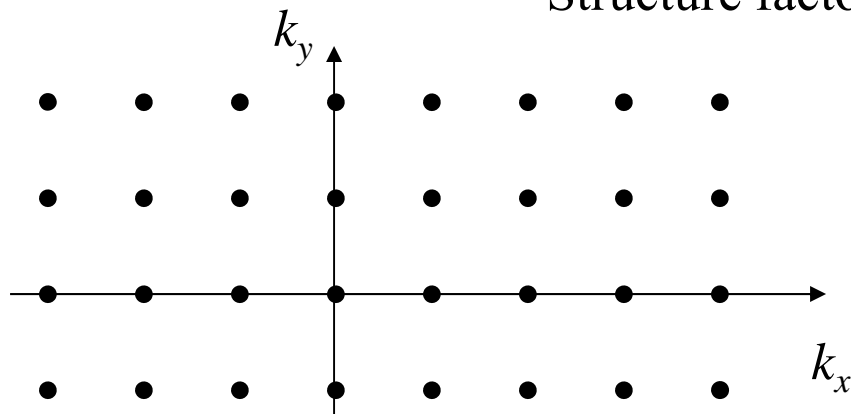# 8. Crystal Diffraction

April 12, 2018

Reciprocal lattice (Reziprokes Gitter)

Any periodic function can be written as a Fourier series

$$f(\vec{r}) = \sum_{\vec{G}} f_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}$$

Reciprocal lattice vector G

Structure factor

$$\vec{G} = \upsilon_1 \vec{b}_1 + \upsilon_2 \vec{b}_2 + \upsilon_3 \vec{b}_3$$

v_i integers

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}, \qquad \vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}, \qquad \vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

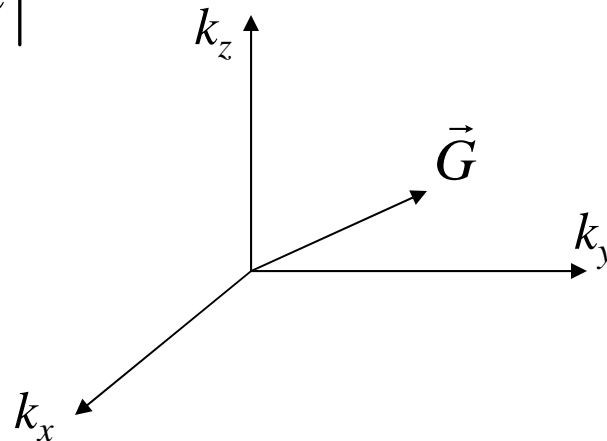$$\vec{a}_i \cdot \vec{b}_j = 2\pi \delta_{ij}$$

Reciprocal space (Reziproker Raum)
k-space (k-Raum)

k-space is the space of all wave-vectors.

A k-vector points in the direction a wave is propagating.

wavelength: $\quad \lambda = \dfrac{2\pi}{\left|\vec{k}\right|}$
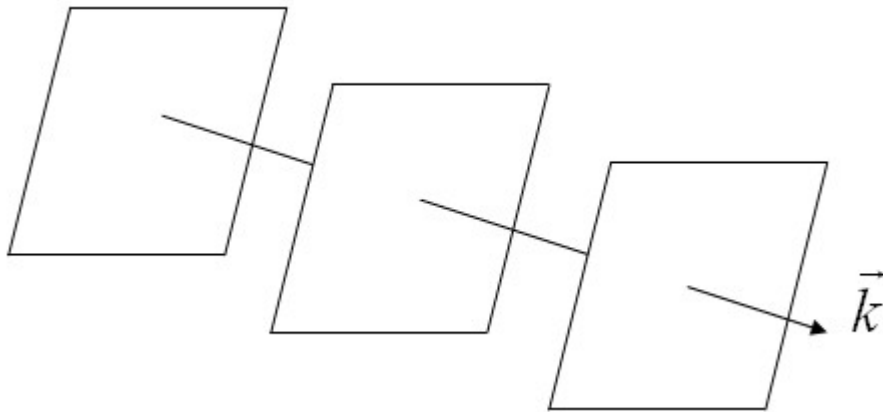$\qquad\qquad\qquad$ momentum: $\quad \vec{p} = \hbar\vec{k}$

Plane wave:

$$\exp(i\vec{G}\cdot\vec{r}) = \cos(G_x x + G_y y + G_z z) + i\sin(G_x x + G_y y + G_z z)$$

Plane waves (Ebene Wellen)

$$e^{i\vec{k}\cdot\vec{r}} = \cos\left(\vec{k}\cdot\vec{r}\right) + i\sin\left(\vec{k}\cdot\vec{r}\right)$$

$$\lambda = \frac{2\pi}{\left|\vec{k}\right|}$$

$$\exp\left(i\vec{k}\cdot\left(\vec{r}+\vec{r}_\perp\right)\right) = \exp\left(i\vec{k}\cdot\vec{r}\right)$$

Most functions can be expressed in terms of plane waves

$$f(\vec{r}) = \int F\left(\vec{k}\right) e^{i\vec{k}\cdot\vec{r}} d\vec{k}$$

A k-vector points in the direction a wave is propagating.

Fourier transforms

Most functions can be expressed in terms of plane waves
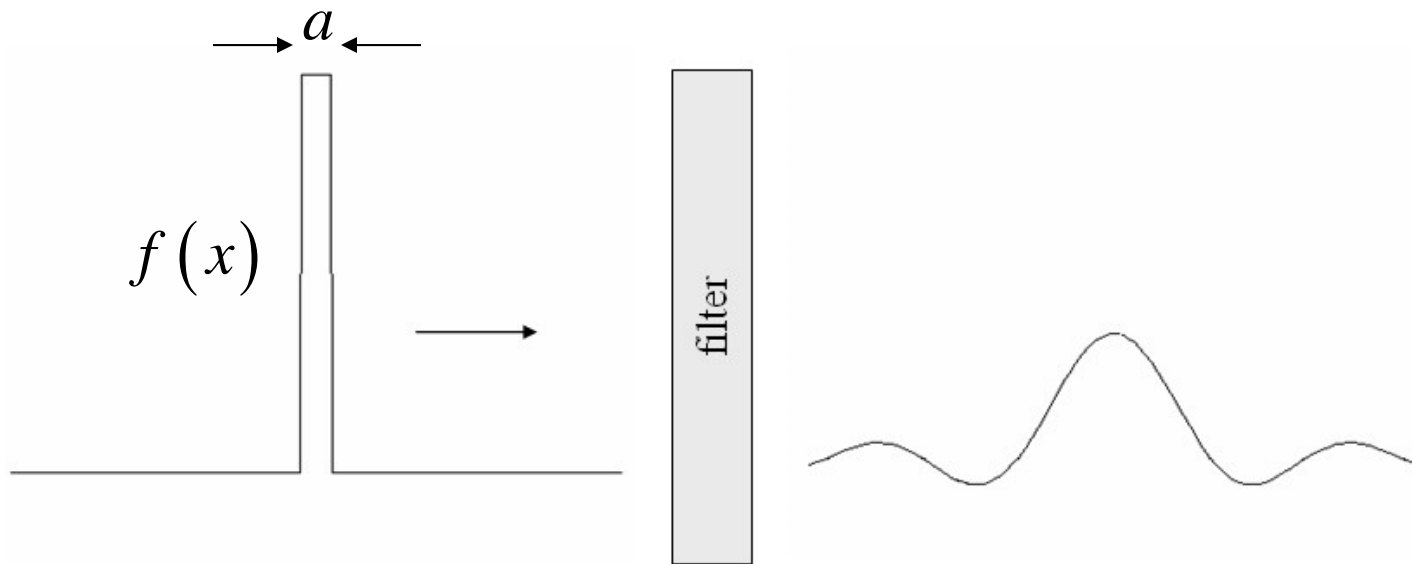
$$f(\vec{r}) = \int F(\vec{k}) e^{i\vec{k}\cdot\vec{r}} \, d\vec{k}$$

This can be inverted for $F(k)$

$$F(\vec{k}) = \frac{1}{(2\pi)^d} \int f(\vec{r}) e^{-i\vec{k}\cdot\vec{r}} \, d\vec{r}$$

Fourier transform of $f(r)$

http://lamp.tu-graz.ac.at/~hadley/ss1/crystaldiffraction/ft/ft.php

Fourier transforms

Fourier transform: $F(k) = \dfrac{1}{2\pi} \displaystyle\int\limits_{-a/2}^{a/2} e^{-ikx}\, dx = \dfrac{\sin(ka/2)}{\pi k}$

Inverse transform: $f(x) = \displaystyle\int\limits_{-\infty}^{\infty} \dfrac{\sin(ka/2)}{\pi k} e^{ikx}\, dk$

Transmitted pulse: $f'(x) = \displaystyle\int\limits_{-k_0}^{k_0} \dfrac{\sin(ka/2)}{\pi k} e^{ikx}\, dk = \dfrac{\mathrm{Si}(k_0 x + \frac{1}{2}) + \mathrm{Si}(k_0 x - \frac{1}{2})}{\pi}$

Sine integral

Notations for Fourier Transforms

$$F_{a,b}\left(\vec{k}\right) = \mathcal{F}_{a,b}\{f(\vec{r})\} = \sqrt{\frac{|b|^d}{(2\pi)^{d(1-a)}}} \int\limits_{-\infty}^{\infty} f(\vec{r})e^{ib\vec{k}\cdot\vec{r}}\,d\vec{r}$$

$$f(\vec{r}) = \mathcal{F}_{a,b}^{-1}\left\{F\left(\vec{k}\right)\right\} = \sqrt{\frac{|b|^d}{(2\pi)^{d(1+a)}}} \int\limits_{-\infty}^{\infty} F_{a,b}\left(\vec{k}\right)e^{-ib\vec{k}\cdot\vec{r}}\,d\vec{k}$$

d = number of dimensions 1,2,3
a,b = constants

Notations for Fourier Transforms

$$F_{-1,-1}\left(\vec{k}\right) = \frac{1}{(2\pi)^d} \int f\left(\vec{r}\right) e^{-i\vec{k}\cdot\vec{r}}\, d\vec{r}.$$

$$f\left(\vec{r}\right) = \int F_{-1,-1}\left(\vec{k}\right) e^{i\vec{k}\cdot\vec{r}}\, d\vec{k}.$$

$f(r)$ is built of plane waves

Notations for Fourier Transforms

$$F_{1,-1}\left(\vec{k}\right) = \int f(\vec{r})e^{-i\vec{k}\cdot\vec{r}}\, d\vec{r}\,.$$

$$f(\vec{r}) = \frac{1}{(2\pi)^d} \int F_{1,-1}\left(\vec{k}\right) e^{i\vec{k}\cdot\vec{r}}\, d\vec{k}\,.$$

Matlab

Notations for Fourier Transforms

$$F_{0,-1}\left(\vec{k}\right) = \frac{1}{(2\pi)^{d/2}} \int f(\vec{r}) e^{-i\vec{k}\cdot\vec{r}} \, d\vec{r}.$$

$$f(\vec{r}) = \frac{1}{(2\pi)^{d/2}} \int F_{0,-1}\left(\vec{k}\right) e^{i\vec{k}\cdot\vec{r}} \, d\vec{k}.$$

Mathematica

Notations for Fourier Transforms

$$F_{0,-2\pi}\left(\vec{q}\right) = \int f(\vec{r})e^{-i2\pi\vec{q}\cdot\vec{r}}\,d\vec{r}.$$

$$f(\vec{r}) = \int F_{0,-2\pi}\left(\vec{q}\right)e^{i2\pi\vec{q}\cdot\vec{r}}\,d\vec{q}.$$

Engineering literature, usually on the 1-d case is considered.

Function		
$\exp(-|a|x)$	$\dfrac{|a|}{\pi(a^2+k^2)}$	$\dfrac{2|a|}{a^2+k^2}$
$\mathrm{sgn}(x)$ $\mathrm{sgn}(x)=-1$ for $x<0$ and $\mathrm{sgn}(x)=1$ for $x>0$	$\dfrac{-i}{\pi\omega}$	$\dfrac{-2i}{\omega}$
$\mathrm{sgn}(x)\exp(-|a|x)$	$\dfrac{-ik}{\pi(a^2+k^2)}$	$\dfrac{-i2k}{a^2+k^2}$
$H(x)\exp(-|a|x)$	$\dfrac{|a|-ik}{2\pi(a^2+k^2)}$	$\dfrac{|a|-ik}{a^2+k^2}$
$\sqcap(x)=H\left(x+\tfrac{1}{2}\right)H\left(\tfrac{1}{2}-x\right)$ Square pulse: height = 1, width = 1, centered at $x=0$.	$\dfrac{\sin(k/2)}{\pi k}$	$\dfrac{2\sin(k/2)}{k}$
$\sqcap\left(\dfrac{x-x_0}{a}\right)$ Square pulse: height = 1, width = a, centered at x_0.	$\dfrac{\sin(ka/2)}{\pi k}\exp(-ikx_0)$	$\dfrac{2\sin(ka/2)}{k}\exp(-ikx_0)$
$\exp\left(i\vec{k}_0\cdot\vec{r}\right)$ Plane wave	$\delta\left(\vec{k}-\vec{k}_0\right)$	$(2\pi)^d\delta\left(\vec{k}-\vec{k}_0\right)$
1	$\delta(k)$	$2\pi\delta(k)$
$\delta(x)$	$\dfrac{1}{2\pi}$	1
$\delta\left(\dfrac{\vec{r}-\vec{r}_0}{a}\right)$	$\left(\dfrac{a}{2\pi}\right)^d\exp\left(-i\vec{k}\cdot\vec{r}_0\right)$	$a^d\exp\left(-i\vec{k}\cdot\vec{r}_0\right)$
$\exp\left(-\dfrac{|\vec{r}-\vec{r}_0|^2}{a^2}\right)$	$\left(\dfrac{a}{2\sqrt{\pi}}\right)^d\exp\left(-\dfrac{a^2k^2}{4}\right)\exp\left(-i\vec{k}\cdot\vec{r}_0\right)$	$(a\sqrt{\pi})^d\exp\left(-\dfrac{a^2k^2}{4}\right)\exp\left(-i\vec{k}\cdot\vec{r}_0\right)$
$H(R-|\vec{r}-\vec{r}_0|)$ Disc of radius R centered at $\vec{r}_0$, $\vec{r}\in\mathbb{R}^2$	$\dfrac{R}{2\pi|\vec{k}|}J_1(|\vec{k}|R)\exp(-i\vec{k}\cdot\vec{r}_0)$	$\dfrac{2\pi R}{|\vec{k}|}J_1(|\vec{k}|R)\exp(-i\vec{k}\cdot\vec{r}_0)$
$H(R-|\vec{r}-\vec{r}_0|)$ Sphere of radius R centered at $\vec{r}_0$, $\vec{r}\in\mathbb{R}^3$	$\dfrac{1}{(2\pi)^3|\vec{k}|^3}\left(\sin(|\vec{k}|R)-|\vec{k}|R\cos(|\vec{k}|R)\right)\exp(-i\vec{k}\cdot\vec{r}_0)$	$\dfrac{4\pi}{|\vec{k}|^3}\left(\sin(|\vec{k}|R)-|\vec{k}|R\cos(|\vec{k}|R)\right)\exp(-i\vec{k}\cdot\vec{r}_0)$

Here $H(x)$ is the Heaviside step function, $\delta(x)$ is the Dirac delta function, $J_1(x)$ is the first order Bessel function of the first kind, and d is the number of dimensions.

Calculate a Fourier transform numerically.

http://lamp.tu-graz.ac.at/~hadley/ss1/crystaldiffraction/ft/ft.php

Properties of Fourier transforms

Linearity and superposition

$\mathcal{F}\{\alpha f(\vec{r}) + \beta g(\vec{r})\} = \alpha \mathcal{F}\{f(\vec{r})\} + \beta \mathcal{F}\{g(\vec{r})\}$ where α and β are any constants.

Similarity

$\mathcal{F}\left\{f\left(\frac{\vec{r}}{a}\right)\right\} = |a|^d \mathcal{F}\{f(\vec{r})\}.$

Shift

$\mathcal{F}\{f(\vec{r} - \vec{r}_0)\} = \mathcal{F}\{f(\vec{r})\} \exp\left(-i\vec{k} \cdot \vec{r}_0\right).$

Convolution (Faltung)

$$f(\vec{r}) * g(\vec{r}) = \int f(\vec{r}') g(\vec{r} - \vec{r}') d\vec{r}$$

Notation [-1,-1]: $\mathcal{F}\{fg\} = \mathcal{F}\{f\} * \mathcal{F}\{g\}, \quad \mathcal{F}^{-1}\{FG\} = \frac{1}{2\pi} \mathcal{F}^{-1}\{F\} * \mathcal{F}^{-1}\{G\}.$
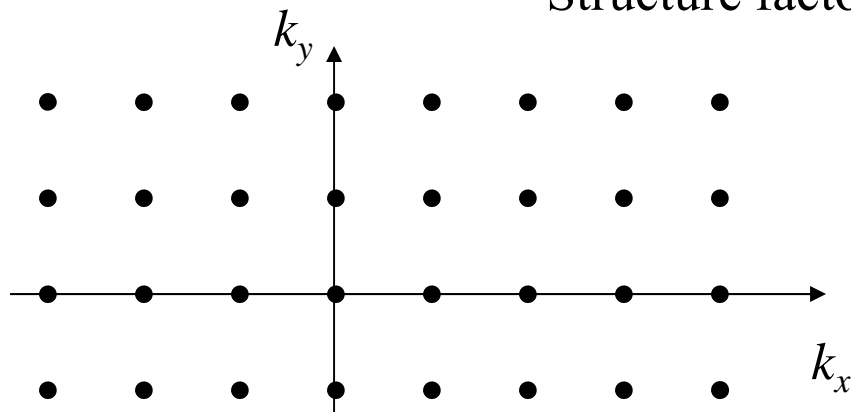
Notation [1,-1]: $\mathcal{F}\{fg\} = \frac{1}{2\pi} \mathcal{F}\{f\} * \mathcal{F}\{g\}, \quad \mathcal{F}^{-1}\{FG\} = \mathcal{F}^{-1}\{F\} * \mathcal{F}^{-1}\{G\}.$

Notation [0,-1]: $\mathcal{F}\{fg\} = \frac{1}{\sqrt{2\pi}} \mathcal{F}\{f\} * \mathcal{F}\{g\}, \quad \mathcal{F}^{-1}\{FG\} = \frac{1}{\sqrt{2\pi}} \mathcal{F}^{-1}\{F\} * \mathcal{F}^{-1}\{G\}.$

Notation [0,-2π]: $\mathcal{F}\{fg\} = \mathcal{F}\{f\} * \mathcal{F}\{g\}, \quad \mathcal{F}^{-1}\{FG\} = \mathcal{F}^{-1}\{F\} * \mathcal{F}^{-1}\{G\}.$

Reciprocal lattice (Reziprokes Gitter)

Any periodic function can be written as a Fourier series

$$f(\vec{r}) = \sum_{\vec{G}} f_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}$$
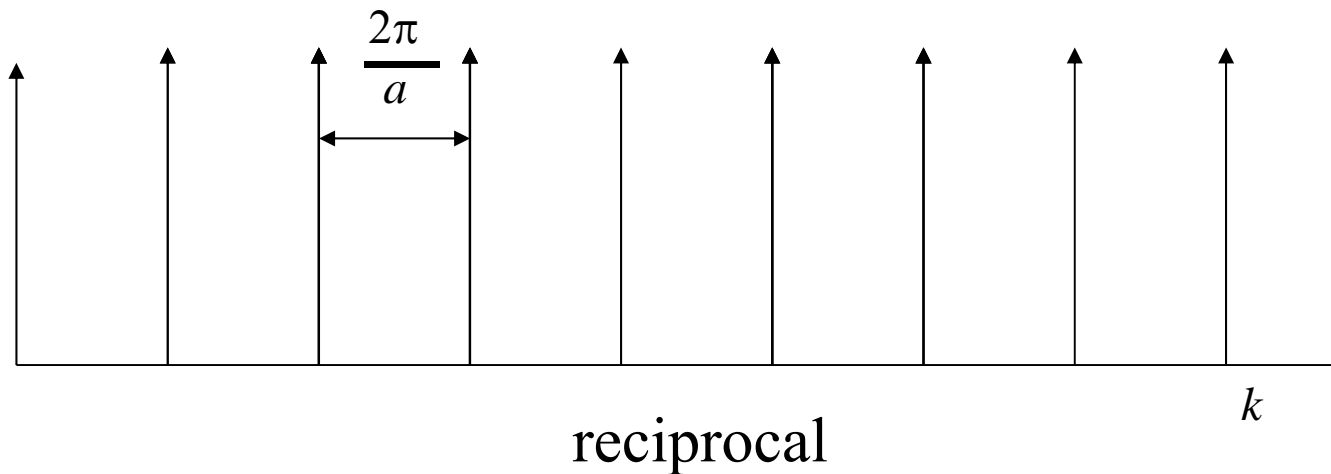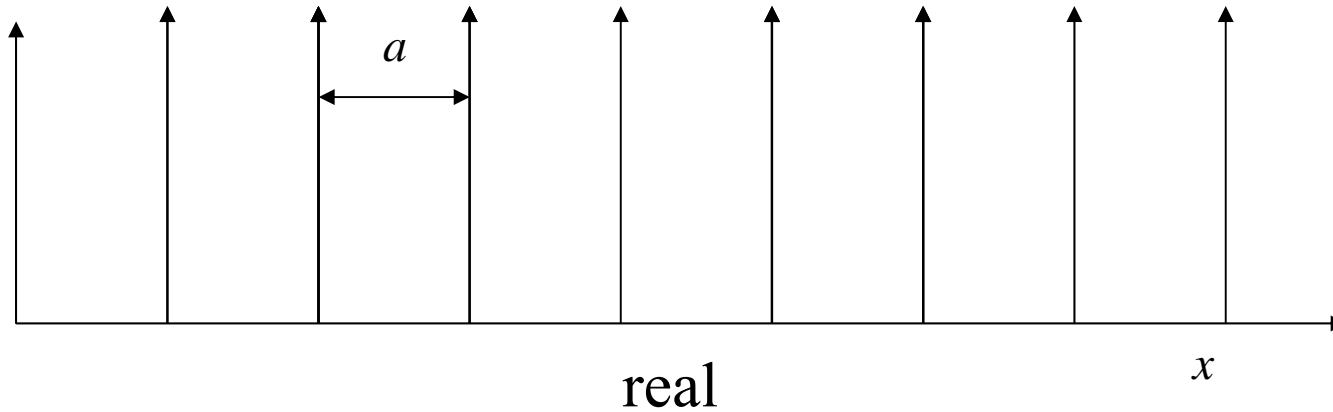
Reciprocal lattice vector G

Structure factor

$$\vec{G} = \upsilon_1 \vec{b}_1 + \upsilon_2 \vec{b}_2 + \upsilon_3 \vec{b}_3$$

v_i integers

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}, \qquad \vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}, \qquad \vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$
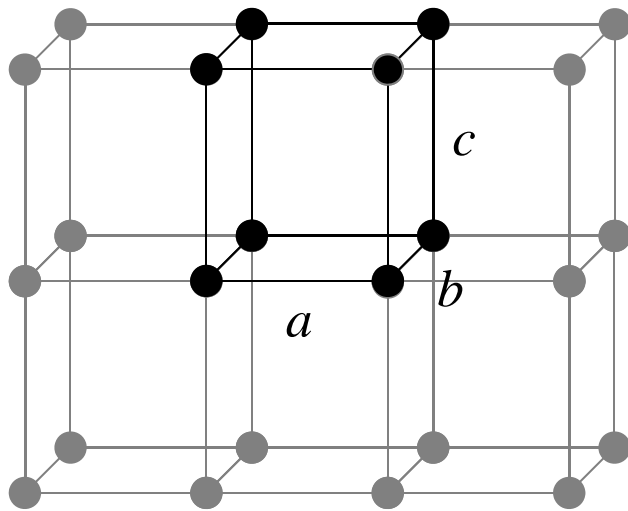
$$\vec{a}_i \cdot \vec{b}_j = 2\pi \delta_{ij}$$

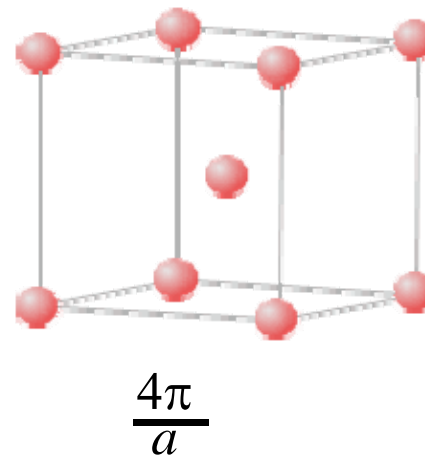# Bravais lattice and reciprocal lattice in 1-D

a

real

x
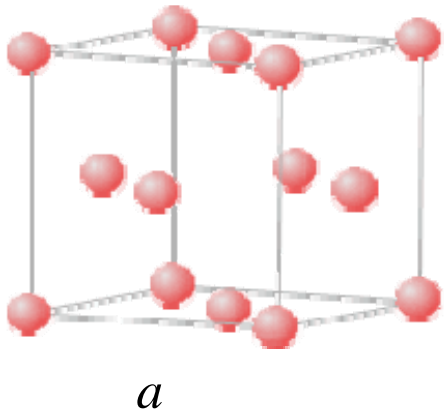
$\dfrac{2\pi}{a}$

reciprocal

k

$$\cos\left(\frac{2\pi p x}{a}\right) \Rightarrow \cos(Gx) \qquad G = p\,\frac{2\pi}{a}$$

Reciprocal lattice of an orthorhombic lattice is an orthorhombic lattice
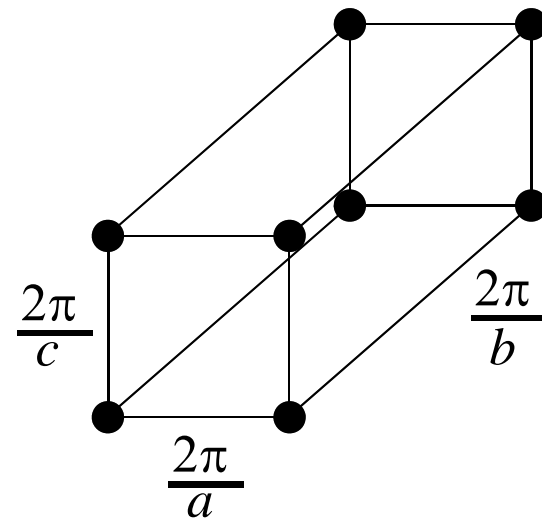
reciprocal lattice

The reciprocal lattice of an fcc lattice is a bcc lattice

a

$\dfrac{4\pi}{a}$

$$\vec{a}_1 = \frac{a}{2}\hat{x} + \frac{a}{2}\hat{y}$$

$$\vec{a}_2 = \frac{a}{2}\hat{x} + \frac{a}{2}\hat{z}$$

$$\vec{a}_3 = \frac{a}{2}\hat{y} + \frac{a}{2}\hat{z}$$

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot \left(\vec{a}_2 \times \vec{a}_3\right)}$$
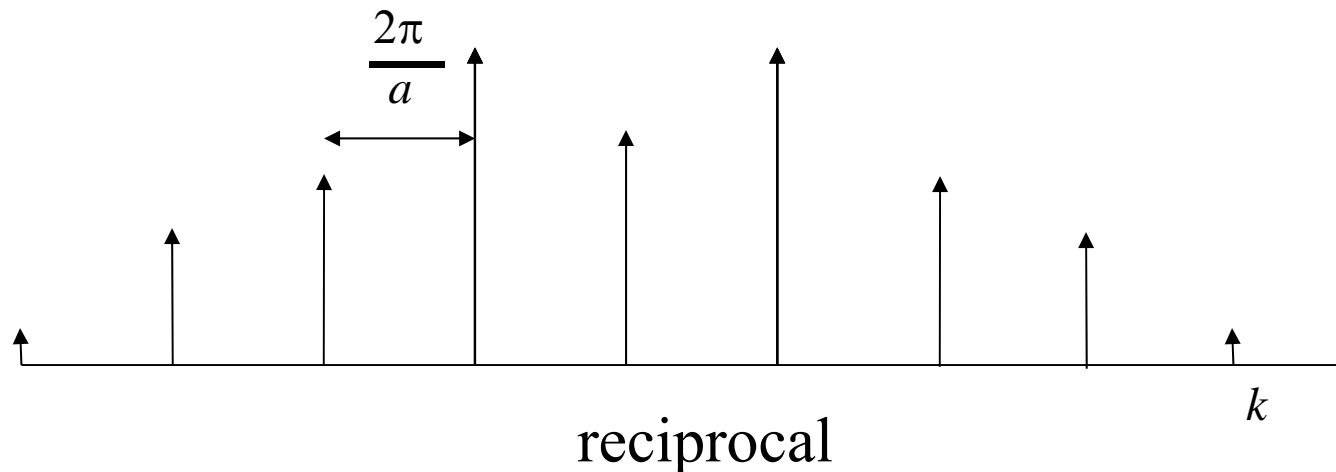
$$\vec{b}_3 = \frac{2\pi}{a}\left(\hat{x} - \hat{y} - \hat{z}\right)$$

$$\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij}$$

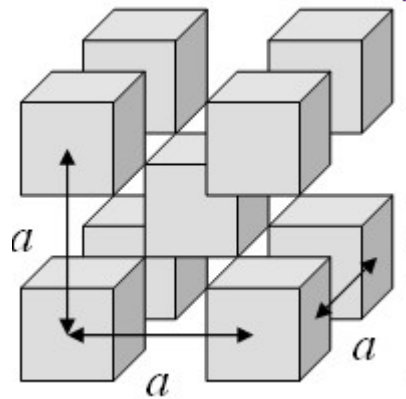# The reciprocal lattice is the Fourier transform of the real space lattice

crystal = Bravais_lattice(r) * unit_cell(r)

$\mathcal{F}$(crystal) = $\mathcal{F}$(Bravais_lattice(r))$\mathcal{F}$(unit_cell(r))

$$\frac{2\pi}{a}$$

reciprocal
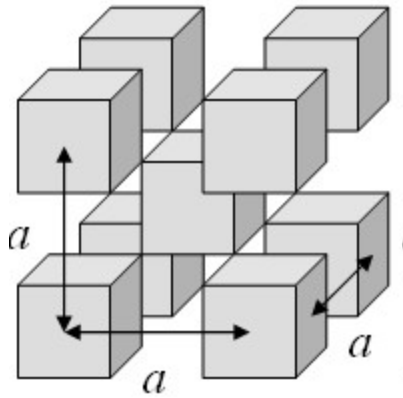
k

Cubes on a bcc lattice

$$f(\vec{r}) = \sum_{\vec{G}} f_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}$$

Multiply by $e^{-i\vec{G}'\cdot\vec{r}}$ and integrate over a primitive unit cell.

$$\int_{\text{unit cell}} f(\vec{r}) e^{-i\vec{G}\cdot\vec{r}} d^3r = f_{\vec{G}} V$$

http://lamp.tu-graz.ac.at/~hadley/ss1/crystaldiffraction/fourier.php

Cubes on a bcc lattice

$$\int_{\text{unit cell}} f(\vec{r})e^{-i\vec{G}\cdot\vec{r}} d^3r = f_{\vec{G}} V$$

V is the volume of the primitive unit cell.

$$f_{\vec{G}} = \frac{1}{V}\int f_{cell}(\vec{r})\exp\left(-i\vec{G}\cdot\vec{r}\right)d^3r$$

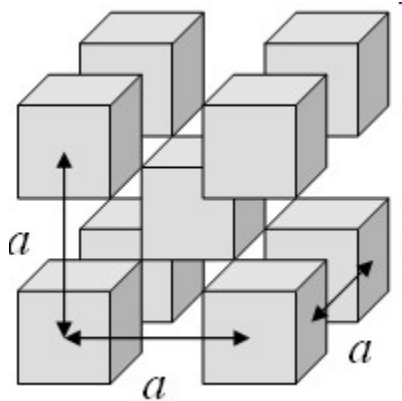f_G is the Fourier transform of f_{cell} evaluated at G.
f_{cell} is zero outside the primitive unit cell.

$$f_{\vec{G}} = \frac{1}{V}\int f_{cell}(\vec{r})\exp\left(-i\vec{G}\cdot\vec{r}\right)d^3r = \frac{2C}{a^3}\int_{-\frac{a}{4}}^{\frac{a}{4}}\int_{-\frac{a}{4}}^{\frac{a}{4}}\int_{-\frac{a}{4}}^{\frac{a}{4}}\exp(-iG_x x)\exp\left(-iG_y y\right)\exp\left(-iG_z z\right)dxdydz$$

Volume of conventional u.c. a^3. Two Bravais points per conventional u.c.

Cubes on a bcc lattice

$$\int_{\frac{-a}{4}}^{\frac{a}{4}} \exp\left(-iG_x x\right) dx = \left.\frac{\exp\left(-iG_x x\right)}{-iG_x}\right|_{\frac{-a}{4}}^{\frac{a}{4}} = \left.\frac{\cos\left(-G_x x\right) + i\sin\left(-G_x x\right)}{-iG_x}\right|_{\frac{-a}{4}}^{\frac{a}{4}} = \frac{2\sin\left(\dfrac{G_x a}{4}\right)}{G_x}$$
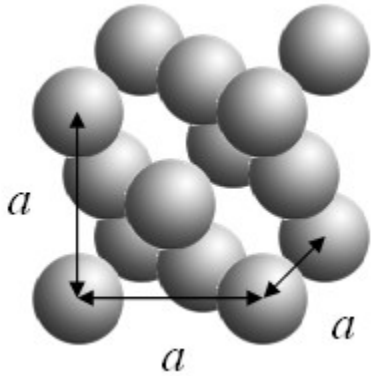

$$f_{\vec{G}} = \frac{16C \sin\left(\dfrac{G_x a}{4}\right) \sin\left(\dfrac{G_y a}{4}\right) \sin\left(\dfrac{G_z a}{4}\right)}{a^3 G_x G_y G_z}$$

The Fourier series for any rectangular cuboid with dimensions $L_x \times L_y \times L_z$ repeated on any three-dimensional Bravais lattice is:

$$f(\vec{r}) = \sum_{\vec{G}} \frac{8C \sin\left(\dfrac{G_x L_x}{2}\right) \sin\left(\dfrac{G_y L_y}{2}\right) \sin\left(\dfrac{G_z L_z}{2}\right)}{V G_x G_y G_z} \exp\left(i\vec{G} \cdot \vec{r}\right)$$

Spheres on an fcc lattice

$$f(\vec{r}) = \sum_{\vec{G}} f_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}$$

Multiply by $e^{-i\vec{G}'\cdot\vec{r}}$ and integrate over a primitive unit cell.

$$f_{\vec{G}} = \frac{1}{V}\int f_{cell}(\vec{r})\exp\left(-i\vec{G}\cdot\vec{r}\right)d^3r = \frac{C}{V}\int_{sphere}\exp\left(-i\vec{G}\cdot\vec{r}\right)d^3r.$$
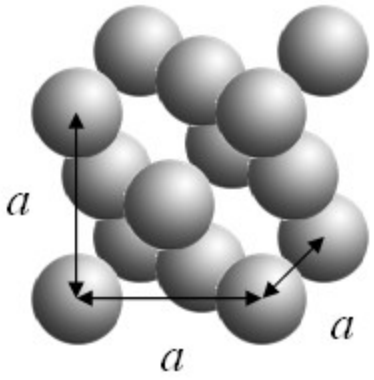
$$f_{\vec{G}} = \frac{C}{V}\int_0^R\int_0^\pi\int_{-\pi}^\pi \exp(-i\vec{G}\cdot\vec{r})r^2\sin\theta\, dr\, d\theta\, d\varphi$$

$$= \frac{C}{V}\int_0^R\int_0^\pi\int_{-\pi}^\pi \left(\cos\left(|G|r\cos\theta\right) - i\sin\left(|G|r\cos\theta\right)\right)r^2\sin\theta\, dr\, d\theta\, d\varphi$$

Integrate over φ

$$f_{\vec{G}} = \frac{2\pi C}{V}\int_0^R\int_0^\pi \left(\cos\left(|G|r\cos\theta\right) - i\sin\left(|G|r\cos\theta\right)\right)r^2\sin\theta\, dr\, d\theta$$

Spheres on an fcc lattice

$$f_{\vec{G}} = \frac{2\pi C}{V} \int\limits_0^R \int\limits_0^\pi \left(\cos\left(|G|r\cos\theta\right) - i\sin\left(|G|r\cos\theta\right) \right) r^2 \sin\theta \, dr \, d\theta$$

Both terms are perfect differentials

$$\frac{d}{d\theta}\cos\left(|G|r\cos\theta\right) = |G|r\sin\left(|G|r\cos\theta\right)\sin\theta \qquad \text{and}$$

$$\frac{d}{d\theta}\sin\left(|G|r\cos\theta\right) = -|G|r\cos\left(|G|r\cos\theta\right)\sin\theta,$$

Integrate over θ:
$$f_{\vec{G}} = \frac{2\pi C}{V} \int\limits_0^R \left. \left(-\sin\left(|G|r\cos\theta\right) - i\cos\left(|G|r\cos\theta\right) \right) \right|_0^\pi r \, dr$$

$$f_{\vec{G}} = \frac{4\pi C}{V} \int\limits_0^R \frac{\sin\left(|G|r\right)}{|G|} r \, dr$$
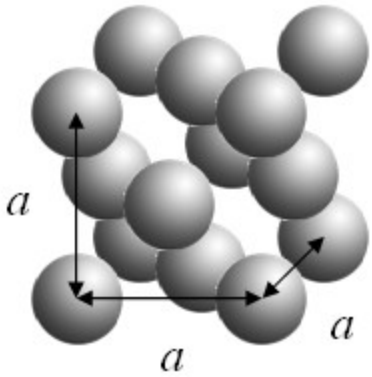
Spheres on any lattice

$$f_{\vec{G}} = \frac{4\pi C}{V} \int_0^R \frac{\sin(|G|r)}{|G|r} r^2 dr$$

Integrate over r

$$f_G = \frac{4\pi C}{V|G|^3} \left(\sin(|G|R) - |G|R\cos(|G|R) \right).$$

The Fourier series for non-overlapping spheres on any three-dimensional Bravais lattice is:

$$f(\vec{r}) = \frac{4\pi C}{V} \sum_{\vec{G}} \frac{\sin(|G|R) - |G|R\cos(|G|R)}{|G|^3} \exp(i\vec{G}\cdot\vec{r}).$$

Molecular orbital potential

$$U(\vec{r}) = \frac{-Ze^2}{4\pi\varepsilon_0} \sum_{r_j} \frac{1}{\left|\vec{r} - \vec{r}_j\right|}$$

position of atom j

The Fourier series for any molecular orbital potential is:

$$U(\vec{r}) = \frac{-Ze^2}{V\varepsilon_0} \sum_{\vec{G}} \frac{\exp\left(i\vec{G}\cdot\vec{r}\right)}{\left|G\right|^2}$$

Volume of the primitive unit cell