Surface Sensitive X-ray Scattering

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Introduction
- Concepts of surfaces
- Scattering (Born approximation)

Crystal Truncation Rods
- The basic idea
- How to calculate
- Examples

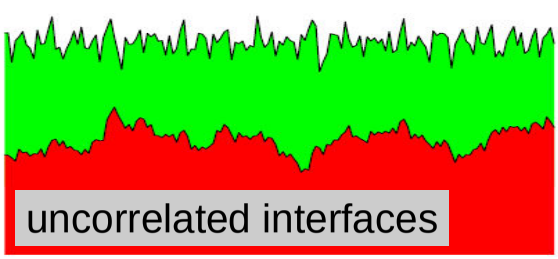
Reflectivity
- In Born approximation
- Exact formalism (Fresnel)
- Examples

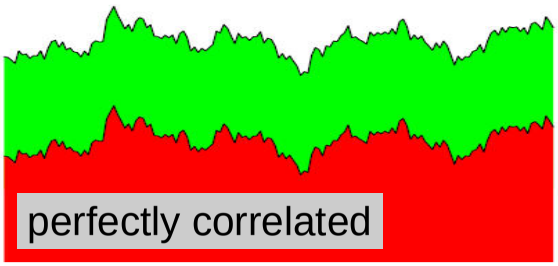
Grazing Incidence Diffraction
- The basic idea
- Penetration depth
- Example

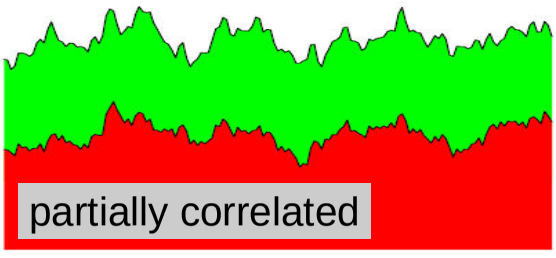
Diffuse Scattering
- Concepts of rough surfaces
- Correlation functions
- Scattering Born-approximation
- DWBA
- Examples

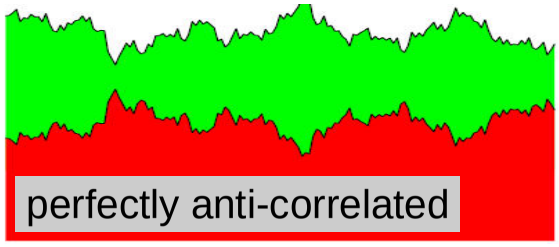
X-ray Diffuse Scattering from Surfaces

- Interfaces and surfaces are usually NEVER perfectly smooth
- Rough interfaces can be described in terms of different models (fractal roughness, capillary waves ...)
- The different models are described by different parameters
- How is the roughness developing from interface to interface in a multilayer system



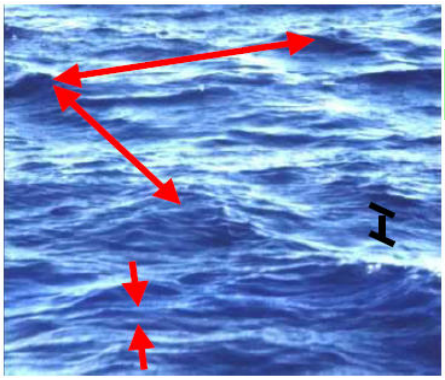






Description of a Single Surface

e.g. macroscopically rough surface (water)

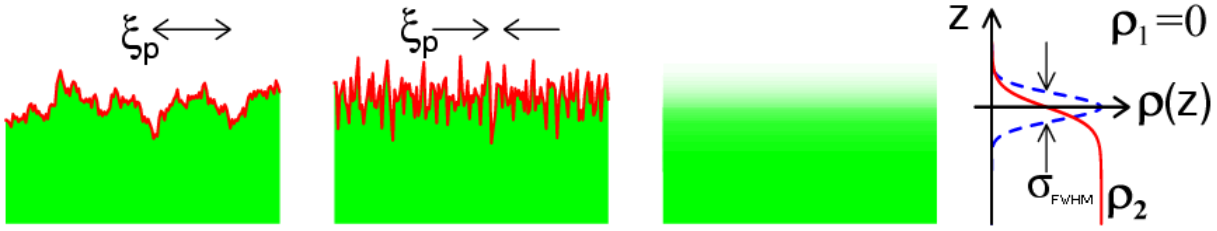


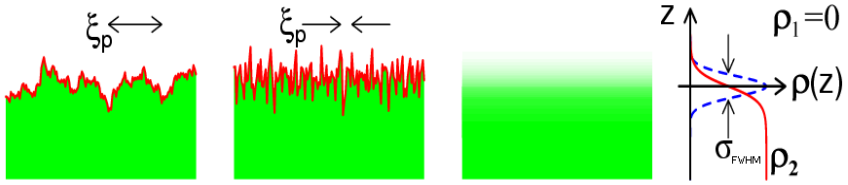
typical in-plane distance (long)

typical amplitude

typical in-plane distance (short)

1-dim cut





How to describe the interface?

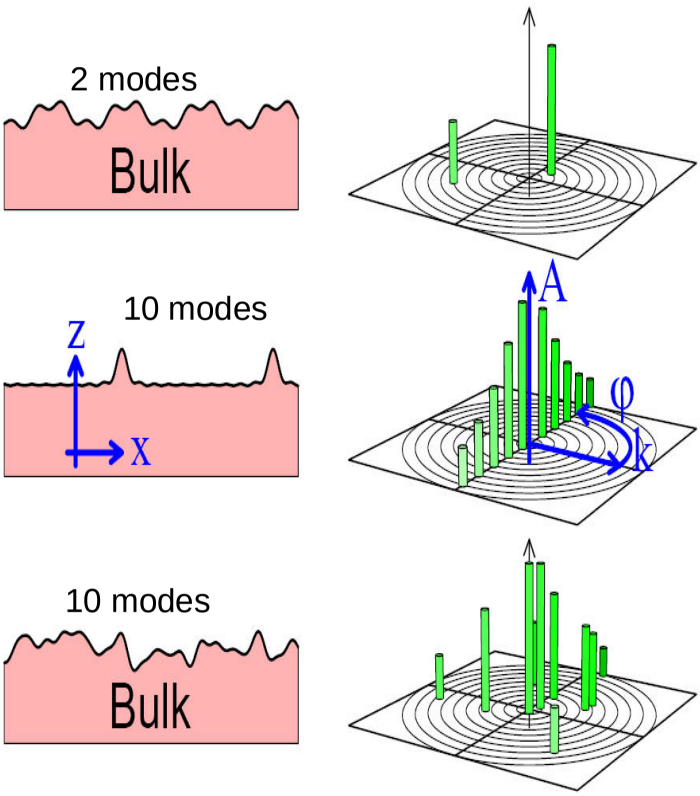
1) Description via a real-space surface function $z(x,y)$
   - is only useful for well-defined structures
   - is useless for statistical surface

2) Description via a surface function in Fourier space

$$\tilde{z}(q_x,q_y)=\int z(x,y)\exp(i[q_x x+q_y y])\,dydx=\mathcal{F}\{z(x,y)\}$$

   - the description in Fourier space is equivalent to real-space
   - what is the advantage ????

Real-space **Fourier-space**



Each oscillation (**so-called modes**) in real-space makes a peak in Fourier-space

Separation of amplitude & phase

$$\tilde{z}(q_x,q_y)=|\tilde{z}(q_x,q_y)|\exp[i\varphi(q_x,q_y)]$$

amplitude phase

Characteristics of the surface are determined by the amplitude

Special realization of the surface is determined by the phase (usually not of interest)

If the phase is not of interest, take absolute square:

$$\tilde{z}(q_x,q_y)\,\tilde{z}(q_x,q_y)^*=|\tilde{z}(q_x,q_y)|^2=\tilde{C}(q_x,q_y)$$

$\tilde{C}(q_x,q_y)$ is the so-called Power Spectral Density (PSD)
The PSD is a measure of the number of waves of a particular wavelength

Good points for the PSD :

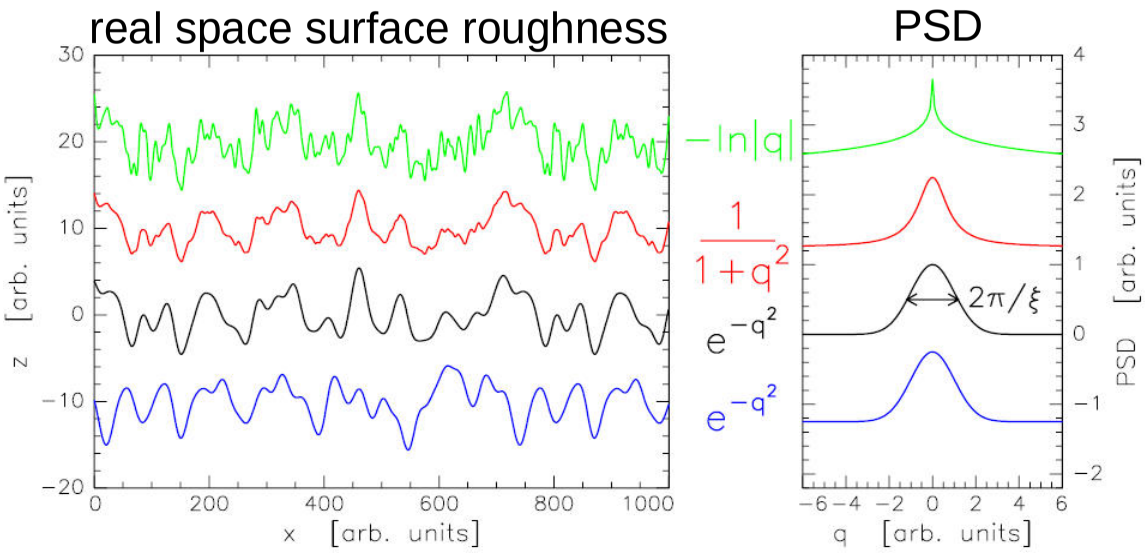
1) is independent from the special realization of the surface
2) is connected with physical properties e.g.
dynamical susceptibility of liquid surfaces

$$\tilde{C}(\boldsymbol{q},\omega)=2k_BT\,\frac{\Im\{\chi_{zz}(\boldsymbol{q},\omega)\}}{\omega}$$

3) Fourierbacktransformation yields the so-called auto-correlation function $C(x,y)$

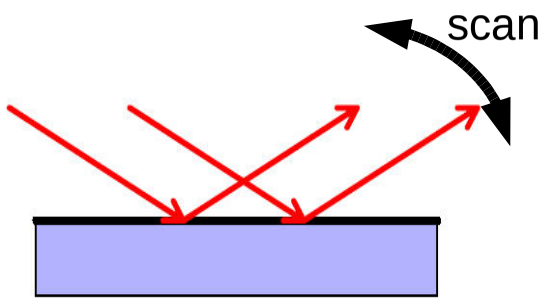
$$C(x,y)=\int z(X,Y)z(X+x,Y+y)\,dX\,dY=\int \tilde{C}(q_x,q_y)\exp(-i[q_x x+q_y y])\,dq_y\,dq_x$$

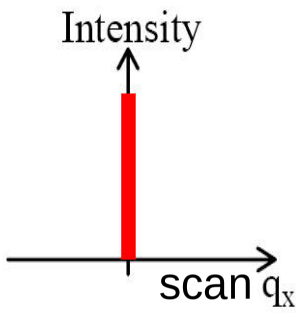
Examples of statistical interfaces



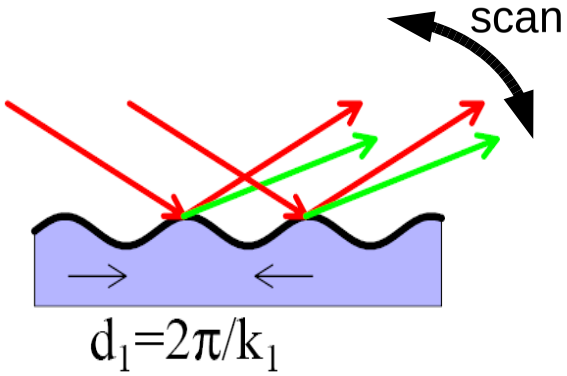
- Same rms-roughness σ used for all surfaces
- Same in-plane correlation length ξ used
- The top three surface are created with the same phase $\varphi(x)$

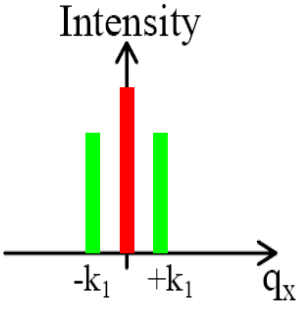
Diffuse X-ray Scattering (Principle)



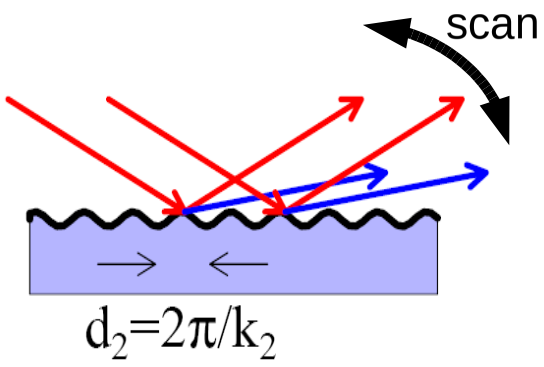


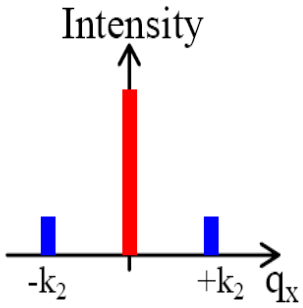
perfectly smooth: only intensity in specular direction (qx = 0)



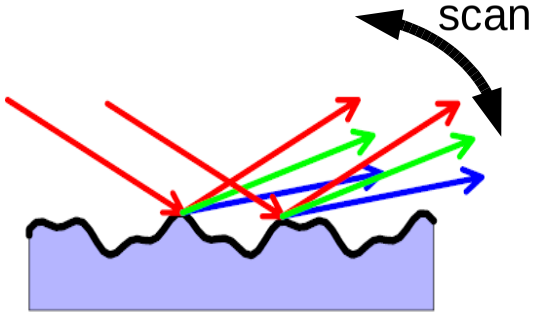


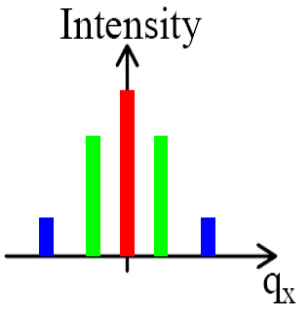
one mode: side peaks at (qx ≠ 0)





different wave vector of the mode shifts also qx

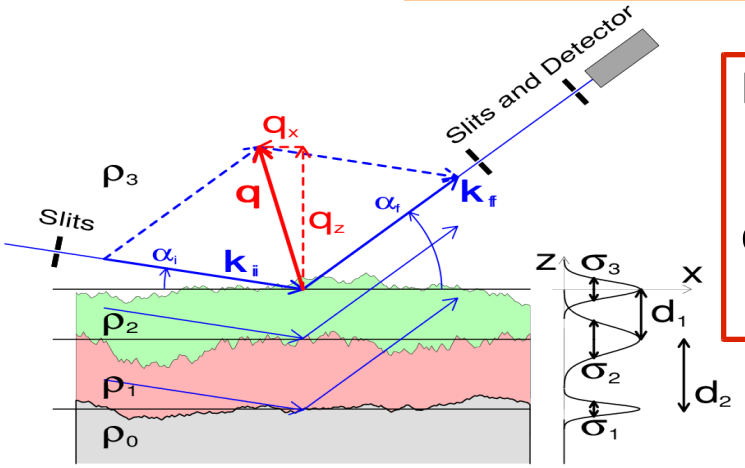




two modes: respective side peaks at (qx ≠ 0)

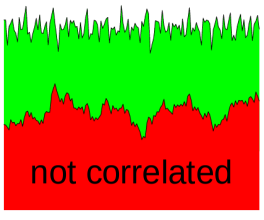
1) Rough surfaces are a collection of modes with different amplitudes, phases and wave vectors.
2) The modes create the respective scattering
   => diffuse scattering

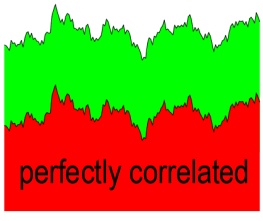
Diffuse X-ray Scattering

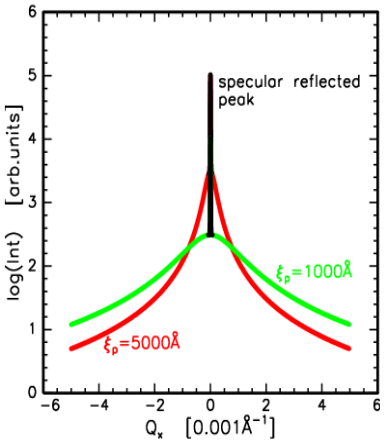


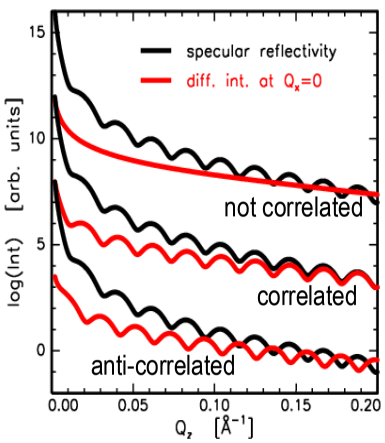
Experiment : incident angle θ ≠ exit angle θ'

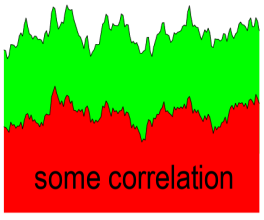
often resolution in q_y bad => Integrated Intensity in q_y

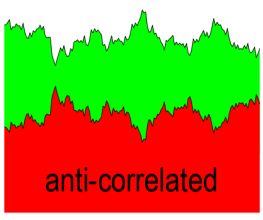












Diffuse Scattering of one Rough Interface in Born Approximation

- multiple scattering effects are neglected
- refraction index is 1 (only the electron density is considered)
- wrong for small incident or exit angles (compared to critical angle)

$$I_{diff}^{BA}(\boldsymbol{q}) = \frac{4\pi}{q_z^2}\Delta\rho\exp(-q_z^2\sigma^2)\int\left(\exp[q_z^2 C(x,y)]-1\right)\cos(q_x x + q_y y)\,dxdy$$

The diffusely scattered intensity depends on:

- the incident and exit angles (via q_x, q_y, q_z)
- the contrast (the density difference at the surface) $\Delta\rho$
- the roughness σ
- the auto-correlation function $C(x,y)$

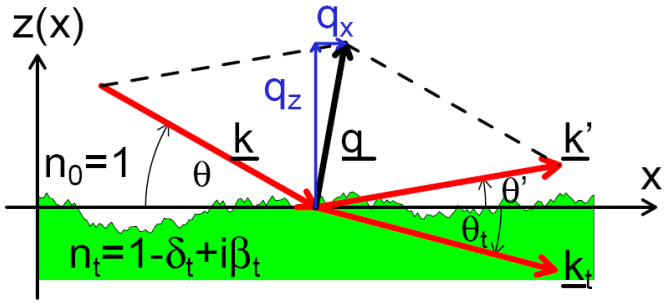
For small q_z :

$$I_{diff}^{BA}(\boldsymbol{q}) \approx 4\pi\Delta\rho\exp(-q_z^2\sigma^2)\tilde{C}(q_x,q_y)$$

In simplest approximation the diffuse scattering proportional to PSD

Diffuse Scattering of one Rough Interface Distorted Wave Born Approximation (DWBA)

- multiple scattering effects are taken into account via transmission functions
- refraction index is considered
- only valid vor small σq_z



For a single surface:

$$I_{diff}^{DWBA}(\boldsymbol{q}) \approx |t_f(\theta)|^2 I_{diff}^{BA}(\boldsymbol{q}) |t_f(\theta')|^2$$

with

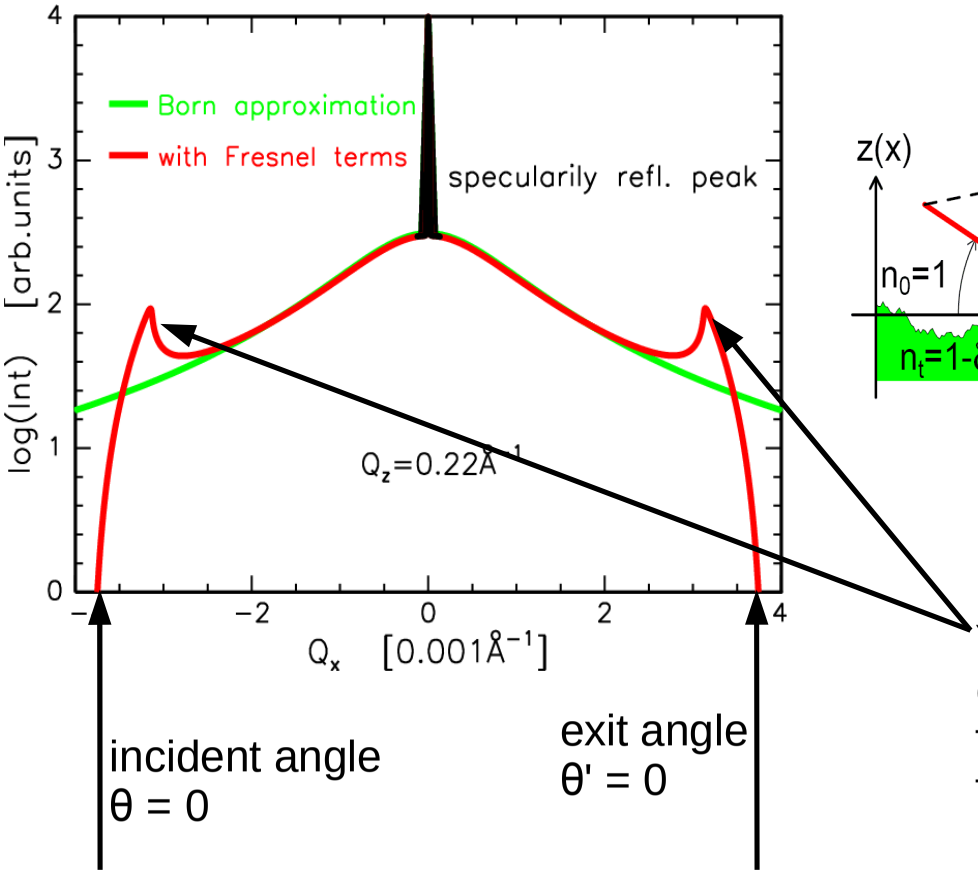
$$t_f = \frac{2k_z}{k_z + k_{t,z}}$$ Fresnel transmission coefficient and

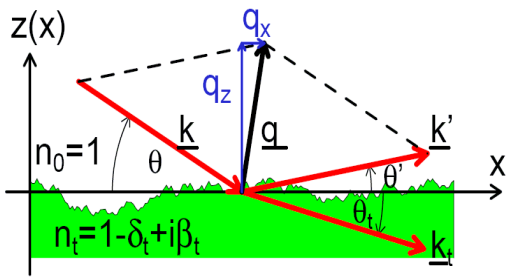
$$k_z = k\sin\theta$$

$$k_{t,z} = k_t\sin(\theta_t) = k\sqrt{n_t^2 - \cos^2\theta}$$

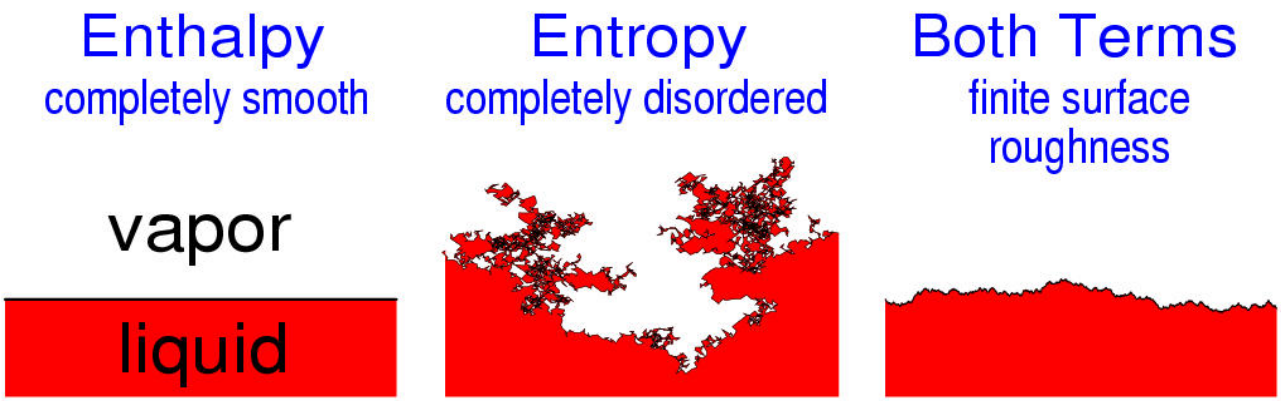
$$k = 2\pi/\lambda$$

Rocking scan (detector angle fixed, rotating sample)



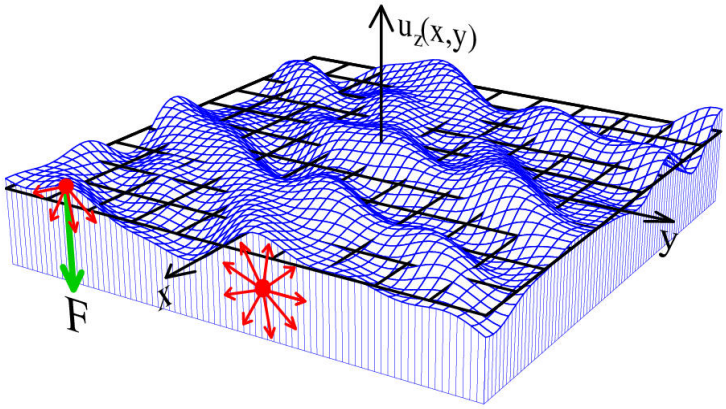


Example : Capillary waves
(thermally induced surface fluctuations of liquid surfaces)



Even liquids do not have a perfectly smooth surface!

Theoretical description by the equilibium of forces at the surface.



Break of symmetry at the surface =>

Resulting force directed to the bulk =>

surface tension

Equilibrium in the liquid: balance of forces => Navier Stokes Eq.

$$\rho \frac{\partial}{\partial t}\boldsymbol{v} = -\nabla p + \eta \, \Delta \, \boldsymbol{v}$$

with boundary conditions:

$$\sigma_{zz} = \gamma \frac{\partial^2}{\partial^2 z} u_z + g \rho u_z$$

ρ : density, v : velocity
p : pressure, η : viscosity
σ_{zz} : from stress tensor
γ : surface tension
g : gravitational constant
u_z : displacement at surface

With this knowledge the **dynamical susceptibility** $\chi_{zz}(q,\omega) = u_z / p_z$ can be calculated.
χ_{zz} describes the response of the surface on extranal forces and depends on the frequency ω and the wave vector q.

The **equipartition theorem** states that each thermally excited surface wave (mode) has in average the energy $k_B T$.
The PSD of the modes can be calculated by:

$$\tilde{C}(\boldsymbol{q},\omega) = 2 k_B T \frac{\Im\{\chi_{zz}(\boldsymbol{q},\omega)\}}{\omega}$$

In the static case for a bulk liquid (average in time)

$$\tilde{C}(\boldsymbol{q}) = \frac{k_B T}{4\pi^2 \gamma}\left[q^2 + \frac{g\rho}{\gamma}\right]^{-1}$$

$$\tilde{C}(\boldsymbol{q}) = \frac{k_B T}{4\pi^2 \gamma}\left[q^2 + \frac{g\rho}{\gamma}\right]^{-1}$$

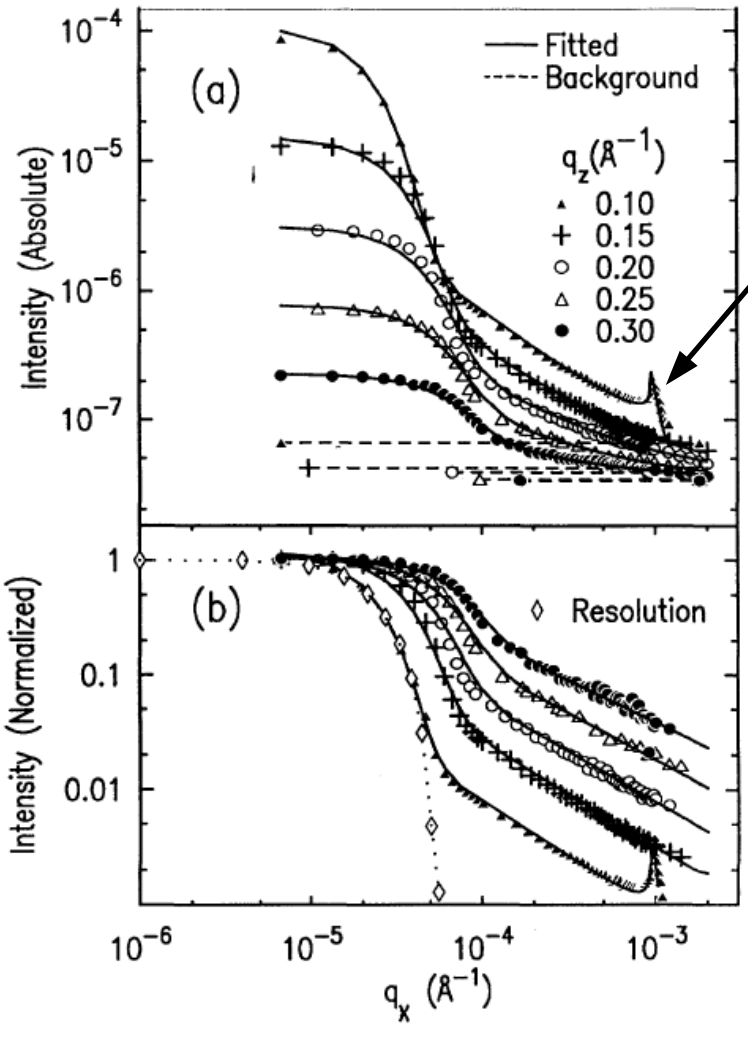
after 2-dim Fourier-backtrans-formation leads to a logarithmic auto-correlation function C(r)

$$C(\boldsymbol{r}) = -\frac{k_B T}{2\pi^2 \gamma}\left[\ln\left(\frac{g\rho}{\gamma} r\right) + 0.5772\right]$$

With logarithmic auto-correlation function C(r) the diffuse scattering in Born approximation is for $q^2 > g\rho/\gamma$ in good approximation given by

$$I^{BA}_{diff,liquid}(\boldsymbol{q}) \sim q_x^{\frac{k_B T}{2\pi\gamma} q_z^2 - 1}$$

q_z -dependent power low: slope contains the surface tension



Yoneda peak

Picture taken from Sanyal et al. Phys.Rev.Lett 66, 628 (1991)

X-ray diffuse scattering at a liquid ethanol surface

From the data extracted parameters:
Roughness = 0.69nm
surface tension = 0.022N/m
(exactly the known value)

Summary

- Rough surfaces and interfaces can be described via their power spectral density (PSD) or their auto-correlation function.
- The PSD is measure of the number of modes in a wave vector interval.
- Rough interfaces will cause diffuse x-ray scattering.
- Diffuse x-ray scattering can be calculated in Born approximation and in DWBA (better). The formular contains the PSD of the interface.
- The PSD of liquids contain macroscopic material parameters such as temperature, surface tension and density.
  These parameters show up in the diffuse scattering.