<u>Summing up what we've done so far</u>

- All we've really been doing is adding vectors
- We showed that waves can be represented by an amplitude, which is a complex number, which is basically a vector
- So, when we add waves we're just adding those vectors (either graphically or as complex numbers)

- When we look at waves scattered from matter, we're really looking at scattering by electrons
- When we observe scattering from many atoms we're looking at the sum of the contribution of each individual electron (it's a sum over many, many terms)
- To simply this we group the electrons into atoms
- We can calculate (from quantum mechanics) the contribution from the individual atoms
- For a molecule we can then sum the contributions from each atom (instead of individually summing the contribution from each electron in the molecule)
- We can also determine the scattering from a collection of molecules, since we already said we can calculate the scattering of individual molecules, we can repeat the same process, and sum the contributions of individual molecules
- This process is a lot like determining the population of a province by adding up the population of individual settlements, then determining the population of a country by adding up the population of individual provinces...

- We have shown that the contribution from each unit (electron, atom, etc.) is given by:

$$\text{(scattering factor of unit)} \times \boxed{e^{2\pi i \vec{S}\cdot\vec{r}}}$$

This is the phase angle that relates to the scattering direction **S** (the direction in which we observe) and the position of this unit relative to the origin **r**

$$\text{scattering factor of unit} = 1 \quad \text{If the unit is an electron}$$
$$= f_{atom}(S) \quad \text{If the unit is an atom}$$
$$= F_M(\vec{S}) \quad \text{If the unit is a molecule}$$

- If you have many units (eg. many atoms in a molecule) you simply sum the contributions from each unit
- The next step is to see if there are specific arrangements of atoms that have special properties in terms of diffraction, one example we've already seen is the one-dimensional array of atoms:


$$\boxed{\vec{r}_n = n\vec{a}}$$

$$\boxed{F(\vec{S})} = \sum_{n=-\infty}^{\infty} f(S)e^{2\pi i \vec{S}\cdot n\vec{a}} = f(S)\cdot\sum_{n} e^{2n\pi i \vec{S}\cdot\vec{a}} = \boxed{f(S)\cdot G(\vec{S})}$$

$$G(\vec{S}) = \begin{cases} \gg 1, & when \ \vec{S}\cdot\vec{a} = h \ (integer) \\ \\ 0, & elsewhere \end{cases}$$

Defines conical surface for **S**

- The above function for the diffraction for the total array is really an amplification of a single atom

- In this specific case the amplification function $G(\vec{S})$ has spikes when $\vec{S}\cdot\vec{a} = integer$ and is 0 elsewhere.

An example Wave 1 has amplitude E_0 and a phase angle of 60° ($\pi/3$ radians). Wave 2 has the same amplitude and a phase angle of -60°. If these two waves add together, what is the total wave?

Im

60°

E_0 E_0

60° E_0 60°

- 60°   → Re

= wave 1
= wave 2
= resultant wave
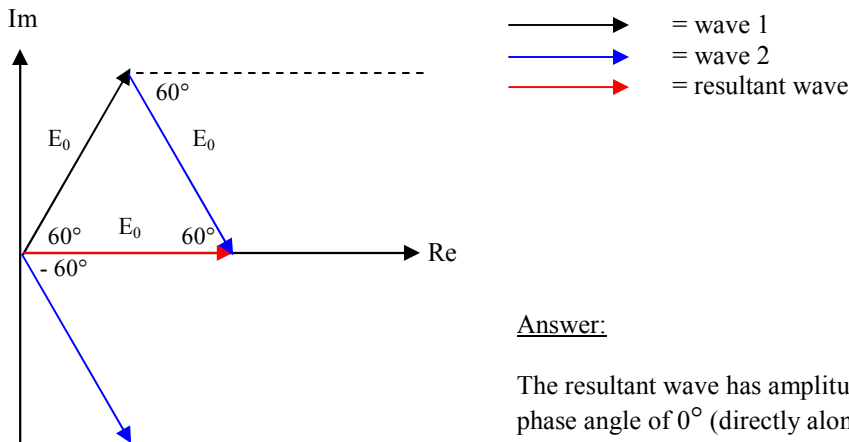
<u>Answer:</u>

The resultant wave has amplitude E_0 (because the triangle is equilateral) and phase angle of 0° (directly along the real axis).

- To add multiple waves, you would do the same thing, just add the waves one at a time

Three Dimensional Array of Atoms

- The one-dimension array of atoms is not that useful in the real world
- We can extend this to a 2D plane of atoms
- We can then stack these planes on top of each other to create a 3D array
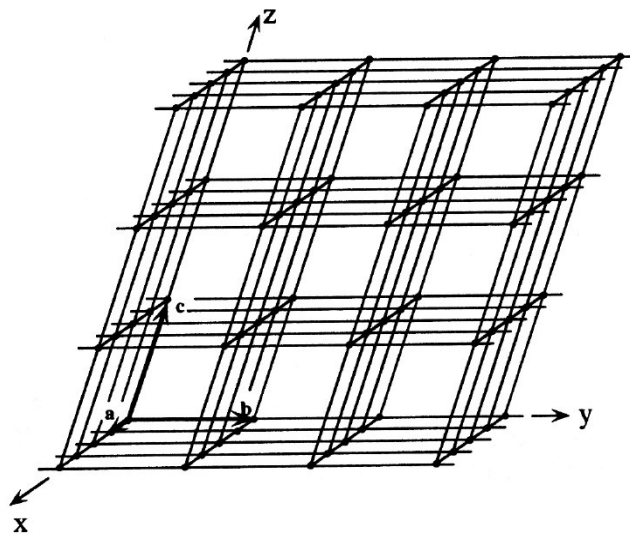
- This array has translational symmetry
- Because of this, the position of any atom in the array can be described by:

$$\vec{r}_n = n\vec{a} + m\vec{b} + p\vec{c}$$

- The network is made up of "bricks" called unit cells:
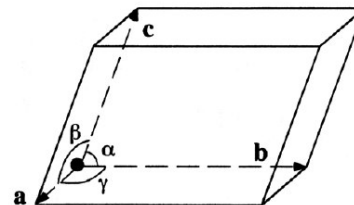
- The unit cell is translated in the x,y,z directions from -∞ to +∞ to create this network

Why are the planes not at right angles?
- Because the unit cell can be any shape, having the planes at right angles would be a special case

2

Scattering From a 3D Array of Atoms:

$$\vec{r}_n = n\vec{a} + m\vec{b} + p\vec{c}$$

$\vec{a}, \vec{b}, \vec{c}$ define the size of the unit cell
They are constant for a given 3D array

$$\boxed{F(\vec{S})} = \sum_{n,m,p=-\infty}^{\infty} F_m(\vec{S}) e^{2\pi i \vec{S} \cdot (n\vec{a}+m\vec{b}+p\vec{c})} = F_m(\vec{S}) \cdot \overbrace{\sum_{n,m,p} e^{2\pi i (n\vec{S}\cdot\vec{a}+m\vec{S}\cdot\vec{b}+p\vec{S}\cdot\vec{c})}}^{G(\vec{S})}$$

$$= \boxed{F_m(\vec{S}) \cdot G(\vec{S})}$$

$$G(\vec{S}) = \begin{cases} \gg 1, & \text{when } \vec{S}\cdot\vec{a} = h, \text{ and } \vec{S}\cdot\vec{b} = k, \text{ and } \vec{S}\cdot\vec{c} = l, \\ & \text{where } h,k,l \text{ are integers} \\ 0, & \text{elsewhere} \end{cases}$$

Laue conditions

Location of G(S) peaks depends only on the size of unit cell (a,b and c vectos)

*Note: In the printed version of the notes **S** is written as a scalar instead of a vector in the above equations. **S** is used a scalar only in the special case where the electron density is spherically symmetric about the origin. This is corrected in the notes posted online.*

- This is not very different from the 1D array
- Because it's in 3D we have to sum over all n,m,p from $-\infty$ to $+\infty$ and the vector **r_n** is a 3D position vector

$F_m(\vec{S})$ is the scattering factor for whatever is in the unit cell

- if the unit cell contains an atom, this would be replaced with $f_{atom}(\vec{S})$ (atomic scattering factor)

- if the unit cell contains a molecule, this would be a molecular scattering factor...etc

$G(\vec{S})$ is the shape function

- this is the phase difference, which depends on where a particular unit cell is located in the array
- it is very similar to the shape function we had for the 1D case, except now there are 3 terms instead of 1
- this function is also very spiky, it spikes when the *Laue conditions* are met, and only when **all three** conditions are met (h,k,l must all be integers)

- for a given value of h $\vec{S} \cdot \vec{a} = h$ describes all the vectors $\vec{S}$ inclined by a certain angle relative to $\vec{a}$

- these vectors lie on the surface of a cone with its axis along $\vec{a}$

- for all possible values of h, this equation describes a **series** of cones along the vector **a**
- similar series of cones lie along the vectors **b** and **c**
- the shape function is non-zero only when **all three** series of cones intersect, therefore this shape function is non-zero only in very specific directions
- h,k,l really describe the value of **S** given a,b,c for a certain lattice

- the equations on the previous page allow us to calculate the scattering from a 3D lattice given the scattering factor of the contents of the unit cells
- we can calculate the scattering factor by summing the contributions to the scattering of all the atoms in the unit cell
- if the unit cell contains a molecule, then we will sum the contributions of the atoms that make up that molecule
- x_n, y_n, z_n define the position of the atoms in the unit cell relative to the dimensions of the unit cell, so they must be between 0 and 1

$$F_m(\vec{S}) = \sum_{n=1}^{N} f_n(S)\, e^{2\pi i \vec{S} \cdot (x_n \vec{a} + y_n \vec{b} + z_n \vec{c})} =$$

$$= \sum_{n}^{N} f_n(S)\, e^{2\pi i (hx_n + ky_n + lz_n)} = F_m^{hkl}$$

Structure Factor:

- For a specific lattice (ie. with given values of a,b,c) every possible vector **S** is described by a combination of h,k,l and each combination of h,k,l describes only one vector **S**

- knowing h,k,l we can calculate $\vec{S}$ and vice-versa
- so the scattering factor for the contents of the unit cell is really a function of h,k,l

- the difference between the $\vec{S}$ vector and h,k,l is that **S** describes a continuous function, but h,k,l describe the discontinuous function where $G(\vec{S})$ is non-zero

- when h,k, or l are **not integers** this corresponds to a vector $\vec{S}$ but for these values of **S** the shape function is zero, so we can ignore them

$$F_{hkl} = \sum_{n=1}^{N} \boxed{f_n(S)} \cdot \boxed{e^{2\pi i (hx_n + ky_n + lz_n)}}$$

Electronic property of atom

Structural property (position)

|	
• this depends on what the individual atom is (C,N,etc) • has been calculated for each element	• this is independent of the type of atom • depends only on the position of the atom within the unit cell

- so, scattering from a molecule depends on the electronic properties of the individual atoms, and the position of the atoms

- similarly, scattering from a lattice (of many molecules) depends on the electronic properties of the molecules and the dimensions of the unit cells
- the **amplitude** of scattering from the lattice is determined by the contents of the unit cell
- the **directions** in which scattering is actually observed is determined by the directions for which the G function is non-zero, that in turn depends only on a,b,c (the dimensions of the unit cell)

- therefore, from the distribution of the directions of scattering we can determine the dimensions of the unit cell
- by looking at the amplitudes of scattering we can determine the contents of the unit cell (the structure of the molecule)
- measurements of distribution of scattering and amplitude of scattering are distinct

Bragg Equation

- The idea of Laue conditions with 3 intersecting cones is not that conceptually straightforward
- The Bragg equation is just **another way of looking at the same thing** (scattering), which may be more useful in some situations
- It allows us to come up with an equation for resolution (on the next page)
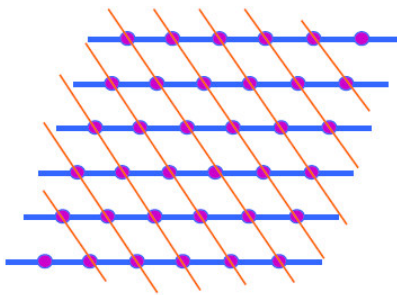
- First we look at a 2D lattice
- When we have atoms in a plane, we can think of them as belonging to the blue set of lines, the orange set of lines, or any other set of lines we want
- The same plane can be described many ways as different sets of lines
- In exactly the same way, a 3D lattice can be described as different sets of planes

- Now we take one particular set of planes that describes a lattice (see diagram below)
- We think of the planes as being semi-transparent mirrors, so some of the X-rays will pass through to the next plane and some will reflect
- Because the plane is like a mirror, the angle at which the X-rays reflect will equal the angle of incidence to the plane (this angle is θ in the diagram)
- We have two incoming rays, one which hits a point directly below the other

- If we look in the direction $\vec{s}$ two waves are scattered in that direction, but they did not go the same distance, the bottom wave traveled $2x$ farther than the top wave
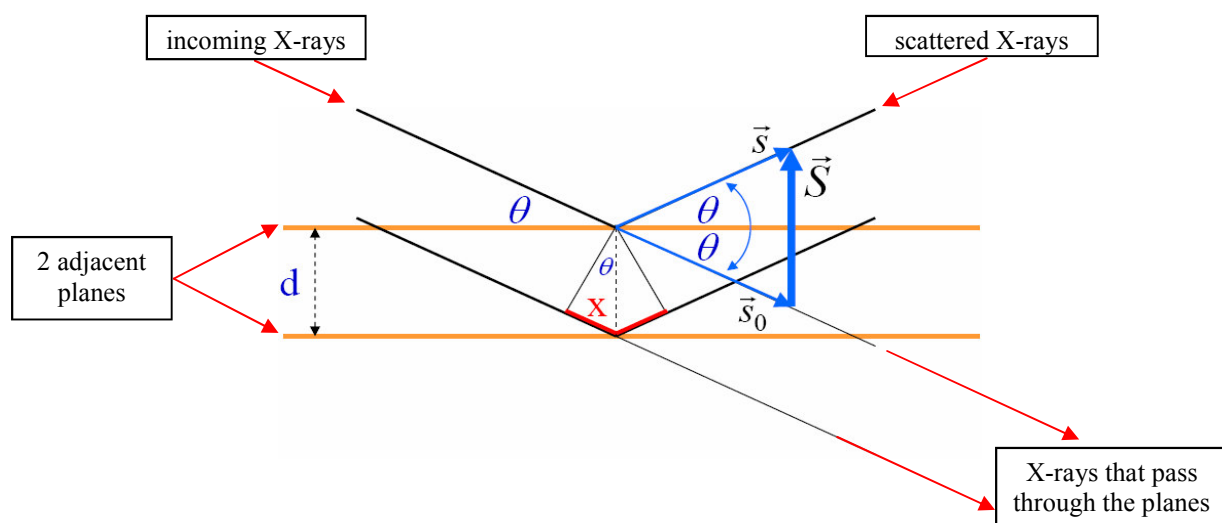
$$\Delta = 2x = 2d\sin\theta$$

Interference in phase when $\Delta = \lambda$ →

$$2d\sin\theta = \lambda \qquad |\vec{S}| = 2\,|s_0|\sin\theta$$

$$\frac{1}{d} = \frac{2\sin\theta}{\lambda} \qquad |\vec{S}| = \frac{2\sin\theta}{\lambda}$$

$$\boxed{|\vec{S}| = \frac{1}{d}}$$

- In order to get addition of the waves in phase, the path difference ($\Delta = 2x = 2d\sin\theta$) must be equal to the wavelength (λ)
- really it could be n x λ, where n is any integer, but we'll just consider the simplest case
- If we have just two planes and the path difference is slightly off λ, then we will have a distribution of intensities, with maximum intensity when $\Delta = \lambda$ and minimum intensity when $\Delta = \lambda / 2$
- But if we have a whole series of planes (as we do with a 3D lattice) then the only direction in which we will observe scattering is the one for which $\Delta = \lambda$, for other directions scattering will be 0 (which is the same property that the shape function had in the previous description)

- the above equations are pretty straight forward based on the diagram, one trick to remember is that $|s_0| = 1 / \lambda$ (because we defined it that way)
- we can conclude that the modulus of the scattering vector equals the inverse of the distance between the planes, this is the Bragg equation
- for a given set of planes this equation tells us what angle incident radiation will have to come in at in order to get diffraction that is non-zero
- for each set of planes we have one scattering condition, since we have many sets of planes in a lattice we have many scattering conditions
- this is analogous the places where the three cones intersect in the previous description

$$|\vec{S}_{max}| = \frac{1}{d_{min}} \leftarrow \text{resolution}$$

- When we measure scattering, we can only measure up to a certain maximum value of the scattering vector (which also corresponds to a maximum value of 2θ)
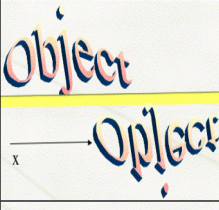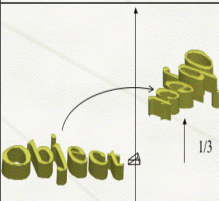- The maximum value of the scattering vector corresponds to a set of planes with minimum distance between them
- We can imagine planes as close together as we want, but beyond a certain point we cannot measure the scattering from those planes
- This minimum distance of planes that we can actually measure is related to the resolution
- When we have a structure with a resolution of 2Å, this really means that we have measured scattering from all planes that are further than 2Å apart

Symmetry

- We've already seen that in a 3D lattice there is translational symmetry, which means if you move the whole lattice the width of a unit cell, it looks exactly the same
- So the whole lattice is symmetrical, but the molecules in the unit cell may have symmetry as well

There are several types of symmetry:

	Point of Inversion • two objects related by a center of symmetry • anything at the point of rotation does not move
	Mirror Plane • for example, two enatiomers of a chiral compound within the unit cell • anything at points along the plane does not move
	Glide Plane • mirror image plus a shift
	Rotation • exactly what it sounds like • this one is about 120°, if we did many of these rotations we would get 3-fold rotational symmetry • 2-fold symmetry is 180°, 3-fold = 120°, 4-fold = 90°, 6-fold = 60° • anything on the rotation axis does not move
	Screw-Rotation • rotation, plus a shift along the rotation axis

- Except for glide plane and screw axis these are called point symmetry, because at least one point does not change position
- If the unit cells have symmetry will the whole lattice have this symmetry as well?
- Only if the unit cell has inversion, mirror plane or 2/3/4/6-fold rotational symmetry, these are the only types of symmetry consistent with the translational symmetry of the lattice
- 5-fold symmetry will not work, because it is **impossible** to fill a plane with pentagons without leaving gaps (the same goes for heptagons, octagons, etc.)

- there can't be a center of symmetry in a lattice made of proteins, because amino acids are chiral and rotating around the center of symmetry would change amino acids from L to D
- so we don't have to worry about many of the point symmetries (ex. mirror plane), we only have to worry about rotational symmetry

Electron Density and Resolution

$$\rho(\vec{r}) = \int_{V^*} F(\vec{S})e^{-2\pi i \vec{S}\cdot\vec{r}} \, dS$$

$$\rho(x,y,z) = \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} F_{hkl} \cdot e^{-2\pi i(hx+ky+lz)}$$

$$\rho_{exp}(x,y,z) = \sum_{h=-min}^{max} \sum_{k=-min}^{max} \sum_{l=-min}^{max} F_{hkl} \cdot e^{-2\pi i(hx+ky+lz)}$$

$$\rho(x,y,z) \approx \rho_{exp}(x,y,z)$$

- Due to limitations of the experimental setup when we measure scattering, we measure only up to a certain maximum value of the scattering vector
- If we measure the scattering amplitudes we can calculate the electron density using the inverse Fourier transform
- In order to calculate this exactly, we need to sum over all possible values of h,k,l, which means many values of $\vec{S}$
- But if we measure only within certain limits, what we calculate is only an approximation to the electron density, the more terms we include the better the approximation (ie. the better the resolution)