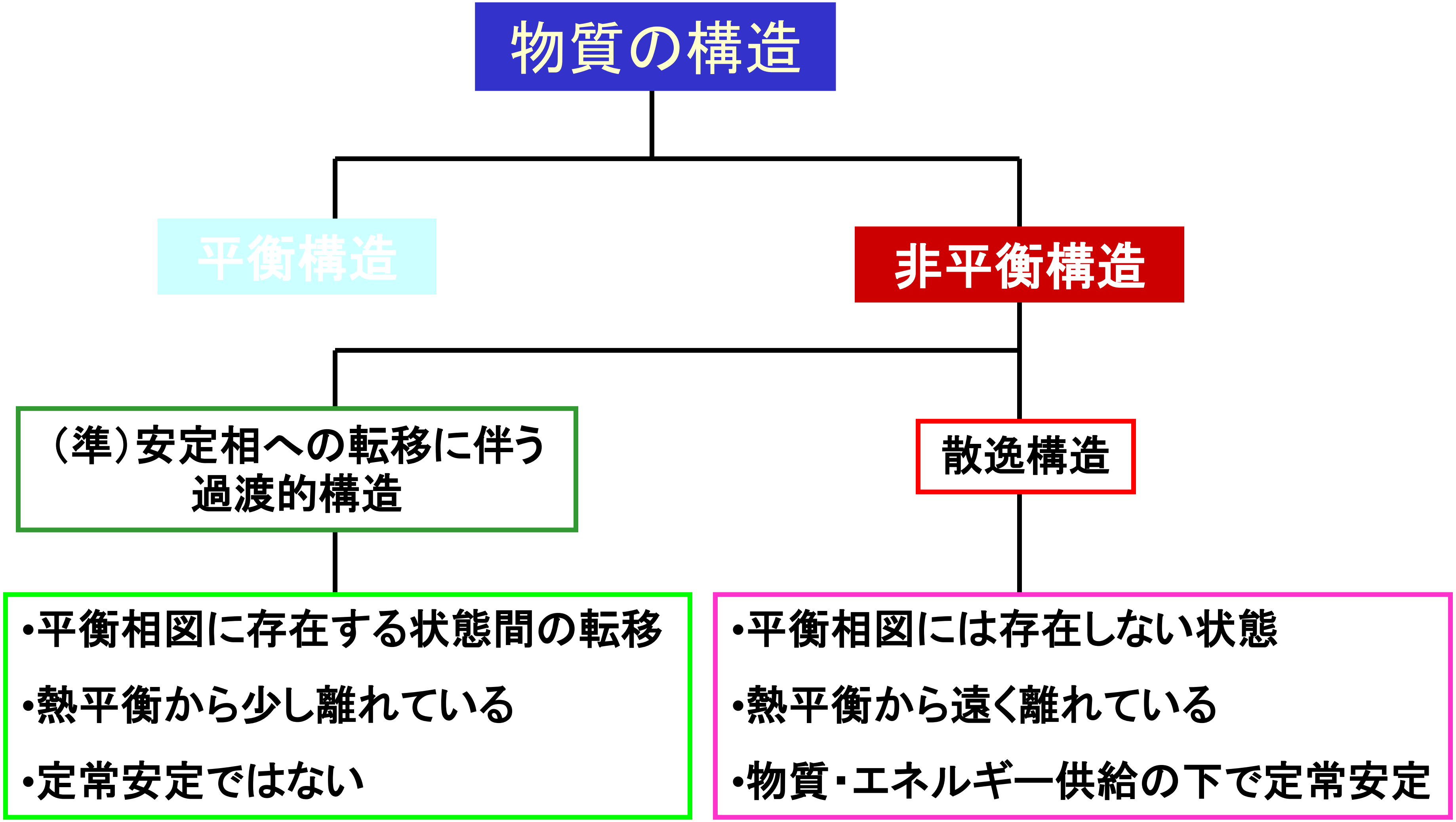
基研研究会2011 非平衡系の物理—ミクロとマクロの架け橋—

湯川記念館パナソニックホール 2011年8月19日

液晶超薄膜に微弱外場で誘起される非平衡構造

多辺由佳

早稲田大学 先進理工学術院
物理学及応用物理学専攻



物質の構造

平衡構造

非平衡構造

（準）安定相への転移に伴う
過渡的構造

散逸構造

- 平衡相図に存在する状態間の転移
- 熱平衡から少し離れている
- 定常安定ではない

- 平衡相図には存在しない状態
- 熱平衡から遠く離れている
- 物質・エネルギー供給の下で定常安定

散逸構造

希薄系

（要素間の直接相互作用：弱）

入力	出力
熱	ベナール対流
電場	液体の対流ロール
	液晶の電気流体力学的不安定性
光	レーザー発振
化学反応	BZ反応 

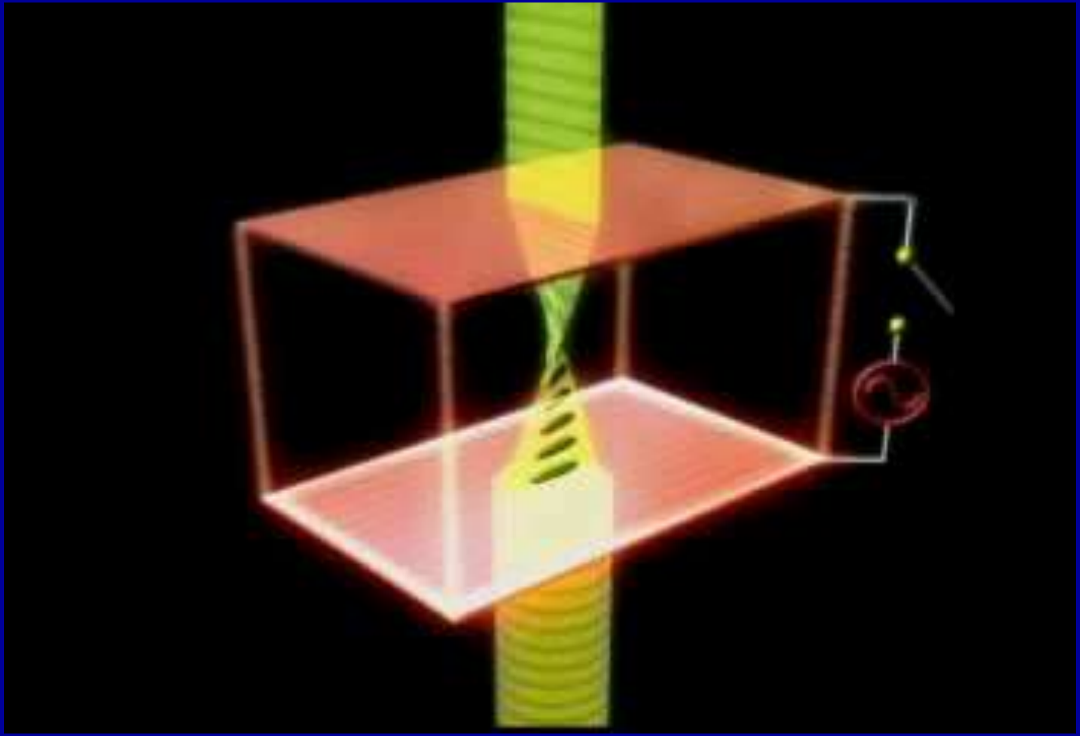
凝縮系

（要素間の直接相互作用：本質的）

入力	出力
電気信号	脳の情報伝達系
化学反応	生体内の代謝
光	液晶単分子膜の配向波
化学ポテンシャル	キラル液晶分子集団歳差運動

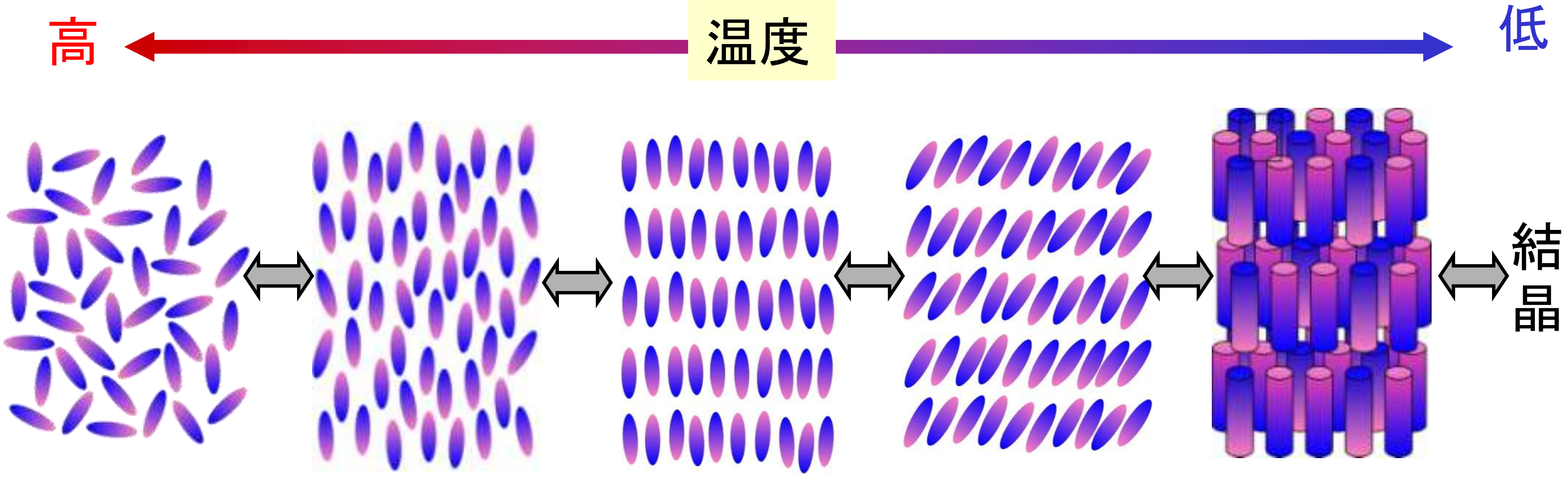
（低分子）液晶の特徴　１

- 構造・光学異方性 ——→ 表示パネルへの応用
- 高い流動性（棒状低分子の非化学結合）



（低分子）液晶の特徴　２

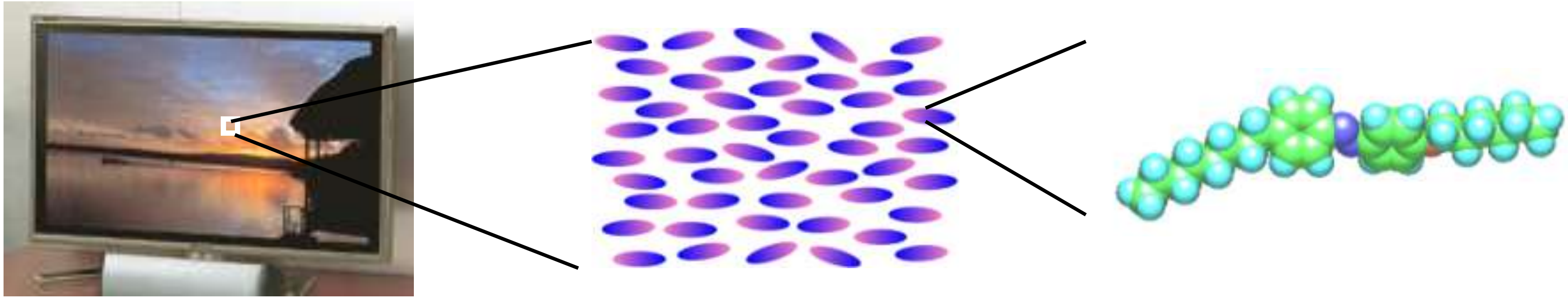
- 多彩な相転移と高次構造
- 次元性、トポロジー、ゆらぎ



高 ← 温度 → 低

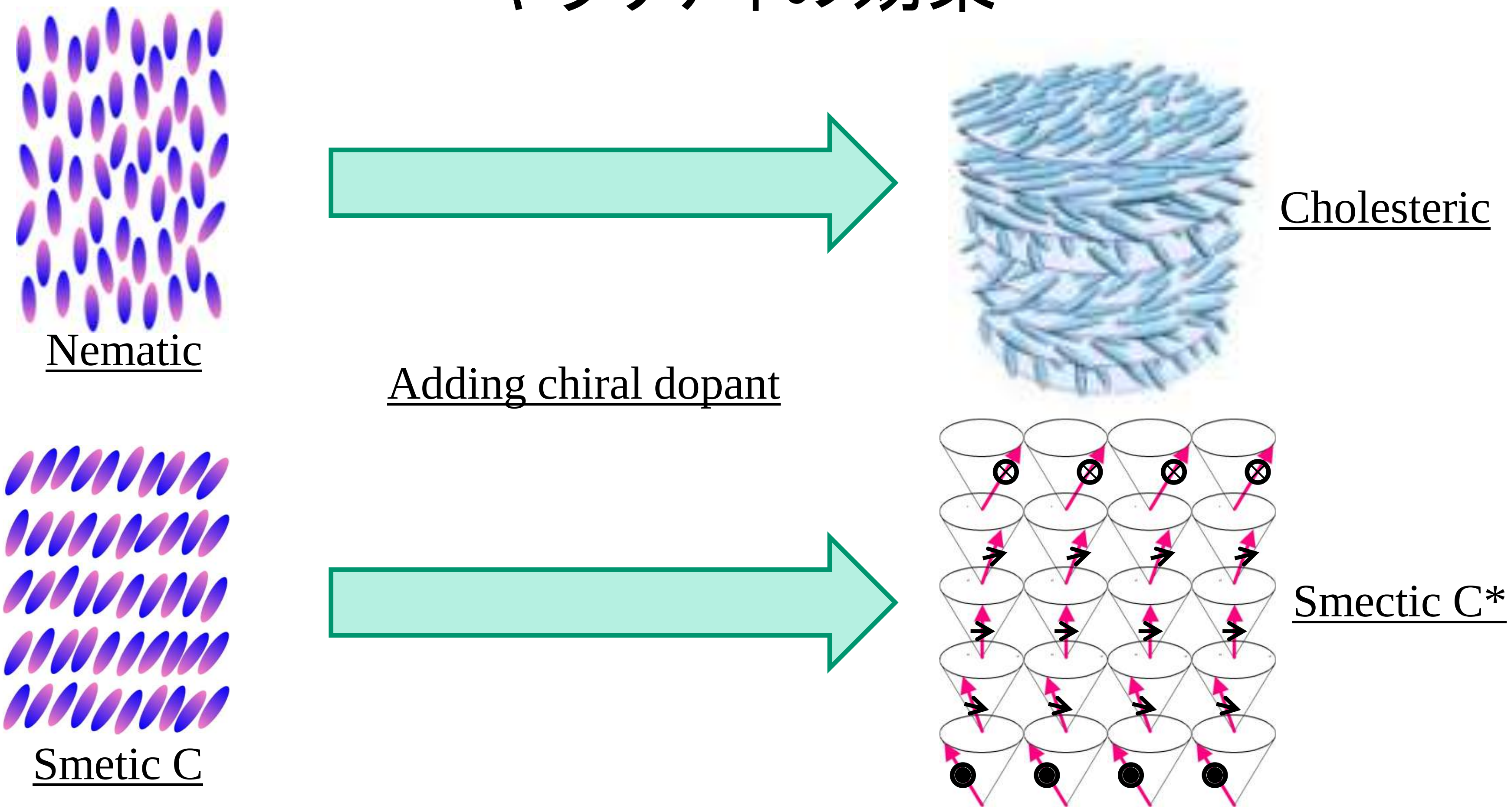
等方液体 ⇔ ネマチック ⇔ スメクチックA ⇔ スメクチックC ⇔ スメクチックE ⇔ 結晶

分子構造とマクロ物性



構成分子の構造 → 液晶の相系列、配向弾性、粘性

キラリティの効果



Nematic

Adding chiral dopant

Cholesteric

Smetic C

Smectic C*

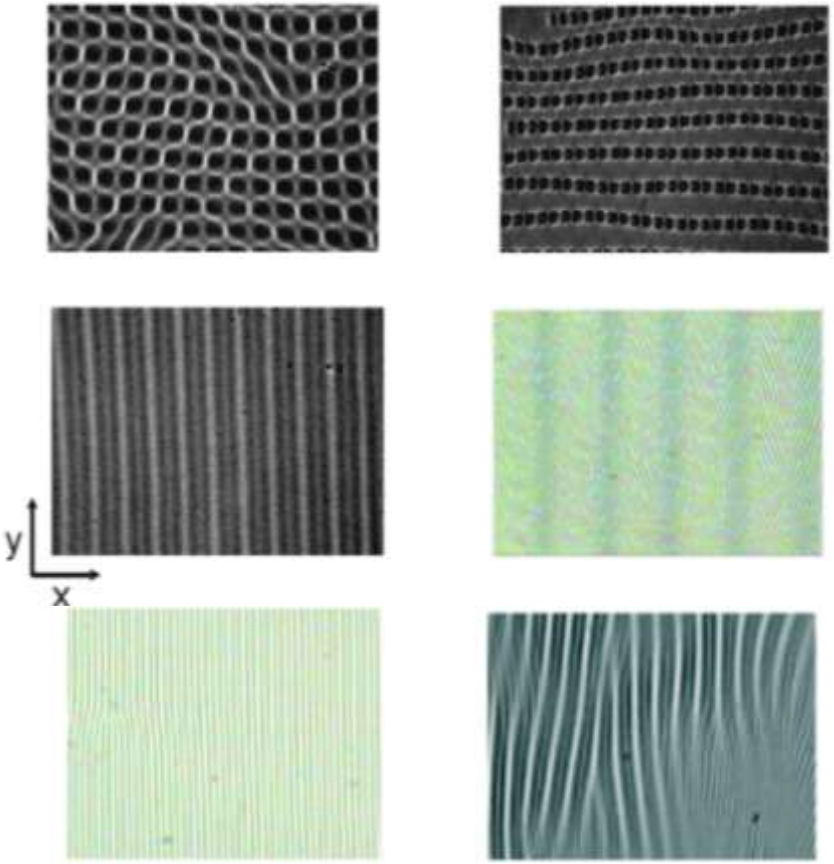
mirror symmetry is broken → Helix, ferroelectricity

構成分子の対称性 → マクロな配向構造の対称性

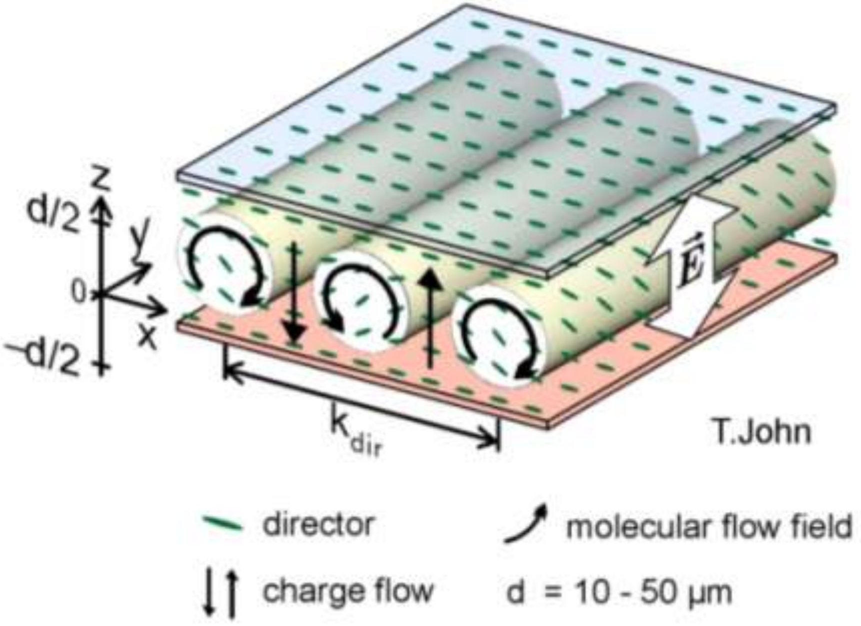
液晶の非平衡ダイナミクス

例① Electrohydrodynamic Instability

Williams domain



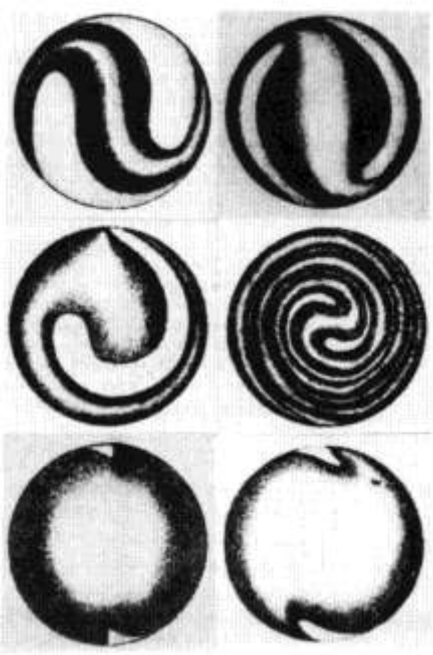
DC or low frequency　　High frequency



http://www.uni-magdeburg.de/anp/projects/pattern_form/index.htm

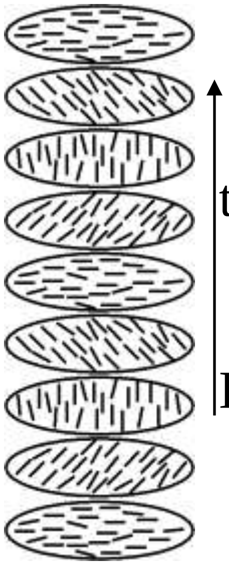
液晶の非平衡ダイナミクス

例② Lehmann effects



under temperature gradient

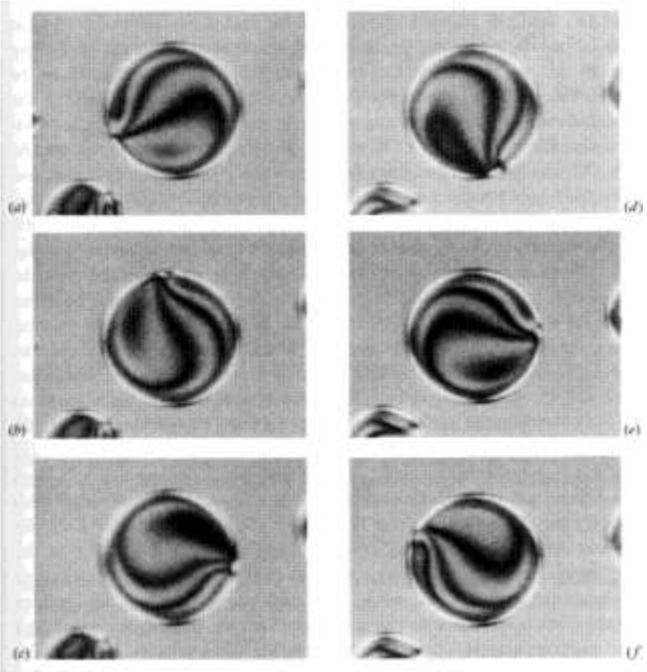
by Lehmann (1900)



thermal flux

or

DC current



under DC electric field

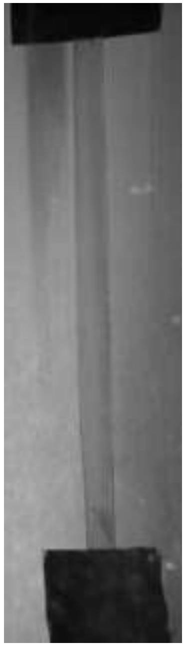
by Madhusudana & Pratibha (1987)

液晶の非平衡ダイナミクス

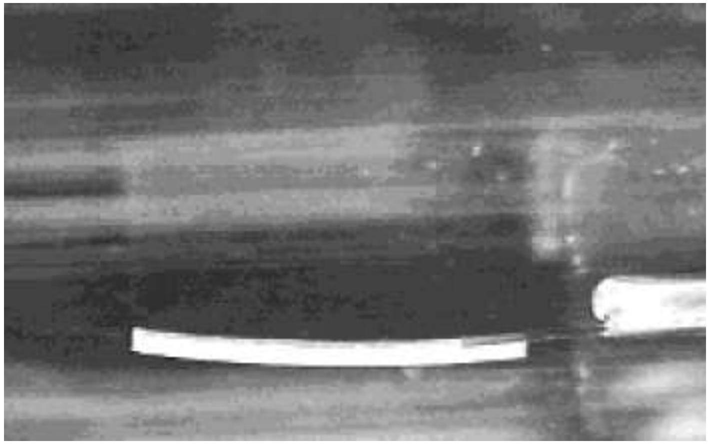
例③ Thermomechanical or photo-mechanical effects in nematic elastomers

under ∇T

under illumination

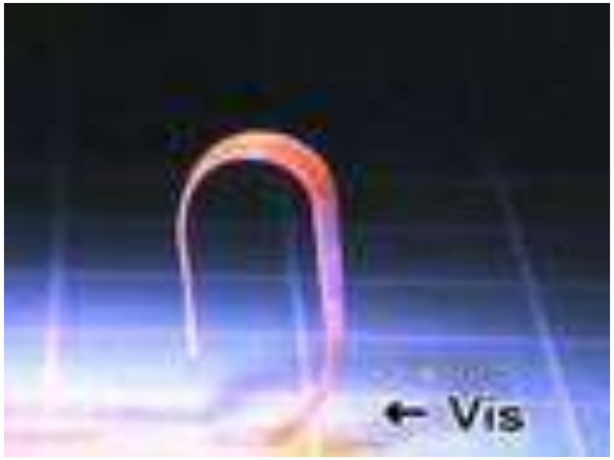


monodomain



birubber

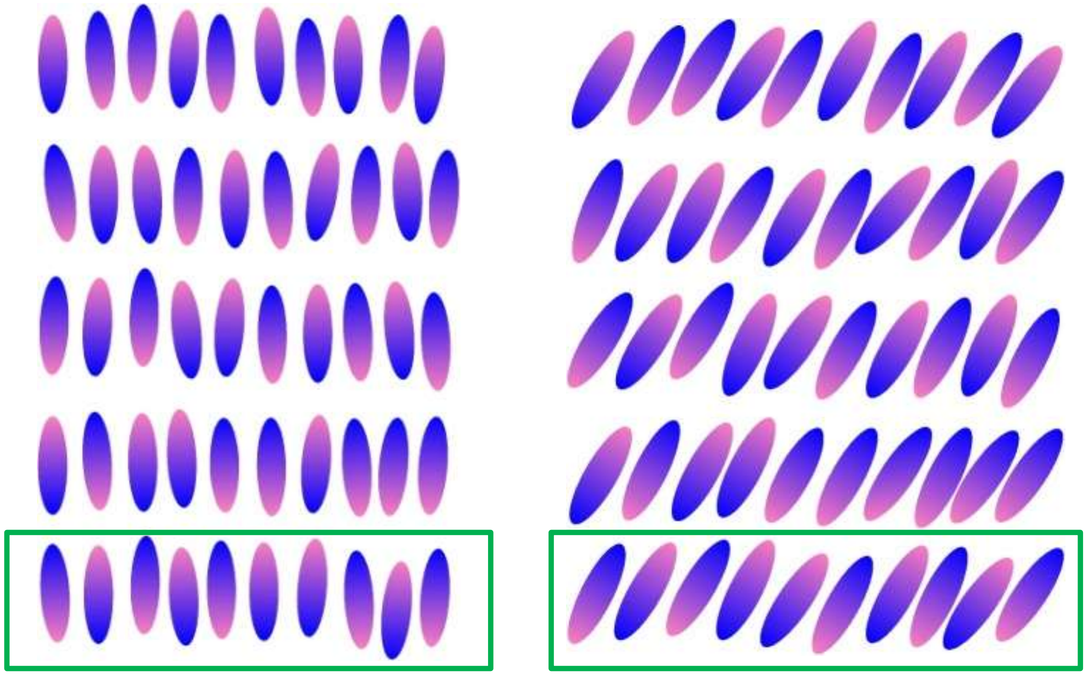
By H. Finkelman



By T. Ikeda

分子の運動 vs マクロなダイナミクス

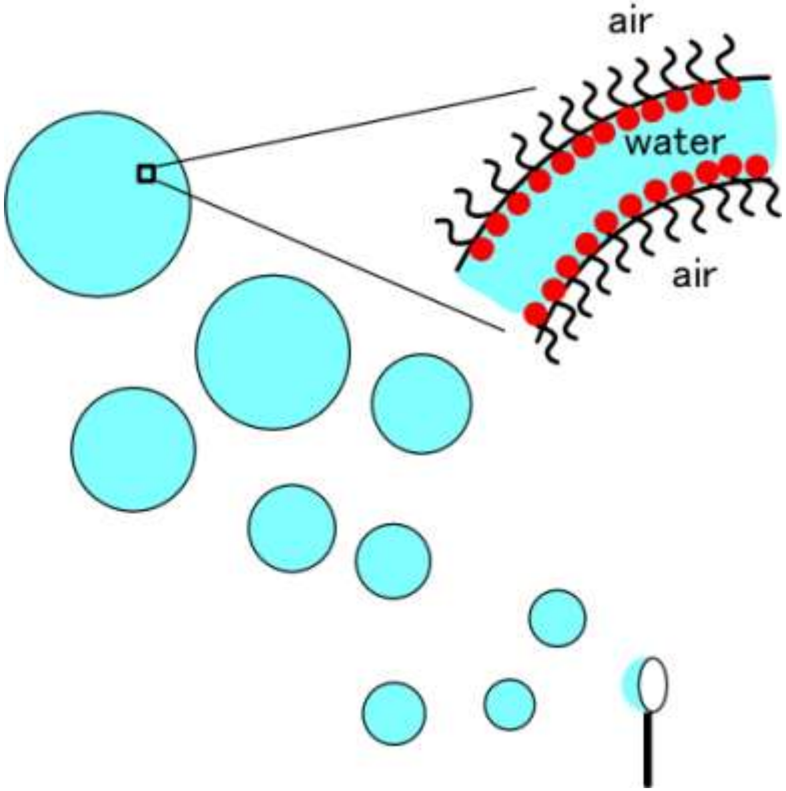
バルクの液晶実験で、両者の関係を追うのは容易ではない



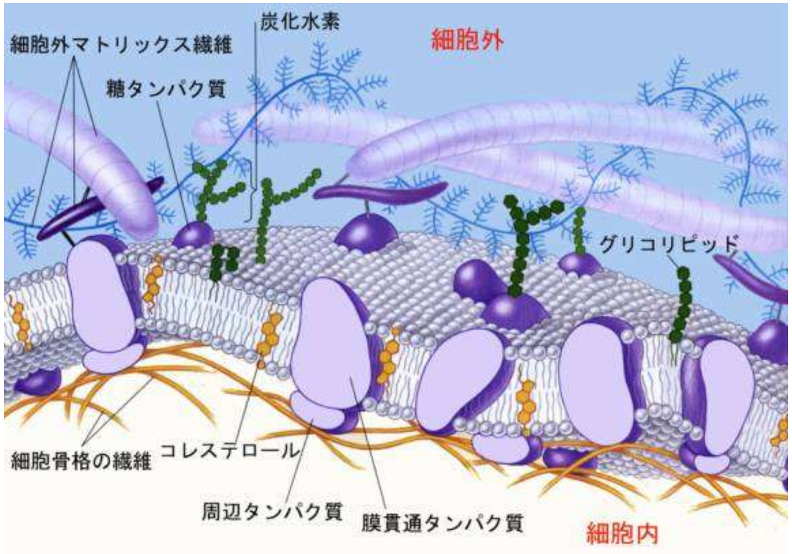
単分子膜:ミクロとマクロの中間

二次元液晶を対象とした分子運動とマクロダイナミクスとの相関

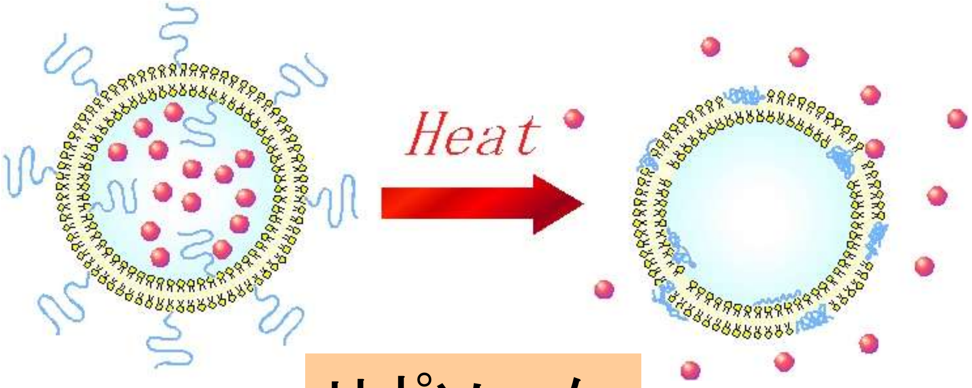
身の回りの二次元液晶



シャボン玉



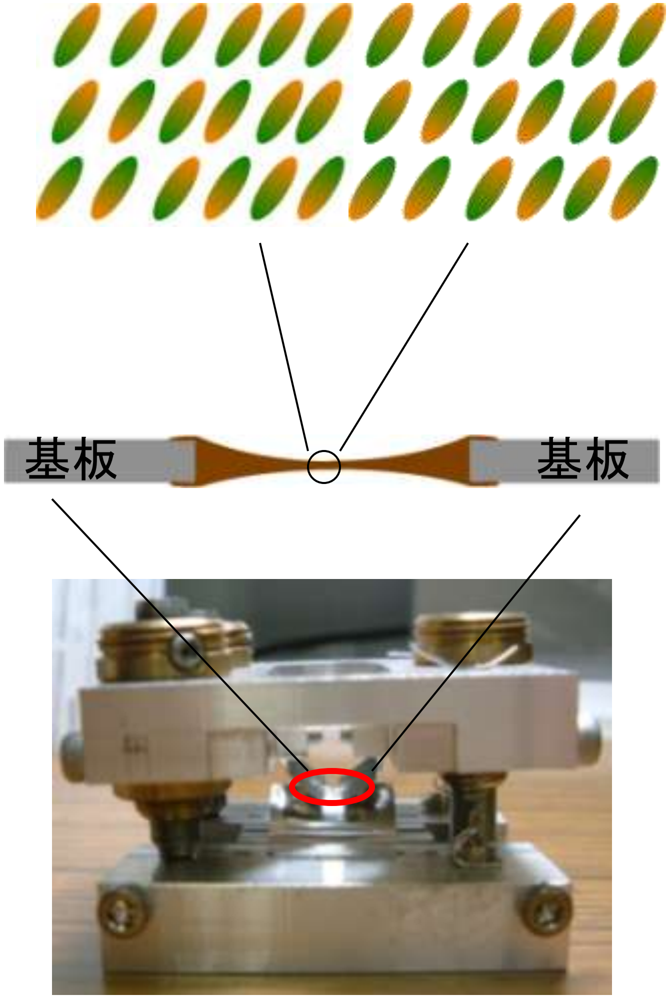
細胞膜



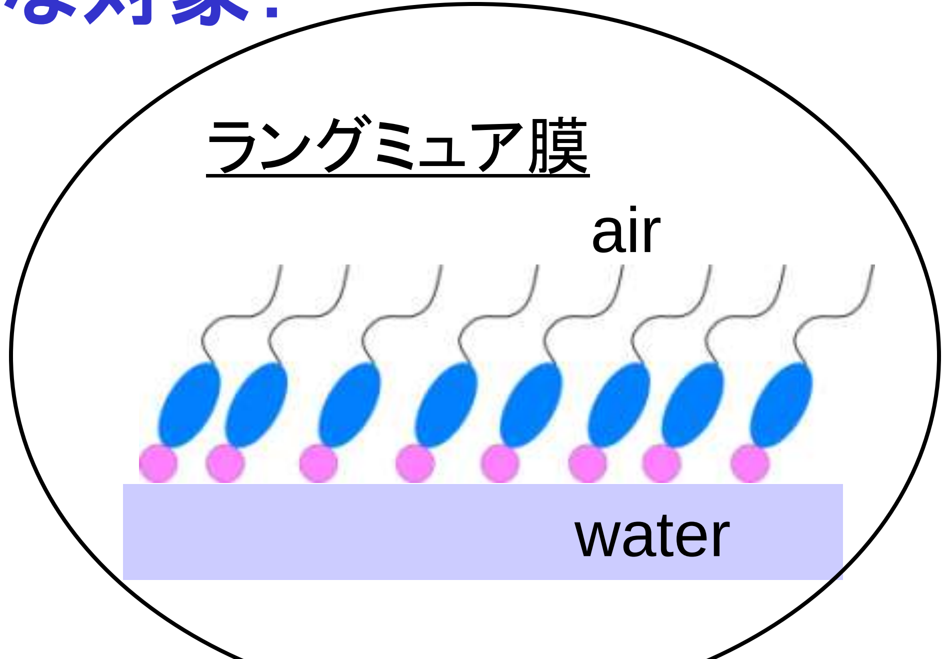
リポソーム

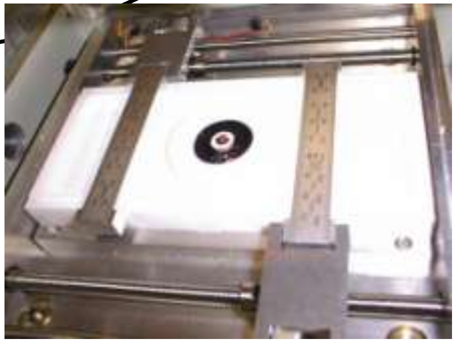
二次元液晶の具体的な対象：

自己保持膜

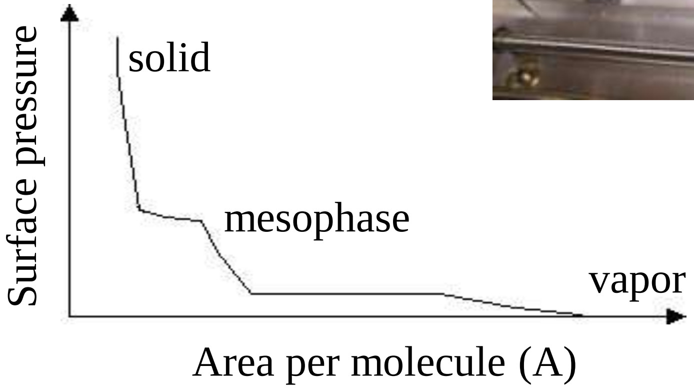


ラングミュア膜

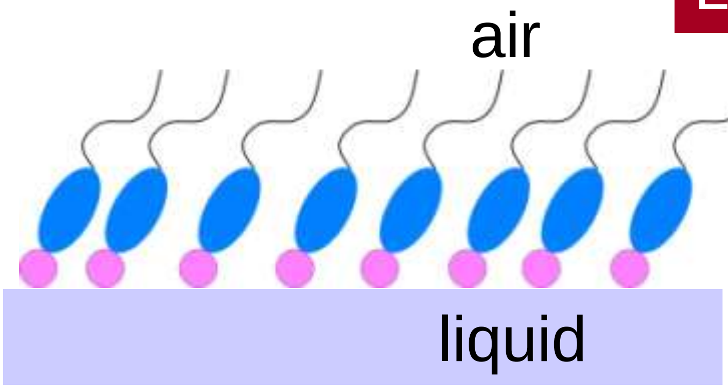




2D phase transition



LC monolayer at air-liquid interface



broken symmetry

low dimensionality

molecular characteristics ⟺ macroscopic properties

Molecular movement → Macroscopic dynamics

Two examples:

- Photo-induced orientational waves in azo LC monolayer
- Coherent molecular precession in chiral LC monolayer

OUTLINE

1. 研究背景と液晶に見られる非平衡構造

2. 二次元液晶の非平衡ダイナミクス

   2-1. 光誘起配向波

   2-2. 物質流透過によるキラル液晶の一方向回転

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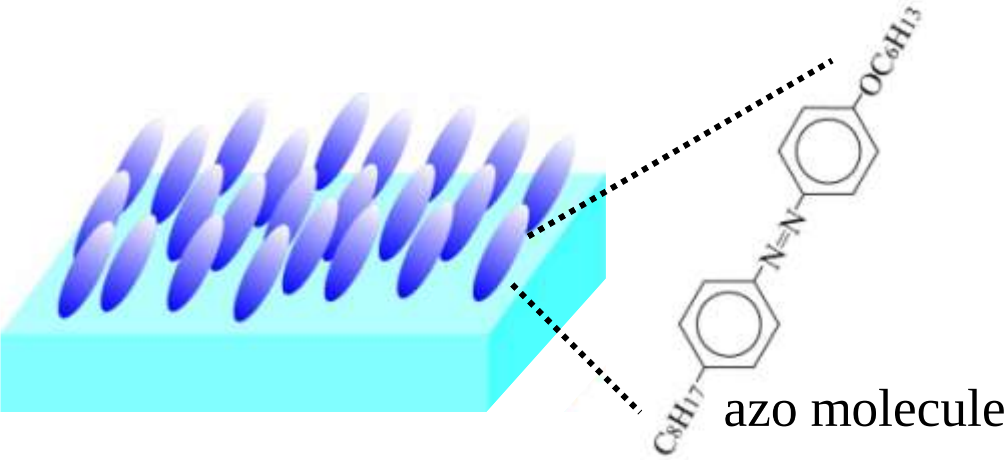
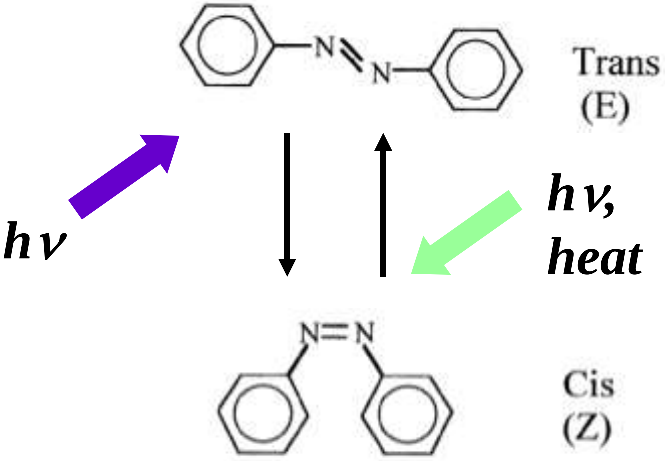
3. まとめ

Dissipative structures in 2D LCs (monolayers)

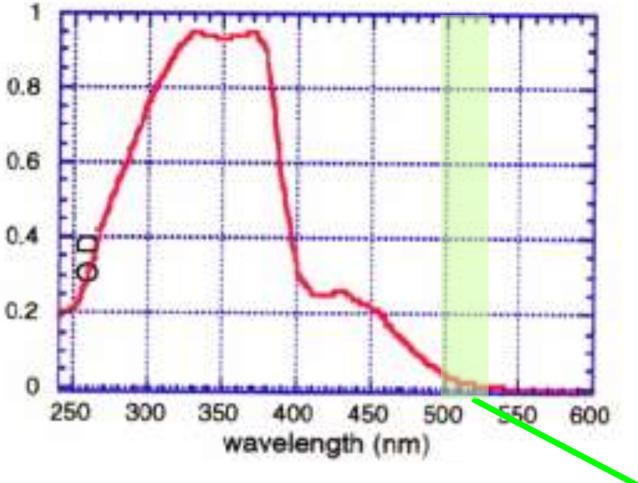
1. Photo-induced orientational waves

Photo-reactive molecule: **azobenzene**

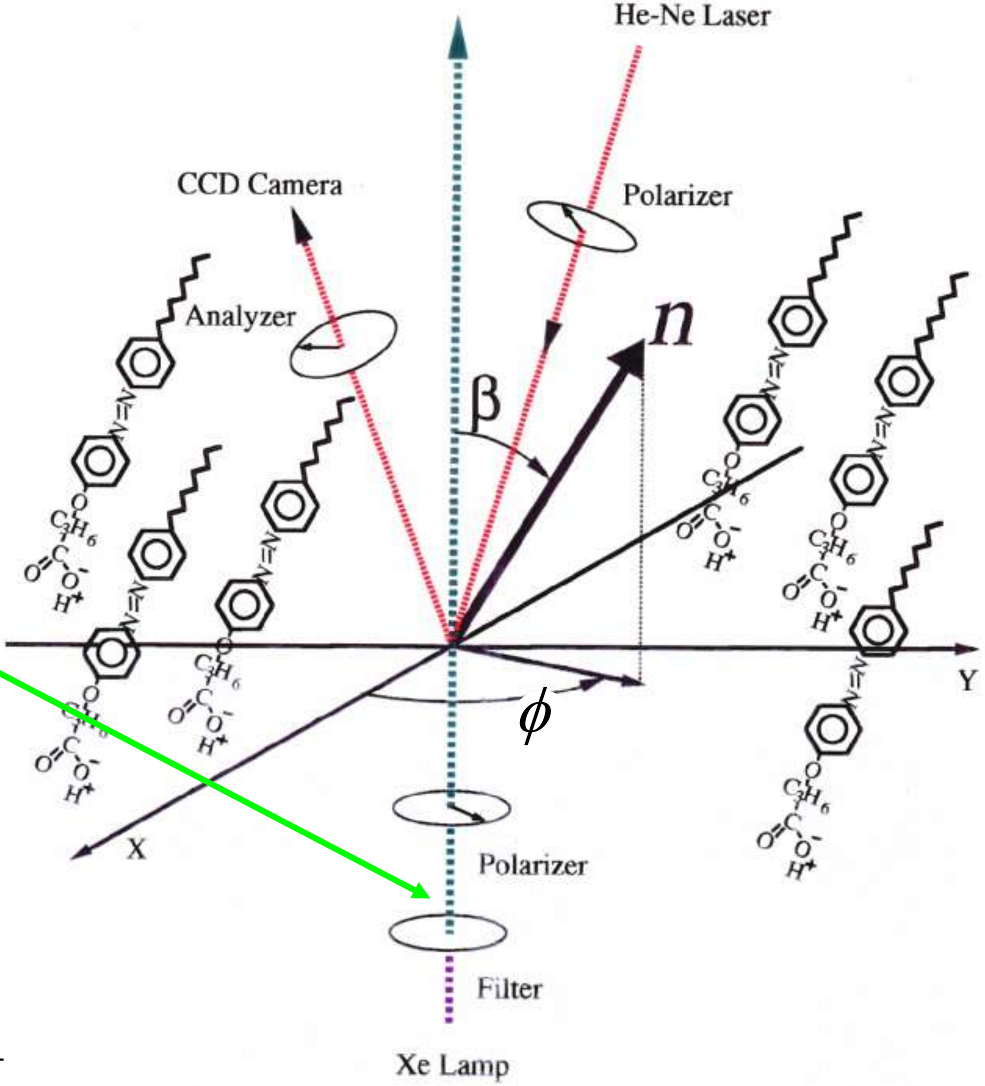




Weakly-excited LC monolayers of azobenzene derivatives



Absorption spectrum of chloroform solution of azobenzene

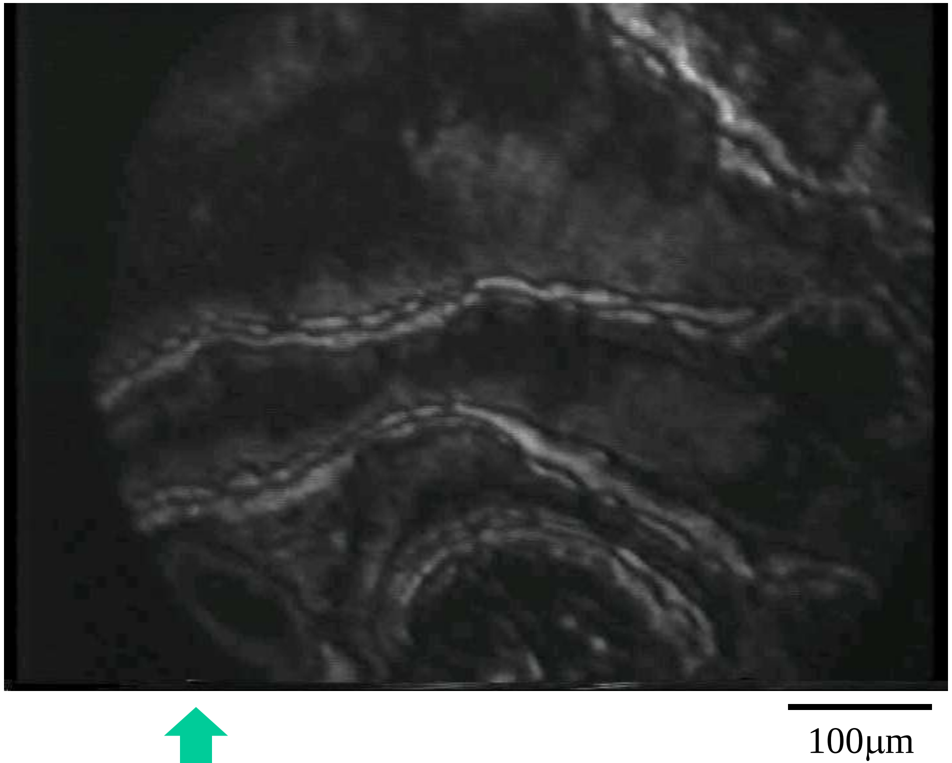


Reflection detected by CCD camera:

$$I = h^2 \sin^2 \phi \left(\cos\phi - f\right)^2$$

$$f = \frac{n^2 \tan\theta_t}{n_0{}^2 \tan\beta}$$

Generation and preparation of LC orientational wave



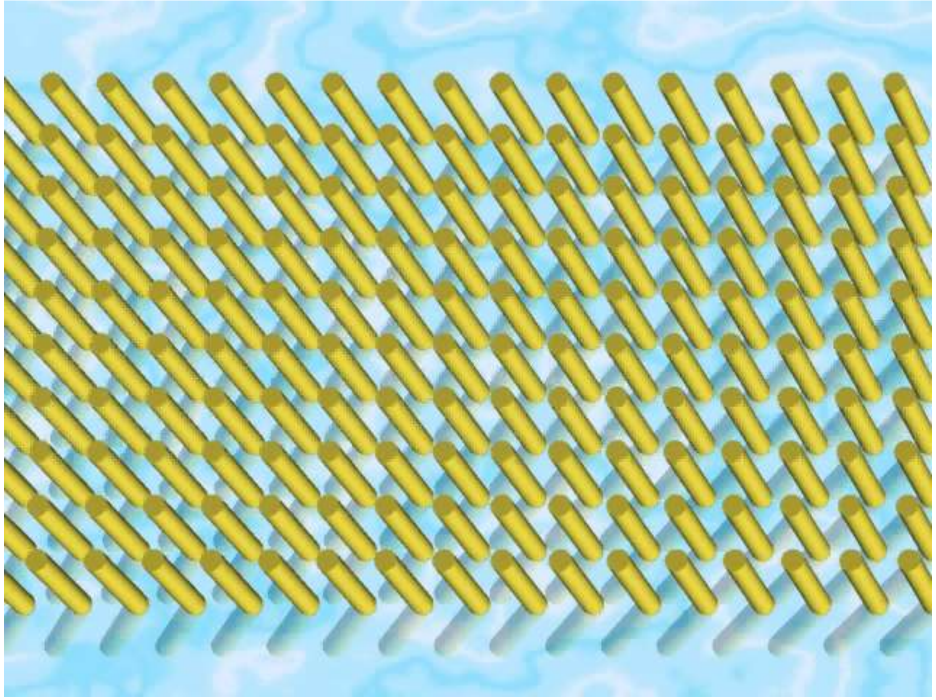
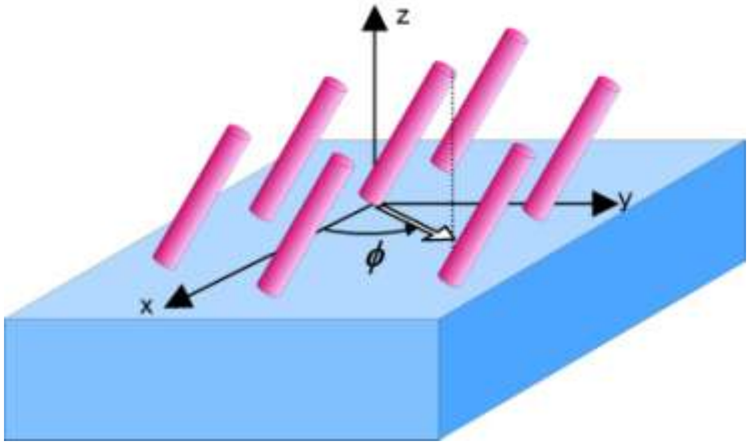


Image under polarizing microscope

Excitation polarization

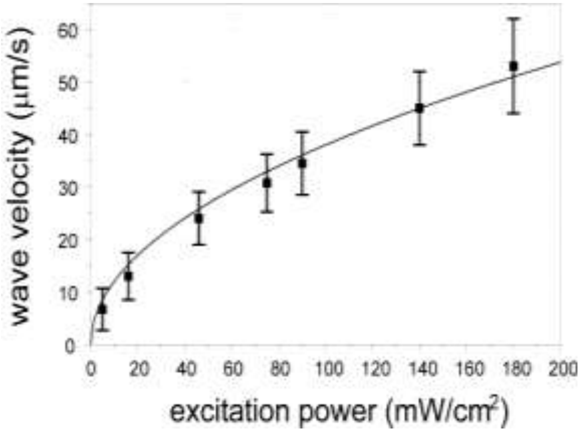
$$I = h^2 \sin^2\phi\left(\cos\phi - f\right)^2$$

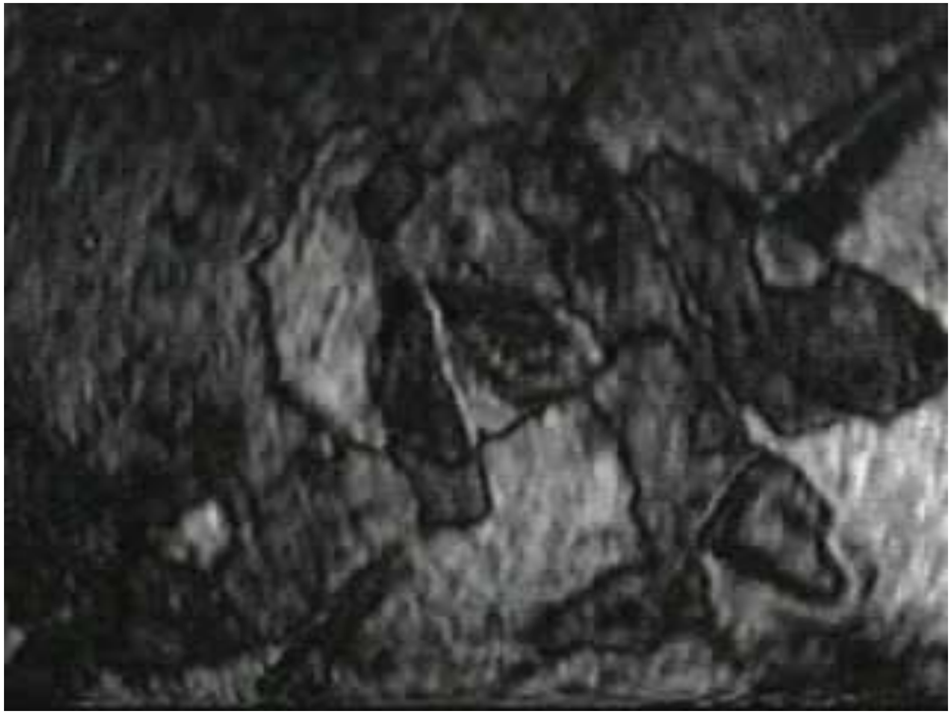
$\longrightarrow$ <u>Oscillation of ϕ</u>



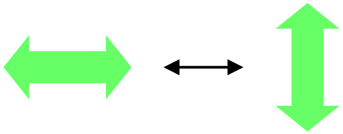
Wave properties

- Periodic rotation of molecular azimuth
- Propagate in the asymmetric film
- Wave velocity $\propto \sqrt{\text{excitation power}}$
- 90° rotation of excitation polarization → 180° inversion of wave direction





180° wave switching by 90° rotation of excitation polarization



Polarization direction of excitation

Y. Tabe & H. Yokoyama; *New J. Phys*. **5**, 65.1-65.11 (2003)

Theory for illuminated LC Langmuir monolayer

T. Okuzono, Y. Tabe & H. Yokoyama; *Phys. Rev. E*, **69** (2004)

free energy

$$F = \int d\mathbf{r} \left[\frac{1}{2} |\nabla c_i|^2 - \frac{\tau}{2} |\mathbf{c}|^2 + \frac{u}{4} |\mathbf{c}|^4 - \lambda \psi \nabla \cdot \mathbf{c} + \frac{D}{2} |\nabla \psi|^2 + \frac{\chi}{2} \psi^2 \right]$$

$\mathbf{c}(\mathbf{r},t)$: projection of the local molecular direction

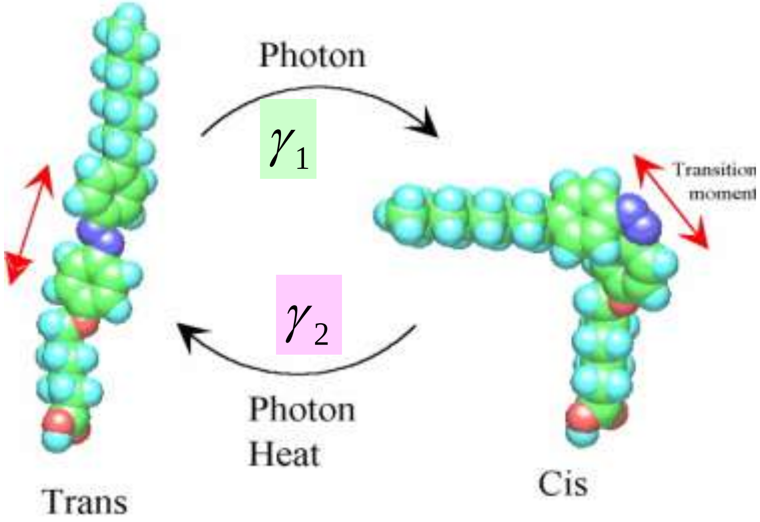
$\psi(\mathbf{r},t)$: local concentration difference between trans and cis isomers

kinetic equation:

$$\frac{\partial \mathbf{c}}{\partial t} = -\frac{\delta F}{\delta \mathbf{c}} + \mathbf{f}, \quad \left(\mathbf{f} \equiv -\gamma_2 \frac{1-\psi}{1+\psi} \mathbf{c}\right)$$

$$\frac{\partial \psi}{\partial t} = M \nabla^2 \frac{\delta F}{\delta \psi} + g,$$

$$g \equiv -(\gamma_1 + \gamma_2)\psi - (\gamma_1 - \gamma_2)$$



anisotropic reaction in LC monolayer:

$$\gamma_1 = g_1 (\mathbf{E} \cdot \mathbf{c})^2$$

γ_2: independent of electric field polarization

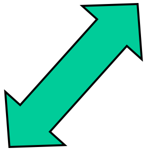
γ_1 : trans → cis reaction rate

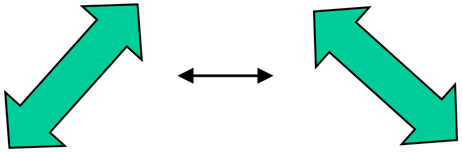
γ_2 : cis → trans reaction rate

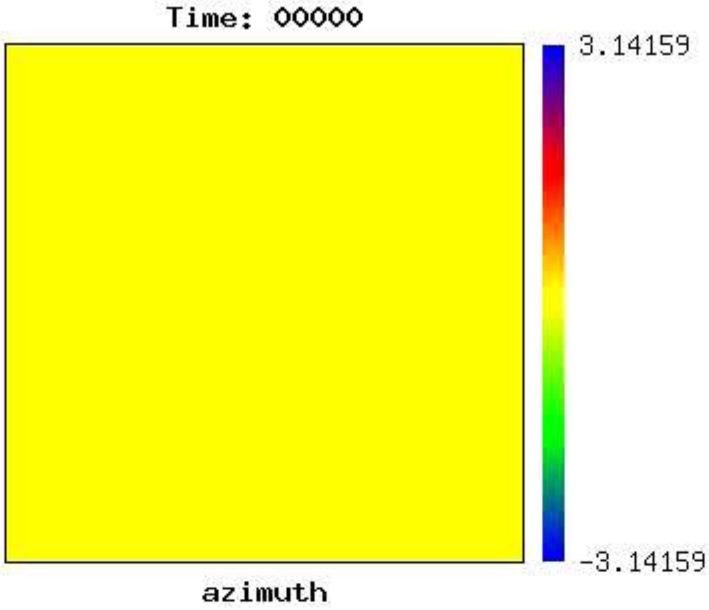
Simulation of wave switching

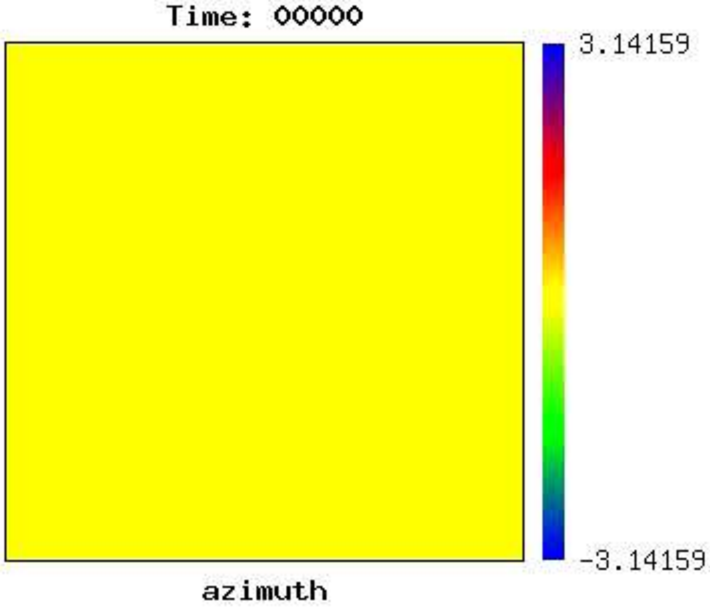
T. Okuzono, Y. Tabe & H. Yokoyama; *Phys. Rev. E,* **69** (2004)

excitation
polarization





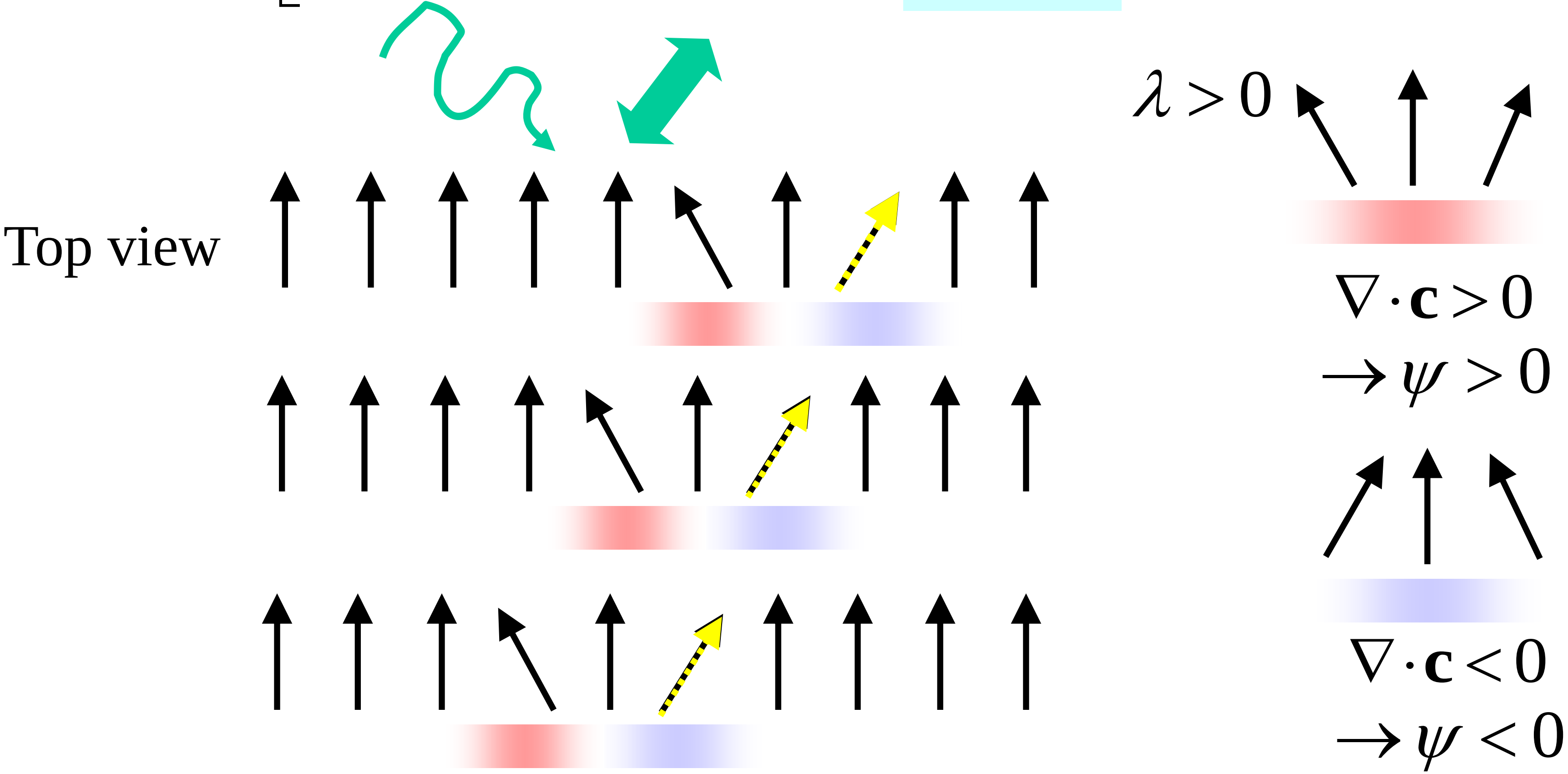




$$g_1 = \gamma_2 = 0.05,\ \tau = u = 2,\ \lambda = 1$$

Possible mechanism of wave propagation

$$F = \int d\mathbf{r}\left[\frac{1}{2}|\nabla c_i|^2 - \frac{\tau}{2}|\mathbf{c}|^2 + \frac{u}{4}|\mathbf{c}|^4 - \lambda\psi\nabla\cdot\mathbf{c} + \frac{D}{2}|\nabla\psi|^2 + \frac{\chi}{2}\psi^2\right]$$



The coupling between the anisotropic absorption & splay distortion & density variation carries the orientational waves

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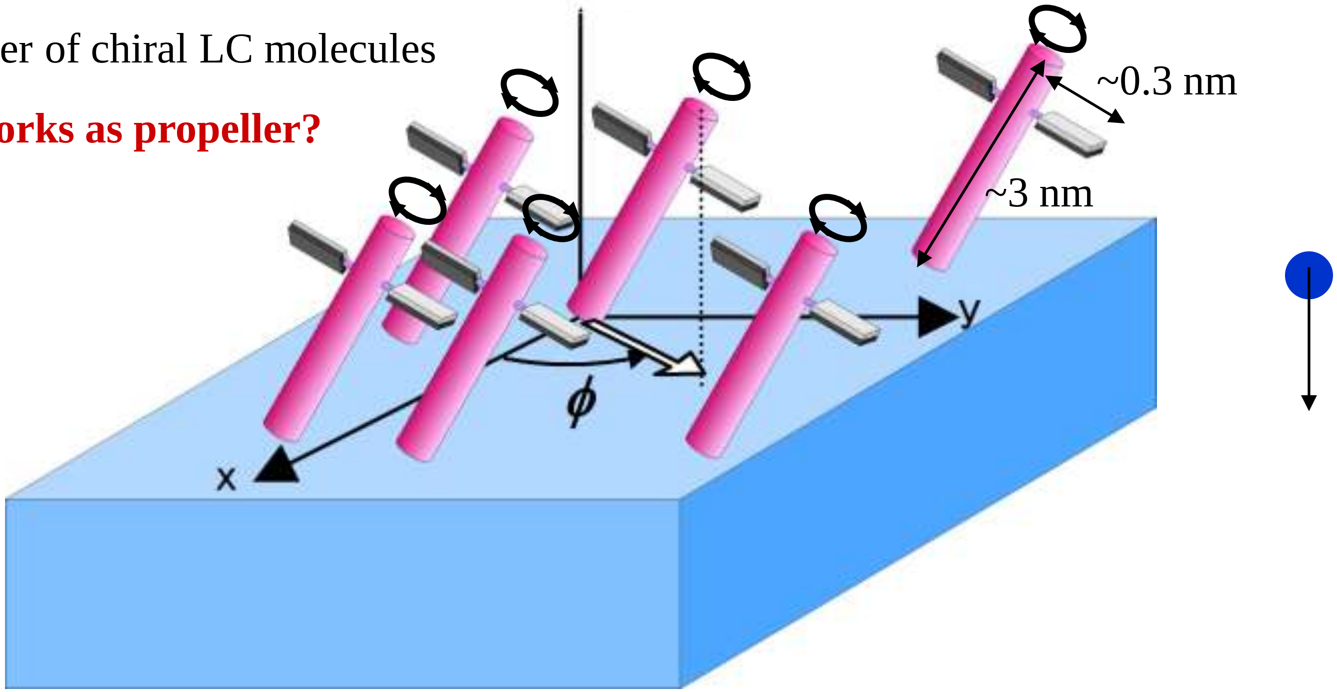
3. まとめ

Dissipative structures in 2D LCs

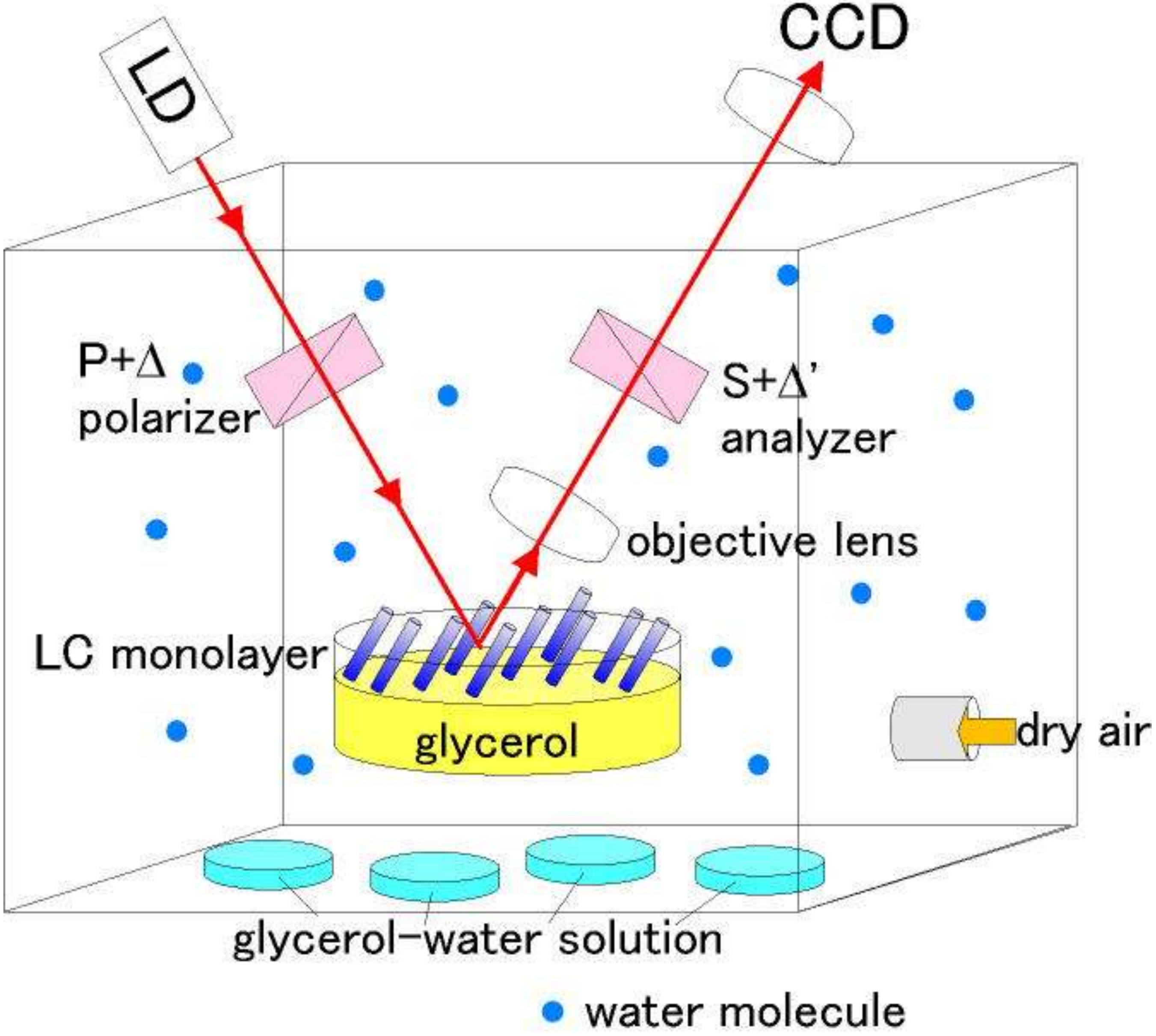
2. Chiral molecular precession driven by transport currents

Langmuir monolayer of chiral LC molecules

→ **chiral part works as propeller?**



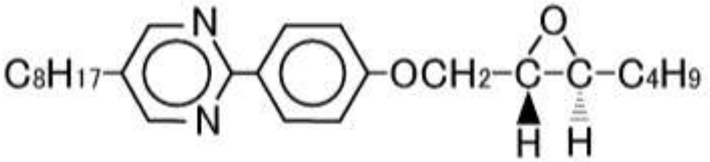
Overview of the experimental setup



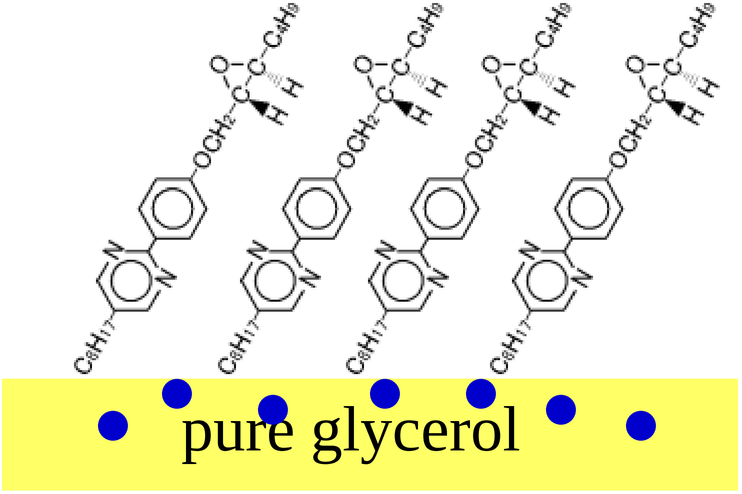
Chiral LC monolayer on pure glycerol

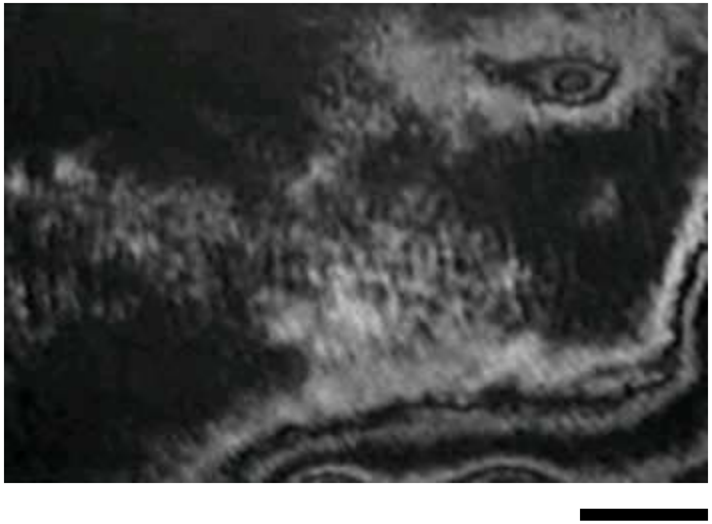
Example 1

(S)-OPOB on pure glycerol



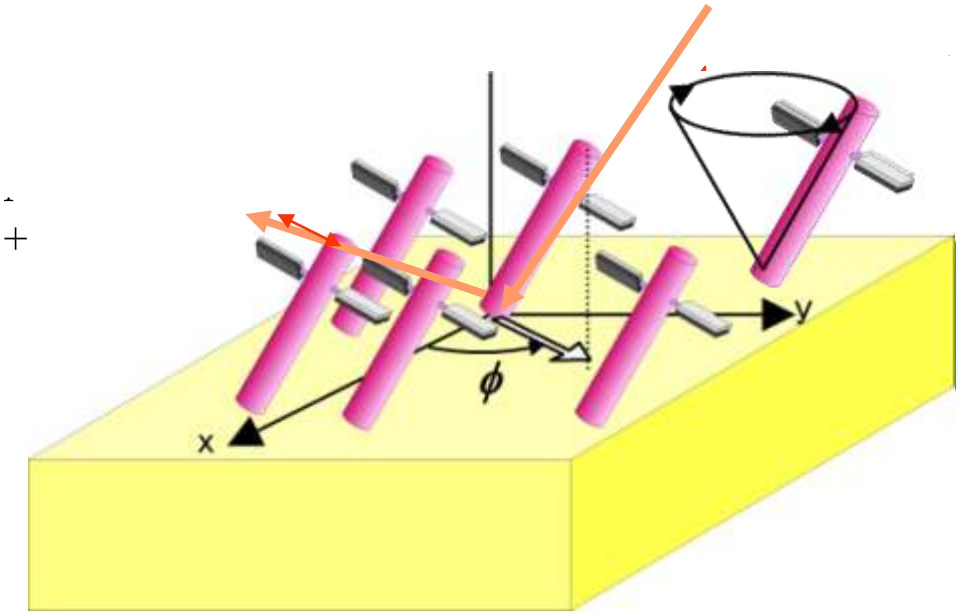
Clariant Japan Ltd.





100µm

Depolarized polarizing light microscopy: CW or CCW ?



Crossed polarizers (P&S):

$$I(\phi)=h\sin^2\phi(\cos\phi-f)^2$$

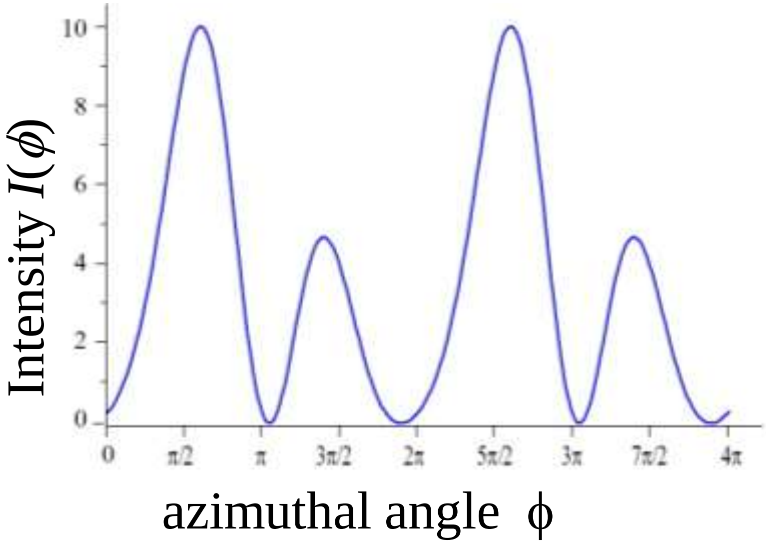
Slightly depolarized (P+2° & S+Δ°):

$$I(\phi)=h\left[\sin^2\phi(\cos\phi-f)^2-\underbrace{g\sin\phi(\cos\phi-f)}_{\uparrow\; I(\phi)\neq I(-\phi)}\right]$$

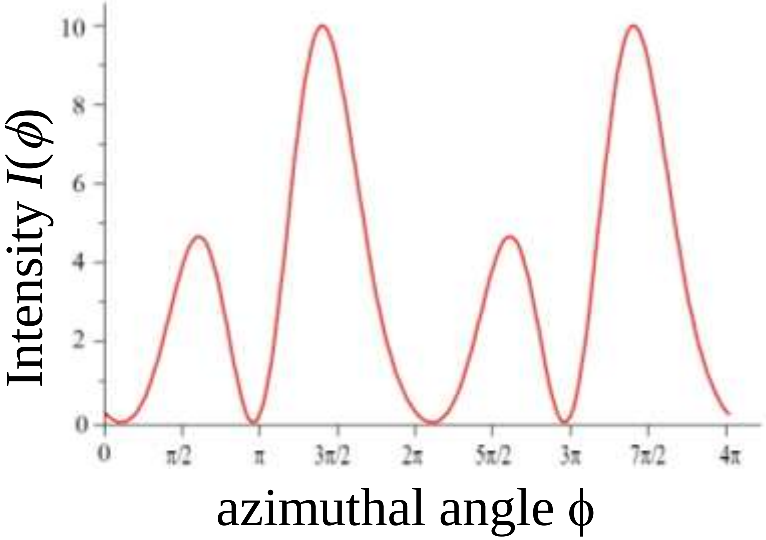
$$\theta_i=30^\circ,\ \Delta P=2^\circ,\ n_g=1.4746;\ \beta=10^\circ,\ \varepsilon_\perp=2,\ \varepsilon_{//}=2.1$$

$$\longrightarrow f=2.5,\ g=1.1$$

Clockwise rotation

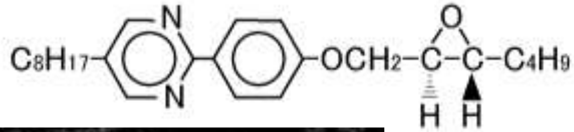


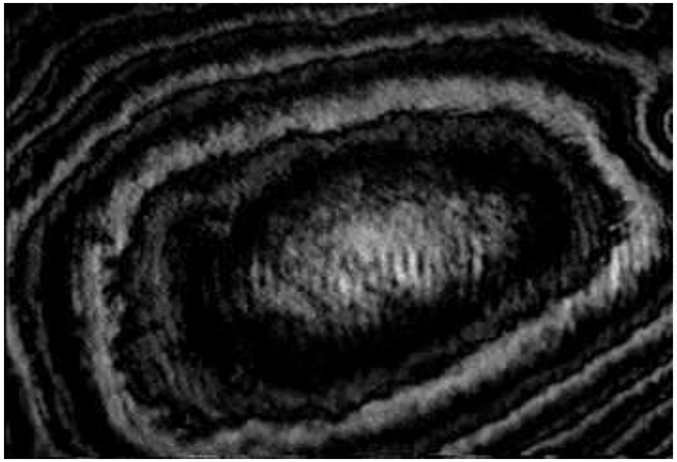
Counter-clockwise rotation



Chirality inversion

(R)-OPOB

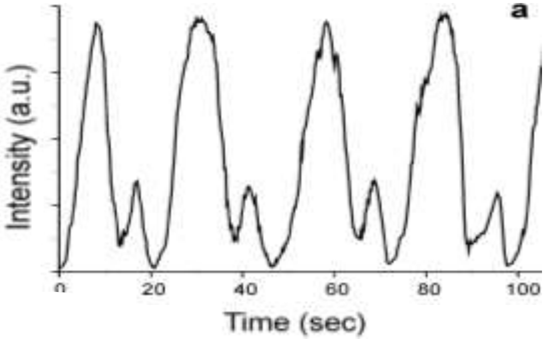




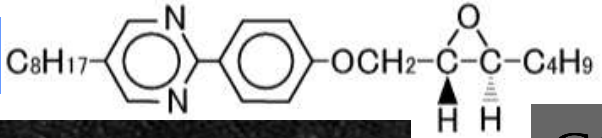
on pure glycerol

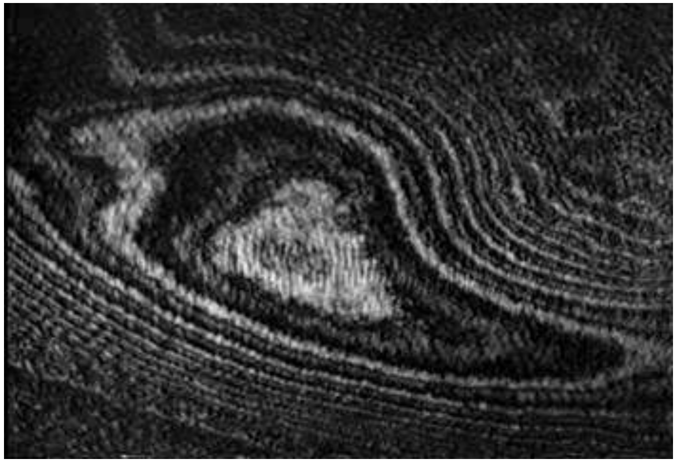
100μm

CW

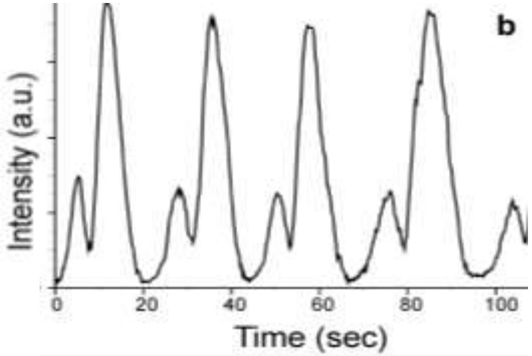


(S)-OPOB

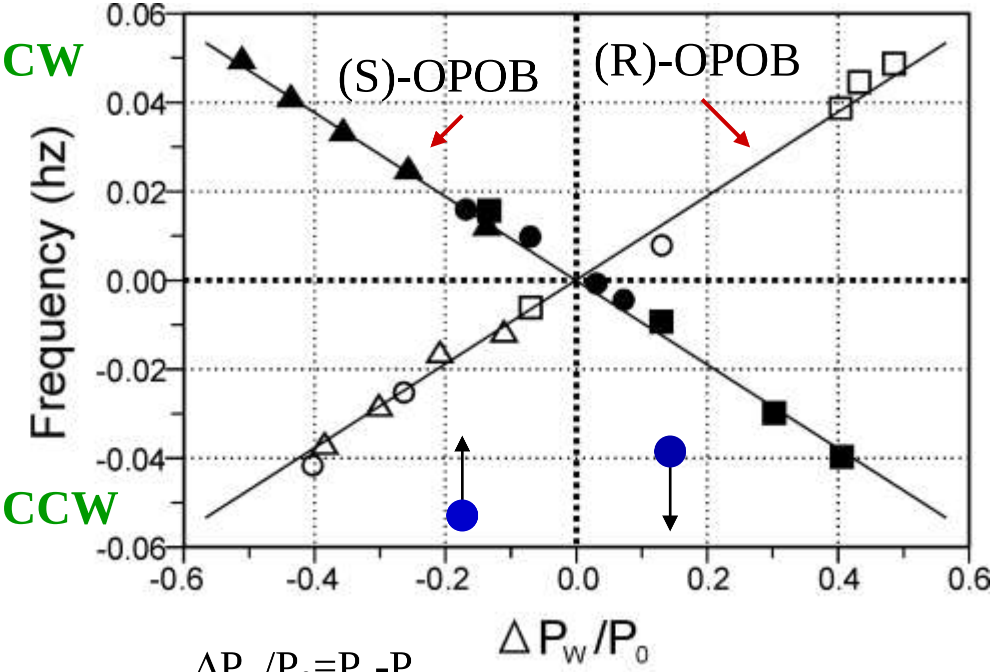




CCW



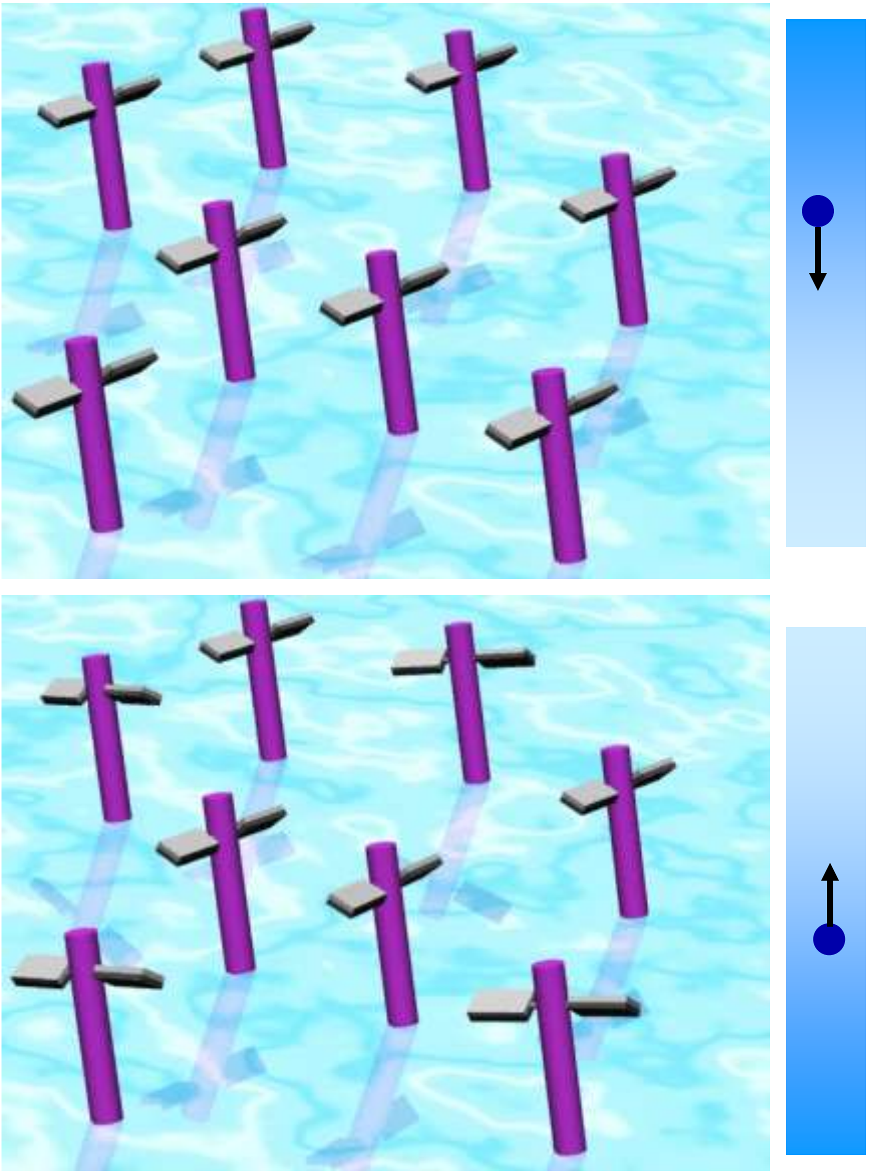
LC motor is driven by water transfer



$\Delta P_w/P_0 = P_v - P_s$

P_v: actual water vapour pressure

P_s: saturated water vapour pressure



molecular rotational speed

∝ vapor pressure difference

Phenomenological equations

Entropy source:

$$T\dot{S}=\tau\frac{\partial\phi}{\partial t}+J\cdot\upsilon_m\Delta P$$

$\Delta P_w/P_0=P_v-P_s$

P_v: actual water vapor pressure

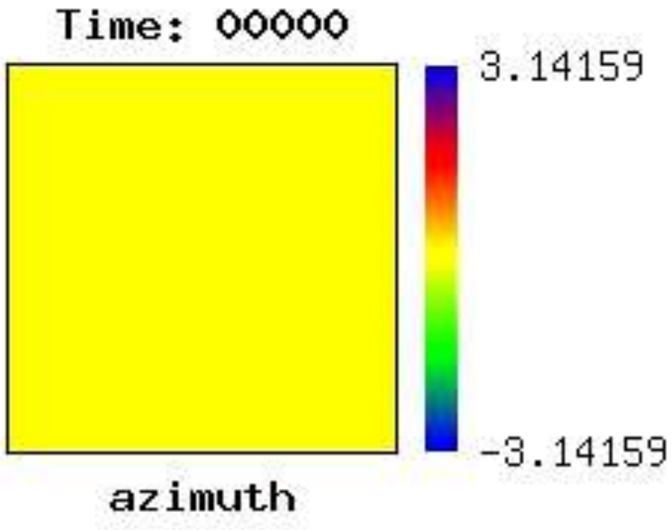
P_s: saturated water vapor pressure

Two forces:

$$\tau,\ \upsilon_m\Delta P$$

Two Fluxes:

$$\frac{\partial\phi}{\partial t},\ J$$



Phenomenological equation:

$$\frac{d\phi}{dt}=\frac{1}{\gamma}\tau+b\ \upsilon_m\ \Delta P$$

$$J=b\tau+\frac{1}{\eta}\upsilon_m\Delta P$$

υ_m: molecular volume of water in vapor

γ: rotational viscosity of LC director

η: water mobility through the film

b: cross-coupling coefficient (depend on chirality)

$$\text{when}\ \tau=0:\frac{d\phi}{dt}=b\ \upsilon_m\ \Delta P$$

$b=10^{24}\ [\mathrm{N}^{-1}\mathrm{m}^{-1}\mathrm{s}^{-1}]$

Molecular Dynamics Simulation

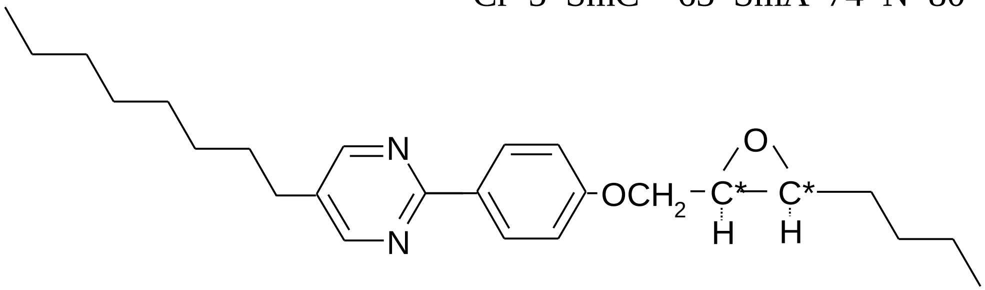
Microscopic interaction between LC molecules & current molecules:

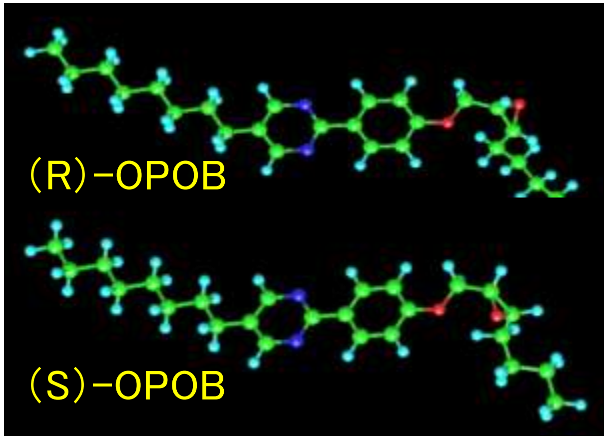
Chiral LC Molecules（detailed atomic model)

OPOB

Phase Sequence（[℃]）

Cr 5 SmC* 63 SmA 74 N 80 I

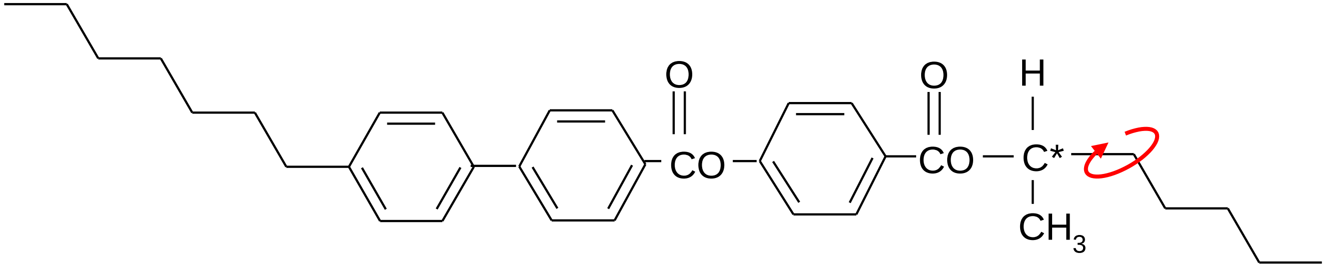




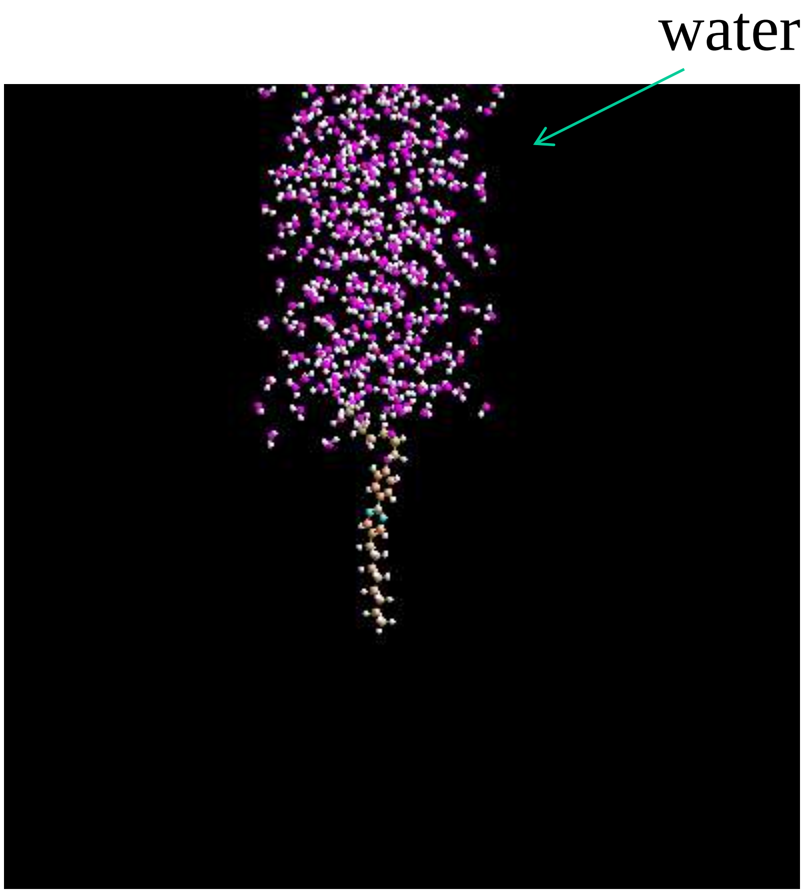
MHPOBC

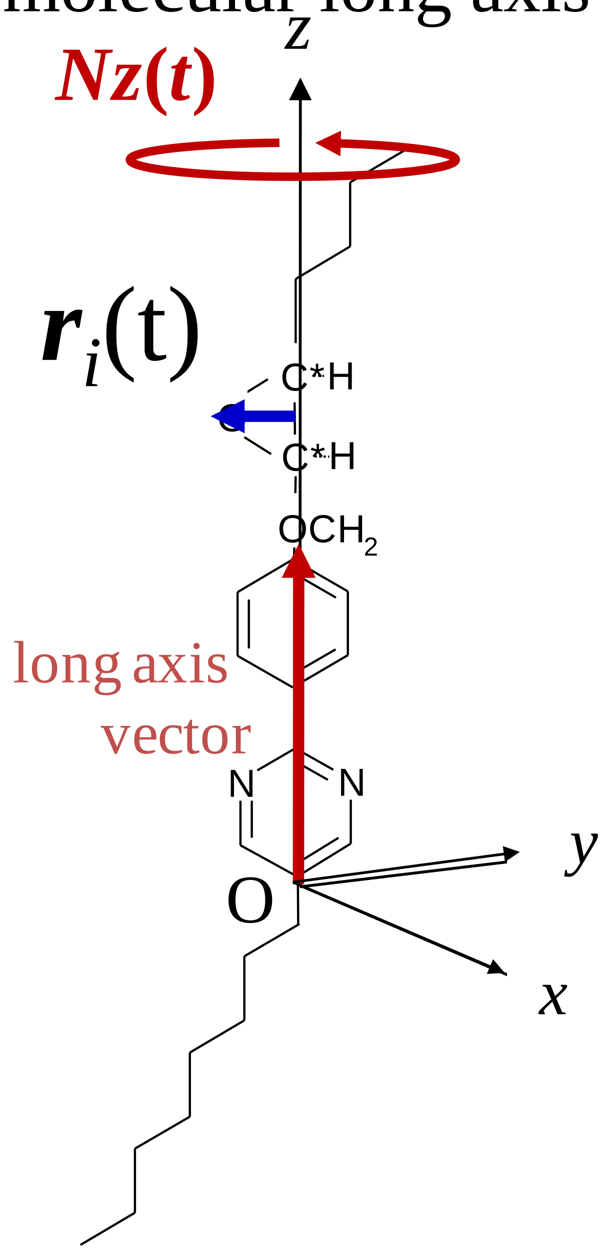
Phase Sequence（[℃]）

Cr 66 SmCA* 118 SmCγ 119 SmC* 120
SmCα* 122 SmA 156 I



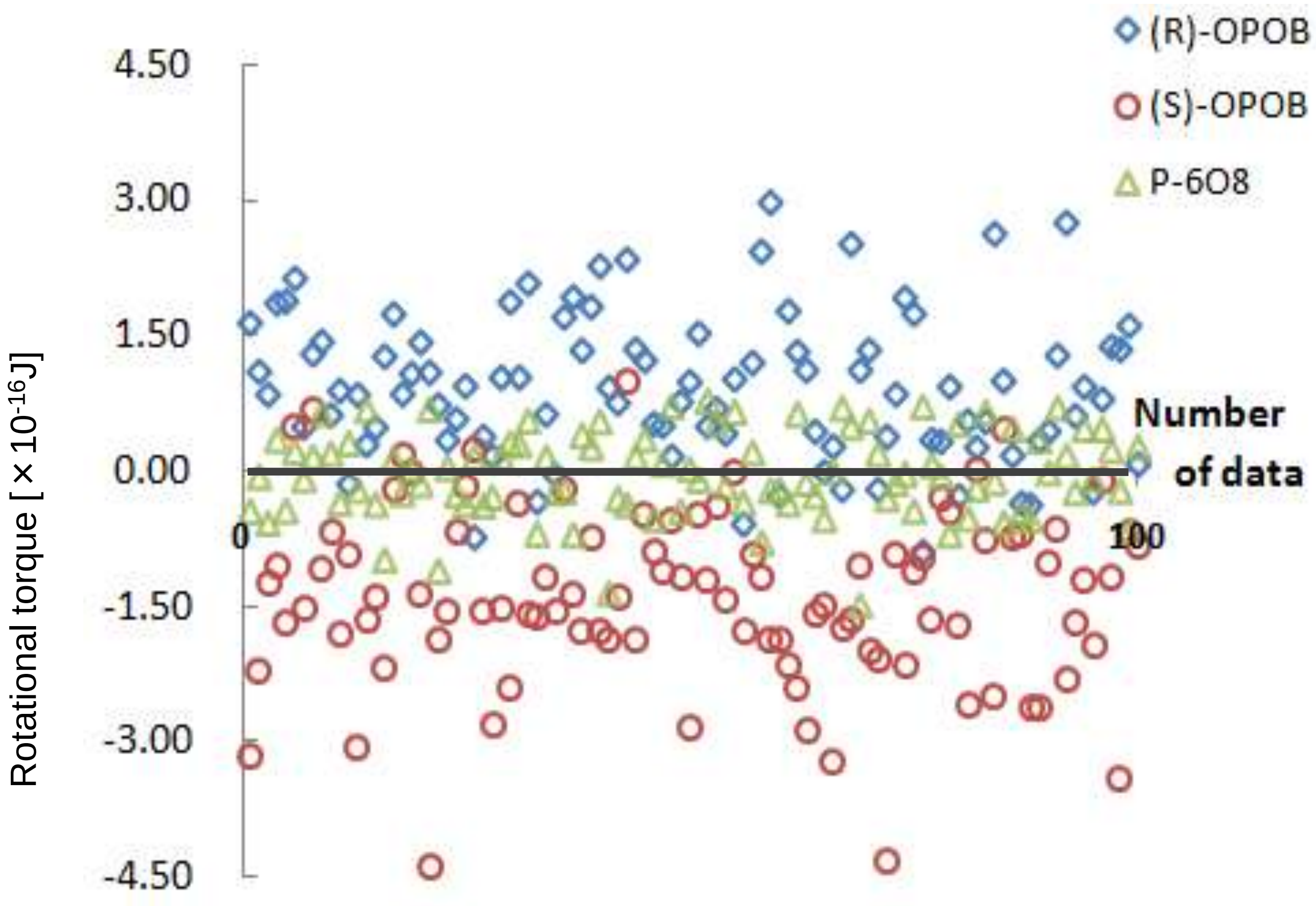
Calculation of torque along the molecular long axis





$$\mathbf{N}_z(t)=\sum_i\left[\mathbf{r}_i(t)\times\mathbf{F}_i(t)\right]_z$$

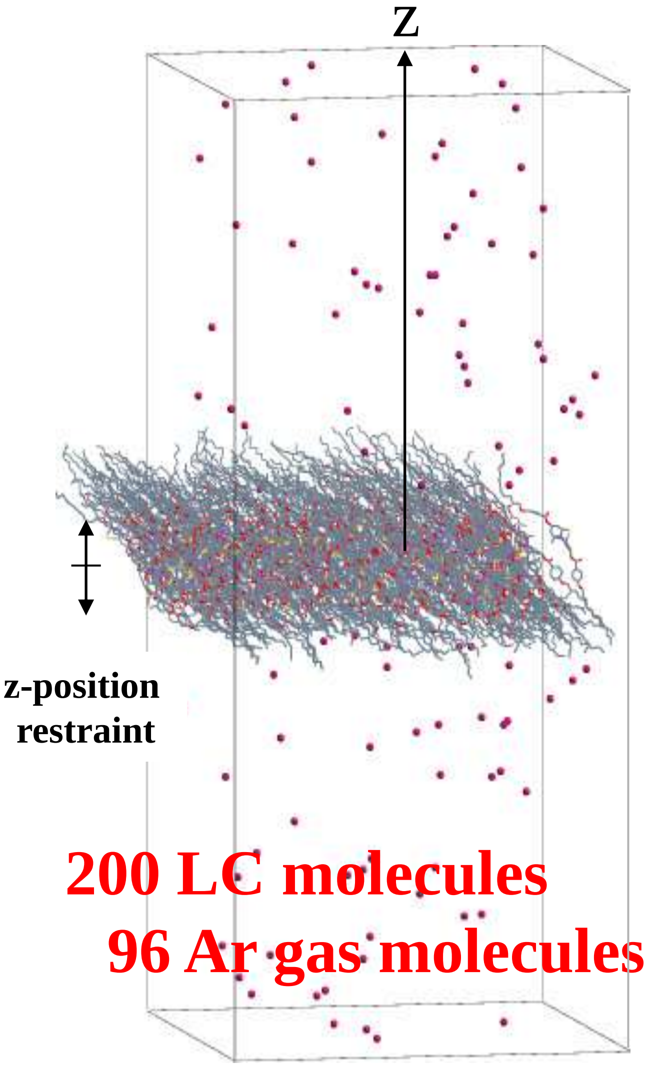
Torque on an isolated LC molecule along the molecular axis per single water collision



	OPOB		P-6O8
	R-isomer	S-isomer	
Mean value	3.23E-19	-4.97E-19	-1.56E-20
Standard deviation	2.91E-20	3.56E-19	1.67E-20

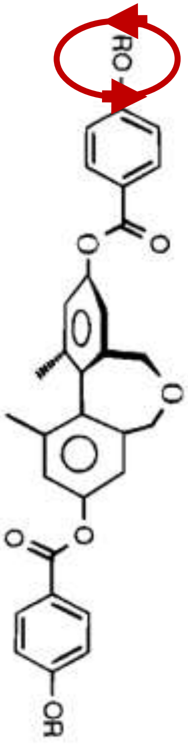
Axial rotation and precession of chiral molecules in monolayer state

M. Yoneya, Y. Tabe and H. Yokoyama
J. Phys. Chem.B *114* (25), 8320 (2010)



200 LC molecules

96 Ar gas molecules

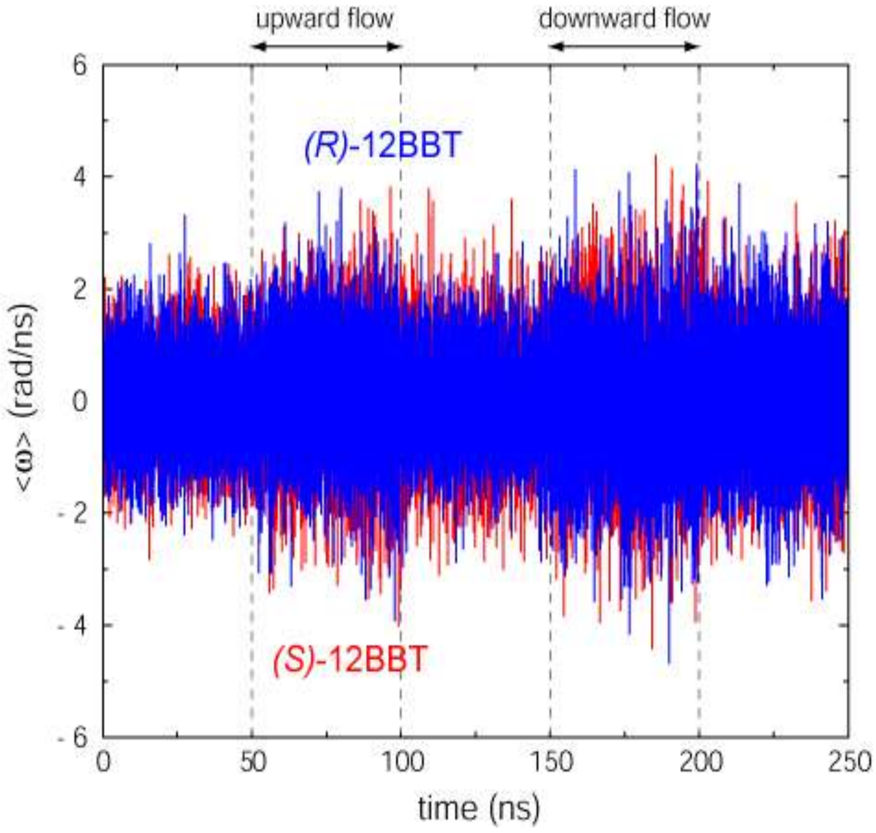


- hydrogens are treated as united atoms CH_n
- Gaussian03 HF/6-31g* RESP fitted atomic charges
- GROMACS force field (with extension)
- Δt=4fs (with fixed bonds), cut-off = 0.9/1.8nm
- z-position restraints on dummy atoms at the mol. center

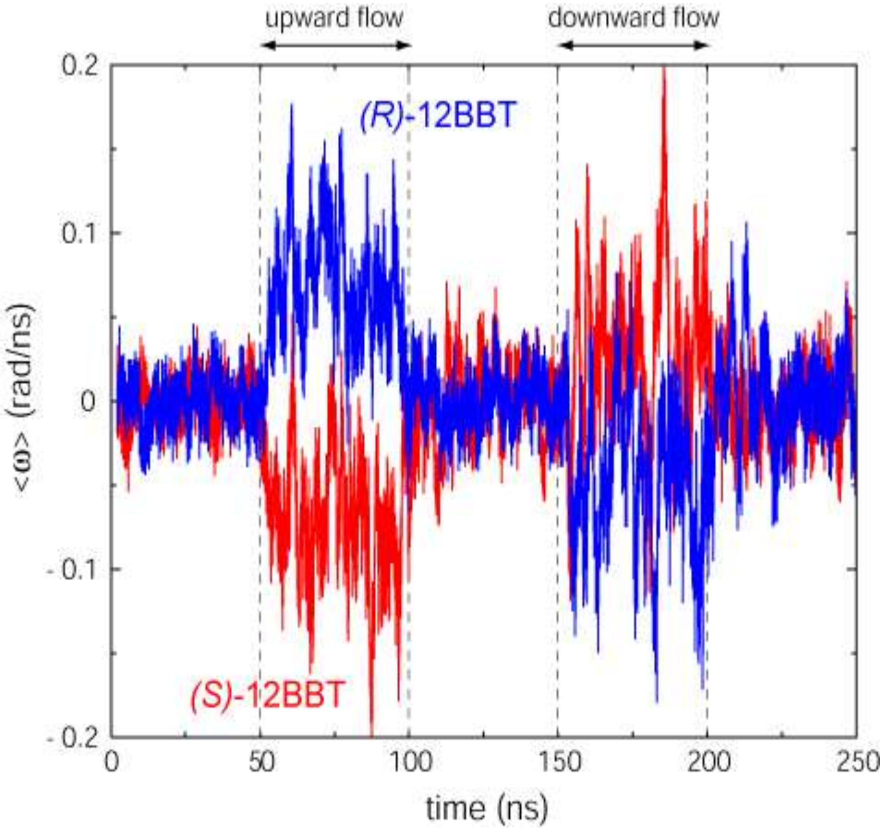
$$V(z_i) = \quad k_{pr} (z_i - z_0)^4$$

Directions of axial rotation under Ar flow

- Dependence on molecular chirality and flow direction

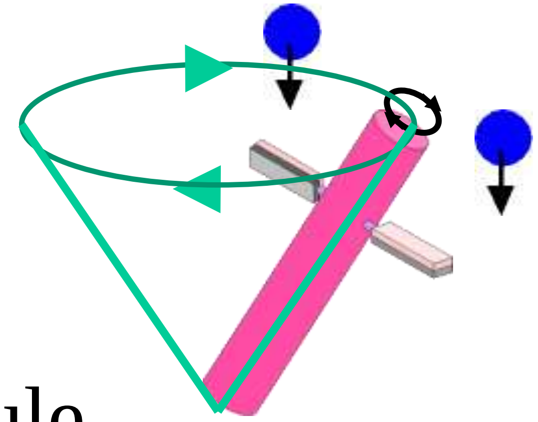


average angular velocity
(calc. without filtering)



average angular velocity
(calc. after high-freq. filtering)

Possible mechanism of flow-driven molecular precession in chiral monolayers:



Collision of flow molecules with the chiral propeller

⬇

axial rotation of each molecule

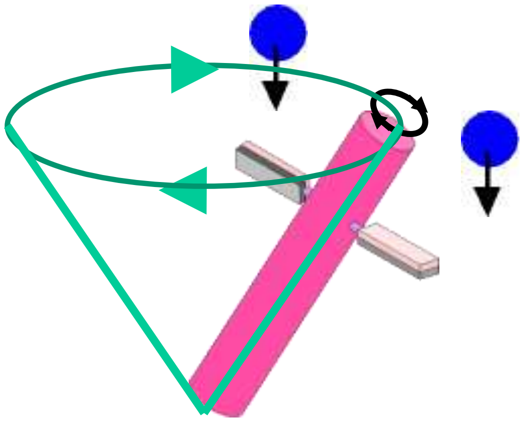
⬇

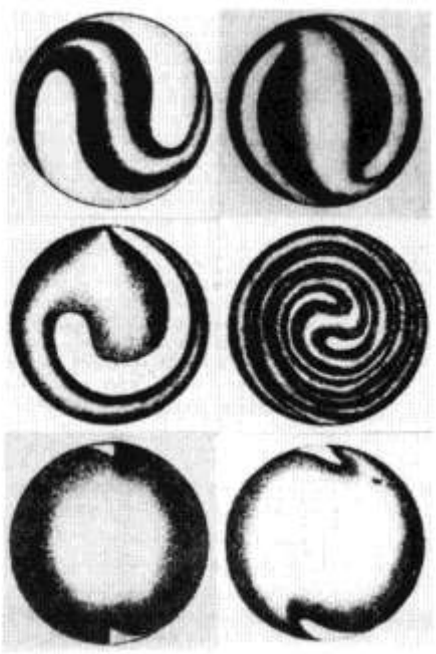
develops into the collective precession

Molecular chiral propeller is essential in monolayers.

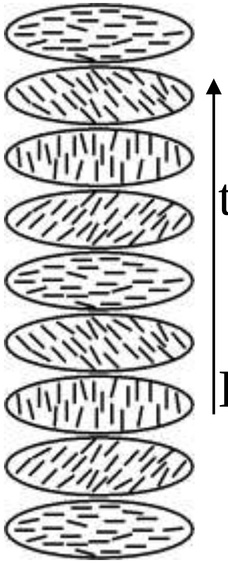
What happens in thick films with macroscopic helix?

Microscopic torque vs macroscopic torque





under temperature gradient
by Lehmann (1900)



thermal flux

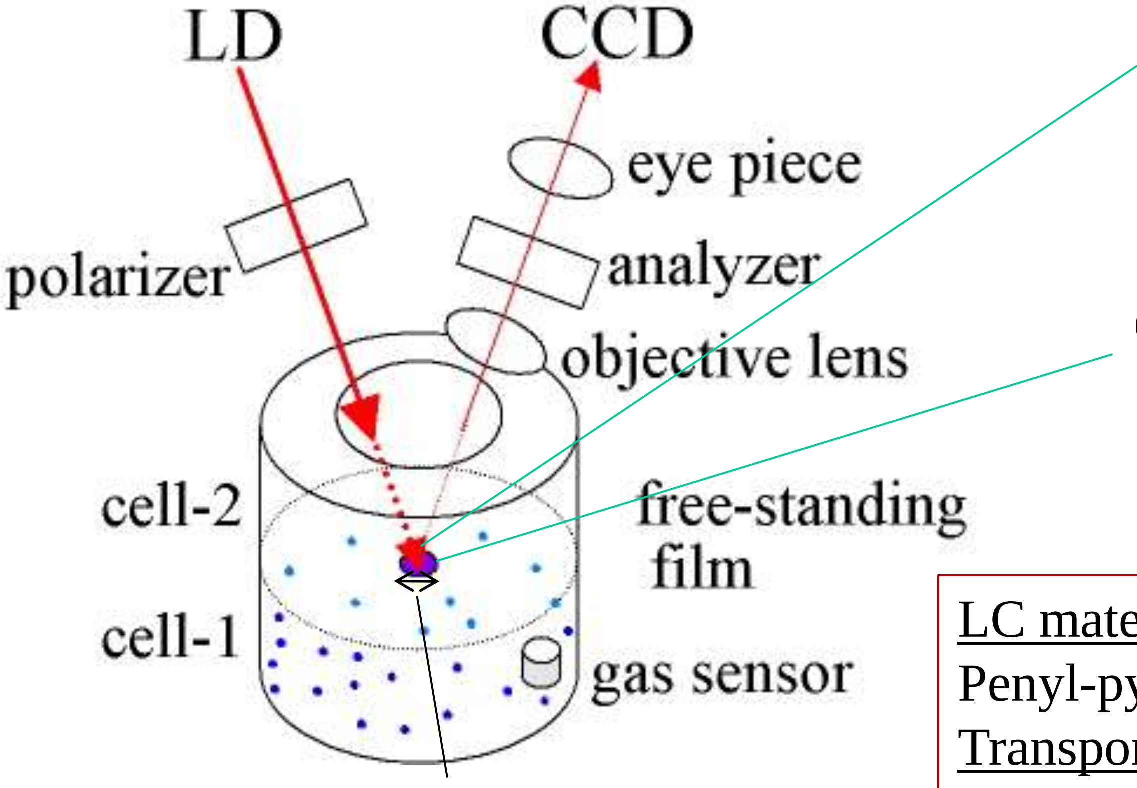
or

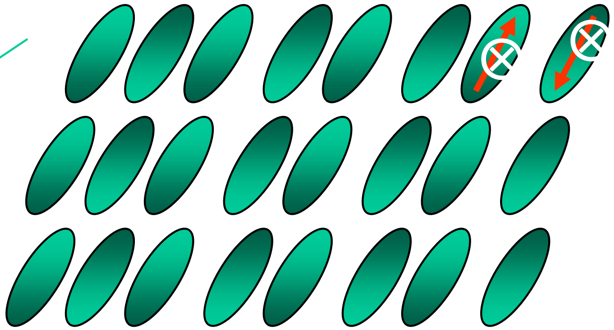
DC current

Experiment with SmC* free-standing films

Merits:

- Changeable film thickness (several nm ~ several μm)
- Wide temperature range
- Free surface
- A variety of flow gas



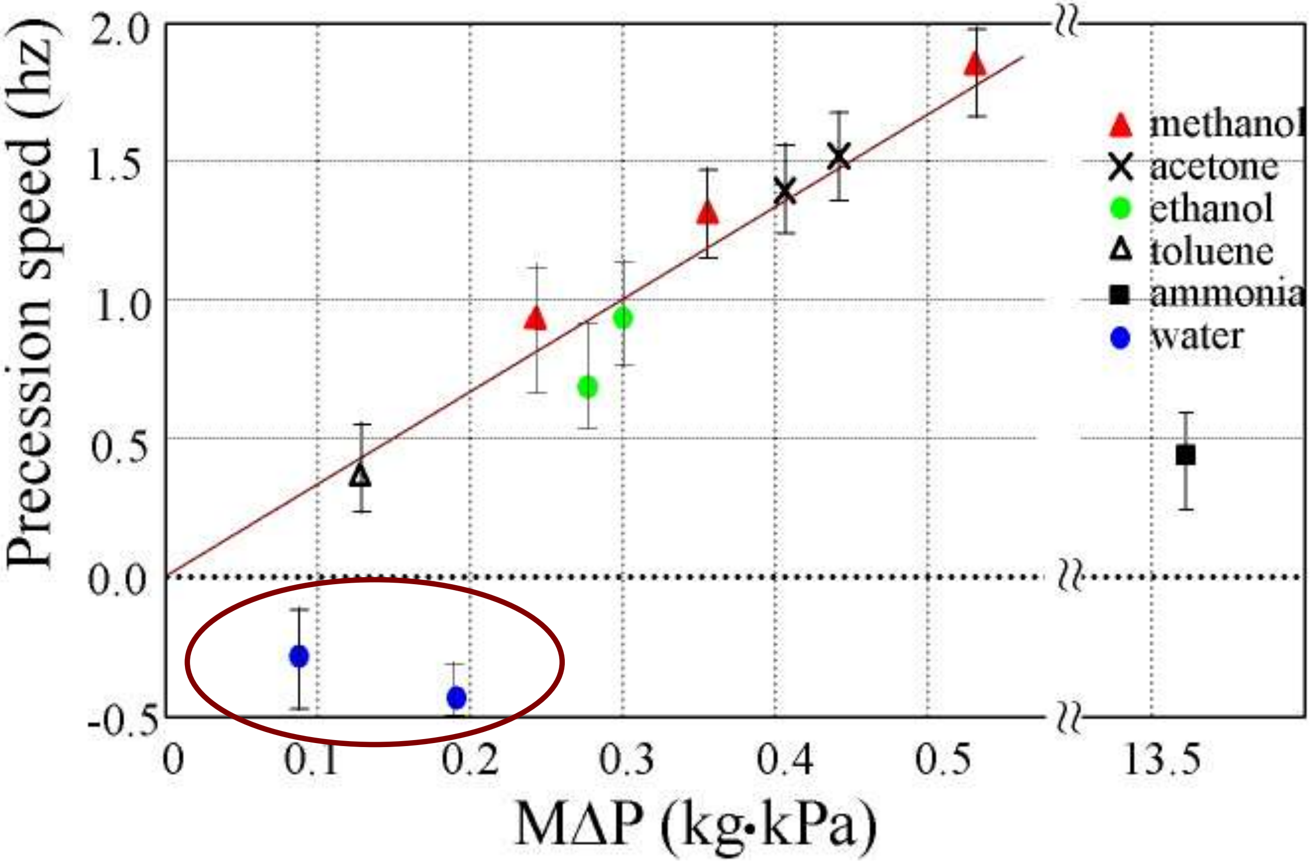


3~20 layers of SmC*

LC materials: Felix (chiral mixture), Penyl-pymiridine with chiral dopants

Transported gas: water, methanol, ethanol, toluene, ammonia

Flux rate vs precession speed
(5 layers film of FELIX013)



{methanol, ethanol, acetone, toluene} in the same group

⇩

coefficients for transforming momentum of the transferred gas into the LC rotational torque are almost same

Characteristics of transferred materials

	water	ammonia	methanol	ethanol	toluene
Vapor pressure (25℃)	3.2 kPa	800 kPa	16.5 kPa	7.4 kPa	2.9 kPa
Molecular weight	18	17	32	46	92
Solubility into LC (calculated, a.u.)	~0.006	~0.007	0.86	0.93	0.85
Dielectric constant	81	22	32	24	2.3

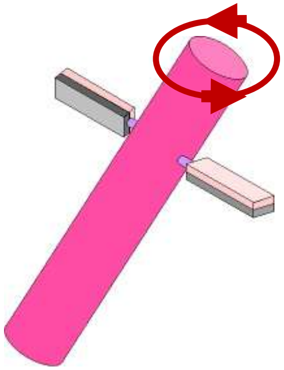
Critical thickness for torque inversion under water transfer

Pitch (um)	Spontaneous polarization (nC/cm^2)	Critical thickness (layer)
6	58	3~4
20	39	7~8
110	42	NA
20	9	NA

Competition between torque caused by helix and by molecular propeller

- ✓Chemical interaction between the molecules is small
- ✓Helix has short pitch

Microscopic torque < Macroscopic torque



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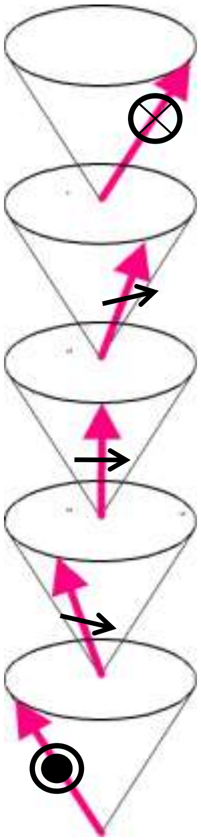


FELIX013: director changes its in-plane direction by 0.06 degree each layer

OUTLINE

1. 研究背景と液晶に見られる非平衡構造

2. 二次元液晶の非平衡ダイナミクス

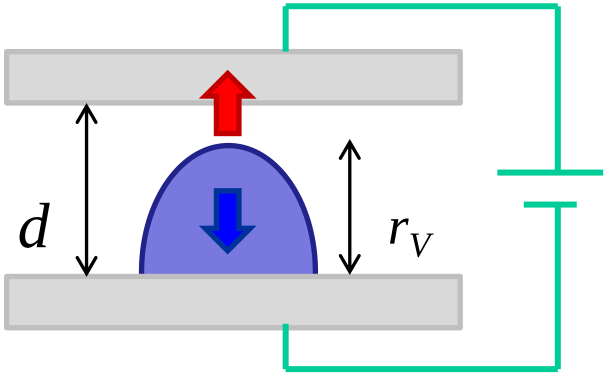
   2-1. 光誘起配向波

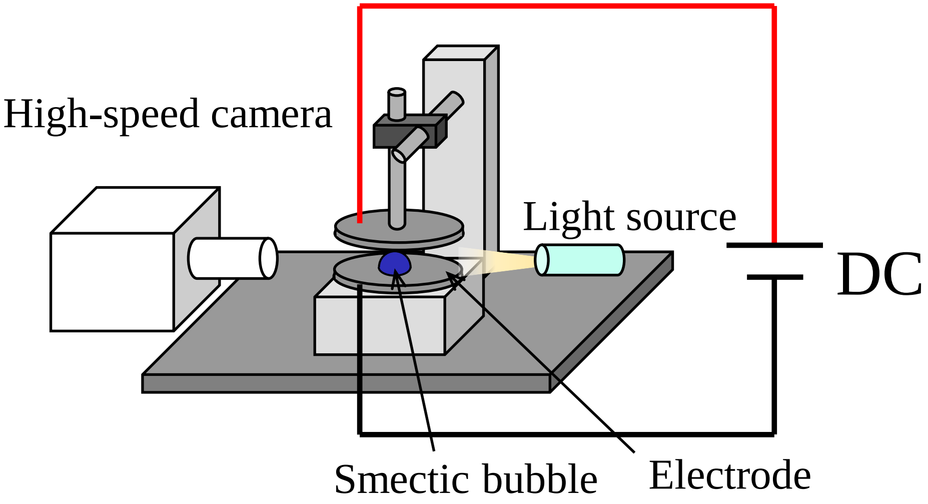
   2-2. 物質流透過によるキラル液晶の一方向回転

   2-3. DC電場による液晶バブルの非平衡ダイナミクス

3. まとめ

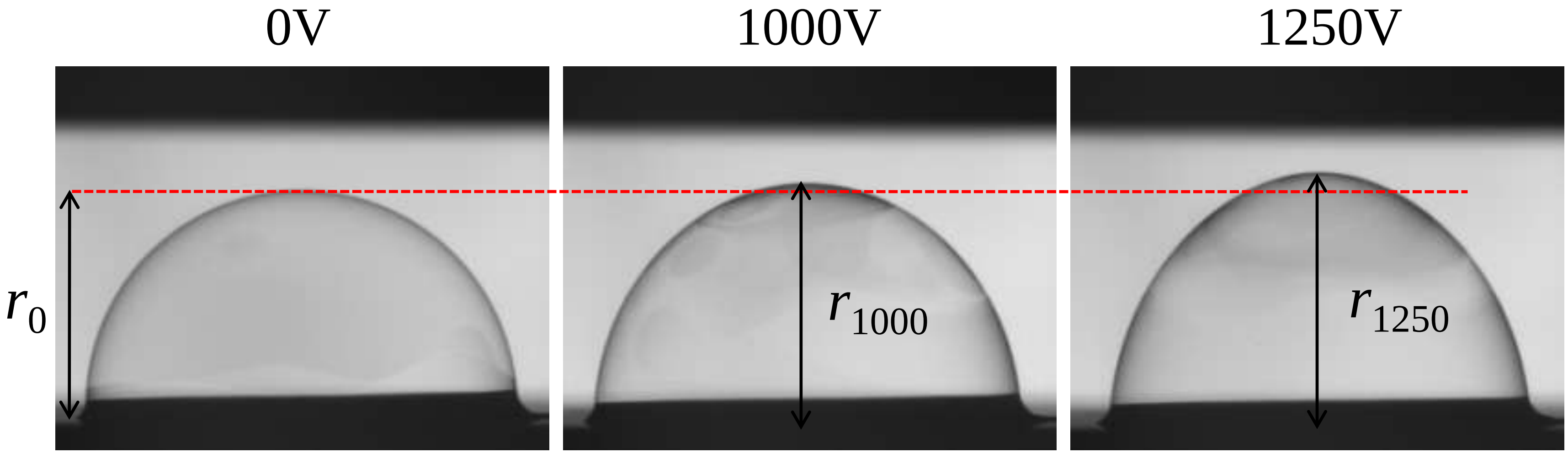
Bubble deformation under DC field





- sample
  - 8CB
- condition
  - r_0 (initial bubble radius): 1.30-3.27mm
  - d (electrode distance): 2.0-4.4mm
  - DC voltage：0-2000V

Static deformation induced by low electric field



Initial bubble radius $r_0 = 2.22\text{mm}$

Distance between electrodes $d = 3.00\text{mm}$

Bubble is pulled by the electrostatic force

Competition between electrostatic force and surface tension

- Force per unit area of bubble surface

$$f_r = \underbrace{\left(p_{in} + \frac{1}{2}\rho E_r\right)}_{\text{expand}} - \underbrace{\left(p_0 + 2\sigma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)\right)}_{\text{shrink}}$$

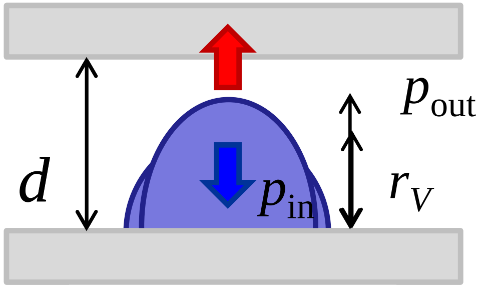
$\rho(z)$: induced charge density

$E_r(z)$: electric field normal to the bubble surface

σ : surface tension

$R_1(z)$, $R_2(z)$: curvature radius

- Assumptions:
  - Bubble shape is ellipsoidal
  - $E_{r\_top} \approx V / (d-h)$
  - Constant molar number inside the bubble



Static deformation in the equilibrium

- $f_r=0$ →

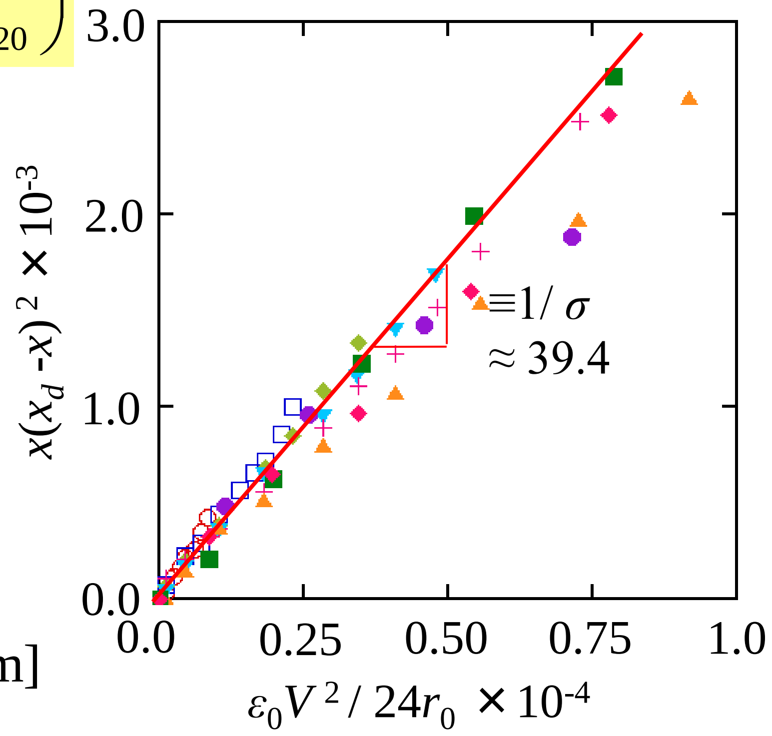
$$\frac{4\sigma}{R_{top}} = \frac{1}{2}\varepsilon_0 E_r^{\ 2} + 2\sigma\left(\frac{1}{R_{10}} + \frac{1}{R_{20}}\right)$$

Normalization

$$x\left(x_d - x\right)^2 = \frac{\varepsilon_0 V^2}{24\sigma r_0}$$

$x = r_V/r_0\text{-}1$

$x_d = d/r_0\text{-}1$



Slope gives:

$\sigma = 0.025$ [N/m]

agree with the reported value $\sigma = 0.024$ [N/m]

By R. Stannarius and C. Cramer (1997)

➡ Derive the surface tension and the induced charge

Under high voltage: Non-equilibrium states

- In the equilibrium state, force must be balanced:

$$\underbrace{x(x_d - x)^2}_{f(x)} = \underbrace{\frac{\varepsilon_0 V^2}{24\sigma r_0}}_{E(V)}$$

$x = r_V / r_0 - 1$:
$x_d = d / r_0 - 1$

⇓

◆ When $V > V_{\mathrm{th}}$, x has no solution except for $x > x_d$

$\Rightarrow$ must touch the electrode

Threshold radius & voltage:

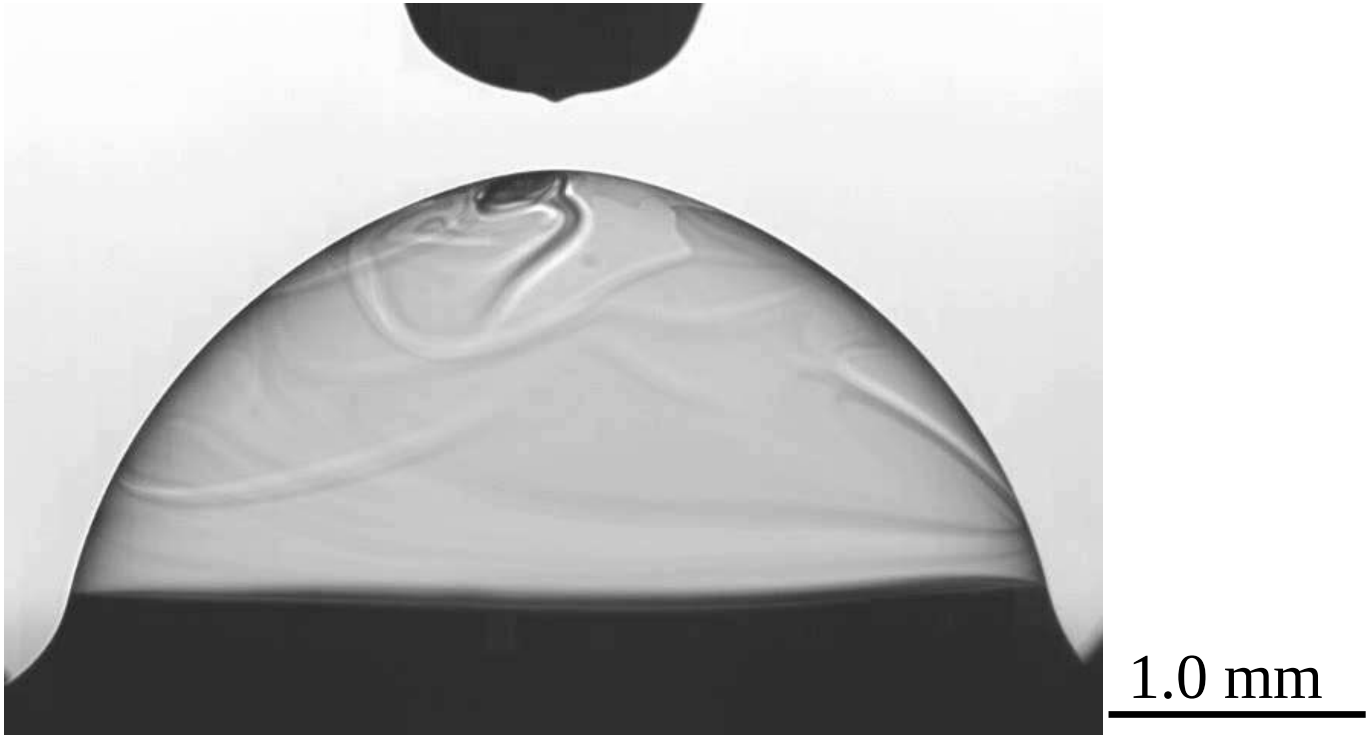
$$x_{\mathrm{th}} = x_d/3 \Leftrightarrow r_{\mathrm{th}} = (2r_0 + d)/3$$

$$E_{\mathrm{th}} = \frac{4}{27} x_d^3 \Leftrightarrow V_{\mathrm{th}} \approx \sqrt{\frac{96\sigma r_0}{27\varepsilon_0} x_d^3}$$

DC電場下での液晶バブルに誘起される不安定性
Oscillation under high DC field

Mass (charge) transport -> interface instability

- Oscillation period：~60ms



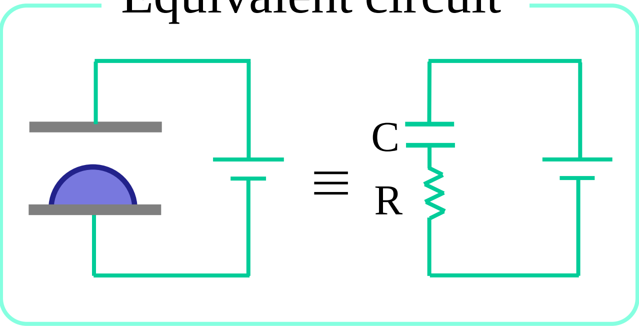
Dynamics of bubble deformation

- Equation of motion of bubble top :

$$\rho_{LC}\frac{d^2 r_v}{dt^2}+\frac{\nu}{r_0}\frac{dr_V}{dt}=\frac{1}{2}\varepsilon_0 E_r{}^2-2\sigma\left(\frac{2}{R_{top}}-\frac{1}{R_{10}}-\frac{1}{R_{20}}\right)$$

- E_r at time t :

Equivalent circuit



$$E_r \approx \frac{V\left(1-\exp\left(-\frac{t}{RC}\right)\right)}{d-r_v}$$

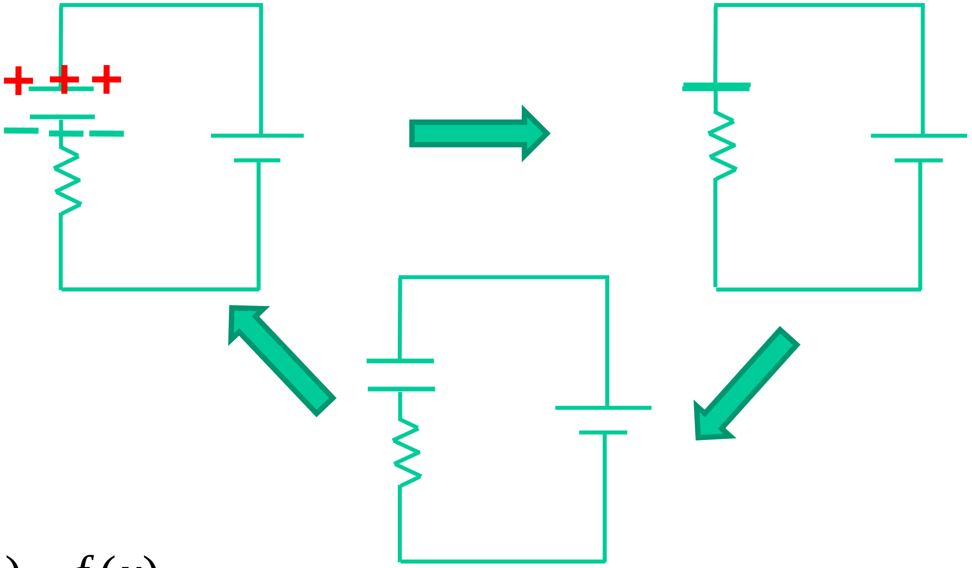
- Normalized equation of motion :

$$\boxed{A\frac{dx}{d\tau}=\frac{E(1-e^{-\tau})}{(x_d-x)^2}-x}$$

$$A=\frac{\nu r_0}{12\sigma RC}<<1 \qquad \tau=\frac{t}{RC}$$

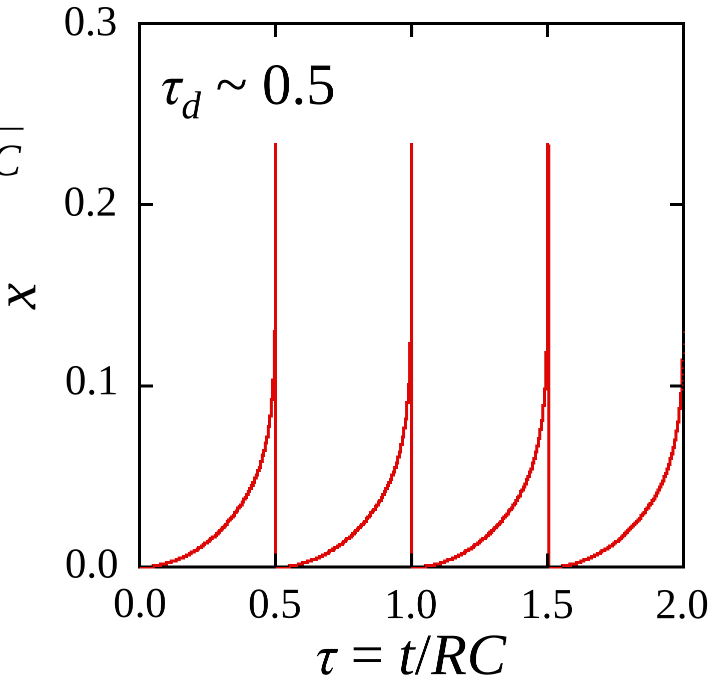
$$E=\frac{\varepsilon_0 V^2}{24\sigma r_0}$$

Charge transfer & re-charge



$$A\frac{dx}{d\tau}=\frac{E(1-e^{-\tau})-f(x)}{(x_d-x)^2}$$

$$:\tau=\frac{t}{RC}$$



まとめ

二次元液晶（単分子膜 or 分子数層からなる自己保持膜）に光・ポテンシャル流・電場により誘起される非平衡構造

✓液晶の強い分子間相互作用が主役
✓二次元系を対象とすることで、分子の運動の偏りがそのままマクロダイナミクスに反映

✓現象論では説明できるが、分子の運動とマクロダイナミクスの間には大きな時空間的隔たりがあり、これを埋めることが課題