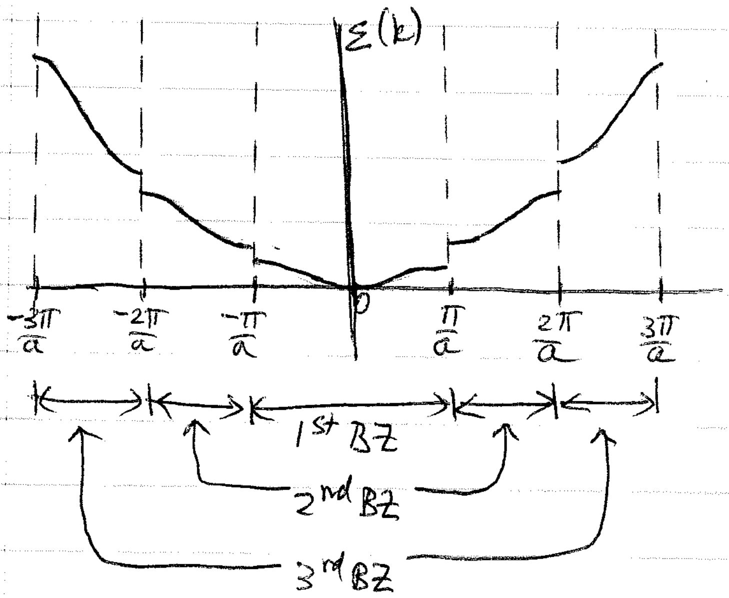
For a 1-dimension B.L. (of lattice constant a) We expect the dispersion relation to look as in the sketch below:



$R = ma$ m integers

$K = nb$, $b = \frac{2\pi}{a}$, n integers

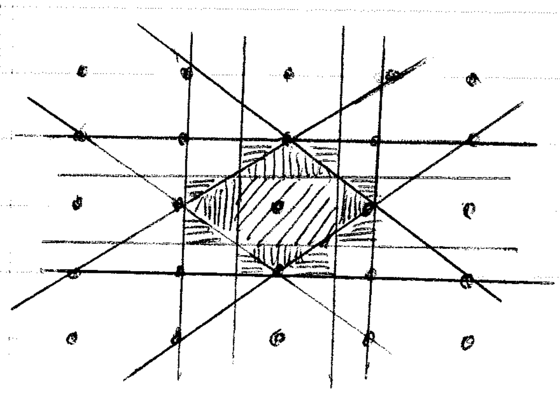
gap open in $\varepsilon(k)$ every time k crosses the boundary of a Brillouin Zone

Bragg Planes are at

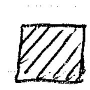
$$\frac{K}{2} = \left(\frac{2\pi n}{a}\right)\left(\frac{1}{2}\right) = \frac{\pi n}{a}$$

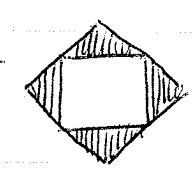
for n integer

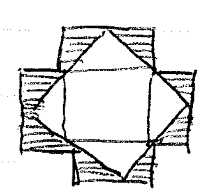
For a 2-dimensional square B.L. of lattice constant a



Bragg Planes divide k-space into Brillouin Zones

1st BZ 

2nd BZ 

3rd BZ 

Whenever $\vec{k}$ crosses the surface of a BZ, there then is a discrete jump in the energy $\varepsilon(\vec{k})$

Each BZ is a primitive cell of the R.L.

Each $\vec{k}$ in k-space can be written as $\vec{k} = \vec{q} + \vec{K}$ with $\vec{K}$ a R.L. vector and $\vec{q}$ a vector in the 1st B.Z. $\vec{q}$ is unique

$\Rightarrow$ each n^{th} BZ may be mapped onto the 1st BZ by translating its pieces by appropriate R.L. vectors $\vec{K}$

It is customary to label the eigenstates and eigenvalues by this $\vec{q}$ and by discrete index n. $\vec{q}$ is called the "crystal momentum" and n the "band index." The state $(\vec{q}, n)$ corresponds to the free electron state in the n^{th} BZ with wave vector $\vec{k} = \vec{q} + \vec{K}$ ($\vec{K}$ is the RL vector that translates $\vec{q}$ into the n^{th} BZ)

The wavefunctions $\psi_{q,n}$ and energies $\varepsilon_n(\vec{q})$ are called the <u>band structure</u>

Born - von Karmen boundary conditions and Fourier transforms for a Bravais Lattice

We generalize the idea of periodic (or Born-von Karmen) boundary conditions to electron states on a Bravais lattice.

B.L. vectors $\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$
n_1, n_2, n_3 integers.

For a BL of finite size we have $0 \leq n_i < N_i$
$N = N_1 N_2 N_3$ is total number of points in the BL.
Total volume of this finite BL is

$$V = \underbrace{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}_{\text{volume of primitive cell}} N$$

We want our electron wave functions to be periodic on such a finite BL

$$\psi(\vec{r} + N_i\vec{a}_i) = \psi(\vec{r})$$

As we saw earlier for free electrons, this imposes a constraint on the wave vectors $\vec{k}$ that can appear in the Fourier transform of $\psi(\vec{r})$.

Write $\psi(\vec{r})$ in terms of its Fourier transform

$$\psi(\vec{r}) = \sum_{k} e^{i\vec{k}\cdot\vec{r}} c_{\vec{k}}$$

Fourier coefficients for $\psi(\vec{r})$

Then

$$\psi(\vec{r} + N_i \vec{a}_i) = \sum_k e^{i\vec{k}\cdot(\vec{r}+N_i\vec{a}_i)} c_k$$

$$= e^{iN_i \vec{k}\cdot\vec{a}_i} \sum_k e^{i\vec{k}\cdot\vec{r}} c_k$$

$$= e^{iN_i \vec{k}\cdot\vec{a}_i} \psi(\vec{r})$$

$\Rightarrow$ must have $e^{iN_i \vec{k}\cdot\vec{a}_i} = 1$ for all $\vec{k}$ that appear in Fourier transform of $\psi(\vec{r})$

Write $\vec{k}$ in terms of the primitive vectors of the RL

$$\vec{k} = x_1\vec{b}_1 + x_2\vec{b}_2 + x_3\vec{b}_3$$ x_i are not in general integers

Then $e^{iN_i \vec{k}\cdot\vec{a}_i} = e^{iN_i 2\pi x_i} = 1$

$$\Rightarrow \quad x_i N_i = m_i \text{ integer}$$

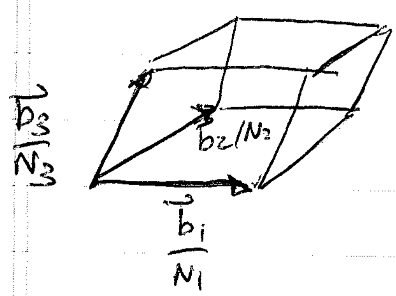
$$x_i = \frac{m_i}{N_i}$$

So the allowed wavevectors are

$$\boxed{\vec{k} = \frac{m_1}{N_1}\vec{b}_1 + \frac{m_2}{N_2}\vec{b}_2 + \frac{m_3}{N_3}\vec{b}_3},$$

where m_1, m_2, m_3 are integers.

This is the Born-von Karman boundary conditions



volume per allowed wavevector in $\vec{k}$-space is the volume of the parallelpiped formed by the vectors $\frac{\vec{b}_i}{N_i}$

$$= \frac{\vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3)}{N_1 N_2 N_3} = \frac{(2\pi)^3}{N\,(\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3))}$$

$$= \frac{(2\pi)^3}{vN} = \frac{(2\pi)^3}{V} \qquad V = vN = \text{total volume BL}$$

where $v = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$ is the volume of the primitive cell of the B.L. and $\frac{(2\pi)^3}{v}$ is the volume of the primitive cell of the R.L.

Note: volume per allowed wavevector $\frac{(2\pi)^3}{V}$ is same as we had for free electrons.

Number of allowed $\vec{k}$ values in any primitive cell of the R.L. is

$$\frac{\left[\frac{(2\pi)^3}{v}\right]}{\left[\frac{(2\pi)^3}{vN}\right]} = N \quad \text{number of ions in BL}$$

$$\boxed{\text{Number of allowed } \vec{k} \text{ values in any primitive cell of the R.L., for example the } 1^{st}\text{ BZ, is } N}$$

$\Rightarrow$ # electron states in 1^{st} BZ is $2N$ (2 from spin $= \pm 1$)
$\Rightarrow$ when valence $Z=1$, ground state occupies half the states of 1^{st} BZ

We now define the Fourier transform and its inverse that is consistent with the allowed wavevectors $\vec{k}$ of the Born - von Karmen boundary conditions

If
$$\boxed{\psi(\vec{r}) \equiv \sum_{k} e^{i\vec{k}\cdot\vec{r}} c_k}$$

sum over all $\vec{k}$ that obey Born - von Karman boundary conditions

then the inverse Fourier transform is

$$\boxed{c_k = \frac{1}{V}\int_V d^3r\, e^{-i\vec{k}\cdot\vec{r}}\,\psi(\vec{r})}$$

Proof:

$$\frac{1}{V}\int_V d^3r\, e^{-i\vec{k}\cdot\vec{r}}\,\psi(\vec{r}) = \sum_{k'} c_{k'}\,\frac{1}{V}\int d^3r\, e^{i(\vec{k}'-\vec{k})\cdot\vec{r}}$$

~~the~~ since both $\vec{k}$ and $\vec{k}'$ satisfy Born - von Karman boundary conditions, we can write

$$\vec{k}' - \vec{k} = \frac{m_1}{N_1}\vec{b}_1 + \frac{m_2}{N_2}\vec{b}_2 + \frac{m_3}{N_3}\vec{b}_3$$

with m_1, m_2, m_3 integers.

Also we can write

$$\vec{r} = x_1\vec{a}_1 + x_2\vec{a}_2 + x_3\vec{a}_3 \qquad 0 \le x_i \le N_i$$

since $\vec{r}$ is not in general a BL vector, the x_i are any real values (not necessarily integers)

Now

$$\int_V d^3r = v \int_0^{N_1} dx_1 \int_0^{N_2} dx_2 \int_0^{N_3} dx_3 \qquad \text{since } V = vN$$

$v =$ vol primitive cell

and

$$(\vec{k}' - \vec{k}) \cdot \vec{r} = 2\pi \left(\frac{m_1}{N_1} x_1 + \frac{m_2}{N_2} x_2 + \frac{m_3}{N_3} x_3 \right)$$

So

$$\frac{1}{V} \int d^3r \, e^{i(\vec{k}'-\vec{k})\cdot\vec{r}} = \frac{v}{V} \prod_{i=1}^{3} \left[\int_0^{N_i} dx_i \, e^{2\pi i \frac{m_i}{N_i} x_i} \right]$$

do for example the x_1 integral

$$\int_0^{N_1} dx_1 \, e^{2\pi i \frac{m_1 x_1}{N_1}} = \frac{e^{2\pi i m_1} - 1}{2\pi i \frac{m_1}{N_1}}$$

$$= \begin{cases} 0 & m_1 \neq 0 \quad \text{since } m_1 \text{ integer} \\ N_1 & m_1 = 0 \quad (\text{take limit } m_1 \to 0) \end{cases}$$

So

$$\frac{1}{V} \int d^3r \, e^{i(\vec{k}'-\vec{k})\cdot\vec{r}} = \frac{v N_1 N_2 N_3}{V} \delta_{k',k}$$

$$= \delta_{k',k}$$

zero unless $\vec{k} = \vec{k}'$

So $\displaystyle\sum_{k'} C_{k'} \frac{1}{V} \int d^3r \, e^{i(\vec{k}'-\vec{k})\cdot\vec{r}} = \sum_{k'} C_{k'} \delta_{k',k} = C_k$

Bloch's Theorem

Now we prove Bloch's theorem by substituting the ~~Fourier~~ transform in the Schrodinger Equ.

$$-\frac{\hbar^2}{2m}\nabla^2\psi + U(\vec{r})\psi = \varepsilon\psi$$

where $U(\vec{r})$ is the ionic potential
and ε is the eigenvalue = electron energy

Substitute in the Fourier transforms

$$\psi(\vec{r}) = \sum_k e^{i\vec{k}\cdot\vec{r}} c_k$$

$$U(\vec{r}) = \sum_{k'} e^{i\vec{k}'\cdot\vec{r}} U_{k'}$$

to get

$$\sum_k e^{i\vec{k}\cdot\vec{r}} \frac{\hbar^2 k^2}{2m} c_k + \sum_{k''}\sum_{k'} e^{i(\vec{k}''+\vec{k}')\cdot\vec{r}} U_{k'} c_{k''}$$

$$= \varepsilon \sum_k e^{i\vec{k}\cdot\vec{r}} c_k$$

Now ~~sta~~ transform summation variable in the 2nd term to $\vec{k} = \vec{k}'' + \vec{k}'$ so $\vec{k}'' = \vec{k} - \vec{k}'$

$$\Rightarrow \sum_k e^{i\vec{k}\cdot\vec{r}} \left[\left(\frac{\hbar^2 k^2}{2m} - \varepsilon\right) c_k + \sum_{k'} U_{k'} c_{k-k'} \right] = 0$$

write $\varepsilon_k^0 = \frac{\hbar^2 k^2}{2m}$

$$\Rightarrow \varepsilon_k^0 c_k + \sum_{k'} U_{k'} c_{k-k'} = \varepsilon c_k$$

Now the ionic potential $U(\vec{r})$ is periodic on the Bravais lattice, ie

$$U(\vec{r}+\vec{R}) = U(\vec{r}) \quad \text{for all } \vec{R} \text{ in BL}$$

$\Rightarrow$ the only wave vectors $\vec{k}$ that appear in its Fourier transform are the wavevectors $\{\vec{K}\}$ of the reciprocal lattice.

$$U(\vec{r}+\vec{R}) = \sum_k e^{ik\cdot(\vec{r}+\vec{R})} U_k = \sum_k e^{i\vec{k}\cdot\vec{R}} e^{i\vec{k}\cdot\vec{r}} U_k$$

$$U(\vec{r}) = \sum_k e^{i\vec{k}\cdot\vec{r}} U_k$$

these can be equal only if $e^{i\vec{k}\cdot\vec{R}} = 1$ for any $\vec{R}$ in BL

$\Rightarrow$ $\vec{k}$ must be a $\vec{K}$ in the R.L.

So the sum on $\vec{k}'$ in above becomes a sum on $\vec{K}$

$$\Rightarrow \boxed{\varepsilon_k^0 c_k + \sum_K U_K c_{k-K} = \varepsilon c_k}$$

note: $U_K = \frac{1}{V} \int_V d^3r \, e^{-i\vec{K}\cdot\vec{r}} U(\vec{r})$

$$= \frac{1}{v} \int_C d^3r \, e^{-i\vec{K}\cdot\vec{r}} U(\vec{r})$$

where C is any primitive cell of the B.L. This follows from fact that $U(\vec{r})$ is periodic on the BL