Protein Structure Determination

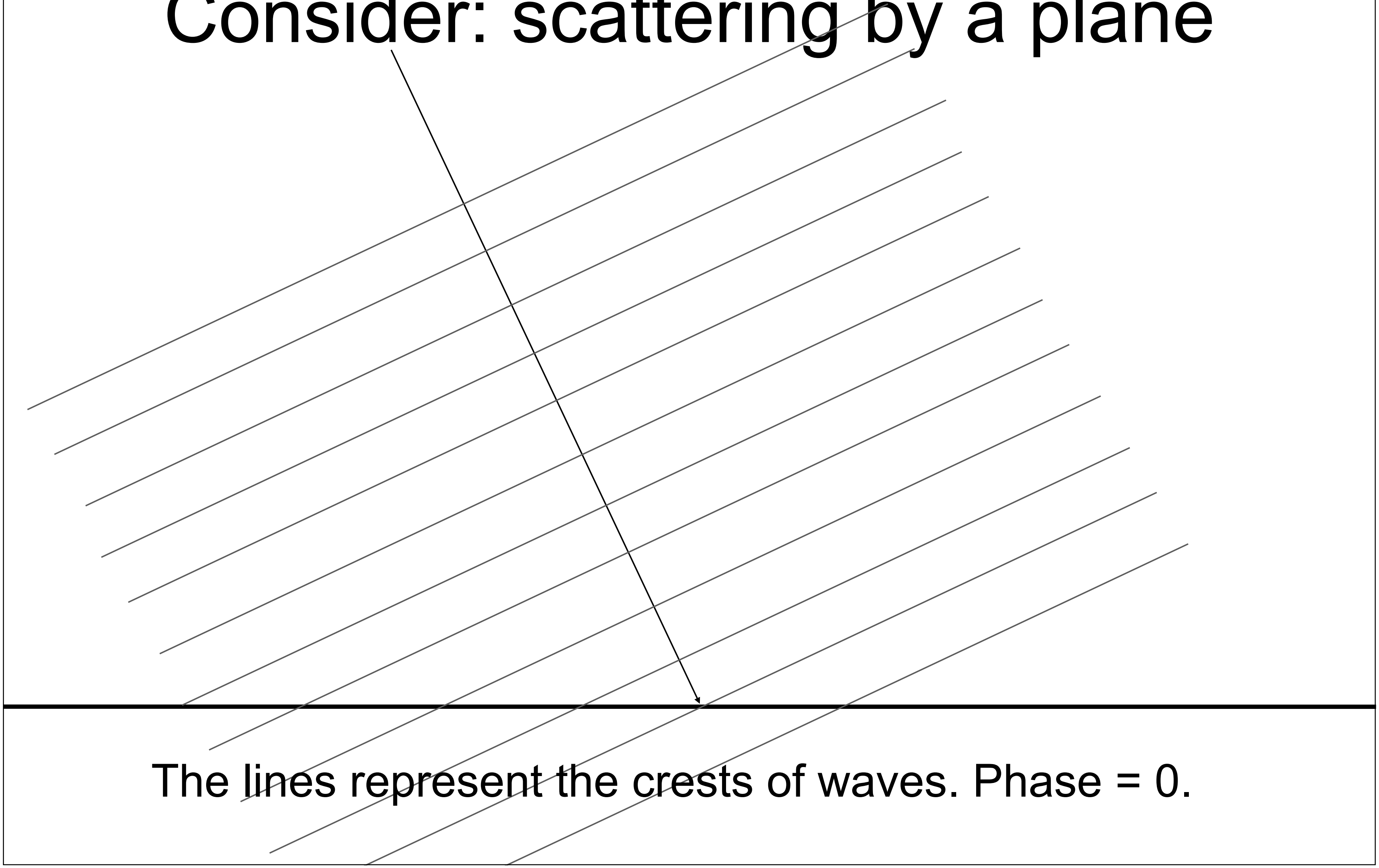
Lecture 3:

Bragg's Law
Diffraction

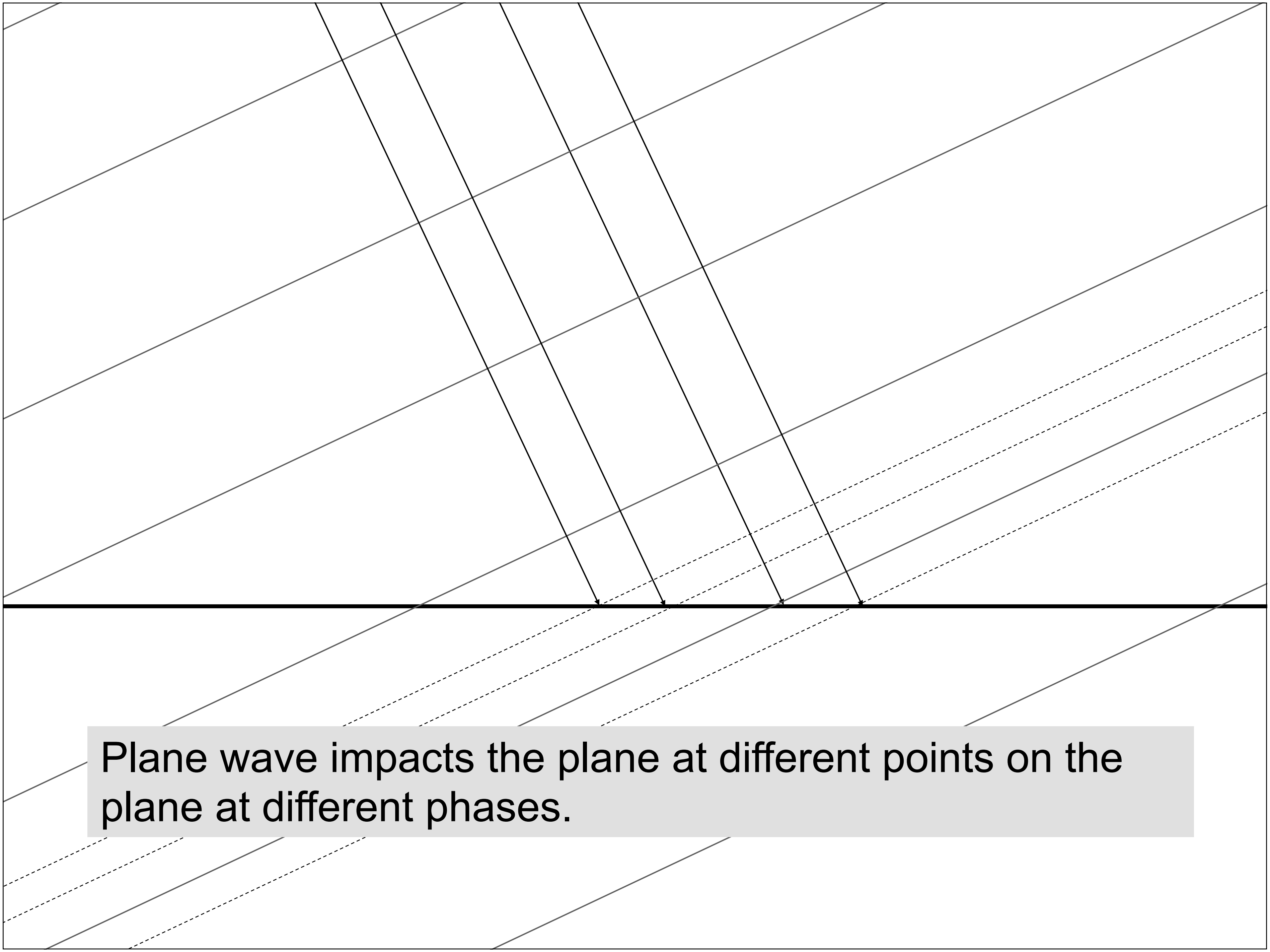
Reflecting on mirrors

Why does light scatter at only one angle from a smooth surface?

Consider: scattering by a plane



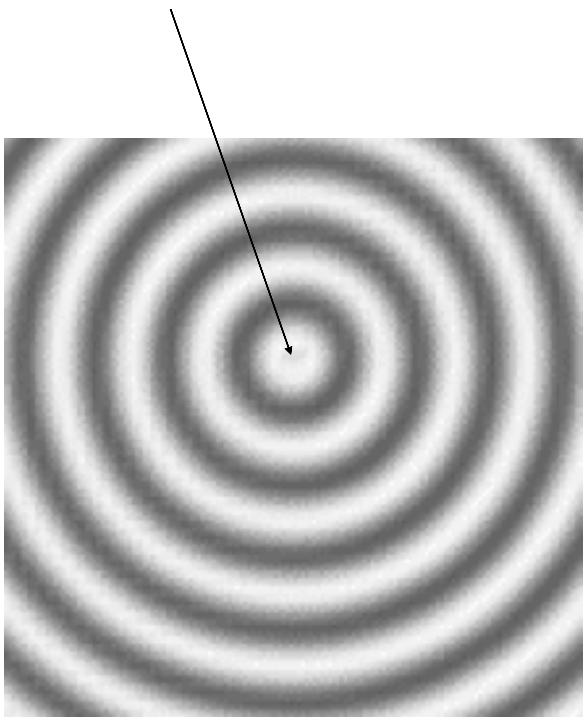
The lines represent the crests of waves. Phase = 0.



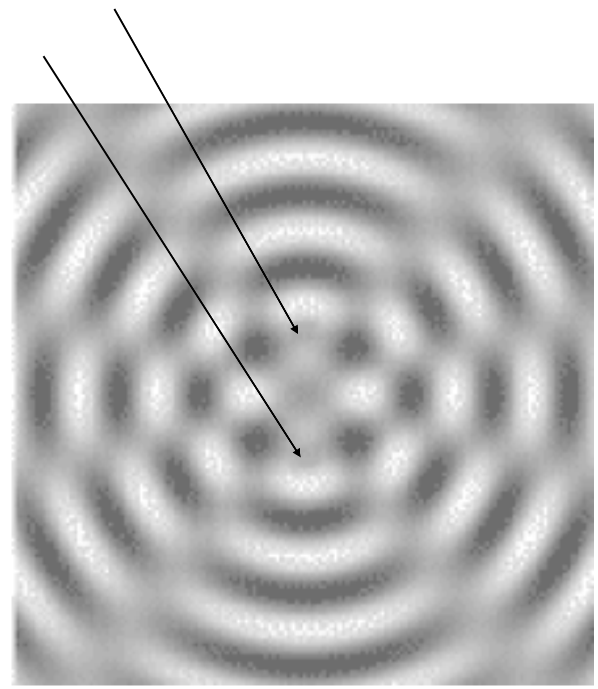
Plane wave impacts the plane at different points on the plane at different phases.

Scatter from a point initiates a spherical wave

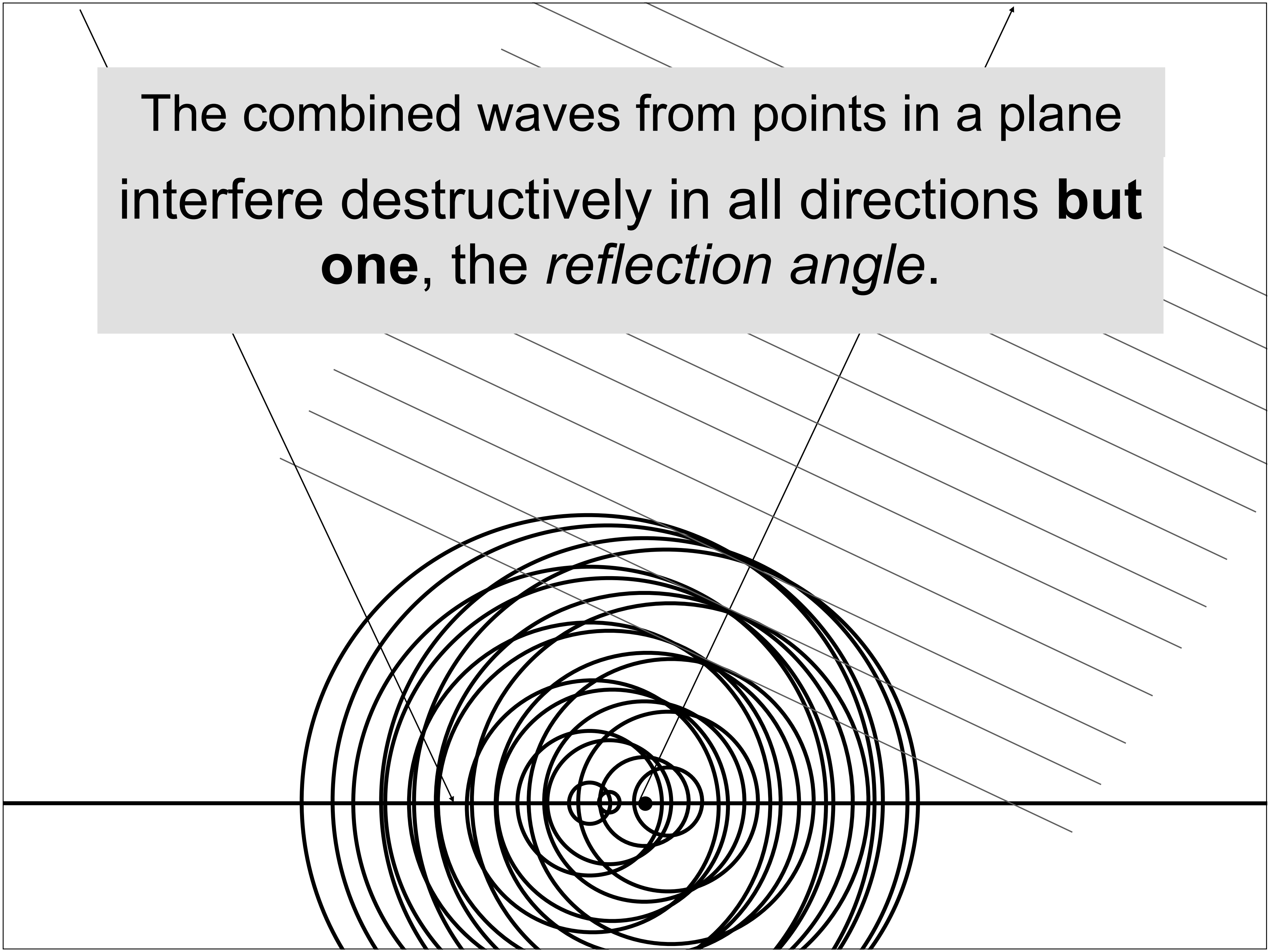
one point



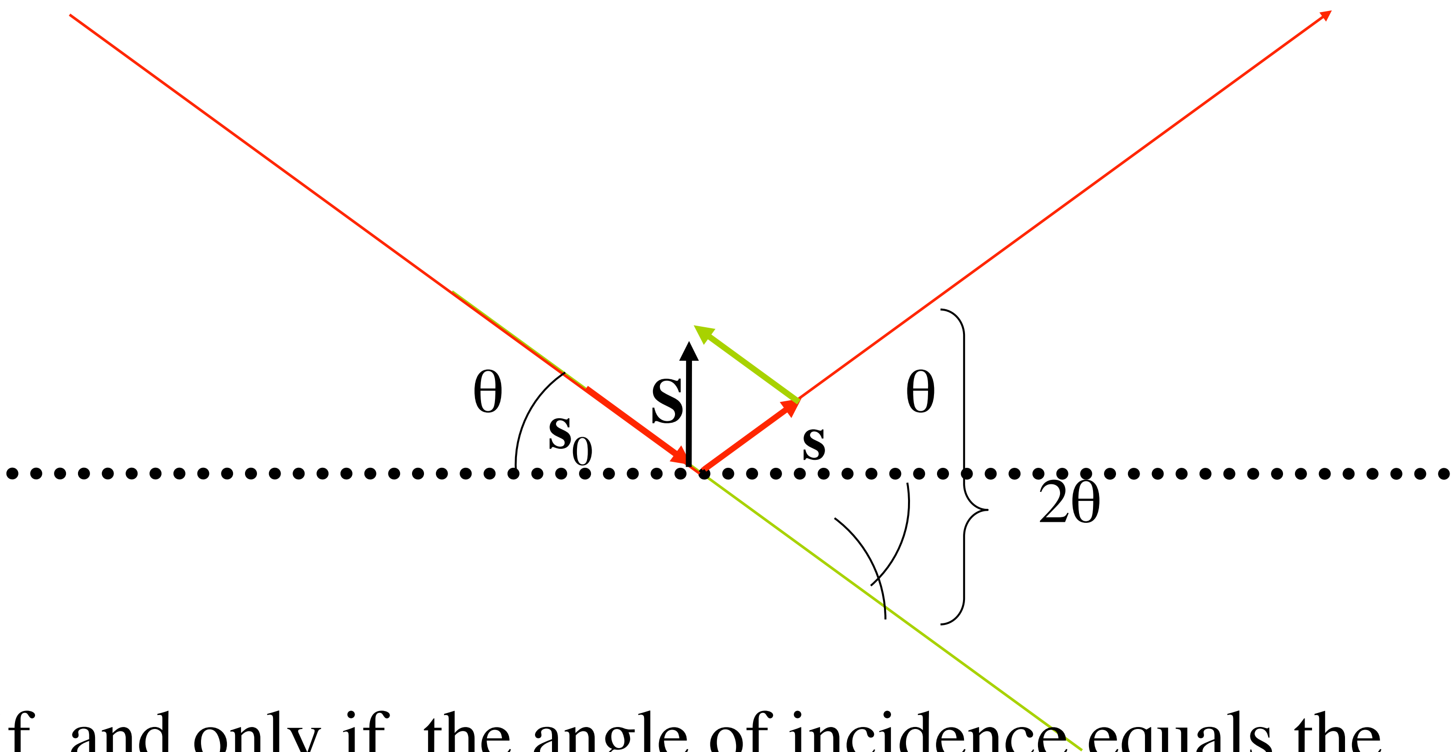
two points



The combined waves from points in a plane interfere destructively in all directions **but one**, the *reflection angle*.



All points on a plane scatter with the same path length...

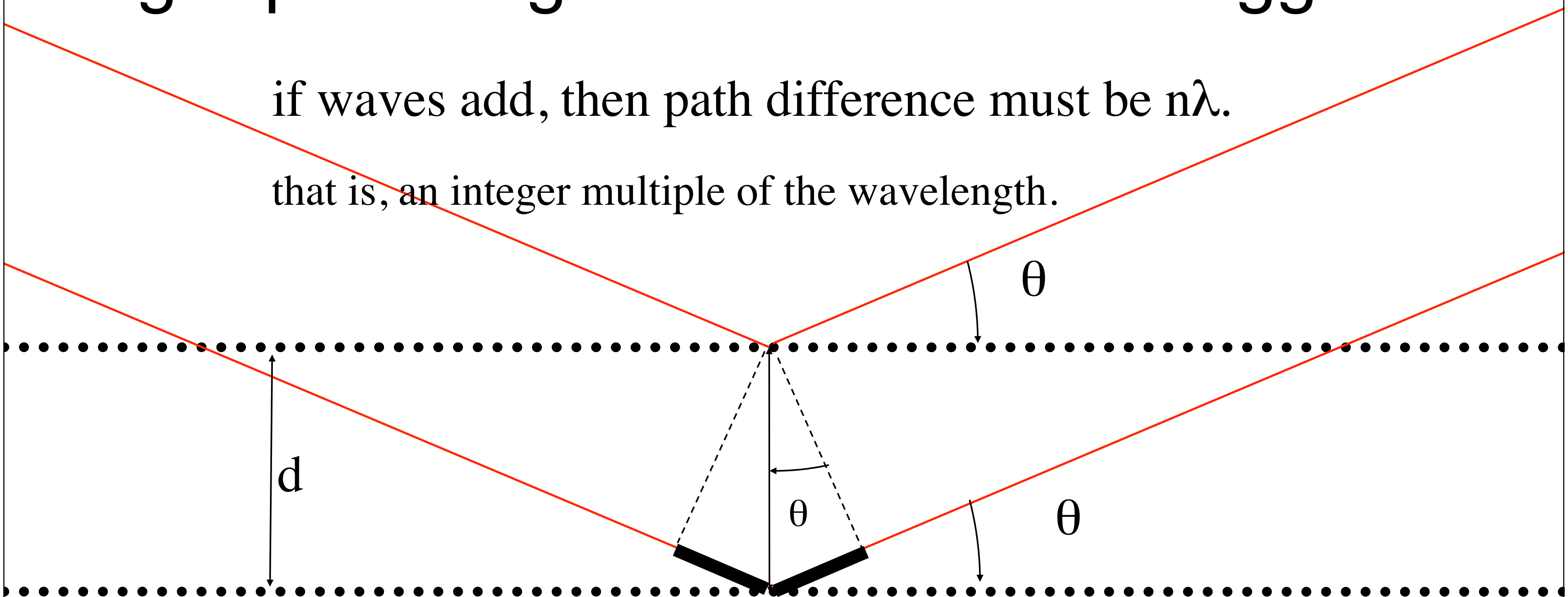


...if, and only if, the angle of incidence equals the angle of scatter. Everywhere else, interference is destructive.

Integer path length differences--> Bragg's Law

if waves add, then path difference must be $n\lambda$.

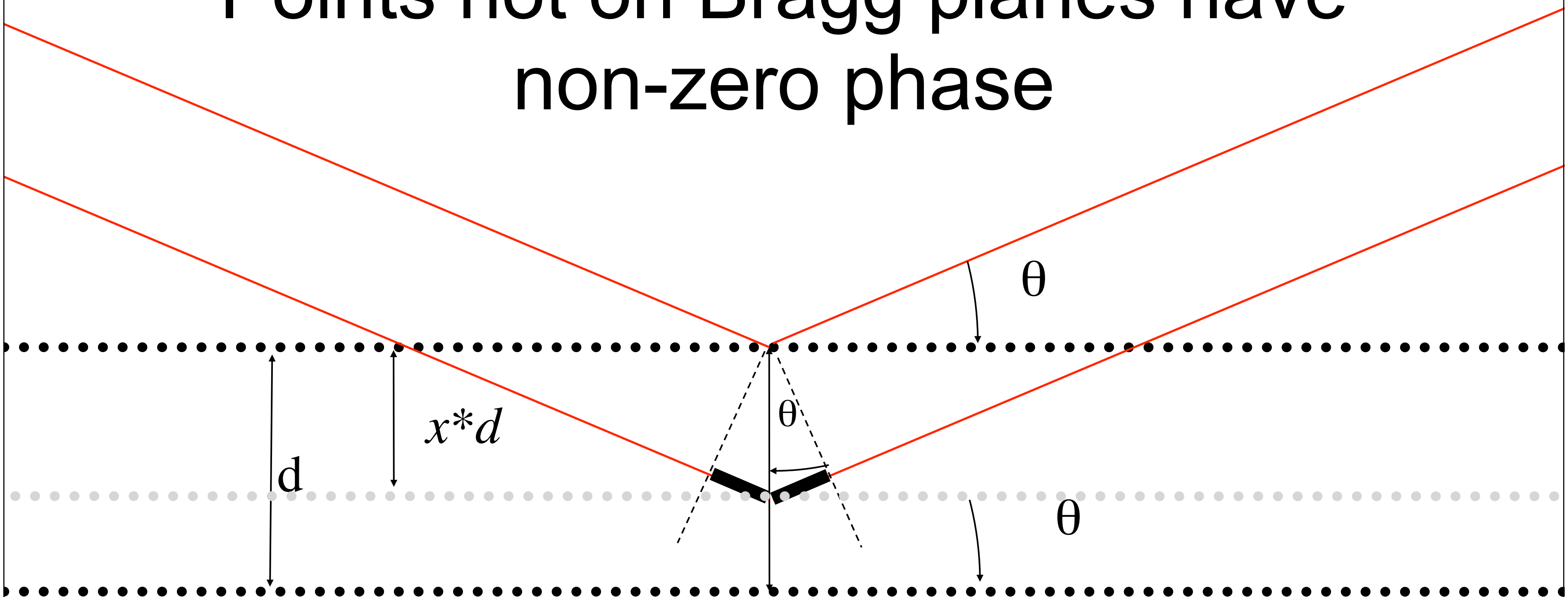
that is, an integer multiple of the wavelength.



path difference=the two bold lines = $2d \sin\theta$

Let path difference equal integer multiple of the wavelength, and you get Bragg's law, $n\lambda=2d\sin\theta$

Points not on Bragg planes have non-zero phase



x = fraction of distance d

Path difference = $2(x^*d) \sin\theta$

Phase difference = $2\pi\, 2(x^*d) \sin\theta / \lambda$ radians

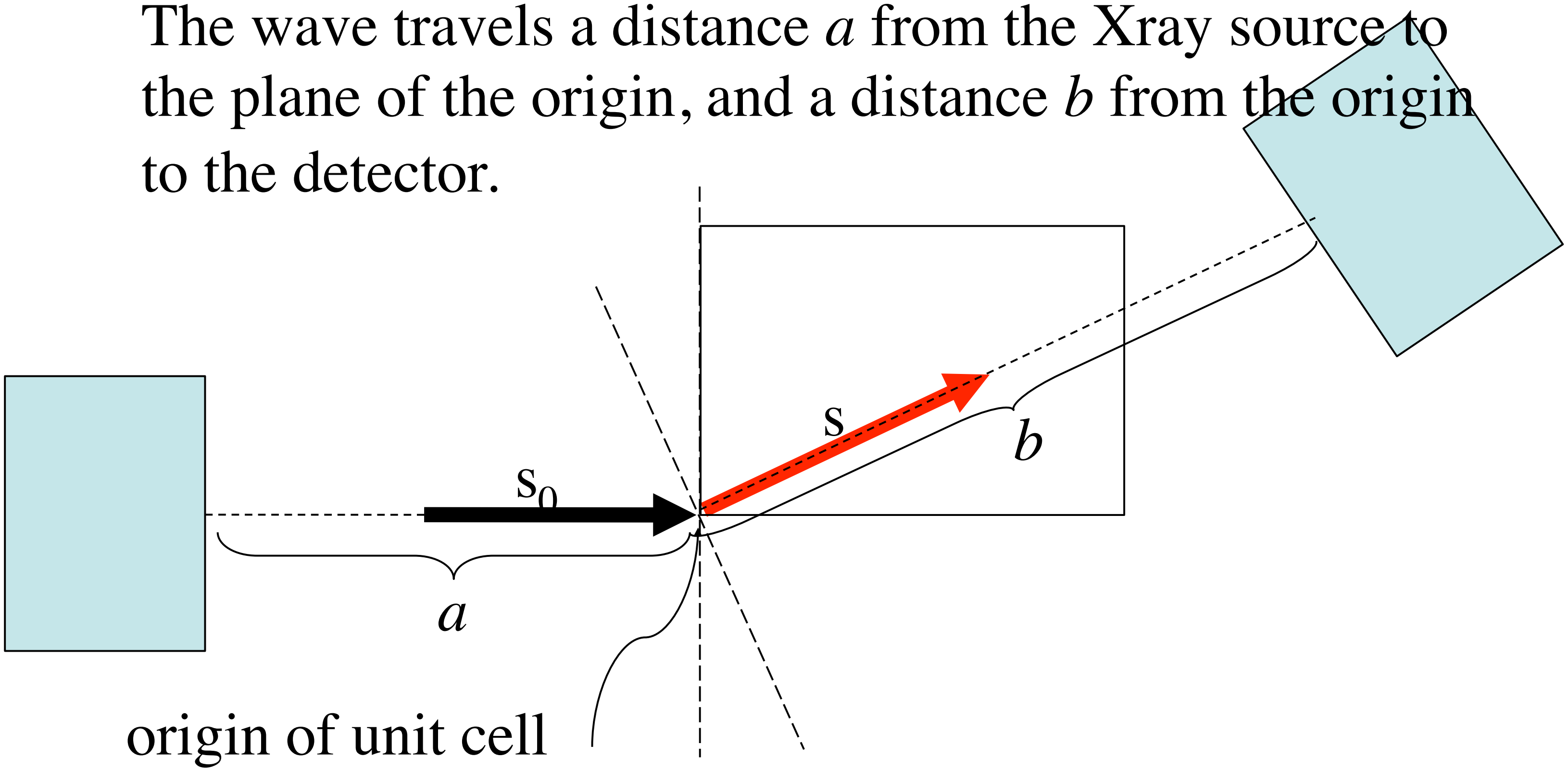
but, $d = \lambda / 2\sin\theta$

therefore, phase difference = $2\pi x$ radians

Scattering from the Origin has phase 0 by definition

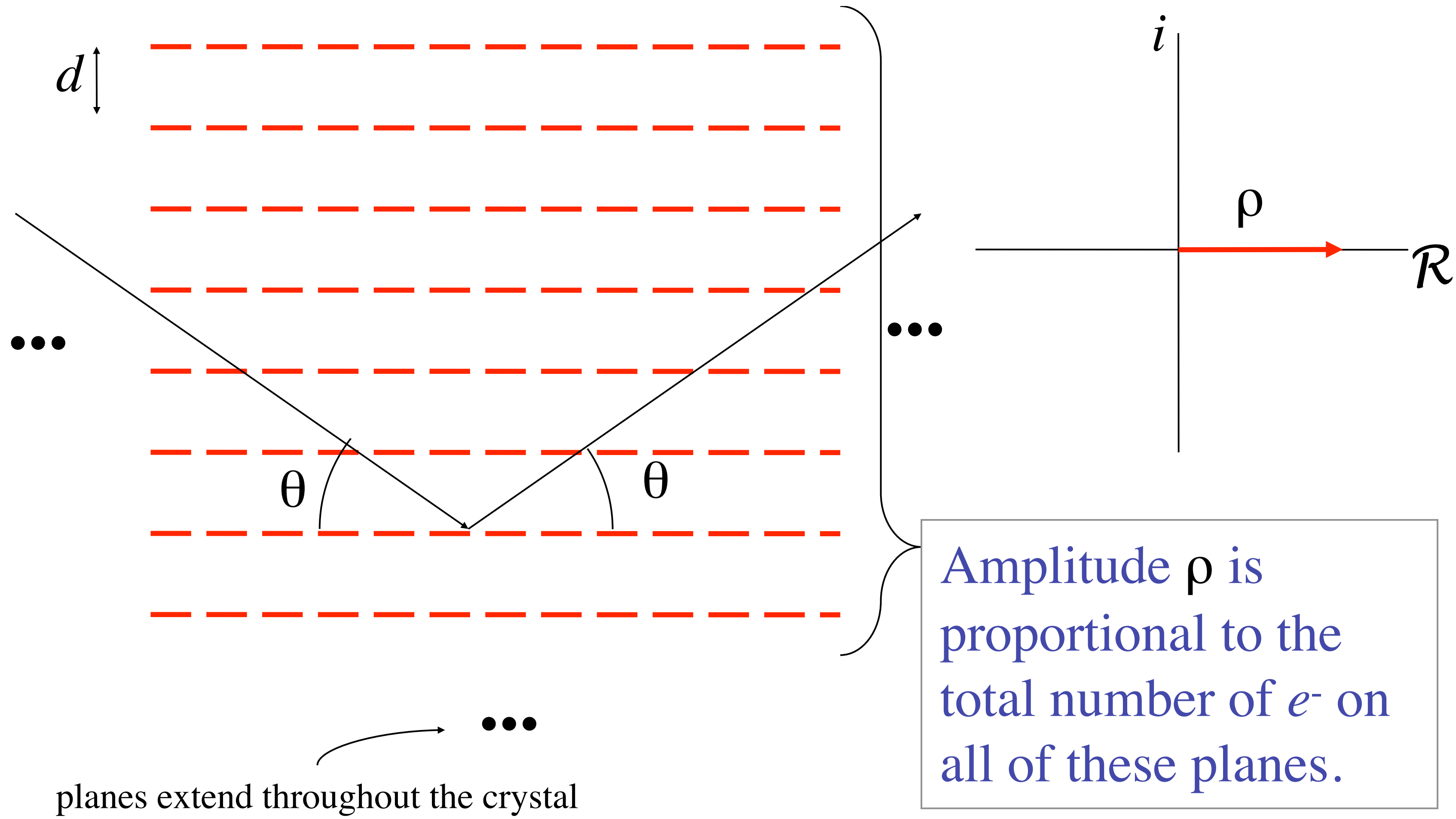
There is only one origin in the crystal (usually this is defined by crystal symmetry)

The wave travels a distance *a* from the Xray source to the plane of the origin, and a distance *b* from the origin to the detector.



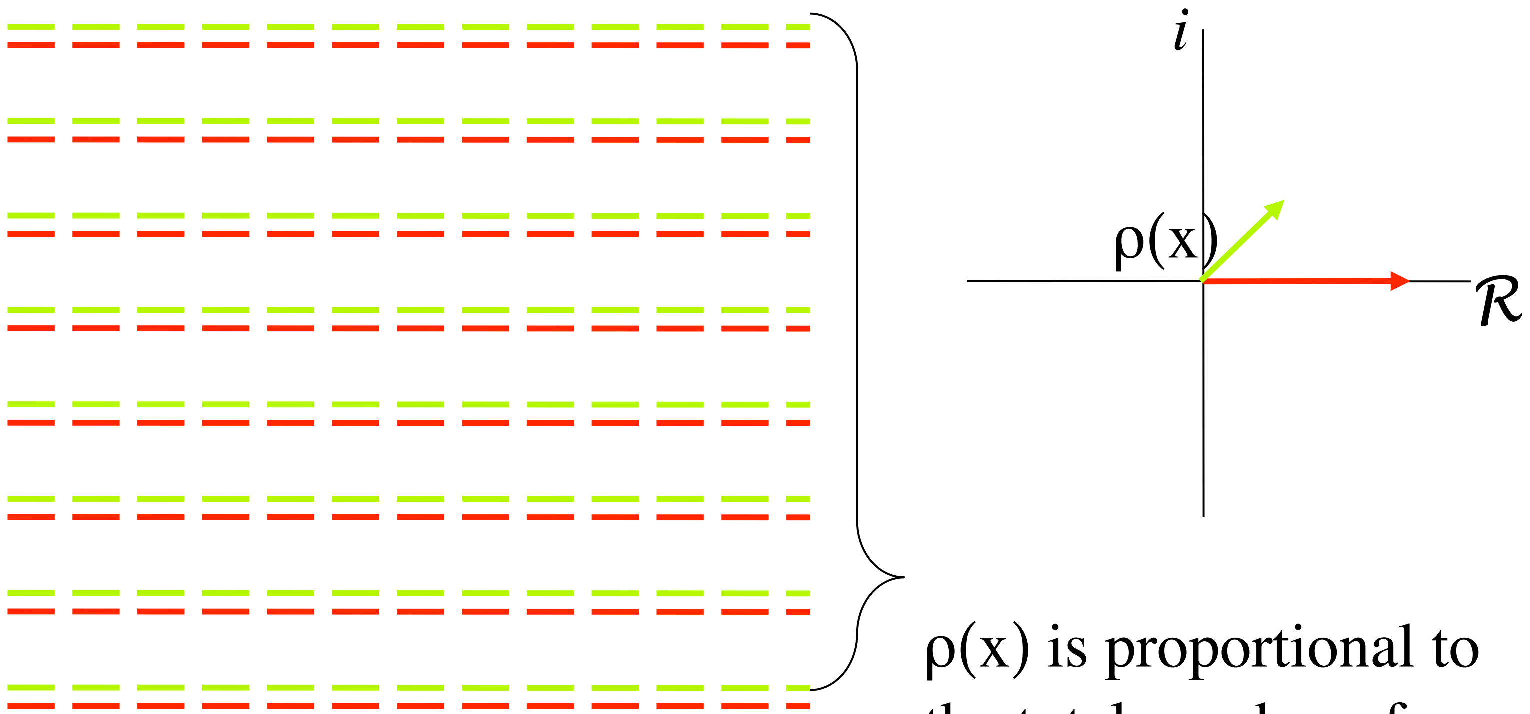
The Fourier transform of Bragg planes

(1) All Bragg planes scatter in phase.
(2) Bragg planes through the origin have phase =0
(3) The amplitude from Bragg planes is the sum of the density



Amplitude ρ is proportional to the total number of e^- on all of these planes.

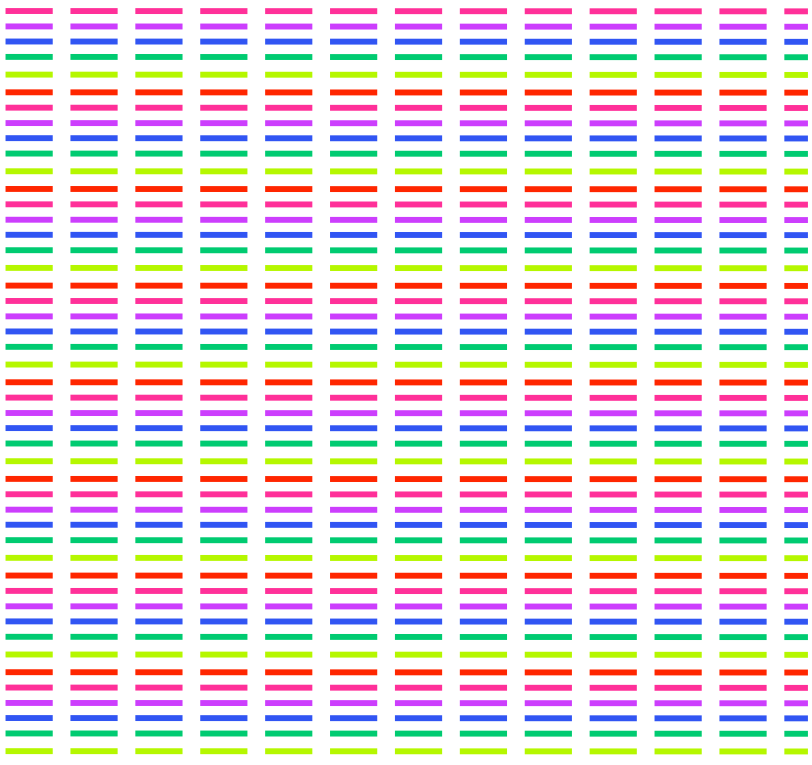
Bragg planes offset by x have phase $2\pi x$



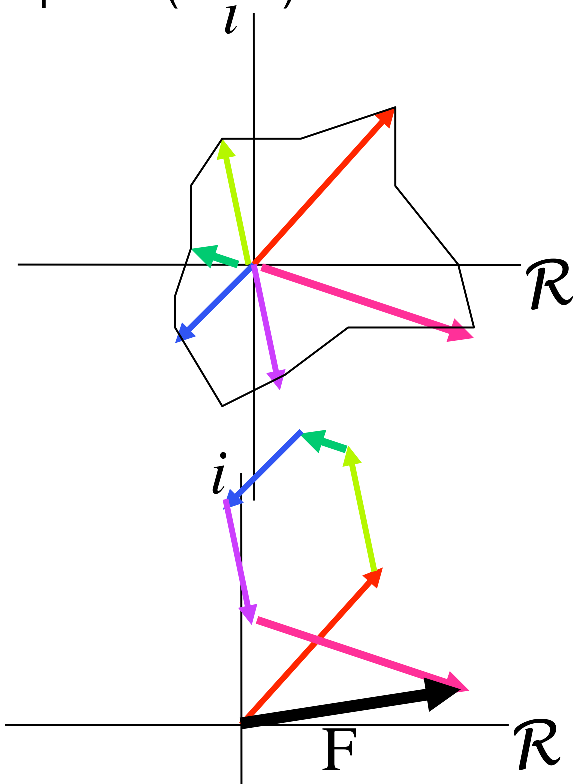
Planes shifted by $x = d/6$ are phase shifted by $2\pi/6$.

$\rho(x)$ is proportional to the total number of e^- on these planes.

Integrating offset Bragg planes from x=0 to 1



Amplitude as a function of phase (offset)



Integral over phase.

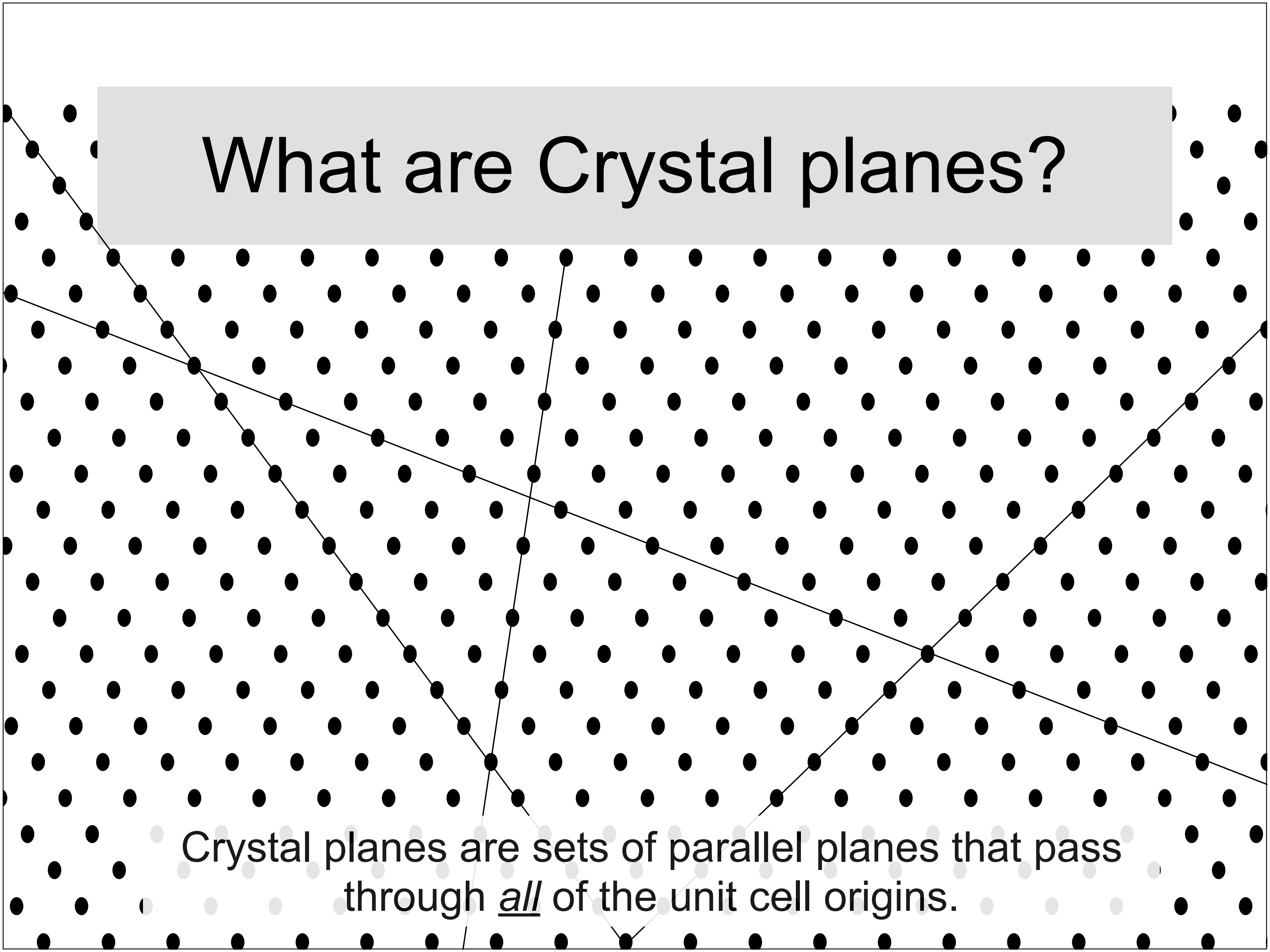
The total F is the wave sum over all offsets.

$$F = \sum_{x=0,1} \rho(x) e^{2\pi i x}$$

The only Bragg planes of interest <u>are</u> crystal planes

proof to follow...

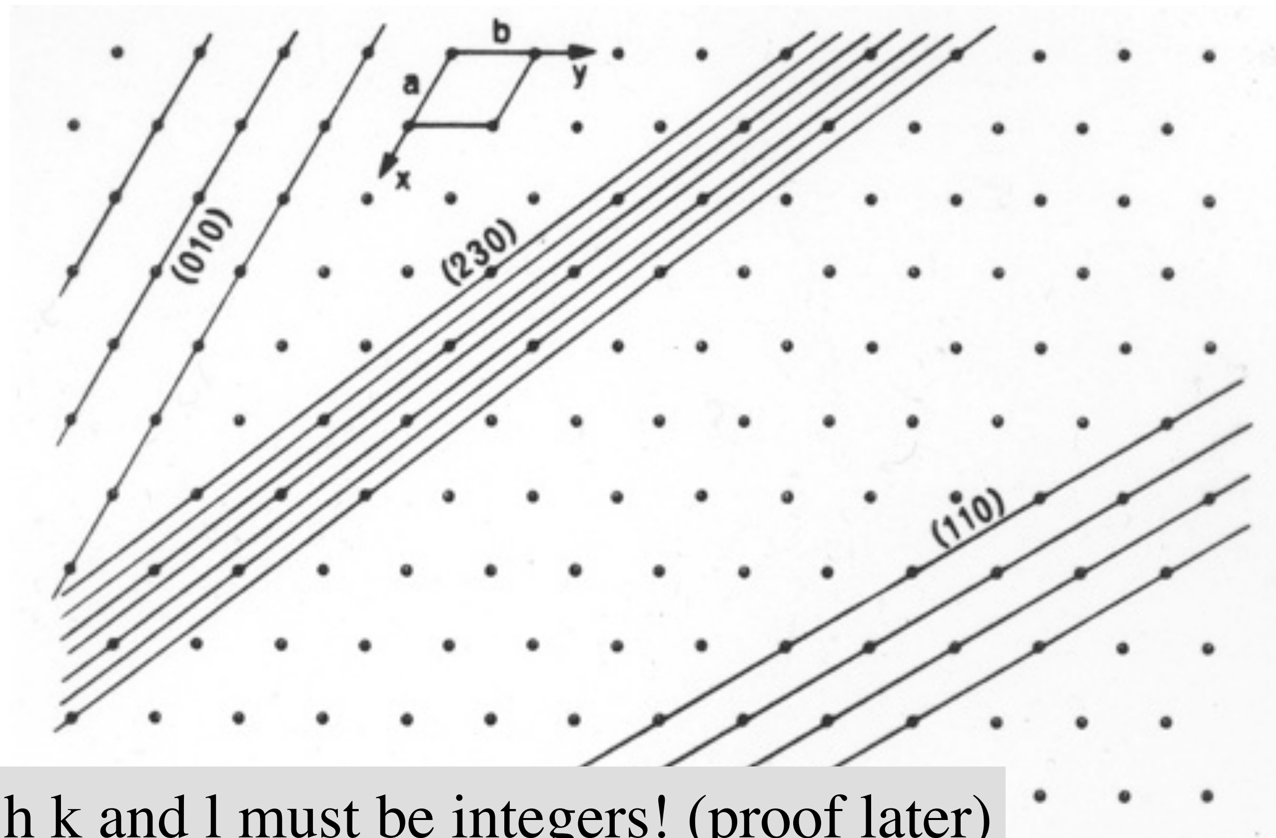
What are Crystal planes?



Crystal planes are sets of parallel planes that pass through *__all__* of the unit cell origins.

Bragg Planes/Crystal Planes naming.

Planes are numbered according to how they intersect the crystal axes. Starting from the Origin and moving to the first Bragg plane, if it intersects the a axis at 1/h, the b axis at 1/k and the c axis at 1/l, then the Bragg planes are called the (h k l) reflection plane. Each set of Bragg planes defines a single diffracted spot, called a "reflection". Reflections are also numbered using (h k l).



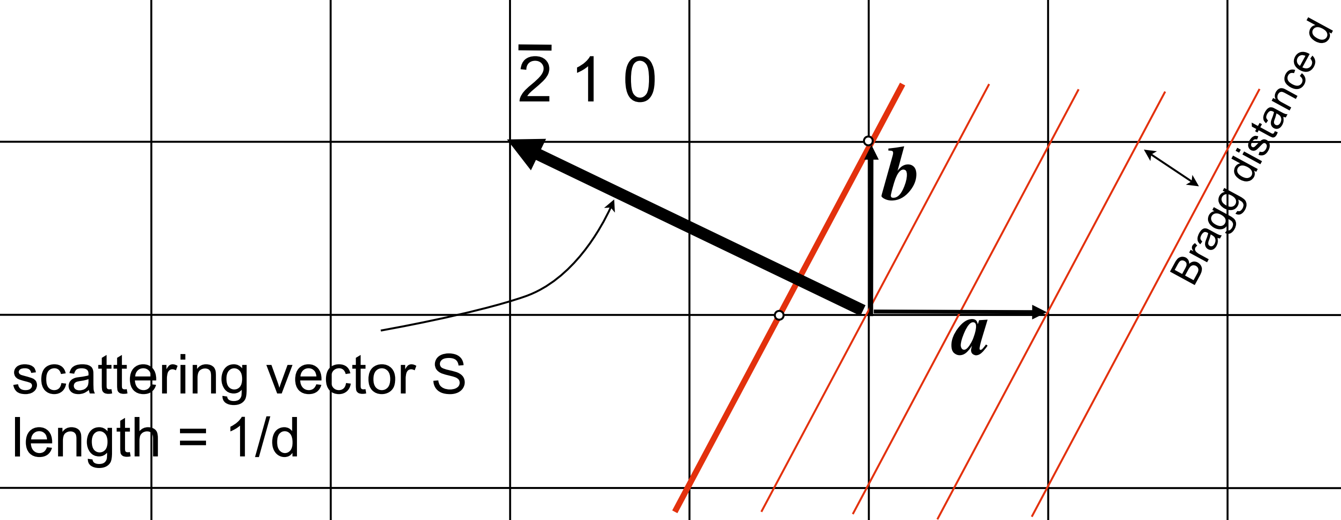
NOTE: h k and l must be integers! (proof later)

How to draw Bragg planes on a lattice

Draw a plane that intersects

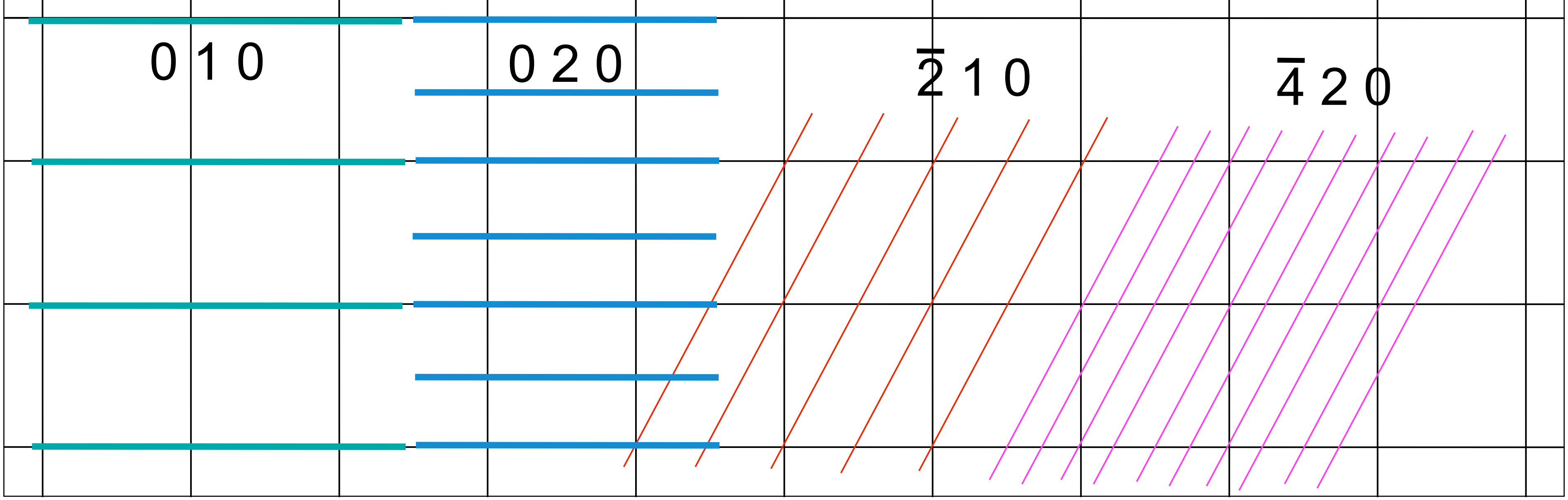
a at $1/h$, ***b*** at $1/k$, ***c*** at $1/l$

Then draw a a parallel plane through the origin.
The position of the *hkl* reflection is normal to these planes
at distance $1/d$ from the beam.



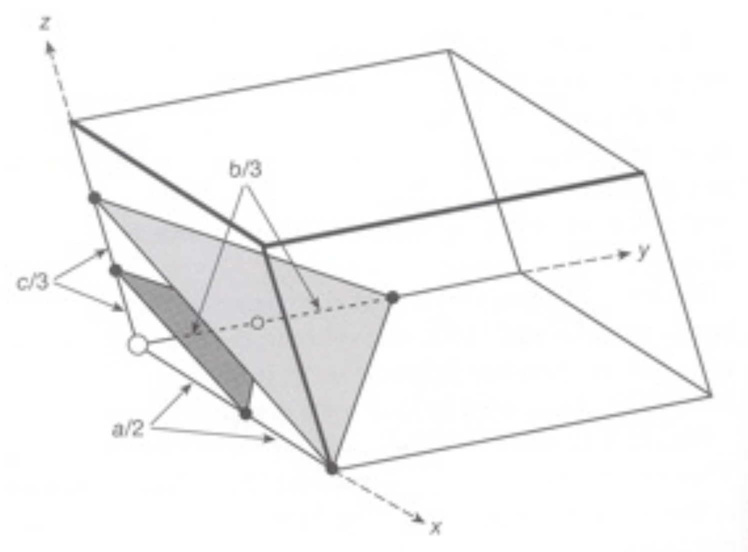
If indeces *hkl* are doubled, Bragg distance *d* is halved.

- All unit cell origins have phase zero. But not all phase-zero Bragg planes must go through a unit cell origin. For example, the n=odd Bragg planes for the 0 2 0 reflection does not touch a single unit cell origin.

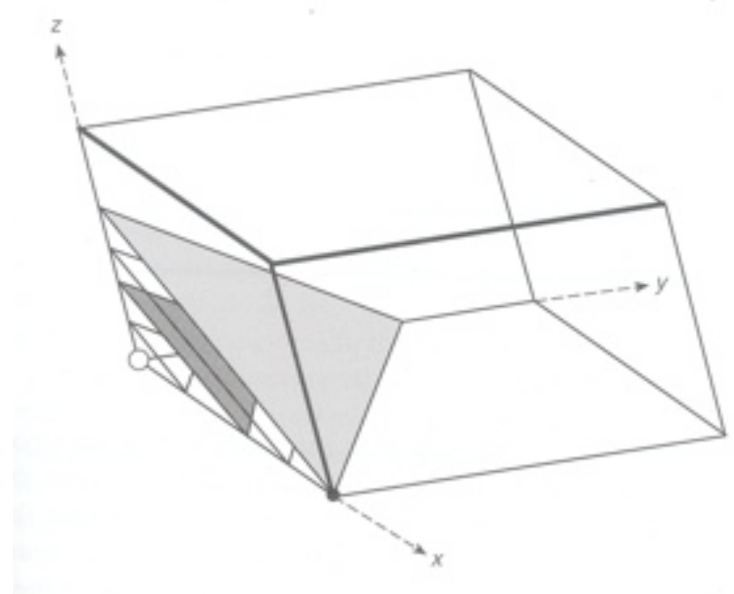


3D Bragg planes/Crystal planes

(2 3 3) Bragg planes



(4 6 6) Bragg planes



Phase-zero planes intersect the cell axes at multiples of fractional coordinates

(1/h,0,0), (0,1/k,0),(0,0,1/l)

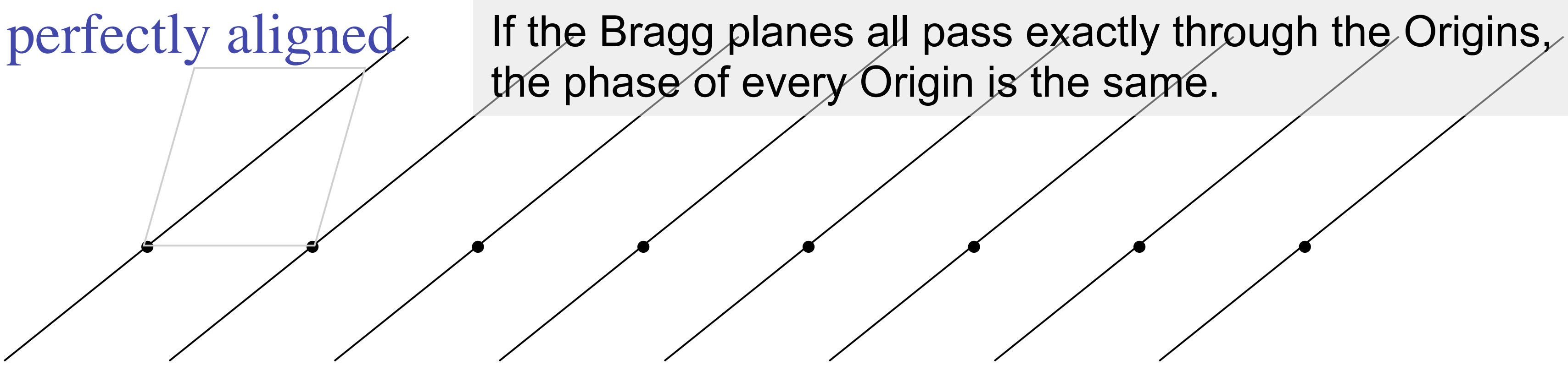
Proof: The only Bragg planes that diffract X-rays are crystal planes.

other planes don't

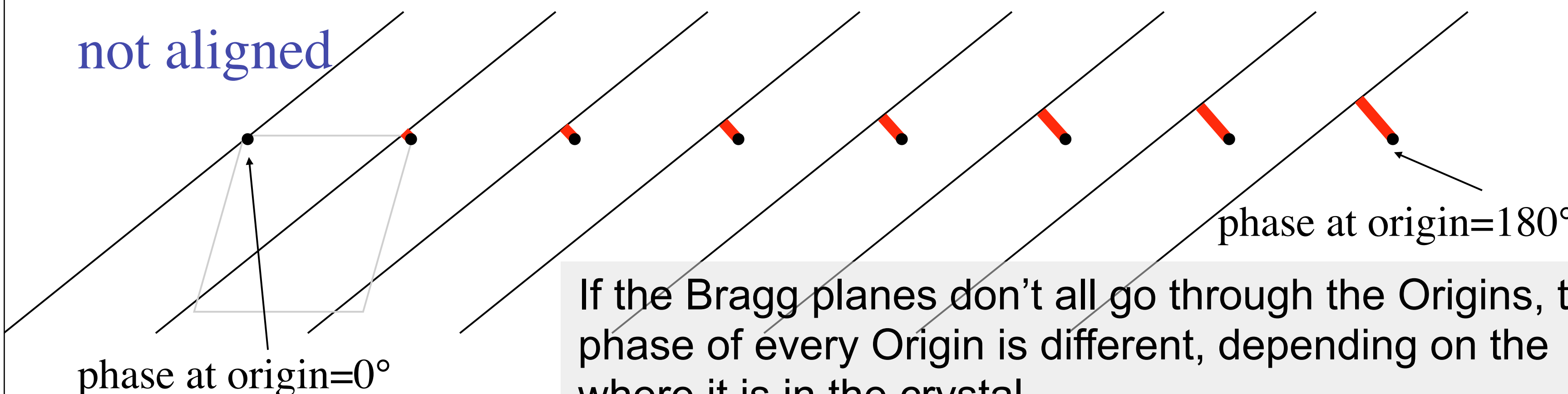
In other words, if we have seen a reflection on the film, that reflection corresponds to a set of crystal planes. Since all crystal planes pass through the unit cell origins, and since the phase of the Origin can be set to zero, *all (observable) Bragg planes of phase zero pass through the Origins*

Proof: All Bragg planes of phase zero pass through the Origins

1. Bragg planes are either aligned with the Unit Cell Origins, or they are not.



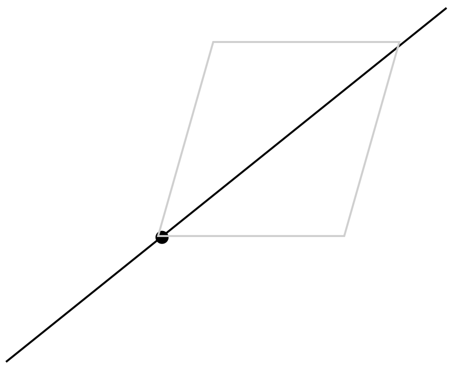
If the Bragg planes all pass exactly through the Origins, the phase of every Origin is the same.



If the Bragg planes don't all go through the Origins, then phase of every Origin is different, depending on the where it is in the crystal.

Proof: All Bragg planes of phase zero pass through the Origins

2. All planes that pass through the Origins have the same number of electrons



The angle and intercept with the Unit Cell determine with atoms are on the plane.

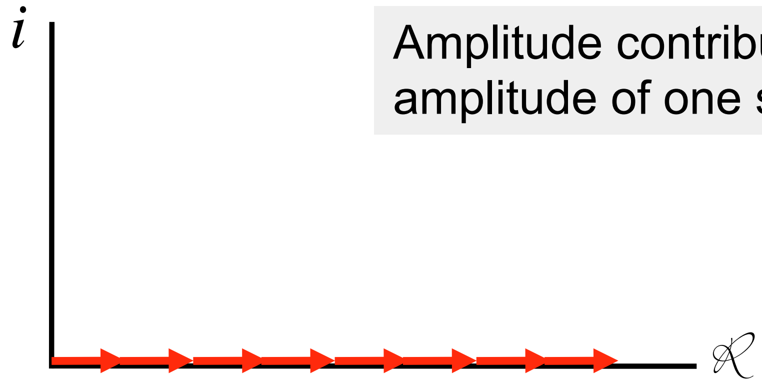
3. All planes that pass through the Origins contribute the same amplitude.

...because amplitude is proportional to number of electrons, and (statement 2).

Proof: All Bragg planes of phase zero pass through the Origins

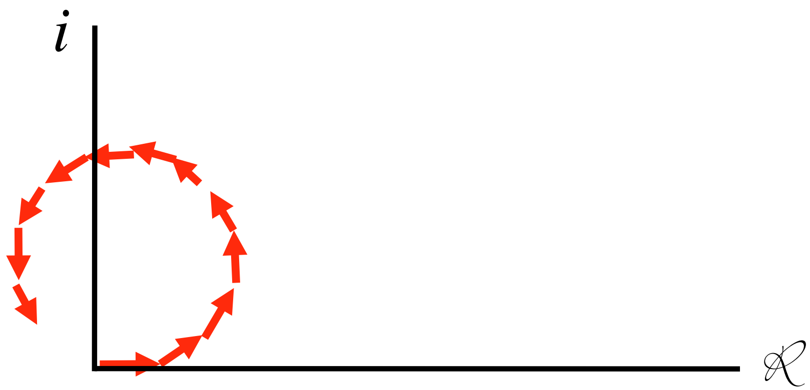
4. Total amplitude is the sum of the amplitudes of the planes if the planes have the same phase.

Amplitude contributed by origin planes is 10K times the amplitude of one such plane, if there are 10K unit cells.



5. Total amplitude is approximately zero if the planes have different phases.

Phase shifts by a constant for each unit cell. Vectors sum in a circle. Summed over 10K unit cells, vector length is small.



Proof: All Bragg planes of phase zero pass through the Origins

6. Any point in the Unit Cell can be the Origin.

7. All equivalent positions by lattice symmetry have the same phase.

Because (statement 6), statements 1-5 apply to any point in the Unit cell.

8. If the Bragg planes do not pass through all Origins, the diffraction amplitude is zero.

Because the total diffraction amplitude is the wave sum over all points in the Unit Cell.

Conclusion: Bragg planes that pass through all of the Origins diffract X-rays. Bragg planes that do not pass through all of the origins do not diffract X-rays.

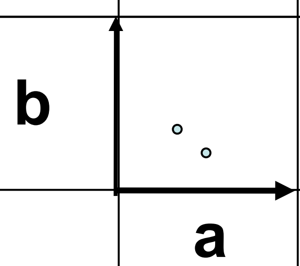
Calculating the structure factors

- Draw a plane that intersects the unit cell axes at 1/h, 1/k, and 1/l (careful to consider the sign of h,k,l)
- Measure the phase of each atom as its distance from the nearest Bragg plane, divided by d and multiplied by 360°.
- Draw the scattering factor for that atom, and sum the scattering factors to get the structure factor.

In class exercise:

Calculate structure factors:
F(1 1 0)
F(-1 1 0)
F(-2 1 0)

For a unit cell with two atoms:
carbon (amplitude 6) @ (0.5, 0.2, 0.0)
oxygen (amplitude 8) @ (0.3, 0.4, 0.0)



Calculating the density

- Given the structure factors F(hkl), find the point(s) of maximum e-density. $F(hkl) = |F(hkl)|e^{i\alpha}$
- Draw Bragg planes with phase = α (Measure phase in the direction (h,k,l))
- Erase Bragg planes with phase = α+180°
- After drawing and erasing all F's, the darkest areas are the locations of the atoms.

In class exercise:

Find the maximum density point given the following structure factors:

$F(1\ \ 1\ \ 0) = 1\ e^{i(108°)}$

$F(0\ \ 1\ \ 0) = 1\ e^{i(180°)}$

$F(1\ \ 1\ \ 0) = 1\ e^{i(-60°)}$

$F(-1\ \ 1\ \ 0) = 1\ e^{i(60°)}$

$F(-2\ \ 1\ \ 0) = 1\ e^{i(-10°)}$