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
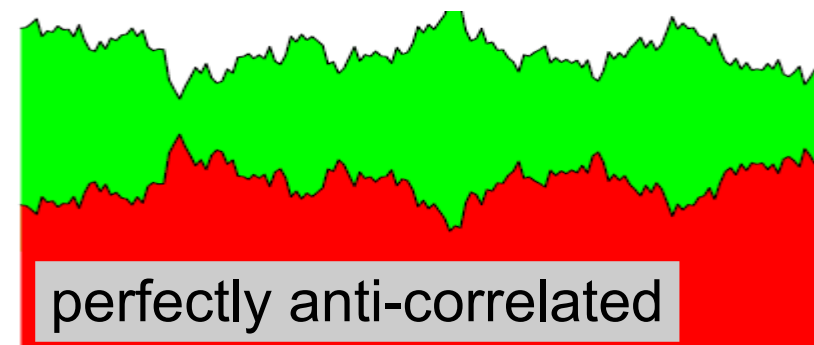- Exact formalism (Fresnel)
- Examples
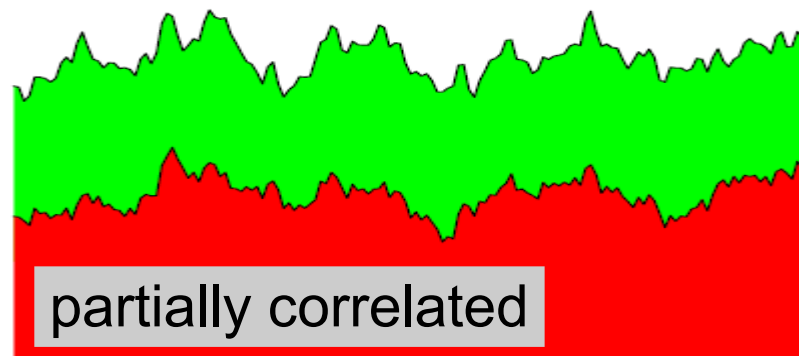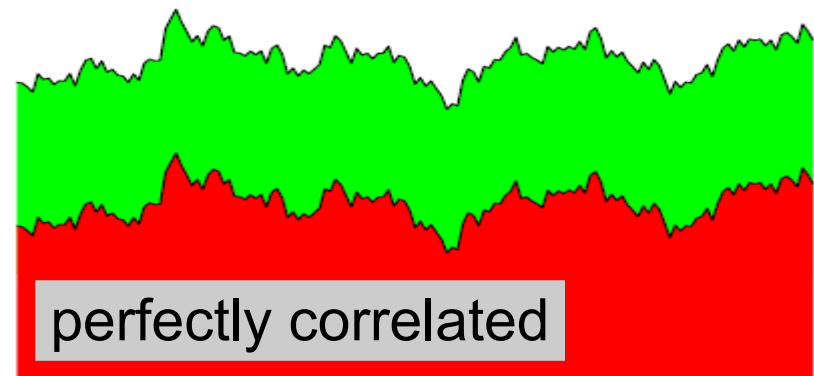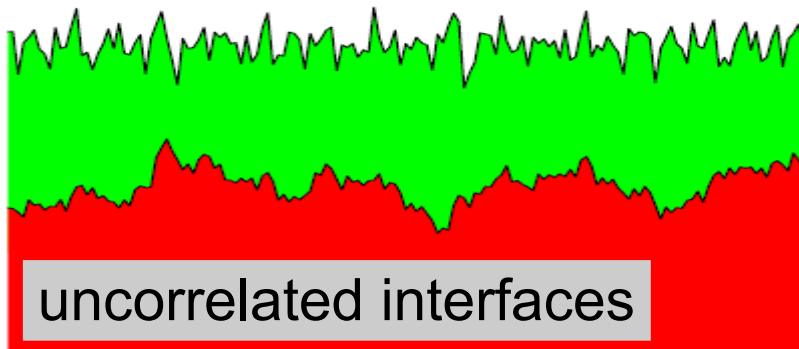
Grazing Incidence Diffraction
- The basic idea
- Penetration depth
- Example

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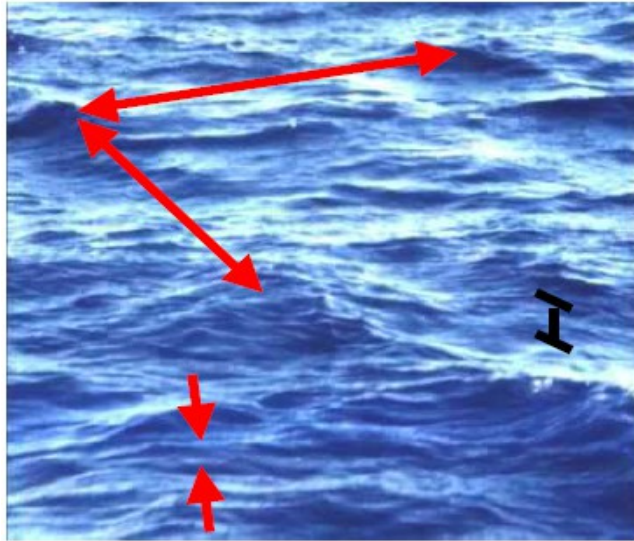- Scattering Born-approximation
- DWBA
- Examples

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

uncorrelated interfaces

perfectly correlated

partially correlated

perfectly anti-correlated

Surface Sensitive X-ray Scattering

Description of a Single Surface
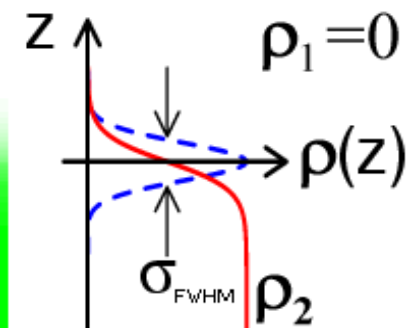
e.g. macroscopically rough surface (water)
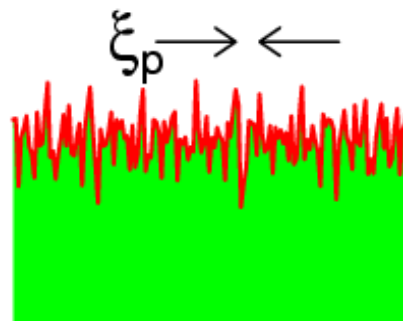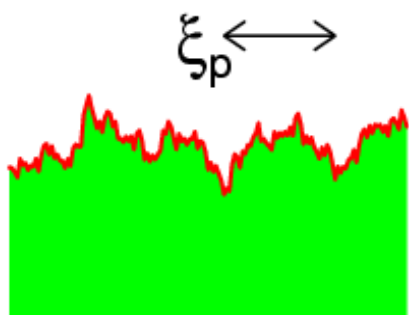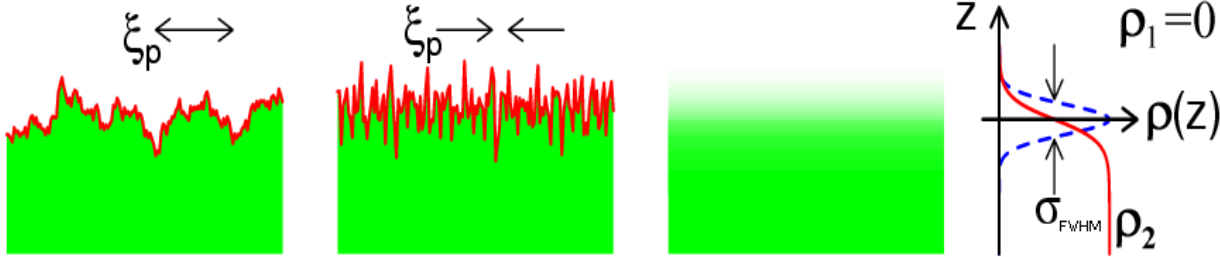
typical in-plane distance (long)

typical amplitude

typical in-plane distance (short)

1-dim cut

$\xi_p \leftrightarrow$ $\xi_p \rightarrow \leftarrow$

Z $\rho_1 = 0$

$\rho(z)$

σ_{FWHM} ρ_2

Surface Sensitive X-ray Scattering

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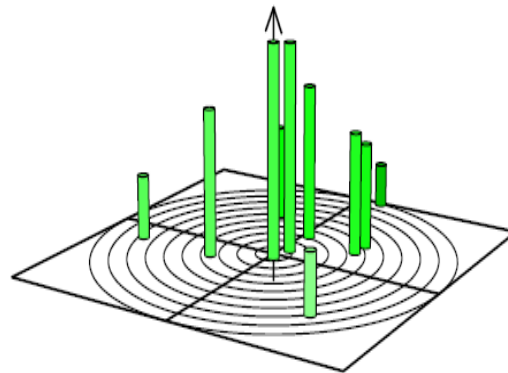
$$\tilde{z}(q_x, q_y) = \int z(x,y) \exp\left(i\left[q_x x + q_y y\right]\right) dydx = \mathscr{F}\{z(x,y)\}$$

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

Surface Sensitive X-ray Scattering

Real-space

Fourier-space

2 modes

Bulk

10 modes

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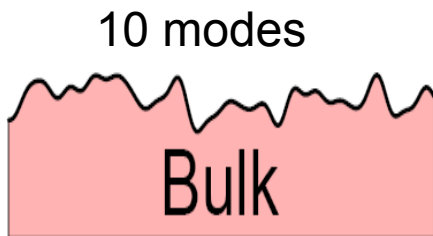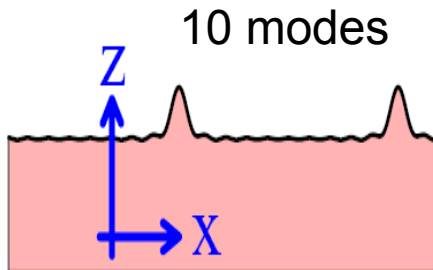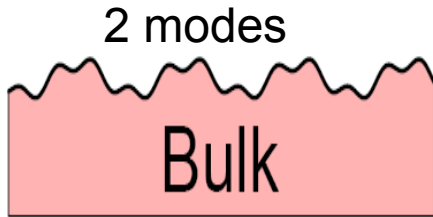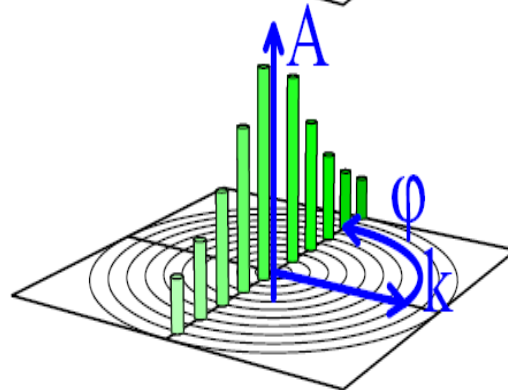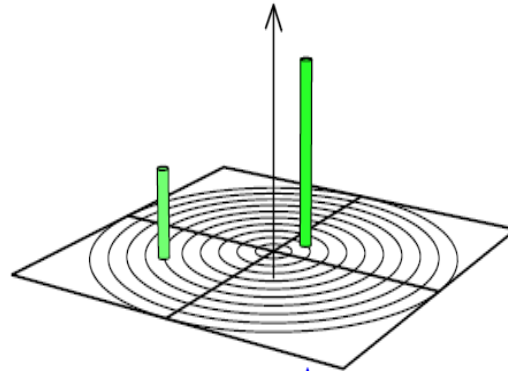
Each oscillation (**so-called modes**) in real-space makes a peak in Fourier-space

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)

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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

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

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

real space surface roughness

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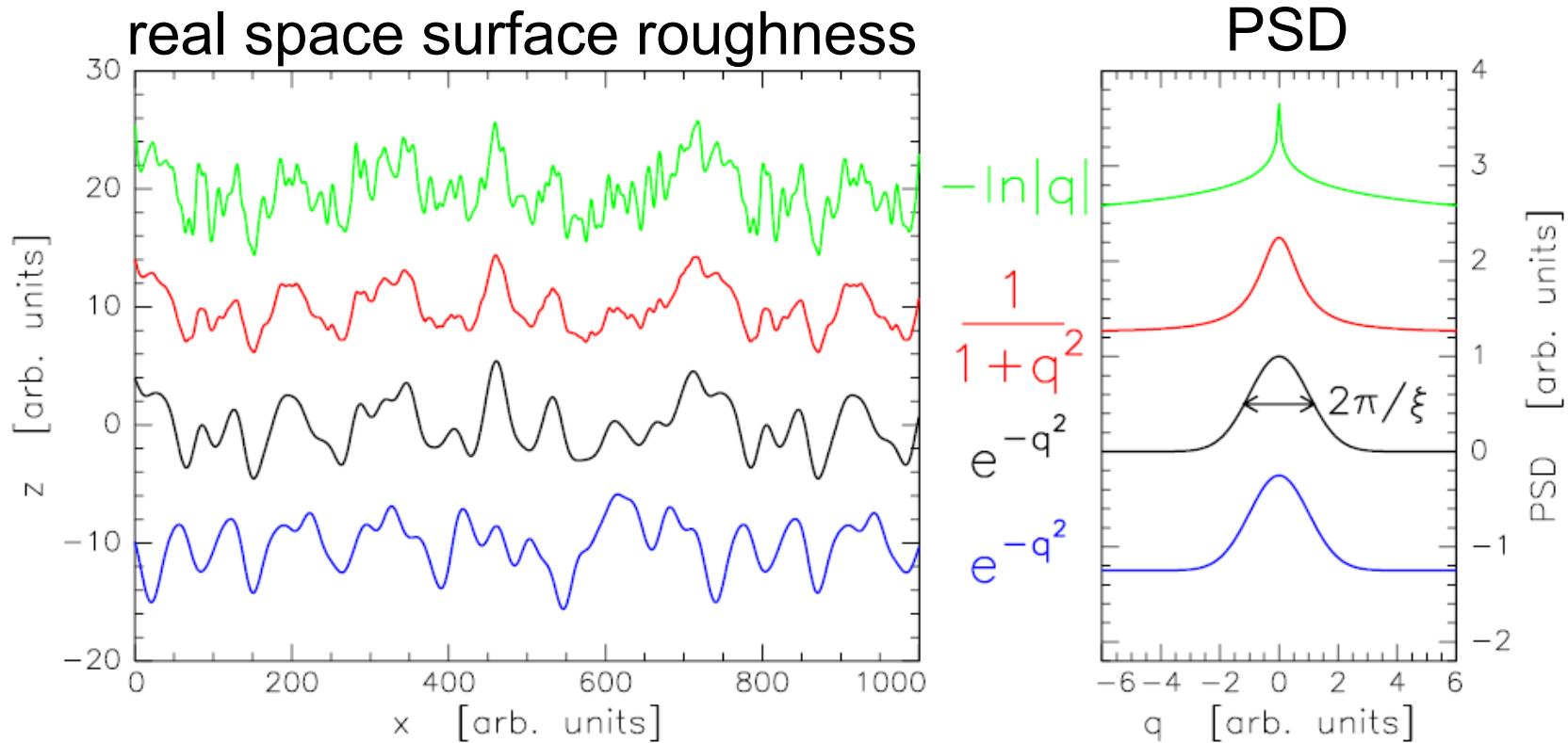
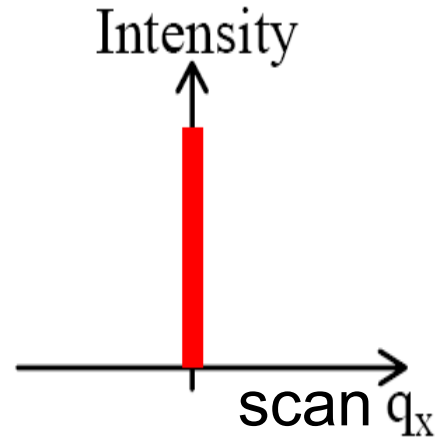- Same rms-roughness σ used for all surfaces
- Same in-plane correlation length ξ used
- The top three surface are created with the same phase $\varphi(x)$

Surface Sensitive X-ray Scattering

Diffuse X-ray Scattering (Principle)

scan

Intensity

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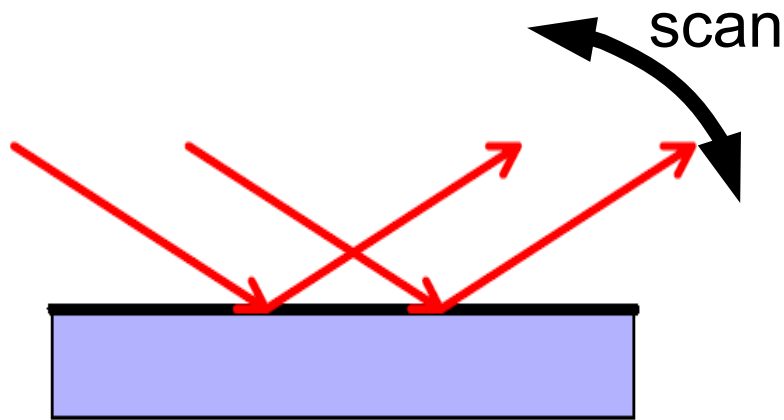
perfectly smooth:
only intensity in
specular direction
($qx = 0$)

scan

Intensity

$d_1 = 2\pi/k_1$

$-k_1$ $+k_1$ q_x
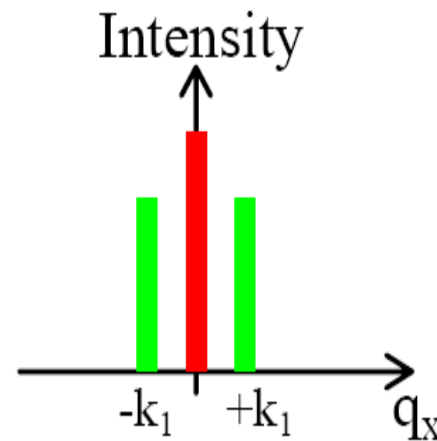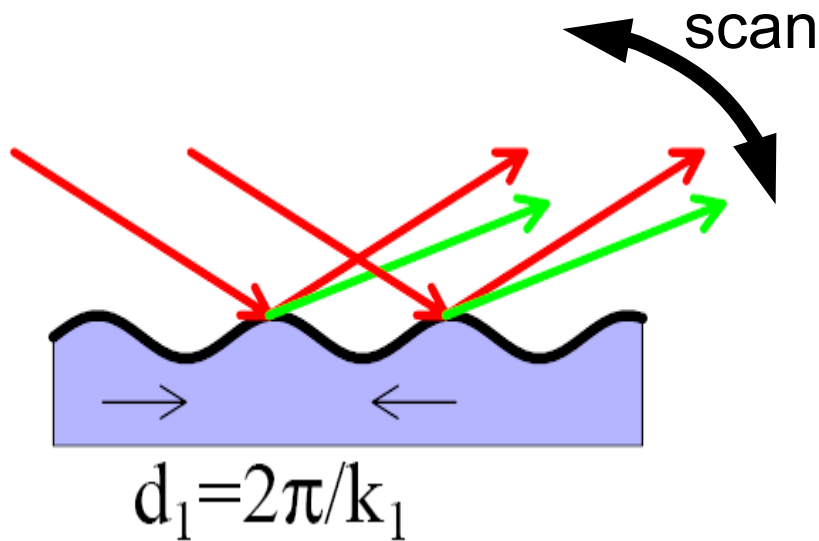
one mode:
side peaks at
($qx \neq 0$)

Surface Sensitive X-ray Scattering

scan

Intensity

$d_2 = 2\pi/k_2$

$-k_2$ $+k_2$ q_x
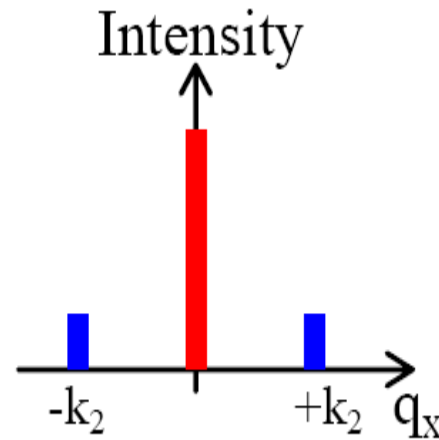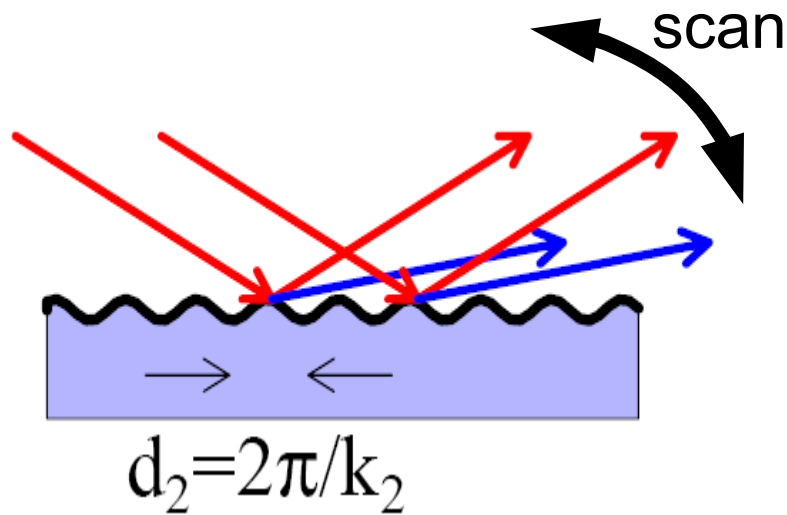
different wave vector of the mode shifts also qx

scan

Intensity

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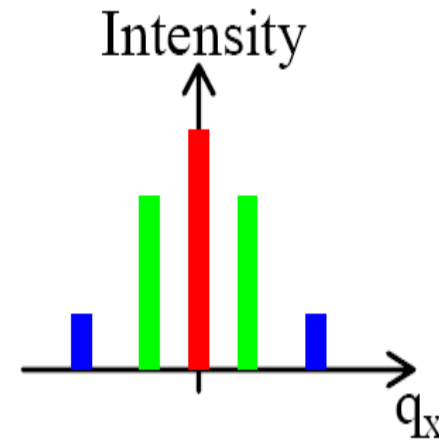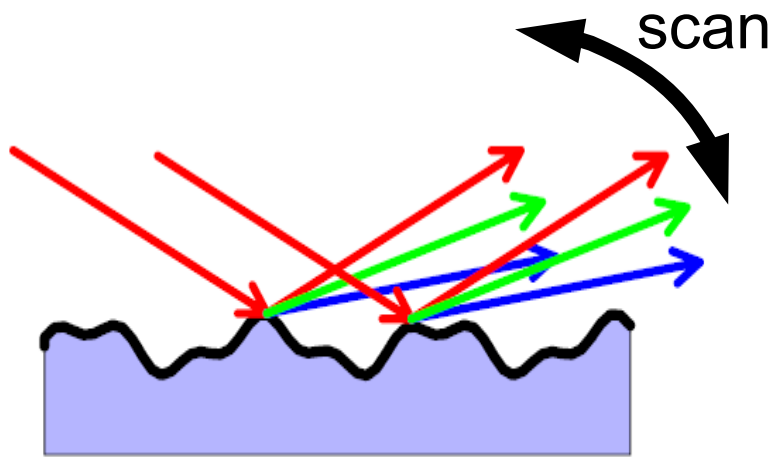
two modes: respective side peaks at (qx ≠ 0)

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

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Diffuse X-ray Scattering
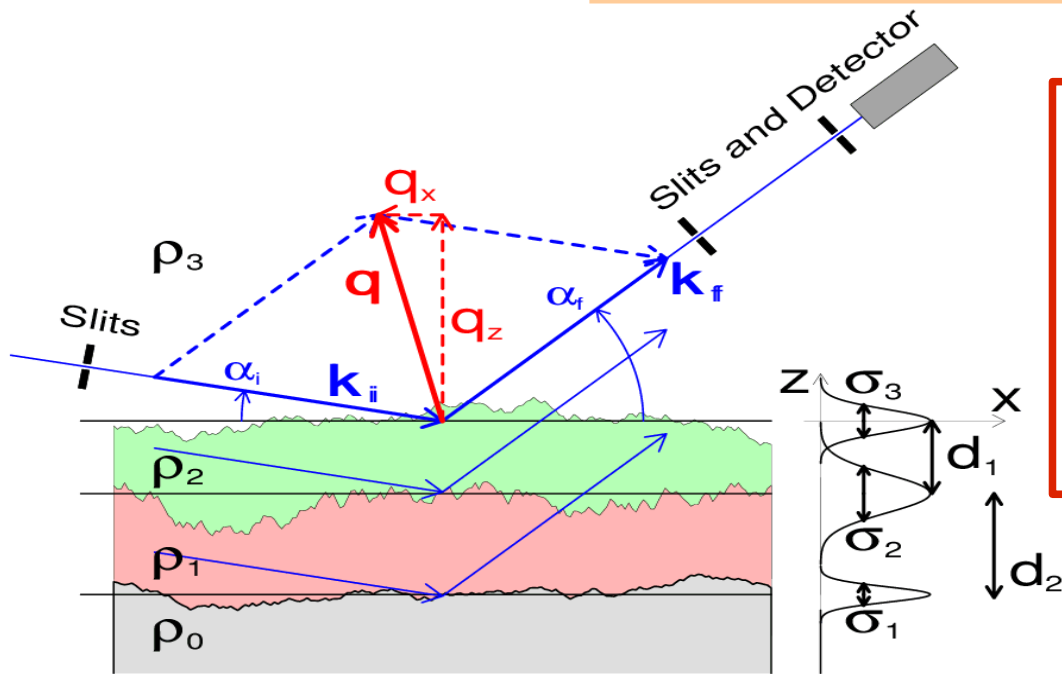
Experiment : incident angle $\theta \neq$ exit angle θ'

often resolution in q_y bad => Integrated Intensity in q_y

not correlated

perfectly correlated

some correlation

anti-correlated

Surface Sensitive X-ray Scattering
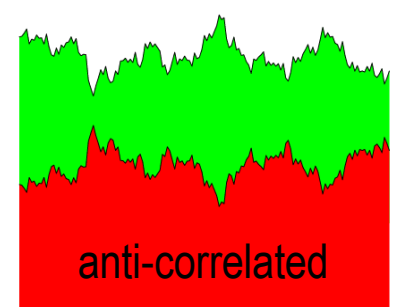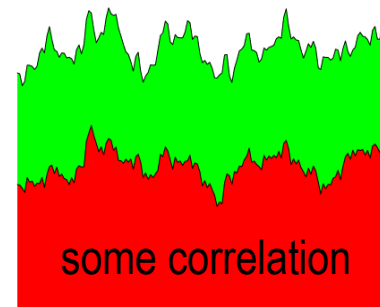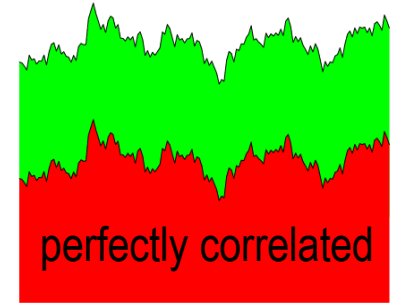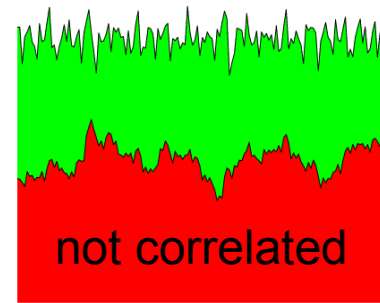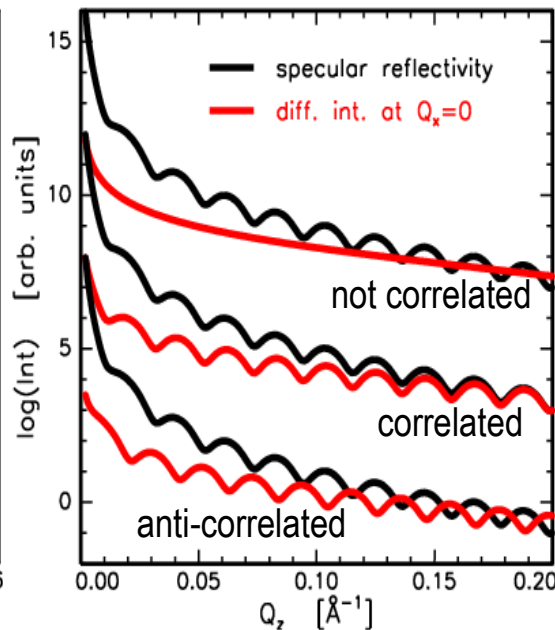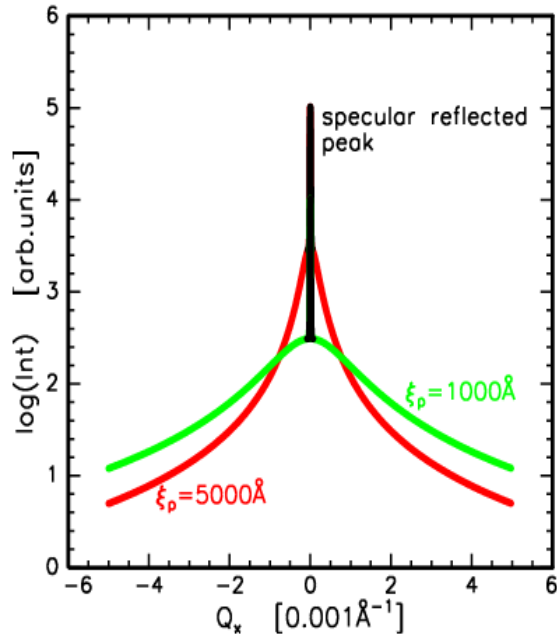
Diffuse Scattering of one Rough Interface in Born Approximation

- 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)

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

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

In simplest approximation the diffuse scattering proportional to PSD

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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
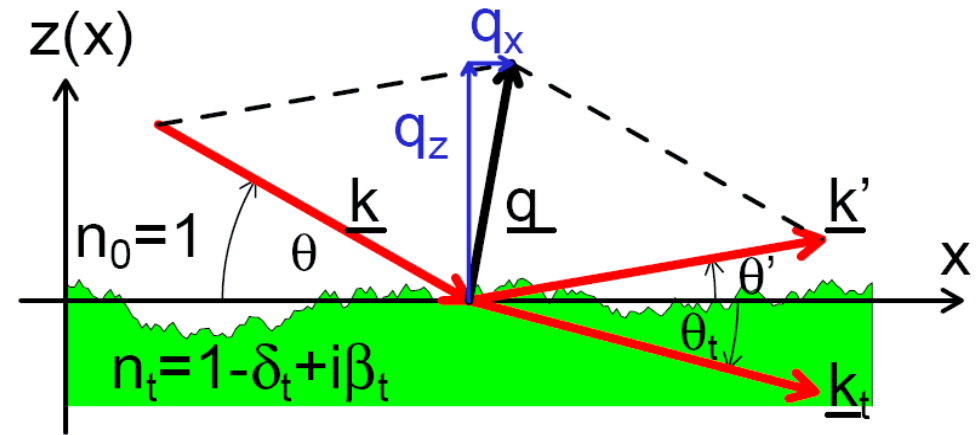
For a single surface:

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

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)

Born approximation
with Fresnel terms

specularily refl. peak

$Q_z = 0.22 Å^{-1}$

log(Int)   [arb.units]

Q_x $[0.001 Å^{-1}]$

incident angle
$\theta = 0$

exit angle
$\theta' = 0$
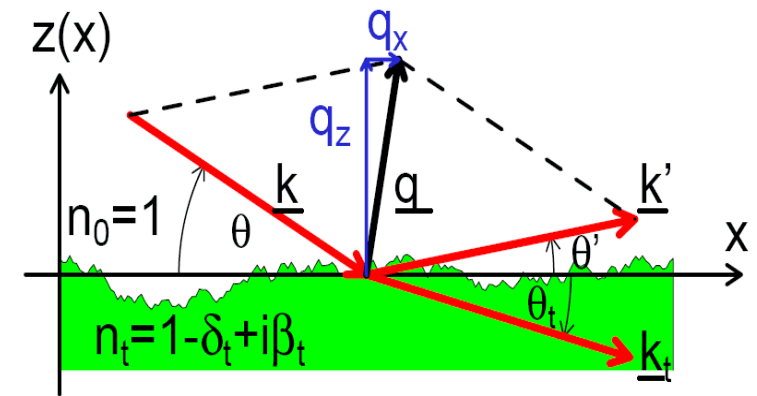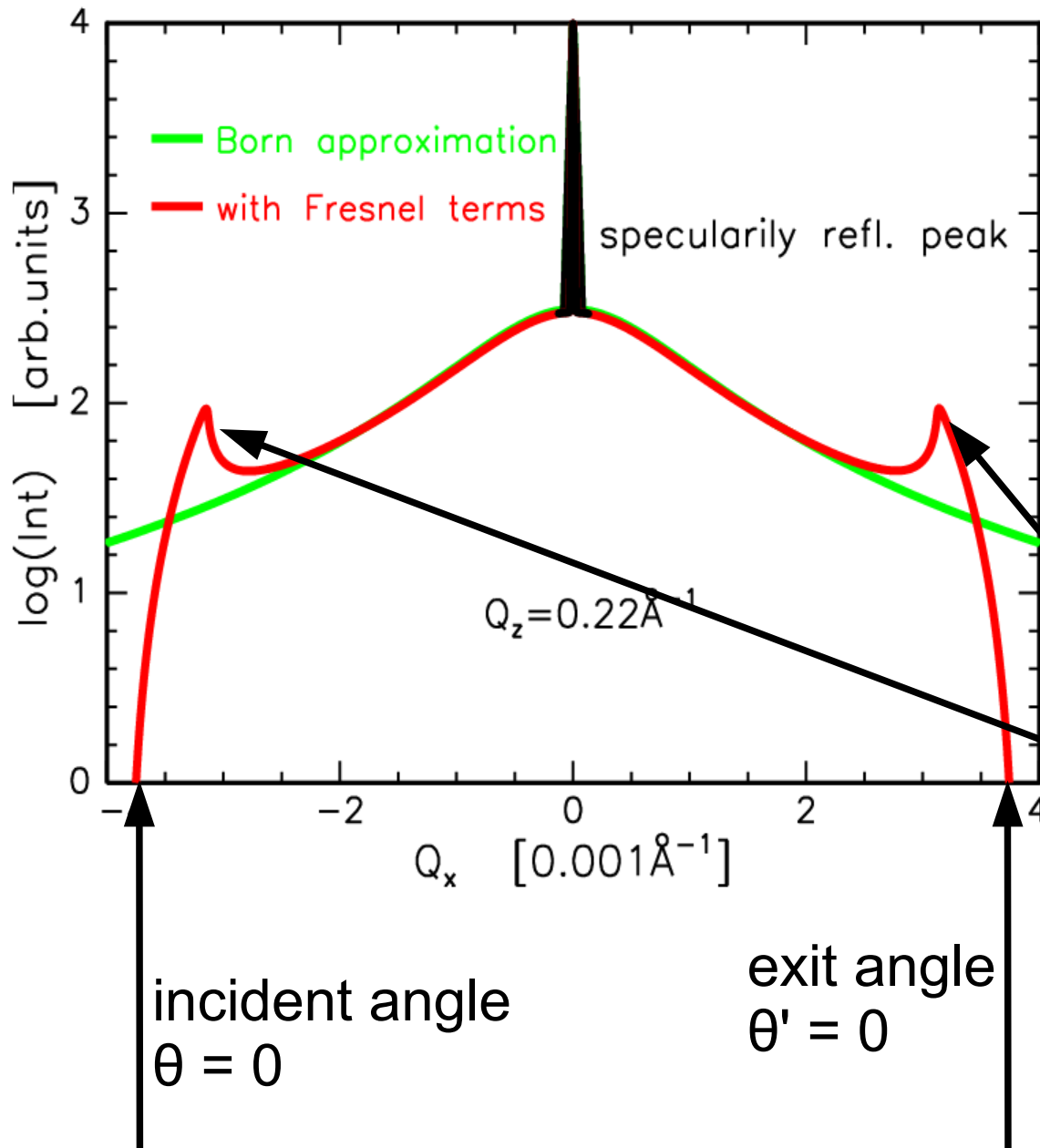
Yoneda-wings
(amplifications of
the scattering at
the critical angle)

$z(x)$

q_x

q_z

$n_0 = 1$

$\underline{k}$

θ

$\underline{q}$

$\underline{k}'$

x

θ'

θ_t

$n_t = 1 - \delta_t + i\beta_t$

$\underline{k}_t$

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Example : Capillary waves
(thermally induced surface fluctuations of liquid surfaces)
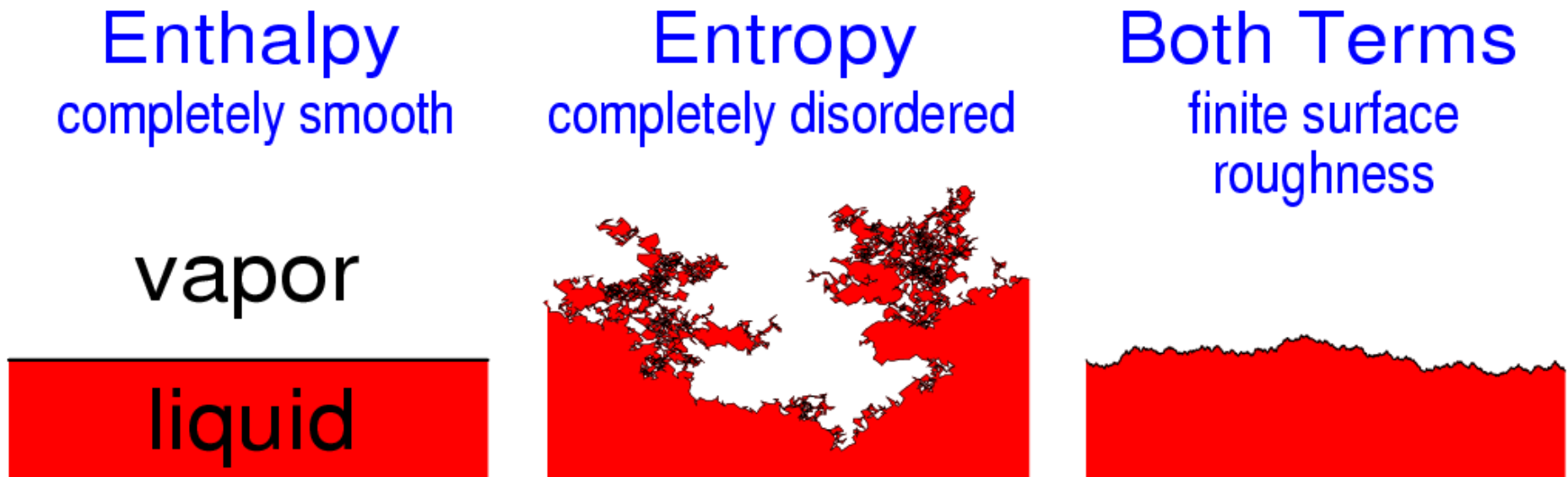
Even liquids do not have a perfectly smooth surface!

Surface Sensitive X-ray Scattering

Theoretical description by the equilibium of forces at the surface.
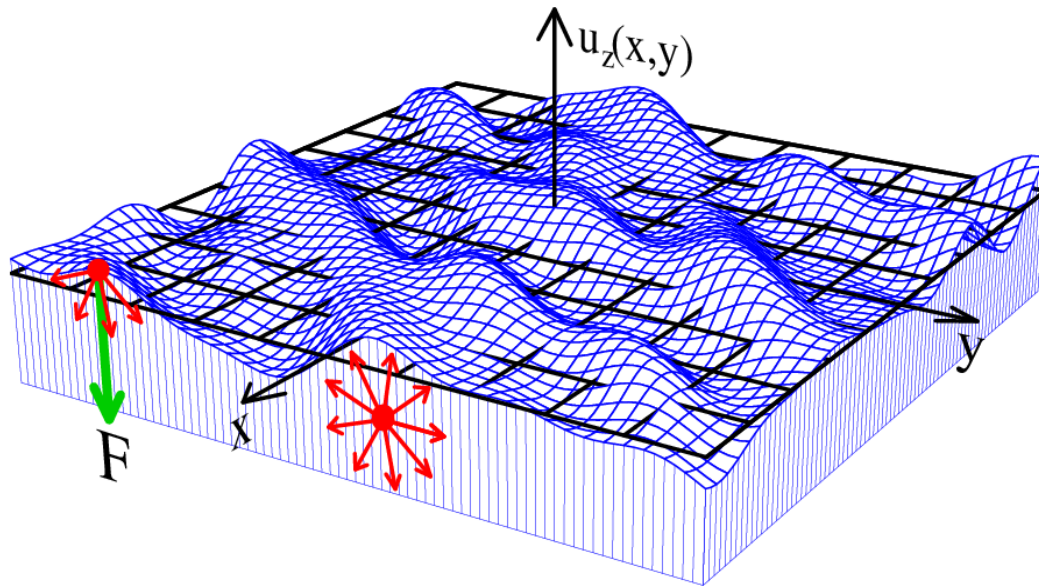
Break of symmetry
at the surface =>

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

Surface Sensitive X-ray Scattering

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:

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

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

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

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

after 2-dim Fourier-backtransformation 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

Surface Sensitive X-ray Scattering
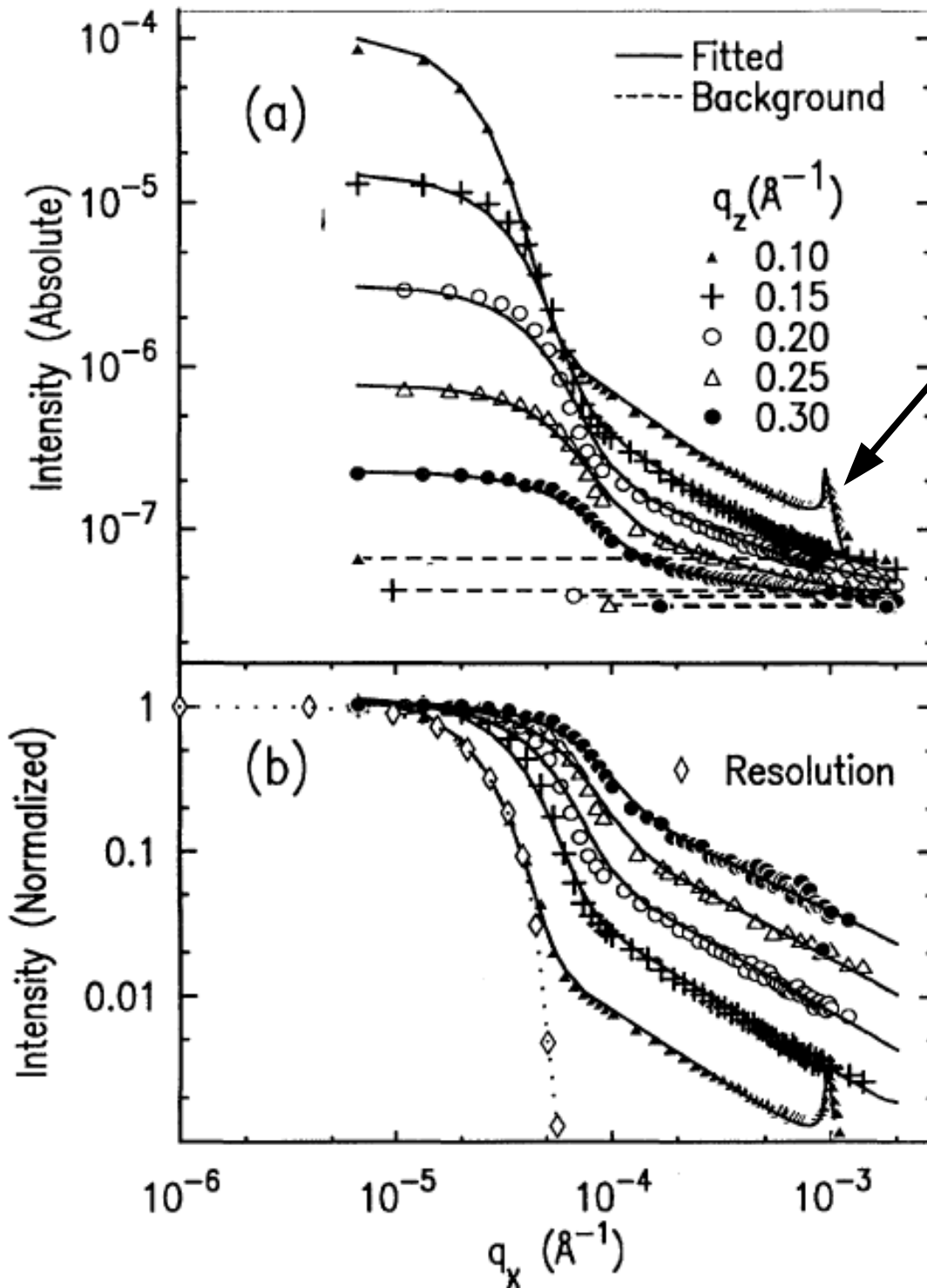
Yoneda peak

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)

Surface Sensitive X-ray Scattering

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.

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