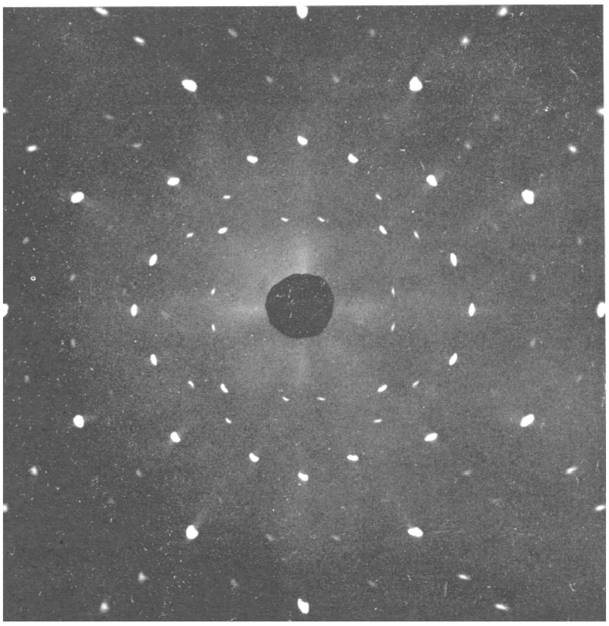

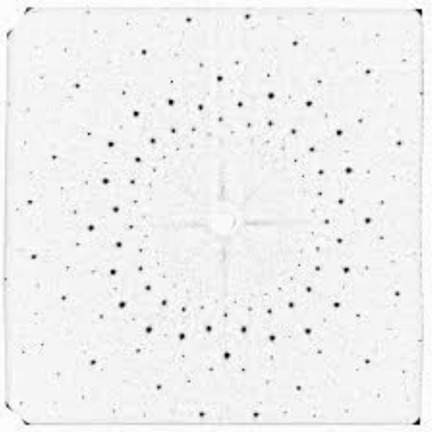

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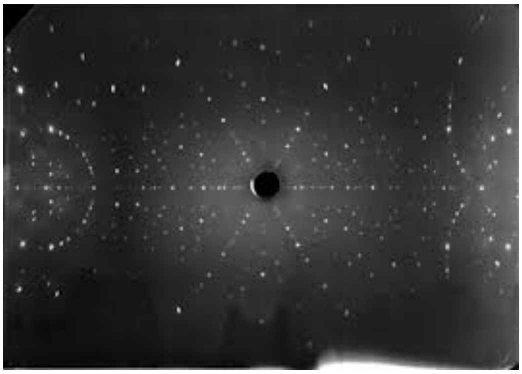
Solid State Physics



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Orientation of Planes in Crystals

Point locations in a crystal are described by coordinates expressed in fractions of the unit cell vectors - the axes do not have to be orthogonal.

Directions are expressed with vectors, specified by two points. Typically one will be at the origin (000). To express the vector in conventional notation, take the endpoint coordinates and reduce to a system where the coordinates have their smallest integer values.

E.g., [110] describes the direction starting from the origin and pointing at the location $x = 1$, $y = 1$, $z = 0$.

Negative directions are conventionally specified with the negative sign written as a bar over the relevant term, e.g., $[\bar{1}01]$ points from the origin to the coordinate –1, 0, 1.

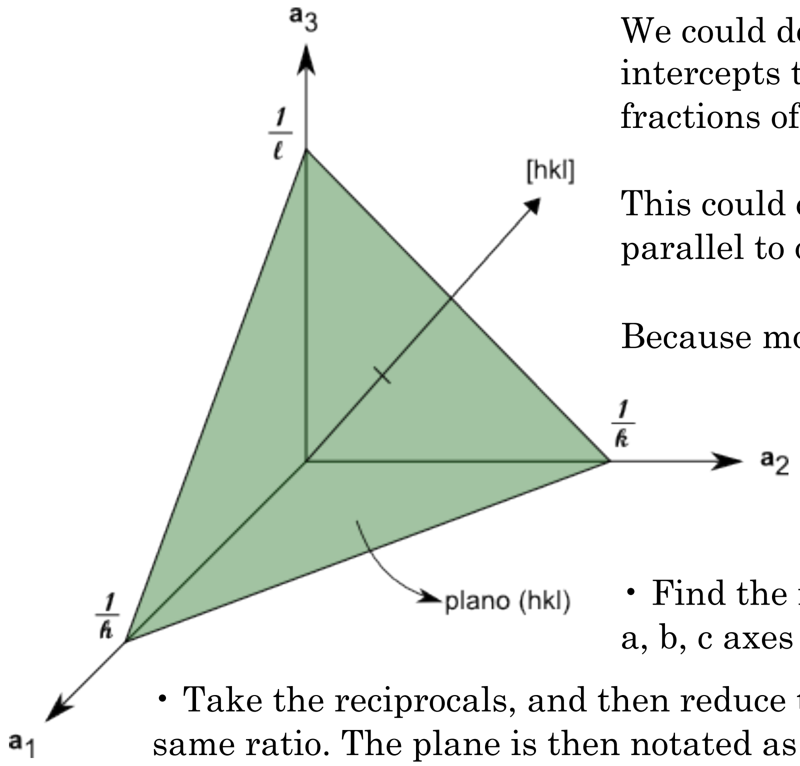
A vector can be used to describe a plane, because it is normal to a plane, but this is not usually the most convenient way to do so.

Orientation of Planes in Crystals

- Crystal structure: Diffraction methods measure the distance between parallel planes of atoms. This information is used to determine the lattice parameters (the angles between lattice points are also measured by diffraction).
- Deformation of of metals: In solids that are ductile (deformable), plastic deformation occurs when atoms slide past one another. This slippage occurs more easily along specific planes within the crystals.
- Transport of electrons and/or heat: In some materials, thermal and electrical conduction happens quickly in certain crystal planes, and slowly outside those planes.

Example: $YBa_2Cu_3O_7$ superconductors: Cu-O planes conduct pairs of electrons (Cooper pairs) responsible for superconductivity. Perpendicular to these planes the material acts as an insulator.

Specifying a Plane with Miller Indices



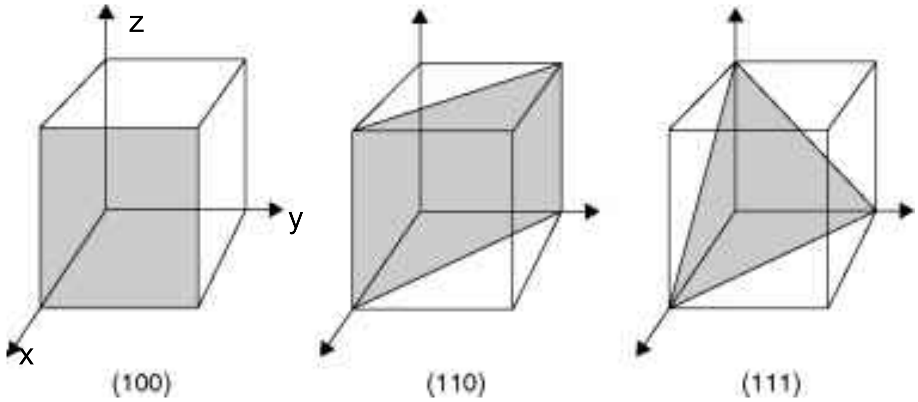
We could define a plane by where it intercepts the three axes, expressed as fractions of the lattice constants a, b, c.

This could cause trouble if the plane is parallel to one axis (intercept = ∞).

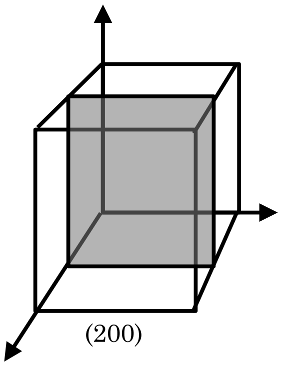
Because most of the information about crystal planes comes from diffraction patterns, the reciprocals of the intercepts turn out to be more useful.

- Find the intercepts $1/h$, $1/k$, $1/l$, on the a, b, c axes respectively.
- Take the reciprocals, and then reduce to three integers having the same ratio. The plane is then notated as (hkl).

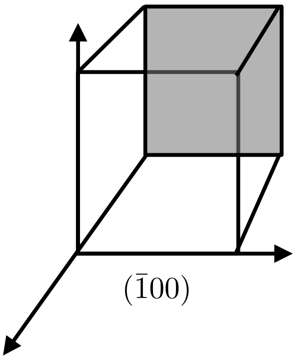
Miller Indices



The indices *hkl* may indicate a single plane or multiple parallel planes. Depending on the lattice, many planes are equivalent due to symmetry (e.g, the faces of a cube).



The plane (200) cuts the x-axis at ½00. It is parallel to (100).



If the plane cuts an axis at a negative value, the index is noted with a bar on top.

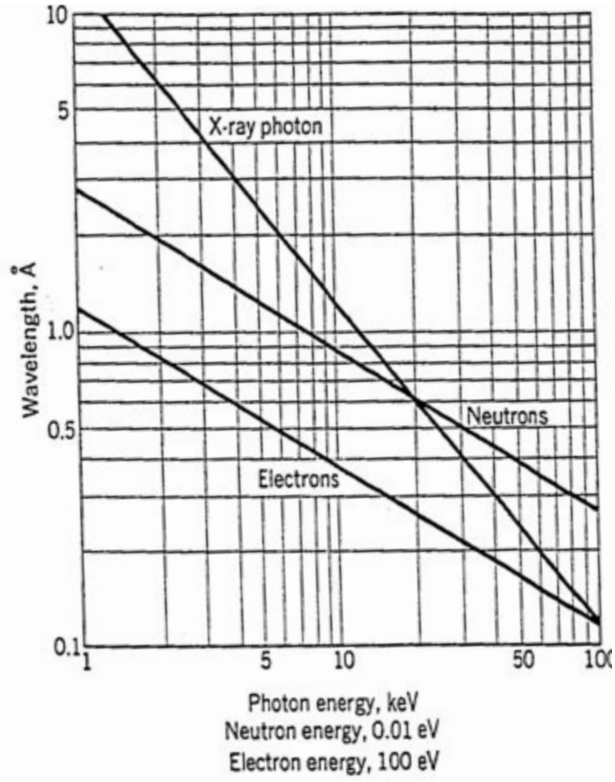
Diffraction and Crystal Structure

Electron microscopy has a practical resolution limit of about 0.5 Å (50 pm).

For fine details of crystal structure, we rely on the diffraction of X-ray photons, neutrons, and sometimes of electrons.

For X-rays, we need photon energies of at least 10-50 keV. These can be generated by the deceleration of electrons in metal targets or by transitions in the most tightly bound energy levels of a target atom.

E.g., the Kα line of Mo has a wavelength of 0.709 Å.



Diffraction and Crystal Structure

Electromagnetic radiation on an atom may be scattered elastically (at the frequency of the incident radiation). The superposition of scattered waves results in reflection and refraction.

If the wavelength of the incident beam is similar to or smaller than the lattice separation constant, one or more diffracted beams may be produced.

X-ray wavelengths: $\lambda(\text{Å}) = \dfrac{12.4}{E(\text{keV})}$

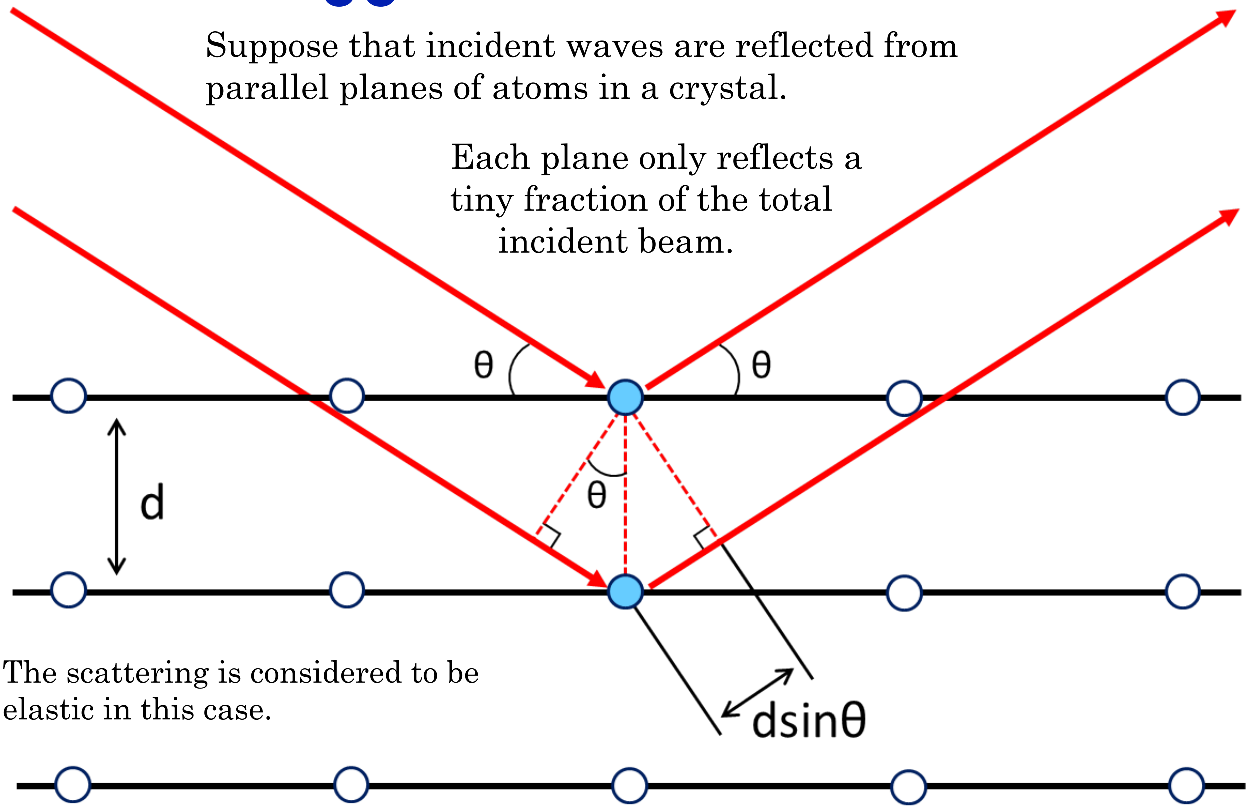
neutron wavelengths: $\lambda(\text{Å}) = h/p = \dfrac{0.28}{E(\text{eV})^{1/2}}$

neutrons are very useful because of their magnetic moment: structure of magnetic crystals can be explored.

electron wavelengths: $\lambda(\text{Å}) = \dfrac{12}{E(\text{eV})^{1/2}}$

strong interactions with matter, only a short useful distance.

Bragg's Law for Diffraction

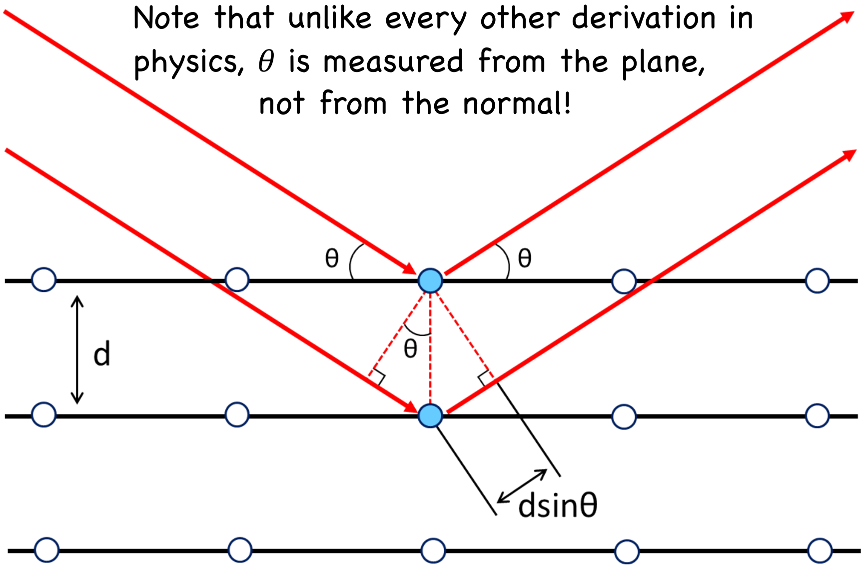


Suppose that incident waves are reflected from parallel planes of atoms in a crystal.

Each plane only reflects a tiny fraction of the total incident beam.

The scattering is considered to be elastic in this case.

Bragg's Law for Diffraction



Note that unlike every other derivation in physics, θ is measured from the plane, not from the normal!

Bright diffraction spots will be observed only where the reflected beams interfere constructively with each other.

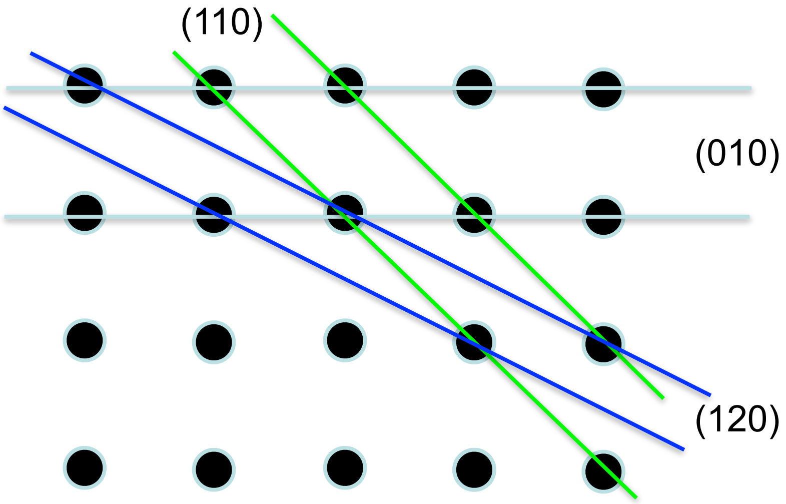
The path difference between two reflected rays is $2d\sin\theta$.

$$\boxed{2d\sin\theta = n\lambda}$$

The Bragg Law results from the strict periodicity of the crystal lattice, and the small amount of reflection from each individual plane. Only defined for $\lambda \leq 2d$. As the wavelength decreases, the angle of incidence must decrease.

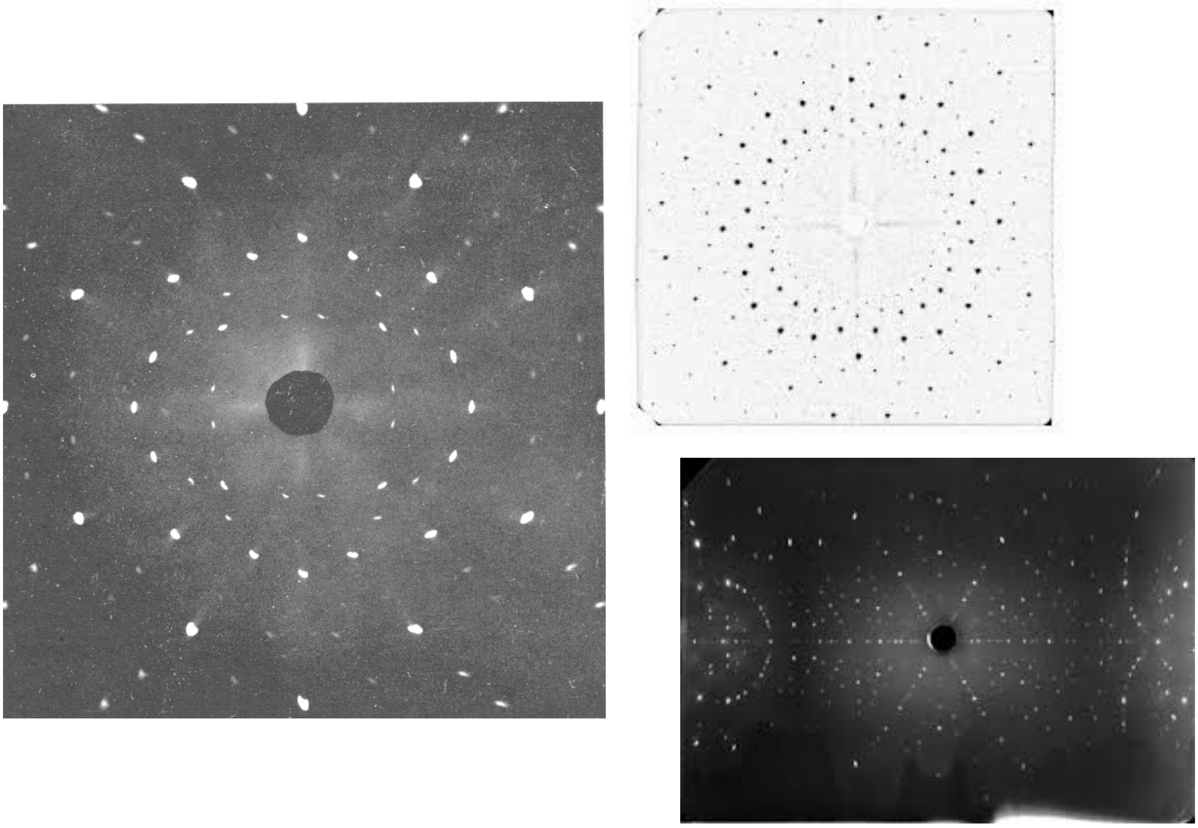
Bragg Diffraction

The planes involved in Bragg diffraction are the planes of the crystal lattice (defined by the Miller indices). This may have little or nothing to do with the surface of the material!



Any given crystal can have enormous numbers of Bragg planes, as it gets larger.

The distance between planes tends to decrease as the indices increase.



Experimental Diffraction Methods

The Bragg Law, $2d\sin\theta = n\lambda$, shows that in general, x-rays of a specific wavelength will not be reflected unless the angle of incidence is has the exact value required.

To use diffraction techniques experimentally we need to scan continuously until we find the right match of θ and λ. (Usually scan through angles).

The **Laue method:** a single crystal is held stationary in a beam of x-rays with a continuous distribution of λ. Only the “correct” wavelengths are diffracted, but there can be multiple correct λ because there are multiple crystal planes. Different orders (n values) may also contribute.

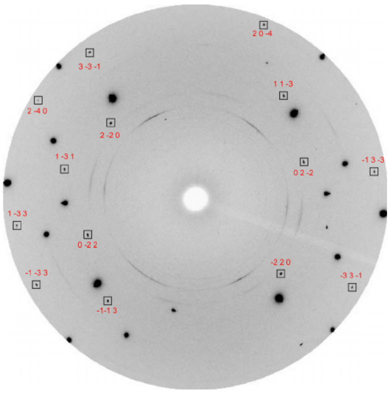
The **rotating crystal method:** a crystal is rotated about a fixed axis in a beam of single-energy neutrons or electrons. The incident beam is made monochromatic by a filter or by reflection from another crystal.

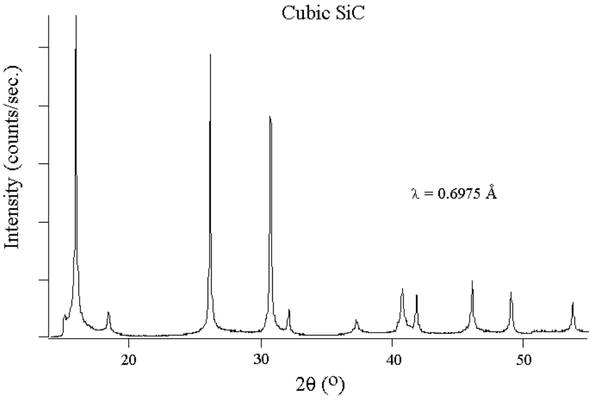
Simple structures were all solved decades ago. Modern use in determining the structure of enzymes with A ~ 10,000 to 100,000.

Experimental Diffraction Methods

The **powder method** produces a continuous distribution of angles simultaneously, by creating a random distribution of crystal orientations. Only the crystals that happen to have the correct orientation will produce bright diffraction spots.

The diffraction is produced by individual crystals, but many different orientations will work- the reflected rays travel outward along a cone centred on the incident beam, with opening angle 2θ, producing a series of concentric rings.





Amplitude of the Scattered Wave

The Bragg condition tells us the scattering angles, but if we want to analyse the crystal structure quantitatively, we need to be able to analyse the intensity of the bright spots as a function of angle.

The Laue method calculates amplitudes by adding up the contributions from many differential volume elements of the crystal, assuming that the response is linear and the scattering is elastic ($\omega' = \omega$, $k' = k$).

Find the scattering vector k' in terms of the incident wavevector k and the primitive vectors of the lattice, a, b, and c .

If we choose an arbitrary origin at a lattice point in the crystal, then the vector linking that origin to any other lattice point is given by

$$\rho = ma + nb + pc$$

where m, n, and p are integers.

If the phase of the incident wave is 1 at the origin,
the phase at ρ is $\exp(ik\cdot\rho)$

Laue method for scattering amplitude

In free space, one component of the incident wave is $E(x) = E_0 e^{i(k\cdot x - \omega t)}$.

An atom at position ρ creates a scattered wave $E_{\text{sc}}(r) = CE(\rho)\,\dfrac{e^{ikr}}{r}$ with normalisation constant C that includes an angular dependence we can ignore for spherically symmetric scatterers.

Substitution gives $E_{\text{sc}}(r) = CE_0 e^{ik\cdot\rho}\,\dfrac{e^{i(kr-\omega t)}}{r}$

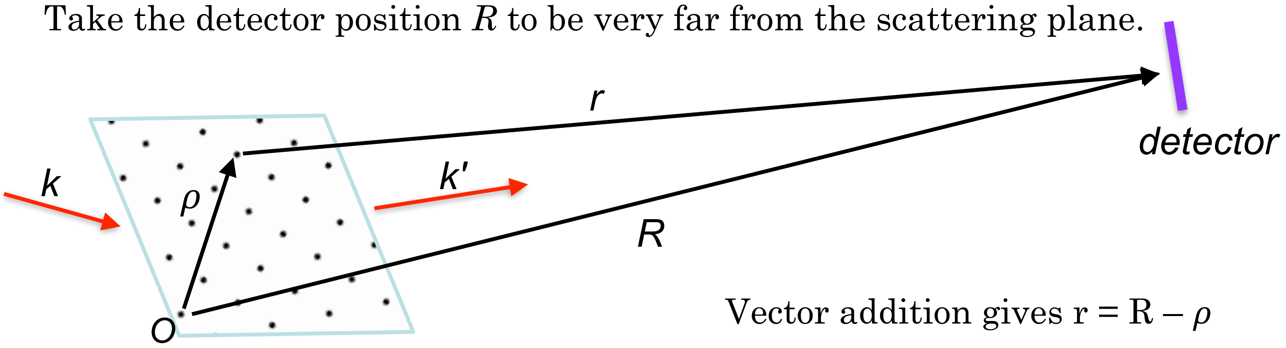
- The scattered wave amplitude is proportional to the incident wave amplitude.
- The 1/r factor is required to conserve scattered energy.
- The whole thing is a solution of the radial wave equation,

$$\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right) E_{\text{sc}}(r) = 0$$

- If we have a photon counting device at position R, we can sum all of the scattered waves from each point in the lattice to get the amplitude at R.

Detected Amplitude

Take the detector position R to be very far from the scattering plane.



Vector addition gives r = R – ρ

If (ρ/R << 1), then r ≈ R – $\rho\cos\theta$. or r ≈ R.

The scattering vector is $\Delta k = k' - k$

In this approximation, we can develop an expression for the partial scattered wave amplitude at R due to the atom at ρ,

$$E_{\text{sc}}(r) = \left(\frac{CE_0 e^{ikR} e^{-i\omega t}}{R}\right)\ \exp(-i\rho\cdot\Delta k)$$

Total Scattering Amplitude

The total scattering at a given point due to a lattice of point atoms is found by summing over the E_{sc} for all possible vectors ρ.

For a finite crystal in the shape of a parallelipiped, there are M individual scatterers. In general these may differ, but for now consider them to be identical. The scattering amplitude A at R is proportional to the sum

$$A \equiv \sum_{mnp} \exp[-i(ma + nb + pc) \cdot \Delta k]$$

This sum has a maximum where $(ma + nb + pc) \cdot \Delta k = 2\pi$

when this condition is met, A is maximised, with value $A = M^3$.

When this condition is not met, A is drastically reduced, such that it very quickly approaches zero in the case of a large number of scatterers.

Scattering by electrons

In a more general case, the scattering will arise due to a nearly continuous distribution of electrons throughout the crystal. In this case we have to consider the scattering from a small volume element dV.

The scattering from a volume element dV is proportional to the density of scatterers (usually electrons), denoted n(ρ), expressed as $\int dV \ n(\rho) e^{-i\rho \cdot \Delta k}$

The rest of the argument is the same: that there are only very few specific scattering vectors that maximise the scattering amplitude.

In real crystals, the scattering amplitude is typically either very close to the maximum value, or very close to zero.

Diffraction Conditions

To satisfy the condition that the phase of the summed wave is unity, there must be definite relationships known as the Laue equations between the lattice parameters and the scattering vector:

$$a \cdot \Delta k = 2\pi h \qquad b \cdot \Delta k = 2\pi k \qquad c \cdot \Delta k = 2\pi l$$

For a scattering vector satisfying the Laue equations, the scattering amplitude

$$A = \sum_{mnp} \exp[-2\pi i(mh + nk + pl)]$$

Since all the parameter are integers, it's easy to show that A = M^3

When the crystal axes are orthogonal (e.g., cubic lattice), it's easy to solve for the allowed values of Δk,

$$\Delta k = 2\pi \left(\frac{h}{a}\hat{x} + \frac{k}{b}\hat{y} + \frac{l}{c}\hat{z} \right)$$

This isn't true for arbitrary crystal geometry. For this we need the concept of the *reciprocal lattice*, developed by J.W. Gibbs.

Reciprocal Lattices

In a general lattice, we have the relationship $\Delta k = hA + kB + lC$ where the vectors A, B, and C need to be determined.

Substitution into the Laue equations

$$a \cdot \Delta k = 2\pi h \qquad b \cdot \Delta k = 2\pi k \qquad c \cdot \Delta k = 2\pi l$$

shows that the following relations must hold: $A \cdot a = B \cdot b = C \cdot c = 2\pi$, and all other dot products (e.g., A·b) must equal 0.

A, B, and C must be mutually perpendicular to each other, and we can find their values by solving for A·a = 2π, etc. This gives

$$A = 2\pi \frac{b \times c}{a \cdot b \times c} \qquad B = 2\pi \frac{c \times a}{b \cdot c \times a} \qquad C = 2\pi \frac{a \times b}{c \cdot a \times b}$$

A, B, and C are the fundamental vectors of the reciprocal lattice.

Every crystal structure with fundamental vectors a, b, c, has the reciprocal lattice vectors A, B, C.

Reciprocal Lattices

The reciprocal lattice is as important as the real lattice:

- An electron microscope image maps the real lattice.
- A diffraction pattern maps the reciprocal lattice.

Vectors in the reciprocal lattice have the units of inverse length.

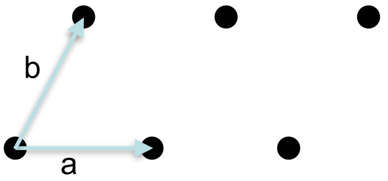
The reciprocal lattice is in fact a lattice in Fourier space, which is the same as the space occupied by wavevectors.

For a crystal with real lattice $\rho = ma + nb + pc$, there will be the reciprocal lattice $G = hA + kB = lC$. (m, n, p, h, k & l are all integers).

The scattering amplitude has its maximum if scattering vector $\Delta k = G$.

Reciprocal Lattice Example in 2D

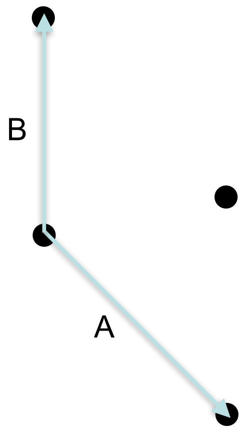
A two-dimensional lattice has the basis vectors $a = 2\hat{x}, \quad b = \hat{x} + 2\hat{y}$.



Find the basis vectors of the reciprocal lattice.

We have a 3D definition for the reciprocal lattice, which we can use if we assume that c is perpendicular to a and b:

$$\begin{aligned} b \times c = \hat{x} \times \hat{z} + 2\hat{y} \times z &= -\hat{y} + 2\hat{x} \\ a \cdot b \times c = 2\hat{x} \cdot (2\hat{x} - \hat{y}) &= 4 \\ A &= \pi(\hat{x} - \hat{y}/2) \end{aligned}$$



$$\begin{aligned} c \times a = \hat{z} \times 2\hat{x} &= 2\hat{y} \\ b \cdot c \times a = (\hat{x} + 2\hat{y}) \cdot 2\hat{y} &= 4 \\ B &= \pi\hat{y} \end{aligned}$$

The "Ewald Construction"

There is an equivalent formulation of the Bragg condition for diffraction that comes from the restrictions on the scattering vector and the requirement that the scattering is elastic.

Thus: $\boldsymbol{k}' = \boldsymbol{k} + \mathbf{G}$, and $\hbar\omega' = \hbar\omega$. The second condition means that the magnitude of k' is equal to the magnitude of k.

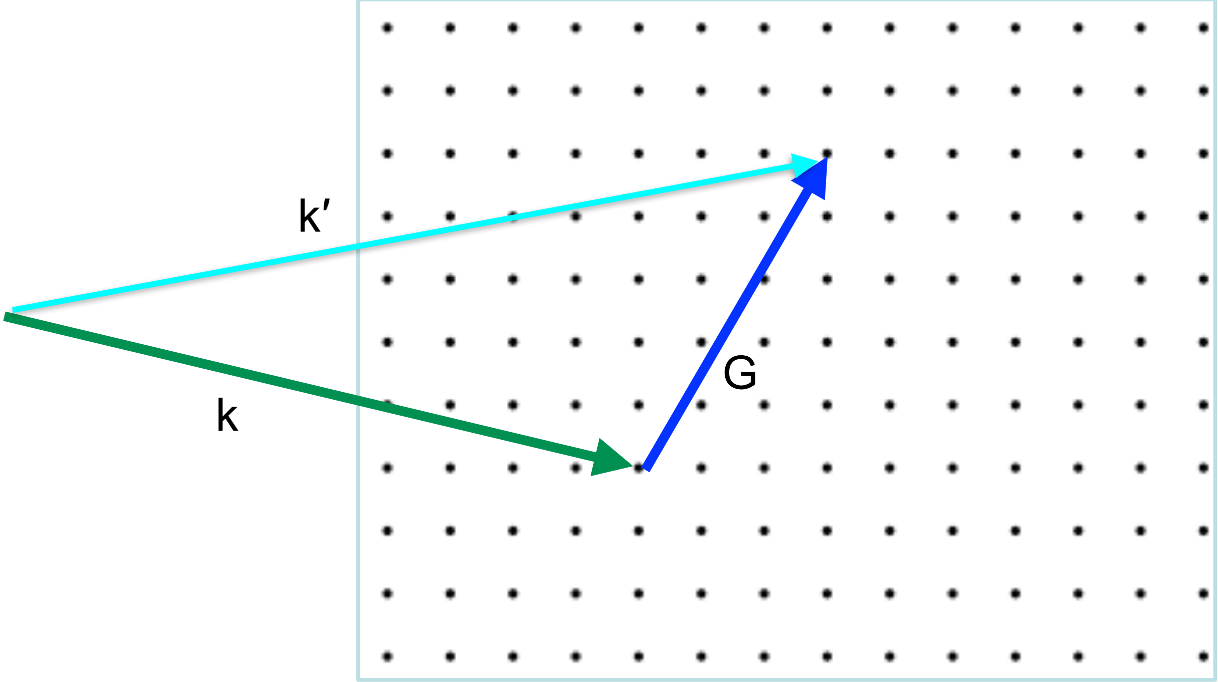
$k'^2 = k^2 + 2(\boldsymbol{k}\cdot\mathbf{G}) + G^2$, so we find that $\boxed{2(\boldsymbol{k}\cdot\mathbf{G}) + G^2 = 0.}$

This requirement can be shown to be a result of conservation of momentum in the (crystal + EM wave) system. It is used far more often than the Bragg condition, to which it is equivalent.

The Ewald construction is a geometric interpretation of the condition above, as vectors in the reciprocal lattice; it is frequently encountered in x-ray diffraction studies.

The "Ewald Construction"

$\boldsymbol{k}' = \boldsymbol{k} + \mathbf{G}$



reciprocal lattice

The Brillouin Zones

The Brillouin construction is more generally applied to mapping electron states in a solid. A Brillouin zone is the equivalent of a Wigner-Seitz cell in Fourier space (the reciprocal lattice). It represents a visualisation of the diffraction condition. We rewrite the diffraction condition: (–G is equiv to G)

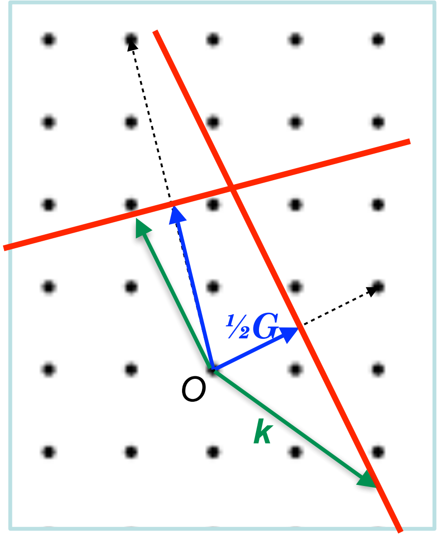
$$2k \cdot G = G^2$$

$$k \cdot (G/2) = (G/2)^2$$

Construct a plane perpendicular to the endpoint of the ½G vector.

Any wavevector *k* that ends on the plane thus defined will satisfy the diffraction condition.

The planes form part of the boundary of a Brillouin zone.



reciprocal lattice

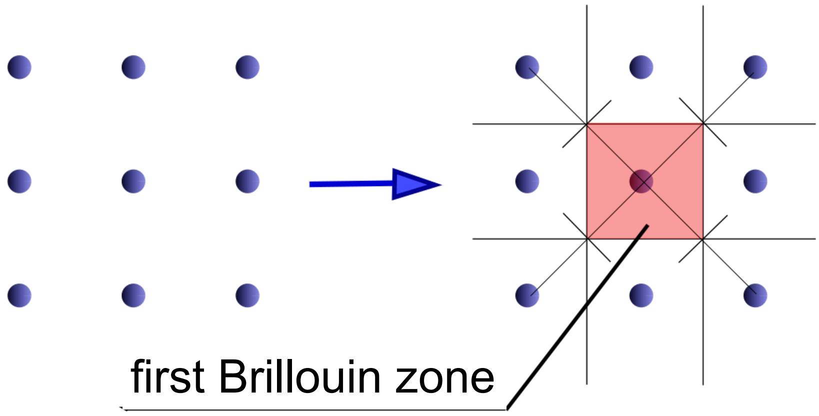
Each vector G takes us from the origin to a unique lattice point. The vectors ½G get us halfway there.

The diffracted beam will have the direction $k' = k + G$

The Brillouin Zones

The central region around the origin of the reciprocal lattice is called the ***first Brillouin zone.*** This is the smallest volume entirely bounded by planes that are the perpendicular bisectors of the reciprocal lattice vectors.

The first Brillouin zone is a primitive cell of the reciprocal lattice. Any incident wavevector *k* on the first Brillouin zone can be Bragg diffracted by the crystal. Knowledge of these zones will be quite important for working out the electronic energy band structure of the crystals.



Example: Reciprocal of the sc Lattice

The simple cubic lattice has primitive translation vectors
$\vec{a} = a\hat{x} \qquad \vec{b} = a\hat{y} \qquad \vec{c} = a\hat{z}$, with cell volume $\vec{a} \cdot \vec{b} \times \vec{c}$.

The translation vectors of the reciprocal lattice are $A = \frac{2\pi}{a}\hat{x}$, etc.

Therefore the reciprocal lattice is also simple cubic, with lengths $2\pi/a$

The planes normal to the six vectors ±½A, etc., define the boundaries of the first Brillouin zone. This creates a cube of edge length $2\pi/a$.

Mechanical Properties of Solids

Brief review of the principles behind the binding of solids by electrostatic forces, according to a few competing principles.

- The positive ions should be kept apart, to minimise Coulomb repulsion.

- The valence electron should be kept apart for the same reason.

- The valence electrons should be close to the ions, to maximise the Coulomb attraction of unlike charges.

- These three rules have to be balanced so that the total energy is minimised; that is, the decrease in potential energy must be larger in magnitude than the accompanying increase in kinetic energy (any localisation of electrons in space tends to increase their K.E.)

The Lennard-Jones Potential

The potential energy of two atoms separated by a distance r is determined by the balance between attractive electrostatic forces and repulsive forces from the Pauli exclusion principle (overlap energy).

The overlap energy depends on the details of the charge density distribution and is awful to calculate. The attractive forces often closely resemble the classical van der Waals energy that characterises the force between two induced dipoles.

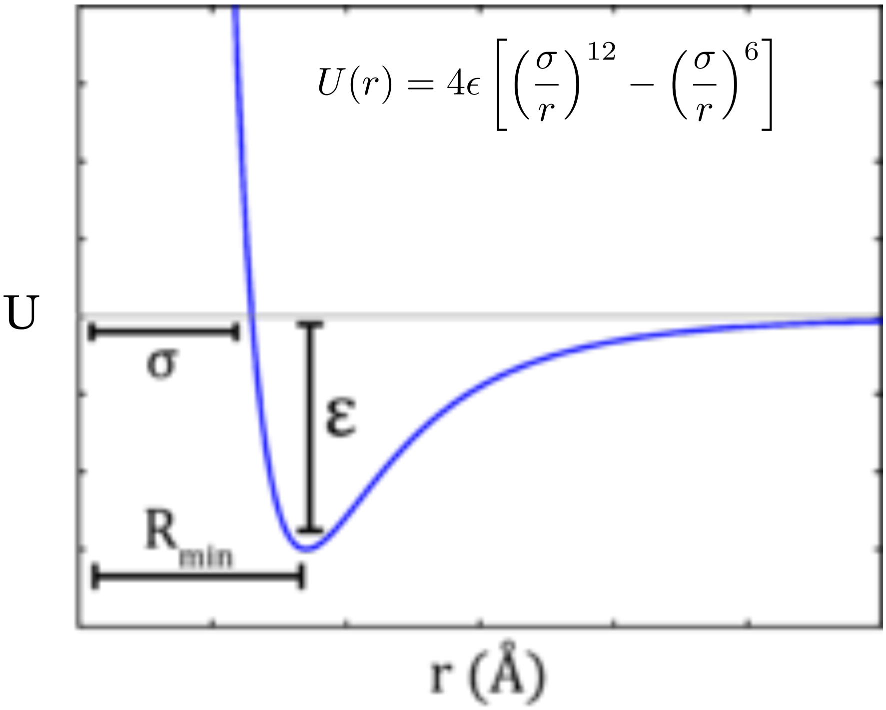
A reasonable approximation to the overlap energy is B/r^{12} with constant B.

The van der Waals interaction is roughly C/r^6 with constant C.

The total energy is conventionally written $U(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$

where $C = 4\epsilon\sigma^6$ and $B = 4\epsilon\sigma^{12}$ define the new parameters ϵ and σ

The Lennard-Jones Potential



The force between two atoms is given by F = –∇U.

Only a good approximation for weakly cohesive molecular solids.

As the Pauli overlap energy is only known approximately, other forms may be more convenient in some circumstances, e.g.,

$U_{\text{repulsive}} \approx \lambda e^{-R/\rho}$

Total Cohesive Energy

At sufficiently low temperatures, the kinetic energy of the atoms can be ignored and the total energy of a solid made up of N pairs of atoms can be found by summation:

$$U_{\text{tot}}(r) = \frac{N}{2} 4\epsilon \left[\sum_{i \neq j} \left(\frac{\sigma}{\rho_{ij} R} \right)^{12} - \sum_{i \neq j} \left(\frac{\sigma}{\rho_{ij} R} \right)^{6} \right]$$

where ρ_{ij} is the separation between atoms *i* and *j*, expressed as a multiple of the nearest-neighbour distance *R*. The leading factor of (1/2) is required to avoid double-counting pairs of atoms.

The summation depends on crystal structure. For example, for *fcc* the terms are

$$\sum_{i \neq j} \rho_{ij}^{-12} = 12.13188 \qquad \sum_{i \neq j} \rho_{ij}^{-6} = 14.45392$$

To interpret this, recall there are 12 nearest-neighbours in the *fcc* structure. The first term is very close to 12, meaning the repulsion is dominated by the nearest neighbours. The attraction has some extra contribution from more distant atoms.

Inert Gas Crystals

The Lennard-Jones potential is particularly useful for gases like He, Ne, Ar, etc., which have great difficulty in forming chemical bonds.

In these cases, we can calculate the predicted equilibrium separation in terms of the parameters of the potential by taking the derivative dU/dR, setting it equal to zero, and solving for R_0.

The Lennard-Jones potential for the face-centred cubic predicts that $R_0 = 1.09\sigma$. Experiments show a good match for all the inert gases except helium. E.g., the multiplier for Ne is 1.14, for Ar 1.11, for Xe 1.09.

Why doesn’t the simple prediction work for He? It is too low mass, so the zeropoint enegy of the system as an oscillator plays an important role. For more massive atoms, the agreement gets better and better.

This calculation assumes that *fcc* is the structure. At absolute zero a detailed calculation shows the *hcp* is energetically preferred, by ~0.01%.

Inert Gas Crystals Cohesive Energy

We can plug the tabulated summations for the *fcc* crystals into the Lennard-Jones potential at R_0 to work out the cohesive energy per atom. Note this formula predicts the same energy for all inert gas crystals, but quantum effects on the lower mass examples make them differ (especially helium).

The heavier the atom, the smaller the quantum correction (e.g., 28% for Ne, just 4% for Xe). The correction comes from confinement of the atom of mass M within a potential well of dimension roughly equal to its wavelength.

This relates back to the deBroglie relation $p = h/\lambda$, with $KE = p^2/2M$. The quantum zeropoint energy correction is inversely proportional to the mass in this model. Observations of neon crystals support this model, based on the lattice constants at a temperature of 2.5 K:

$$Ne^{20}, \quad a = 4.4644\ \text{Å}$$
$$Ne^{22}, \quad a = 4.4559\ \text{Å}$$

Compressibility and Bulk Modulus

The bulk modulus of a material is defined $B \equiv -V\frac{dP}{dV}$, and the compressibility is defined as 1/B.

B is a measure of the stiffness of the crystal: the energy required to produce a given deformation to the lattice. The higher B, the stiffer the material.

The connection to energy is explicit if we assume that the compression is a reversible (adiabatic) process, with no change in entropy. Then $-PdV = dU$, and $dP/dV = -d^2U/dV^2$, so that in that special case, $B = V\, d^2U/dV^2$.

Our crystal lattice parameters can give us B for a given structure, e.g., the *fcc* case already considered.

$V_{fcc} = Na^3/4$ for N atoms. In terms of the nearest-neighbour distance, $R = 2^{-1/2}a$.

Compressibility and Bulk Modulus

$V_{fcc} = Na^3/4$ for N atoms. In terms of the nearest-neighbour distance, $R = 2^{-1/2}a$.

Substitution into the expression for U_{tot} using the summed quantities [slide 5] lets us write $U_{\text{tot}}(V) = \frac{b_{12}}{V^4} - \frac{b_6}{V^2}$, where proper accounting allows us to say

$$b_{12} \equiv \frac{1}{2} 12.132 N^5 \epsilon \sigma^{12} \qquad b_6 \equiv 14.454 N^3 \epsilon \sigma^6$$

At equilibrium, $dU_{tot}/dV = 0$ so $\frac{4b_{12}}{V^5} = \frac{2b_6}{V^3}$

Solving for V, we find $V_0 = \left(\frac{12.132}{14.454}\right)^{1/2} N\sigma^3$.

And the bulk modulus is $B = V_0 \left(\frac{d^2U}{dV^2}\right)_{V_0}$ which is $\sqrt{2}\,\frac{b_6^{5/2}}{b_{12}^{3/2}}$

Compressibility and Bulk Modulus

The coefficients will change depending on crystal type, but the main functional form, B proportional to ϵ/σ^3, will be maintained.

The big picture: bulk properties like compressibility can be determined without too much difficulty from the following properties of a molecule: the lattice type, binding energy ϵ, and minimum separation σ.

For the example of a van der Waals/molecular solid, with binding described by the Lennard-Jones potential, this was relatively straightforward.

For more complex systems, we need to develop a more general method.

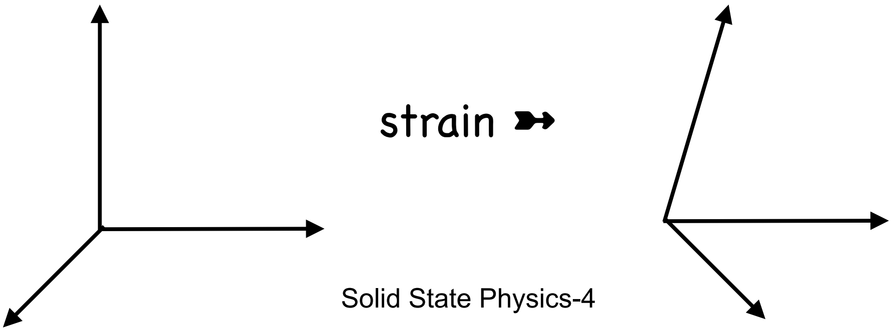
Elastic Strains and Waves

For many disturbances, we can treat a crystal as a homogeneous, continuous medium rather than an array of discrete atoms.

This *continuum approximation* will be valid for periodic disturbances with wavelength much larger than the size of the crystal lattice, e.g., $\lambda > 100$ Å.

For small strains only, we will find that Hooke's law is empirically valid for a broad range of solids: in an elastic solid, the strain is directly proportional to the stress.

The effect of a small strain is to take an orthogonal coordinate system embedded in the solid, and deform it



Elastic Strains

In a uniform deformation, every primitive cell is deformed in the same way.

The new, distorted coordinate axes are given by

$$\begin{aligned} x' &= (1+\epsilon_{xx})\hat{x} + \epsilon_{xy}\hat{y} + \epsilon_{xz}\hat{z} \\ y' &= \epsilon_{yx}\hat{x} + (1+\epsilon_{yy})\hat{y} + \epsilon_{yz}\hat{z} \\ z' &= \epsilon_{zx}\hat{x} + \epsilon_{zy}\hat{y} + (1+\epsilon_{zz})\hat{z} \end{aligned}$$

where the components $\epsilon_{\alpha\beta}$ define the deformation. These are dimensionless and have values <<1 when the deformation is small.

The original unit vectors may change length; e.g., to first order $x' = x + \epsilon_{xx}$

An atom initially at position **r** will now be found at **r**′, with displacement $R \equiv r' - r \;= (x' - \hat{x})x + (y' - \hat{y})y + (z' - \hat{z})z$

Instead of writing out all the $\epsilon_{\alpha\beta}$, we introduce more general and flexible notation, $R = u(r)\hat{x} + v(r)\hat{y} + w(r)\hat{z}$

Elastic Strains

If we take the deformation at the origin equal to 0, we can Taylor series expand R and find that

$$\epsilon_{xx} = \frac{\partial u}{\partial x} \qquad \epsilon_{yx} = \frac{\partial u}{\partial y} \qquad \epsilon_{xy} = \frac{\partial v}{\partial x} \quad \text{, etc.}$$

It's conventional and convenient to make a small change of notation to what are called the **strain components**, $e_{\alpha\beta}$. If $\alpha = \beta$, then $e_{\alpha\alpha} = \epsilon_{\alpha\alpha}$.

For $\alpha \neq \beta$, $e_{\alpha\beta} = \hat{\alpha} \cdot \hat{\beta} \qquad \approx \epsilon_{\beta\alpha} + \epsilon_{\alpha\beta}$

E.g., $e_{yz} \approx \epsilon_{zy} + \epsilon_{yz} \quad = \dfrac{\partial v}{\partial z} + \dfrac{\partial w}{\partial y}$ where the equality holds to 1st order.

The point is: we have six dimensionless coefficients that completely define the strain.

Dilation

The fractional increase in volume from a deformation is called dilation.

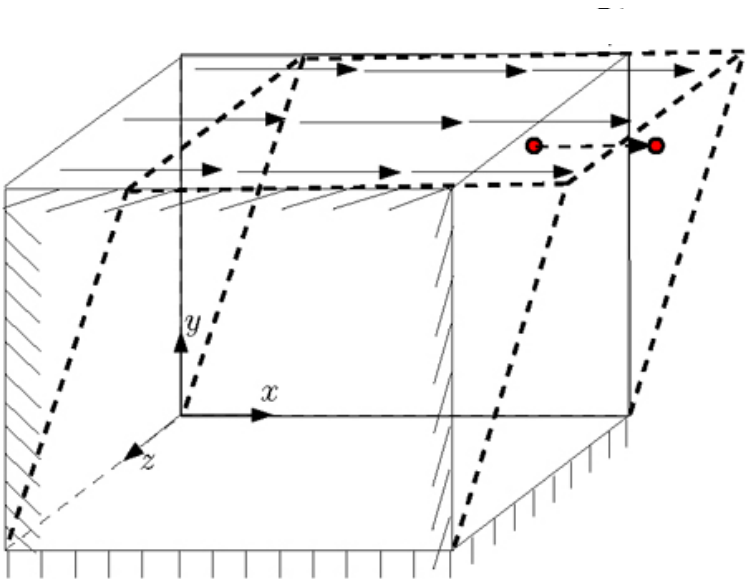
Before deformation, the unit cube has volume $V = \hat{x}\hat{y}\hat{z} = 1$.

Afterward, $V' = x' \cdot y' \times z'$.

From the definitions of the deformation coefficients and the conversion to strain components, it can be shown that

$x' \cdot y' \times z' \approx 1 + e_{xx} + e_{yy} + e_{zz}$

(accurate to first order).

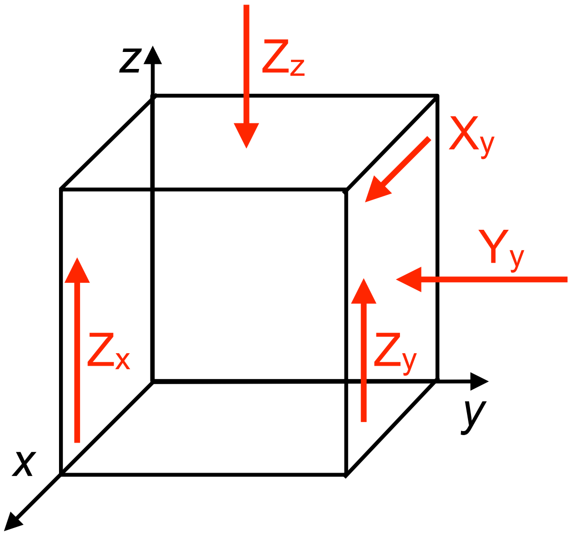


The dilation $\delta \equiv \dfrac{V' - V}{V}$

Here, $\delta \approx e_{xx} + e_{yy} + e_{zz}$

Stress Components

The force per unit area defines the stress. Stress is a tensor, because the area is a vector and so is the force. We define 9 components of the stress tensor, X_x, X_y, X_z, etc. The variable indicates the direction of the force, and the subscript gives the normal vector to the plane across which the force is applied.



The stress tensor can be written

$$(\sigma_{ij}) = \begin{pmatrix} X_x & X_y & X_z \\ Y_x & Y_y & Y_z \\ Z_x & Z_y & Z_z \end{pmatrix}$$

If the net angular acceleration is zero, then only certain combinations of the off-diagonal elements can work- there are only 6 independent components:

$Y_z = Z_y$ $\quad Z_x = X_z$ $\quad X_y = Y_x$

Dimensions: force per unit area, OR energy per unit volume

Elastic Compliance and Stiffness

Hooke's Law holds when the deformation is small, so the strain is linearly proportional to the stress. In this case we can write the stress tensor in terms of the strain components, $(\sigma_{ij}) = (C_{ij})\,(e_{ij})$ where the **elastic stiffness coefficients** or **moduli of elasticity** C_{ij} are the analogue to the spring constant *k* in the elementary Hooke's law expression. C has dimensions of force per unit area.

Remember that 3 of the terms are degenerate, so writing out all the components in full would result in an expression with 6 lines of 6 terms each.

It is also common to define the inverse, that is, to give the strain components as a function of the stress tensor, $(e_{ij}) = (S_{ij})\,(\sigma_{ij})$, where S_{ij} gives the **elastic compliance constants**, with units area/force.

Elastic Energy Density

There are 36 independent compliance (or stiffness) constants, but in many cases this can be reduced by approximations or by the specifics of the problem.

In the small strain approximation, the energy density U is a quadratic function of the strains. The analogue to stored energy in a spring is

$$U = \frac{1}{2}\sum_{\lambda=1}^{6}\sum_{\mu=1}^{6}\tilde{C}_{\lambda\mu}e_{\lambda}e_{\mu}$$

where it is conventional to define the indices 1-6 as *xx, yy, zz, yz, zx, xy*.

Because $e_\lambda e_\mu = e_\mu e_\lambda$, there are only 21 independent terms rather than 36.

These may be reduced further if there is significant symmetry in the crystal. For example, in a cubic crystal there are 4 threefold symmetry axes. Rotation by $2\pi/3$ around any of these interchanges the axes but doesn't alter the overall shape.

Elastic Stiffness Constants: Cubic Crystal

By requiring that the stored energy density remains invariant under the symmetry rotations, such that the result does not depend on the coordinate system chosen, it turns out that a cubic crystal has only three independent stiffness constants:

	e_{xx}	e_{yy}	e_{zz}	e_{yz}	e_{zy}	e_{xy}
X_x	C_{11}	C_{12}	C_{12}			
Y_y	C_{12}	C_{11}	C_{12}			
Z_z	C_{12}	C_{12}	C_{11}			
Y_z				C_{44}		
Z_x					C_{44}	
X_y						C_{44}

Bulk Modulus

Consider the uniform dilation $e_{xx} = e_{yy} = e_{zz} = \delta/3$.

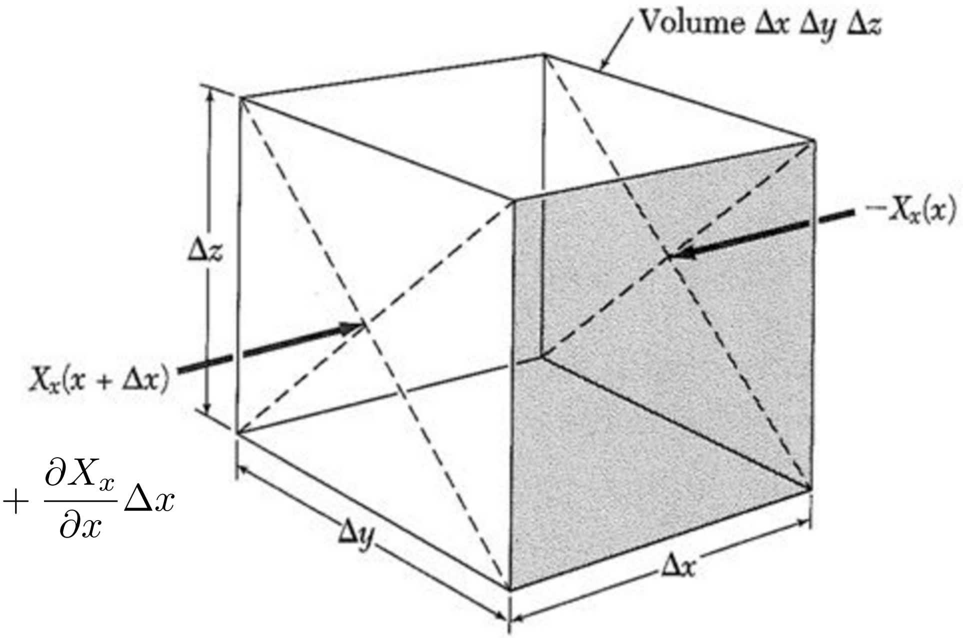
For a cubic crystal, the energy density is $U = \frac{1}{6}(C_{11} + 2C_{12})]\delta^2$

Because δ is the fractional change in volume, we can relate the bulk modulus B to the stiffness constants by substitution, $U = \frac{1}{2}B\,\delta^2$.

So for a cubic crystal, the bulk modulus B is related to the stored energy in the crystal bonds, $B = (C_{11} + 2C_{12})/3$

Elastic Waves (Cubic Crystals)

Consider the forces acting on a volume element of a crystal when it is subject to a stress in the *x* direction, on the *x*-facing planes.

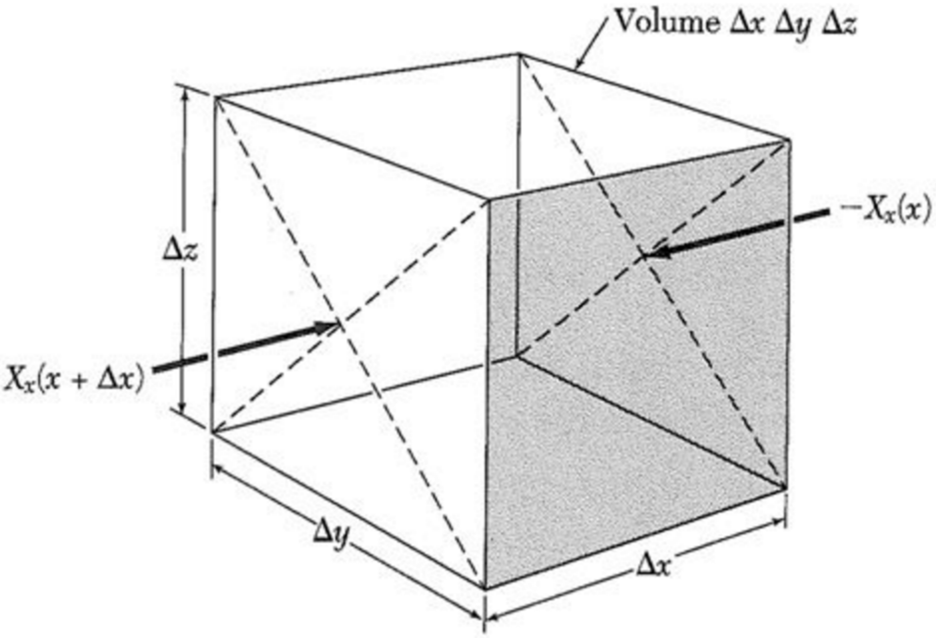


$$X_x(x + \Delta x) \approx X_x(x) + \frac{\partial X_x}{\partial x}\Delta x$$

The net force is $\left(\frac{\partial X_x}{\partial x}\Delta x\right)\Delta y \Delta z$. Including X_y and X_z (shear forces),

$$F_x = \left(\frac{\partial X_x}{\partial x} + \frac{\partial X_y}{\partial y} + \frac{\partial X_z}{\partial z}\right)\Delta x \Delta y \Delta z$$

Elastic Waves (Cubic Crystals)



The mass of the cube is $\rho \Delta x \Delta y \Delta z$

The acceleration in the *x* direction $\partial^2 u/\partial t^2$ can now be calculated

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The equation of motion in the *x* direction can be worked out from considering the forces on a unit volume of the crystal:

$$\rho \frac{\partial^2 u}{\partial t^2} = \frac{\partial X_x}{\partial x} + \frac{\partial X_y}{\partial y} + \frac{\partial X_z}{\partial z}$$

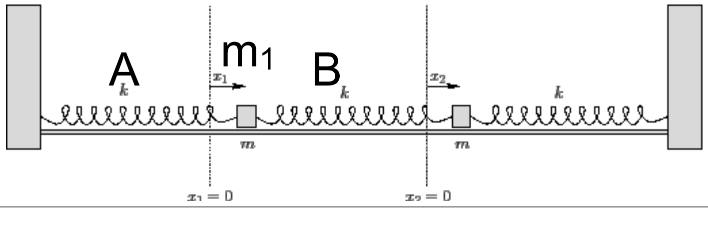
(with similar expressions for *y* and *z*)

For a cubic crystal, we can substitute the stress and strain components from the table above (reduced to the three independent terms). For other lattice types, a similar simplification can usually be found.

For the cubic, $\rho \frac{\partial^2 u}{\partial t^2} = C_{11} \frac{\partial e_{xx}}{\partial x} + C_{12} \left(\frac{\partial e_{yy}}{\partial x} + \frac{\partial e_{zz}}{\partial x} \right) + C_{44} \left(\frac{\partial e_{xy}}{\partial y} + \frac{\partial e_{zx}}{\partial z} \right)$

This may look a little opaque, but the key points are that 1) there are compressive/tensile terms, torque/shear terms, and terms due to the deformation by stresses in the orthogonal directions, and 2) *uniform stresses do not produce a net force.* (Only terms proportional to the variation of these come into play).

Analogy: if springs A and B are equally compressed, there is no acceleration of mass 1.



Elastic Waves in Cubic Crystals

The definitions of the strain components $e_{\alpha\beta}$ allow the substitution of displacements u, v, w into the equation, so for the cubic case:

$$\rho \frac{\partial^2 u}{\partial t^2} = C_{11}\frac{\partial^2 u}{\partial x^2} + C_{44}\left(\frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2}\right) + (C_{12}+C_{44})\left(\frac{\partial^2 v}{\partial x \partial y} + \frac{\partial^2 w}{\partial z \partial x}\right)$$

-the full equation of motion also has the $\partial^2 v/\partial t^2$ and $\partial^2 w/\partial t^2$.

The equation shows that curvature in the displacements across the surface of the unit volume (or, more generally, along planes of the crystal) are directly related to the variation of the displacement with time.

General solution can be quite challenging, but some special cases will be of interest and give a feel for the full range of possibilities.

Waves in the [100] Direction

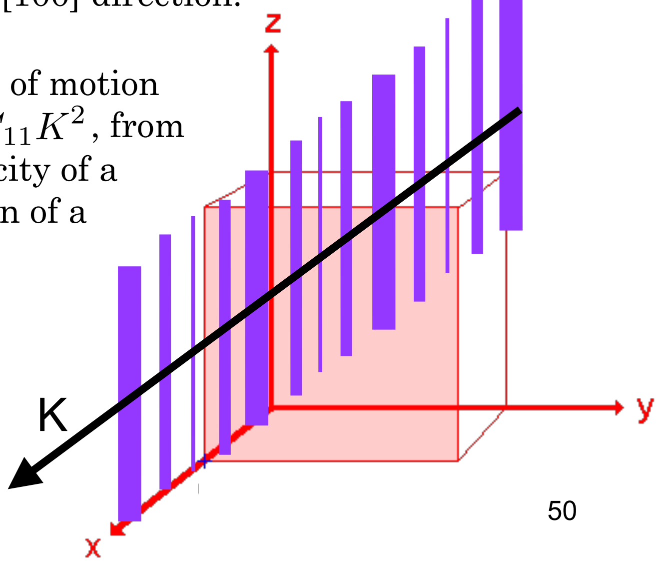
One solution of the equation of motion in the x direction is the longitudinal (compressive) wave, $u(x,t) = u_0 \exp\left[i(Kx - \omega t)\right]$.

u is the x-component of the displacement, $K = 2\pi/\lambda$, and $\omega = 2\pi\nu$.

Both the particle motion and the wavevector K are directed along the x edge of the cube, so it is a wave in the [100] direction.

Explicit substitution into the equation of motion gives the dispersion relation $\omega^2\rho = C_{11}K^2$, from which we can work out the phase velocity of a longitudinal wave in the [100] direction of a cubic lattice,

$\mathrm{v}_{1,100} = \omega/K = (C_{11}/\rho)^{1/2}$



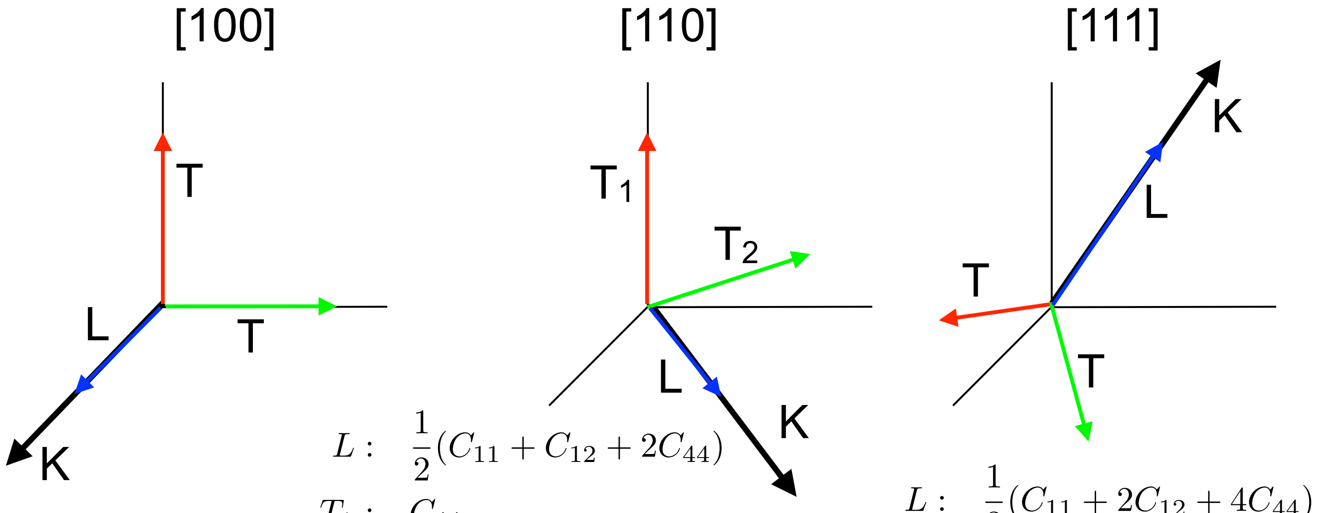
Waves in the [100] Direction

There are also two transverse (shear) wave solutions to the equation, $v(x,t) = v_0 \exp\left[i(Kx - \omega t)\right]$ and $w(x,t) = w_0 \exp\left[i(Kx - \omega t)\right]$. The wavevector is still in the [100] plane, but the displacement oscillates perpendicular to the plane, and the speed is $\mathrm{v}_{t,100} = (C_{44}/\rho)^{1/2}$.

Transverse waves and longitudinal waves will in general have different velocities, because the potential energy of compression and expansion within a plane is likely to be different from the energy required to push atoms slightly in/out of the plane.

For the cubic crystal, the transverse waves in the [100] plane have the same velocity, but this need not be true for other crystal types or for arbitrary crystal lattices.

Wave Propagation in Cubic Crystals



$L:\quad C_{11}$

$T:\quad C_{44}$

$L:\quad \frac{1}{2}(C_{11} + C_{12} + 2C_{44})$

$T_1:\quad C_{44}$

$T_2:\quad \frac{1}{2}(C_{11} - C_{12})$

$L:\quad \frac{1}{3}(C_{11} + 2C_{12} + 4C_{44})$

$T:\quad \frac{1}{3}(C_{11} - C_{12} + C_{44})$

L stands for longitudinal, T for transverse. Arrows show the direction of displacement oscillations. In the [100] and [111] directions, the two transverse modes are degenerate (for a cubic crystal). Effective elastic constants are listed.

Waves in the [110] Direction

Waves that propagate across the face diagonal of a cubic crystal can be used to derive the three elastic constants of the material by observing the different wave speeds (one longitudinal wave, two transverse ones).

The velocities of the first and second transverse waves are different in this case because for one of them K is along a principal axis of the crystal, but the other one is not.

A shear wave travelling in the *xy* plane is $w(x,y,t) = w_0 \exp\left[i(K_x x + K_y y - \omega t)\right]$

The wave vector $K = (K_x + K_y)^{1/2}$ and $\omega^2 \rho = C_{44} K^2$ independent of the propagation direction in the plane (because of the cubic symmetry).

Waves in the [110] Direction

The waves in the plane have two different characters: there must be one longitudinal wave in the direction *K*, and one transverse wave with displacement at right angles to *K* but still in the plane.

The freedom to choose any propagation direction in the plane means that the solutions for *u* and *v* are mixed together.

$$u(x,y,t) = u_0 \exp\left[i(K_x x + K_y y - \omega t)\right]$$
$$v(x,y,t) = v_0 \exp\left[i(K_x x + K_y y - \omega t)\right]$$

The dispersion relations for these waves can be found by substitution into the equations of motion, thus

$$\omega^2 \rho u = (C_{11} K_x^2 + C_{44} K_y^2) u + (C_{12} + C_{44}) K_x K_y v$$
$$\omega^2 \rho v = (C_{11} K_y^2 + C_{44} K_x^2) v + (C_{12} + C_{44}) K_x K_y u$$

The [110] has the specific useful quality that $K_x = K_y = 2^{1/2} K$.

Waves in the [110] Direction

Solving for the dispersion relation means setting the determinant of the coefficients on u and $v = 0$:

$$\begin{vmatrix} -\omega^2\rho + \frac{1}{2}(C_{11}+C_{44})K^2 & \frac{1}{2}(C_{12}+C_{44})K^2 \\ \frac{1}{2}(C_{12}+C_{44})K^2 & -\omega^2\rho + \frac{1}{2}(C_{11}+C_{44})K^2 \end{vmatrix} = 0$$

This leads to two different wave speeds:

$$\omega^2\rho = \frac{1}{2}(C_{11}+C_{12}+2C_{44})K^2 \qquad \omega^2\rho = \frac{1}{2}(C_{11}-C_{12})K^2$$

One of these is the longitudinal wave and one is the shear wave. Which is which? Substitute into the matrix equations for $\omega^2\rho u$ and $\omega^2\rho v$.

The first root of the equation corresponds to the displacements $u = v$, which is the condition to be in the [110] direction, along K. This is the longitudinal wave.

The second root produces $u = -v$: displacement perpendicular to K

Waves in Cubic Crystals: Summary

Disturbances to a crystal structure caused by spatial variation in the stresses will produce travelling waves.

There are three normal modes of oscillation for a crystal for a given magnitude and direction of wave vector K. In general the polarizations and propagation directions will not be mutually perpendicular, although in a cubic crystal they can be, if K is along the crystal axes.

A high degree of complexity is expected, depending on the direction of wave propagation. Even for a cubic crystal with waves along a symmetry plane, transverse and longitudinal waves will in general have different speeds.

If the waves are along certain planes, then the two transverse waves can have different speeds as well. This has the benefit of allowing a direct measure of the stiffness constants from the wave speeds.

Adiabatic Stiffness Constants

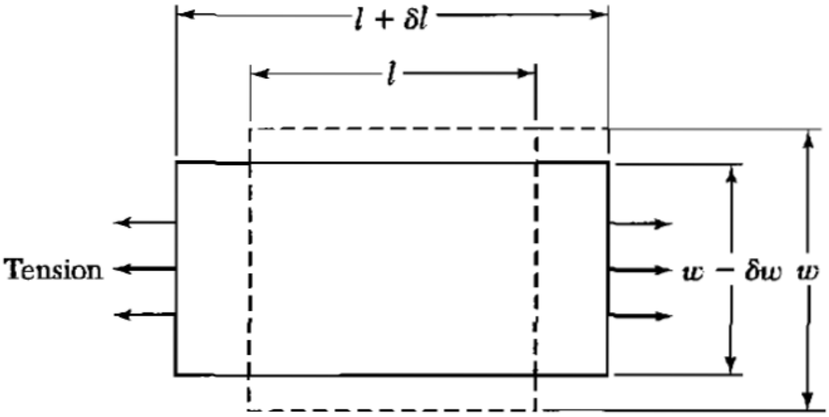
The C values for solids are typically observed to be temperature dependent (decreasing at higher temperature). Conventionally they are measured at several temperatures and extrapolated down to 0 K.

Some typical values for cubic crystals at 300 K are shown for reference, in units of 10^{11} pascals:

W:	$C_{11} = 5.233$;	$C_{12} = 2.045$;	$C_{44} = 1.607$
Cu:	1.684;	1.214;	0.754
K:	0.0370;	0.0314;	0.0188
KCl:	0.403;	0.066;	0.063
Diamond:	10.76;	1.25;	5.76

Young's Modulus & Poisson's Ratio

For tension acting in one dimension, Young's modulus (or the elastic modulus) is defined as the ratio of the stress/strain, (F/A) / ($\delta l/l$)



Poisson's ratio gives the strain perpendicular to the tension as a function of the strain in the direction of the tension.
For many solids, these two numbers plus the bulk modulus are sufficient to describe many of the deformations due to small stresses.

Third-Order Elastic Constants

All of the preceding discussion assumed the validity of Hooke's Law, that is, a linear stress-strain relationship. In this regime the elastic energy density is quadratic in the strain.

For larger stresses, higher-order terms are required. The third-order terms involve products of the strain components, and will be required in order to evaluate coefficients of thermal expansion, and the quantization of sound waves (phonons).