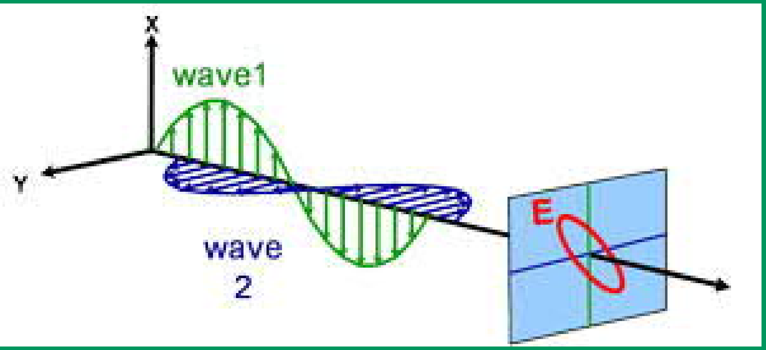
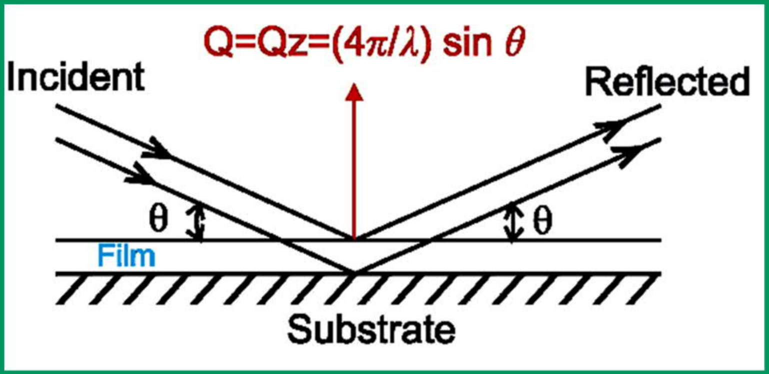
Ellipsometry
X-ray reflectivity
—
CHEM-L2000





Eero Kontturi

11th March 2022

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Learning objectives

- To roughly understand the principles of ellipsometry and XRR
- To be aware of their applications and restrictions when analysing polymeric (soft) materials
- To be able to point out what kind of information one can gain from applying ellipsometry and XRR on soft materials

Outline

(1) General aspects of both techniques

(2) Ellipsometry
- theory
- measuring / interpreting
- applications

(3) X-ray Reflectivity (XRR)
- theory
- measuring / interpreting
- applications

Important requirements

- Both ellipsometry and XRR are analytical techniques for *supported ultrathin films*
- The substrate (support) must reflect light (ellipsometry) or X-rays (XRR)
- Free-standing films (without a reflecting substrate) *cannot* be analyzed by either of the techniques

General applications

- Both ellipsometry and XRR are generally used for inorganic ultrathin films (hard materials)

- Soft, organic materials like natural polymers are less frequently analyzed and the interpretation methods for inorganic materials do not necessarily work for organic materials

Ellipsometry

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General considerations

- Ellipsometry analyzes the dielectric properties of a supported ultrathin film

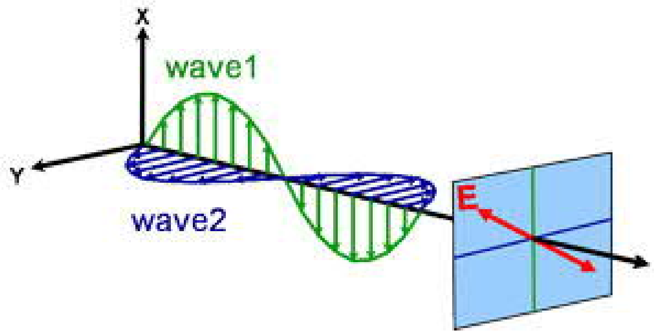
- Usually, film thickness and/or optical constants (like refractive index) are qualities measured with an ellipsometer

Theory: polarization

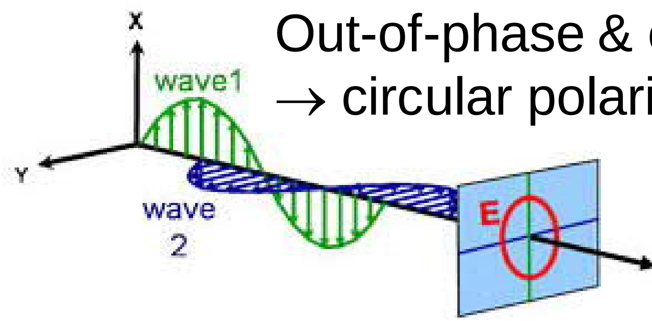
- Electric field of an electromagnetic wave is always perpendicular to its direction
- Polarized light: electric field follows a specific path with a distinct shape at any point

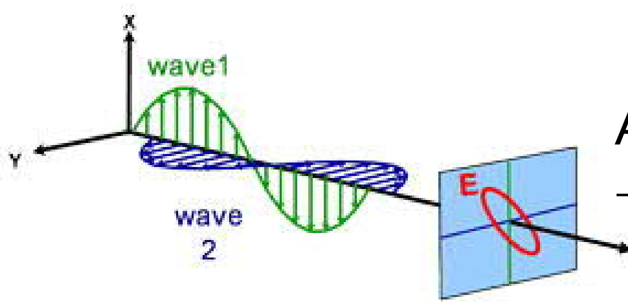
Two orthogonal light waves travelling at z-direction:

In-phase & different in amplitude
$\rightarrow$ linear polarization



Out-of-phase & equal in amplitude
$\rightarrow$ circular polarization

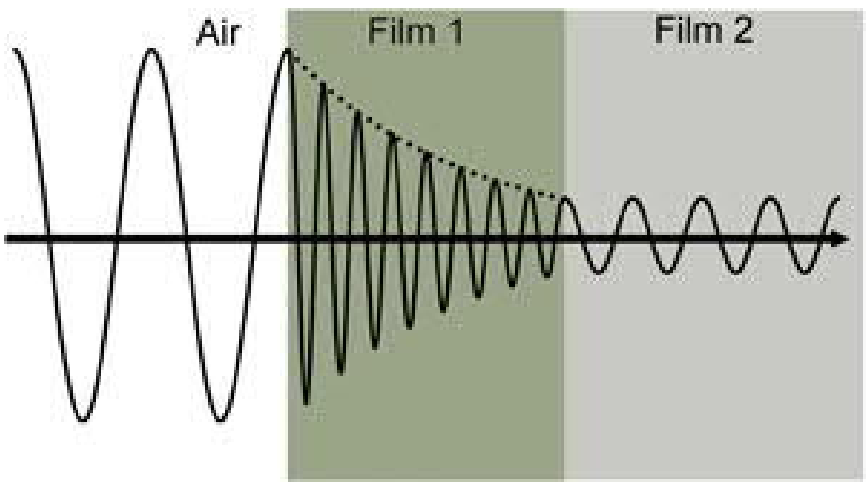




Arbitrary amplitude & phase
$\rightarrow$ ellipsoidal polarization

Theory: interaction between light and material

- Light slows when it becomes in contact with material
- Because the energy of light stays the same, its frequency increases and, therefore, the wavelength decreases



Complex refractive index:

$$\tilde{n} = n + \mathrm{i}k$$

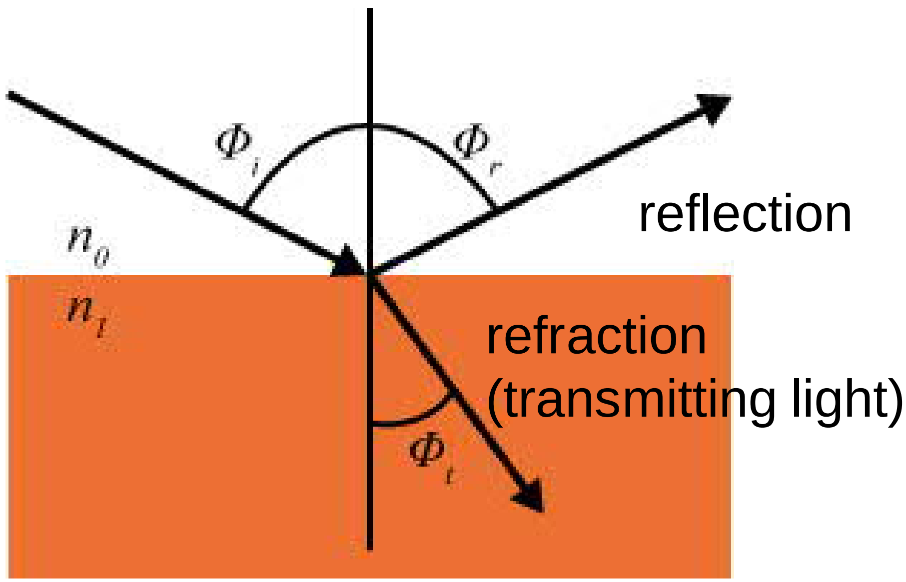
n – refractive index
k – extinction coefficient

Theory: interaction between light and material

At an interface, part of the light reflects and the remained transmits and refracts.

Snell's law: $n_0 \sin(\Phi_i) = n_1 \sin(\Phi_t)$

The mathematical expression of the phenomena of reflection/refraction is simple.



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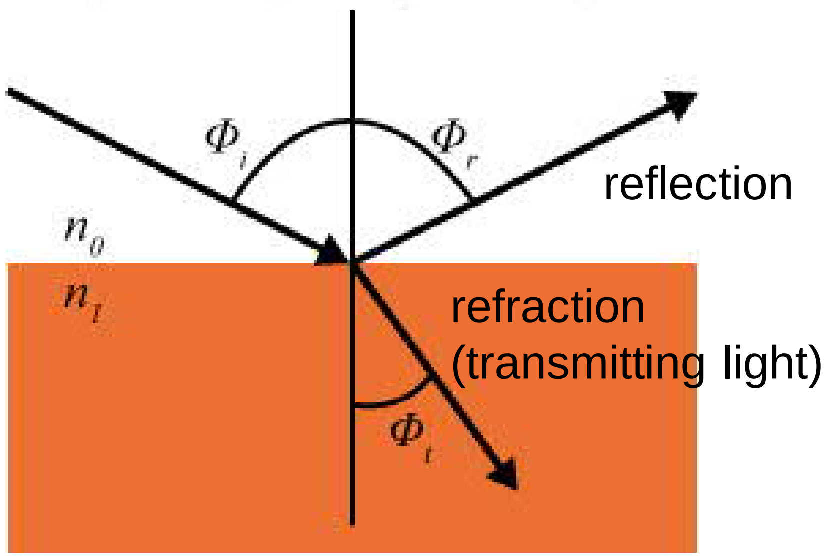
Theory: interaction between light and material

In terms of wave mechanics, the mathematical expression is more complex.

Snell's law:

$$n_0 \sin(\Phi_i) = n_1 \sin(\Phi_t)$$



Fresnel equations

$$r_s = \left(\frac{E_{0r}}{E_{0i}}\right)_s = \frac{n_i \cos(\Phi_i) - n_t \cos(\Phi_t)}{n_i \cos(\Phi_i) + n_t \cos(\Phi_t)}$$

$$r_p = \left(\frac{E_{0r}}{E_{0i}}\right)_p = \frac{n_t \cos(\Phi_i) - n_i \cos(\Phi_t)}{n_i \cos(\Phi_t) + n_t \cos(\Phi_i)}$$

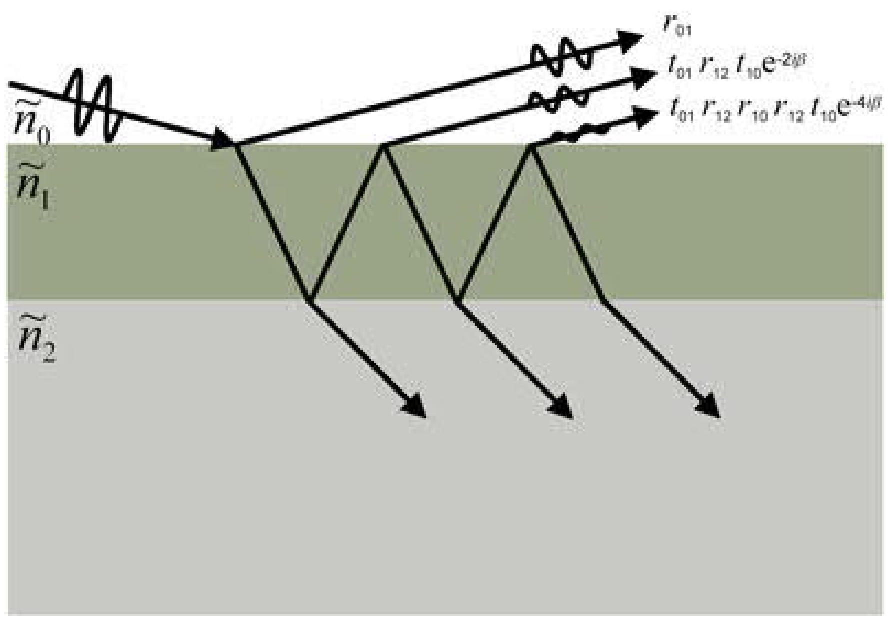
$$t_s = \left(\frac{E_{0t}}{E_{0i}}\right)_s = \frac{2 n_i \cos(\Phi_i)}{n_i \cos(\Phi_i) + n_t \cos(\Phi_t)}$$

$$t_p = \left(\frac{E_{0t}}{E_{0i}}\right)_p = \frac{2 n_i \cos(\Phi_i)}{n_i \cos(\Phi_t) + n_t \cos(\Phi_i)}$$

r – reflectance; t - transmittance
p – parallel; s – perpendicular
E – electric field

Theory: interaction between light and material

In terms of wave mechanics, the mathematical expression is more complex.



Fresnel equations

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r – reflectance; t - transmittance
p – parallel; s – perpendicular
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Measurements

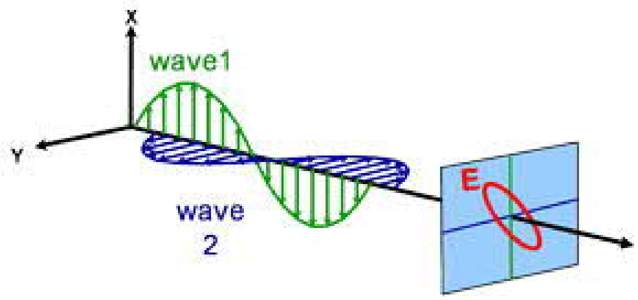
Ellipsometry actually measures the complex reflectance ratio (ρ), which can be denoted also as the ratio of the amplitudes of p (parallel) and s (perpendicular) components after reflection (r_p/r_s) :

$$\rho = \frac{r_p}{r_s} = \tan(\psi) e^{i\Delta}$$

$\tan(\psi)$ – amplitude ratio upon reflection
Δ - phase shift upon reflection

Change in polarization upon reflection

Remember



arbitrary amplitude & phase
$\rightarrow$ ellipsoidal polarization

Interpretation of data

- Ellipsometry is an indirect method

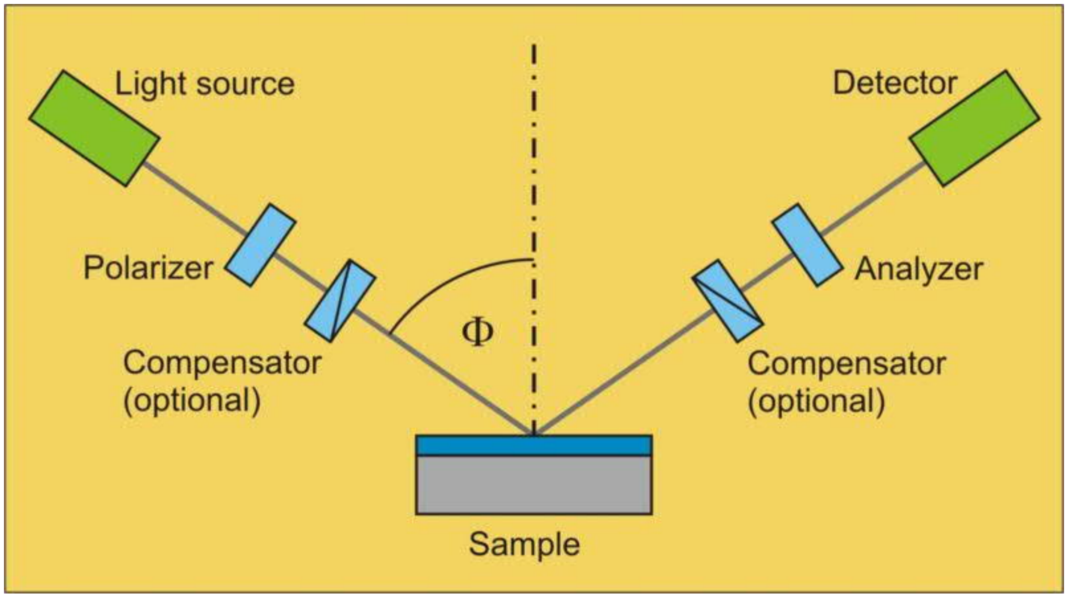
- Reflectance ratio (r_p/r_s) does not yield any concrete physical information on the sample

- Modelling is required to yield actual physical values

→ One must iterate values for k (extinction coefficient) and n (refraction coefficient) which would give a reasonable fit to the measurement values

→ Values for film thickness

Experimental setup



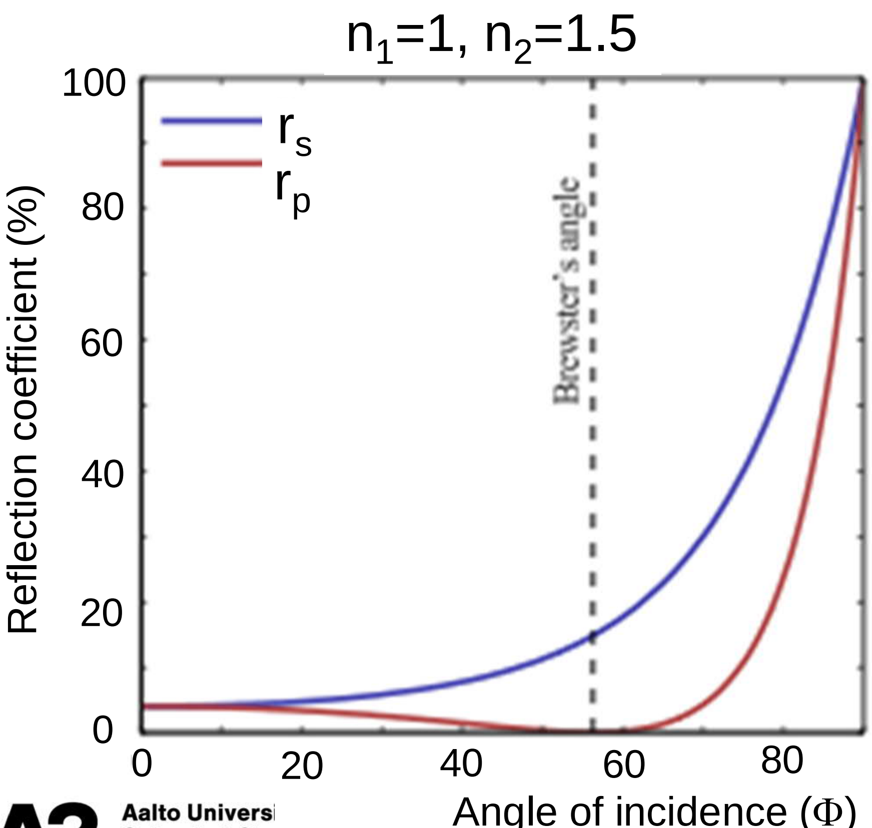
In a conventional ellipsometry measurement mode:

- monochromatic wavelength is used
- incident angle (Φ) is varied manually by a goniometer

(Spectroscopic ellipsometry is based on varying the wavelength of light)

Interpretation of data

The actual data that you get out of an ellipsometry measurement is the reflection coefficient as a function of angle of incidence for s- and p-components.



Reflectance coefficient is the ratio of light that has reflected from the sample, i.e., that has not been transmitted:

$r_s = 1 - t_s$
$r_p = 1 - t_p$

Note: when p-component is zero, the angle is called *Brewster's angle*.

Interpretation of data

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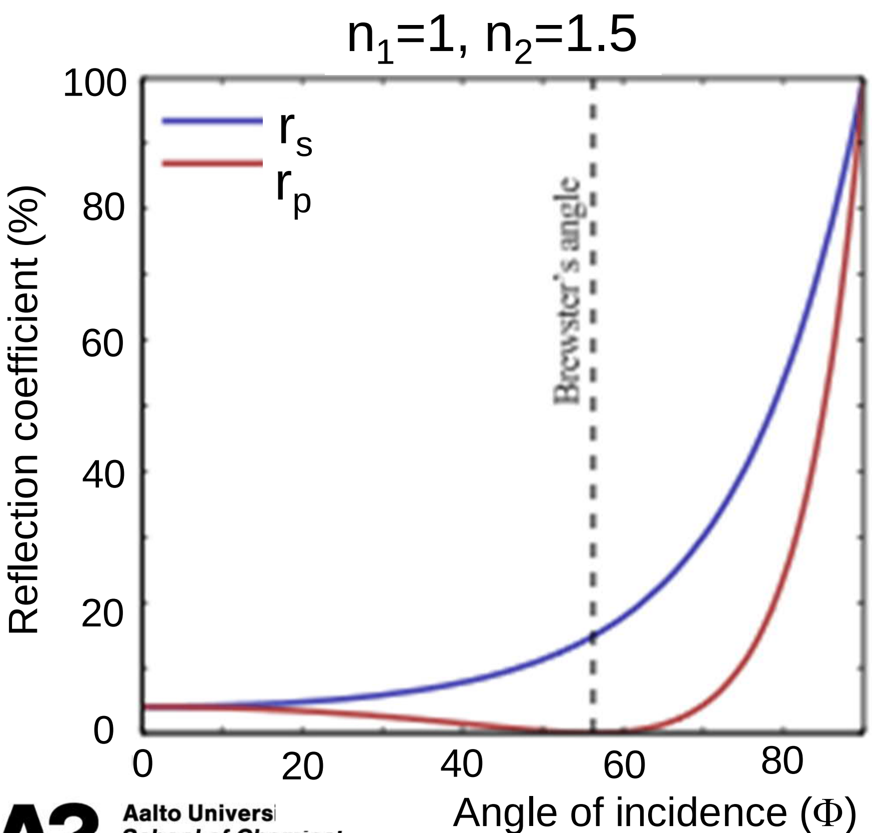


$$n_0 \sin(\Phi_i) = n_1 \sin(\Phi_t)$$

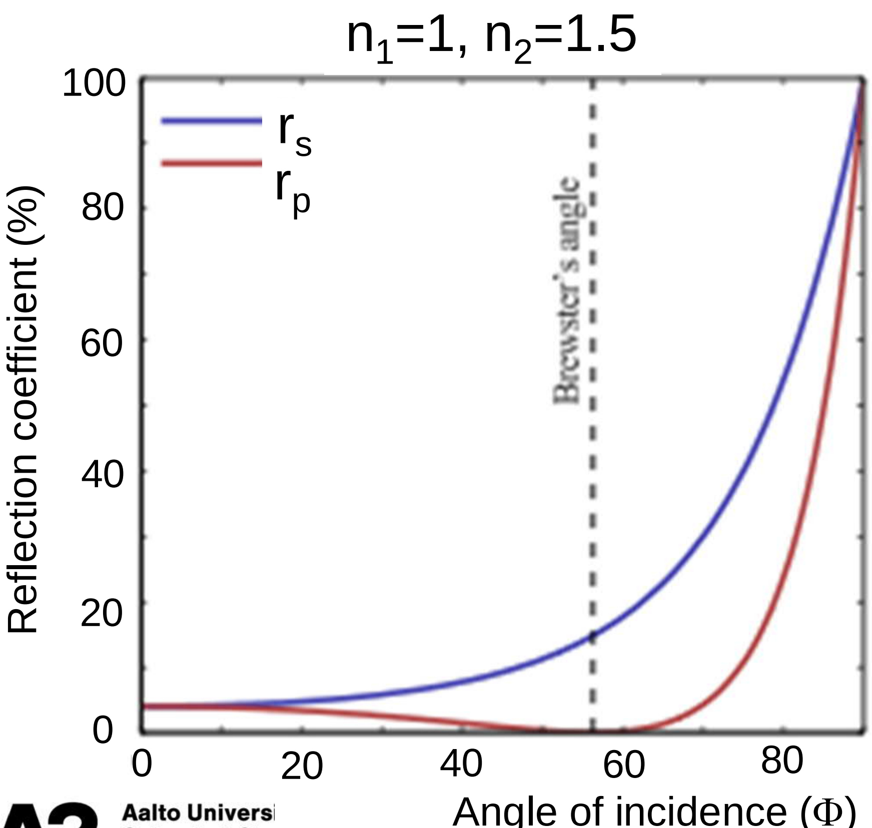
$$\tilde{n} = n + ik$$

n – refractive index
k – extinction coefficient

Modelling: n and k values are iterated to simulate the reflection curve with Fresnel equations.

Interpretation of data

The actual data that you get out of an ellipsometry measurement is the reflection coefficient as a function of angle of incidence for s- and p-components.



Fresnel equations

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r – reflectance; t - transmittance
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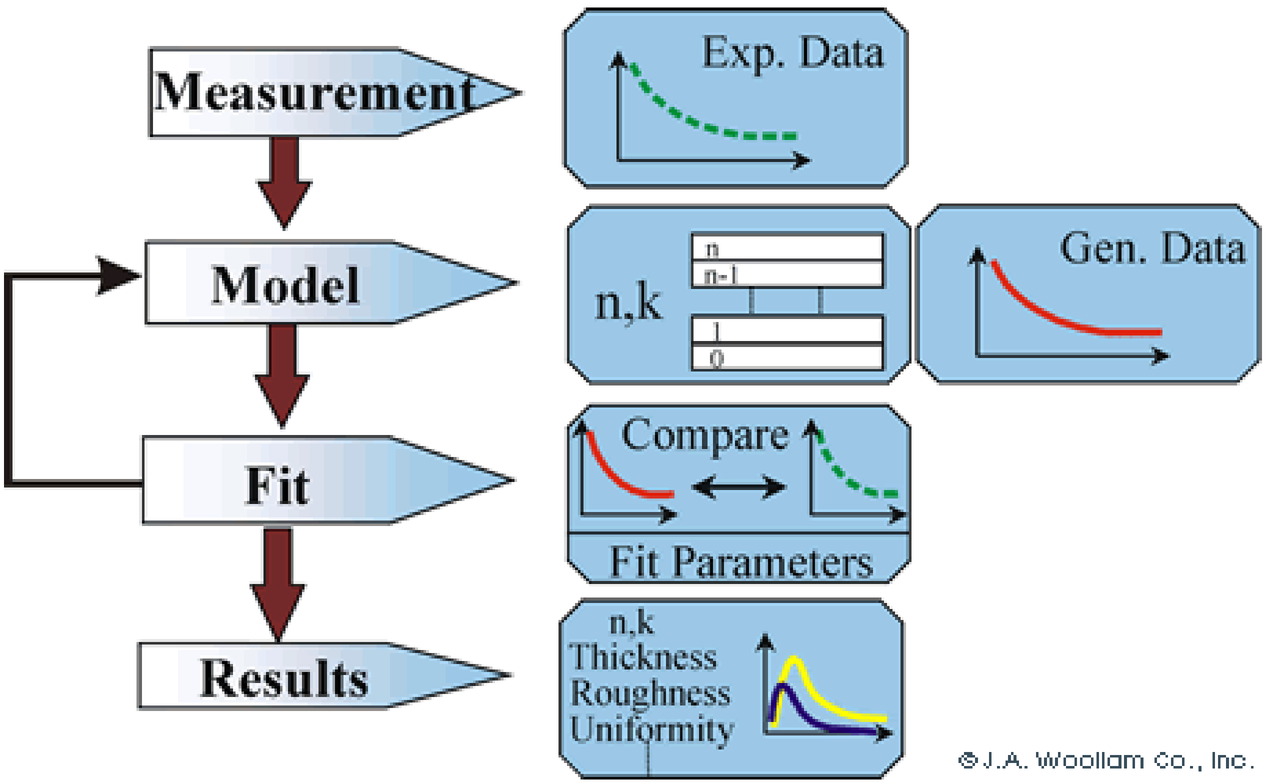
E – electric field

Interpretation of data



Important practical notions

- Probably the most common use of ellipsometry is to determine the film thickness
- Film thickness can be probed from a submonolayer (<nm) thickness to several micrometers
- It helps if you know what you are measuring: if you know the refractive index (n) of the film material, you only have to iterate the k-value
  $\rightarrow$ more reliable modelling of the reflectivity graph
  $\rightarrow$ more reliable film thickness value

Application example: *in situ* determination of enzyme activity

- Cellulase enzymes degrade cellulose into sugars
- Mechanisms of degradation are complex and difficult to interpret

→ Ultrathin model films can provide clarification to degradation mechanisms

- The enzymes first adsorb on cellulose, after which degradation begins
- This can be followed with in situ ellipsometry

$$\Gamma = 3d_1 \frac{\frac{n_1 - n_0}{(n_1^2+2)(n_0^2+2)}}{\frac{A}{M} - v\frac{n_0^2-1}{n_0^2+2}}(n_1 - n_0).$$

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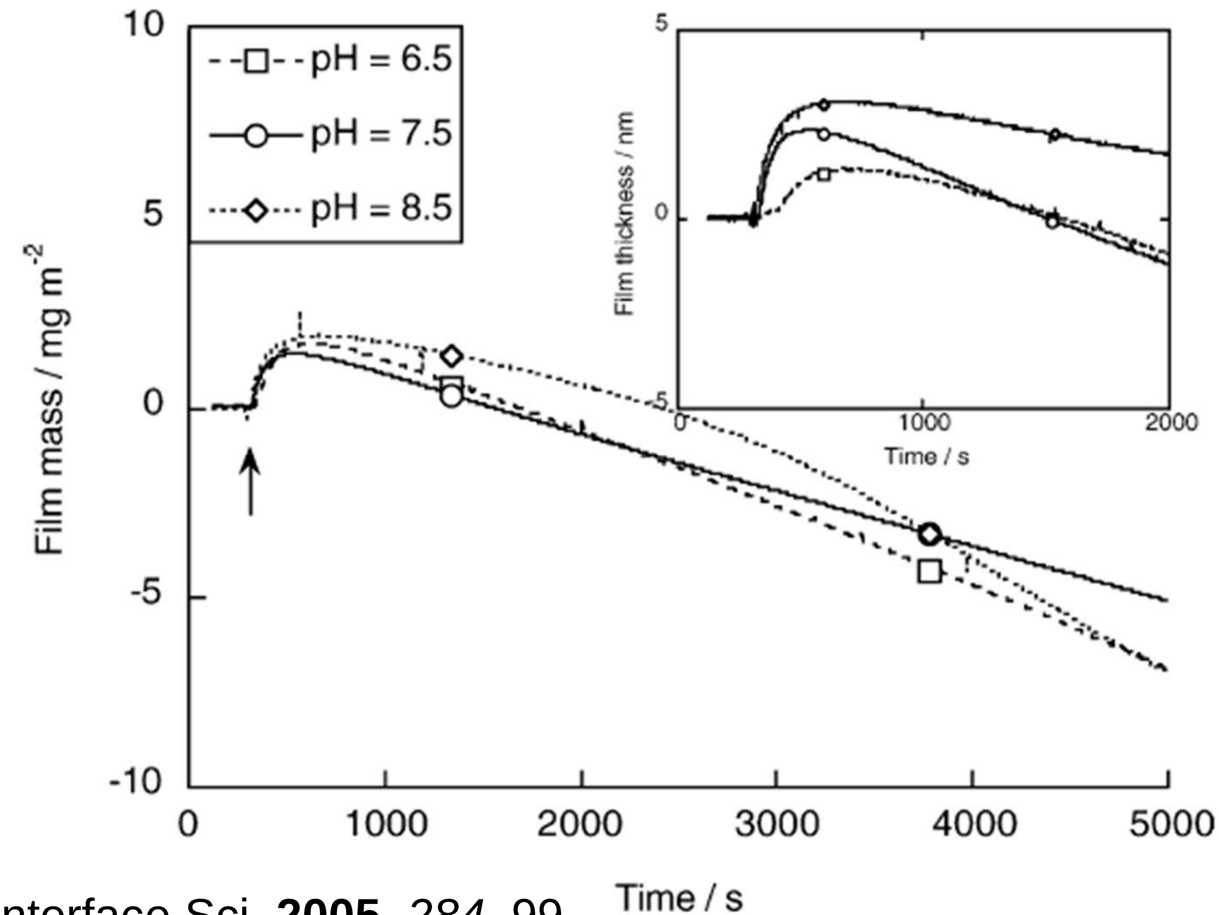
Application example: *in situ* determination of enzyme activity

(1) The enzymes adsorb
→ increase in film mass

(2) The enzymes start to
degrade cellulose
→ decrease in film mass

Effect of pH



J. Colloid Interface Sci. **2005**, *284*, 99.

Application example: *in situ* determination of enzyme activity

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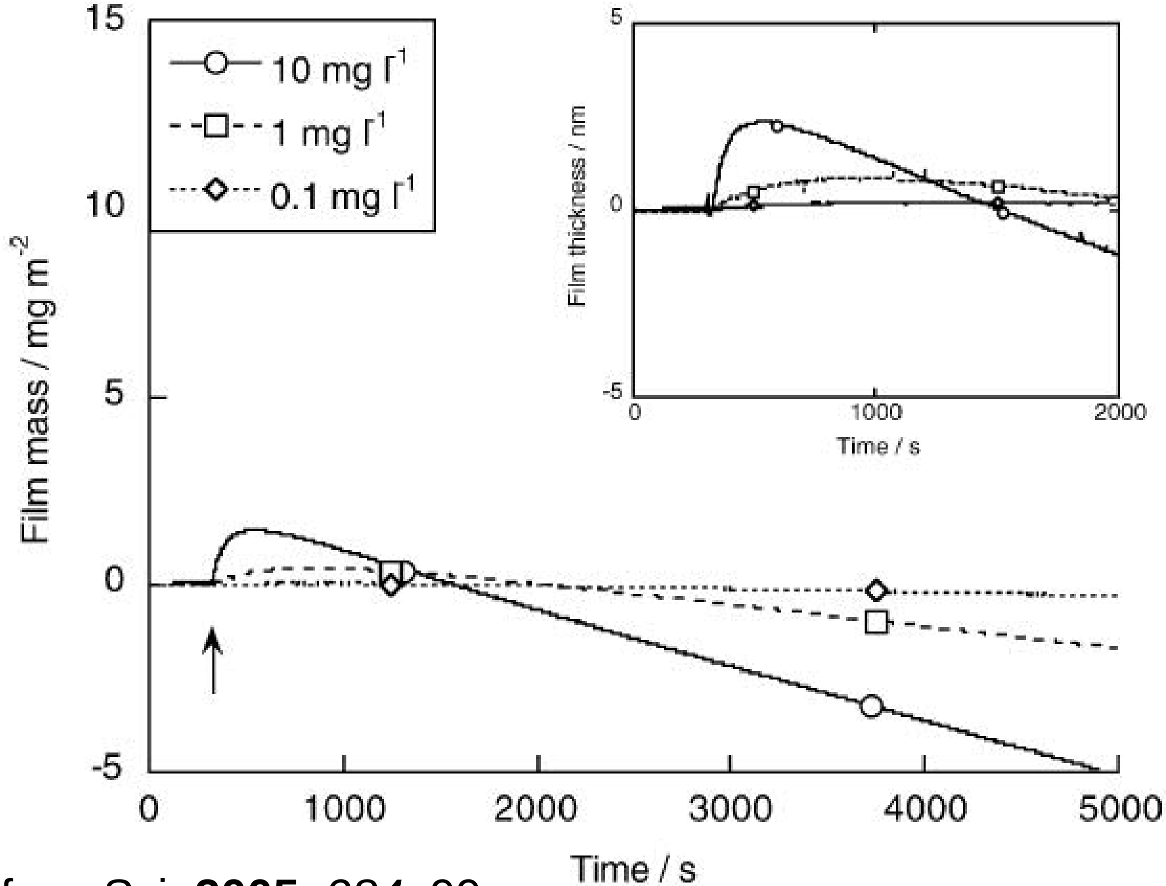

Effect of temperature

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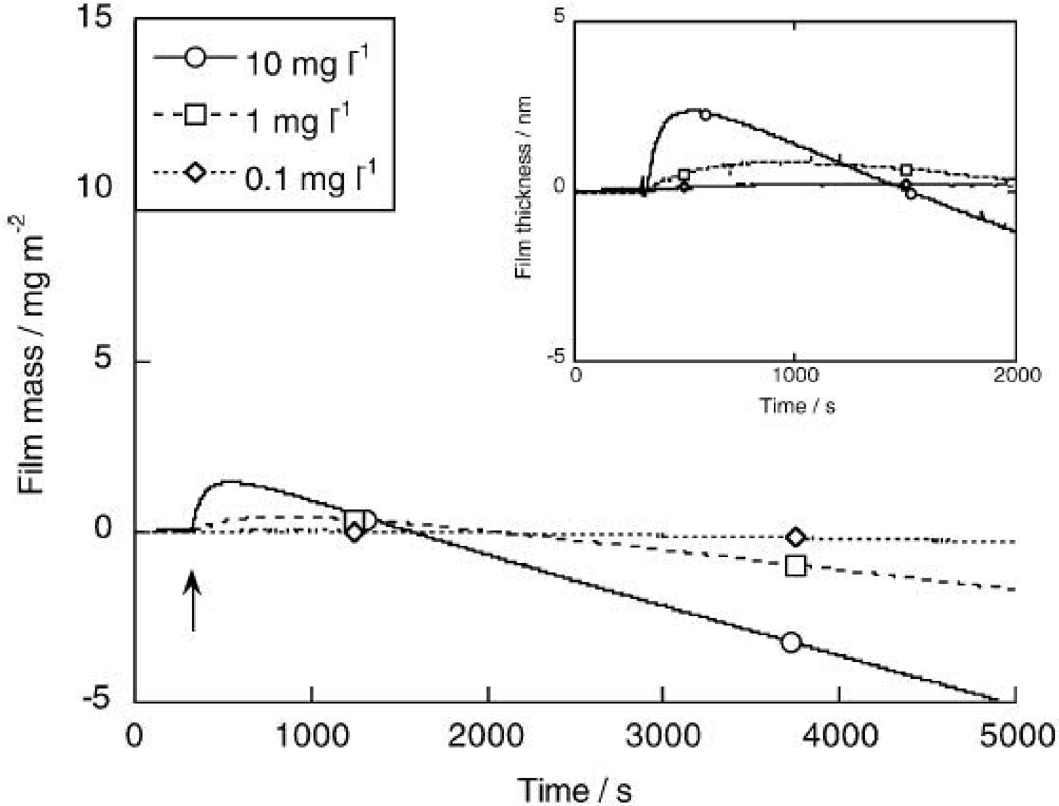
J. Colloid Interface Sci. **2005**, *284*, 99.

Application example: *in situ* determination of enzyme activity

(1) The enzymes adsorb
→ increase in film mass

(2) The enzymes start to
degrade cellulose
→ decrease in film mass

Effect of enzyme concentration



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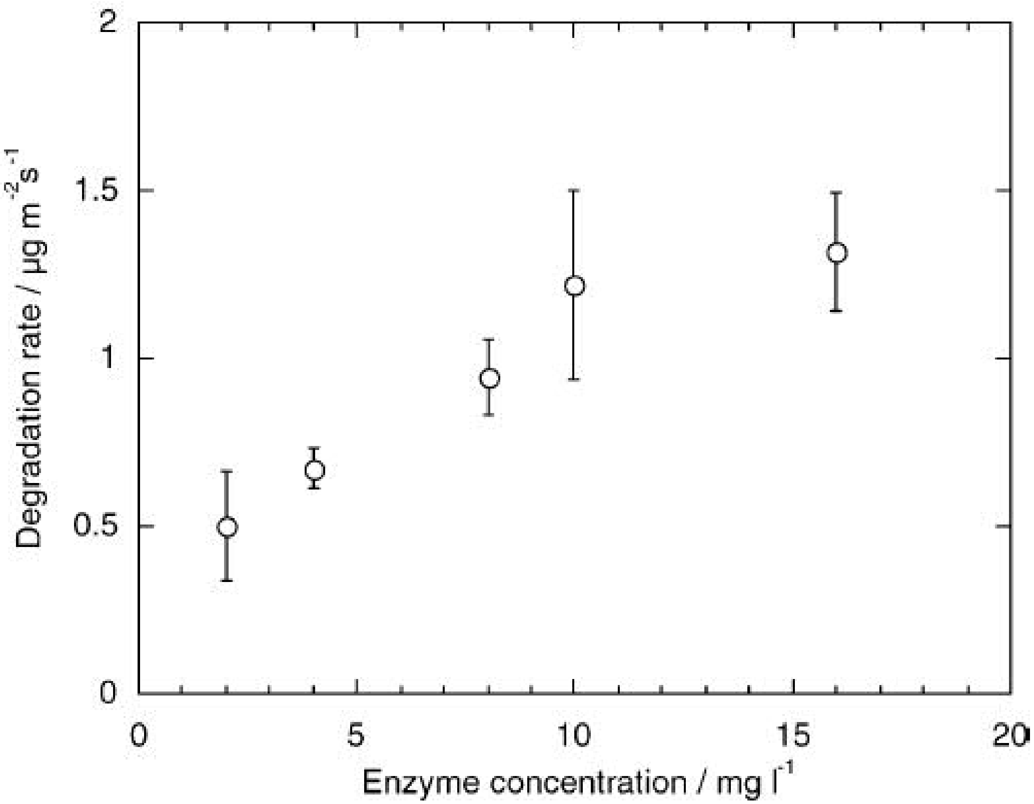
Application example: *in situ* determination of enzyme activity

With ellipsometry data, it is easy to calculate the degradation rate of cellulose exposed to the enzymes.



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Note on adsorption and ellipsometry

- Because of ambiguities in interpretation and the scant availability of in situ setups, ellipsometry is not used very often in *in situ* adsorption studies

- QCM and SPR are nowadays for more common in solution-based adsorption studies

X-ray reflectivity (XRR)

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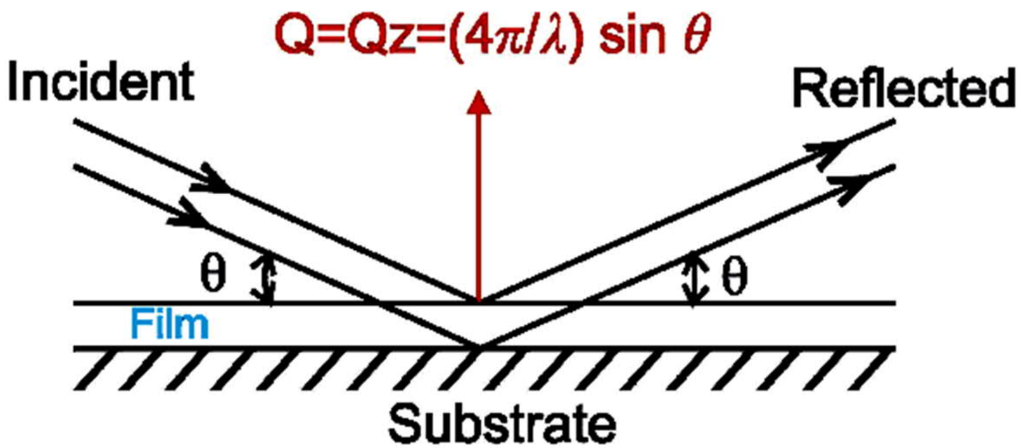
Theory

- Sample is exposed to monochromatic X-rays coming in at grazing angle
- The reflected intensity is plotted as a function of scattering vector (or reflection angle θ)

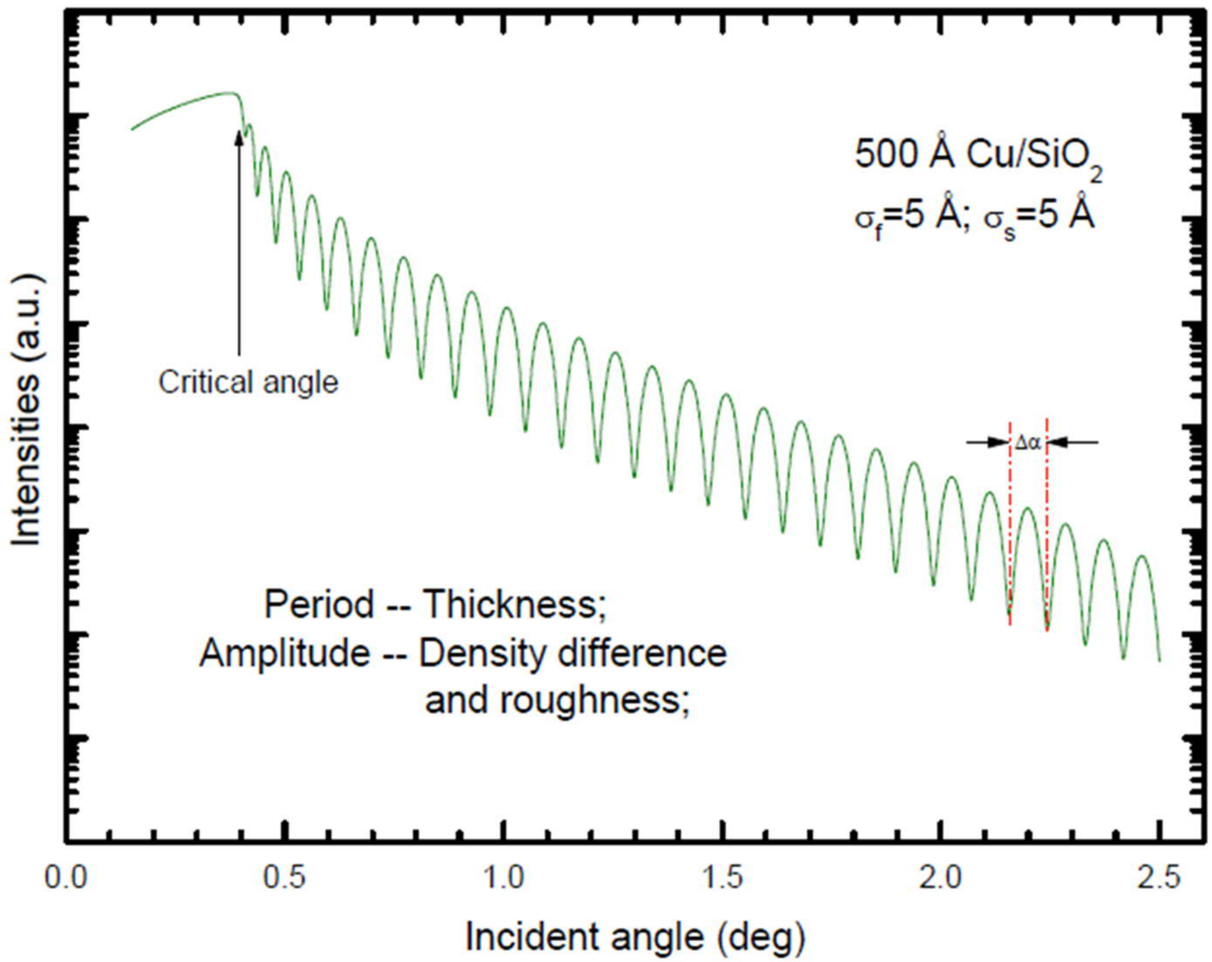
Scattering vector



Reflectivity presents periodical oscillations in reciprocal space.
Reason: constructive interference at substrate-film and substrate-air interface.
Result: accurate determination of film thickness.

Theory

Example: 50 nm Cu film on silica (SiO_2)



First, total reflection occurs with very small reflection angles.

After the **critical angle (α_c)**, interference fringes occur.

Note: the interference fringes are also called *Kiessig fringes*.

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Theory

Complex refractive index:

$n = 1 - \delta - i\beta$

Note that refraction depends also on mass density of the film.

$$\delta = \left(\frac{2\pi}{k_0^{\ 2}}\right) r_e N_a \rho \left(\frac{Z + f'}{M_a}\right)$$

$$\beta = \left(\frac{2\pi}{k_0^{\ 2}}\right) r_e N_a \rho \left(\frac{f''}{M_a}\right)$$

$k_0 = 2\pi/\lambda$ (with λ being the wavelength) is the length of the x-ray wave vector

r_e is the classical electron radius

N_a is Avogadro's number

ρ is the mass density

Z is the atomic number

M_a is the atomic mass

f' is the real part of the dispersion coefficient

f'' is the imaginary parts of the dispersion coefficient

Theory

Reflectance coefficient (R_F):

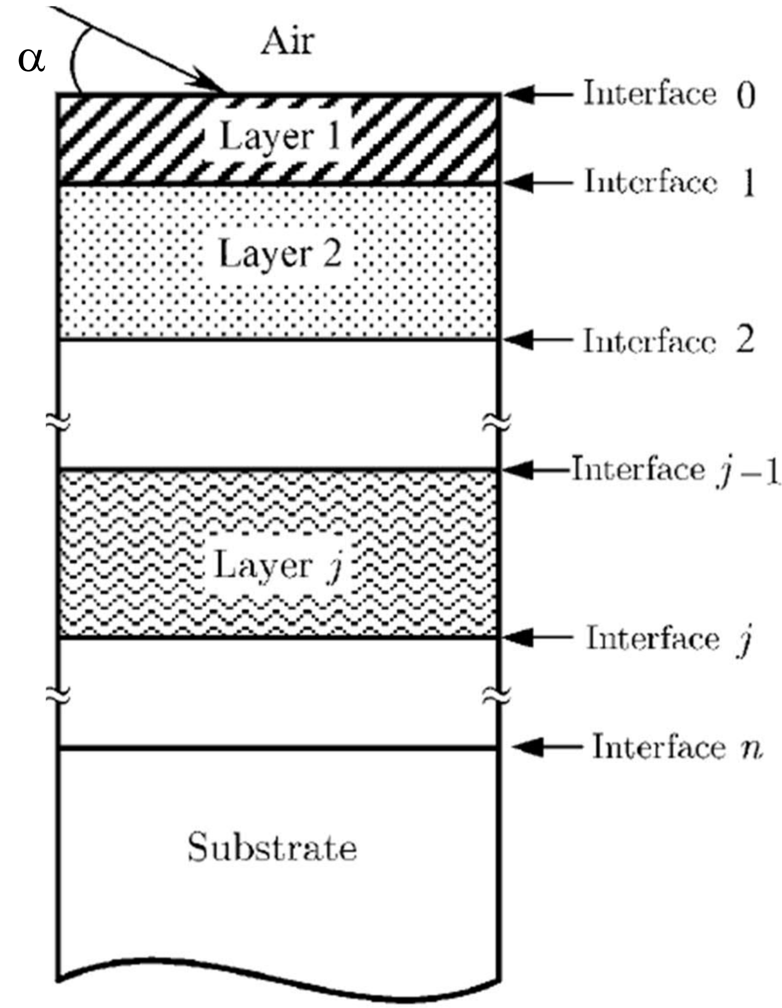
$$R_F = \left| \frac{r_0^{N-C} F_0 + r_1^{N-C} F_1 \exp(-i2k_0 f_1 h)}{1 + r_0^{N-C} r_1^{N-C} F_0 F_1 \exp(-i2k_0 f_1 h)} \right|^2 = \left| \frac{R_F'}{R_F''} \right|$$

h – film **thickness**

$$r_j^{N-C} = \exp(-2k_0^2 \sigma_j^2 f_j f_{j+1})$$

Roughness factor

$$F_j = \frac{f_j - f_{j+1}}{f_j + f_{j+1}}$$



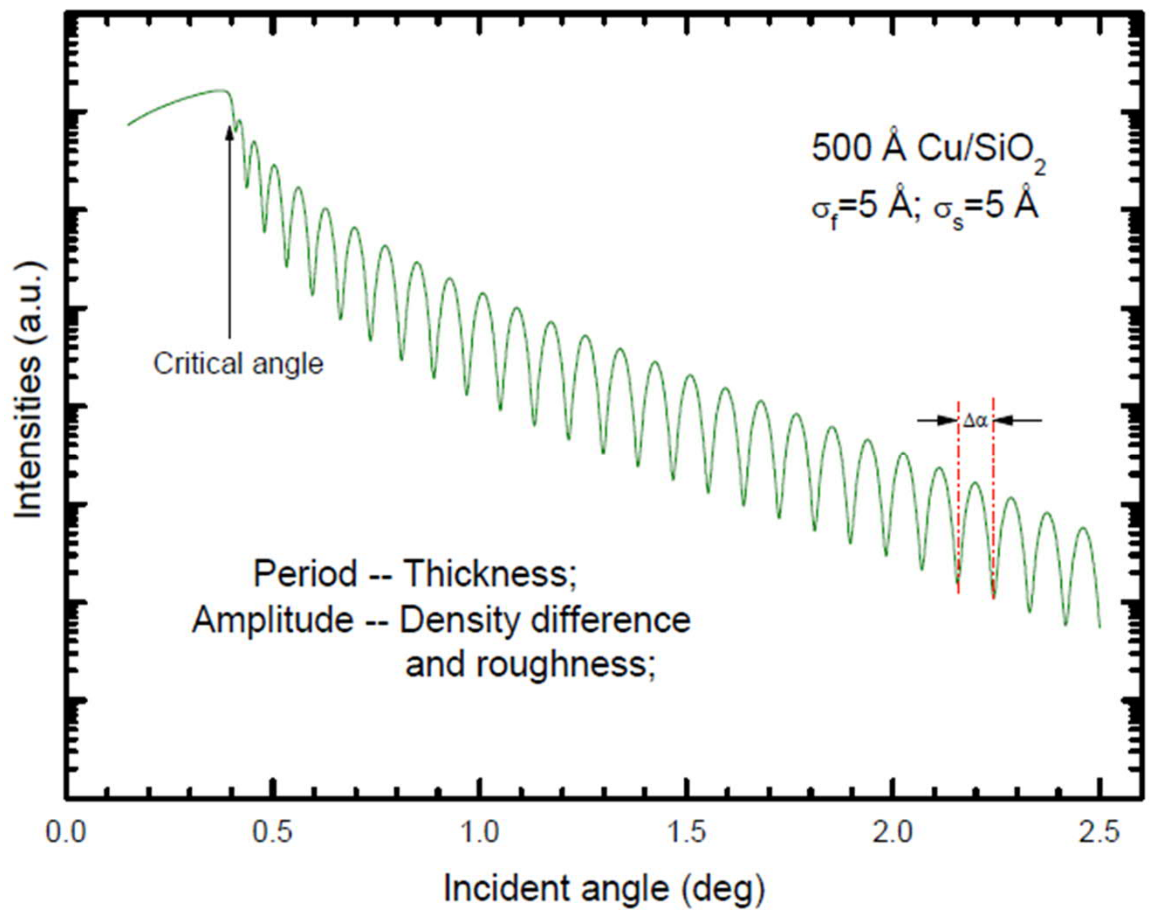
$$f_j = \sqrt{\alpha^2 - 2\delta_j - i2\beta_j}$$

Dependence on incident angle and complex refractive index (incl. mass **density**)

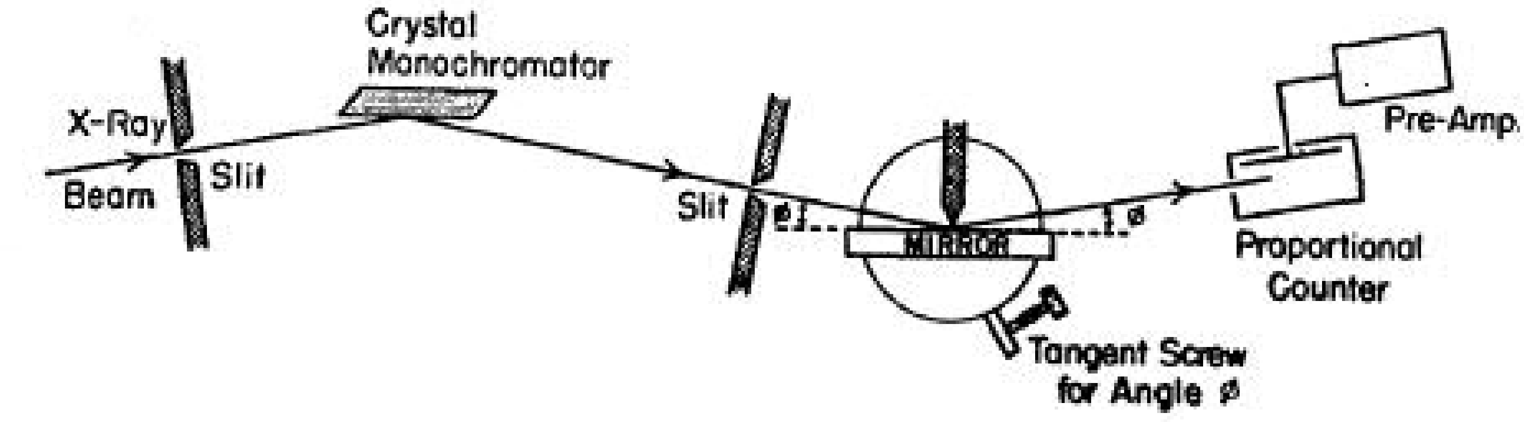
Theory

Overall, the determining factors for the reflectivity curve are:

- film thickness
- film roughness
- mass density of the film



Instrumentation



- Angle of incidence is varied manually during the measurement
- The sample area should be maximized
- XRR is usually feasible to operate with an X-ray diffractometer

Phys. Rev. **1954**, *95*, 359.

Instrumentation

- X-ray reflectivity may also be performed at a synchrotron facility (particle accelerator that produces an x-ray beam of unusual intensity)

- Synchrotron sources are expensive and laborious to use but the data quality is excellent

Interpretation of data

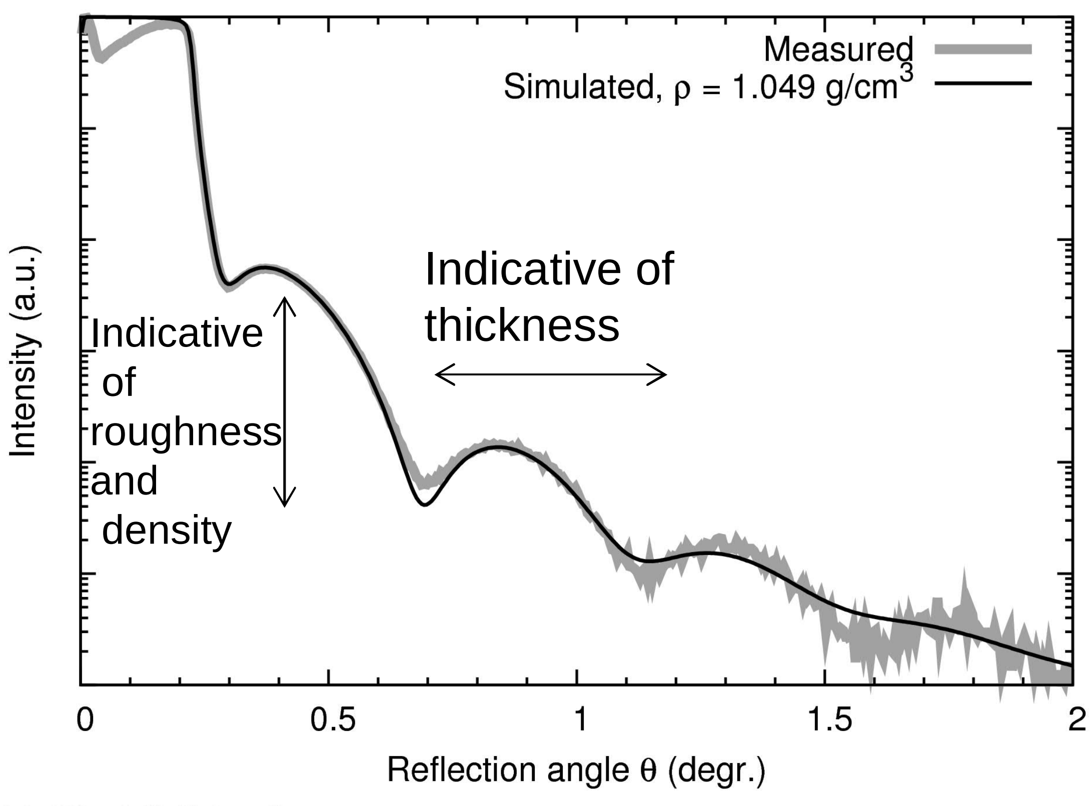
- Like ellipsometry, XRR is an indirect method
- Reflected intensity does not yield any concrete physical information on the sample
- Modelling is required to yield actual physical values

→ One must iterate values for thickness, density, and n roughness which would give a reasonable fit to the measurement values

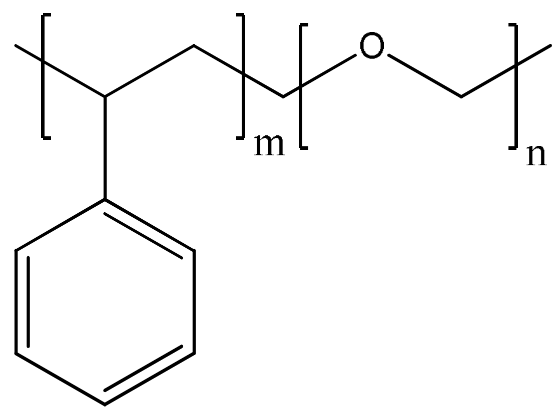
→ Values for film **thickness, density, and roughness**

- In general, the values for film thickness are highly reliable, but the values for mass density are less reliable, particularly with soft materials

Example of simulating the reflectivity curve



Polystyrene-*block*-polyethyleneoxide



Thickness: 9.9 nm
Roughness: 1.8 nm
Density: 1.05 g cm^{-3}

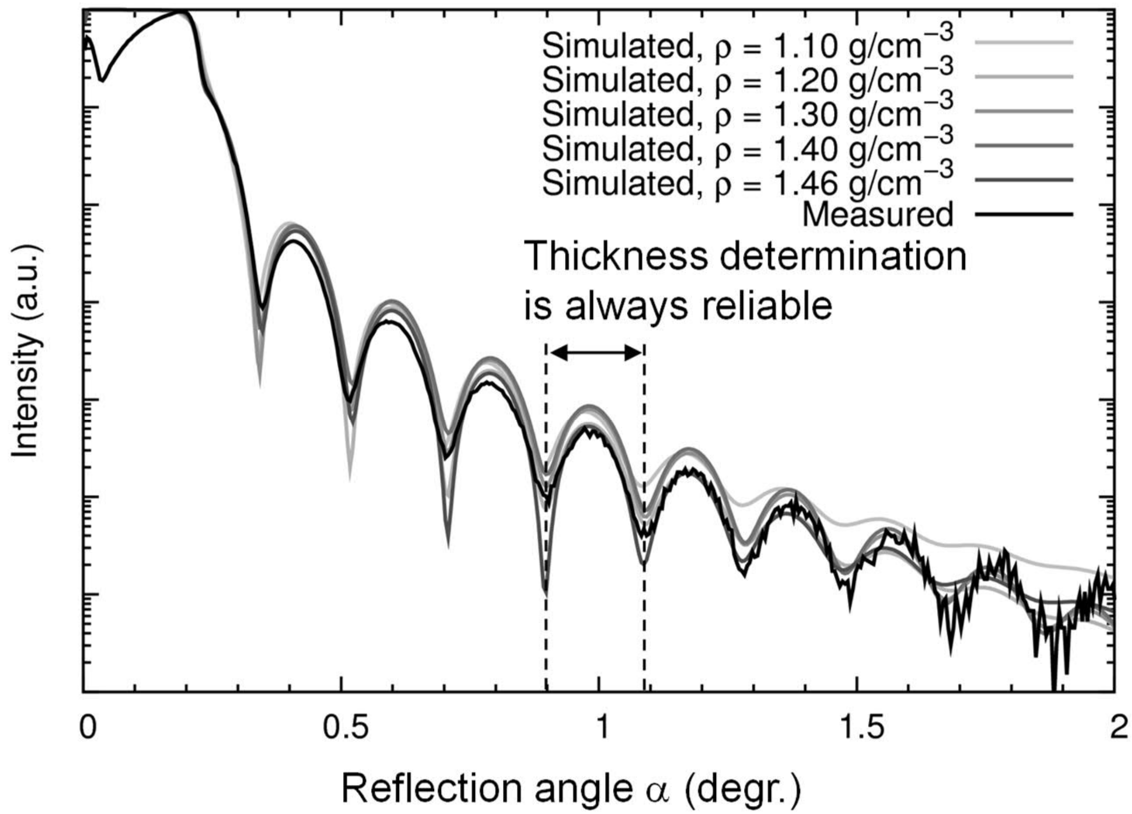
Mass density of organic thin films

PROBLEM WITH SOFT MATERIALS IN DENSITY APPROXIMATION

Different density values yield very similar fits.

UNRELIABLE

XRR profile of 20 nm cellulose film

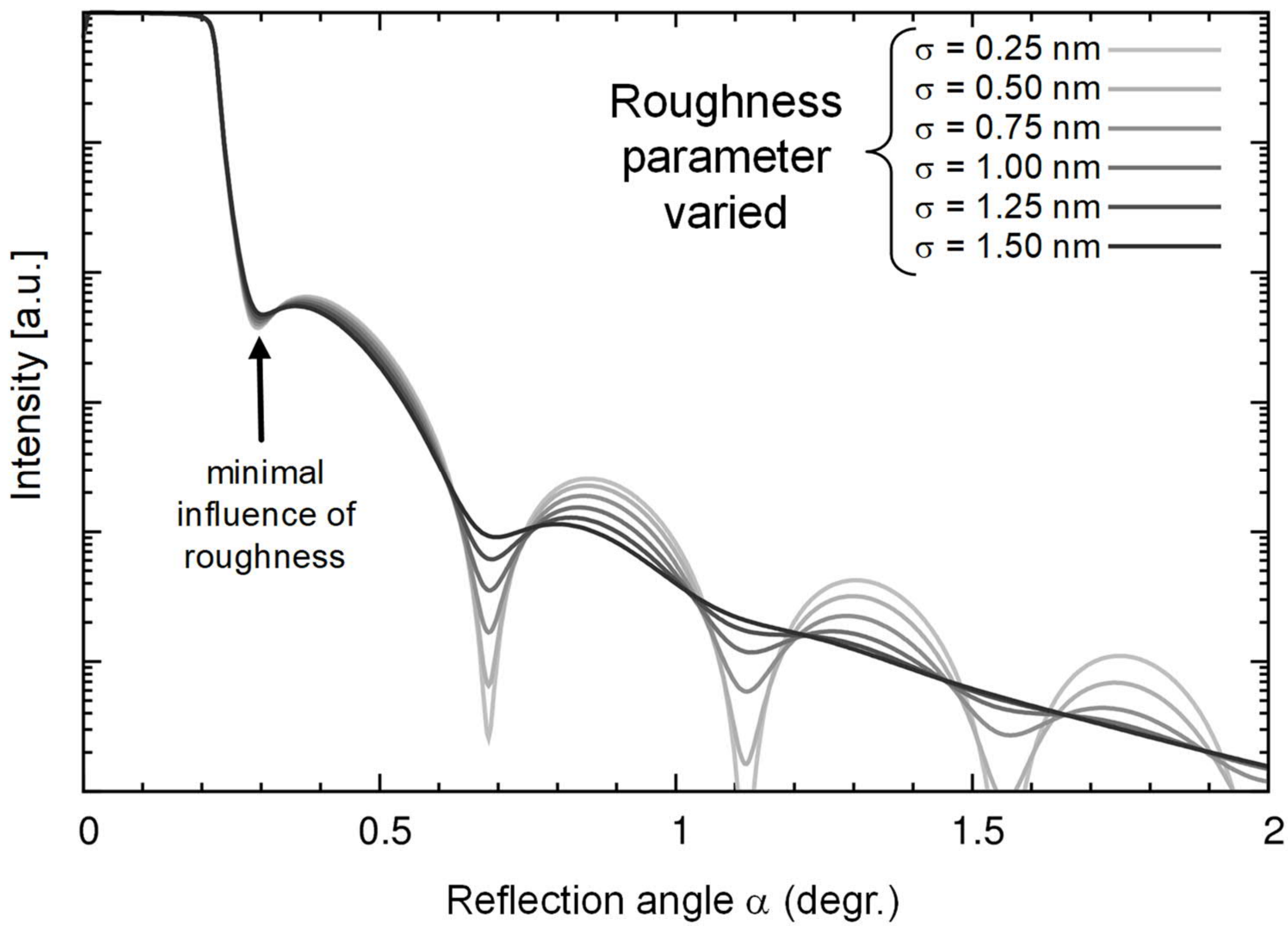


Why the density fit is unreliable

Thickness = 10 nm
density of polystyrene ~1.05

Roughness affects the positions of local minima more than density does.

Simulated XRR curve of polystyrene-like material



Can the density fit be reliable?

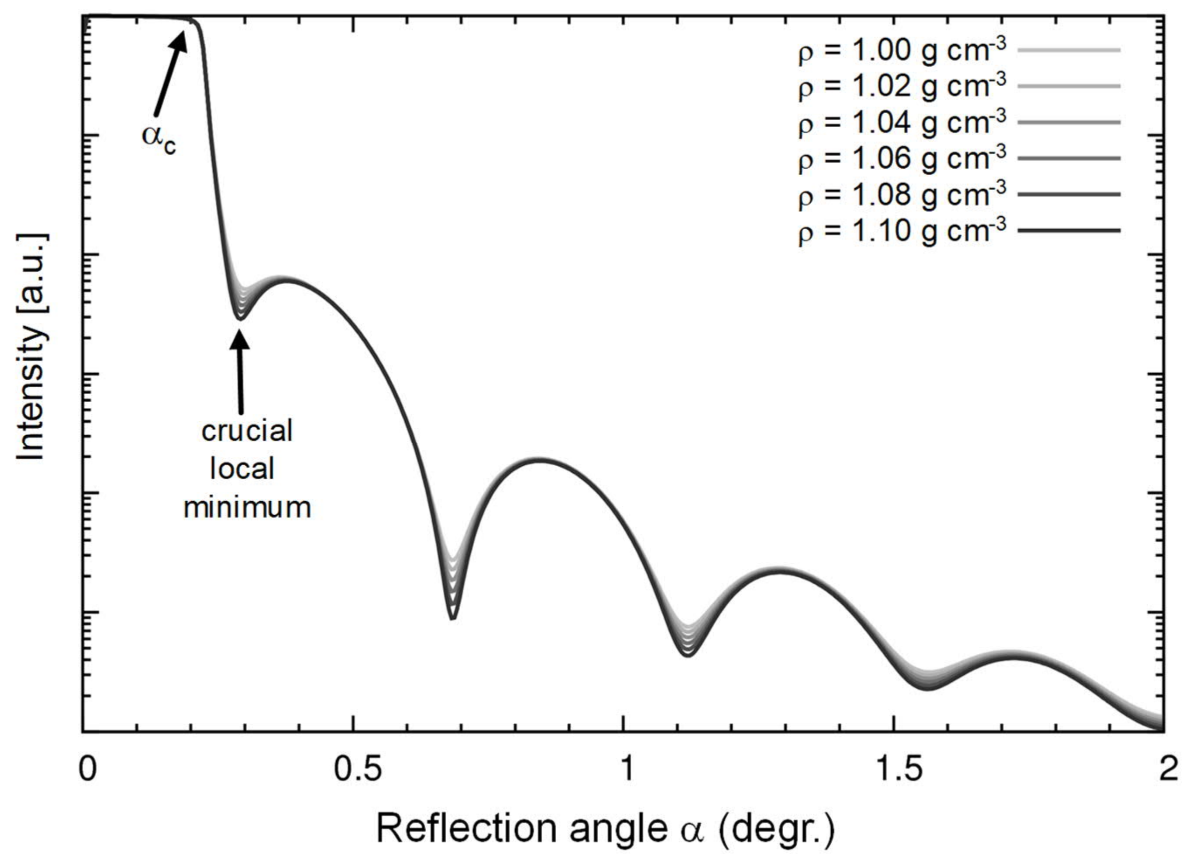
DISCOVERY: DENSITY DETERMINATION RELIABLE AT CERTAIN FILM THICKNESS VALUES (e.g. 5-17 nm)

In ca. 10 nm films,
small changes in density
parameter yield
already different fits.

↕

Reliable density determination
at 5-17 nm film thickness.

XRR profile of 10 nm polystyrene film



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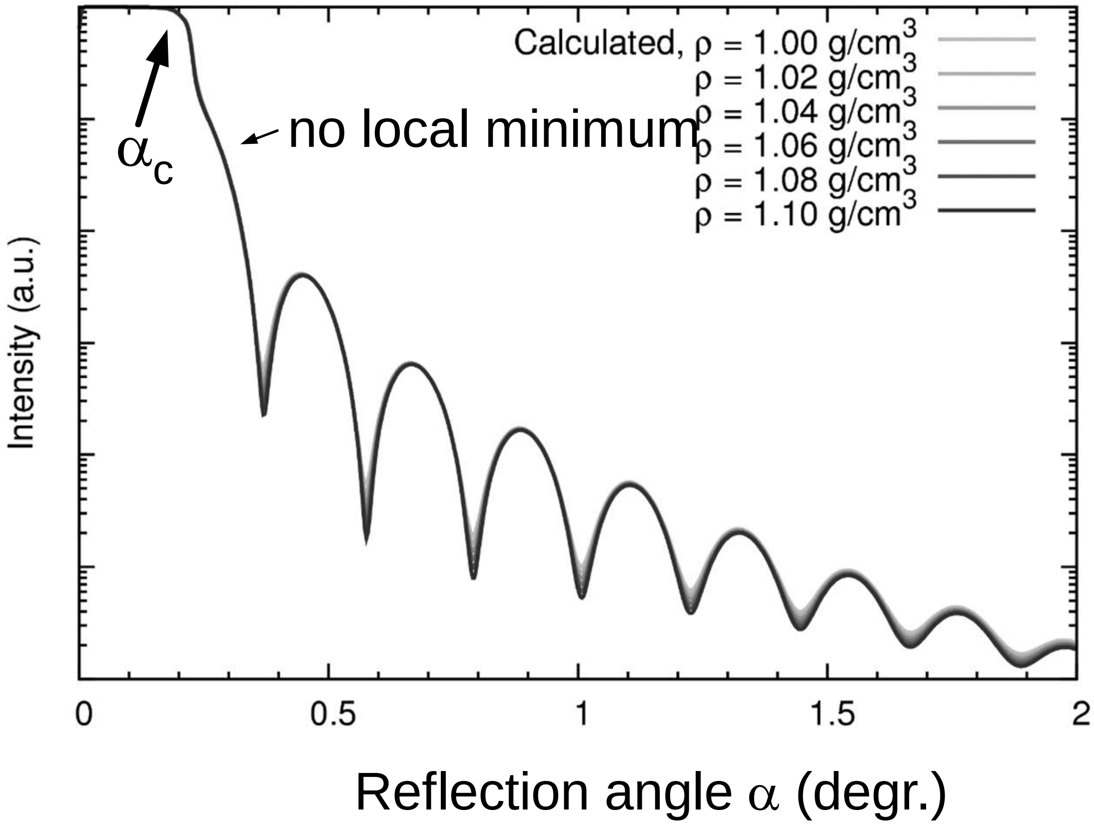
Can the density fit be reliable?

DISCOVERY: DENSITY DETERMINATION UNRELIABLE AT MANY THICKNESS VALUES (e.g. 20-40 nm)

XRR profile of 20 nm polystyrene film



Local minimum just next to α_c must be present – otherwise the density determination is unreliable.

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Experimental data on density

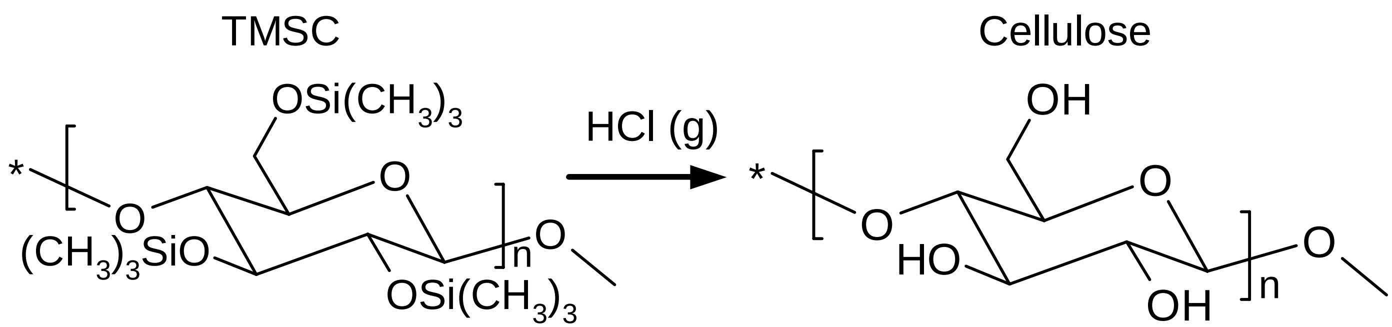
Sample	*Thickness [nm]*	*Roughness [nm]*	*Density [g cm^{-3}]*	**Density in bulk [g cm^{-3}]**
Polystyrene	15.0	0.39	1.03	1.047[a]
Poly(methyl methacrylate)	16.4	0.62	1.15	1.188[a]
Polystyrene-*block*-polyethyleneoxide	9.9	1.18	1.05	1.065[b]
Cellulose	6.7	0.52	1.51	1.52[c]
Trimethylsilyl cellulose	14.7	0.55	0.99	n.a.
Carboxymethyl cellulose	17.0	0.15	1.56	1.59[a]

→ Reasonable correlation with bulk values

Application example: following reaction kinetics in ultrathin film

From XRR data: - thickness - density ➡ **Molar mass**

Example: Hydrolysis of trimethylsilyl cellulose (TMSC) to cellulose



With 0.5 M HCl, the reaction spans ~10 min.

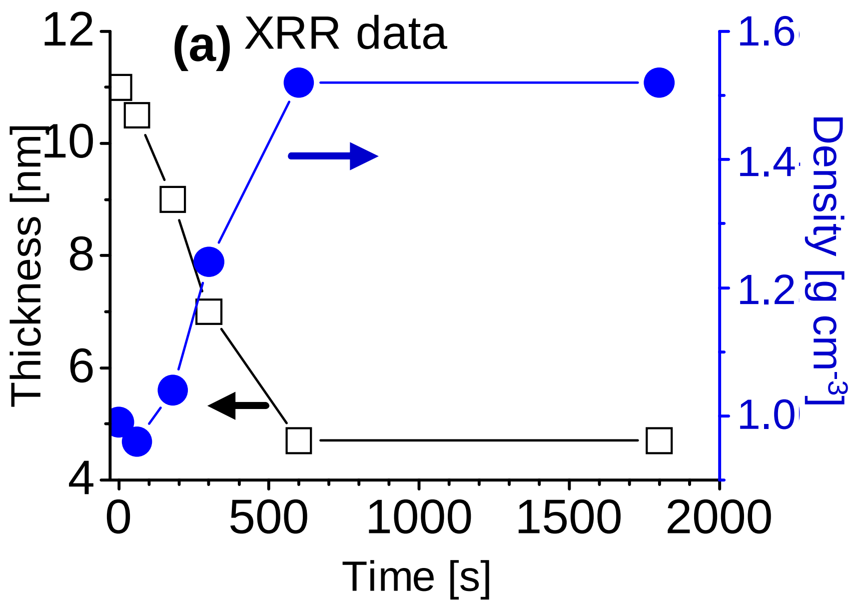
Reaction kinetics with XRR

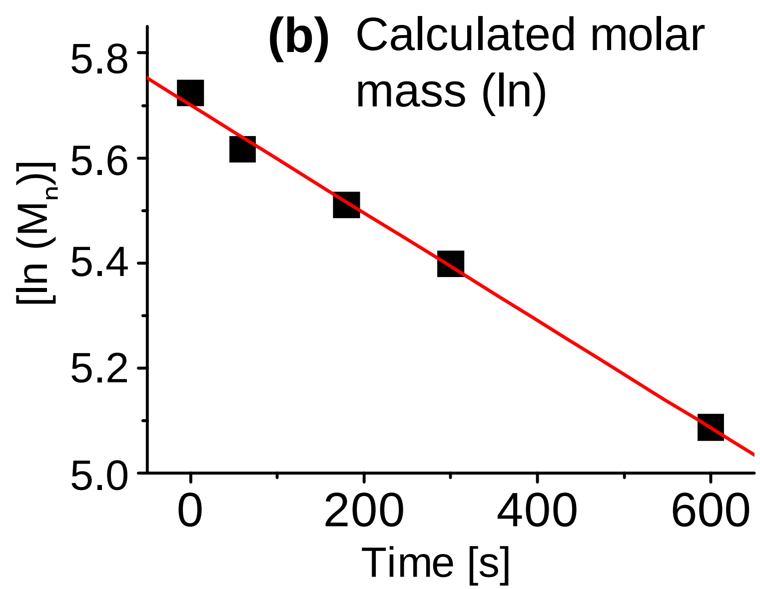
$$M_n = M_0 - \frac{h_0 d_0 - h_n d_n}{h_0 d_0 - h_k d_k}(M_0 - M_k)$$

M_0 is the molar mass of the starting material
M_k is the molar mass of the final material
h_0 is the initial film thickness,
d_0 is the initial mass density of the film
h_k is the final film thickness,
d_k is the final density of the film
h_n is the film thickness at a certain point of the reaction
d_n is the mass density of the film at a certain point of the reaction

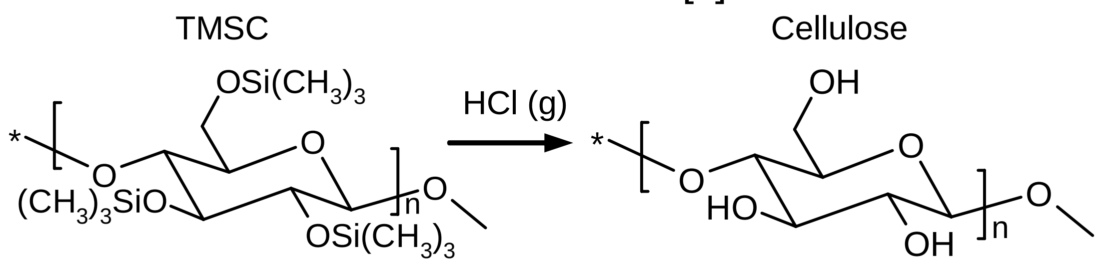
Reaction kinetics with XRR

Hydrolysis of TMSC to cellulose with 0.5 M HCl was followed at RT





First order reaction
$K=1.2\times10^{-3}\ s^{-1}$



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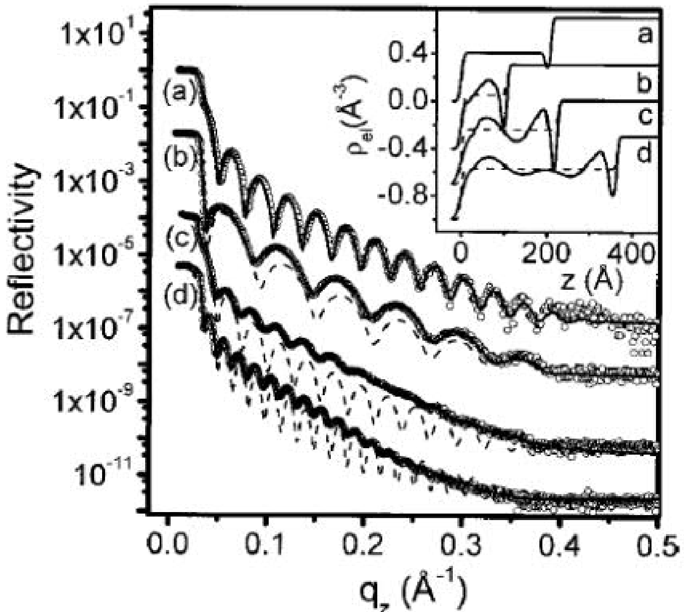
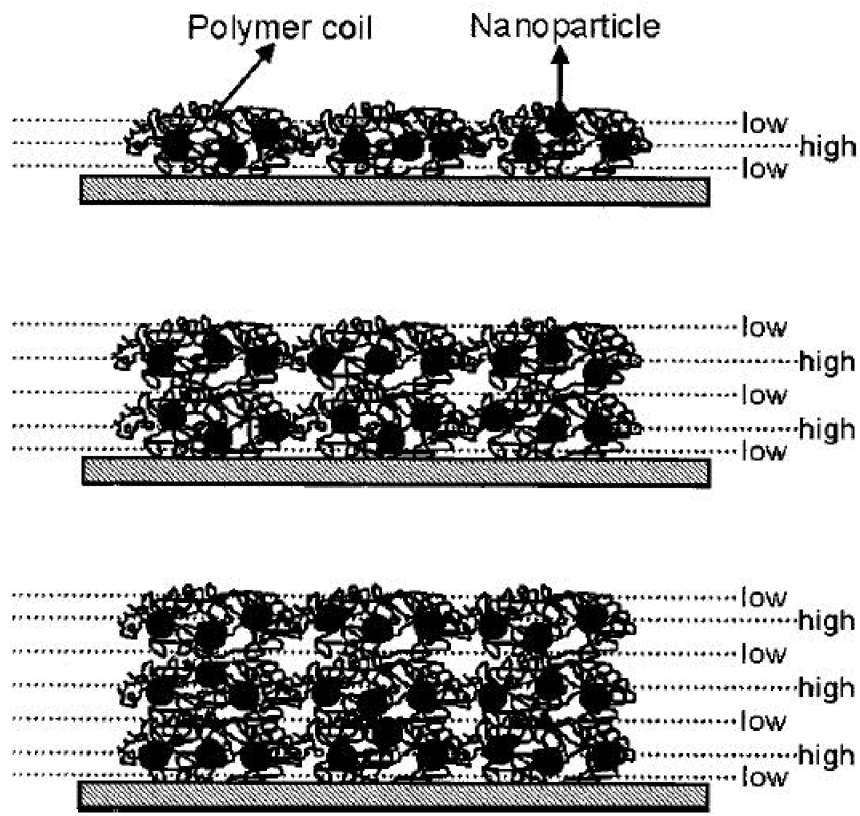
School of Chemical Engineering

J. Am. Chem. Soc. **2010**, *132*, 3678.

Application example: ordered nanocomposites



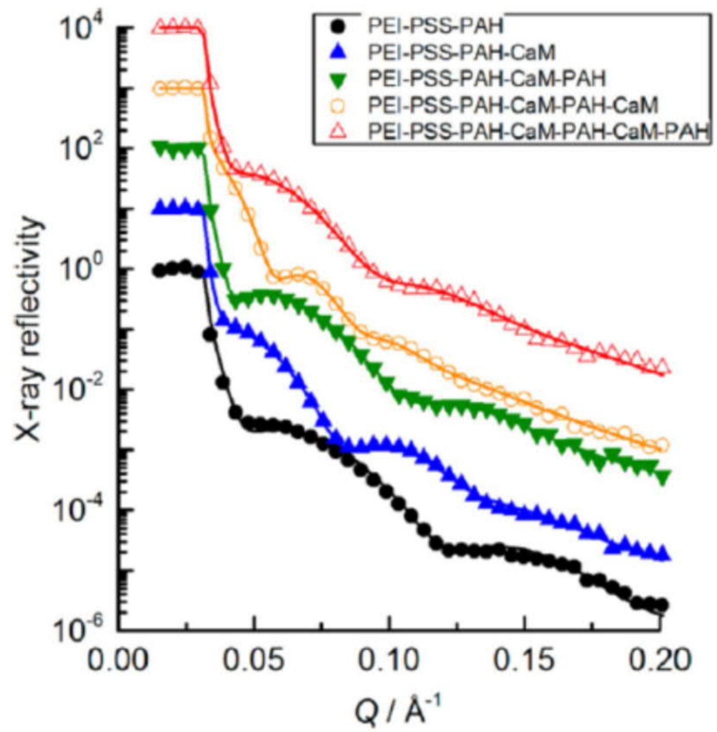


Reflectivity curves reveal that polyacrylamide spin coated with CdS nanoparticles to an ultrathin film is an ordered nanocomposite (discrete layers).

Aalto University
School of Chemical
Engineering

Phys. Rev. E **2004**, *70*, 051608.

Application: Layer-by-layer films with polymers



Protein called calmodulin (CaM) is mixed in an LbL film of cationic (PEI, PAH) and anionic (PSS) polyelectrolytes

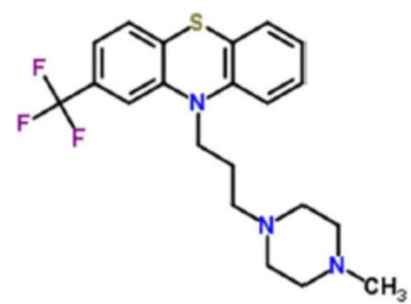
multilayer	d/Å
PEI-PSS-PAH	79
PEI-PSS-PAH-CaM	116
PEI-PSS-PAH-CaM-PAH	89
PEI-PSS-PAH-CaM-PAH-CaM	173
PEI-PSS-PAH-CaM-PAH-CaM-PAH	96

Langmuir **2017**, *33*, 3982.

Application: Layer-by-layer films with polymers

- Layer thickness values within the multilayers are probed by XRR
- It turns out CaM thickness inside the multilayer is very little affected by trifluoperazine (TFP), a ligand that changes CaM conformation in bulk

deposition unit	Δd/Å by XR
PEI-PSS-PAH	+62 ± 14 (23)
PEI-(PSS-PAH)$_2$	
first CaM	+50 ± 21 (7)
first CaM(TFP)	+49 ± 18 (11)
second CaM	+87 ± 15 (3)
second CaM(TFP)	+74 ± 8 (3)
CaM-PAH	+14 ± 7 (17)[c]



Langmuir **2017**, *33*, 3982.

Summary

- Ellipsometry and XRR are both based on electromagnetic radiation reflecting from a substrate of an ultrathin film
- Both yield data for film thickness with excellent accuracy
- With ellipsometry, it helps if you know the refractive index of the material; with XRR you don't need any preliminary information of the sample
- XRR gives you roughness and density of the film with precautions
- Both are extensively used for film thickness characterization