

Surface Sensitive X-ray Scattering

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

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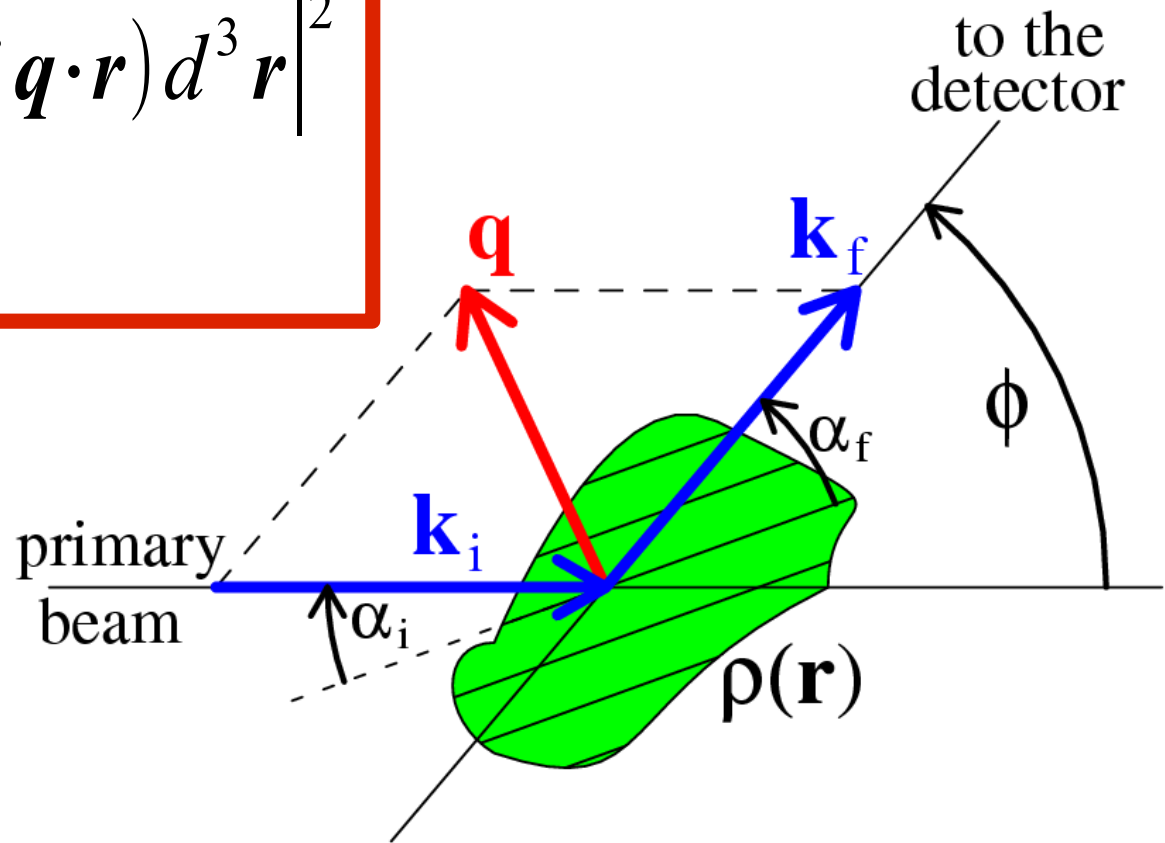
Introduction

No samples are infinite. A surface always exist!

In simplest approximation (**Born approximation**) the scattered intensity is given by the **Fourier Transformation of the electron density**.

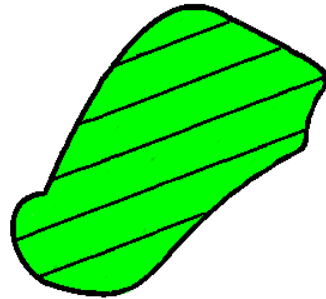
$$I(\mathbf{q}) \propto \left| \int \rho(\mathbf{r}) \exp(i\mathbf{q} \cdot \mathbf{r}) d^3 r \right|^2 \\
 = |\mathcal{F}\{\rho(\mathbf{r})\}|^2$$

How does the presence of a surface effects the scattered signal?



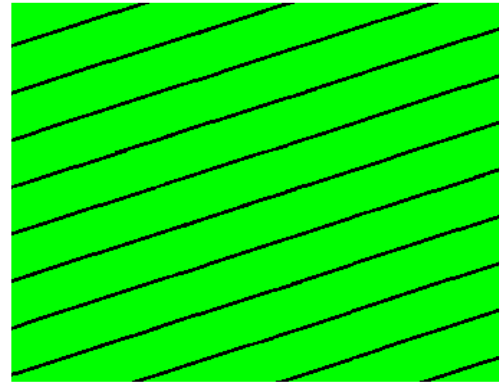
Estimate of the surface effects on the scattering

real sample = infinite sample · shape function



$$\rho(\mathbf{r})$$

=



=

$$\rho_{\infty}(\mathbf{r})$$

·



·

$$S(\mathbf{r})$$

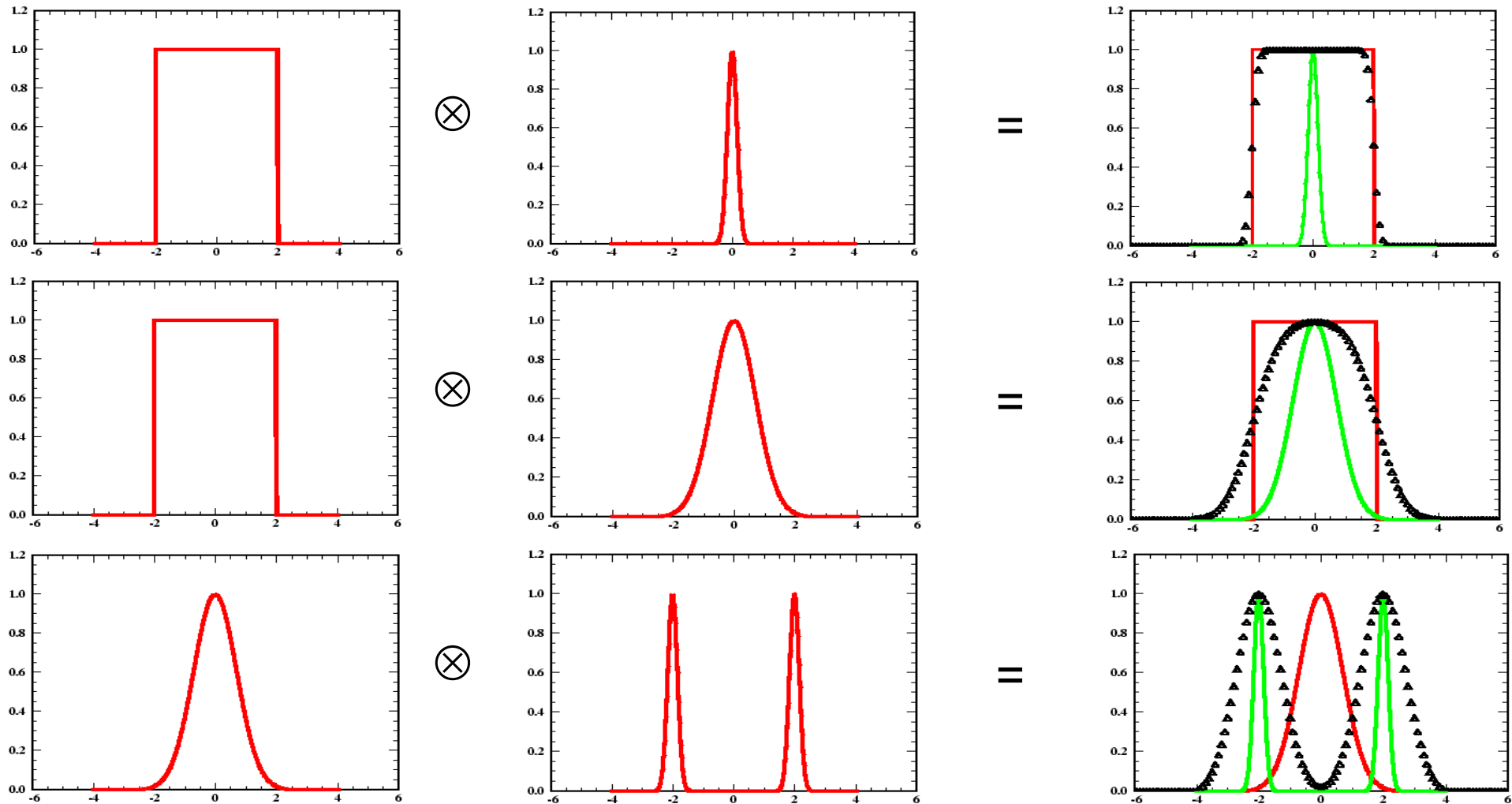
$$I(\mathbf{q}) = |\mathcal{F} \{ \rho(\mathbf{r}) \}(\mathbf{q})|^2 = |\mathcal{F} \{ \rho_{\infty}(\mathbf{r}) S(\mathbf{r}) \}(\mathbf{q})|^2$$

The infinite sample density could be a crystal lattice (→ **Bragg peaks**)

The shape function could be a cube (for a cube shaped sample)

In the following the so called **convolution** $f_1(y) \otimes f_2(y)$ of two functions $f_1(y), f_2(y)$ is important

Definition : $\{f_1(y) \otimes f_2(y)\}(x) = \int f_1(y)f_2(y-x)dy$



In Born approximation the scattered intensity is given by:

$$I(\mathbf{q}) = |\mathcal{F} \{ \rho(\mathbf{r}) \}(\mathbf{q})|^2 = |\mathcal{F} \{ \rho_{\infty}(\mathbf{r}) S(\mathbf{r}) \}(\mathbf{q})|^2$$

Extremely important: **The Convolution Theorem**

$$\mathcal{F} \{ f_1 \otimes f_2 \}(\mathbf{q}) = \mathcal{F} \{ f_1 \}(\mathbf{q}) \cdot \mathcal{F} \{ f_2 \}(\mathbf{q})$$

Proof of the Convolution Theorem:

$$\begin{aligned}
 \mathcal{F} \{ f_1 \otimes f_2 \}(\mathbf{q}) &= \mathcal{F} \left\{ \int f_1(\mathbf{y}) f_2(\mathbf{x}-\mathbf{y}) d\mathbf{y} \right\}(\mathbf{q}) \\
 &= \iint f_1(\mathbf{y}) f_2(\mathbf{x}-\mathbf{y}) d\mathbf{y} \exp(i\mathbf{q}\mathbf{x}) d\mathbf{x} && \text{substitute : } \mathbf{x}-\mathbf{y} = \mathbf{w} \\
 &= \iint f_1(\mathbf{y}) f_2(\mathbf{w}) \exp(i\mathbf{q}[\mathbf{w}+\mathbf{y}]) d\mathbf{w} d\mathbf{y} \\
 &= \int f_1(\mathbf{y}) \exp(i\mathbf{q}\mathbf{y}) d\mathbf{y} \int f_2(\mathbf{w}) \exp(i\mathbf{q}\mathbf{w}) d\mathbf{w} \\
 &= \mathcal{F} \{ f_1 \}(\mathbf{q}) \mathcal{F} \{ f_2 \}(\mathbf{q})
 \end{aligned}$$



From the Convolution Theorem follows :

$$\mathcal{F}\{f_1 \cdot f_2\}(\mathbf{q}) = \{\mathcal{F}\{f_1\} \otimes \mathcal{F}\{f_2\}\}(\mathbf{q})$$

Proof:

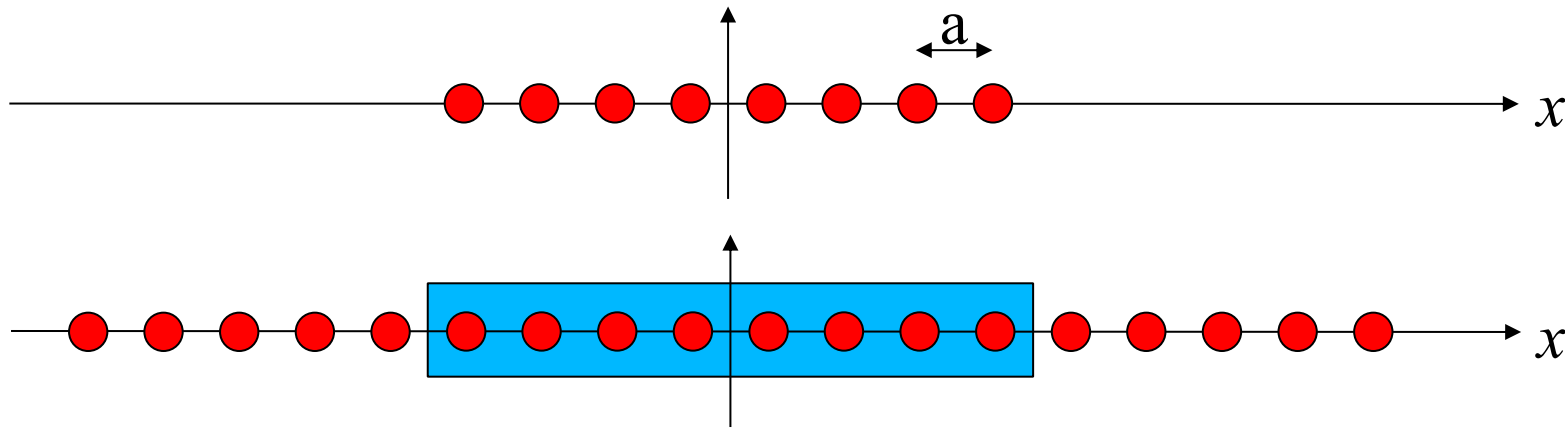
$$\begin{aligned}
 \mathcal{F}^{-1}\{f_1 \cdot f_2\} &= \mathcal{F}^{-1}\{\mathcal{F}\{\mathcal{F}^{-1}\{f_1\}\} \cdot \mathcal{F}\{\mathcal{F}^{-1}\{f_2\}\}\} \\
 &= \mathcal{F}^{-1}\{\mathcal{F}\{F_1\} \cdot \mathcal{F}\{F_2\}\} \quad \text{with } F = \mathcal{F}^{-1}\{f\} \\
 &= \mathcal{F}^{-1}\{\mathcal{F}\{F_1 \otimes F_2\}\} = F_1 \otimes F_2 \\
 &= \mathcal{F}^{-1}\{f_1\} \otimes \mathcal{F}^{-1}\{f_2\}
 \end{aligned}$$

The Inverse Fourier Transformation Operator \mathcal{F}^{-1} can be replaced by the Fourier Transformation \mathcal{F} without violating the proof.

Thus:

$$\begin{aligned}
 I(\mathbf{q}) &= |\mathcal{F}\{\rho(\mathbf{r})\}(\mathbf{q})|^2 = |\mathcal{F}\{\rho_\infty(\mathbf{r})S(\mathbf{r})\}(\mathbf{q})|^2 \\
 &= |\{\mathcal{F}\{\rho_\infty(\mathbf{r})\} \otimes \mathcal{F}\{S(\mathbf{r})\}\}(\mathbf{q})|^2 = |\mathcal{F}\{\rho_\infty\} \otimes \mathcal{F}\{S\}|^2
 \end{aligned}$$

1. Example: N atoms on a 1-dimensional crystal lattice
 lattice distance is a



$$I(q) = \left| \int S(x) \cdot \sum_{n=-\infty}^{\infty} \rho_0 \delta(x-na+a/2) \exp(iqx) dx \right|^2 = \left| \mathcal{F} \left\{ S(x) \cdot \sum_{n=-\infty}^{\infty} \rho_0 \delta(x-na+a/2) \right\} (q) \right|^2$$

With the **delta-function** $\delta(x-x_0) = \begin{cases} \infty & : x = x_0 \\ 0 & : x \neq x_0 \end{cases}$ and $\int \delta(x-x_0) dx = 1$

and the **shape function** $S(x) = \begin{cases} 1 & : -Na/2 < x < +Na/2 \\ 0 & : \text{otherwise} \end{cases}$

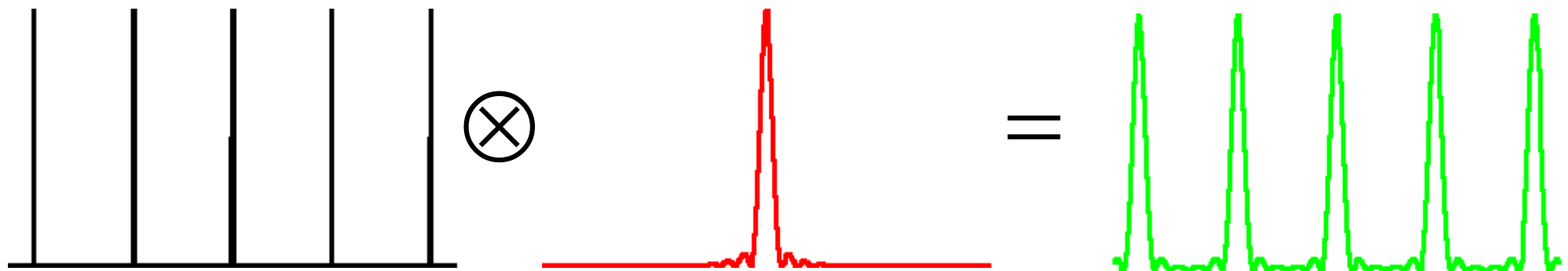
$$I(q) = \left| \mathcal{F} \left\{ S(x) \cdot \sum_{n=-\infty}^{\infty} \rho_0 \delta(x-na+a/2) \right\} (q) \right|^2 = \left| \mathcal{F}\{S(x)\} \otimes \mathcal{F} \left\{ \sum_{n=-\infty}^{\infty} \rho_0 \delta(x-na+a/2) \right\} \right|^2$$

Fourier transformation of an infinite lattice:

$$\mathcal{F} \left\{ \sum_{n=-\infty}^{\infty} \rho_0 \delta(x-na+a/2) \right\} \sim \sum_{n=-\infty}^{\infty} \delta(q-2\pi n/a)$$

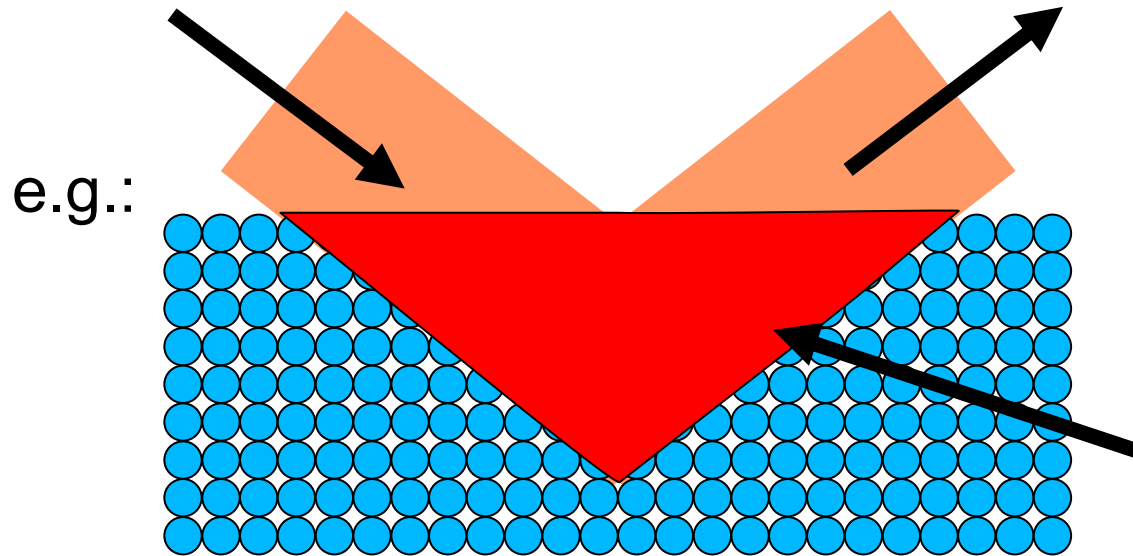
Fourier transformation of the shape function :

$$\mathcal{F}\{S(x)\}(q) \sim \frac{2}{q} \sin\left(\frac{Naq}{2}\right)$$



Bragg peaks are modified: Laue oscillations

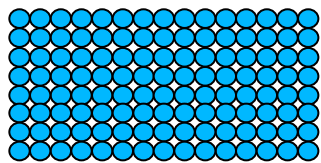
Result: Due to the **convolution** with the **shape function** the **scattered signal** from the sample is **modified**.



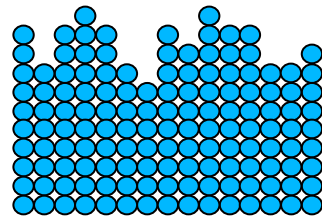
- (1) Limited beam size
- (2) Limited penetration
- (3) Beam size >> penetration

Illuminated part contains only one surface

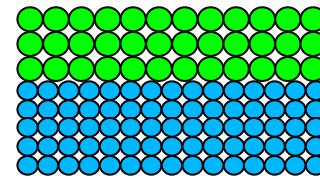
Scattering becomes sensitive to all properties of the illuminated surface via the special shape function $S(r)$.



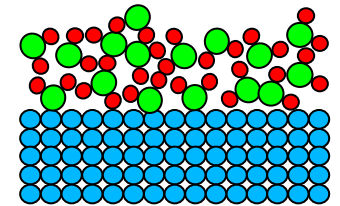
Single surface



Rough surface



Layer system



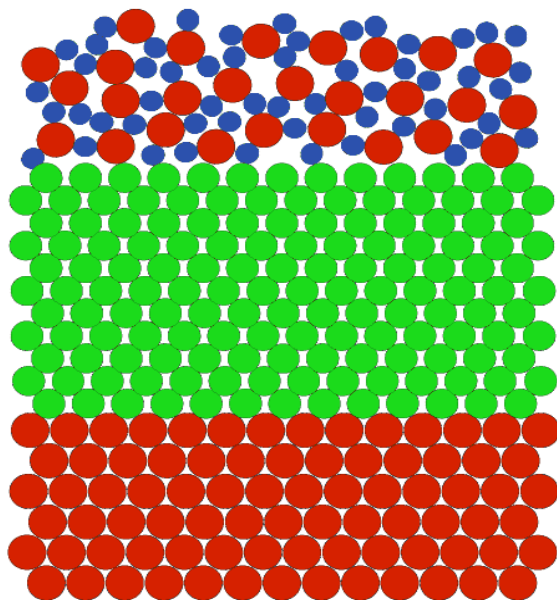
Amorphous

Scattering methods:

- (1) If the samples are **crystalline**: The shape of the Bragg-peaks are modified \Rightarrow **Crystal Truncation Rods (CTR)**
- (2) **Non-crystalline** samples \Rightarrow no real Bragg-peaks, but the zero order Bragg-peak at (0,0,0) (the primary beam) is modified \Rightarrow **Reflectivity**
(Is also used for crystalline samples, if the crystallinity is of no interest).
- (3) **Grazing Incidence Diffraction (GID)** to analyze **crystalline in-plane properties** (also depth dependent).
- (4) **Diffuse scattering** around the CTR or the reflectivity to learn about **non-crystalline in-plane properties**.

Crystal Truncation Rods (CTR)

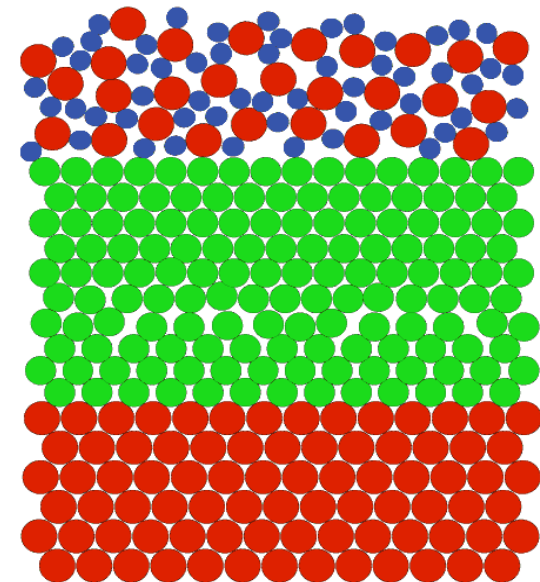
With **Crystal Truncation Rod measurements (CTR)** structural properties of surfaces and thin film systems at **CRYSTALLINE** samples can be investigated on a **nanoscale**.



CTR insensitive

CTR sensitive

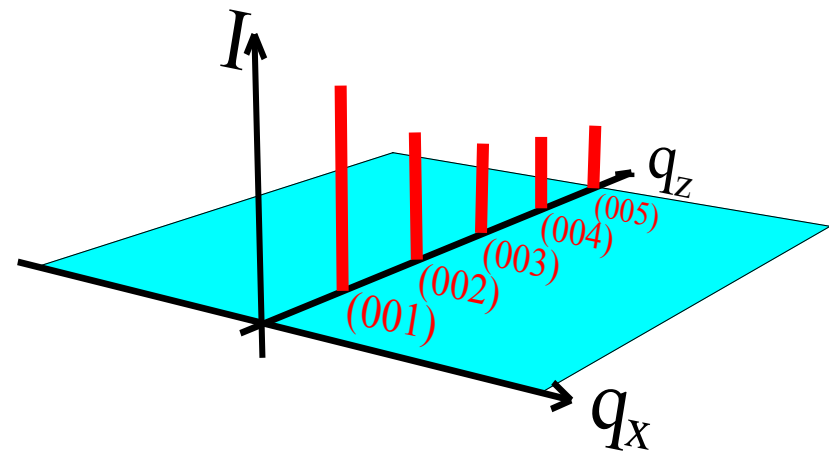
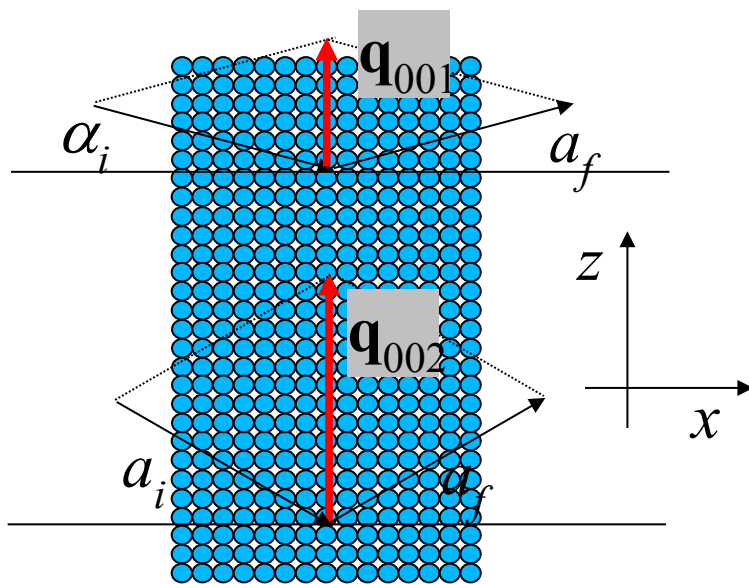
CTR sensitive



An infinite **crystal lattice** has **δ -like Bragg-peaks**: At a particular q -vectors (depending on the incident and exit angles) scattered intensity can be found. In Born approximation ($I_{scatt} \ll I_0$):

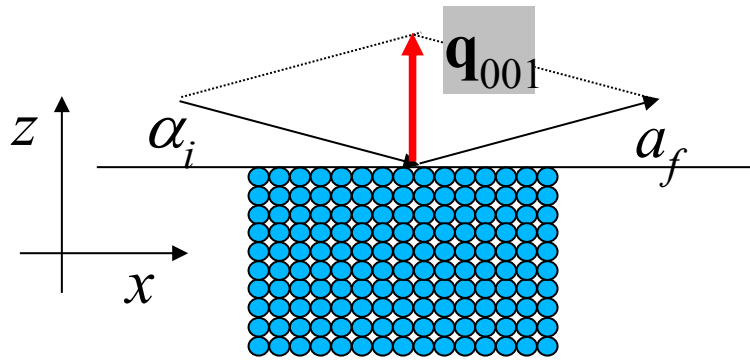
$$I(\mathbf{q}) = |\mathcal{F} \{ \rho(\mathbf{r}) \}(\mathbf{q})|^2 = |\mathcal{F} \{ \rho_\infty(\mathbf{r}) S(\mathbf{r}) \}(\mathbf{q})|^2$$

e.g.: [001]-orientation of the crystal
 scan-mode : incident angle = exit angle
 (001), (002) ... -reflections will appear during the scan

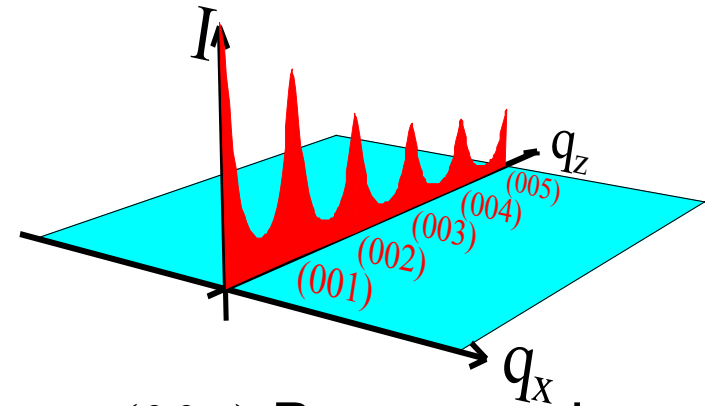


(00n) Bragg-peaks
 in q -space

Considering a simple surface

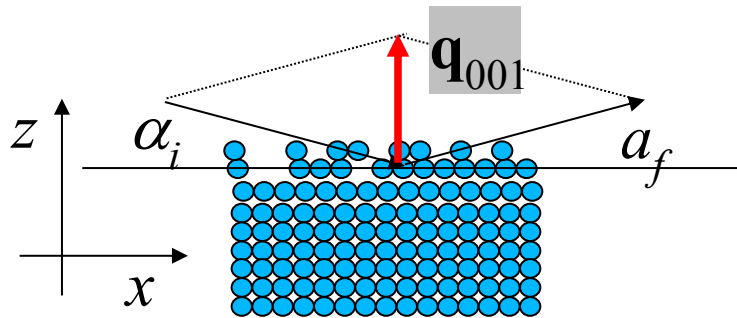


$$\mathcal{F}\left\{ \begin{array}{c} \text{2D lattice} \\ \text{in } xz\text{-plane} \end{array} \right\} \otimes \mathcal{F}\left\{ \begin{array}{c} \text{Step function} \\ \text{along } z \end{array} \right\}$$

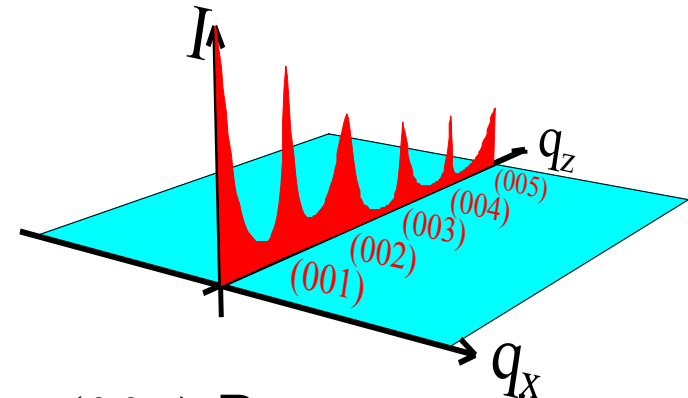


(00n) Bragg-peaks
 and crystal truncation
 rods along q_z

Considering a more complicate surface



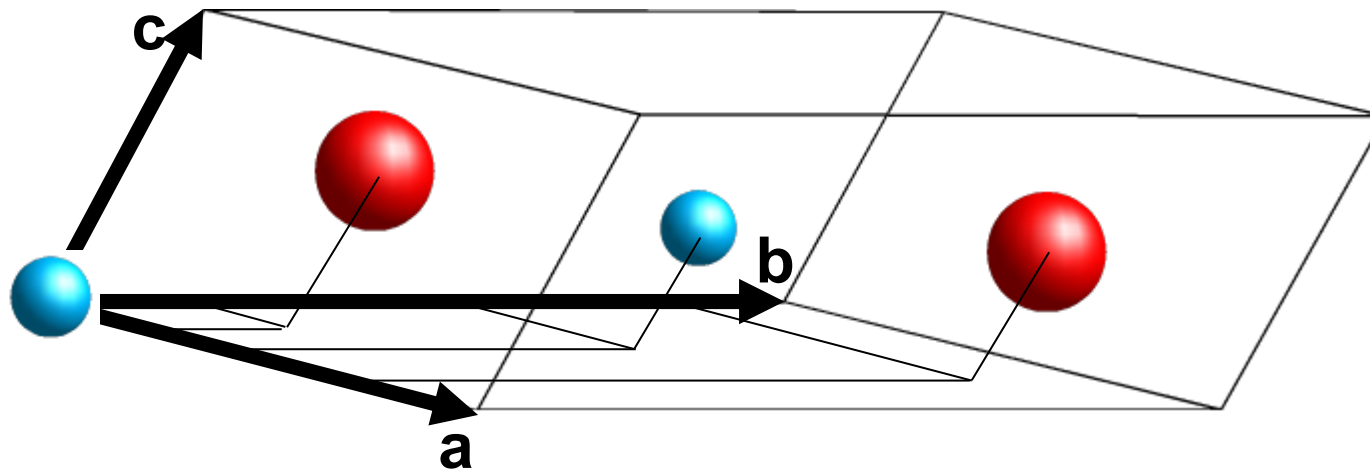
$$\mathcal{F}\left\{ \begin{array}{c} \text{Irregular 2D lattice} \\ \text{in } xz\text{-plane} \end{array} \right\} \otimes \mathcal{F}\left\{ \begin{array}{c} \text{Asymmetric step function} \\ \text{along } z \end{array} \right\}$$



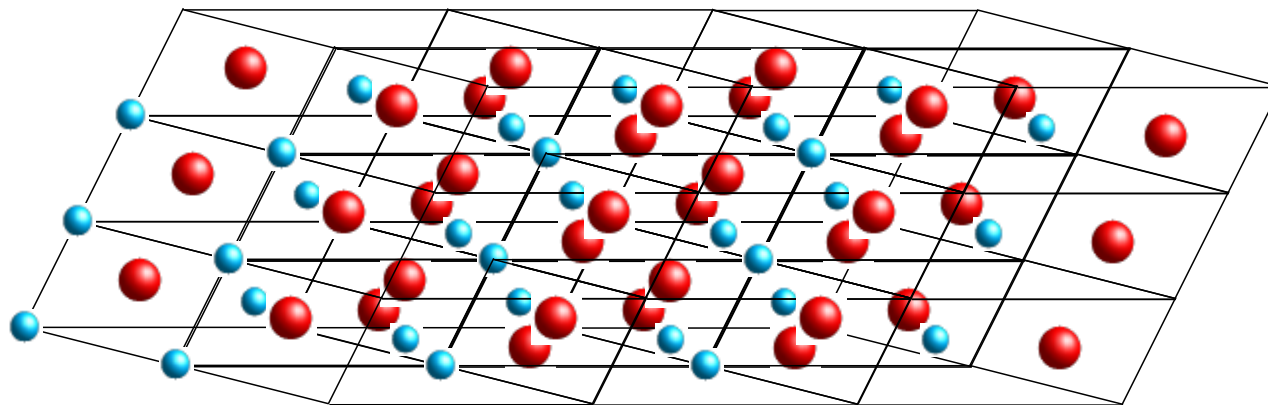
(00n) Bragg-peaks
 and asymmetric
 crystal truncation rods

Calculation of CTRs

Crystals are made from unit cells with base vectors **a**, **b**, **c** [volume $\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})$] containing M atoms with density $\rho_j(\mathbf{r})$ at the positions $\mathbf{R}_j = \mu_j \mathbf{a} + \nu_j \mathbf{b} + \phi_j \mathbf{c}$ with $\mu_j, \nu_j, \phi_j < 1$



each unit cell repeats at $n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c}$ with $n_1, n_2, n_3 \in \mathbb{N}$



electron density of the crystal:

$$\rho(\mathbf{r}) = \sum_{n_1=1}^{N_1} \sum_{n_2=1}^{N_2} \sum_{n_3=1}^{N_3} \sum_{j=1}^M \rho_j(\mathbf{r} + n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c} + \mathbf{R}_j)$$

$$= \sum_{n_1, n_2, n_3} \sum_j \int \rho_j(\mathbf{u}) \delta(\mathbf{u} - \mathbf{r} - n_1 \mathbf{a} - n_2 \mathbf{b} - n_3 \mathbf{c} - \mathbf{R}_j) d\mathbf{u}$$


scattering amplitude $A(\mathbf{q})$:

$$A(\mathbf{q}) = \int \rho(\mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r} = \int \int \sum_{n_{1,2,3}} \sum_j \rho_j(\mathbf{u}) \delta(\mathbf{u} - \mathbf{r} - n_1 \mathbf{a} - n_2 \mathbf{b} - n_3 \mathbf{c} - \mathbf{R}_j) e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{u} d\mathbf{r}$$


$$= \int \sum_{n_{1,2,3}} \sum_j \rho_j(\mathbf{u}) \int e^{i\mathbf{q}\cdot\mathbf{r}} \delta(\mathbf{u} - \mathbf{r} - n_1 \mathbf{a} - n_2 \mathbf{b} - n_3 \mathbf{c} - \mathbf{R}_j) d\mathbf{r} d\mathbf{u}$$

$$= \sum_{n_{1,2,3}} \sum_j \int \rho(\mathbf{u}) e^{i\mathbf{q}\cdot(-\mathbf{u} + n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c} + \mathbf{R}_j)} d\mathbf{u} = \sum_{n_{1,2,3}} e^{i\mathbf{q}\cdot(n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c})} \sum_j e^{i\mathbf{q}\cdot\mathbf{R}_j} \left[\int \rho_j(\mathbf{u}) e^{-i\mathbf{q}\cdot\mathbf{u}} d\mathbf{u} \right]$$

$$= \sum_{n_{1,2,3}} e^{i\mathbf{q}\cdot(n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c})} \sum_j f_j(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{R}_j} = S_f(\mathbf{q}) \sum_{n_{1,2,3}} e^{i\mathbf{q}\cdot(n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c})}$$



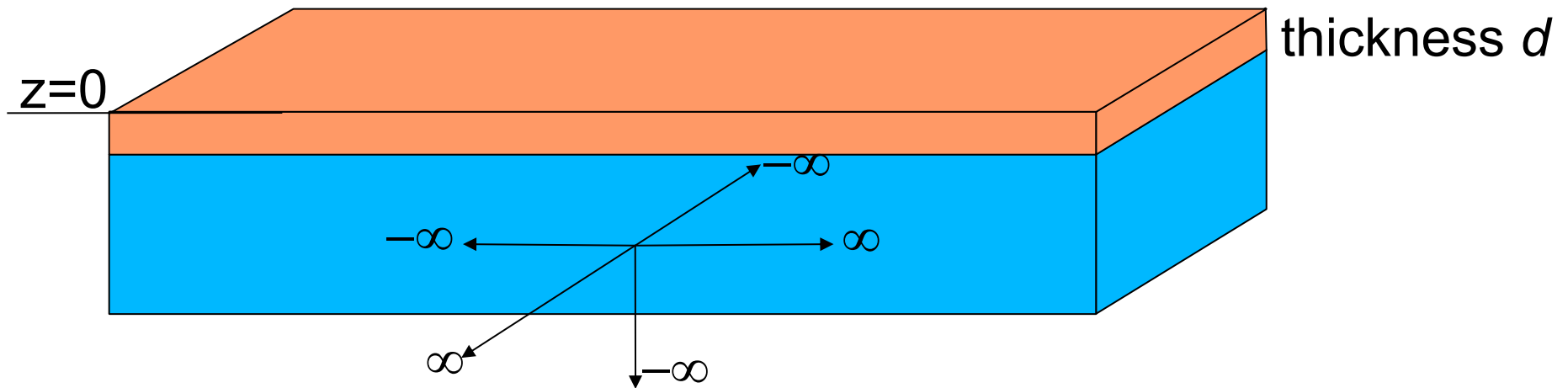
$S_f(\mathbf{q})$ structure factor



$f_j(\mathbf{q})$
form factor



e.g. Bulk crystal and a thin film crystal, infinity in x and y and -z



Bulk scattering amplitude (truncated at $z=0$ and shifted by $-d$)

$$A_{bulk}(\mathbf{q}) = e^{-iq_z d} S_{f,bulk}(\mathbf{q}) \sum_{n_x=-\infty}^{n_x=\infty} \sum_{n_y=-\infty}^{n_y=\infty} \sum_{n_z=-\infty}^{n_z=0} e^{i\mathbf{q} \cdot (n_x \mathbf{a}_{bulk} + n_y \mathbf{b}_{bulk} + n_z \mathbf{c}_{bulk})}$$

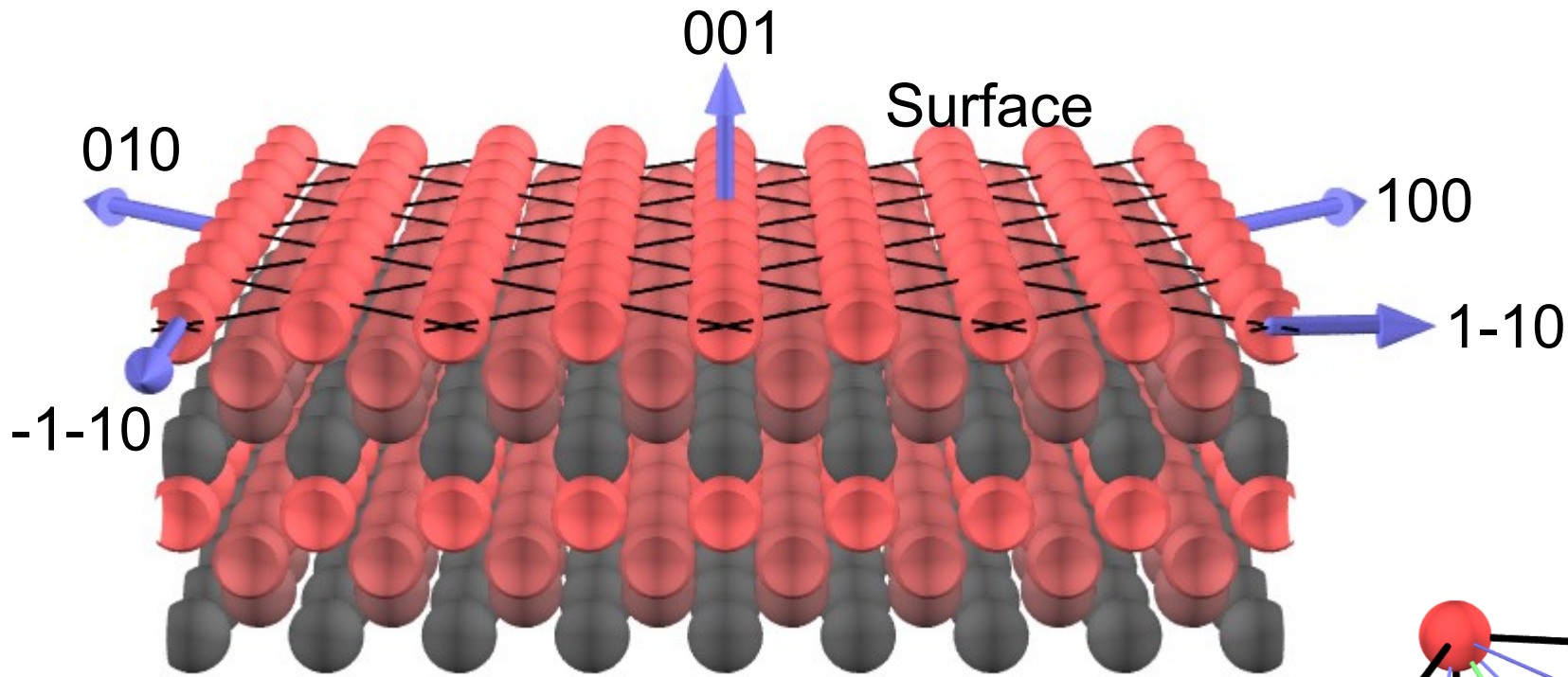
Film scattering amplitude (truncated at $z=0$ and $z = -N$ unit cells)

$$A_{film}(\mathbf{q}) = S_{f,film}(\mathbf{q}) \sum_{n_x=-\infty}^{n_x=\infty} \sum_{n_y=-\infty}^{n_y=\infty} \sum_{n_z=-N}^{n_z=0} e^{i\mathbf{q} \cdot (n_x \mathbf{a}_{film} + n_y \mathbf{b}_{film} + n_z \mathbf{c}_{film})}$$

Scattered Intensity

$$I(\mathbf{q}) = |A_{film}(\mathbf{q}) + A_{bulk}(\mathbf{q})|^2$$

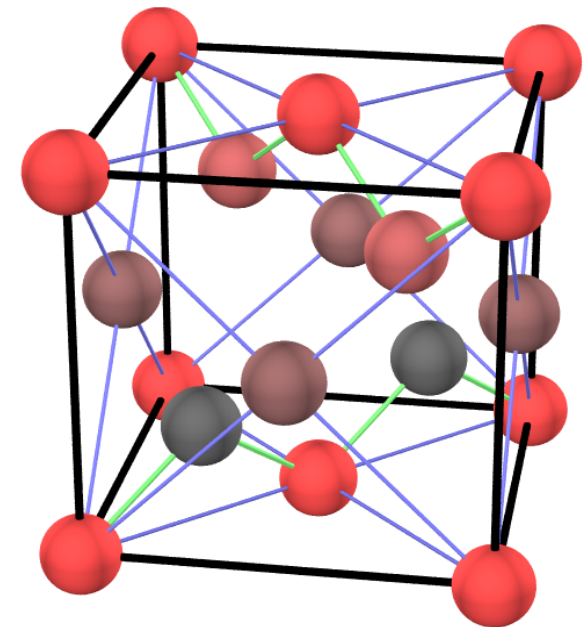
Example: Reconstruction of Si-(001)Surface



↓
Bulk

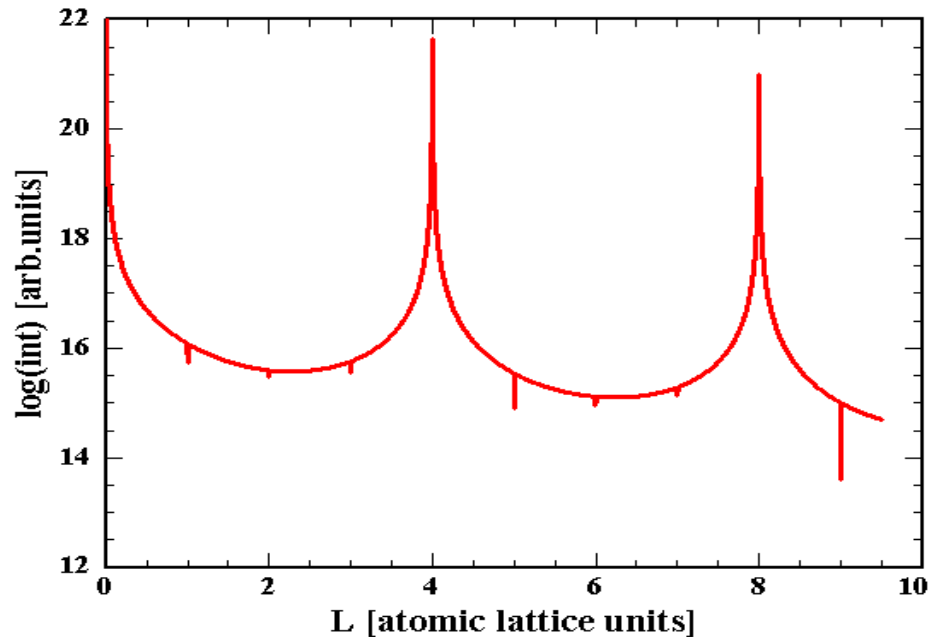
Cut of crystal results into unterminated bonds (orbitals)

Silicon unit cell (diamond structure with $a = 5.431\text{\AA}$)

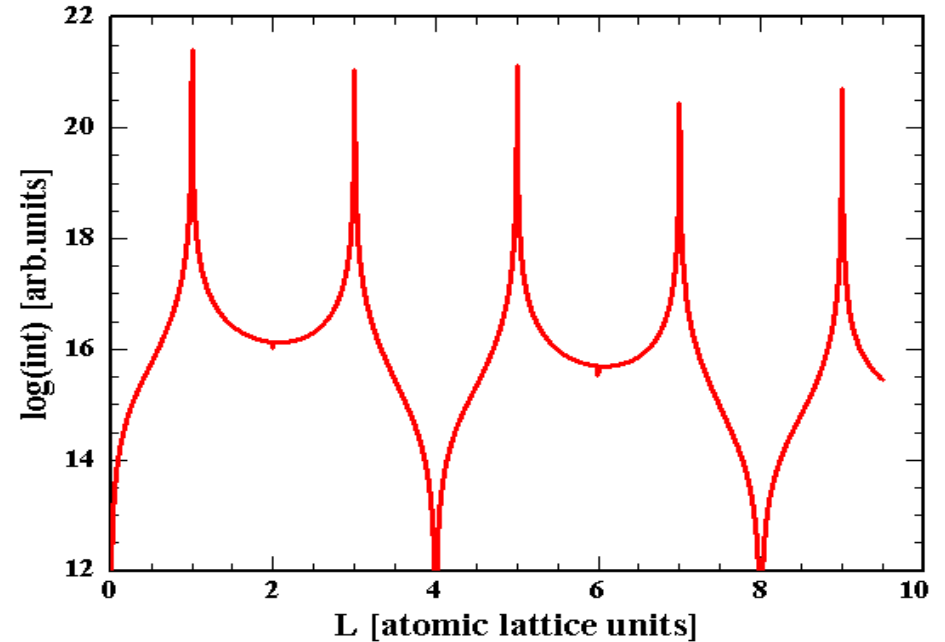


CTRs of un-reconstructed Si-(001)Surface

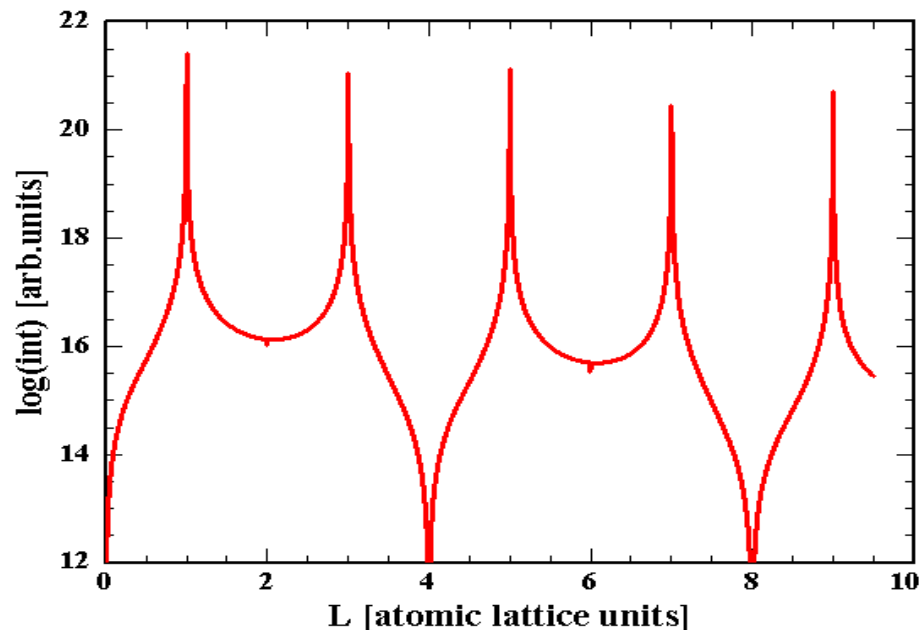
unrelaxed 00L-scan



unrelaxed 11L-scan



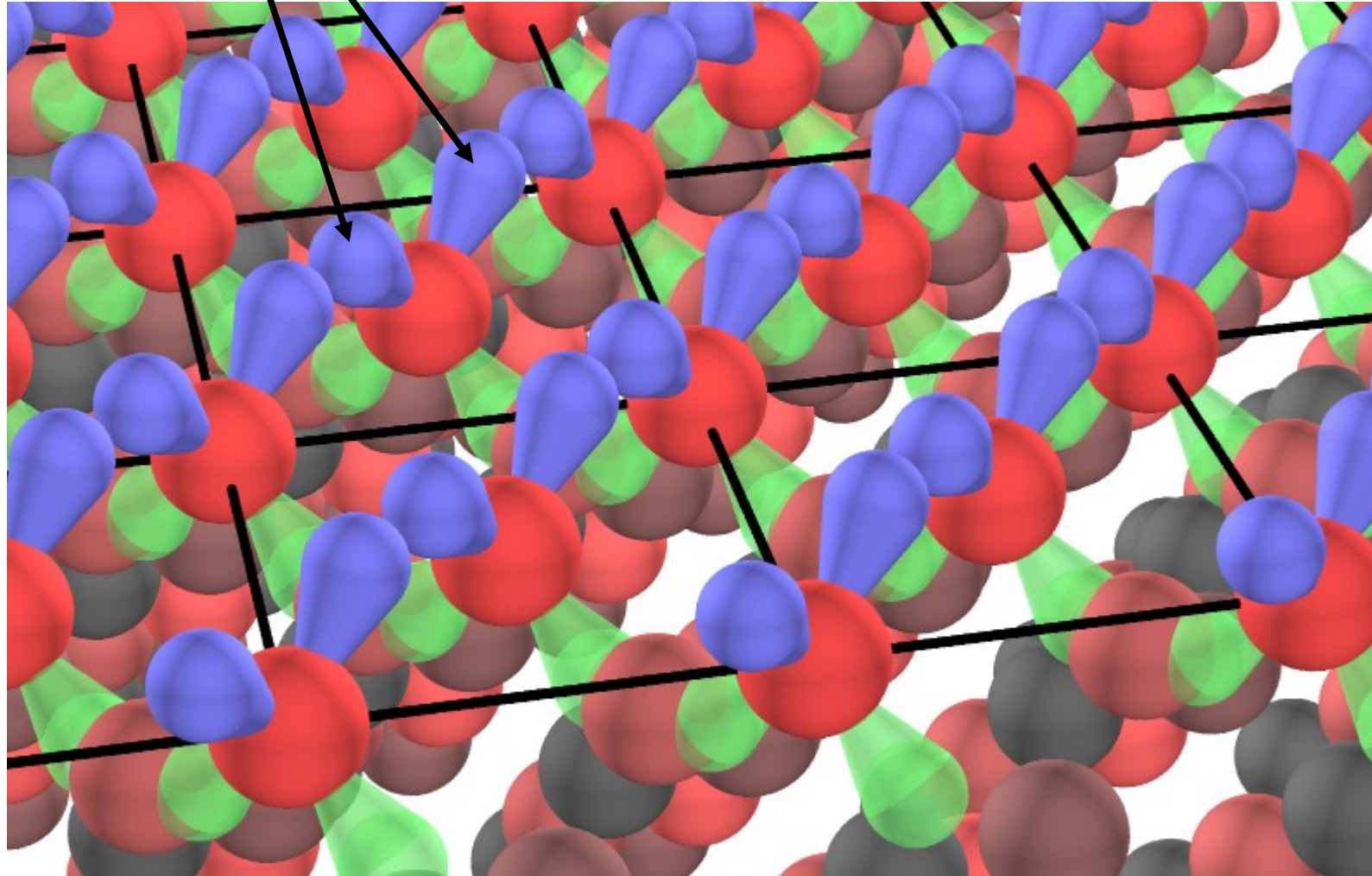
unrelaxed 1-1L-scan



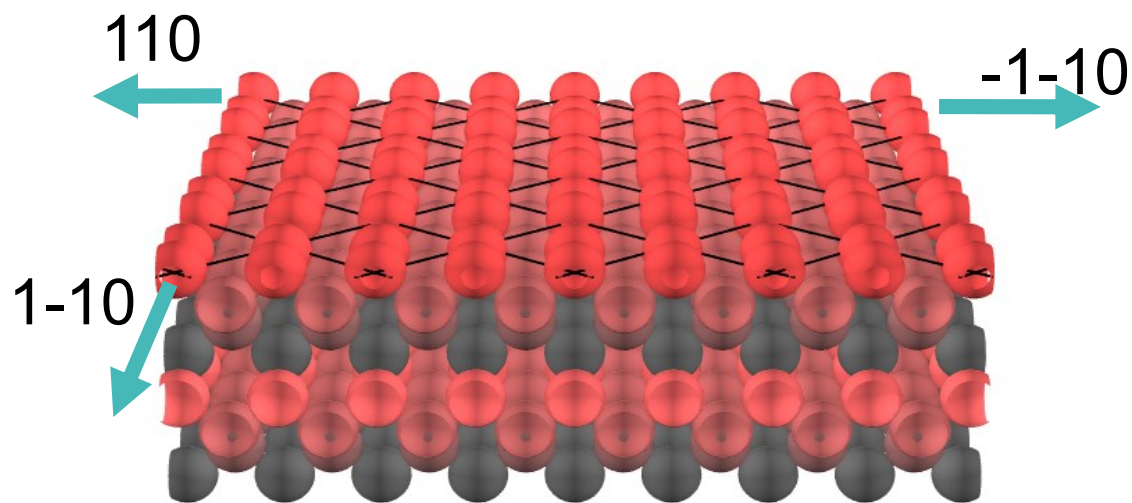
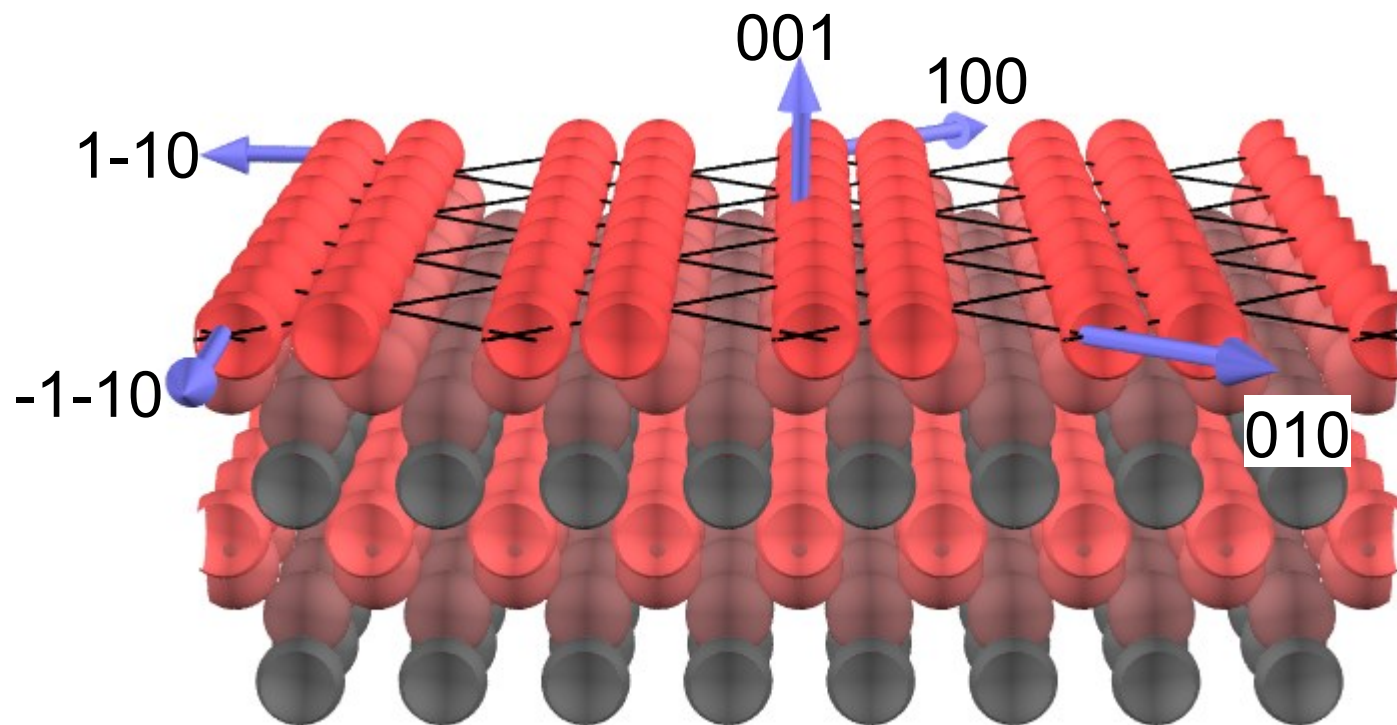
- 1) 00L scan looks easy
(the dips mark the position of forbidden reflections and are caused by numerical problems)
- 2) 11L and 1-1L scans are identical

To lower the free energy the orbitals un-terminated orbitals try to bond. This deforms the lattice.

un-terminated orbitals



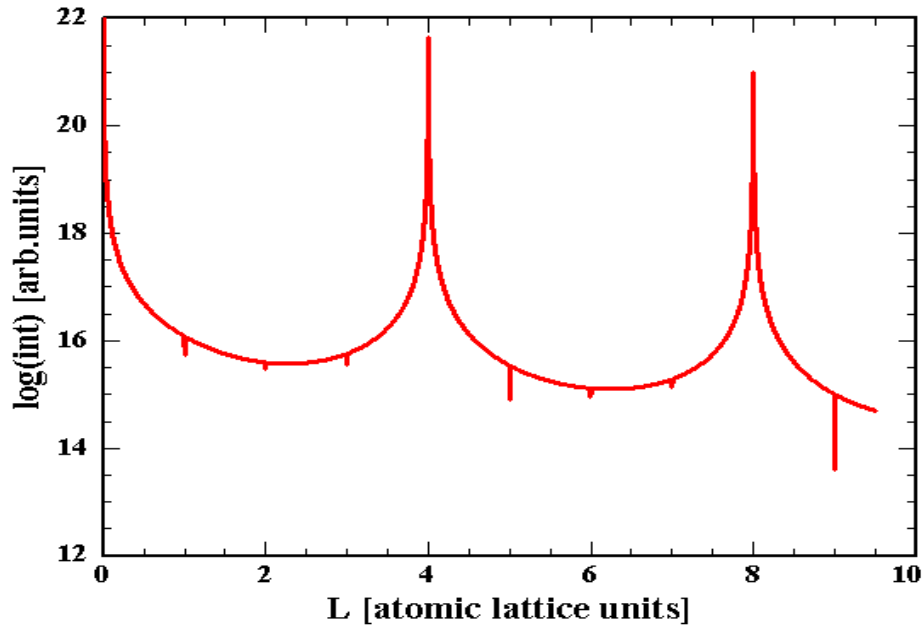
Possible relaxation: Forming "double rods" along 110-direction



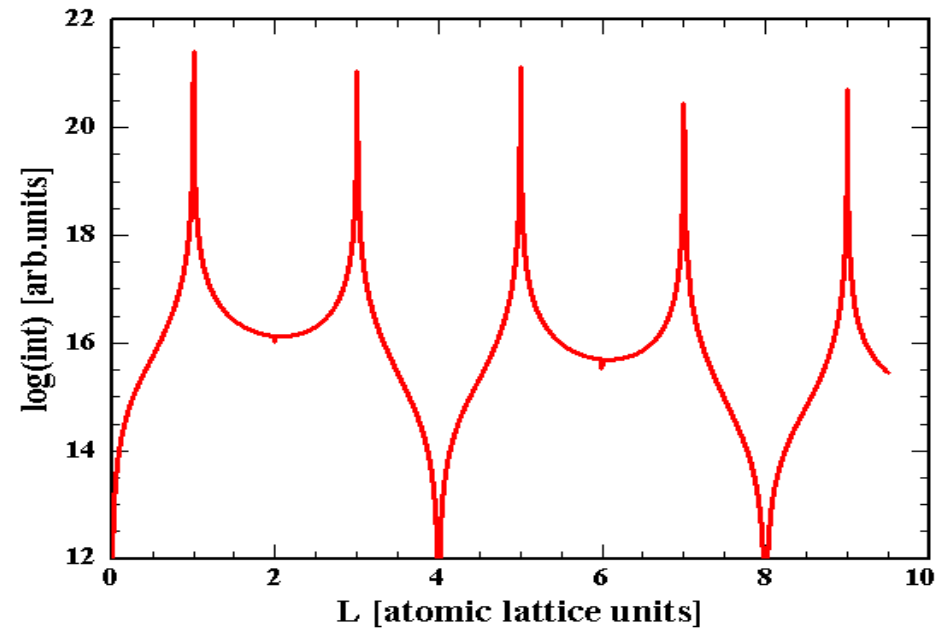
90° turn looks pretty much like unrelaxed surface

CTRs of simple “dimer rod” reconstructed Si-(001)Surface

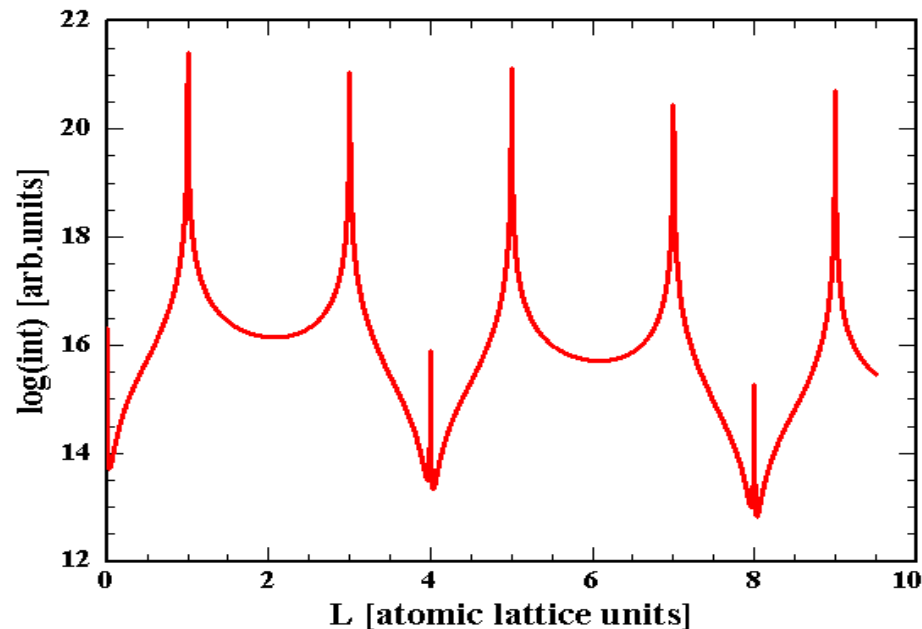
double-rod relaxed 00L-scan



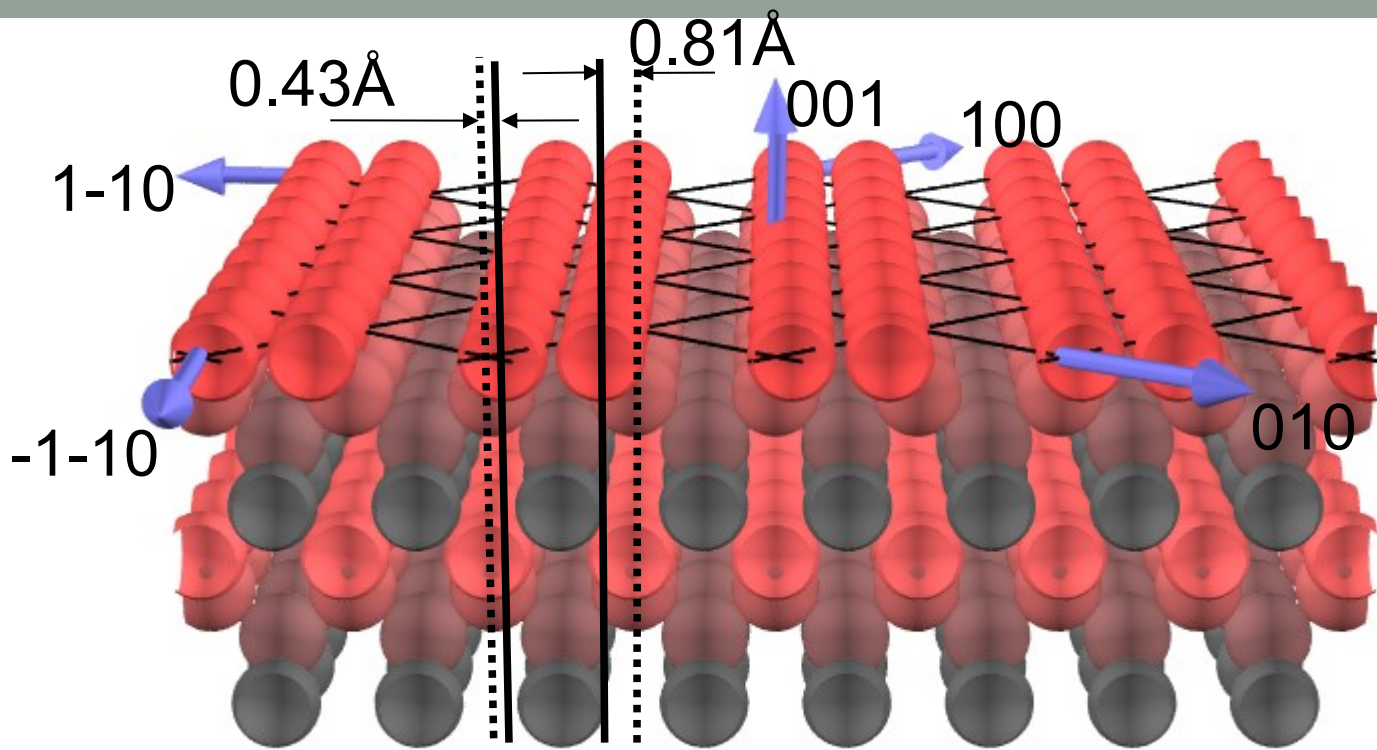
double-rod relaxed 11L-scan



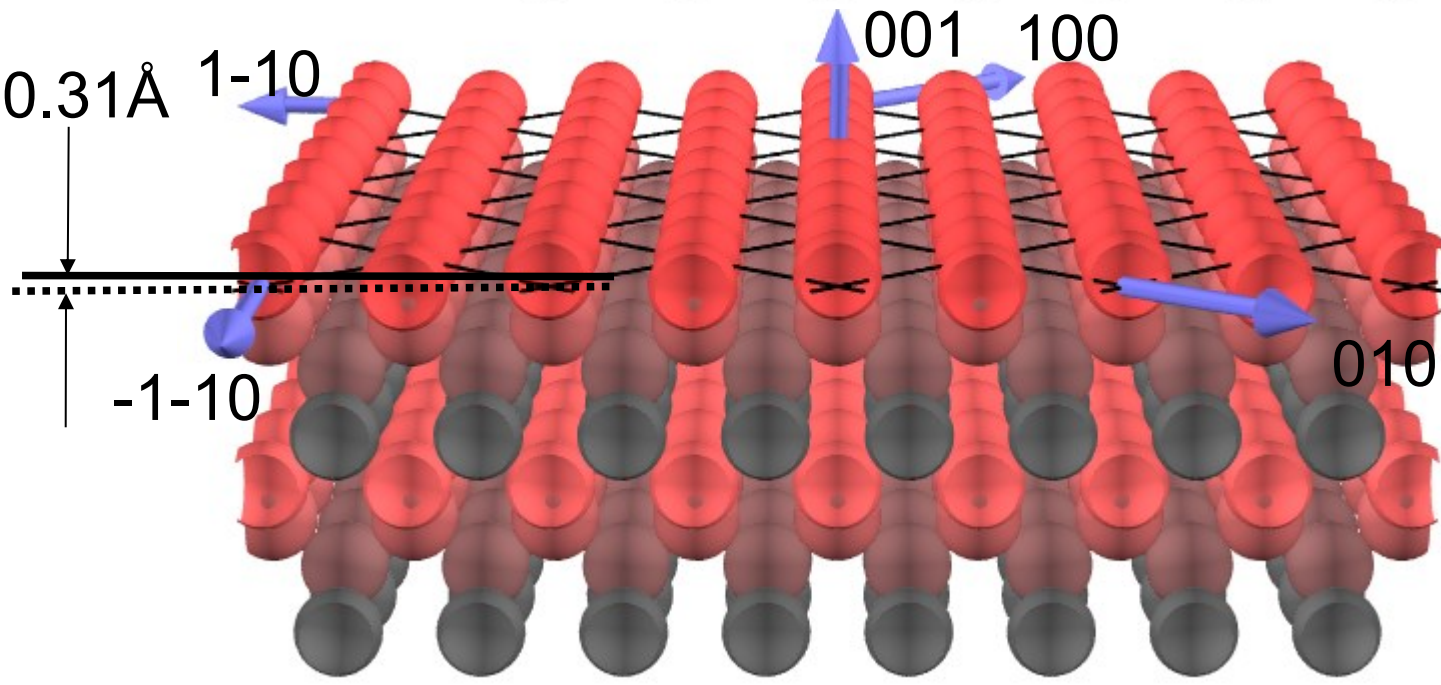
double-rod relaxed 1-1L-scan



- 1) 00L scan has not changed (no change in z-direction)
- 2) 11L has not changed (in this direction identical to unrelaxed lattice)
- 3) slight changes is 1-1L : breaking of symmetry -> additional small peaks

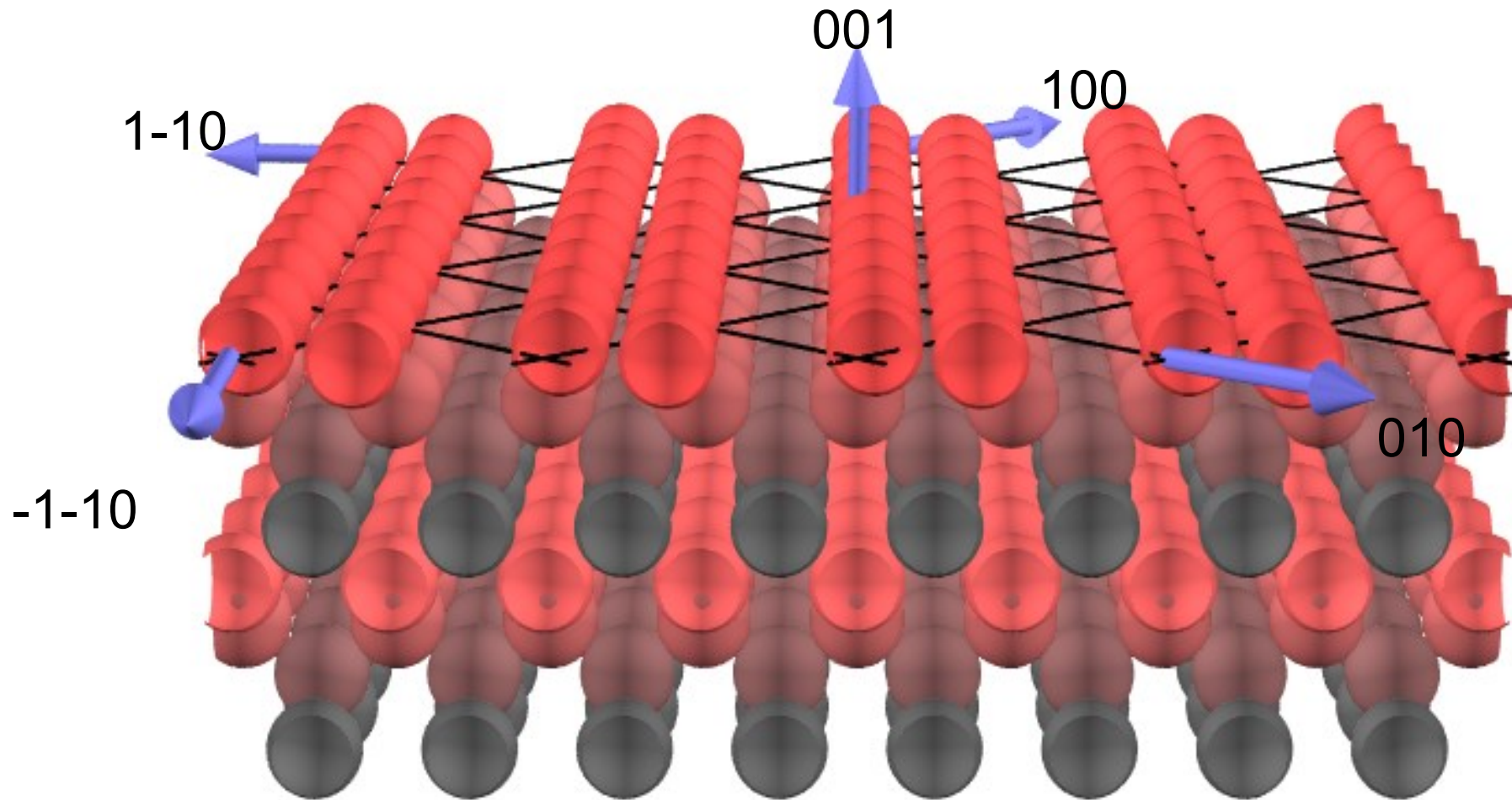


actual situation:



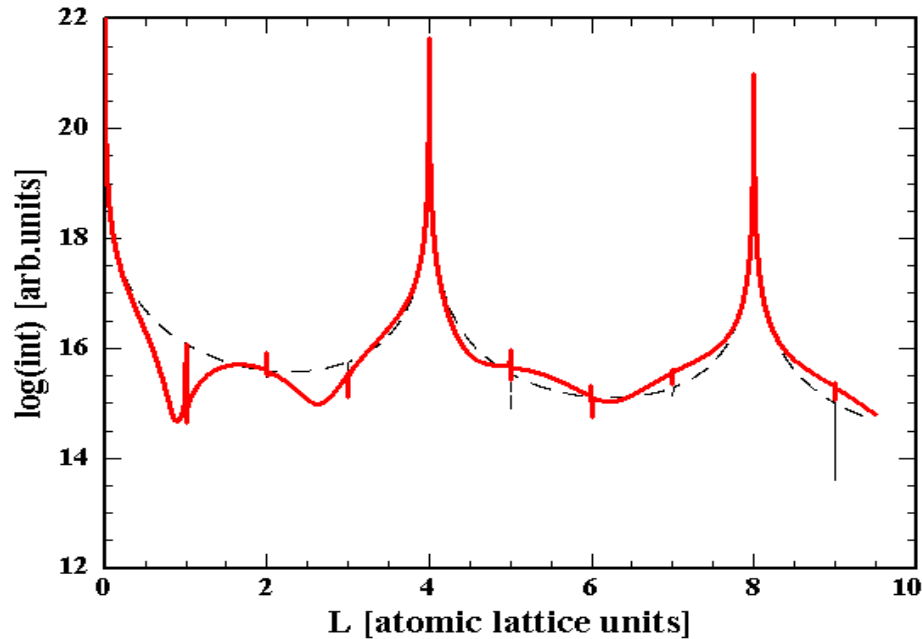
strained
"dimer rod"

Resulting 2x1 lattice reconstruction the of 001 Silicon surface

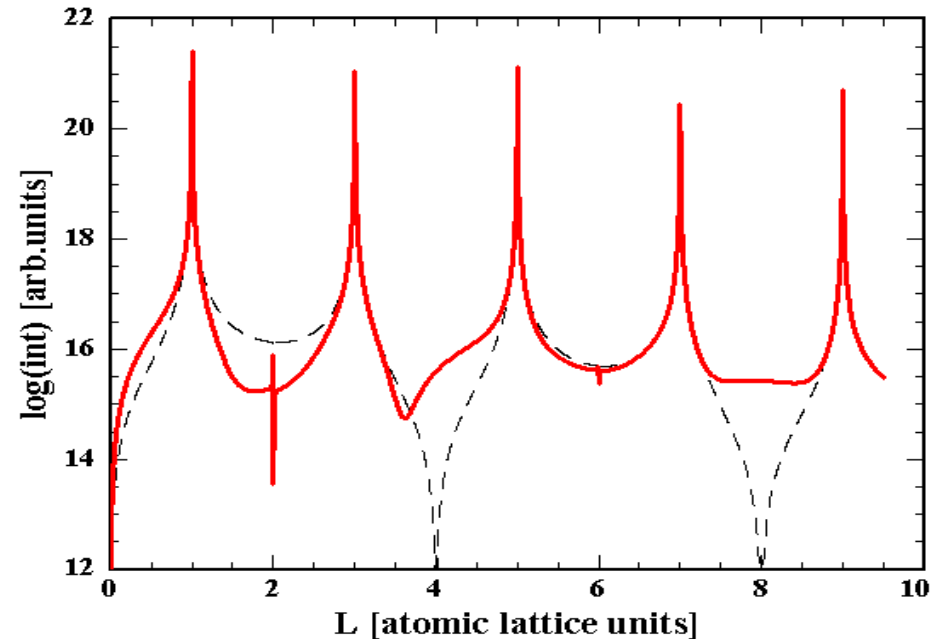


CTRs of “strained dimer rod” reconstructed Si-(001)Surface

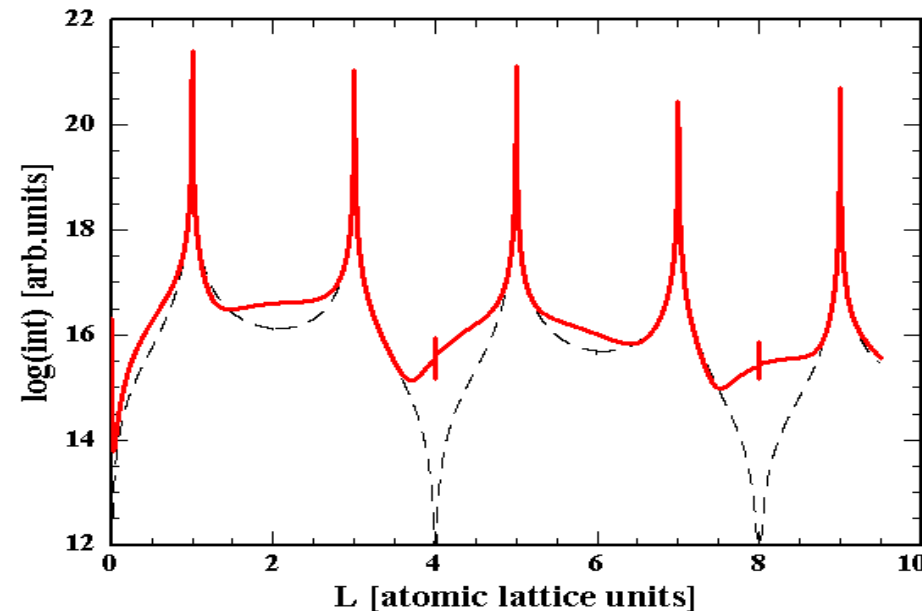
double-rod relaxed 00L-scan



double-rod relaxed 11L-scan



double-rod relaxed 1-1L-scan



- 1) 00L has changed (atoms lifted)
- 2) the additional break in symmetry causes the 11L and 1-1L to be different.

Crystal Truncation Rods

- CTR measurements are applicable for **crystalline samples ONLY**
- They are sensitive to **very small displacements of atoms near the surface**
- For full information about the sample, **three or more linear independent CTRs are necessary**
- In Born approximation ($I_{scatt} \ll I_0$)

$$I(\mathbf{q}) = |\mathcal{F} \{ \rho(\mathbf{r}) \}(\mathbf{q})|^2 = |\mathcal{F} \{ \rho_\infty(\mathbf{r}) S(\mathbf{r}) \}(\mathbf{q})|^2$$

with $\rho_\infty(\mathbf{r})$ the periodic infinite electron density and $S(\mathbf{r})$ the shape function.