6.730 Physics for Solid State Applications

Lecture 7: Periodic Structures (cont.)

February 18, 2004

Outline

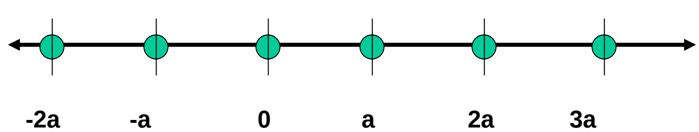
- Review
- 2D & 3D Periodic Crystal Structures: Mathematics
- X-Ray Diffraction: Observing Reciprocal Space

Point Lattices: Bravais Lattices

Bravais lattices are point lattices that are classified topologically according to the symmetry properties under rotation and reflection, without regard to the absolute length of the unit vectors.

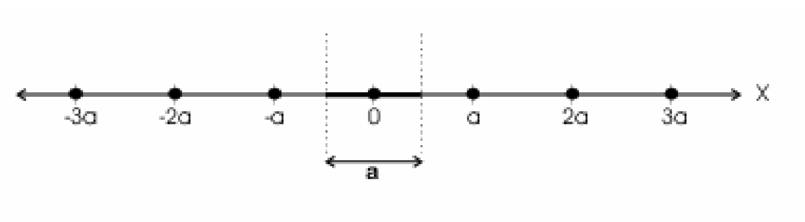
A more intuitive definition:
At every point in a Bravais lattice the "world" looks the same.

1D: Only one Bravais Lattice

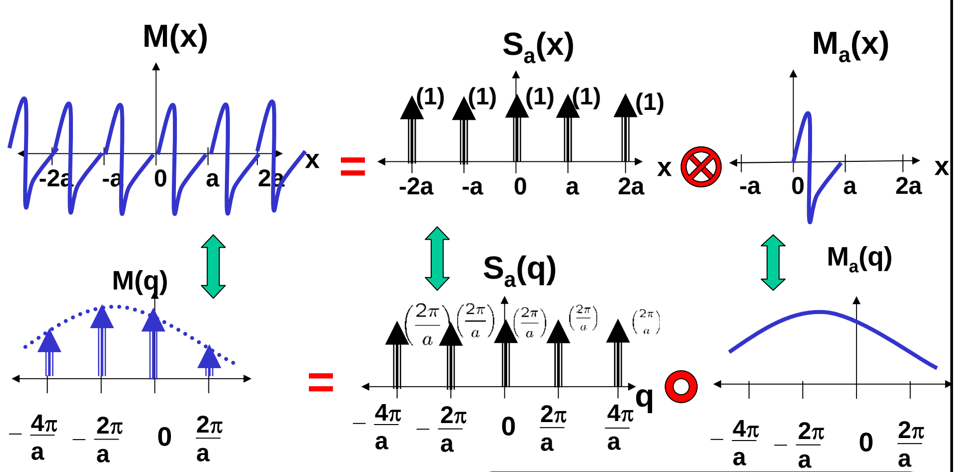


Wigner-Sietz Cell

1. Choose one point as the origin and draw lines from the origin to each of the other lattice points.
2. Bisect each of the drawn lines with planes normal to the line.
3. Mark the space about the origin bounded by the first set of planes that are encountered. The bounded space is the Wigner-Sietz unit cell.



1D Periodic Crystal Structures



$$M(x) = \sum_{m=-\infty}^{\infty} M[K_m] e^{iK_m x}$$

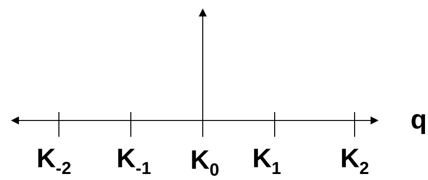
$$M(q) = 2\pi \sum_{m=-\infty}^{\infty} M[K_m]\delta(q - K_m)$$

$$M[K_m] = \frac{1}{a}\int_0^a M(x) e^{-iK_m x} dx$$

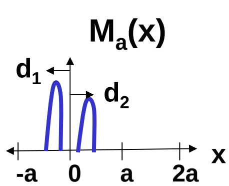
Reciprocal Lattice Vectors

1. The Fourier transform in q-space is also a lattice
2. This lattice is called the **reciprocal lattice**
3. The lattice constant is $2\pi / a$
4. The **Reciprocal Lattice Vectors** are

$$K_m = m\frac{2\pi}{a} \qquad \text{where} \qquad m = 0, \pm 1, \pm 2$$

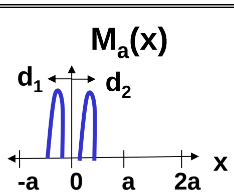


Atomic Form Factors & Geometrical Structure Factors



Different Atoms (1) and (2)

$$\underbrace{M_a(K_m)}_{\text{Structure Factor}} = \underbrace{f_a^{(1)}(K_m)}_{\text{Atomic Form Factor}} e^{-iK_m d_1} + f_a^{(2)}(K_m)\, e^{-iK_m d_2}$$



Same atoms at d_1 and d_2

$$M_a(K_m) = \underbrace{f_a(K_m)}_{\text{Atomic Form Factor}} \cdot \underbrace{\left[e^{iK_m d_1} + e^{iK_m d_2}\right]}_{\text{Geometrical Structure Factor } S(K_m)}$$

2D & 3D Crystal Structures

$$\mathbf{R}_i = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$$

A. Orthogonal Primitive Lattices Vectors

Then choose primitive lattice vectors along the x, y and z axes

$$\mathbf{R}_i = n_1 a_1\hat{\mathbf{x}} + n_2 a_2\hat{\mathbf{y}} + n_3 a_3\hat{\mathbf{z}}$$

The 3D sampling function is

$$S_p(\mathbf{r}) = \sum_{i=-\infty}^{+\infty} \delta^3(\mathbf{r} - \mathbf{R}_i)$$

Fourier Transform of Sampling Function

$$\begin{aligned} S_p(\mathbf{q}) &= \int\int\int \left(\sum_{i=-\infty}^{+\infty} \delta^3(\mathbf{r} - \mathbf{R}_i)\right) e^{-i\mathbf{q}\cdot\mathbf{r}} d^3\mathbf{r} \\ &= \int\int\int \sum_{n_1}\sum_{n_2}\sum_{n_3} \delta(x - n_1 a_1)\delta(y - n_2 a_2)\delta(z - n_3 a_3) \cdot e^{-iq_x x} e^{-iq_y y} e^{-iq_z z} dx dy dz \\ &= \left(\int_{-\infty}^{\infty} \sum_{n_1} \delta(x - n_1 a_1) e^{-iq_x x} dx\right) \left(\int_{-\infty}^{\infty} \sum_{n_2} \delta(y - n_2 a_2) e^{-iq_y y} dy\right) \cdot \\ &\quad \left(\int_{-\infty}^{\infty} \sum_{n_3} \delta(z - n_3 a_3) e^{-iq_z z} dz\right) \end{aligned}$$

This is a product of three independent 1D sampling functions

Reciprocal Lattice

Therefore,

$$\begin{aligned} S_p(\mathbf{q}) &= \left[\frac{2\pi}{a_1}\sum_{m_1=-\infty}^{+\infty}\delta(q_x - m_1\frac{2\pi}{a_1})\right]\left[\frac{2\pi}{a_2}\sum_{m_2=-\infty}^{+\infty}\delta(q_y - m_2\frac{2\pi}{a_2})\right]\left[\frac{2\pi}{a_3}\sum_{m_3=-\infty}^{+\infty}\delta(q_x - m_3\frac{2\pi}{a_3})\right] \\ &= \frac{(2\pi)^3}{\mathbf{a}_1\cdot(\mathbf{a}_2\times\mathbf{a}_3)}\sum_{i=-\infty}^{+\infty}\delta^3(\mathbf{q}-\mathbf{K}_i) \end{aligned}$$

The reciprocal lattice vectors are

$$\mathrm{K} = m_1\frac{2\pi}{a_1}\hat{\mathbf{x}} + m_2\frac{2\pi}{a_2}\hat{\mathbf{y}} + m_3\frac{2\pi}{a_3}\hat{\mathbf{z}}$$

with primitive lattice vectors

$$\mathrm{b}_1 = \frac{2\pi}{a_1}\mathbf{i}_x \quad \mathrm{b}_2 = \frac{2\pi}{a_2}\mathbf{i}_y \quad \mathrm{b}_3 = \frac{2\pi}{a_3}\mathbf{i}_z$$

3D Periodic Functions

A periodic function

$$M(\mathbf{r}) = M(\mathbf{r}+\mathbf{R}_i)$$

can be written as a convolution

$$M(\mathbf{r}) = M_p(\mathbf{r}) \otimes S_p(\mathbf{r})$$

when $M_p(\mathbf{r}) = \begin{cases} M(\mathbf{r}) & \mathbf{r} \text{ confined to a primitive unit cell} \\ 0 & \text{otherwise} \end{cases}$

and

$$S_p(\mathbf{r}) = \sum_{i=-\infty}^{\infty}\delta^3(\mathbf{r}-\mathbf{R}_i)$$

Reciprocal Space Representation

The convolution in real space becomes a product in reciprocal space

$$M(\mathbf{q}) = M_p(\mathbf{q}) S_p(\mathbf{q})$$

since S(k) is a series of delta functions at the reciprocal lattice vectors, Mp(k) only needs to be evaluated at reciprocal lattice vectors:

$$\begin{aligned} M_p(\mathbf{K}) &= \int_{-\infty}^{\infty} M_p(\mathbf{r}) e^{-i\mathbf{K}\cdot\mathbf{r}} d^3\mathbf{r} \\ &= \int_{\mathrm{PC}} M(\mathbf{r}) e^{-i\mathbf{K}\cdot\mathbf{r}} d^3\mathbf{r}\,. \end{aligned}$$

Here PC mean to integrate over one primitive cell, such as the Wigner-Seitz cell

Therefore, M(q) is crystal structure in q-space

$$M(\mathbf{q}) = \sum_i \frac{(2\pi)^3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} M_p(\mathbf{K}_i)\, \delta^3(\mathbf{q} - \mathbf{K}_i)$$

Generalized Fourier Transform

$$\begin{aligned} M(\mathbf{r}) &= \int_{-\infty}^{\infty} M(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}} \frac{d^3\mathbf{q}}{(2\pi)^3} \\ &= \int_{-\infty}^{\infty} \sum_i \frac{(2\pi)^3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} M_p(\mathbf{K}_i) \delta^3(\mathbf{q} - \mathbf{K}_i) e^{i\mathbf{q}\cdot\mathbf{r}} \frac{d^3\mathbf{q}}{(2\pi)^3} \\ &= \sum_i \frac{1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} M_p(\mathbf{K}_i) e^{i\mathbf{K}_i\cdot\mathbf{r}} \end{aligned}$$

Therefore this is a generalized Fourier Transform in 2D and 3D

$$M(\mathbf{r}) = \sum_i M[\mathbf{K}_i] e^{i\mathbf{K}_i\cdot\mathbf{r}}$$

with

$$M[\mathbf{K}_i] = \frac{1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \int_{PC} M(\mathbf{r}) e^{-i\mathbf{K}_i\cdot\mathbf{r}} d^3\mathbf{r}$$

Form factors and Structure Factors

$$M(\mathbf{q}) = M_p(\mathbf{q}) S_p(\mathbf{q})$$

Mp(q) is the FT of atoms in one primitive cell. Let each atom j of an n atom basis have a density function $f_a^j(r)$ and be located a position d_j. The Fourier components that are needed for Mp are

$$M_p(\mathbf{K}) = \sum_{j=1}^{n} f_a^{(j)}(\mathbf{K}) e^{-i\mathbf{K}\cdot\mathbf{d}_j}$$

where the atomic form factor is $f_a^j(K)$.

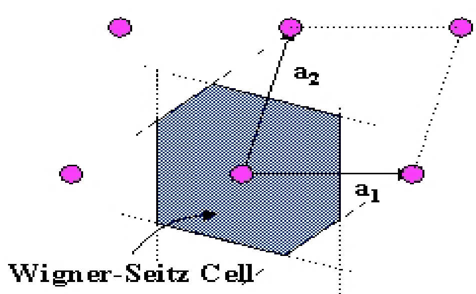
If the basis consist of all the same type of atoms then,

$$M_p(\mathbf{K}) = \underbrace{f_p(\mathbf{K})}_{\text{Atomic form factor}} \underbrace{\sum_{j=1}^{n} e^{-i\mathbf{K}\cdot\mathbf{d}_j}}_{\text{Geometrical Structure Factor}}$$

Atomic form factor

Geometrical Structure Factor

Oblique Primitive Lattice Vectors



$$\mathbf{a}_1 \cdot \mathbf{a}_2 \neq 0$$

Periodic functions with oblique lattice vectors

Periodic function $M(\mathbf{r}) = M(\mathbf{r} + \mathbf{R}_i)$

$$M(\mathbf{r}) = \int_{-\infty}^{\infty} M(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}} \frac{d^3\mathbf{q}}{(2\pi)^3}$$

$$\begin{aligned} M(\mathbf{r}+\mathbf{R}_i) &= \int_{-\infty}^{\infty} M(\mathbf{q}) e^{i\mathbf{q}\cdot(\mathbf{r}+\mathbf{R}_i)} \frac{d^3\mathbf{q}}{(2\pi)^3} \\ &= \int_{-\infty}^{\infty} e^{i\mathbf{q}\cdot\mathbf{R}_i} M(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}} \frac{d^3\mathbf{q}}{(2\pi)^3}\,. \end{aligned}$$

Therefore need to find a set {K_i} of all possible vectors q such that

$$e^{i\mathbf{K}_j\cdot\mathbf{R}_i} = 1 \quad \Longrightarrow \quad \mathbf{K}_j \cdot \mathbf{R}_i = 2\pi(\text{integer})$$

Reciprocal Lattice Vectors for Oblique vectors

Let $\mathbf{R}_i = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$

And assume that {K_j} also forms a lattice with primitive vectors b_k

$$\mathbf{K}_j = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3$$

Then to have $\mathbf{K}_j \cdot \mathbf{R}_i = 2\pi(\text{integer})$ **we need** $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\,\delta_{i,j}$

By construction, the primitive reciprocal lattice vectors are

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

Sampling function for oblique vectors

Write all vectors in real space in terms of the a_i's and write all vectors in reciprocal space in terms of the b_j's

$$\mathbf{r} = \alpha_1 a_1 \hat{\mathbf{a}}_1 + \alpha_2 a_2 \hat{\mathbf{a}}_2 + \alpha_3 a_3 \hat{\mathbf{a}}_3$$

$$\mathbf{q} = \gamma_1 b_1 \hat{\mathbf{b}}_1 + \gamma_2 b_2 \hat{\mathbf{b}}_2 + \gamma_3 b_3 \hat{\mathbf{b}}_3$$

Then the dot product is simply

$$\mathbf{q} \cdot \mathbf{r} = 2\pi \left(\gamma_1 \alpha_1 + \gamma_2 \alpha_2 + \gamma_3 \alpha_3\right)$$

And as proven in the notes, even for the oblique vectors,

$$S_p(\mathbf{r}) = \sum_{i=-\infty}^{\infty} \delta^3(\mathbf{r} - \mathbf{R}_i) \quad \Longleftrightarrow \quad S_p(\mathbf{q}) = \frac{(2\pi)^3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \sum_i \delta^3(\mathbf{q} - \mathbf{K}_i)$$

Rectangular Lattice

The primitive lattice vectors are orthogonal in this case.

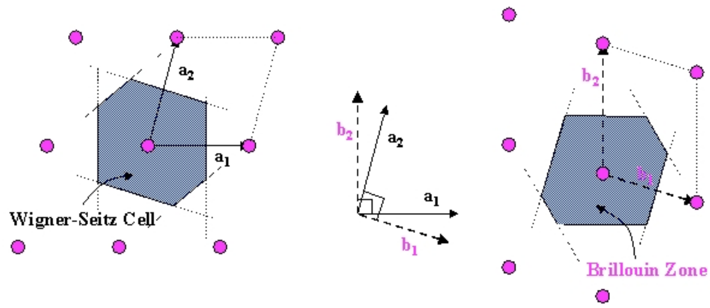
$$\mathbf{a}_1 = a_1 \mathbf{i}_x \qquad \mathbf{a}_2 = a_2 \mathbf{i}_y \qquad \mathbf{a}_3 = a_3 \mathbf{i}_z$$

The primitive reciprocal lattice vectors are also define a rectangular lattice, but rescaled inversely.

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

$$\mathbf{b}_1 = \frac{2\pi}{a_1} \mathbf{i}_x \qquad \mathbf{b}_2 = \frac{2\pi}{a_2} \mathbf{i}_y \qquad \mathbf{b}_3 = \frac{2\pi}{a_3} \mathbf{i}_z$$

Real & Reciprocal lattices in 2 D



- Two lattices associated with crystal lattice
- b_1 perpendicular to a_2 , b_2 perpendicular to a_1
- Wigner-Seitz Cell of Reciprocal lattice called the "First Brillouin Zone" or just "Brillouin Zone"

BCC ⟺ FCC

BCC in real space

$$a_1 = \frac{a}{2}(i_y + i_z - i_x) \qquad a_2 = \frac{a}{2}(i_z + i_x - i_y) \qquad a_3 = \frac{a}{2}(i_x + i_y - i_z)$$

has an FCC reciprocal lattice with

$$b_1 = \frac{2\pi}{a}(i_y + i_z) \qquad b_2 = \frac{2\pi}{a}(i_z + i_x) \qquad b_3 = \frac{2\pi}{a}(i_x + i_y)$$

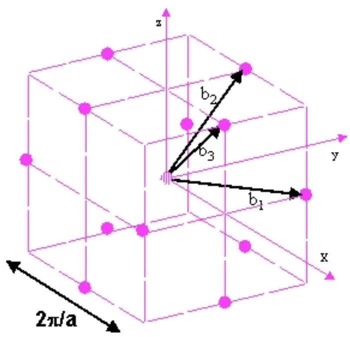
FCC in real space

$$a_1 = \frac{a}{2}(i_y + i_z) \qquad a_2 = \frac{a}{2}(i_z + i_x) \qquad a_3 = \frac{a}{2}(i_x + i_y)$$

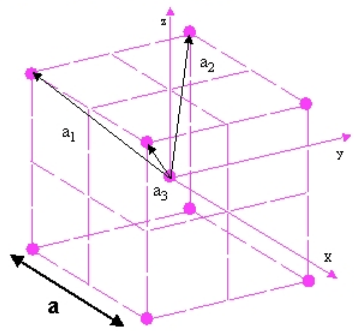
has a BCC reciprocal lattice with

$$b_1 = \frac{2\pi}{a}(i_y + i_z - i_x) \qquad b_2 = \frac{2\pi}{a}(i_z + i_x - i_y) \qquad b_3 = \frac{2\pi}{a}(i_x + i_y - i_z)$$

Face Centered - Body Centered Cubic Reciprocal to one another



Reciprocal lattice is Face Centered Cubic



Primitive vectors and the conventional cell of bcc lattice

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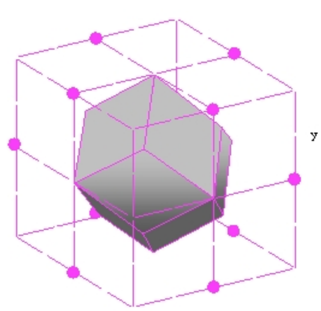
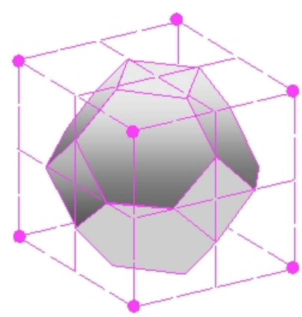
Face Centered Cubic



Wigner-Seitz Cell for Face Centered Cubic Lattice



Brillouin Zone = Wigner-Seitz Cell for Reciprocal Lattice

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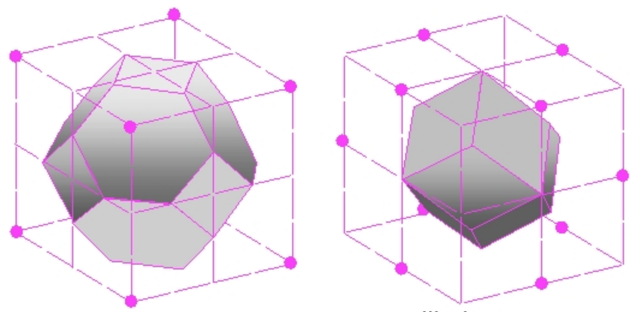
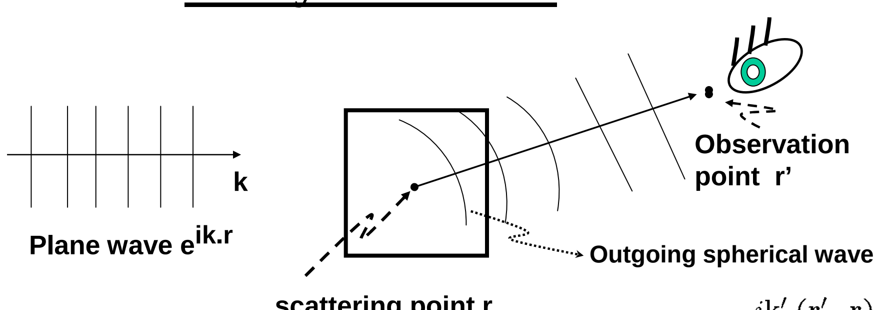
Body Centered Cubic



Wigner-Seitz Cell for
Body Centered Cubic Lattice

Brillouin Zone =
Wigner-Seitz Cell for
Reciprocal Lattice

X-Ray Diffraction



$$\phi(\mathbf{r}' - \mathbf{r}) = A \frac{e^{i\mathbf{k}' \cdot (\mathbf{r}' - \mathbf{r})}}{|\mathbf{k}' \cdot (\mathbf{r}' - \mathbf{r})|}$$

The total amplitude of the wave arriving at r' from all the r points in the sample located with density n(r) is

$$\Phi(\mathbf{r}') = \int_{\text{sample}} e^{i\mathbf{k}\cdot\mathbf{r}} n(\mathbf{r}) \phi(\mathbf{r} - \mathbf{r}')\, d^3\mathbf{r}$$

Scattering in the Far-field

In the far-field region, | r'- r| >> L and we can use the approximation

$|\mathbf{r}' - \mathbf{r}| \approx |\mathbf{r}' - \mathbf{r}_o|$ **so that**

$$\Phi(\mathbf{r}') \approx \frac{Ae^{i\mathbf{k}'\cdot\mathbf{r}'}}{|\mathbf{k}'\cdot(\mathbf{r}_o - \mathbf{r}')|}\int_{\text{all space}} n(\mathbf{r})e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}\, d^3\mathbf{r}$$

Because the density is a periodic function, $n(\mathbf{r}) = \sum_{\mathbf{K}_\ell} n[\mathbf{K}_\ell]e^{i\mathbf{K}_\ell\cdot\mathbf{r}}$

So that

$$\Phi(\mathbf{r}') = \frac{Ae^{i\mathbf{k}'\cdot\mathbf{r}_o}}{|\mathbf{k}'\cdot(\mathbf{r}_o - \mathbf{r}')|}\sum_{\mathbf{K}_\ell} n[\mathbf{K}_\ell]\,\delta^3(\mathbf{k}' - \mathbf{k} + \mathbf{K}_\ell)$$

Therefore, the amplitude is zero unless k'= k – K_j.

The Bragg Condition

Squaring the condition k'= k – Kj gives

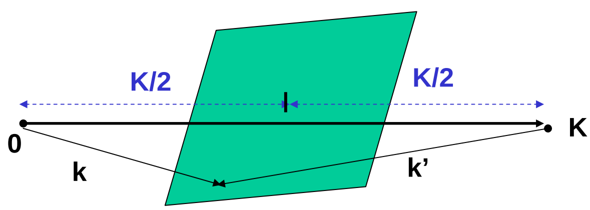
$$|\mathbf{k}'|^2 = |\mathbf{k}|^2 - 2\mathbf{k}\cdot\mathbf{K}_\ell + |\mathbf{K}_\ell|^2$$

X-ray diffraction is *elastic*, it does not change the magnitude of the wave vector, so that |k| = |k'|, which gives the Bragg Condition

$$\mathbf{k}\cdot\underbrace{\widehat{\mathbf{K}}_\ell}_{\text{unit vector}} = \frac{1}{2}|\mathbf{K}_\ell|$$

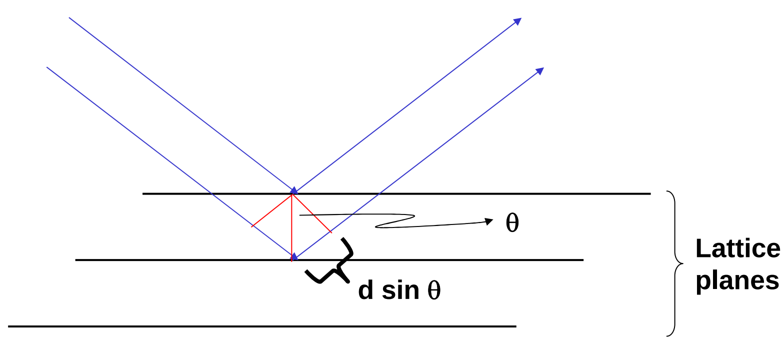
Bragg Condition

This sweeps out a plane at the perpendicular bisector of K. These are the same planes that define the Wigner-Sietz cell construction, and for this reciprocal space define the First Brillioun zone.



$$\mathbf{k} \cdot \widehat{\mathbf{K}}_\ell = \frac{1}{2}|\mathbf{K}_\ell|$$

Bragg Condition



$$\mathbf{k} \cdot \widehat{\mathbf{K}}_\ell = \frac{1}{2}|\mathbf{K}_\ell| \Rightarrow k \sin\theta = \frac{\pi}{a} m$$

Or $$\sin\theta = \frac{n\lambda}{2a}$$