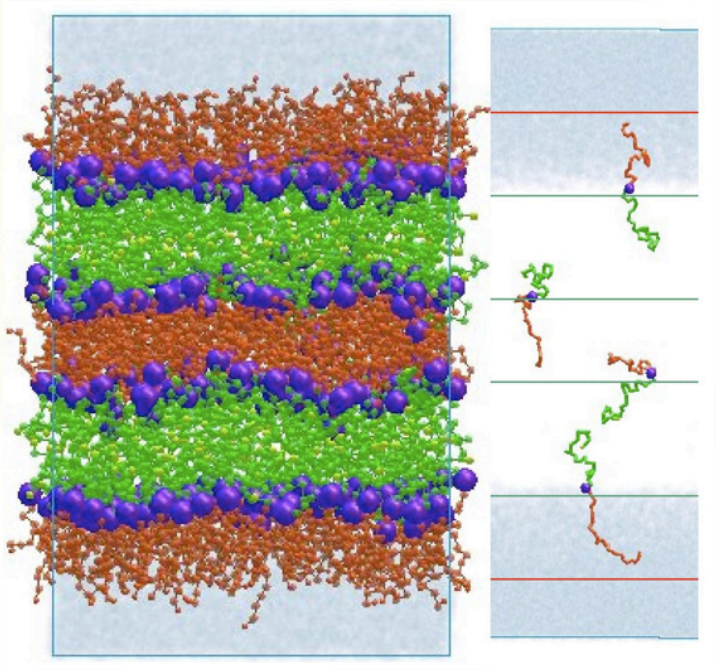
# discotic columnar phases

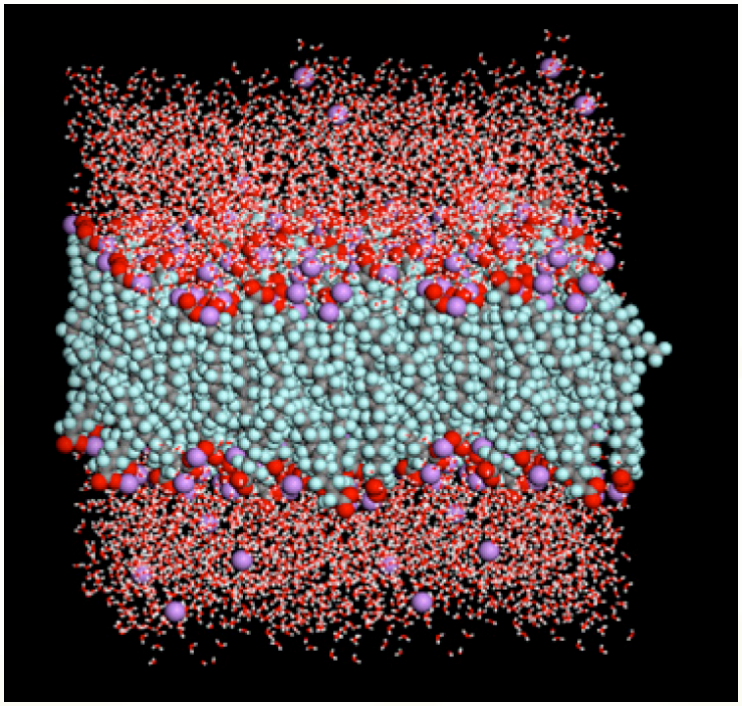


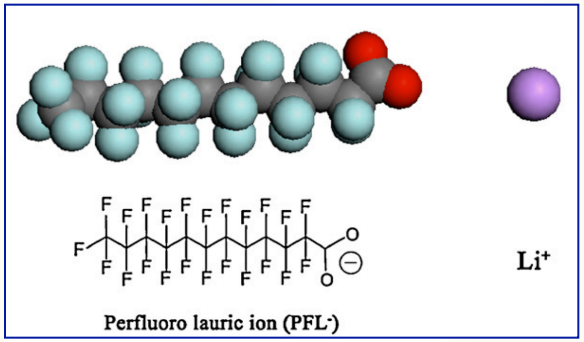


# pathways - fluid interfaces generate anisotropy





*hydrophobic*
*hydrophillic*
*water*

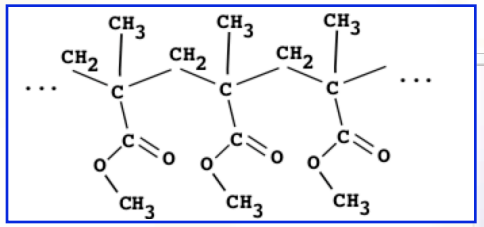



*G. Srinivas, IBM Almaden*

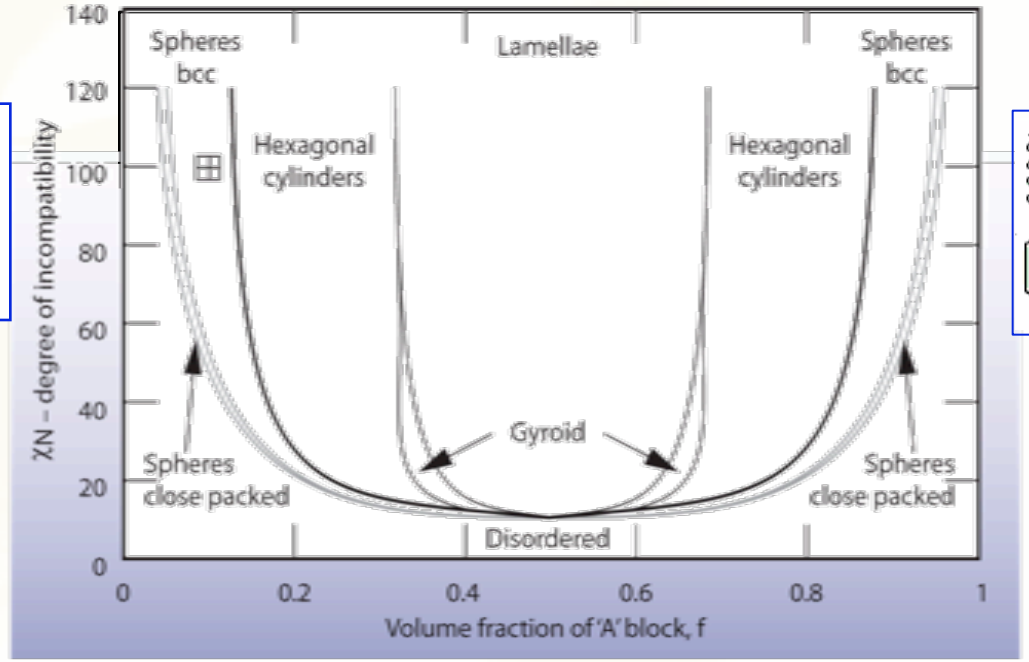
*Long et al. J Fluor Chem (2012)*

# block copolymers

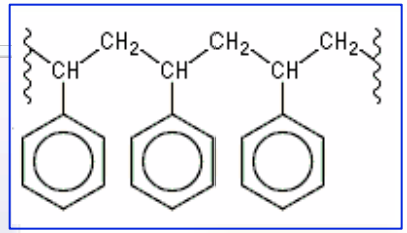

Controlling Order in Block Copolymer Thin Films for Nanopatterning Applications



PMMA

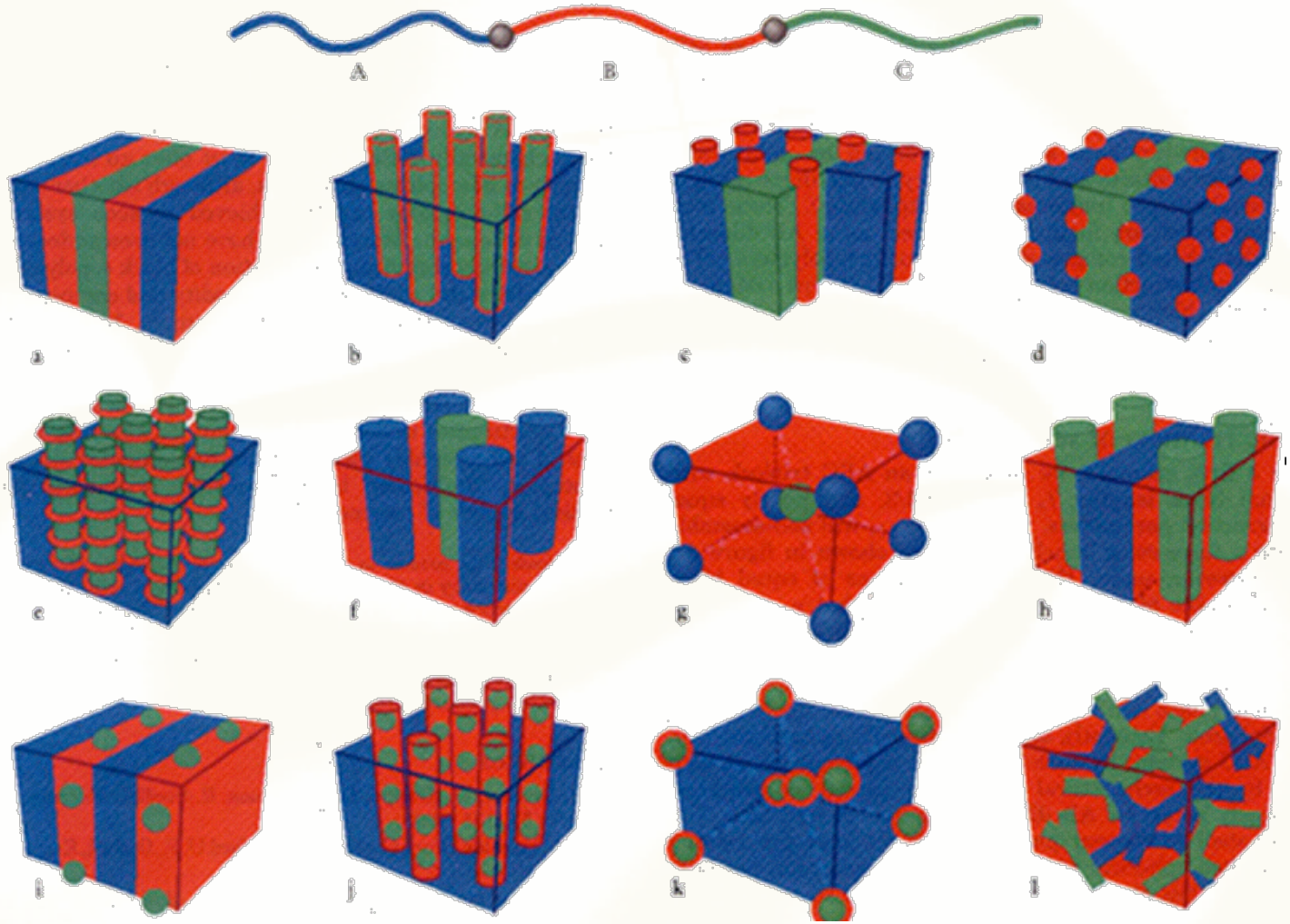



Phase diagram for polystyrene and PMMA, predicted using self-consistent mean field theory

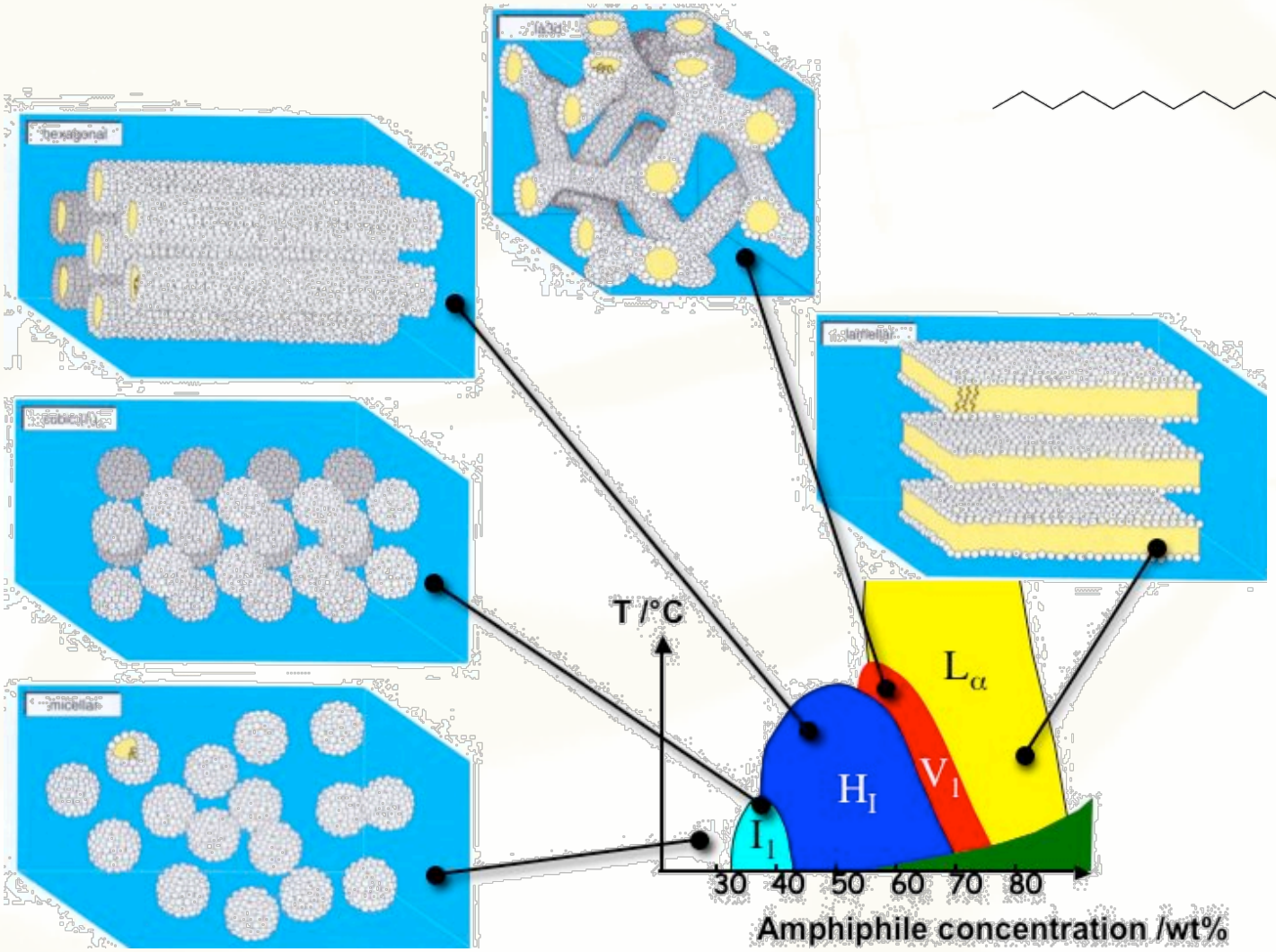


polystyrene

# triblock copolymers

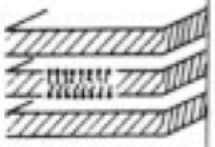
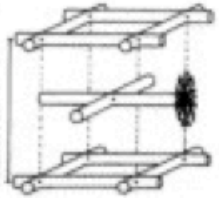
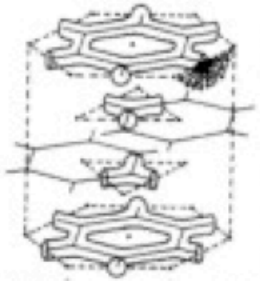
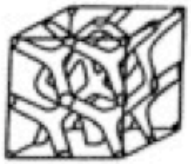
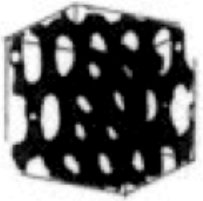
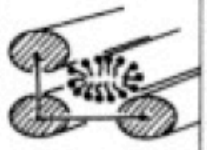
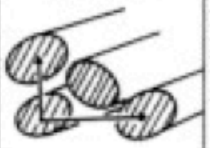


# lyotropics

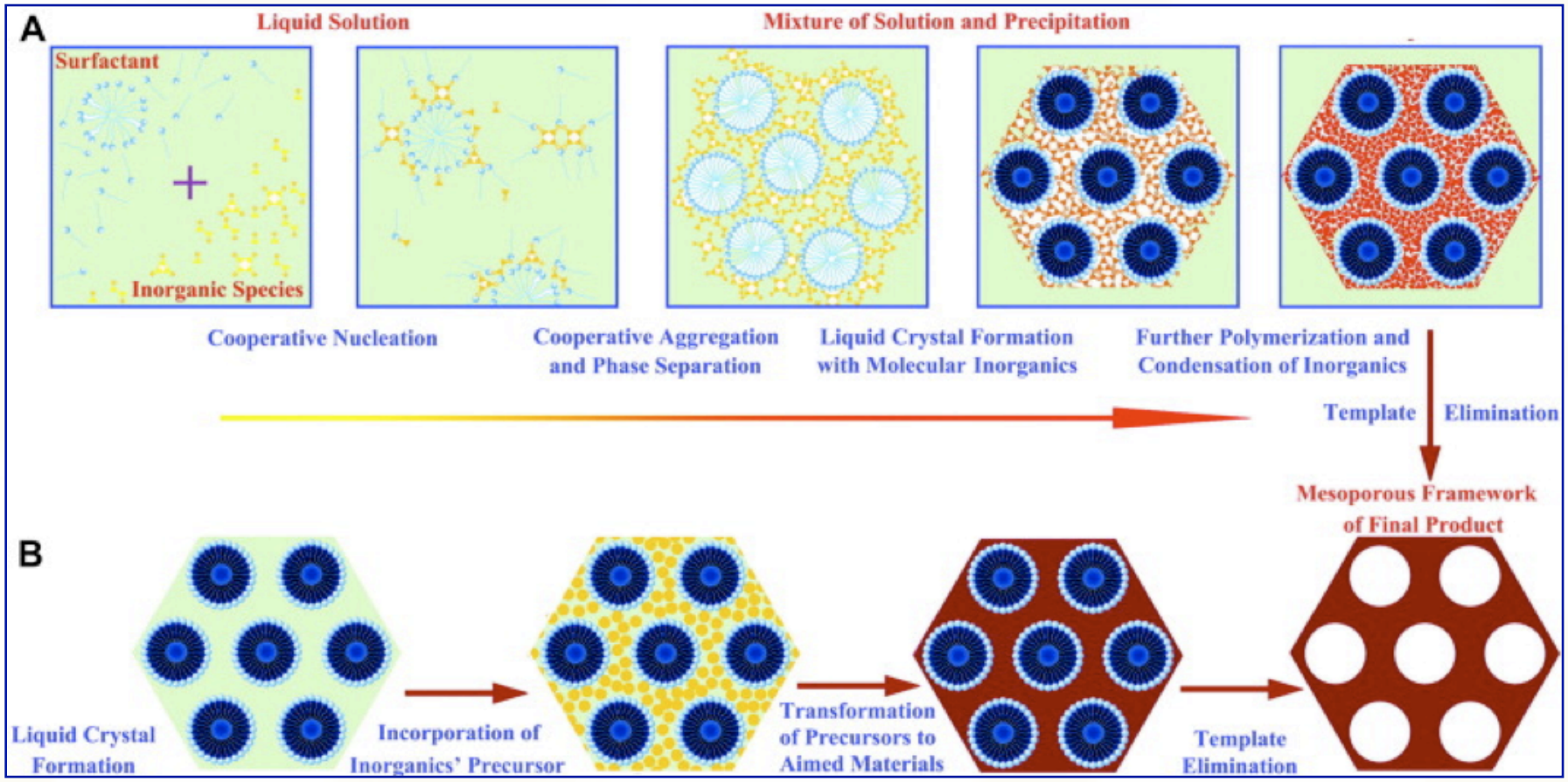

hexagonal
T /°C
$L_\alpha$
$H_I$
$V_I$
$I_I$
30 40 50 60 70 80
Amphiphile concentration /wt%


O
O
S
O
O⁻ Na⁺

# lyotropic variations

| Flat layers | Undulated layers | Perforated layers | Bicontinuous networks | Ribbon-phases | Columns |
|---|---|---|---|---|---|
|  SmA $L_\alpha$ |  Egg-cartoon  Undulated  Superundulated |  Random mesh  Square mesh  Hexagonal mesh  Tetragonal *I4mm*  Rhombohedral *R3m* |  *Im3m*  *Ia3d*  *Pn3m*  *R3c* |  *c2mm*  *p2gg* |  $Col_h$ *p6mm* |

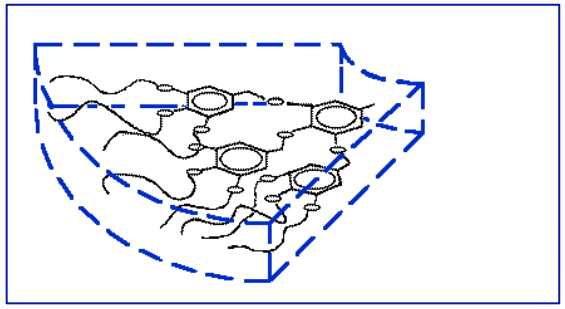
# *nanoporous silica from lyotropic liquid crystals*

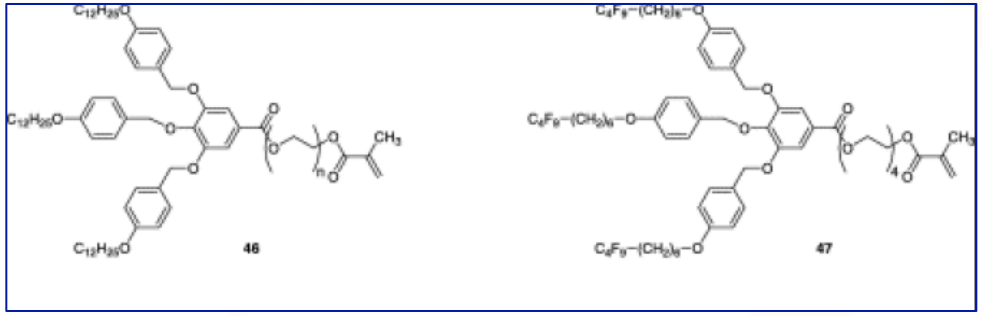


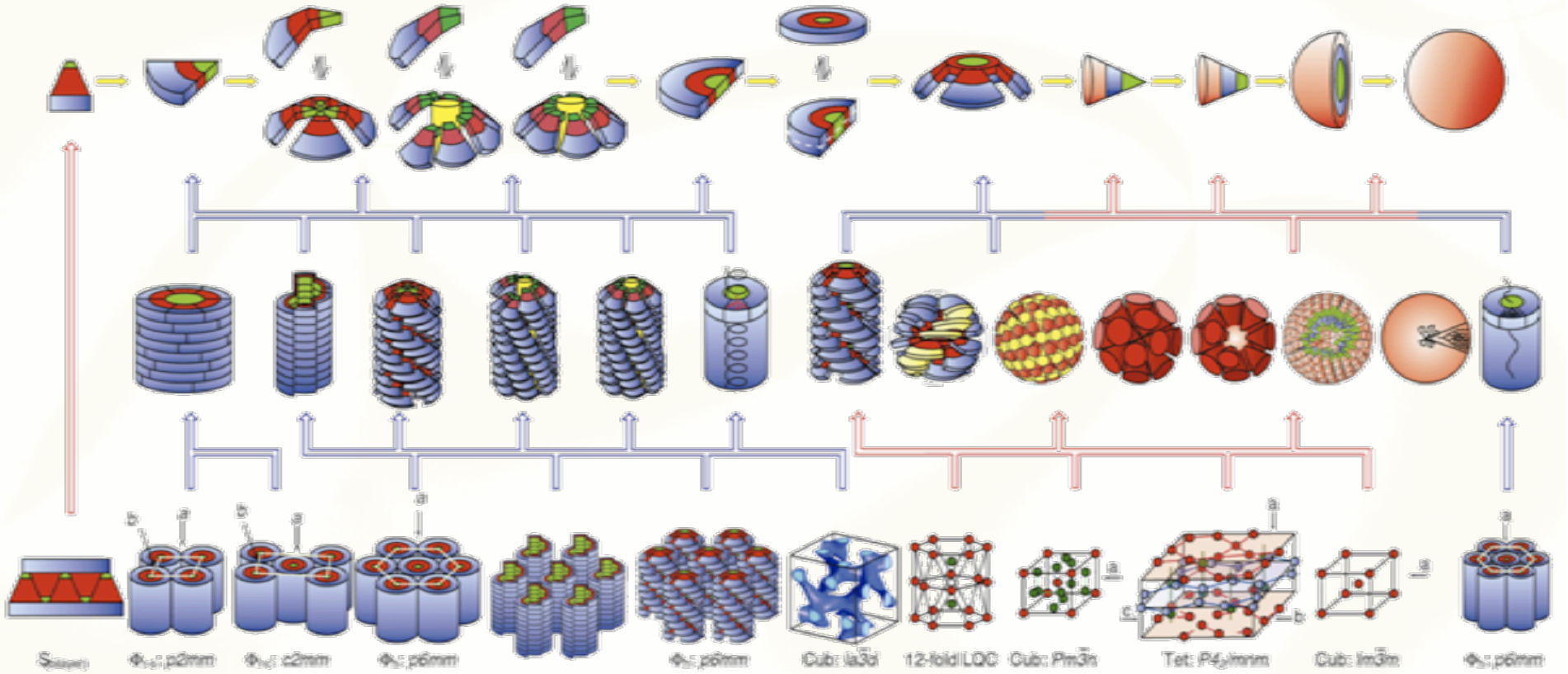

1. Title: **ORDERED MESOPOROUS MOLECULAR-SIEVES SYNTHESIZED BY A LIQUID-CRYSTAL TEMPLATE MECHANISM**
Author(s): KRESGE CT; LEONOWICZ ME; ROTH WJ; et al.
Source: NATURE Volume: **359** Issue: **6397** Pages: **710-712** DOI: **10.1038/359710a0** Published: **OCT 22 1992**
Times Cited: **9,613** (from Web of Science)

***~ 10 of the 20 most cited liquid crystal papers***

# hierarchical self assembly

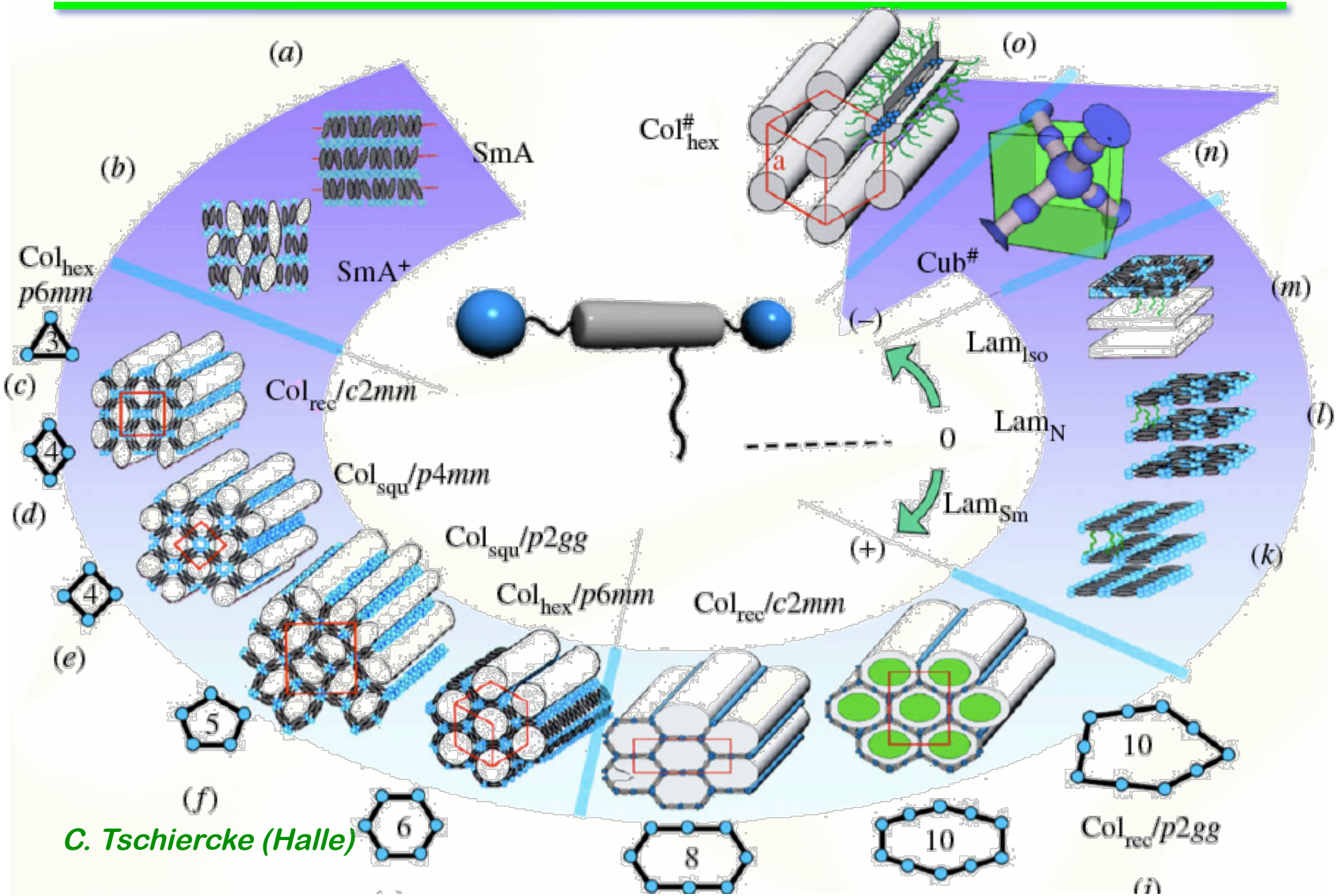




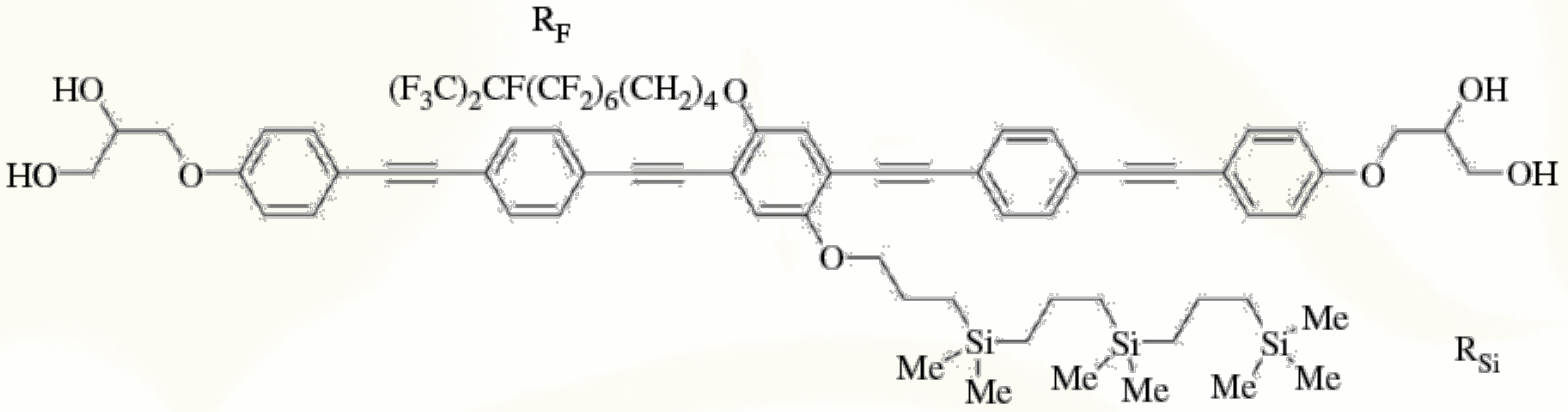

V. Percec (Penn)

# bola-amphiphiles

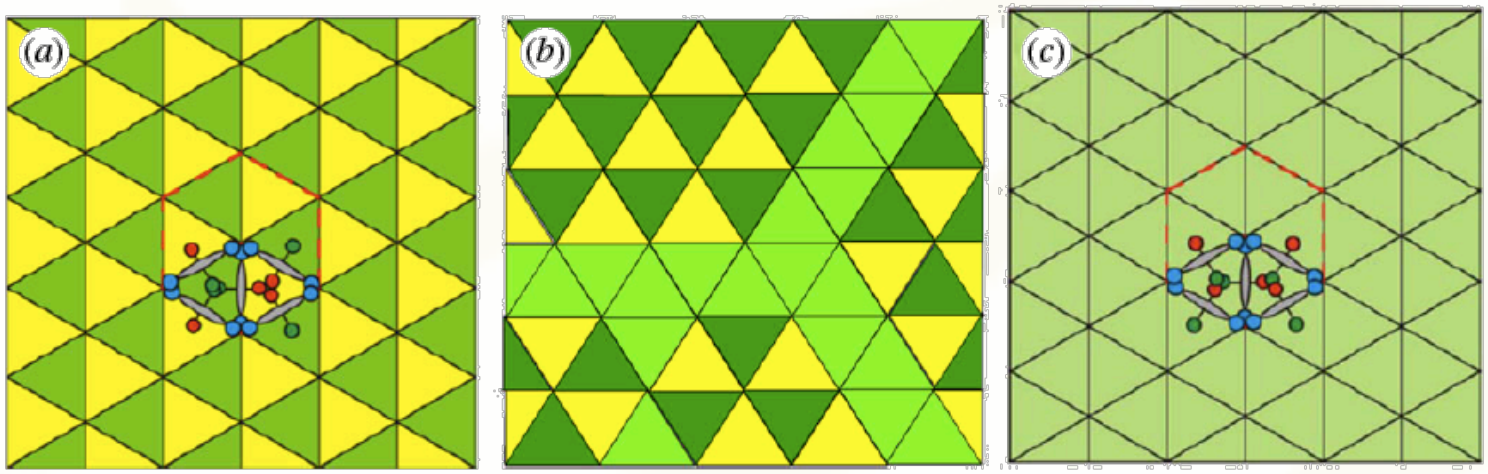



C. Tschiercke (Halle)

# bola-amphiphiles



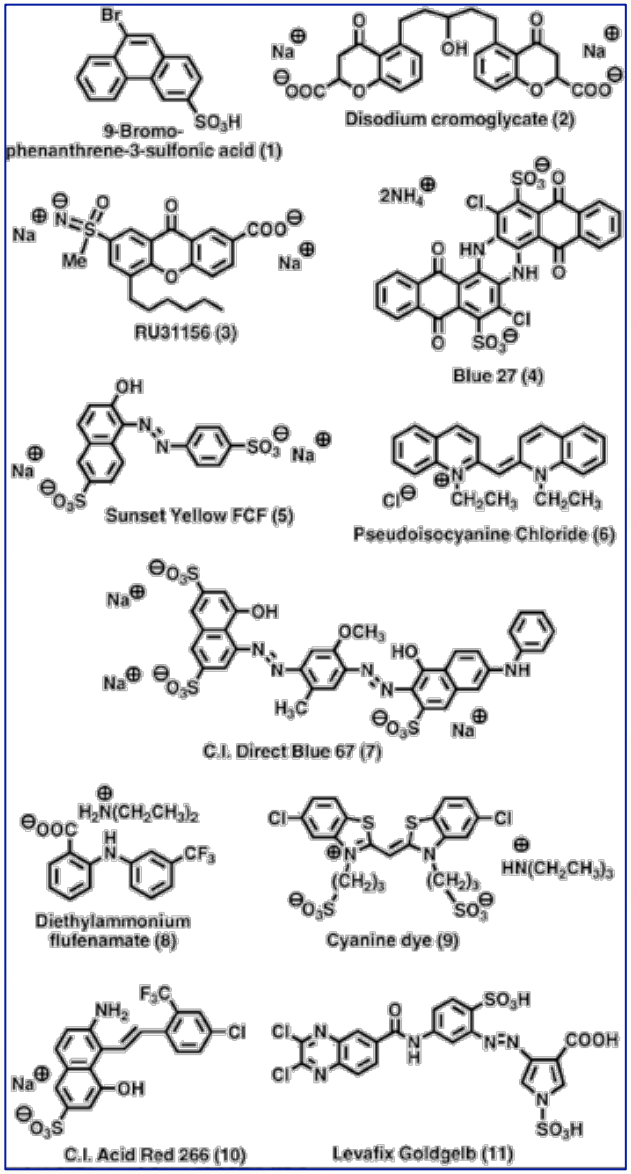

Cr 83 $Col_{hex}/p3m1$ 85 $Col_{hex}/p6mm$ 189 Iso (°C)

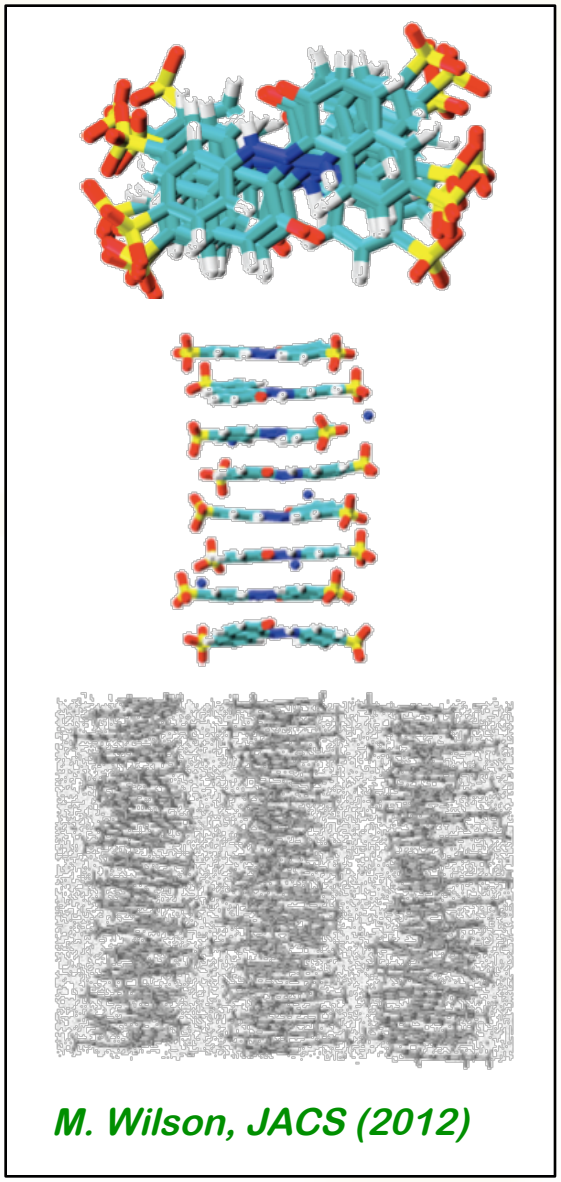


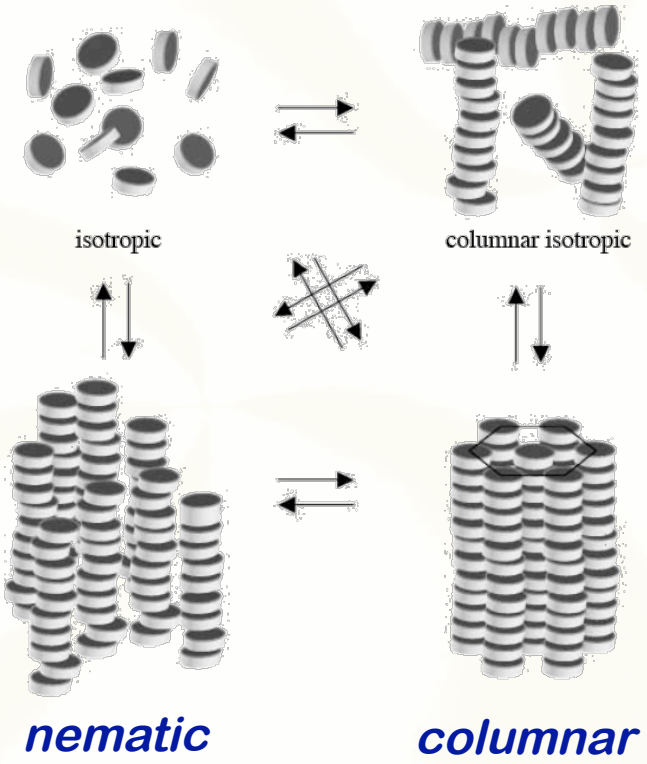

$Col_{hex}/p3m1$ $Col_{hex}/p6mm$ $Col_{hex}/p6mm$

*C. Tschiercke (Halle)*

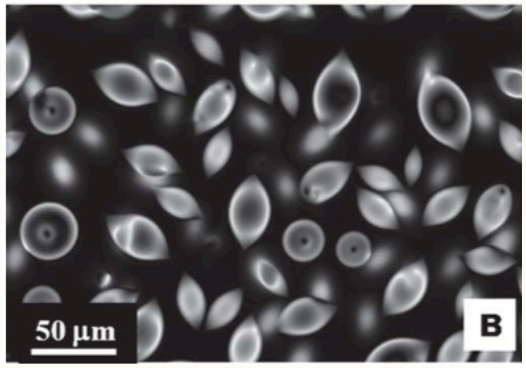
# chromonic liquid crystals

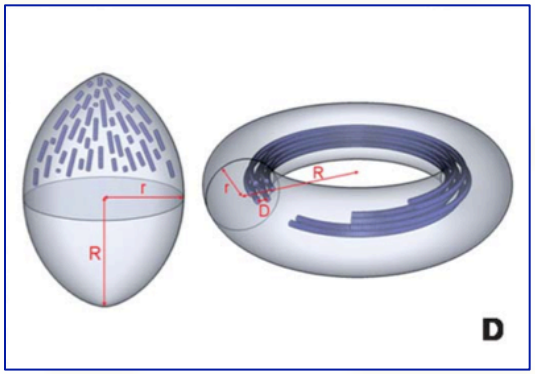


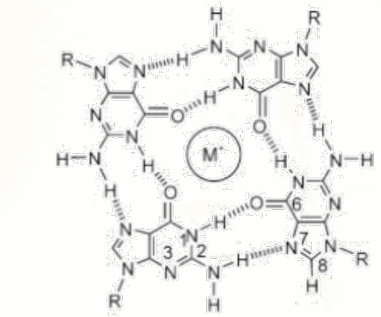



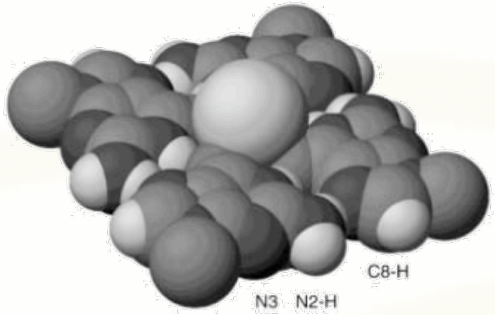
# chromonic liquid crystals



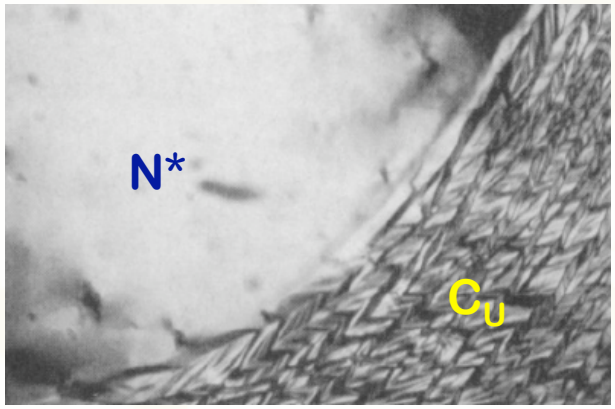




Lavrentovich (Kent State)

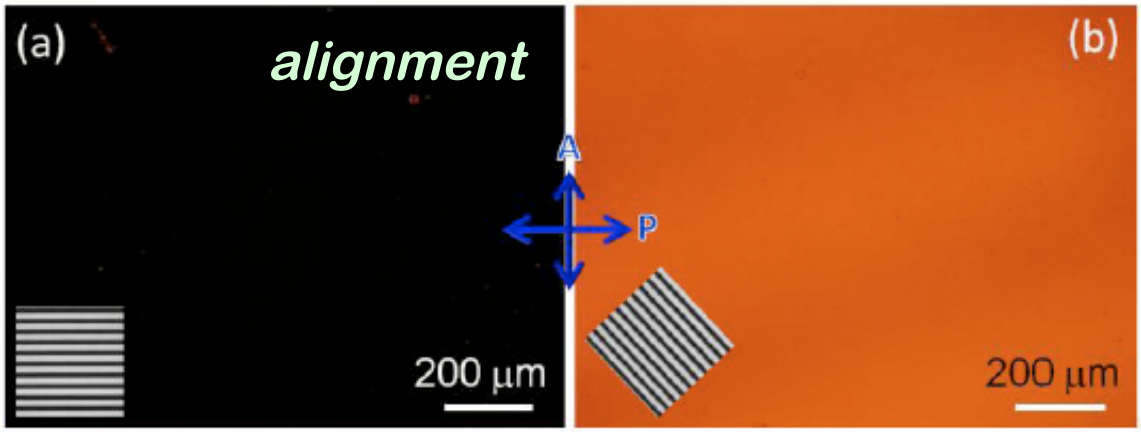


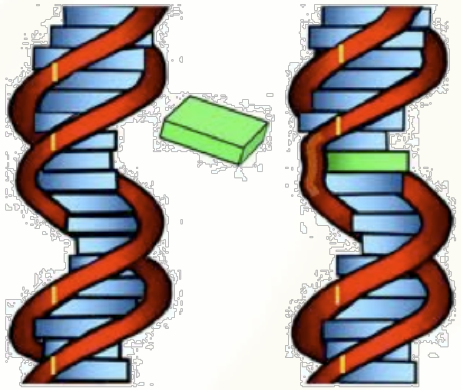




## guanine quartets




Spada, JACS (1989)



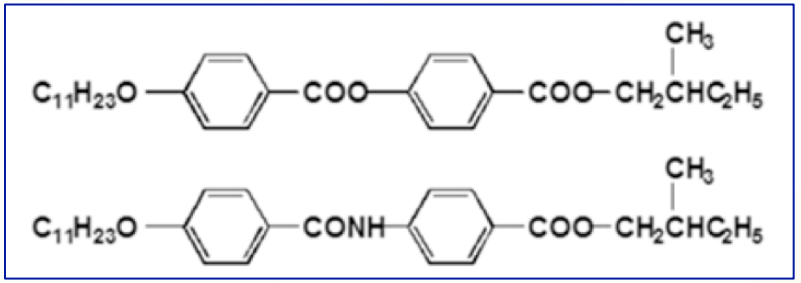



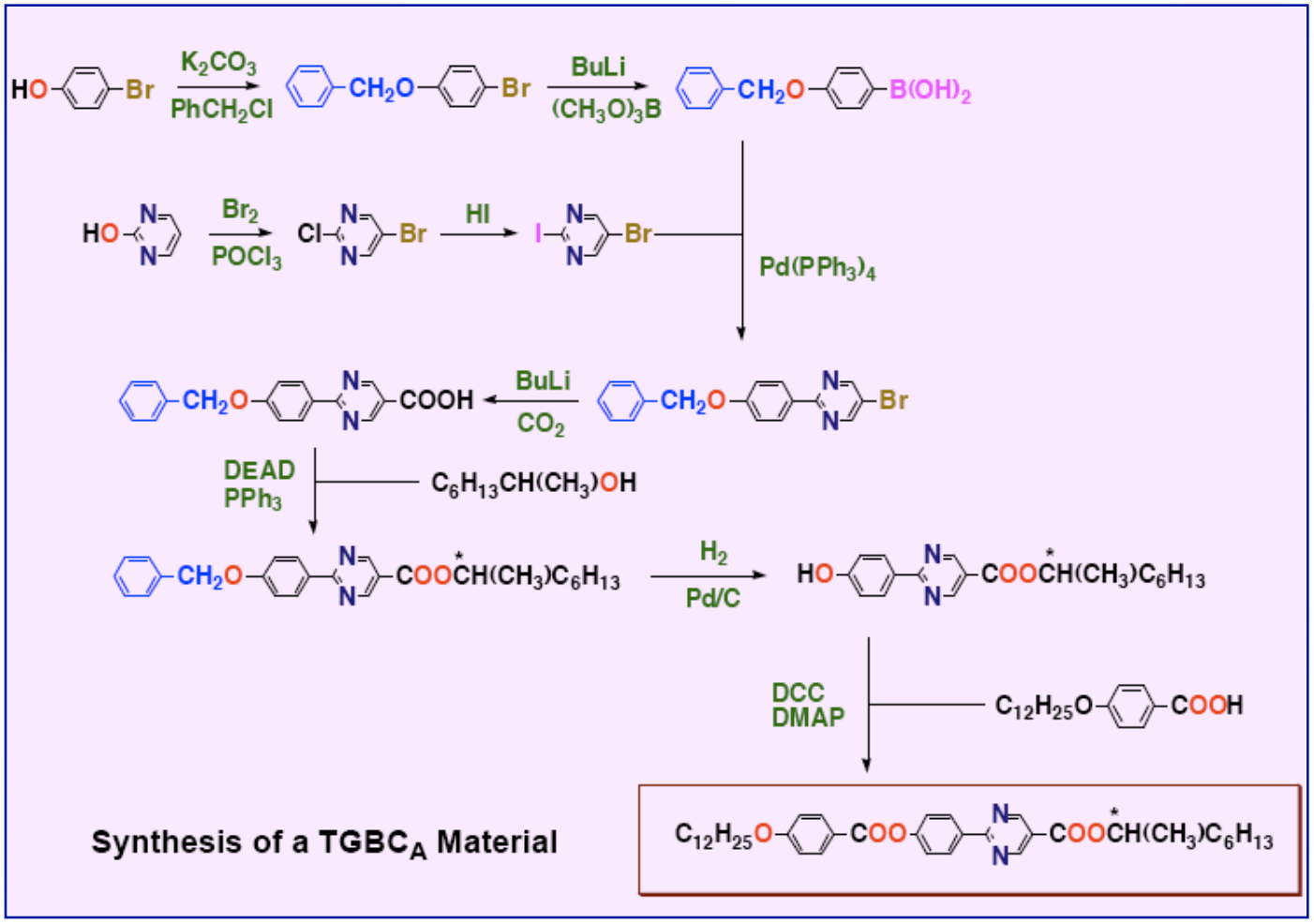
DNA

# molecules

*Iso – Smectics - Xtal*

*Iso - Xtal*




*J. Goodby (York)*