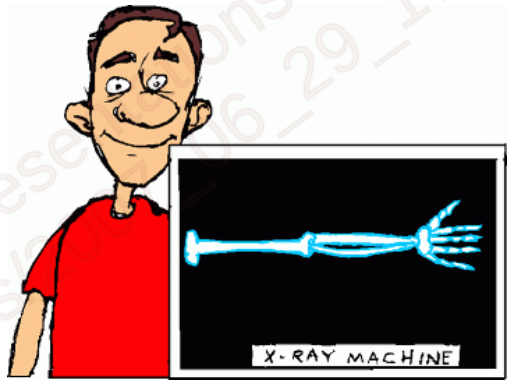
Contrast variation X-ray scattering in studying lyotropic liquid crystals

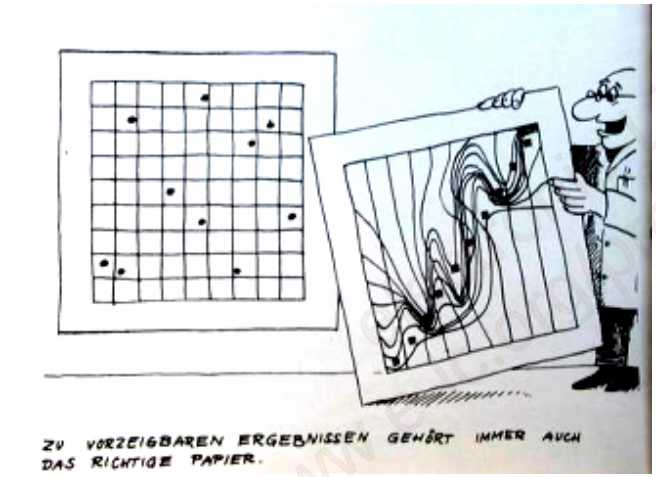
Zoltán Varga, Attila Bóta, Günter Goerigk

Budapest University of Technology and Economics
Department of Physical Chemistry and Material Sciences

Outline

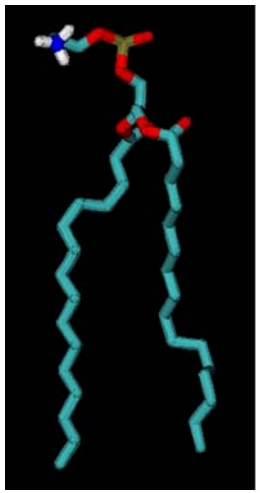
- Phospholipid bilayers
- Small angle X-ray scattering from vesicles
- Interpretation of the scattering curves
- Experimental details

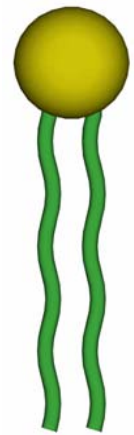




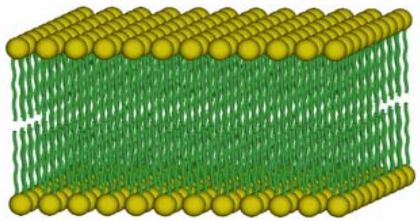
- Special problem: Localization of guest molecules in the lipid bilayer
- Contrast variation methods

Phospholipid/water mixtures as model-membrane systems



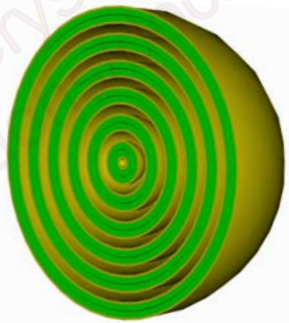


phospholipid

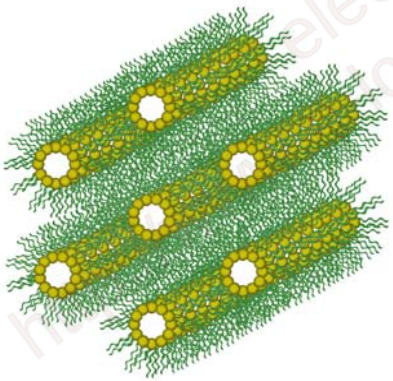


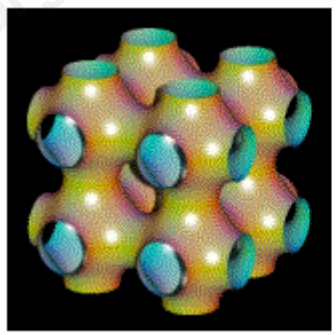
bilayer

vesicle
(liposome)

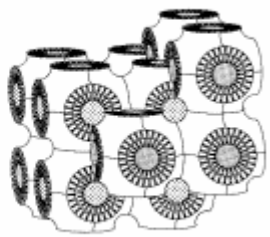


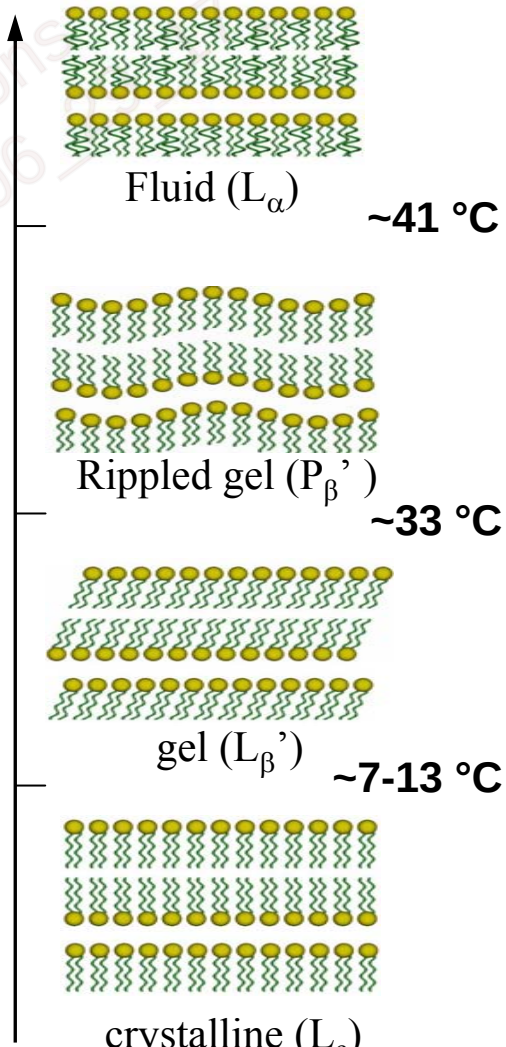
2D and 3D self-assembly of lipids also occures:





Im3m



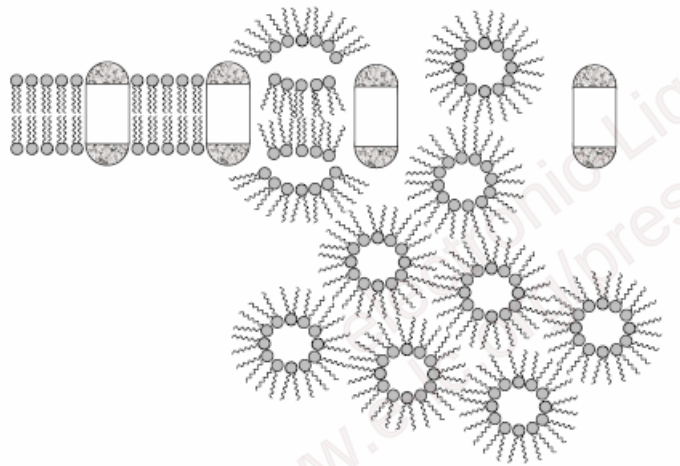


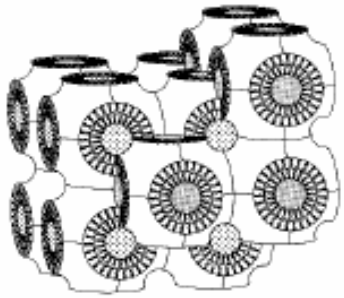
Lipid polymorphism

3D: Cubic phases

They have biological relevance:

- Thylakoid membranes of plants
- Bacterial cell membranes



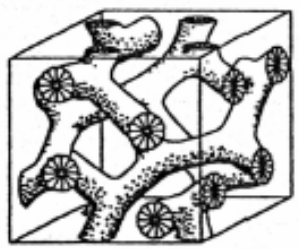


Im3m

P-surface

Pn3m

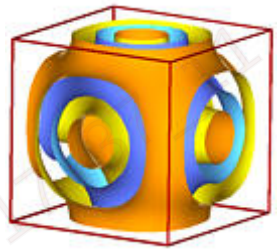
D-surface

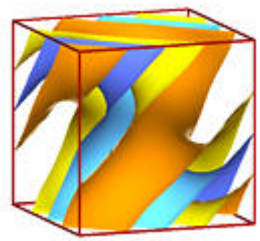


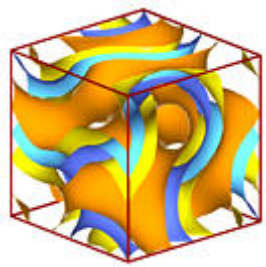
Ia3d

G-surface

IPMS



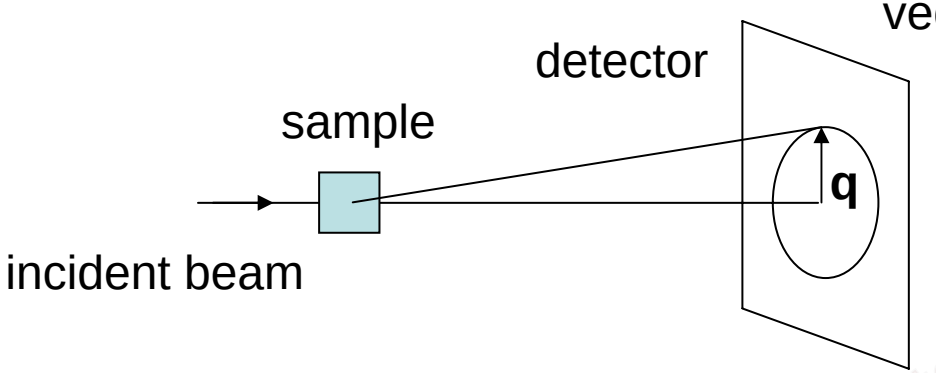




IPMS were first described around 1900.

Small angle X-ray scattering from multilayer strucures:

q: Scattering vector



Layered structure:
Bragg-peaks appear

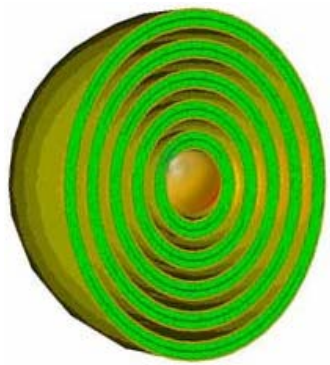
Their positions are related to periodic distance.

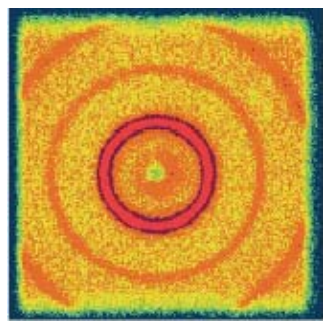
Bragg's law: $n\lambda = 2d\sin\theta$

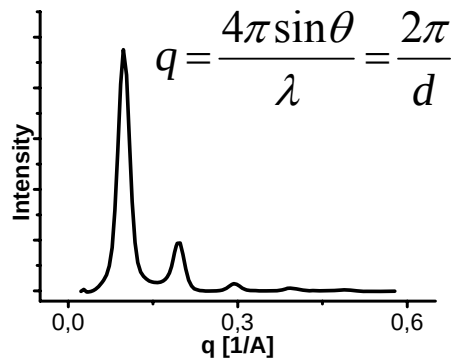
Oriented sample:
Supported lipid multilayer

In the case of an unoriented sample, the intensity depends on the magnitude of the scatterirng vector.

Unoriented sample:
Liposome (or vesicle)

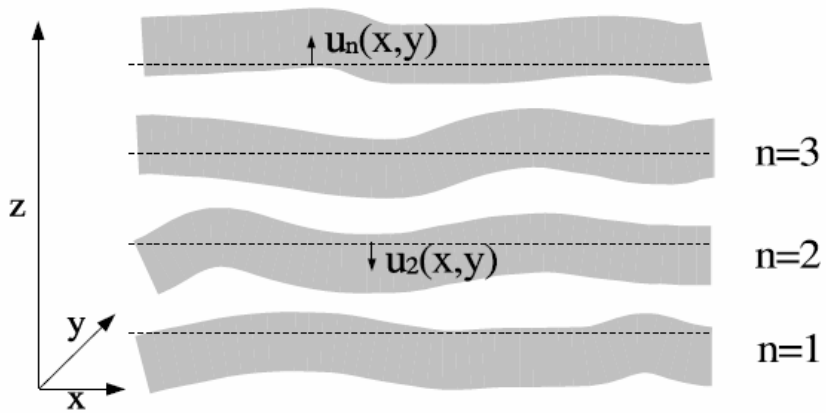






Interpretation of scattering curves:

Periodic electron density along the layer normal:



$$\rho(\mathbf{r}) = \sum_n \rho_n(x,y,z)$$

$$\rho_n(x,y,z) = \rho_n(z - nd - u_n(x,y))$$

The scattered intensity:

$$I(\mathbf{q}) = \left\langle \left| A(\mathbf{q}) \right|^2 \right\rangle = \left\langle \left| \int_V \rho(\mathbf{r}) \exp(-i\mathbf{q}\mathbf{r}) d\mathbf{r} \right|^2 \right\rangle$$

$$I(\mathbf{q}) = \left\langle \left| \sum_n \int_V \rho_n(z - nd - u_n(x,y)) e^{-iq_z z - iq(-nd - u_n(x,y))} dxdydz \right|^2 \right\rangle =$$

$$= \left| \int \rho_n(z) e^{-iq_z z} dz \right|^2 \left\langle \left| \sum_n \int e^{-indq_z - iq_z u_n(x,y) - i(q_x x + q_y y) u_n(x,y)} dxdy \right|^2 \right\rangle =$$

$$= \left| F(q_z) \right|^2 S(\mathbf{q})$$

Models for the **F**orm and **S**tructure factors:

$$S_{PT}(q) = N + 2\sum_{n=1}^{N-1}(N-n)\cos(nqd)e^{-n^2q^2\Delta^2/2}$$

Paracrystalline theory (unoriented sample)

$$\rho_{bilayer} = \sum_i \rho_i e^{-(z-z_i)^2/2\sigma_i^2}$$

$$F(q) = \sqrt{2\pi}\sum_i \rho_i \sigma_i e^{\sigma_i^2 q^2/2}\cos(qz_i)$$

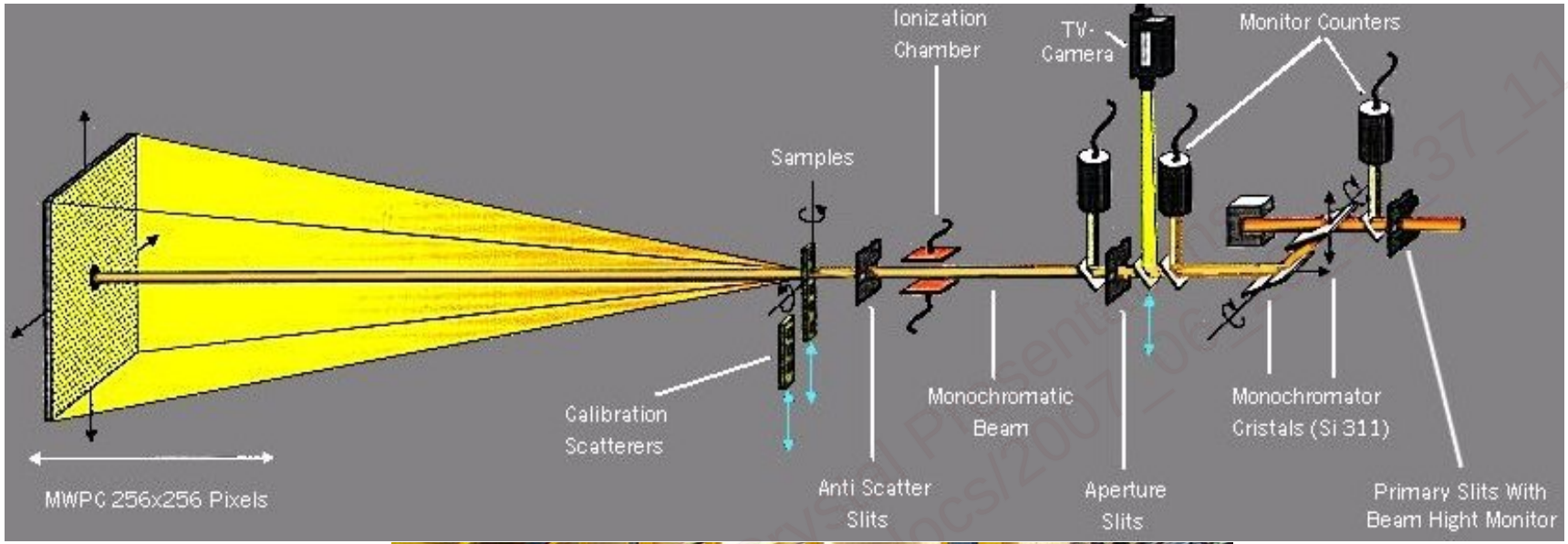
Gaussian model:
the electron density is described by the linear combinations of Gaussians

<u>Special case:</u>

Fourier reconstruction (needs 4-5 Bragg-peaks)

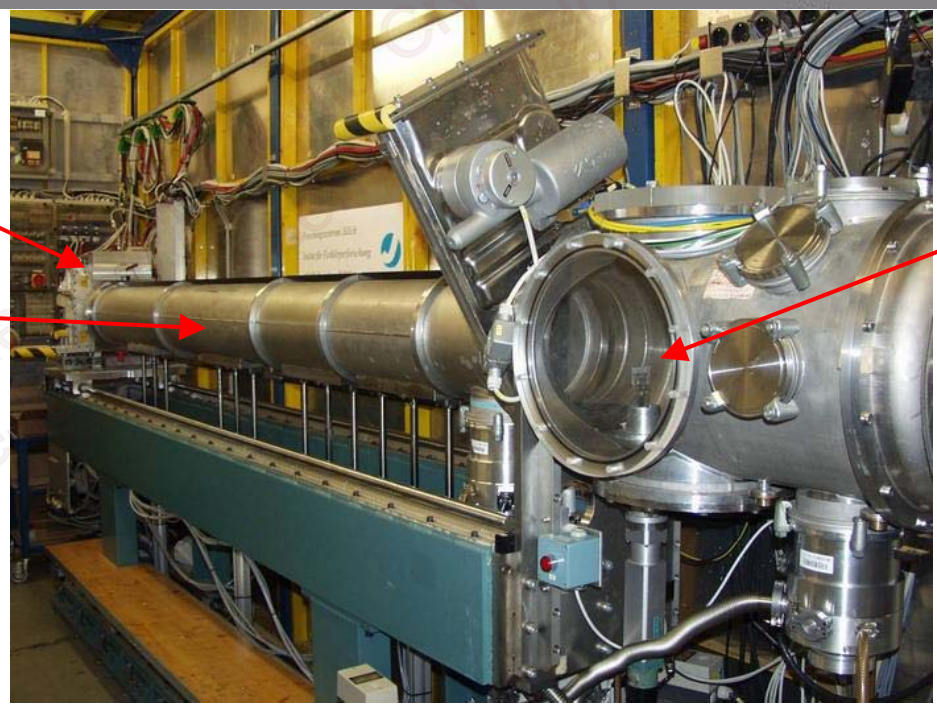
$$\rho(z) = \frac{const}{d\sum_k k^2 I_k}\sum_{k=1}^{k_{max}} sig[I_k]\sqrt{k^2 I_k}\cos\left(\frac{2\pi kz}{d}\right)$$

ASAXS beamline (JUSIFA) at DESY/HASYLAB (Hamburg, Germany)



2D detector

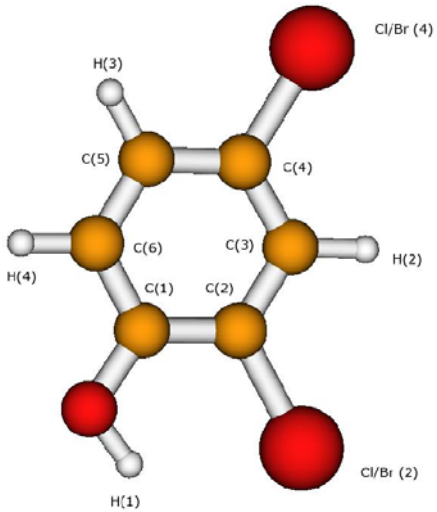
vacuum tube



sample chamber

Localization of guest molecules in vesicle systems

Halogenated phenols:



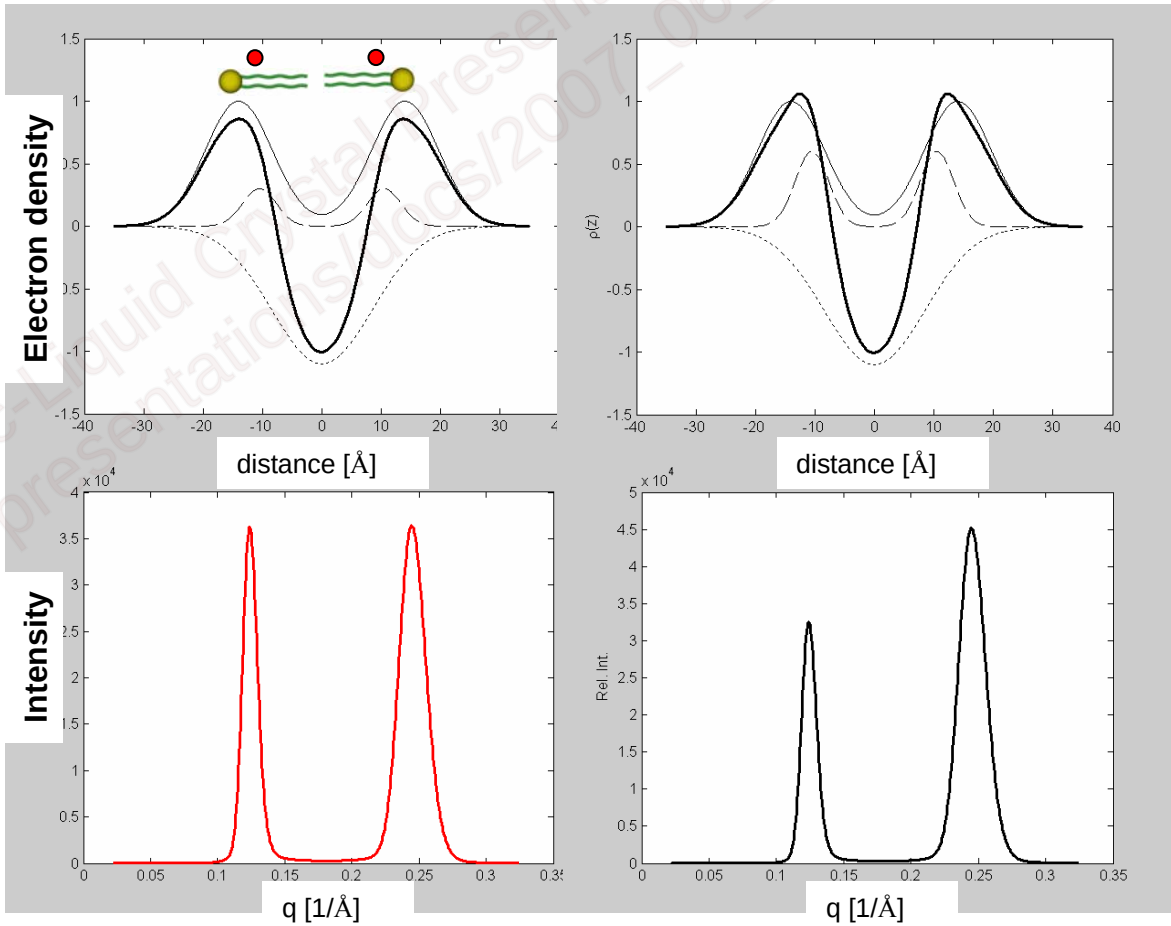
2,4-dichloro(dibromo)-phenol

- Used as flame retardants and biocides
- Toxic and carcinogenic

Used lipid: DPPC

1.) Contrast variation by isomorphous replacement:

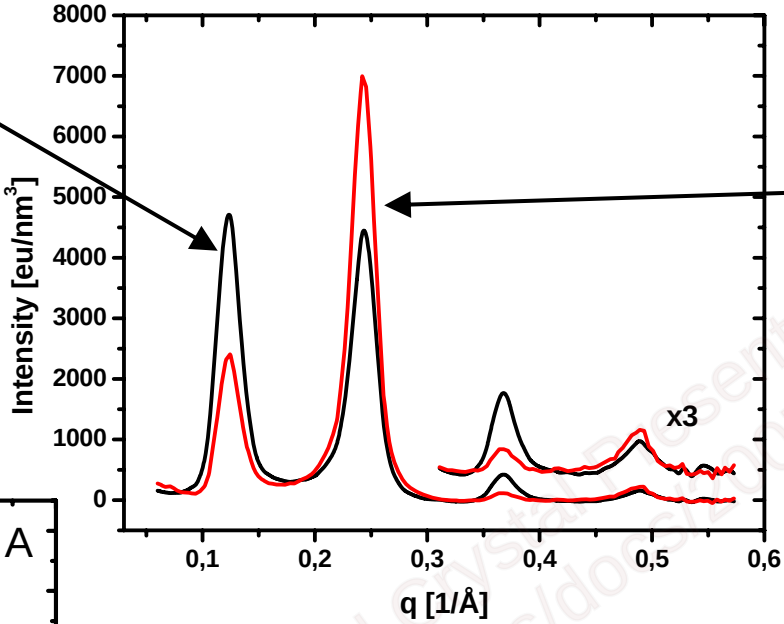
- assumption: same localization of the guest molecules
- changes in the electron density causes changes in the scattered intensity

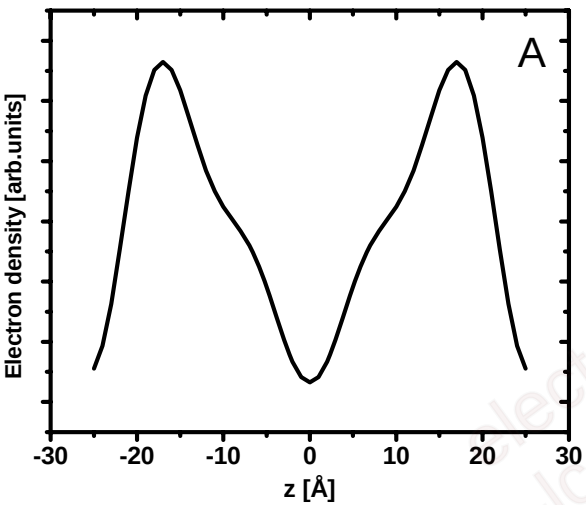


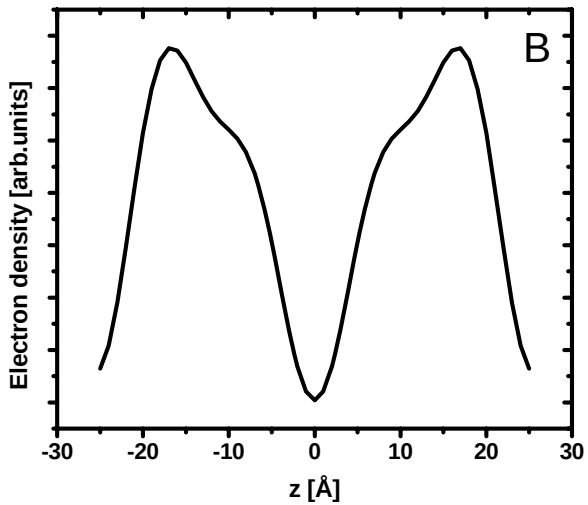
Results, Isomorphous replacement:

dichlorophenol

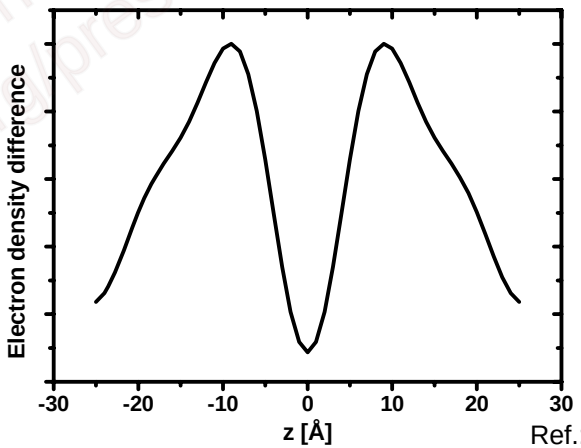
dibromophenol







Four Bragg-peaks:
Fourier reconstruction
can be used.

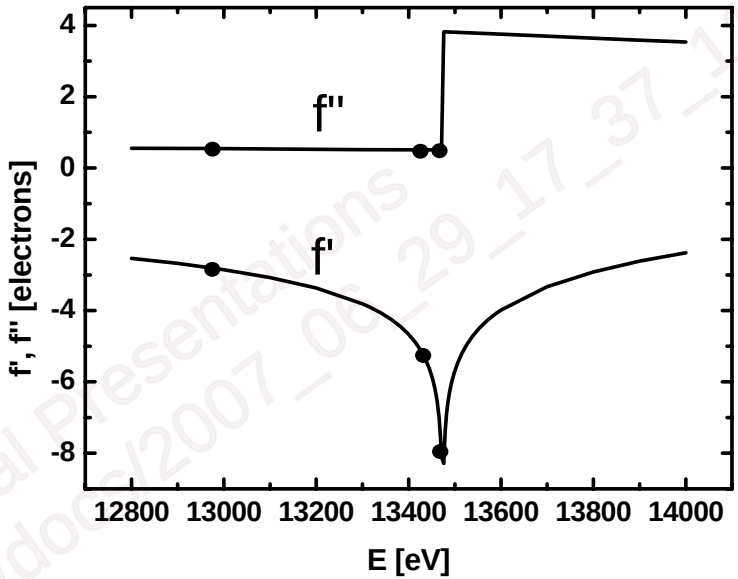


The difference describes the position of halogen atoms along the bilayer normal.

Ref.: Z. Varga, A. Bóta and G. Goerigk, J. Appl. Cryst., 2007

2.) Contrast variation by means of anomalous (or resonant) scattering:

At certain X-ray energy, absorption occures.



The contrast of an atom can be changed by changing the energy of the used X-ray near the absorption edge of that atom.

The scattering length density:

$$\rho(z) = \rho_0(z) + n(z)(f_0 + f'(E) + if''(E))$$

(in classical case this is the electron density)

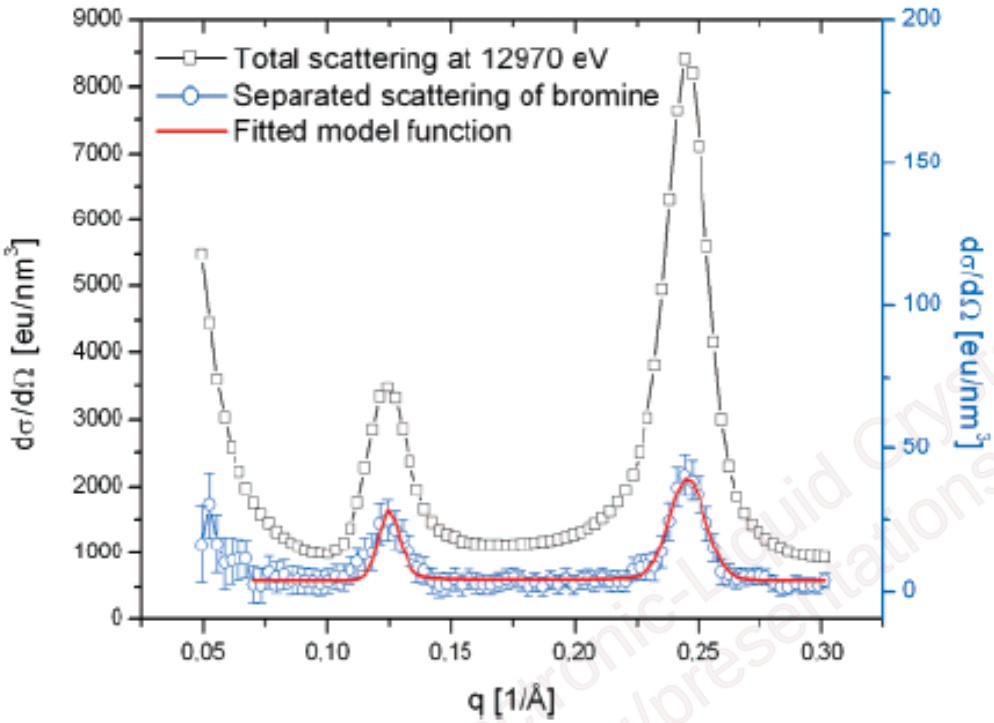
$$I(q,E_1) \rightarrow \Delta I(q,E_1,E_2)$$
$$I(q,E_2)$$
$$I(q,E_3) \rightarrow \Delta I(q,E_1,E_3)$$

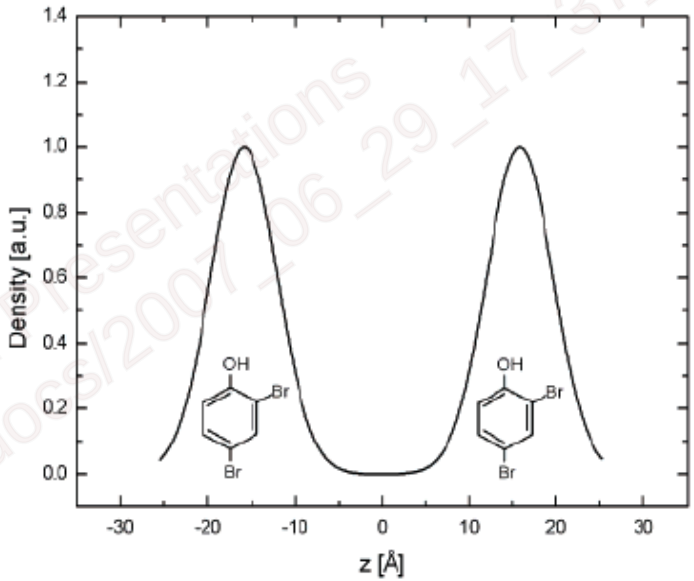
The scattering from the resonant atom can be separated from that of the whole system:

$$I_{\text{bromine}}(q) = \frac{1}{C(E_1,E_2,E_3)}\left[\frac{\Delta I(q,E_1,E_2)}{f'(E_1)-f'(E_2)} - \frac{\Delta I(q,E_1,E_3)}{f'(E_3)-f'(E_3)}\right]$$

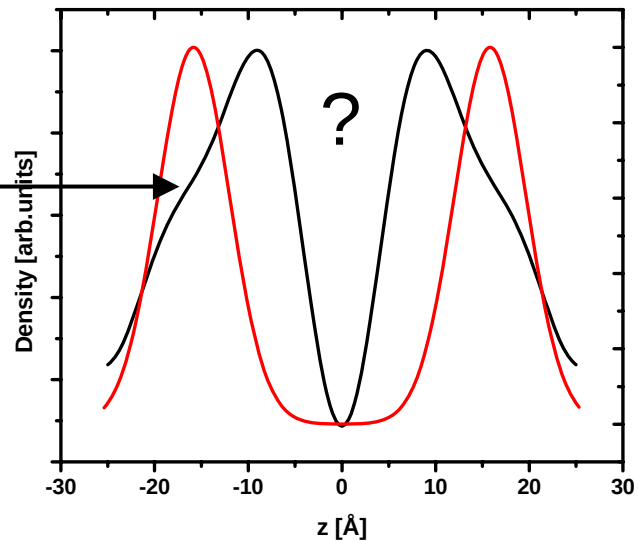
Results, ASAXS:

There are only 2 Bragg-peaks ⇨ model fitting is required





Results from the isomorphous replacement



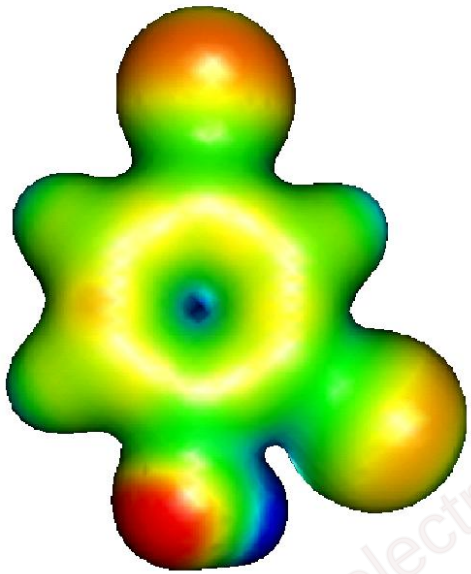
The periodical, inhomogenious localisation is confirmed, but…

Ref.: Z. Varga, A. Bóta, G. Goerigk. J. Phys. Chem. B., 2006, 110(23), 11029-11032

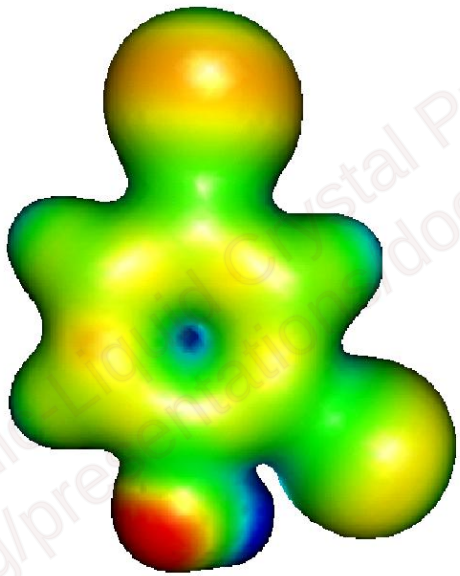
Checking the assumption:

First principles calculations on 2,4-dichloro- and dibromophenol:

DFT(B3LYP), 6-31+G*, Gaussian03



dichlorophenol



dibromophenol

$$V_{MEP} = \sum_A \frac{Z_A}{|R_A - r|} - \int \frac{\rho(r')dr'}{|r - r'|}$$

Next step: constructing the force field for molecular dynamics.

Thank you for your attention!