Chemical Surface Transformation 1

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- **Chemical reactions** at **Si–H** surfaces (inorganic and organic) can generate very thin films (sub–nm thickness up to μm):

⇒ **inorganic** layer formation by:

– thermal conversion: $Si + O_2 \rightarrow SiO_2$ (~1000°C)

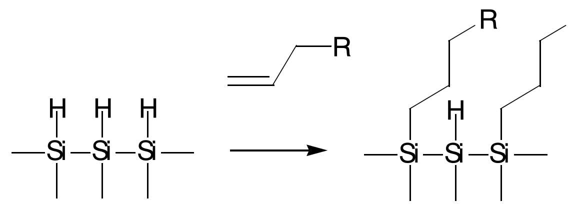
$Si + N_2 \rightarrow Si_3N_4$ (~900°C)

– chemical vapor conversion

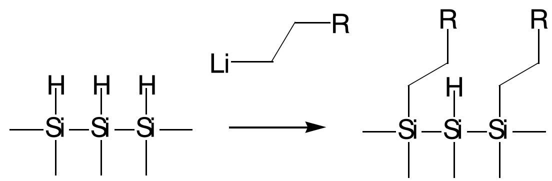
– electrolytic deposition (electro– and electroless plating)

⇒ **organic** layer formation by:

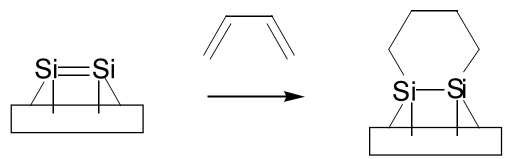
– hydrosilylation (radical, thermal, photochem., catalytic):



– alkyl / aryl carbanions (Grignard, alkyl lithium):



– [2+2] and [4+2] reactions (UHV):



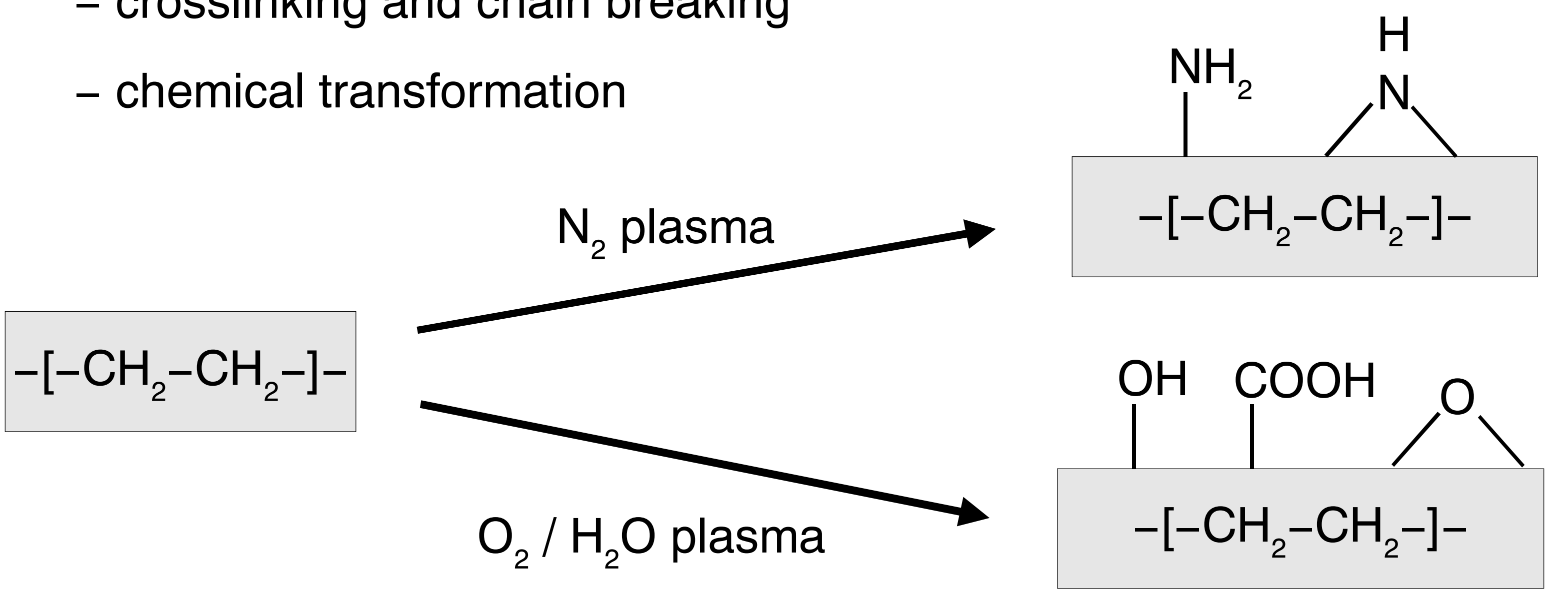
Chemical Surface Transformation 2

- **Chemical modification** of **polymer** surfaces with **plasma**:

⇒ **inorganic** and **organic** layer formation by plasma treatment of polymer surface:

low pressure ~ 1 torr, high frequency (≥ 1 MHz) **discharge** generates **electrons** (bond breaking), **reactive atoms** and molecular **fragments** (radicals, ions)

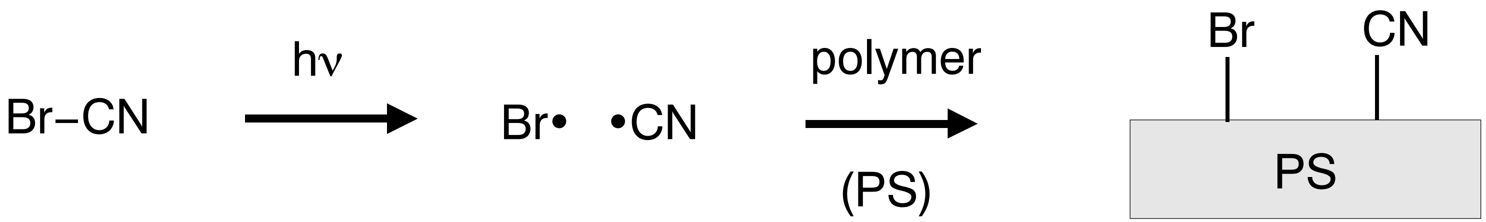
- – cleaning (remove organic contaminants)
- – ablation / etching (remove substrate material)
- – crosslinking and chain breaking
- – chemical transformation



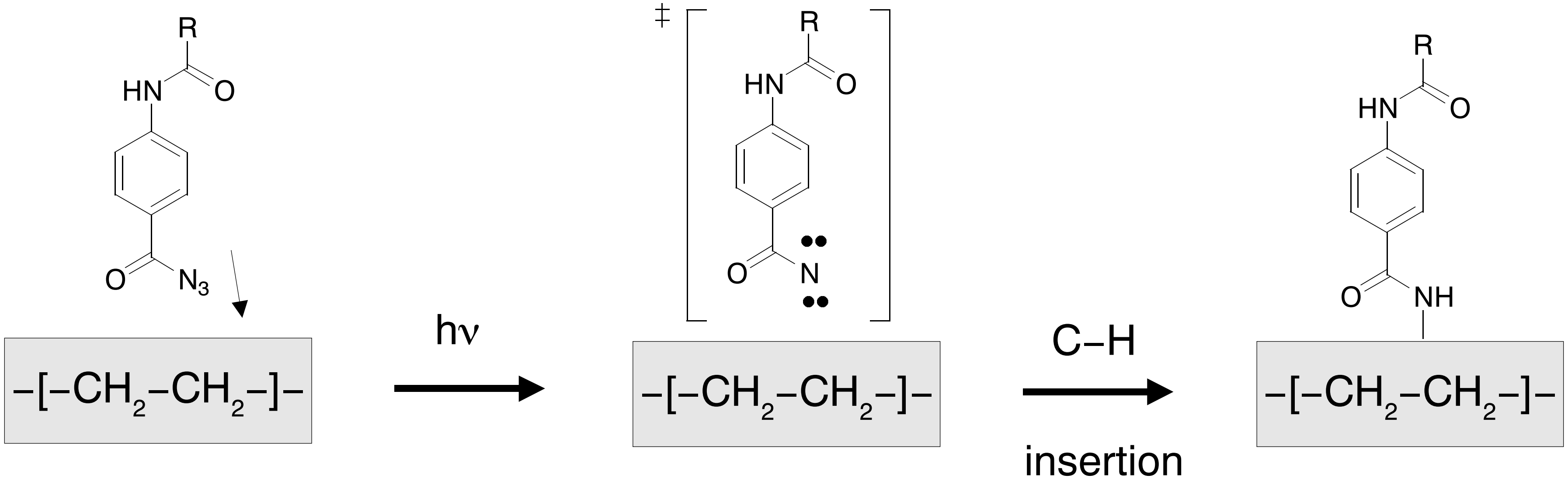
Chemical Surface Transformation 3

- **Chemical modification** of **polymer** surfaces with **photochemically**:

  – **activation** of reactive molecules by **light** in the **gas** phase:

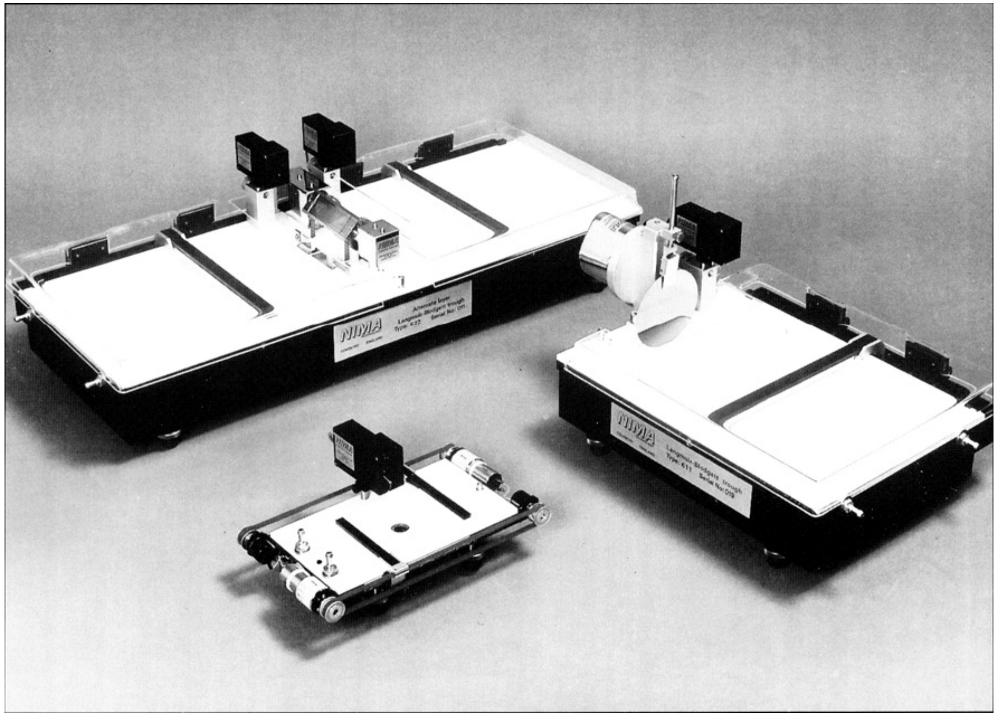


  – photochemical **activation** of molecules **adsorbed** onto the **polymer surface**:

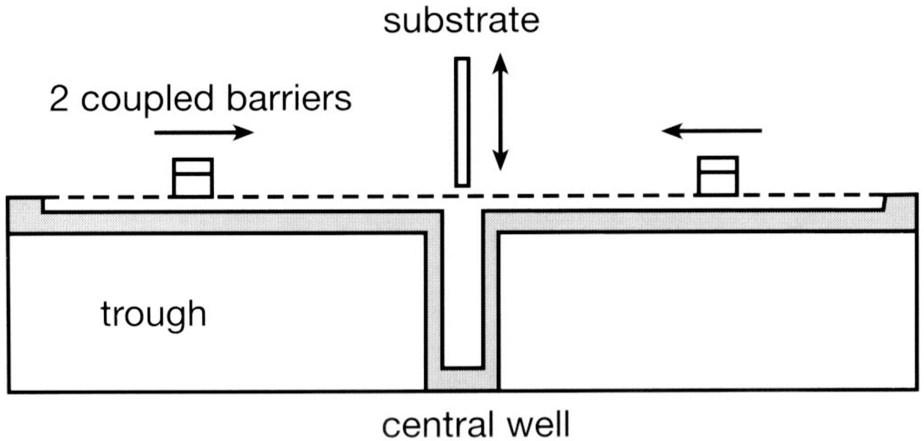


Langmuir–Blodgett (LB) Technique: Troughs

trough made of **hydrophobic** material (→ Teflon) is filled with a **subphase** (water, salt solution,...); **barrier** of hydrophobic material **confines** surface **region** → total **area** of **air–water interface** can be controlled by **barrier position**; device to measure **surface tension** of subphase (→ Wilhelmi plate, Langmuir pressure pickup / floating barrier); **dipping** device to pass a substrate through a floating film (→ LB transfer); **computer control** to set barrier position / movement (direction and speed), to measure surface tension with respect to barrier position (→ film compression and expansion), to control dipper speed / direction with respect to surface pressure and barrier movement (→ LB transfer)

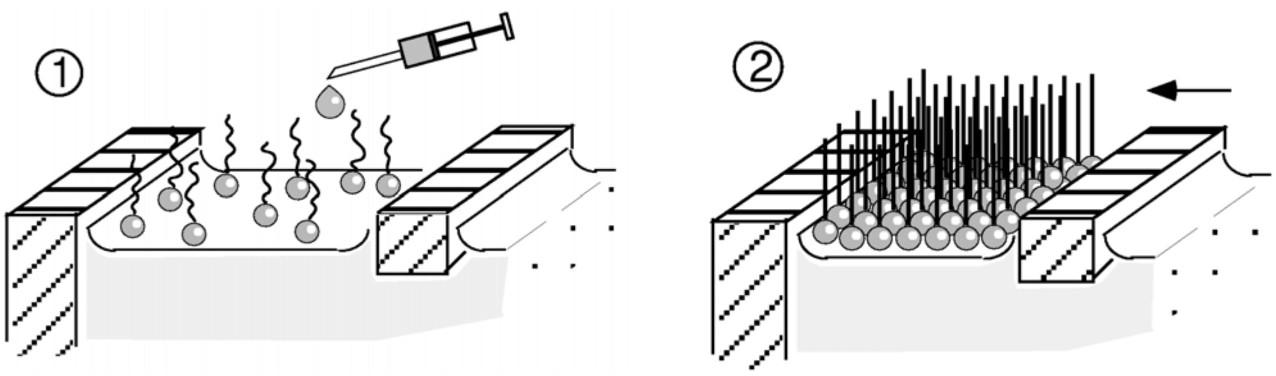


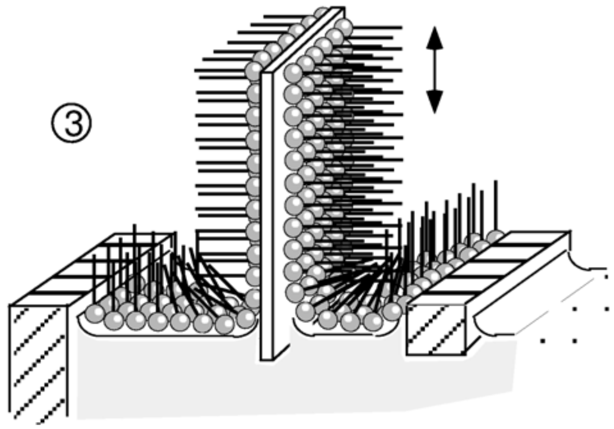
optional equipment:
(fluorescence) microscope, surface potential probe, IR (reflection mode), x–ray reflection ...

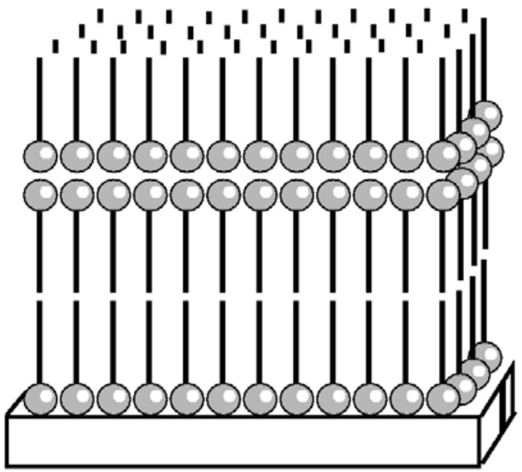


LB Technique: Spreading and Film Transfer

1) spreading of an amphiphile solution in a water immiscible solvent at the air−water interface
2) compressing of the amphiphile monolayer after solvent evaporation
3) transfer of the monolayer to a solid substrate by vertical dipping







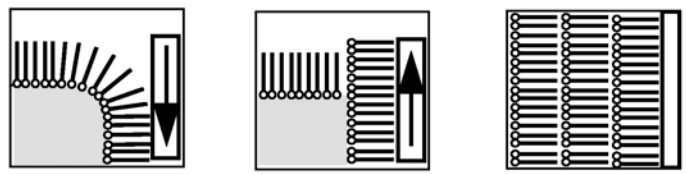
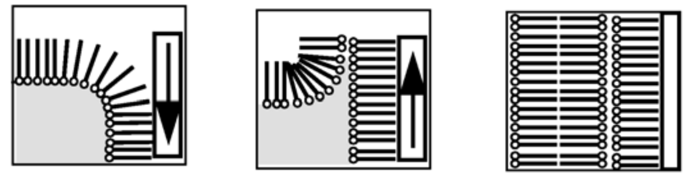
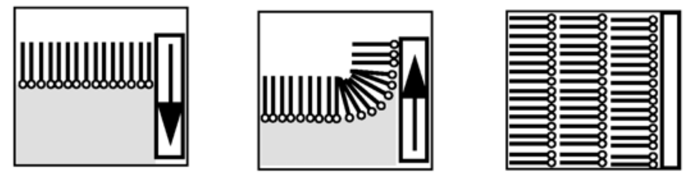
structure of an LB film
(3 layers) after transfer

different transfer behavior and resulting LB multilayer structures

– transfer only upon down stroke:
(x−type)

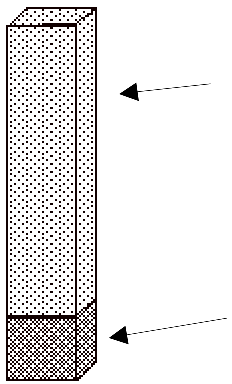
– transfer on up and down stroke:
(y−type)

– transfer only on up stroke:
(z−type)

LB Technique: Structure of Amphiphilic Molecules

amphiphile: molecule with a **polar** region / head group (hydrophilic) and an **apolar** rest / tail (hydrophobic) $\rightarrow$ leads to a preferential molecular orientation at the air–water interface



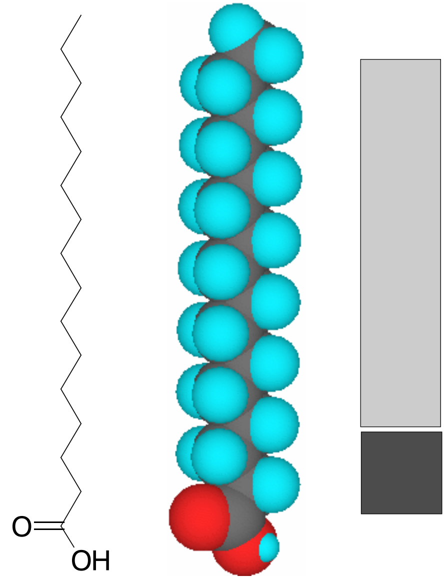
apolar tail: $-(CH_2)_nCH_3$, $-(CF_2)_nCF_3$

– aromatic units, –polymers, $-(SiMe_3O)Me$

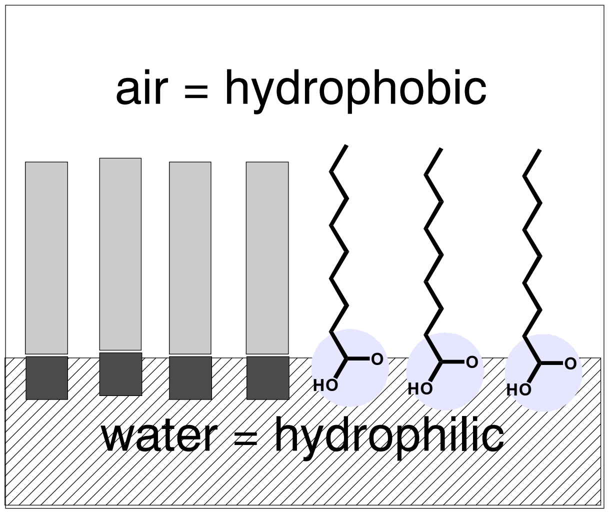
$\rightarrow$ longer chains increase layer stability (intermol. i.a.)

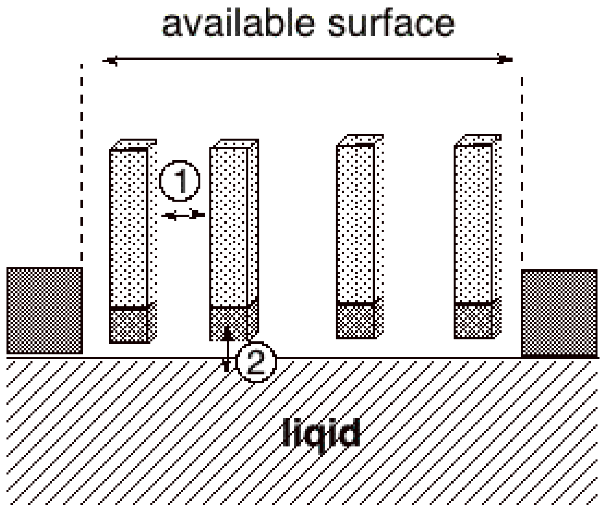
polar head group: $-OH$, $-COOH$, $-CONH_2$, $-NH_2$, $-NMe_3^+$, $-NO_2$, $-CN$, $-PO(OH)_2$, $-SO_2OH$, $-(OCH_2CH_2)_nOH$

$\rightarrow$ more polar head groups increase layer stability



example: palmitic acid





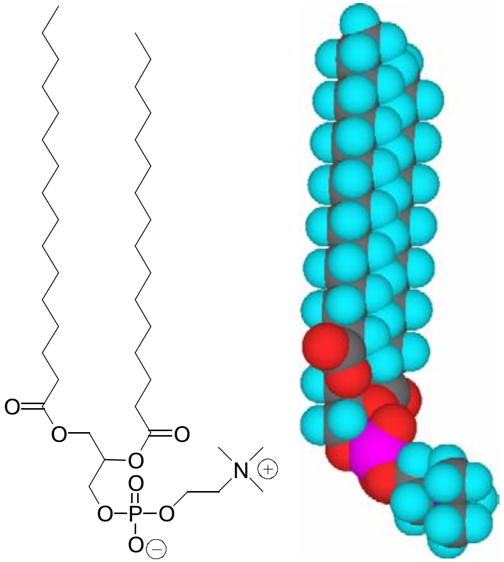
<u>interactions:</u>

1. intermolecular $\rightarrow$ bulk
2. molecule - liquid surf.

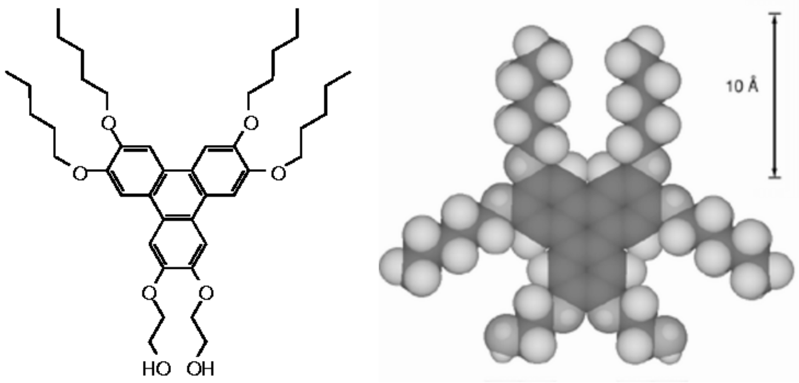
$\Rightarrow$ surface coverage $(^N/_A) \rightarrow$ lateral pressure important !

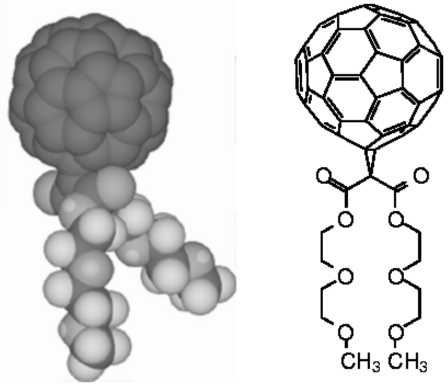
LB Technique: Spreadable Molecules

phospholipid DPPC
(→ cell membranes...)



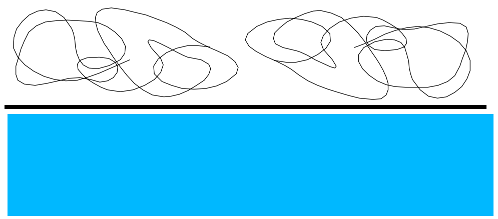
amphiphilic **triphenylene** derivative and **fullerene** derivative



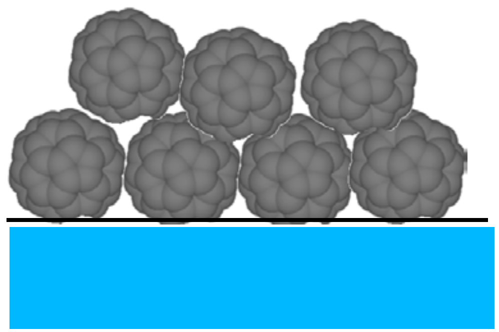


→ also **nonpolar** materials can be spread which form often less stable or very rigid Langmuir films (not necessarily monolayers) depending on the intermolecular interactions:

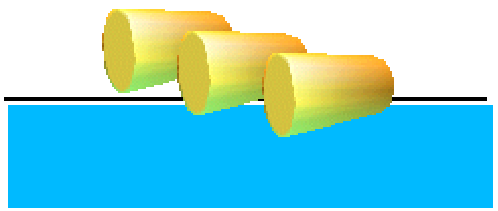
apolar polymers
(soft film)



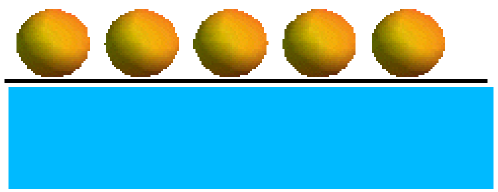
fullerenes (rigid film)



rigid rod polymers



colloidal particles
(polymer latex,
Ag nanoparticles)

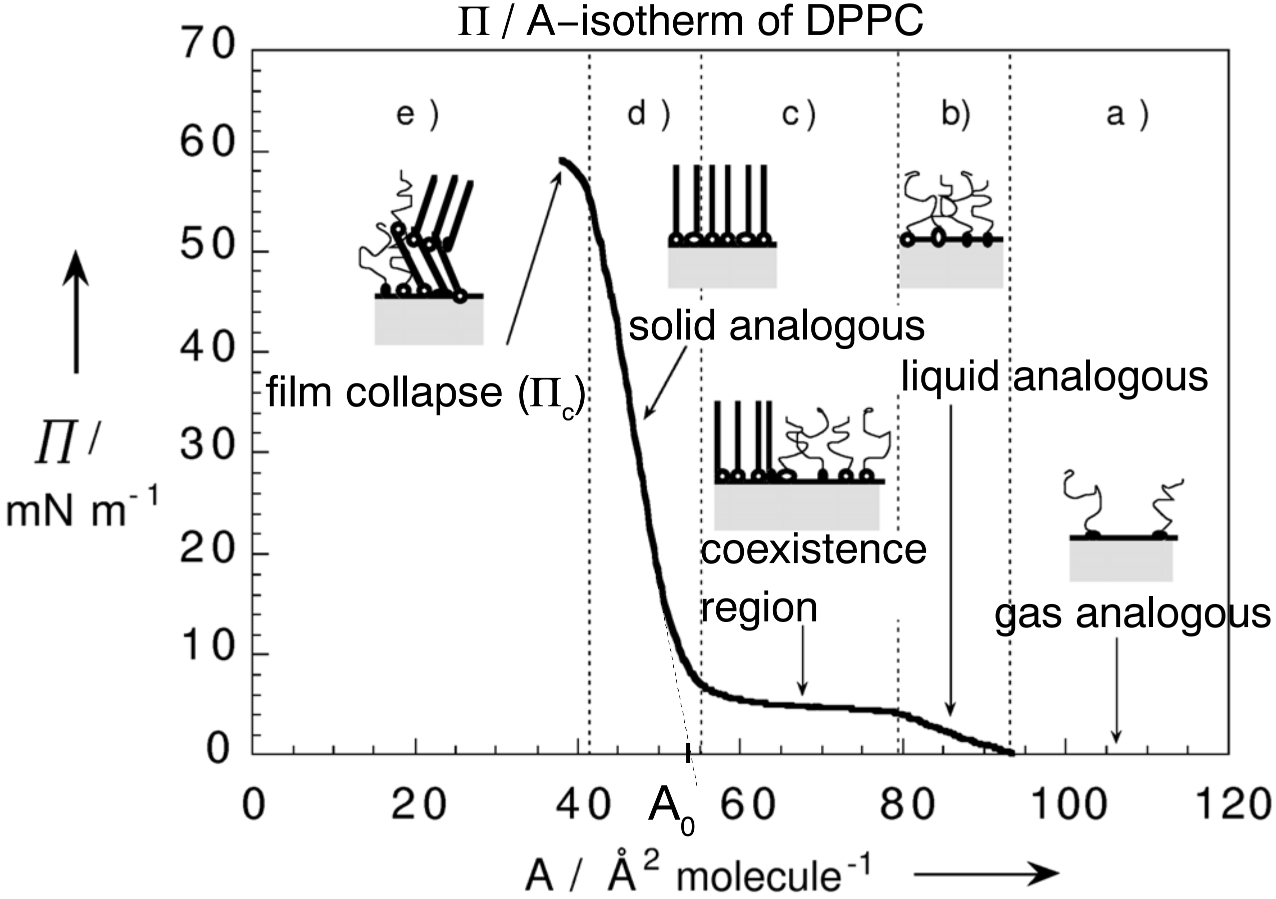


LB Technique: Phase Diagram of Monolayers

amphiphiles at the air–water interface can show in two dimensions a phase behavior (gas–, liquid–, solid analogous) similar to states in 3 D, differences in density and order

→ Π / **A–isotherm**: measurement of surface tension / pressure (mN m^{-1}) with respect to molecular area (Å^2 molecule^{-1}) at a given temperature, allows the measurement of the molecular footprint / projection area

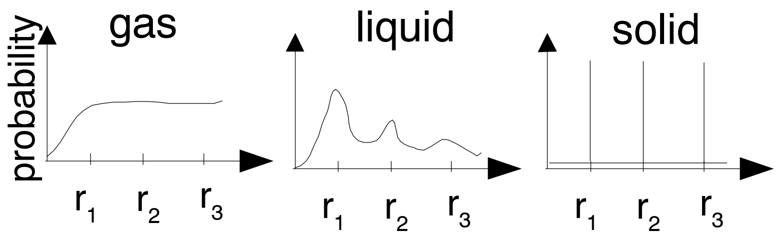
Π / A–isotherm of DPPC



characterization of phases by **translational** and **orientational** order

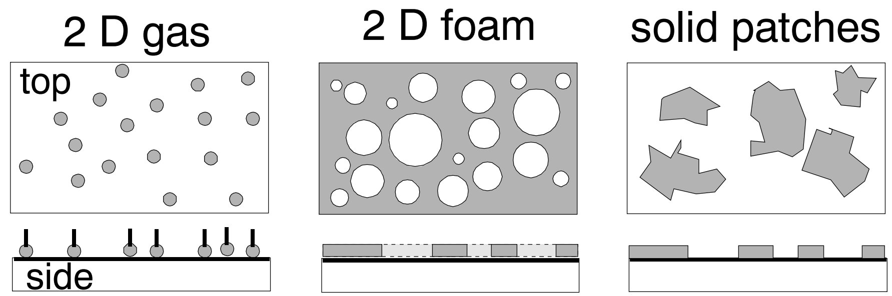
state	***translational order***	***orientational order***
gas	no	no
liquid	yes	no
solid	yes	yes

pair correlation function:



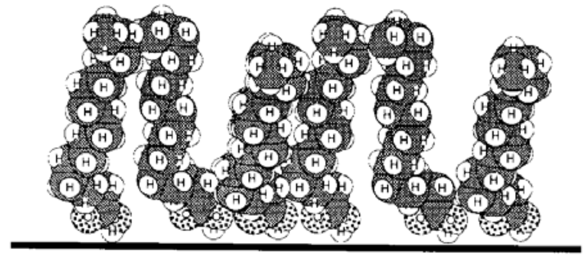
LB Technique: Molecular Packing in Monolayers

gas analogous regime: 1) at sufficiently high temperature amphiphiles might show no intermolecular attraction → 2 D gas, molecules equally / isotropically distributed over surface

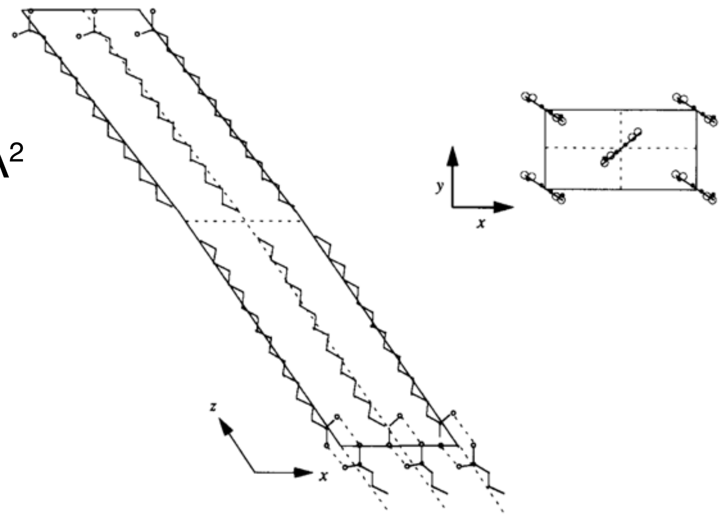


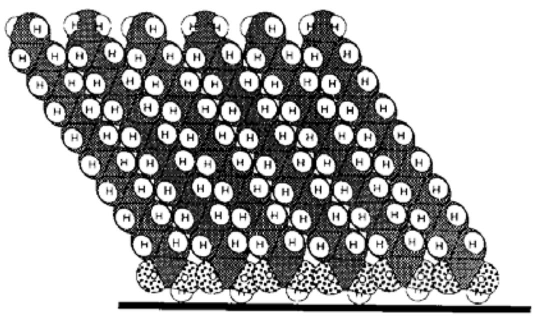
2) if strong intermol. attractions exist → formation of 2 D foam (liquid analogous phase with holes) or patches (solid analogous rafts)

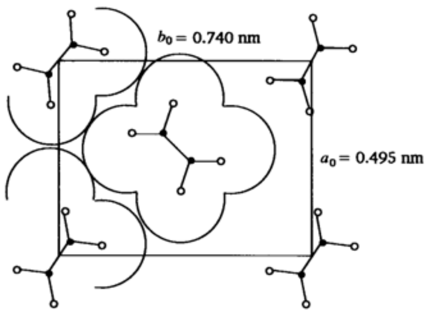
liquid analogous regime: amphiphilic molecules are in contact without translational order, alkyl chains show multiple conformations (gauche / trans), high inplane mobility (diffusion) and intramolecular dynamics (rotation around single bonds / conformation)



solid analogous regime: amphiphilic molecules are tightly packed with similar crystalline order of alkyl chains as in 3 D bulk crystal → mol. area (cross section) of alkyl chain 18−21 Å^2



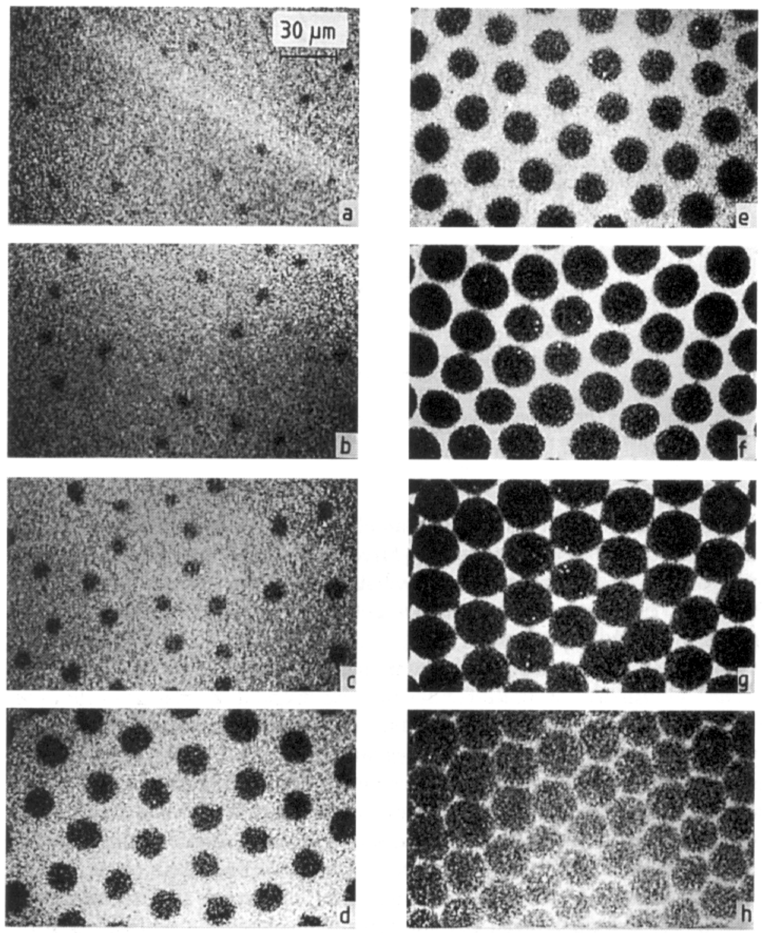


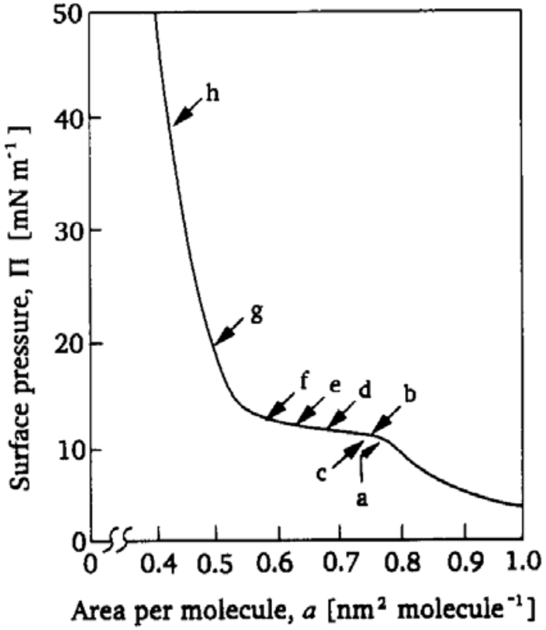


LB Technique: Observation of Monolayers Phases

monolayer states (gas−, liquid−, solid analogous) at the air−water interface can be observed by microscopy techniques (fluorescence, Brewster angle)

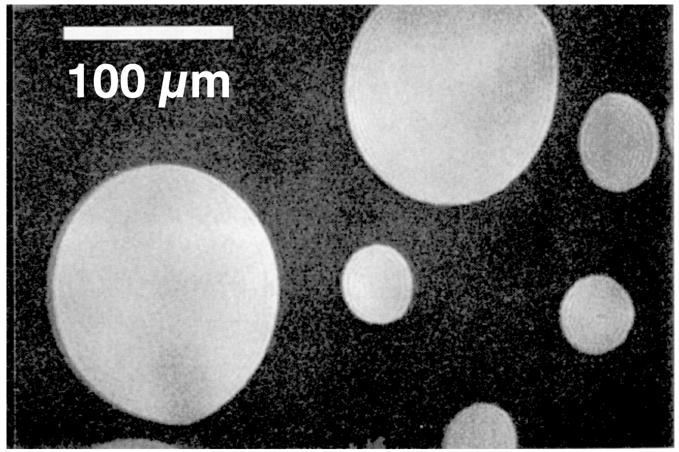
fluorescence microscopy of dimyristol−phosphatic acid doped with fluorescent dye



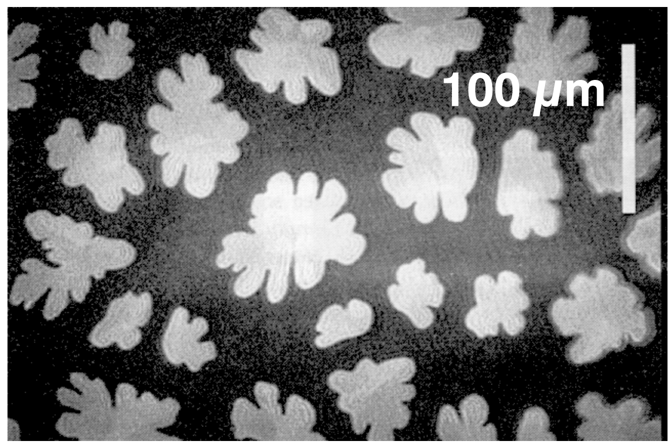


Brewster angle microscopy:

pentadecanoic acid (5 mN m^{-1})

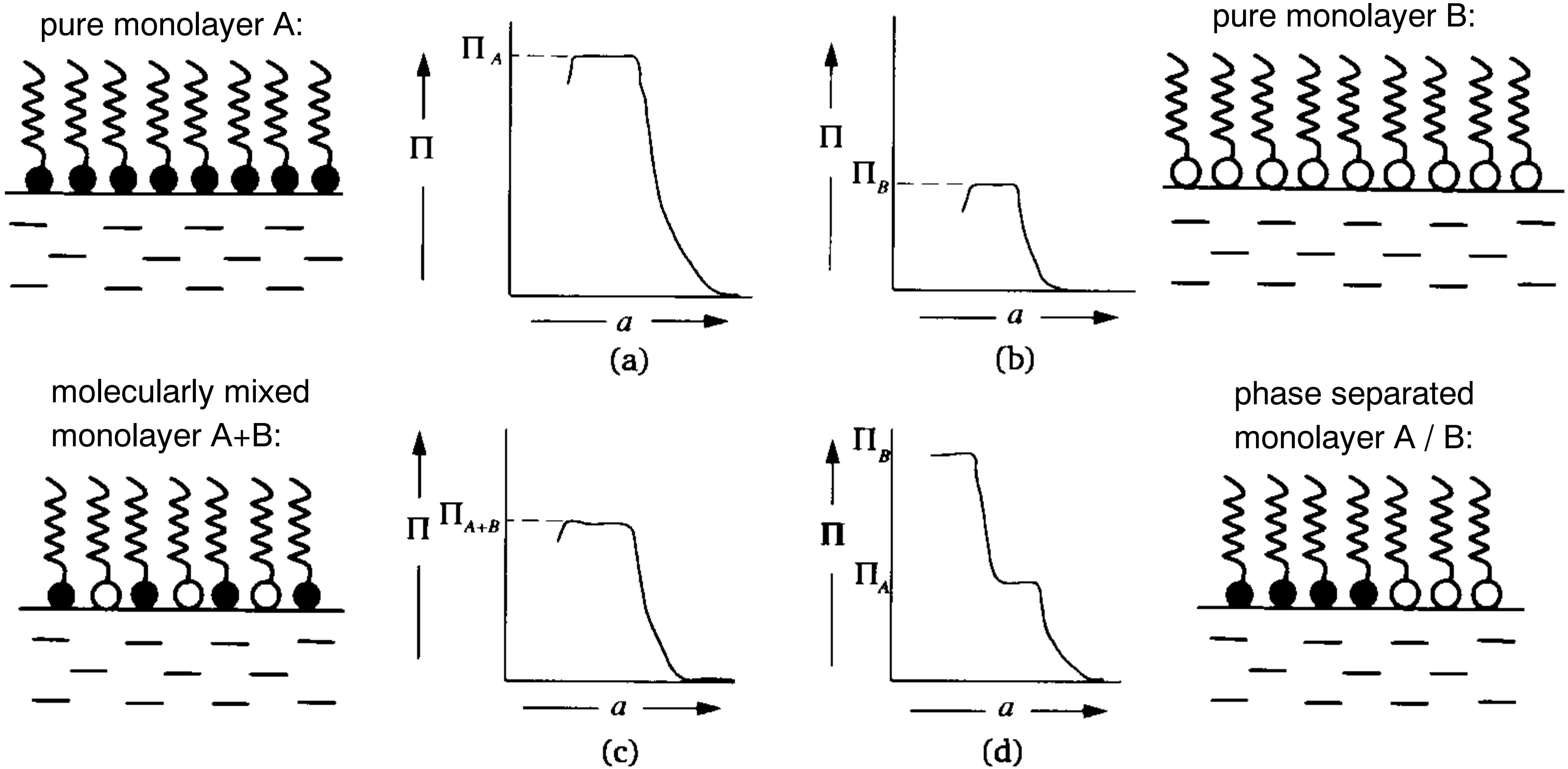


dimyristoyl−phosphatidyl−ethanolamine (8 mN m^{-1})



LB Technique: Mixed Monolayers

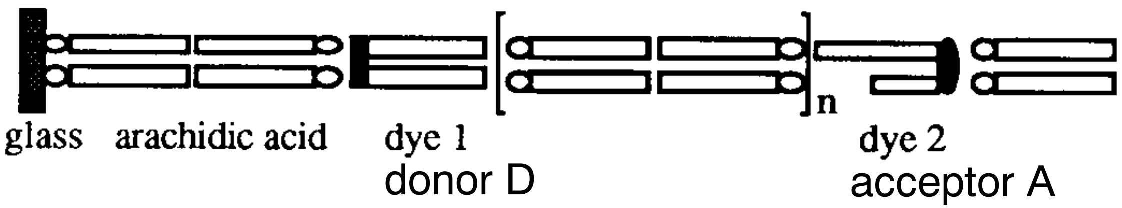
depending on the **miscibility** of the individual monolayer **constituents** the isotherm will show distinct features for a **phase separated** system (individual collapses) or a **molecularly mixed** situation (intermediate collapse)

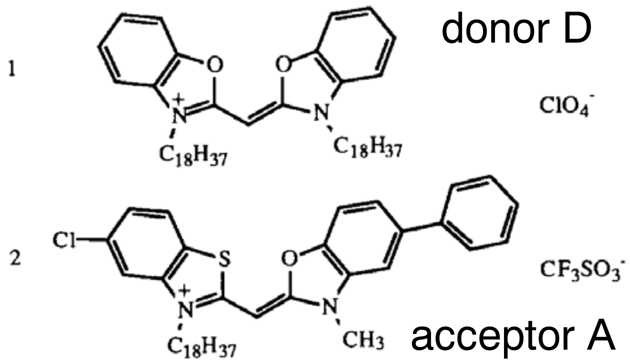


LB Technique: Energy Transfer in LB Films

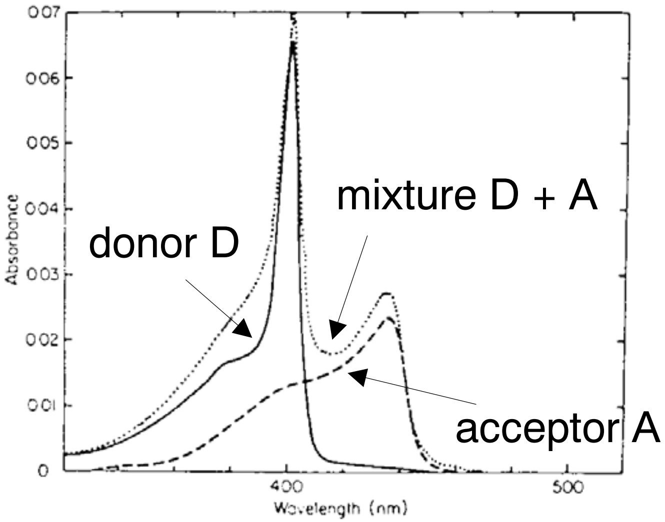
energy transfer (Förster transfer) between energy **donor D** (high energy fluorescence) and energy **acceptor A** (absorption at wavelength of D emission) depends on **D−A separation** (d^{-6} in solution, d^{-4} in LB films) based on electric dipole interaction → **separation** can very well be **controlled** in mixed **LB films** (alternating deposition of different amphiphiles)

schematic LB film structure:

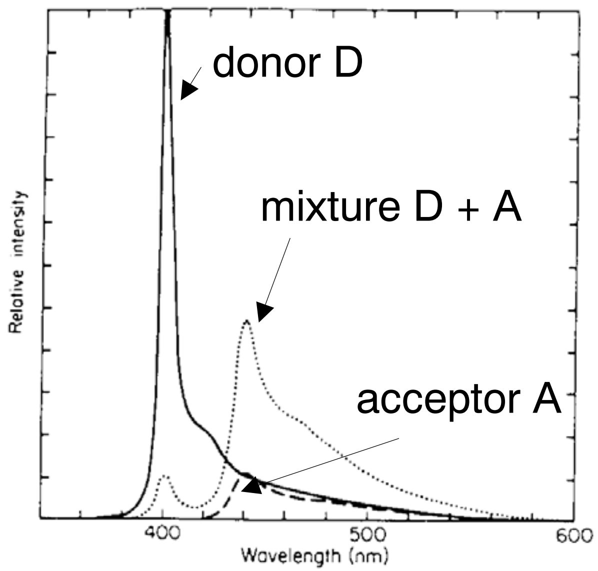


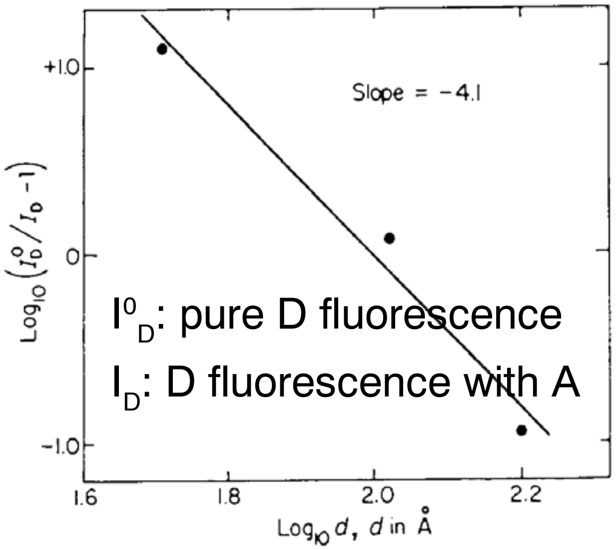


absorption spectra



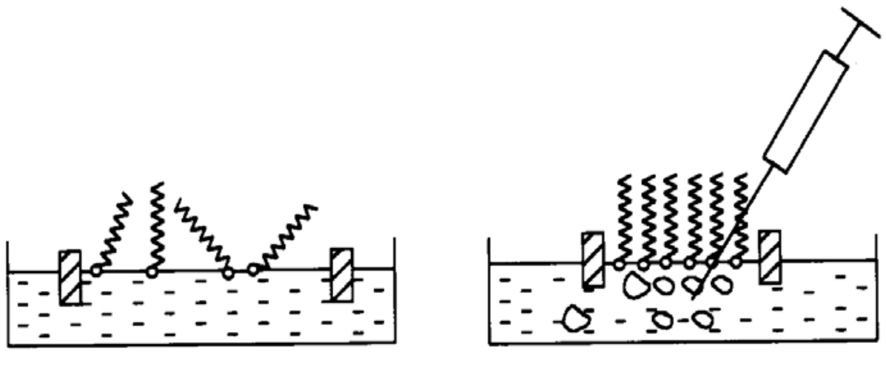
fluorescence spectra





LB Technique: Protein Crystallization at the Air−Water Interface

by adsorbing / binding proteins at ordered monolayer with appropriate ligands at the air−water interface protein crystallization might be induced (sometimes hard to achieve in 3 D)



(a) (b)

a) compression of amphiphile monolayer with protein ligand (e.g. biotin) attached to amphiphiles

b) injection of target protein into the subphase which binds to the ligand in the monolayer
→ example: streptavidin crystallization at a biotinylated monolayer