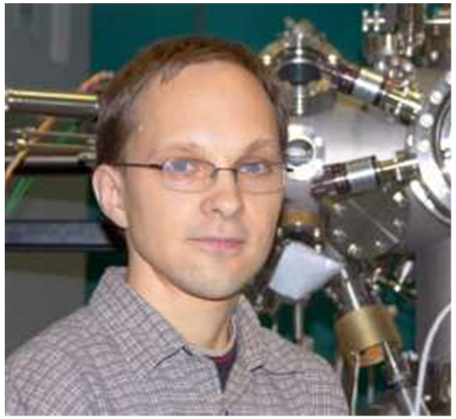
Some common themes on C7 (experiment / theory / simulations) in soft / molecular and biological matter

→ Structure formation
→ Scattering
→ Optical spectroscopy
→ ...

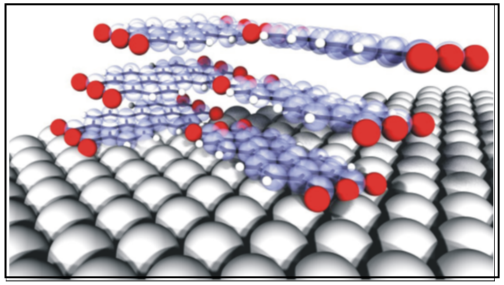
Alexander Gerlach

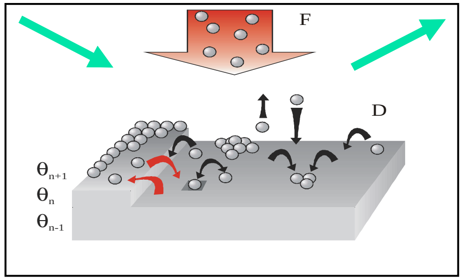


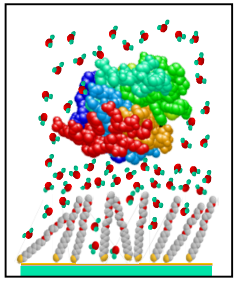
Katharina Broch

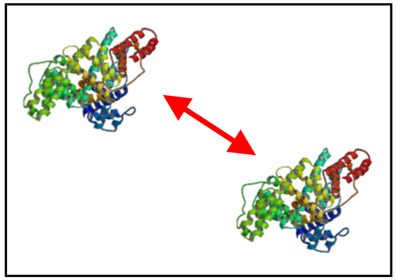
Fajun Zhang

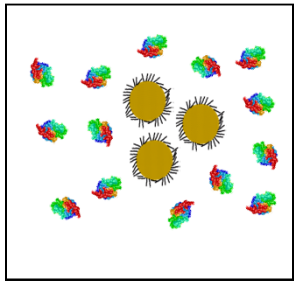
Hajo Schöpe





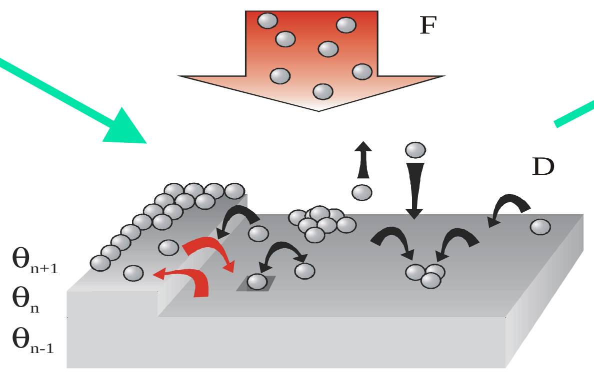


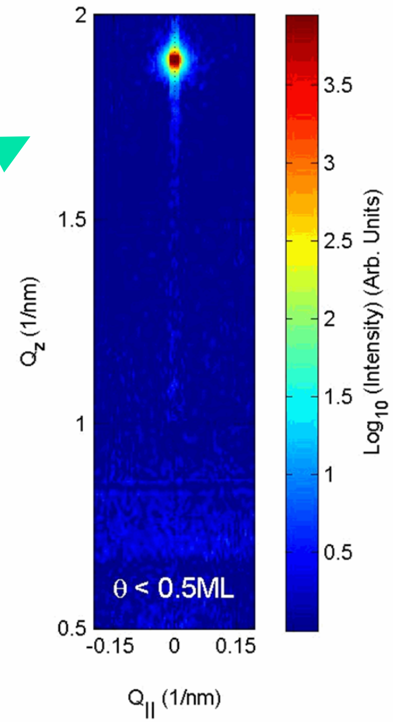




Watch them as they grow: Following thin film formation in real time

Frank Schreiber
http://www.soft-matter.uni-tuebingen.de





Outline

- **Part 1 Film Growth: Concepts and Applications**
- Part 2 Model Studies of Film Growth
  - specular reflectivity
  - off-specular scattering: GIXD, GISAXS, ...
  - complementary methods: optical spectroscopy, transport ...
- Part 3 Multi-Component Systems and Devices

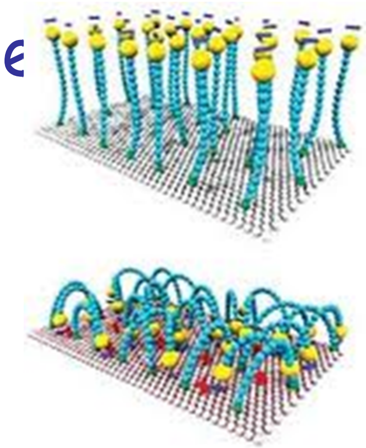
with many thanks to various funding agencies and large-scale facilities

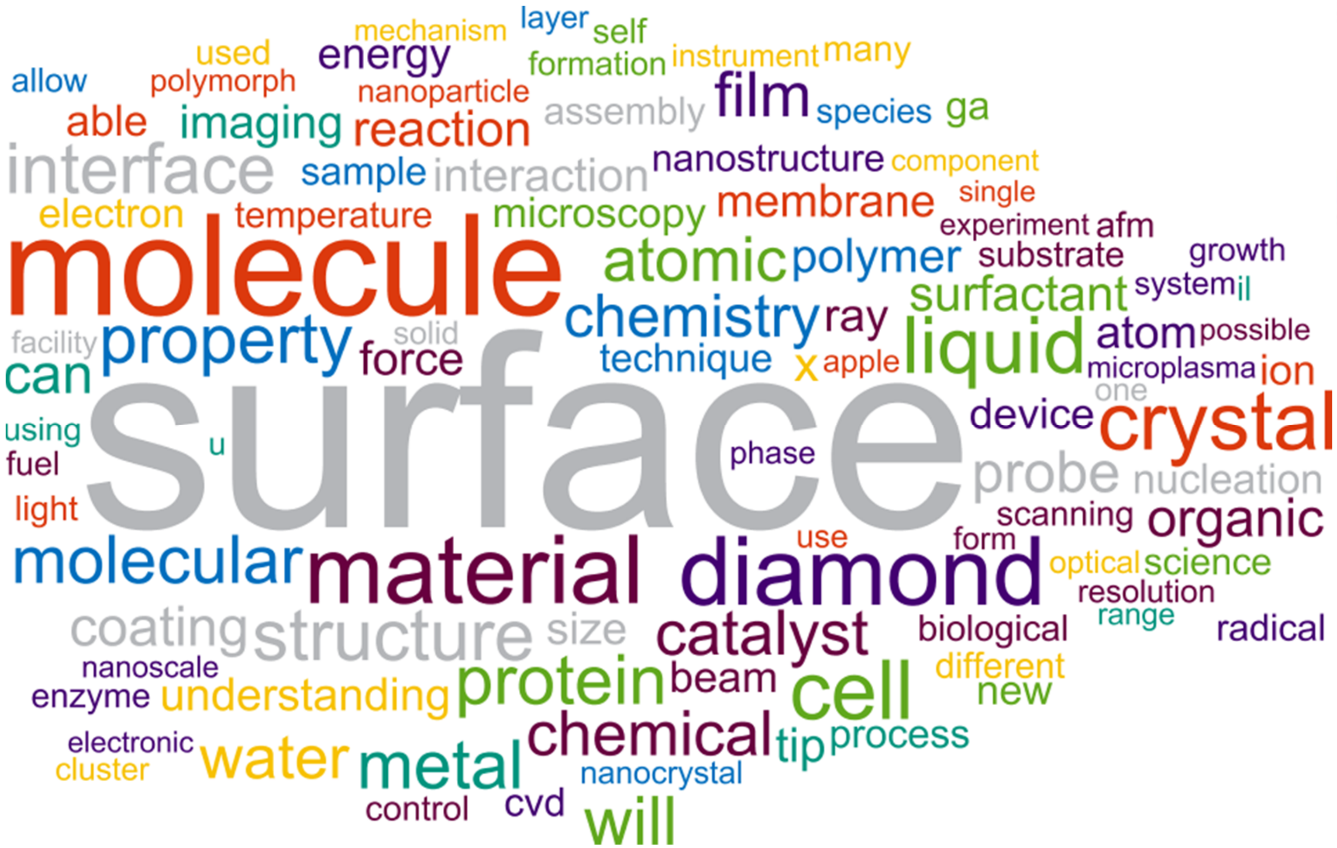
Part 1
Film Growth: Concepts and Applications

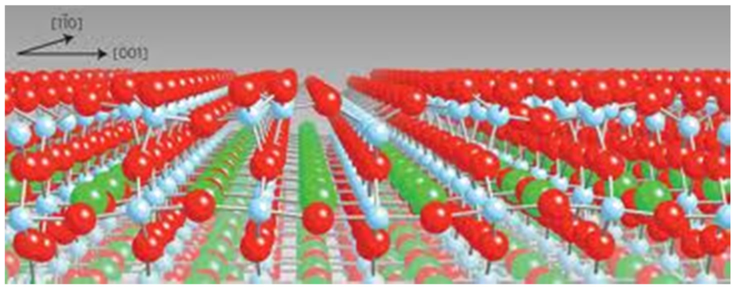
1. Relevance and applications
   --- thin films and interfaces
   --- growth

2. Concepts
   --- growth phenomena
   --- growth modes of thin films
   --- thermodynamics
   --- non-equilibrium issues and statistics

Thin films and interfaces are everywhere







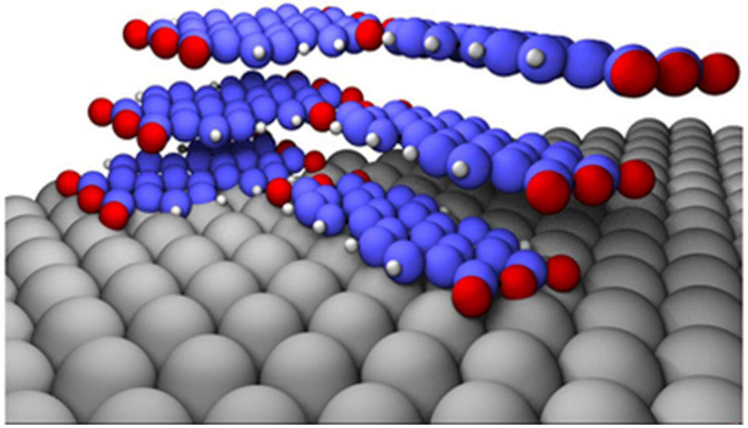
http://pubs.acs.org/cen/coverstory/8151/8151sciencereview13.html

Nature Materials 9 (2010) 185

Thin films and interfaces are everywhere

Applications of Thin Films and Interfaces

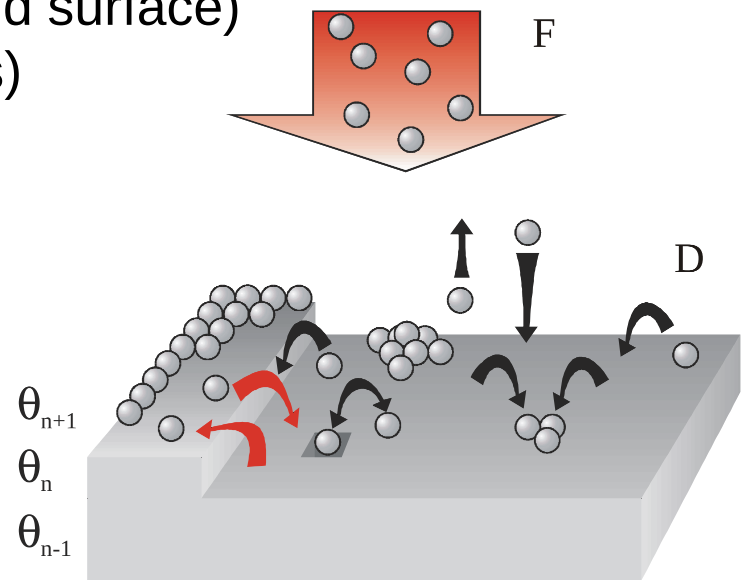
- protective coatings (corrosion protection etc.)
- catalysis
- optical elements / mirrors
- nanostructuring
    - micromechanics
    - microelectronics
- organic electronics
    - organic transistors (OFETs)
    - organic light emitting diodes (OLEDs)
    - organic photovoltaics (OPV)
- bio-compatible interfaces (implants etc.)
- growth of crystals (including protein crystals and biominerals)
- surface freezing / melting
- surface magnetism / magnetic storage
- …



Thin films and interfaces are everywhere

<u>Film Growth Methods</u>

- Molecular beam epitaxy (MBE)
- Organic molecular beam epitaxy / deposition (OMBE / OMBD)
- Langmuir films (amphiphilic molecules at gas-liquid interface)
- Langmuir-Blodgett (LB) films
  (Langmuir films transferred to a solid surface)
- Self-assembled monolayers (SAMs)
- Spin-coating
- …

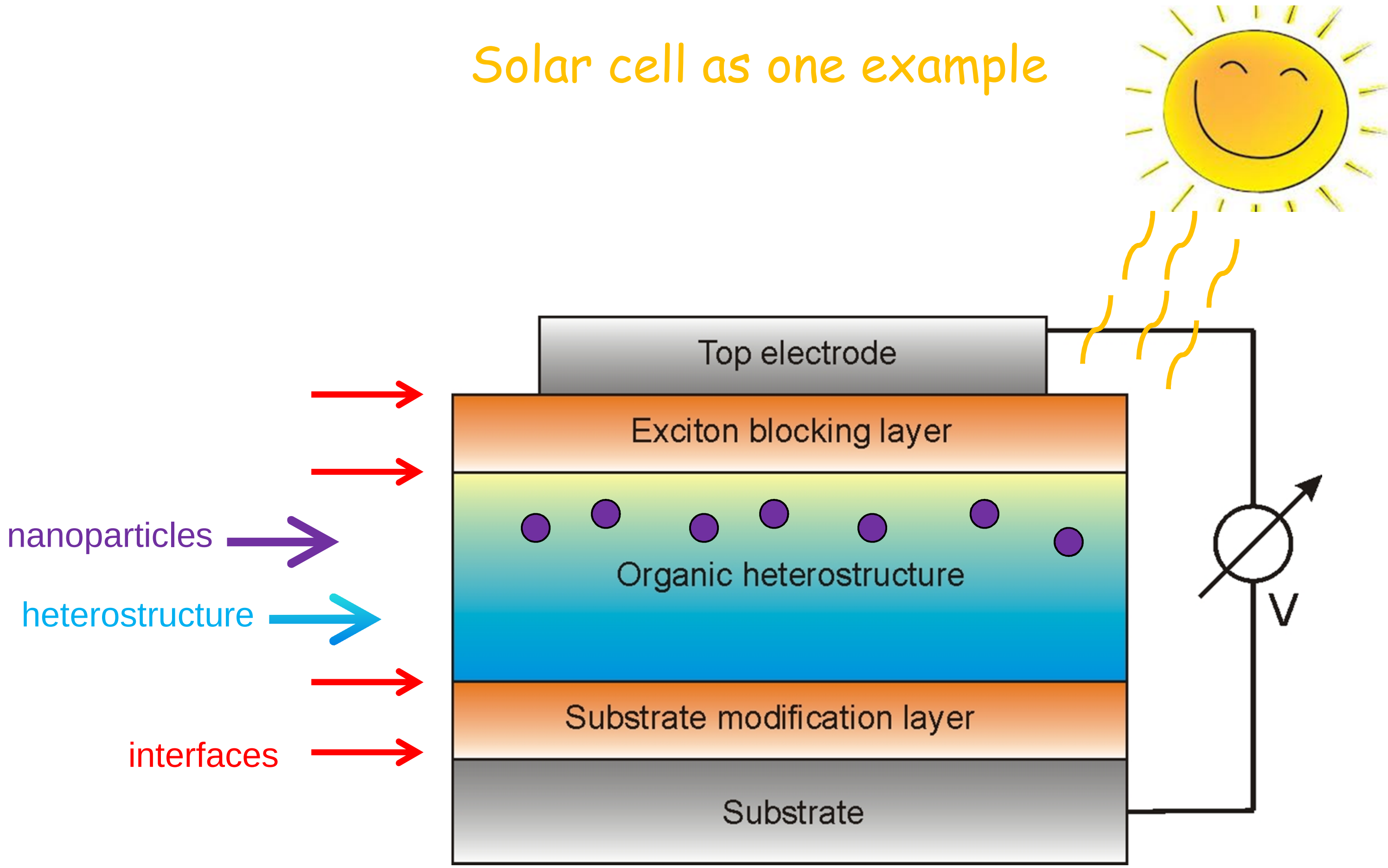


Thin films and interfaces are everywhere

Samsung Galaxy S III with AMOLED display

Thin films and interfaces are everywhere

Solar cell as one example



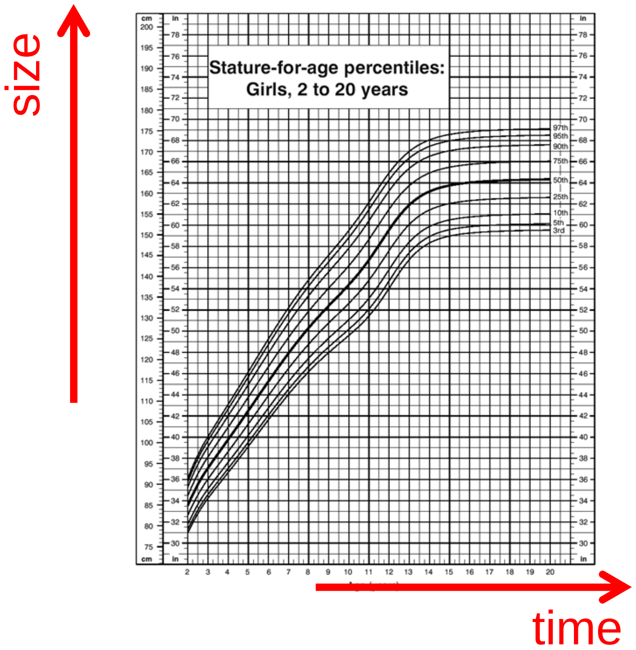
→ This is a *very* complicated architecture !

→ It poses many questions on growth !

based on Alexander Hinderhofer and Frank Schreiber, ChemPhysChem, 13 (2012) 628

Growth phenomena are everywhere

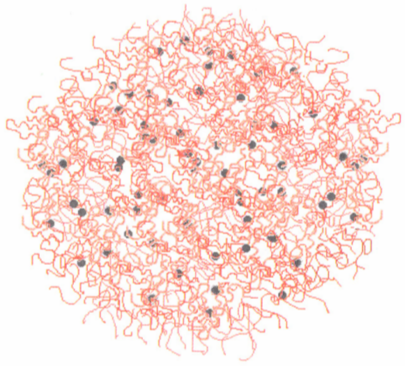
Typical growth rates
~ 1 m / 10 years
~ 30 Å / sec
~ “1 protein / sec”

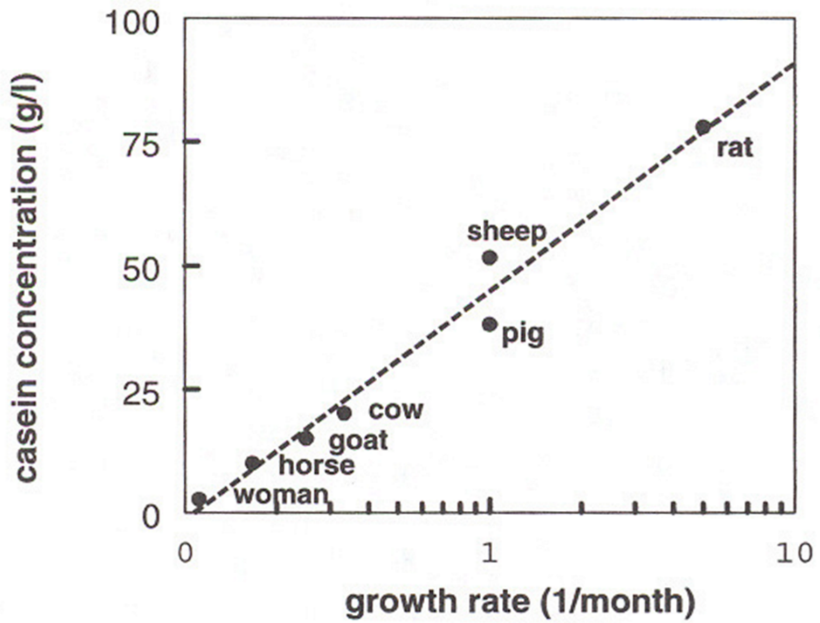


Growth phenomena are everywhere

What can we learn from the growth *rate* ?

Example:
Uptake of calciumphosphate,
$CaPO_4$ via casein-micelles in milk





Result:
Superlinear behaviour of rate as f(*c*) ?
(see rate vs pig; *c* differs by a factor of ~ 2, but rate by a factor of ~ 6)

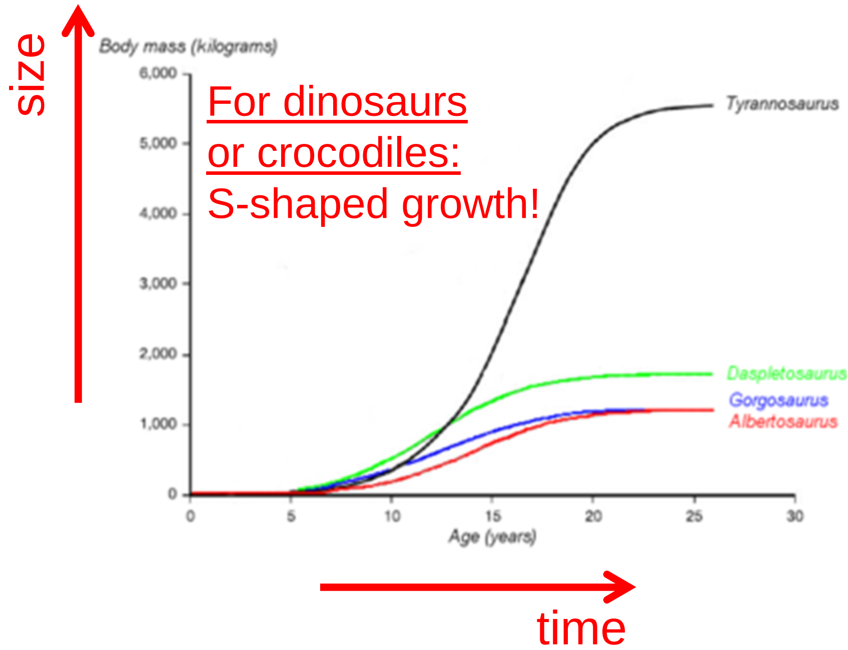
Conclusion:
Need to study *shape* of growth curve to understand *mechanism* !

Growth phenomena are everywhere

Humans:
First 0.5 years high rate, then ~ constant rate for ~ 14 years
Dinosaurs:
S-shaped curve
Note Aptosaurus max. rate of 5.5 tons / year

Different shape implies different mechanism!

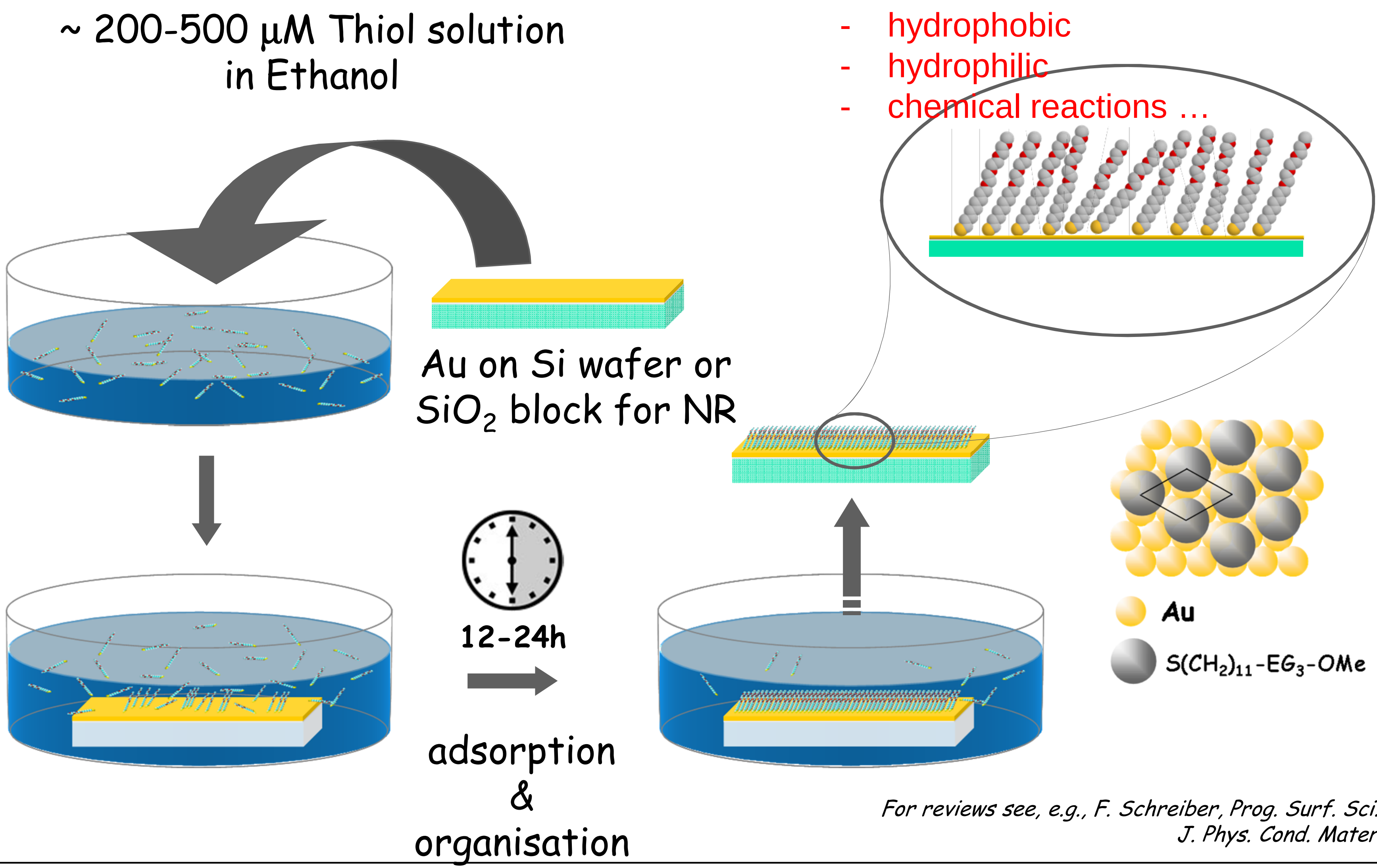
Watch growth as f(time), ideally on molecular level !



Growth phenomena are everywhere

Self-Assembled Monolayers (SAMs) as an example

Endgroup can be changed almost at will for
- hydrophobic
- hydrophilic
- chemical reactions …



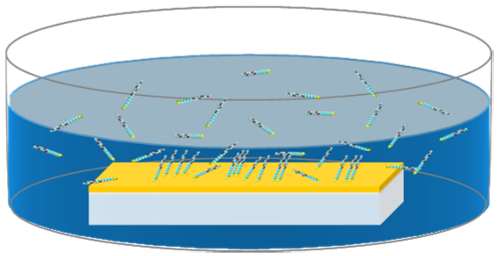
For reviews see, e.g., F. Schreiber, Prog. Surf. Sci. 2000
J. Phys. Cond. Mater 2004

Growth phenomena are everywhere

Self-Assembled Monolayers (SAMs) as an example

What can we learn from the growth *curve (i.e., its shape)* ?

Example:
Growth of a monolayer



Model 1:
Langmuir growth

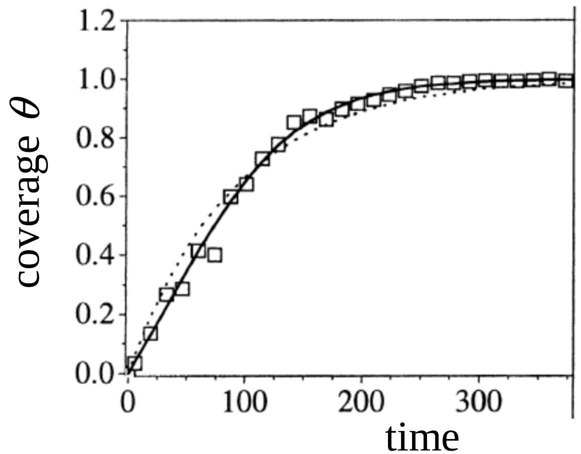
$$\frac{d\Theta}{dt} = R(1 - \Theta)$$

$$\Theta = 1 - e^{-Rt}$$

Model 2:
as above,
but diffusion-limited

$$\Theta = 1 - e^{-R' t^{1/2}}$$

Model 3:
… many other scenarios possible



Conclusion:
Deduce (or rule out) *mechanism* from *shape of curve* !

Part 1
Film Growth: Concepts and Applications

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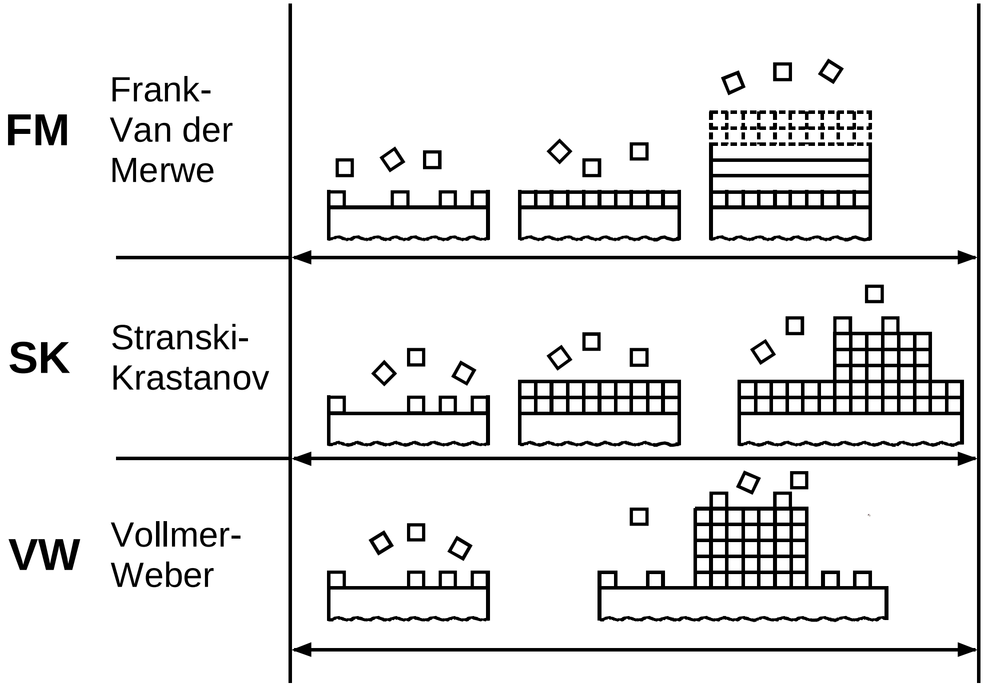
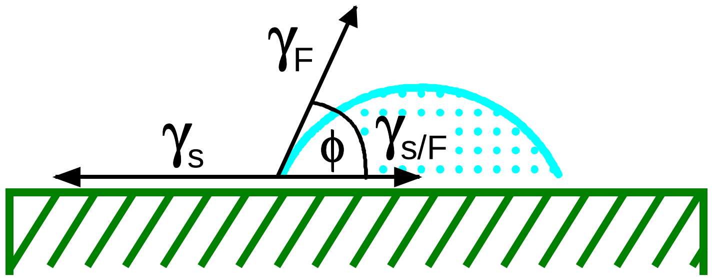
Growth: Modes of Film Growth and Interface Tension



Interface tension



$$\gamma_s - \gamma_{s/F} + \gamma_F \cos(\phi)$$

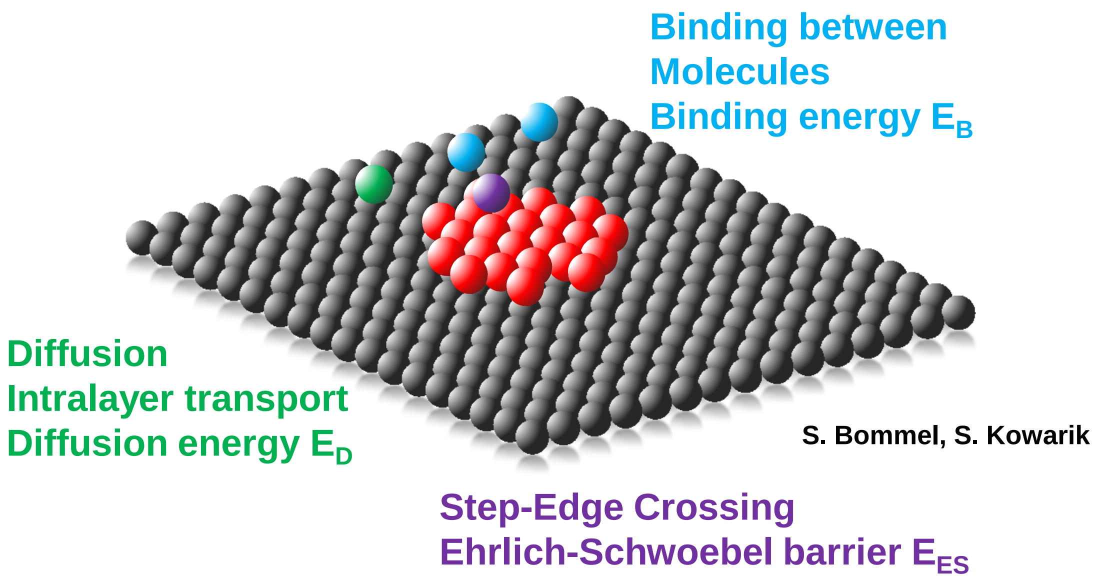
FM Layer-by-layer growth $\phi = 0$: $\gamma_s \geq \gamma_F + \gamma_{s/F}$

SK Layer + island ("mixed")

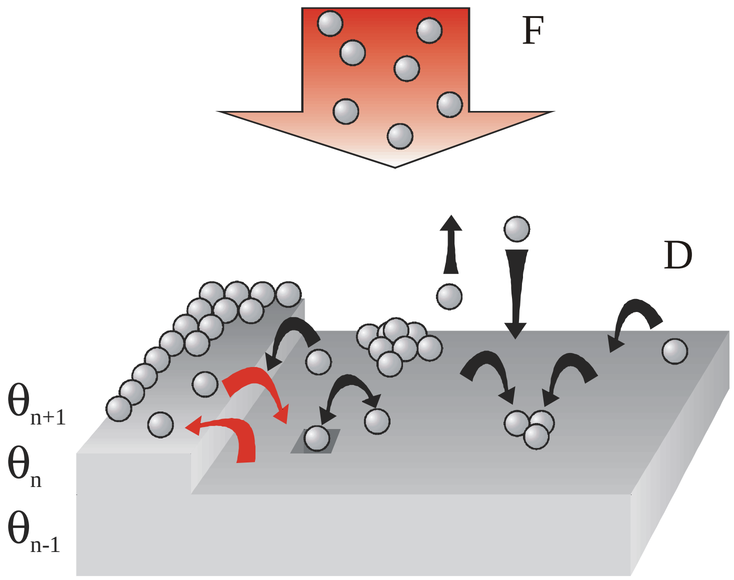
VW island growth $\phi > 0$: $\gamma_s > \gamma_F + \gamma_{s/F}$

Growth: Microscopic processes on the surface

Surface processes during the growth



Growth: What are the relevant quantities ?



typical observables
→ coverage $\theta_n(t)$; island size $L(t)$; …

dependent on microscopic processes
→ diffusion D; Schwöbel barrier ΔE; …

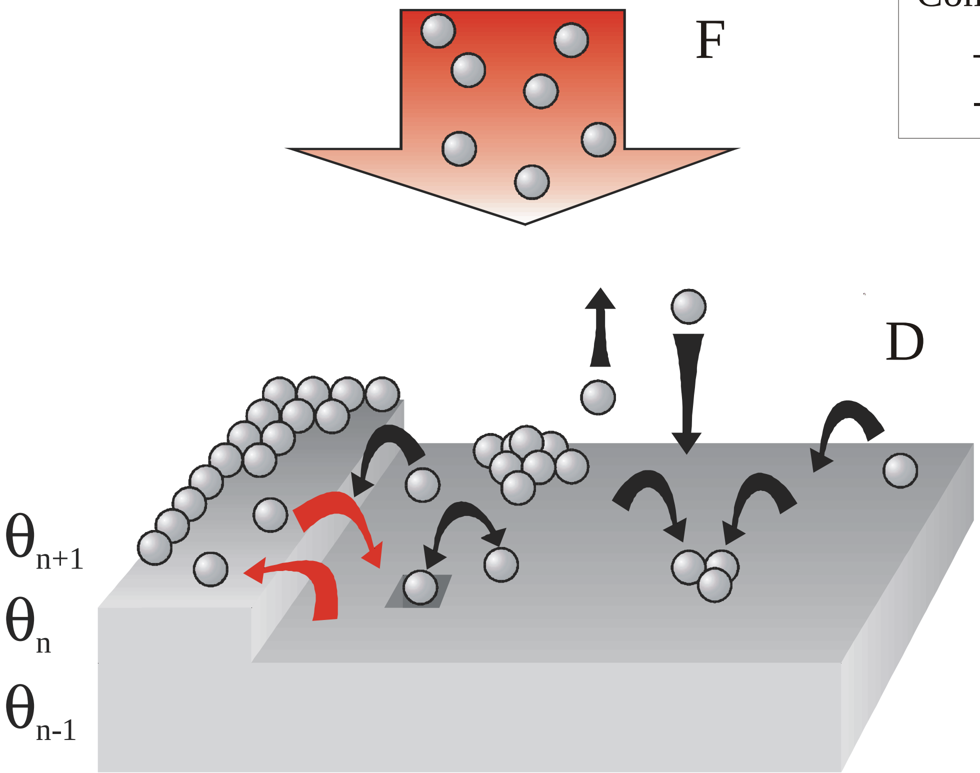
real-time observation required
feedback for models needed
→ Trofimov model and others

also relevant (but not in the focus here)
→ adsorption structure (XSW)

see e.g.
Romaner et al., PRL 99 (2007) 256801
Schreiber et al., PRL 99 (2007) 059601
Koch et al., JACS 130 (2008) 7300
Yamane et al., PRL 105 (2010) 046103
Gerlach et al., PRL 106 (2011) 156102
Heimel et al., Nature Chemistry 5 (2013) 187

Growth: Non-Equilibrium Statistical Aspects

Many competing processes on the surface;
full description very difficult



Competition between flux F and surface diffusion D

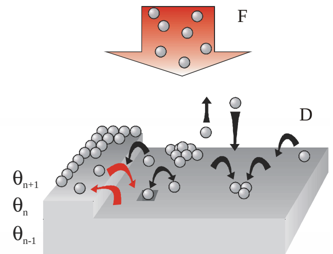
→ determines adsorbate diffusion length L
→ determines adsorbate island distribution

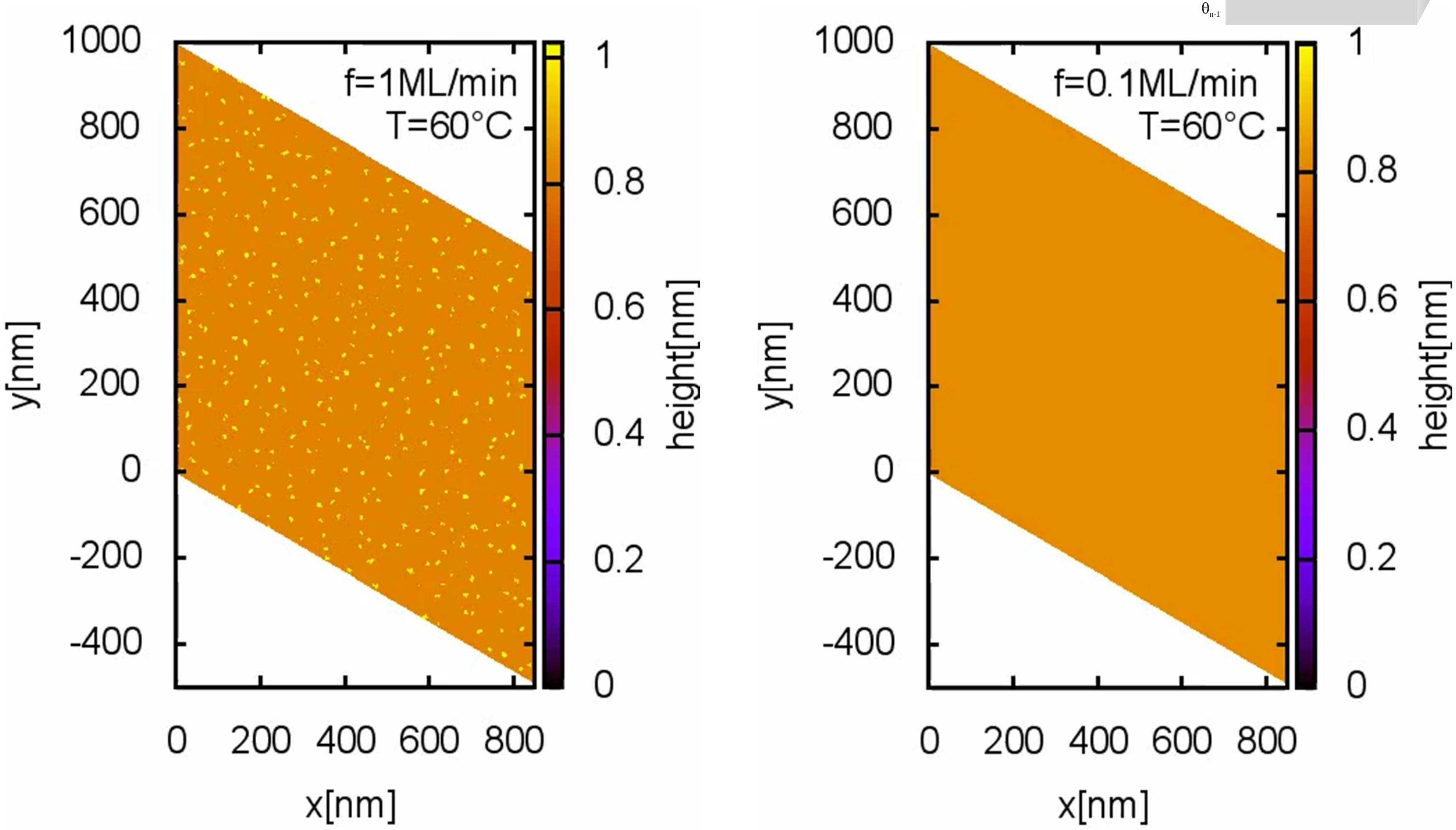
Simplest case

$$L \sim \left(\frac{D}{F}\right)^{1/6}$$

if stable island size = 2
if sticking coefficient = 1
if no structural changes during growth

Growth: Effects of flux and temperature on nucleation and island size evolution

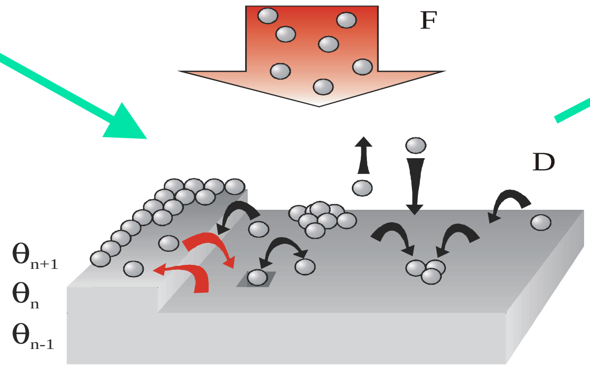


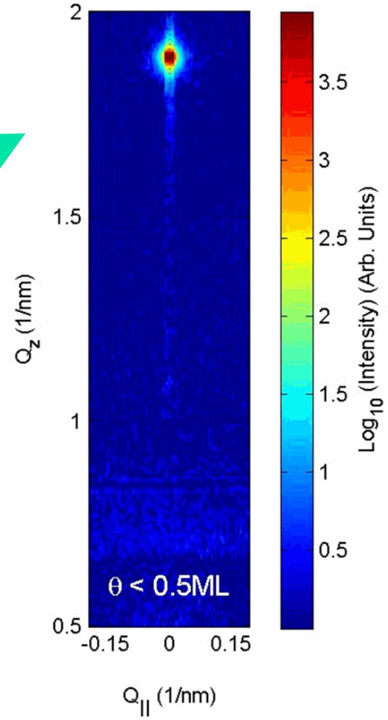


simulations by Nicola Kleppmann and Sabine Klapp

Watch them as they grow: Following thin film formation in real time

Frank Schreiber
http://www.soft-matter.uni-tuebingen.de





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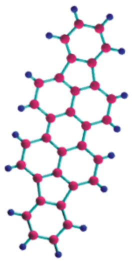
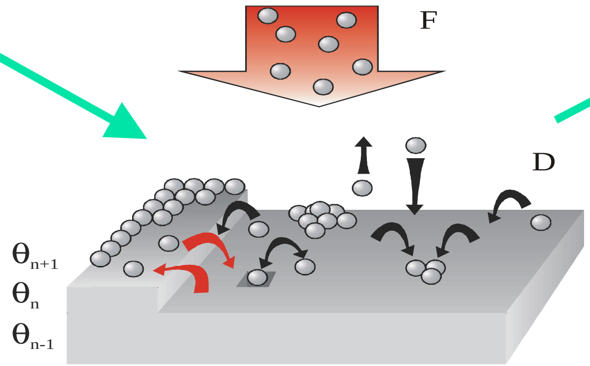
with many thanks to various funding agencies and large-scale facilities

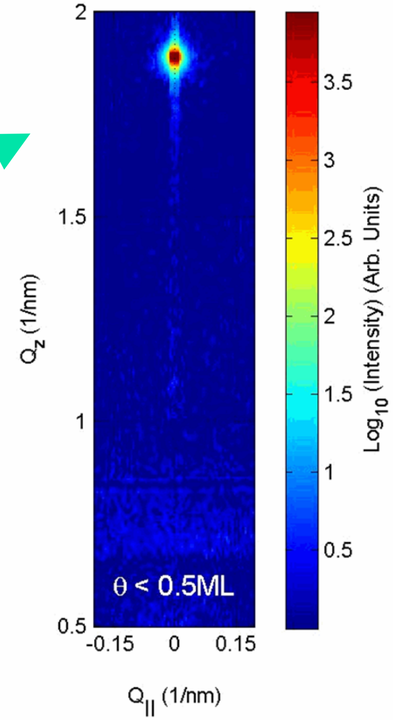
Part 2
Model studies of film growth

Frank Schreiber
http://www.soft-matter.uni-tuebingen.de

DIP



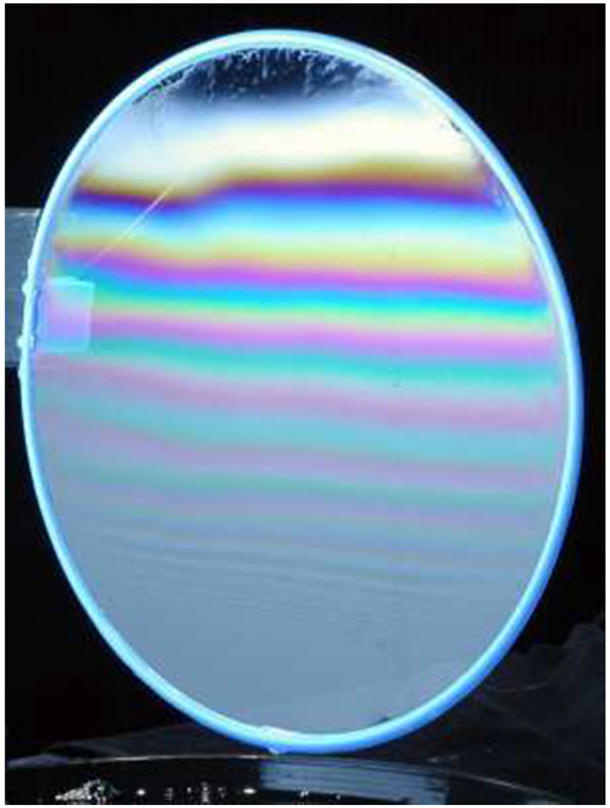


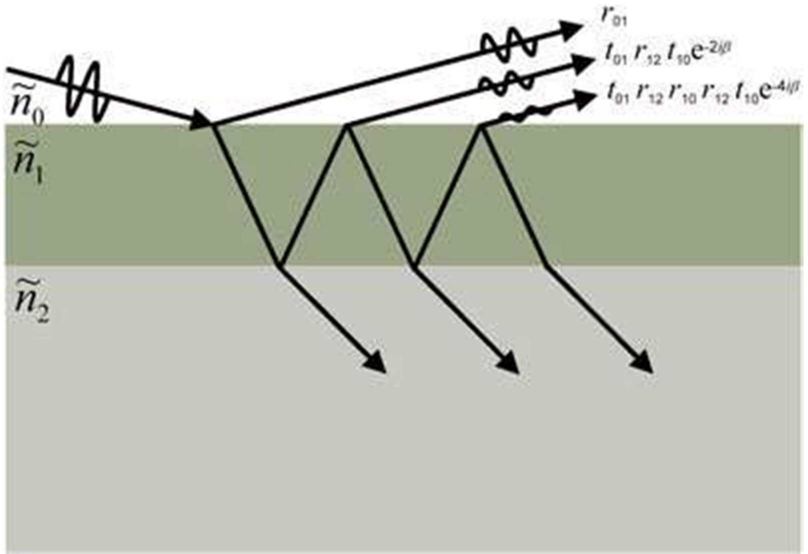


1. post-growth reflectivity (specular)
2. real-time reflectivity (specular)
3. real-time GIXD
4. real-time optical spectroscopy
5. real-time GISAXS

Scattering: Some remarks on interferences

Remember Physics III
or picture on blackboard



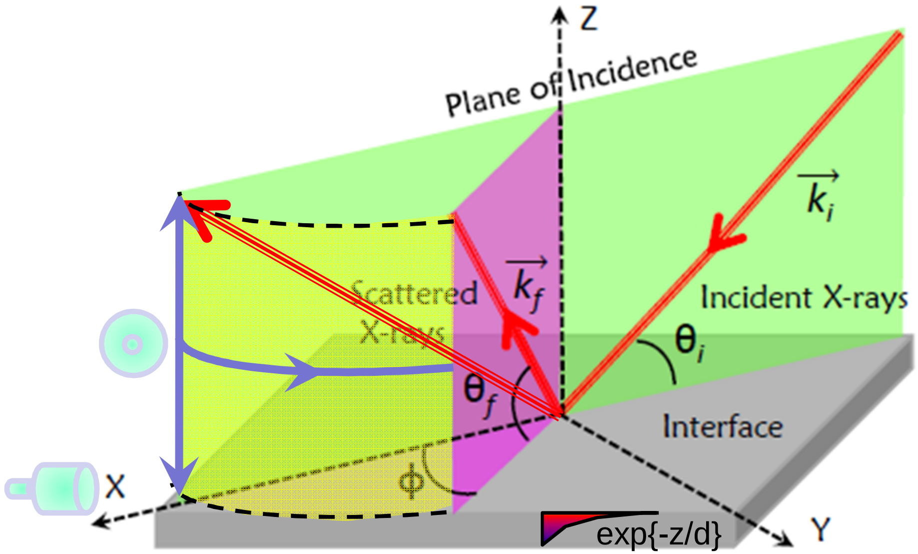


Scattering: Information from thin films and surfaces

X-ray reflectivity (XRR):
Out-of-plane structure
Roughness
thickness

Grazing incidence diffraction (GID):
In-plane structure
Crystallite size
Strain, defects

Grazing incidence small angle X-ray scattering (GISAXS):
In-plane correlation lengths
Shape, distribution of nanostructures



Evanescent field : highly surface sensitive techniques!!!

More details come with the application examples
Animation courtesy of Rupak Banerjee
Theoretical background on surface scattering see previous lectures

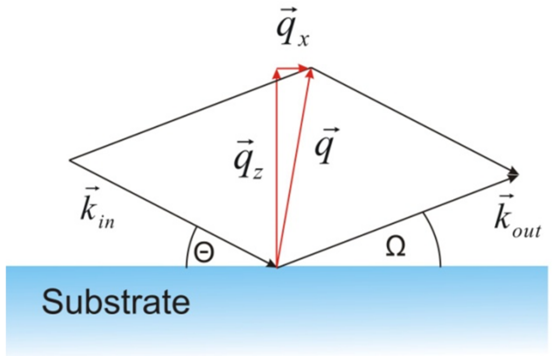
Scattering: Information from thin films and surfaces

Scattering vector q

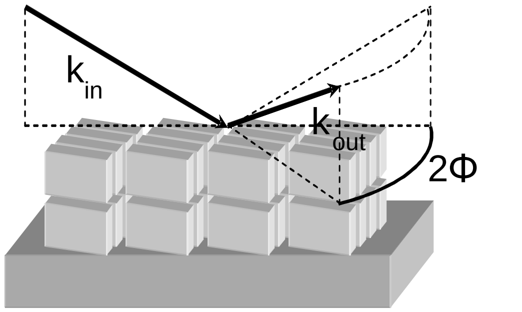
$$q_x = \frac{2\pi}{\lambda}\left(\cos\Omega\cos\Phi - \cos\Theta\right)$$

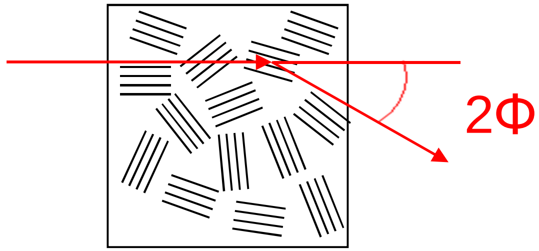
$$q_y = \frac{2\pi}{\lambda}\left(\sin\Phi\cos\Theta\right)$$

$$q_z = \frac{2\pi}{\lambda}\left(\sin\Omega + \sin\Theta\right)$$



Grazing incidence diffraction (GIXD):





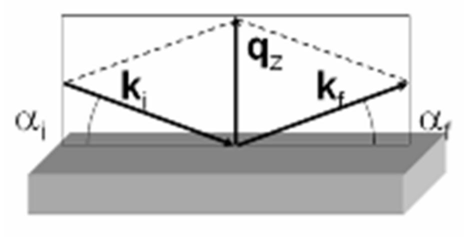
$$\Omega = \Theta = const$$

$$\Phi \neq 0$$

q_z constant

q_{xy} varied

X-ray reflectivity (XRR):



$$\Omega = \Theta$$

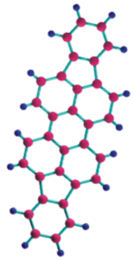
$$\Phi = 0$$

variation of q_z

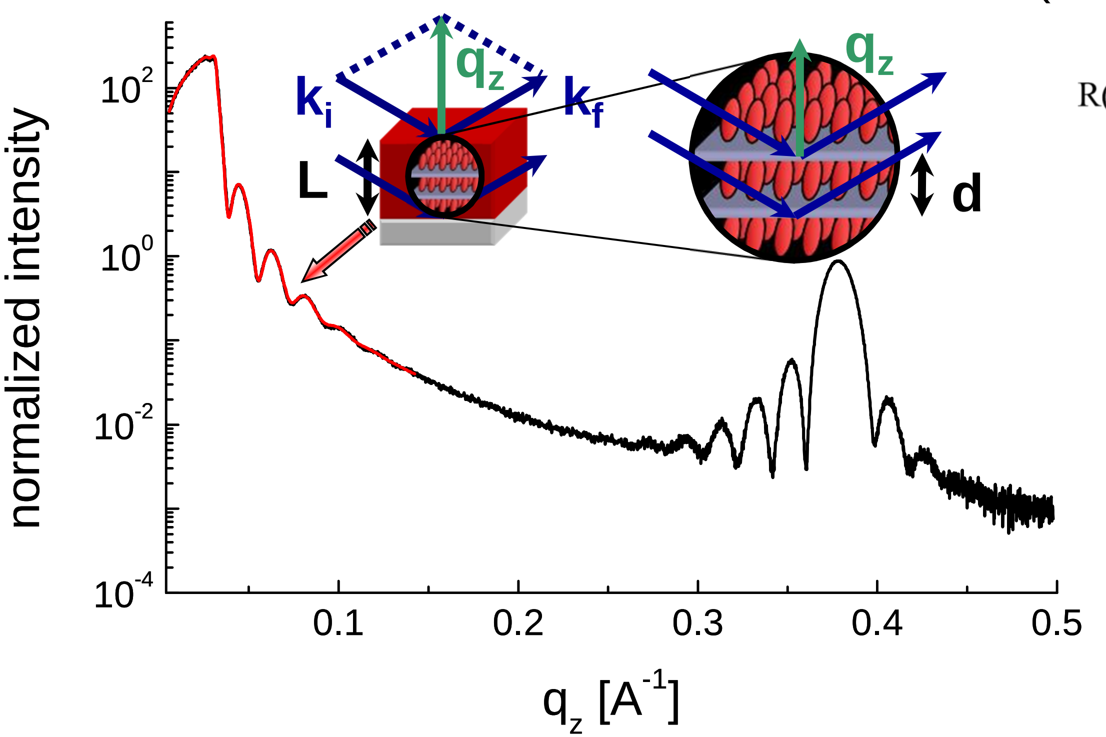
$q_{xy} = 0$

1. post-growth reflectivity (specular)
2. real-time reflectivity (specular)
3. real-time GIXD
4. real-time optical spectroscopy
5. real-time GISAXS

Structural Quality of DIP on SiO_2



thin films of
diindenoperylene (DIP)



kinematic approximation
(Master formalism):

$$R(Q) = R_F \left| \frac{1}{\rho_{el}(z \rightarrow \infty)} \int_{-\infty}^{+\infty} \frac{d\rho_{el}}{dz} e^{iQz} dz \right|^2$$

- X-ray reflectivity:
  - electron density
  - film thickness
  - roughness

- Bragg reflection:
  - lattice spacing
  - coherent thickness (Laue oscillations)

1. post-growth reflectivity (specular)
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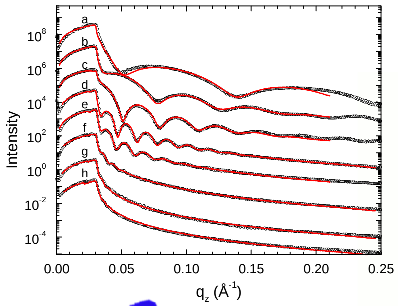
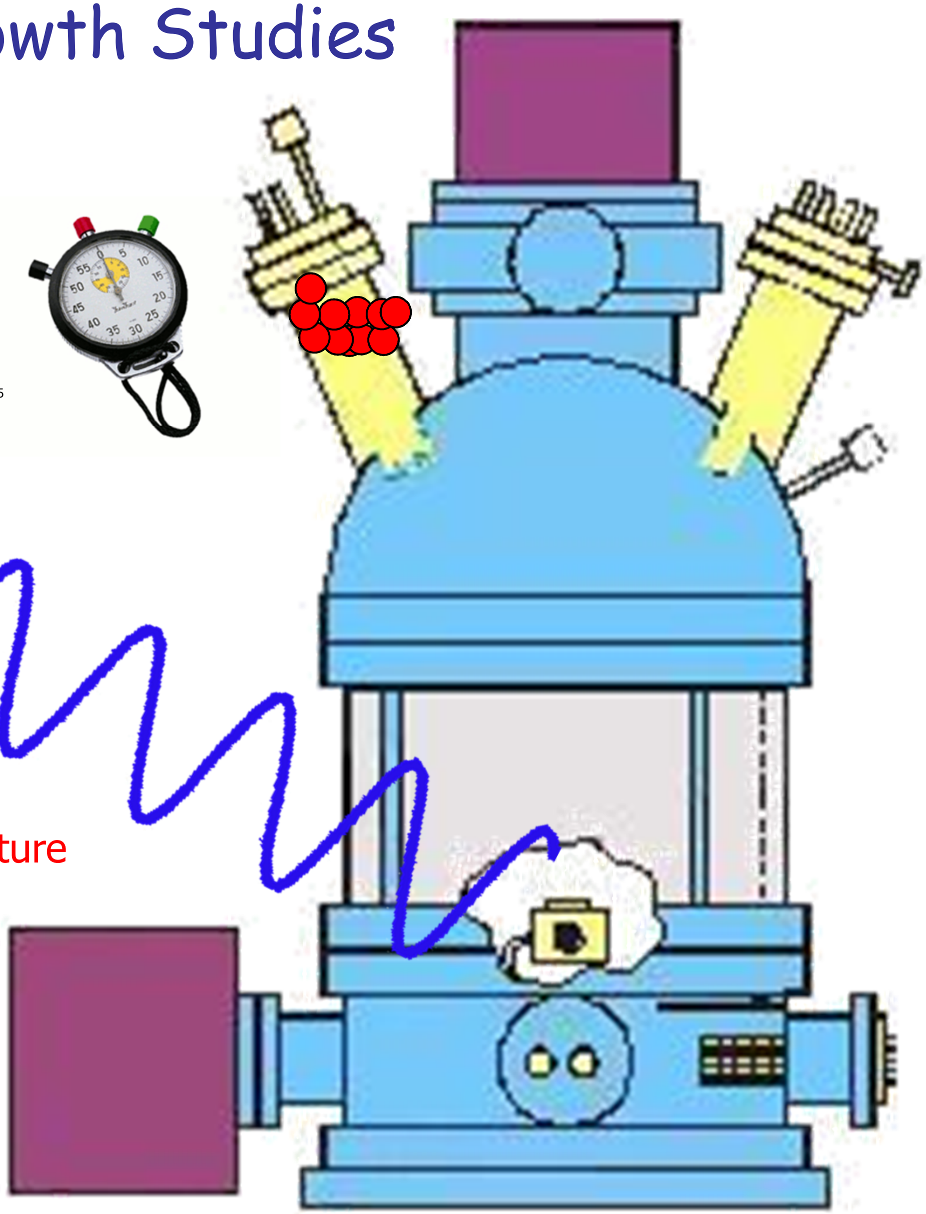
In-Situ Growth Studies

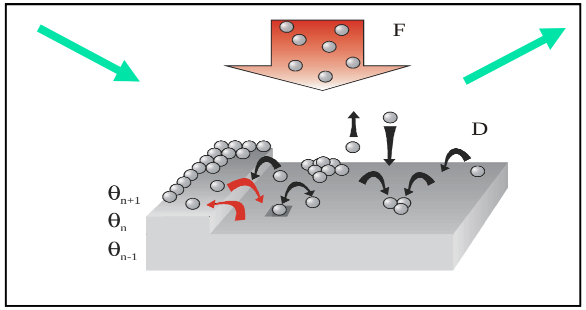


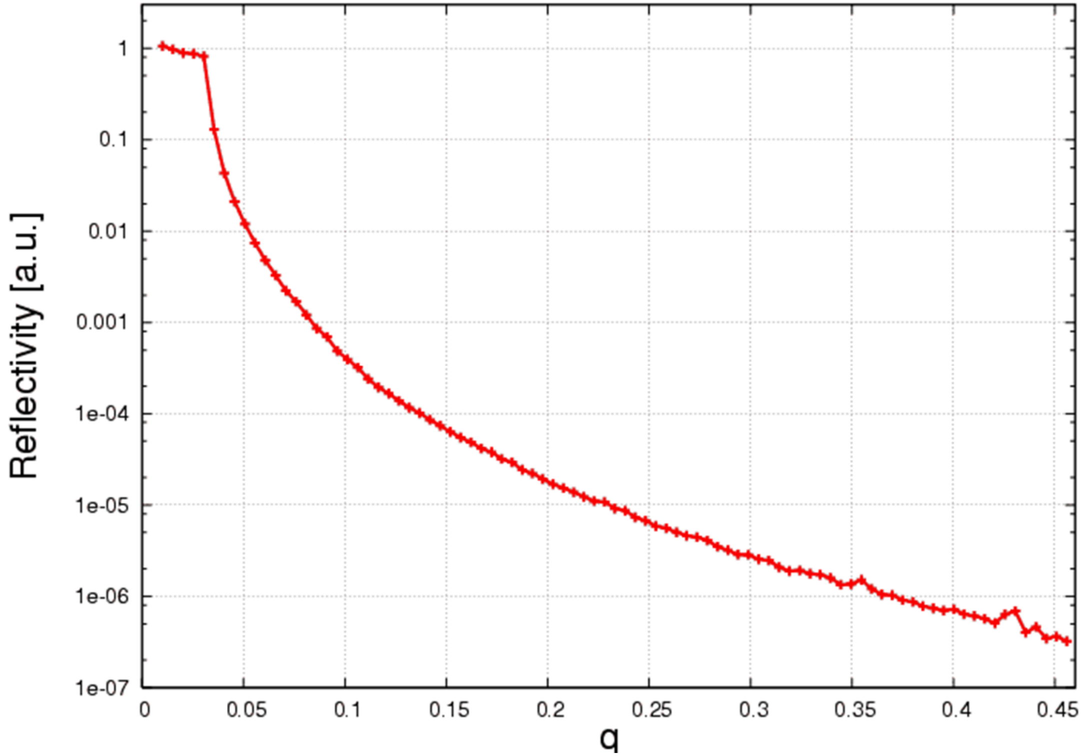


→ out-of-plane structure
→ in-plane structure

Growth data as I(q,t)

i.e. scanning the angles quickly





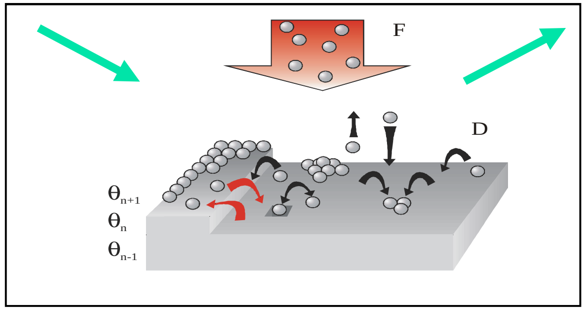
DIP on Si-oxide
growth at 130 deg. C
substrate temperature

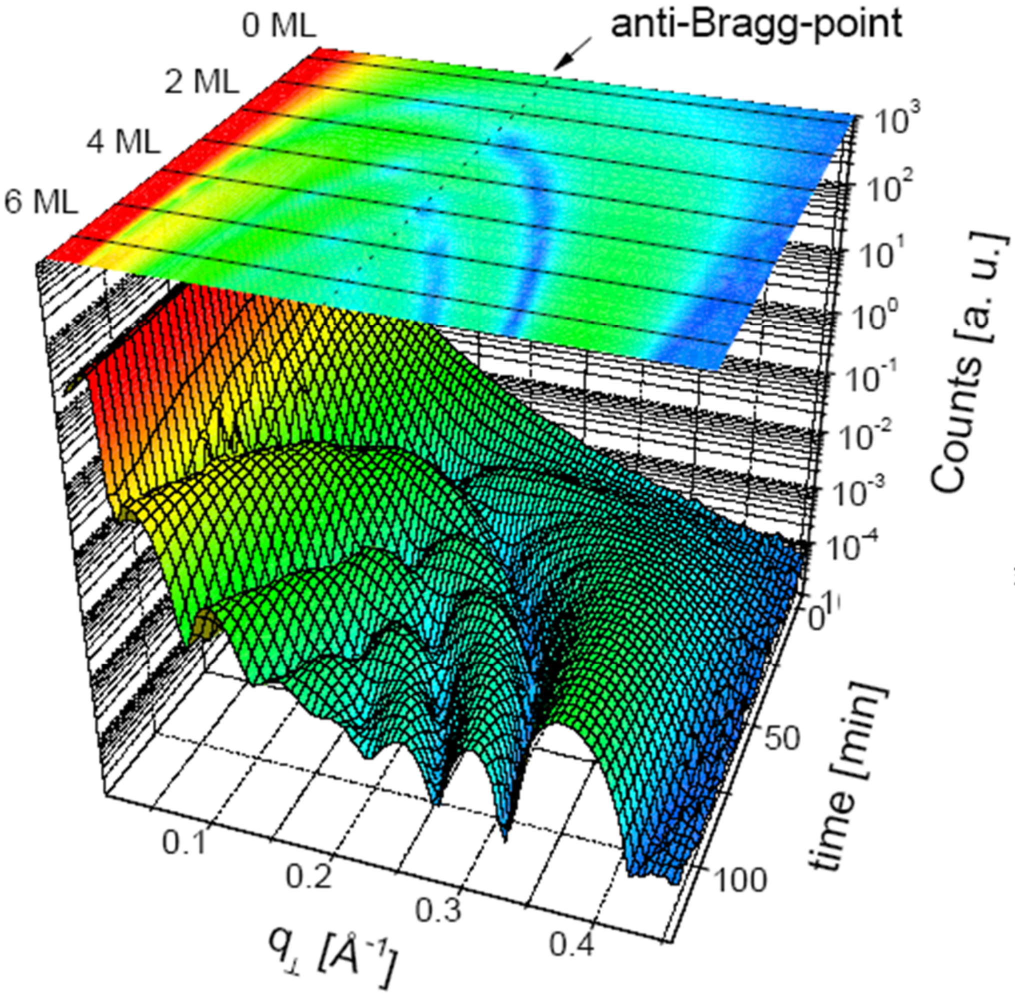
Growth Rate 3 A / min
1 ML (standing up) is 16.5 A

Total growth time 100 min
Total thickness 300 A

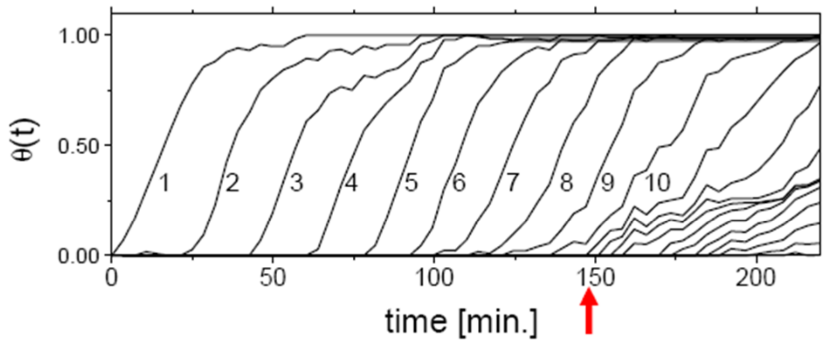
0 10 19 Monolayers (standing up)

Growth data I(q,t) --- Out of plane





Convert I(q,t) data into coverage q(t)



Onset of rapid roughening

S. Kowarik, A. Gerlach, M.W.A Skoda, S. Sellner, and F. Schreiber, Eur. Phys. J. Special Topics **167**, 11 (2009)
S. Kowarik, A. Gerlach, S. Sellner, F. Schreiber, L. Cavalcanti, and O. Konovalov, Physical Review Letters **96**, 125504 (2006)

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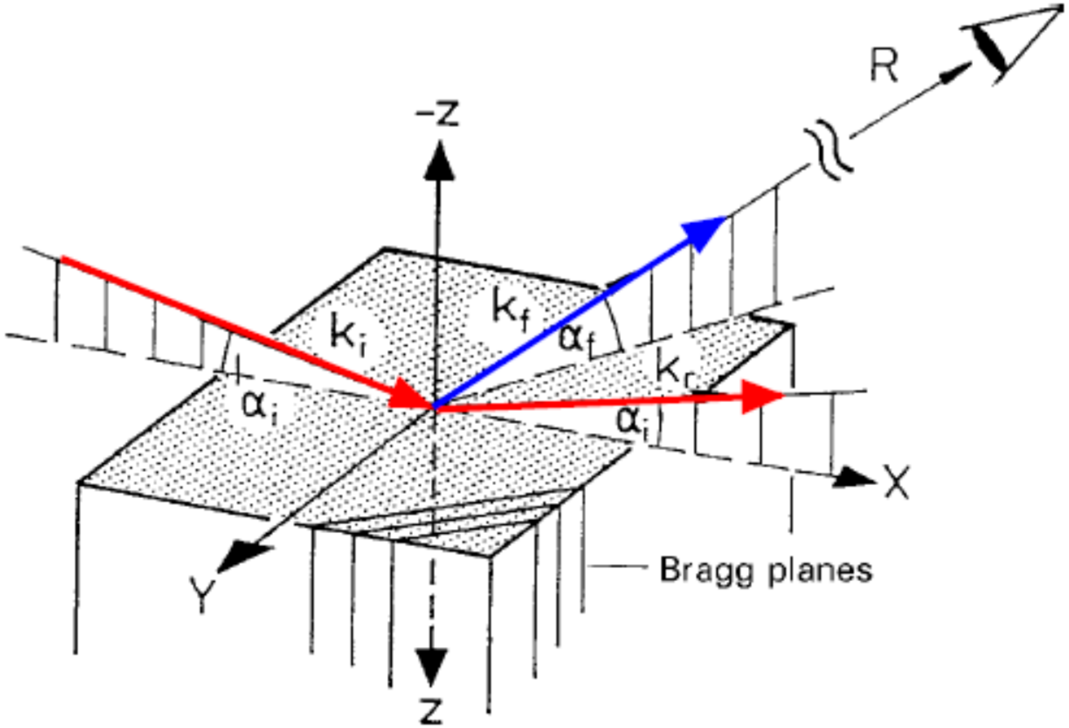
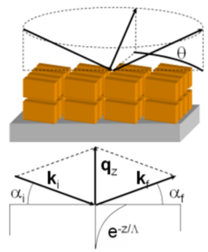
In-plane structure:

Grazing-incidence X-ray diffraction (GIXD)





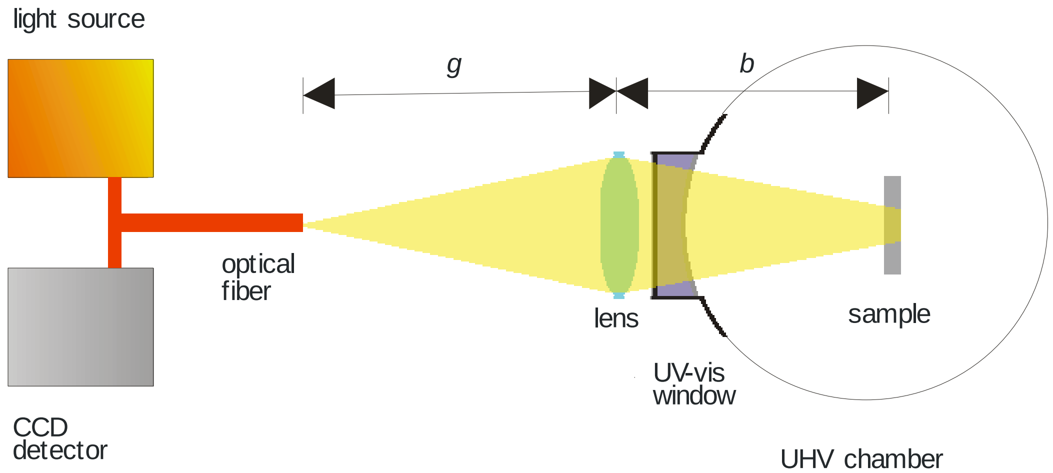
1. post-growth reflectivity (specular)
2. real-time reflectivity (specular)
3. real-time GIXD
4. real-time optical spectroscopy
5. real-time GISAXS

Real-time growth studies: Optics

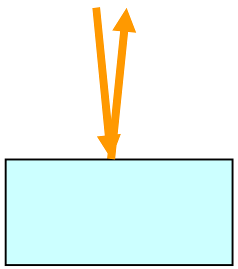
<u>Differential reflectance spectroscopy (DRS)</u>

(a very simple and efficient technique)

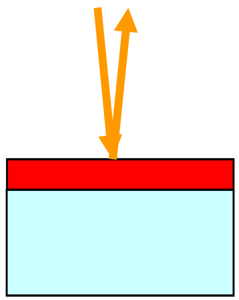
$$\frac{\Delta R}{R} = \frac{R - R_s}{R_s}$$



$$R_s = \frac{I_s^r}{I_0}$$



$$R = \frac{I_{f+s}^r}{I_0}$$



Measure reflected intensity @

$\Rightarrow$ Normal incidence

(sensitive to in-plane component only)

$\Rightarrow$ In-situ

Proehl et al., PRB 71 (2005) 165207

Hosokai et al., APL 97 (2010) 063301

Heinemeyer et al., PRL 104 (2010) 257401

Real-time growth studies: Optics

Differential reflectance spectroscopy (DRS)

(a very simple and efficient technique)

3-phase system

(1) ambient ε_a

(2) film ε_f

(3) substrate ε_s

+

Fresnel coefficient

$$r_{12} = \frac{E^r}{E^0}$$

$$R = (r_{12})^2$$

=

$$r_{123} = \frac{r_{12} + r_{23} e^{-2i\beta}}{1 + r_{12} r_{23} e^{-2i\beta}}$$

$$\beta = \frac{2\pi n_f d \cos(AOI)}{\lambda}$$

Simplifications (very thin films):

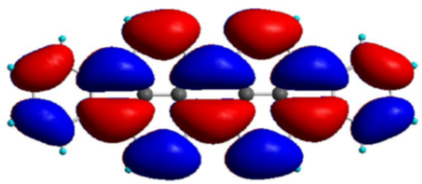
- ⇒ **Thin film limit d «λ** (expand to first order in β)
- ⇒ transparent substrate
- ⇒ normal incidence (AOI = 0°)

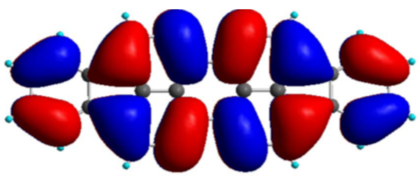
$$\frac{\Delta R}{R} = \frac{8\pi d}{\lambda} \frac{\varepsilon_2}{1 - n^2_{substrate}}$$

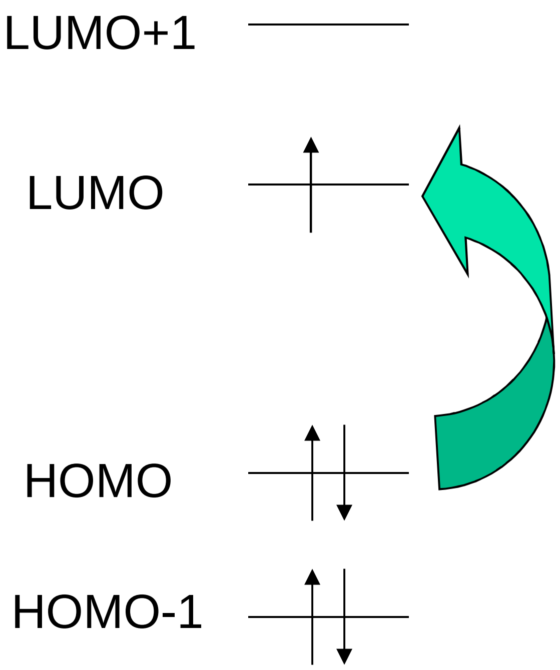
Proehl et al., PRB 71 (2005) 165207
Hosokai et al., APL 97 (2010) 063301
Heinemeyer et al., PRL 104 (2010) 257401

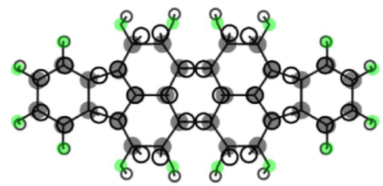
Real-time growth studies: Optics

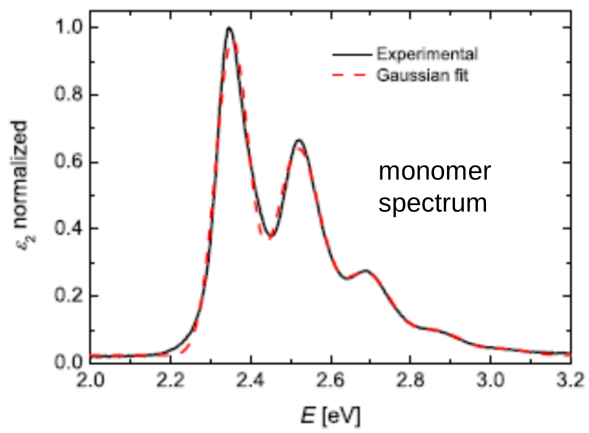
→ follow in real time during growth (DIP, PEN, PFP)
→ spectra coupled to structure (Franck-Condon etc.)
  → coupling to vibrations
  → coupling to neighbours
→ relevant for electronic transport and solar cells









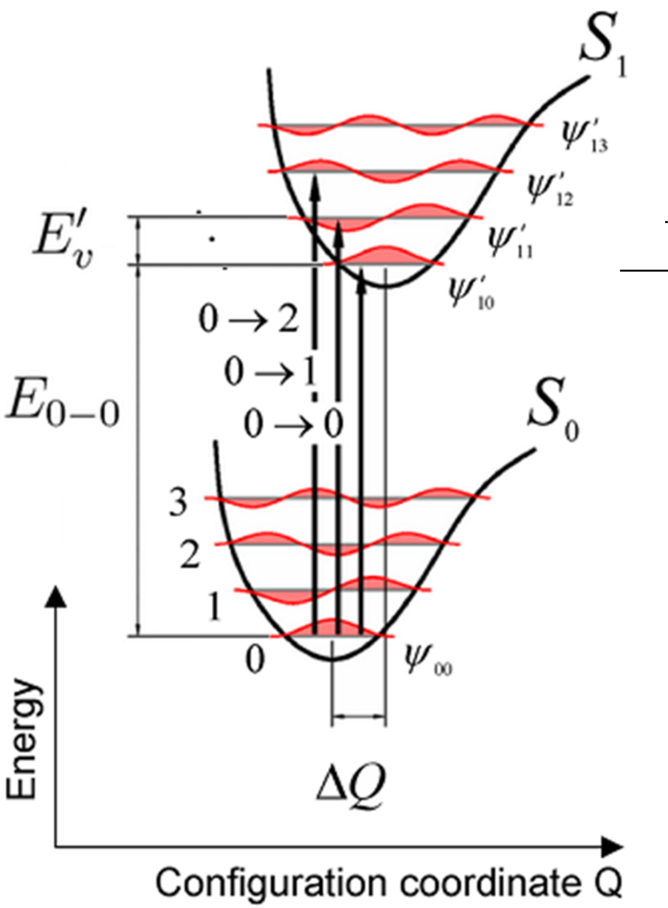


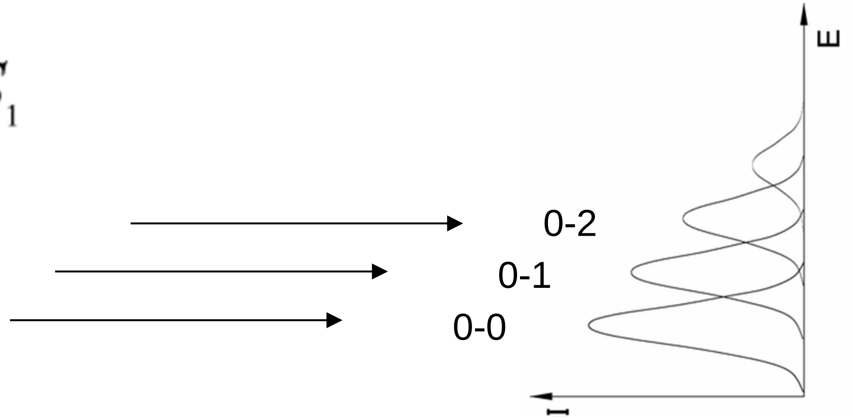
Zhang et al., PRL 104 (2010) 056601
Hosokai et al., APL 97 (2010) 063301
Heinemeyer et al., PRL 104 (2010) 257401

Optical Properties: Theory

Electron-phonon coupling (Huang-Rhys-parameter *S*)

energy levels → resulting spectrum





Possible effects during growth

- → overall shift of energies (solvent shift) ?
- → transitions appearing / disappearing ?
- → intensity redistribution (changes in S) ?
- → fluorescence quenching ?

1. post-growth reflectivity (specular)
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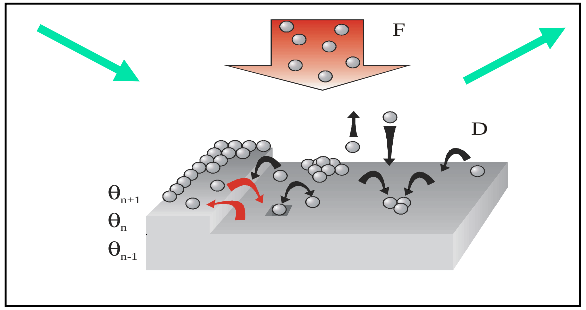
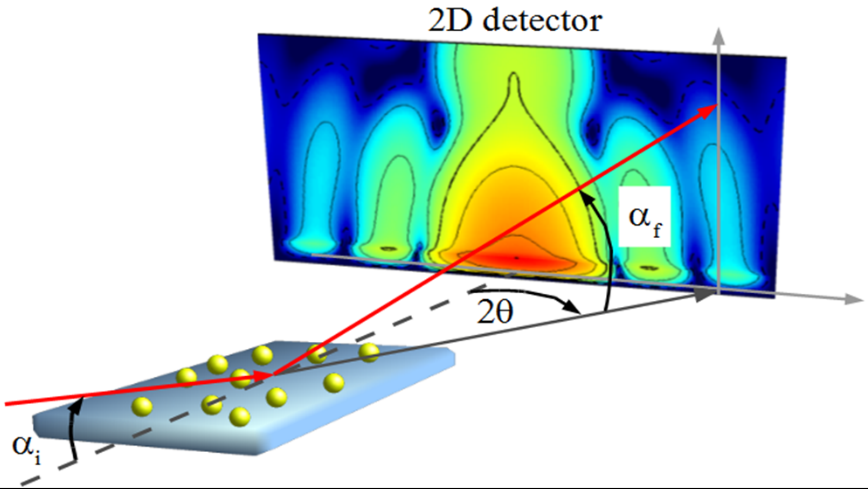
Real-time growth studies

→ Structure
→ Optics
→ Island Evolution ?



diffuse scattering
in real time
→ essentially GISAXS geometry
→ strongly benefits from improved detectors

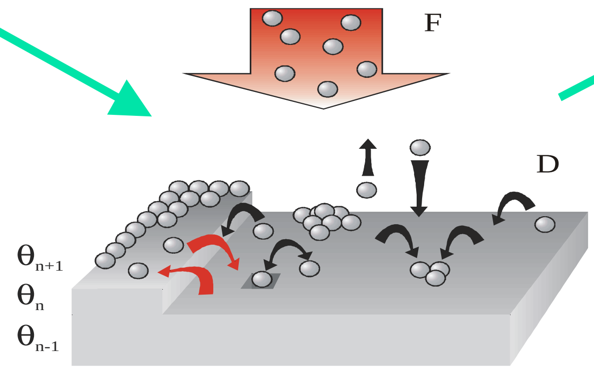


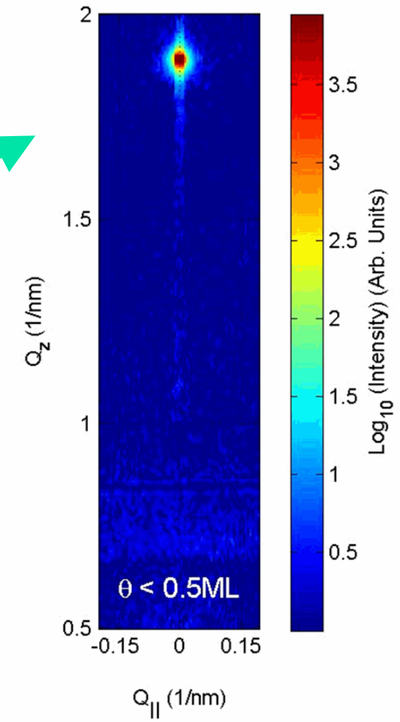
Kowarik et al., PRL 96 (2006) 125504
Heinemeyer et al., PRL 104 (2010) 257401
Hosokai et al., APL 97 (2010) 063301
Frank et al., in preparation

Part 2
Model studies of film growth

Frank Schreiber
http://www.soft-matter.uni-tuebingen.de

C. Frank, J. Novak, R. Banerjee, A. Gerlach (Tübingen)
and many collaborators in Stuttgart, Berlin, Grenoble, …



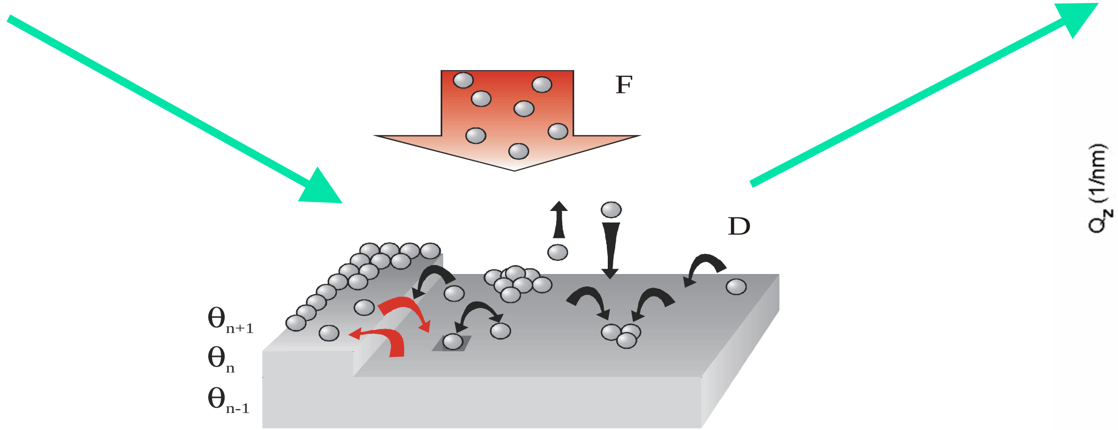


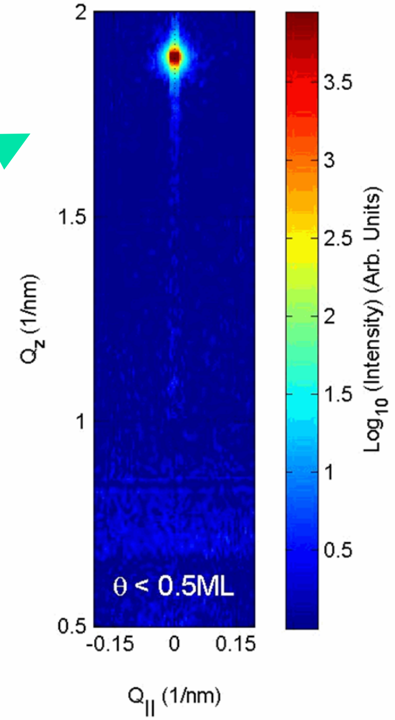
Conclusions

- roughening transition visible in coverage $\Theta_n(t)$
- consistent with unusual growth exponents
- structural changes as f(t)
- optical properties also change as f(t)
- island correlations followed as f(t) and diffusion barriers deduced

Watch them as they grow:
Following thin film formation in real time

Frank Schreiber
http://www.soft-matter.uni-tuebingen.de





Outline

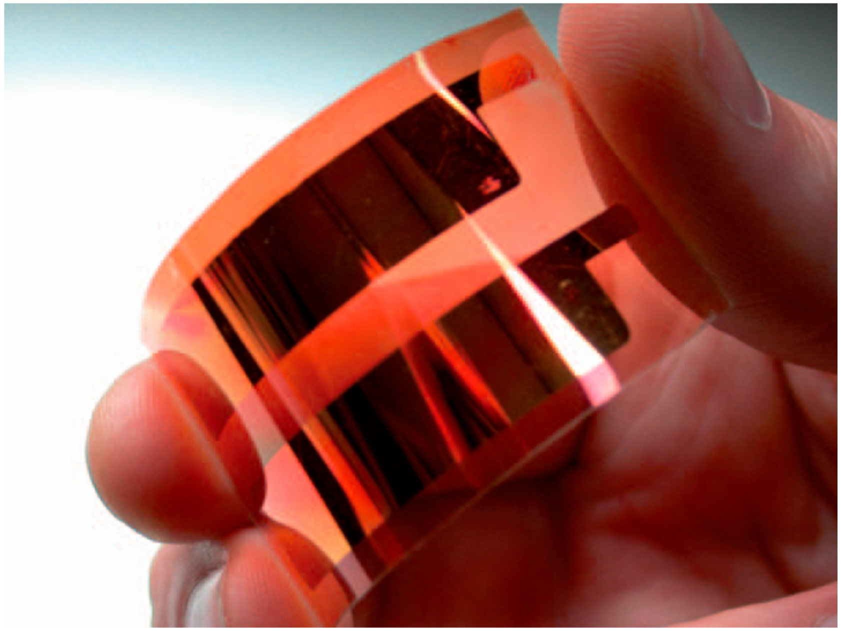
- Part 1 Film Growth: Concepts and Applications
- Part 2 Model Studies of Film Growth
  - specular reflectivity
  - off-specular scattering: GIXD, GISAXS, ...
  - complementary methods: optical spectroscopy, transport ...
- Part 3 Multi-Component Systems and Devices

with many thanks to various funding agencies and large-scale facilities

Organic Photovoltaics

Frank Schreiber
http://www.soft-matter.uni-tuebingen.de

C. Lorch and A. Gerlach
as welll as many collaborators



Organic Semiconductors: Applications

Organic Electronics and Optoelectronics

… assuming that they work as semiconductors,
essentially everything is possible

Organic materials

Organic light emitting diodes

Photovoltaic cells

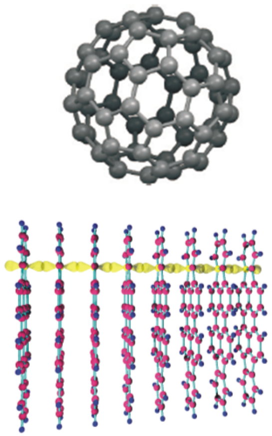
Transistors and memory

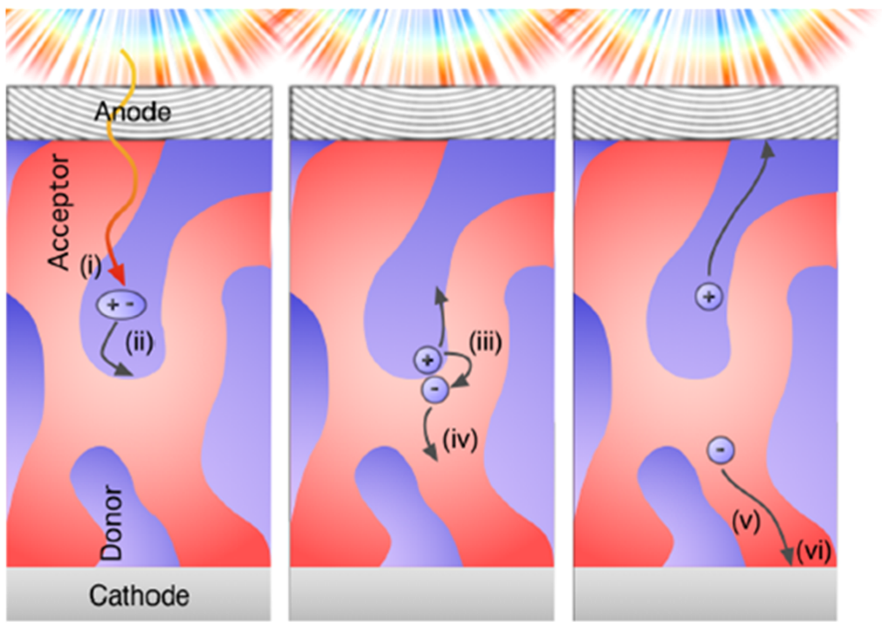
Applications and Binary Mixtures

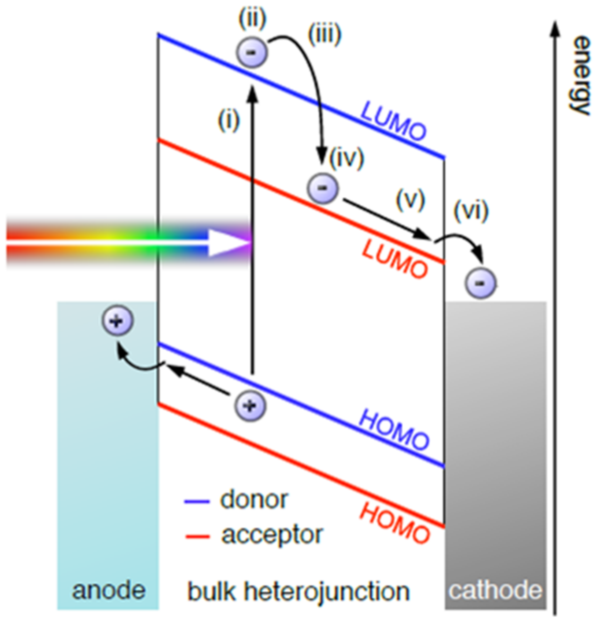
Co-evaporated organic semiconductors

→ phase separation of donor & acceptor ?

→ length scale relevant for photovoltaics !



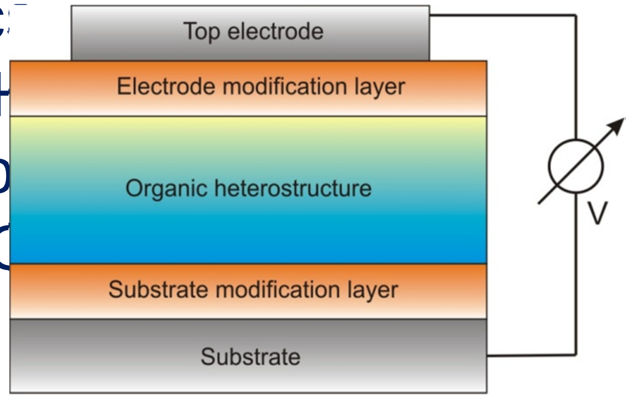




Five Lessons in Growth of Organic Heterostructures

Outline

1. Growth of Single-Component Organics
2. Growth of A:B Blended Structures (BHJ)
   → Mean-Field Theory of Binary Mixtures
   → Geometric Structure
   → Electronic Structure and Optic
3. Growth of A/B Layered Structures (PH
4. Growth on Metal Contacts (Organic-o
5. Growth of Metal Contacts (Metal-on-C

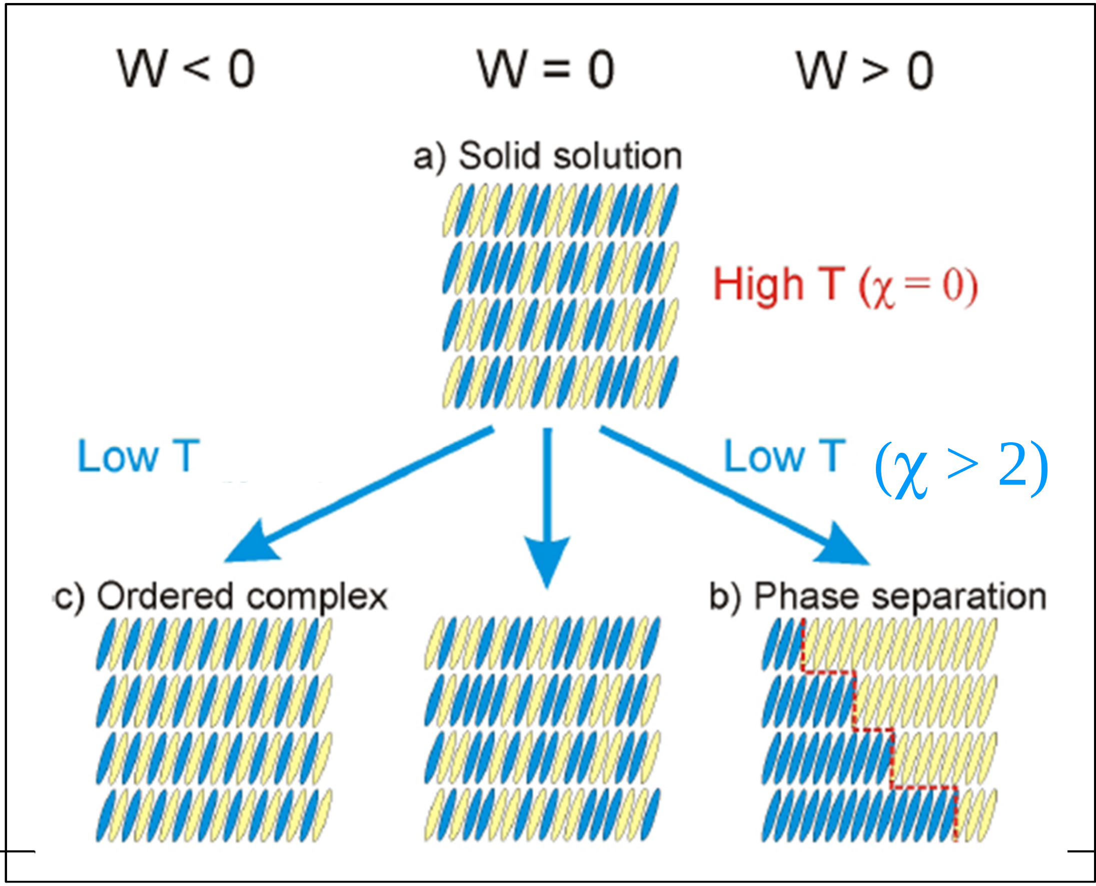


 based on Alexander Hinderhofer and Frank Schreiber, ChemPhysChem (2012)

Binary Mixtures: Mean-Field Theory

$$\frac{F_{mix}}{k_B T} = x_A \ln x_A + x_B \ln x_B + \chi x_A x_B$$

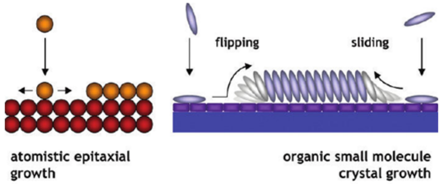
$$\chi = \frac{1}{k_B T}[W_{AA} + W_{BB} - 2W_{AB}] = \frac{1}{k_B T} W$$



Note:
This is equilibrium theory;
kinetics changes picture

based on Alexander Hinderhofer and Frank Schreiber, ChemPhysChem, 13 (2012) 628

Conclusions

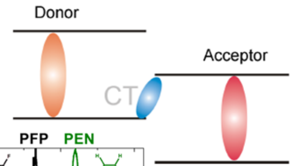


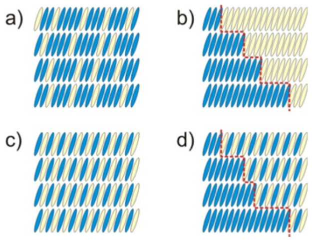
1. Growth of Single-Component Organics

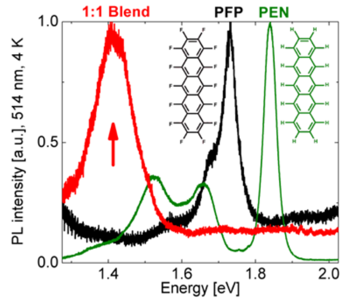
→ *… more sources of disorder than elemental systems (orientation; phase coexistence; …)*

→ *… makes epitaxy and defect-free and smooth layers harder to grow*

→ *… structural and optical changes* during *growth*







2. Growth of A:B Blended Structures (BHJ)

→ *… various scenarios depending on shape and interaction (phase separation; intermixing; …)*

→ *… optical evidence for coupling (absorption; emission; …)*

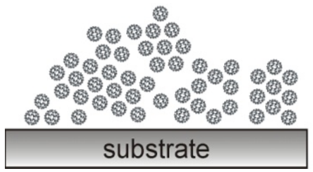
3. Growth of A/B Layered Structures (PHJ)

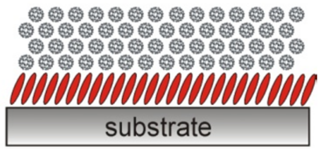
→ *… templating*

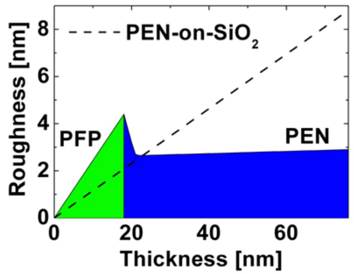
→ *… smoothing*

→ *… roughening*

→ *… interdiffusion / layer exchange*

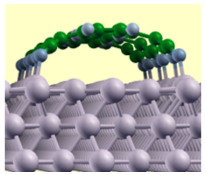






4. Growth on Metal Contacts (Organic-on-Metal)

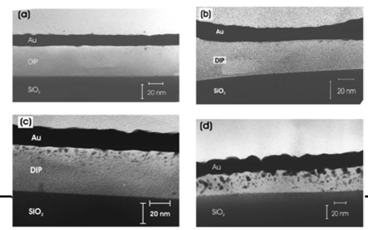
→ *… binding (frequently) means bending*



5. Growth of Metal Contacts (Metal-on-Organic)

→ *… penetration of metal into organic difficult to avoid;*

→ *… may be reduced by low T*



 based on Alexander Hinderhofer and Frank Schreiber, ChemPhysChem (2012)

Organic Semiconductors: Conclusions

- Organic semiconductors allow exciting new products
  → Organic electronic circuits:
  Interesting ideas, but "killer product" is missing
  → OLED have achieved sizable market in display, lighting on the verge
  → Organic solar cells: encouraging progress

- Potential advantages
  → flexible
  → low material and energy consumption
  → tunability (colour)
  → large area production

- Preparation of organic heterostructures and devices:
  → metal-organic interfaces
  → structural definition of organic semiconductor
  → associated optical properties