In Chapter 3 we studied the interaction of atoms in a solid. We learned that the interaction consists of a repelling and an attracting term. We can understand the cohesive energy, the melting point, bulk modulus from the interaction energy. We discussed the:

1. Van der Waals-London Interaction:

$$U(R) = 4\varepsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^{6} \right]$$
[1]

This expression is often referred to as the Lennard-Jones potential. R is the distance between two neighboring atoms. The first term is the repulsive term and originates from the Pauli exclusion principle. Two electrons that occupy the same space cannot have the same wavefunction, or have the same quantum numbers. So if the electron distribution of atoms with closed shells overlap, one of the two electrons need to be partial promoted to unoccupied high energy states, so electron overlap increases the total energy of the system and gives thus a repulsive contribution to the interaction energy. One sometimes models the repulsive energy by an exponential form i.e.

$$\lambda e^{-R/\rho}$$
[2]

The 2nd term of the lennard-Jones potential is the attractive term . This term originates from the electrostatic interaction between the atoms. Two neighboring atoms can be considered to be two electrostatically coupled harmonic oscillators. This combined system has a lower ground state energy than the total energy of two non-coupled oscillators. The difference is larger the closer the atoms are together, so this results in an attractive term. Van der Waals interactions plays a crucial role in the formation of solids of noble gasses.

2. Ionic interaction:

$$U(R) = \lambda e^{-R/\rho} - \frac{q^2}{R}$$
[3]

The first term is the repulsive term originating from the Pauli exclusion principle and the 2nd term is the attractive term originating from the electrostatic interaction. The 2nd term is often referred to a the Madelung energy. Note that the electrostatic interaction in an ionic crystal is much more long range than the Van der Waals interaction mentioned under (1). This type of interaction is important to describe the forces that keep the atoms of salts together.

Above given equations can be used to calculate the total cohesive energy of a material. To do so we have to know the crystal structure as one needs to sum up the U(R) contributions of all atom/ion combinations. So for a Xenon solid the total cohesion energy is given by the following expression:

$$U_{tot} = \frac{1}{2} N(4\varepsilon) \left[\sum_j \left(\frac{\sigma}{p_{ij}R} \right)^{12} - \sum_j \left(\frac{\sigma}{p_{ij}R} \right)^{6} \right] \qquad [13]$$

Where $p_{ij}R$ is the distance between atom I and j. U_{tot} is an estimate of the total cohesive energy as it multiplies the energy of the ith atom with 0.5N, i.e. the total number of atoms. The factor 0.5 makes sure that we do not count the interaction energy double. As both the repulsive and attractive terms in the Lennard-Jones potential are very local one normally only sums over next neighbors. For an fcc structure the summation over the next neighbors are given by:

$$\sum_j p_{ij}^{-12} = 12.13188 \qquad \sum_j p_{ij}^{-6} = 14.45392 \qquad [14]$$

For the hcp structure the terms are:

$$\sum_j p_{ij}^{-12} = 12.13229 \qquad \sum_j p_{ij}^{-6} = 14.45489 \qquad [15]$$

And for the bcc structure the terms are:

$$\sum_j p_{ij}^{-12} = 9.11418 \qquad \sum_j p_{ij}^{-6} = 12.2533 \qquad [16]$$

Note that strictly speaking equation [13] gives the dependence of the cohesive energy on the lattice distance R. The experimental cohesive energy of the system is the minimum of equation [13]. So one first determines the minimum of [13] to find the equilibrium constant and then plugs Ro into equation [13] to determine the cohesive energy of the crystal. So for an fcc lattice we find:

$$R_o = 1.09\sigma \qquad U_{tot}(R_o) = -2.15(4N\varepsilon) \qquad [17]$$

For an ionic crystal the cohesive energy expression is done over more than just the nearest neighbors. Note that the Madelung interaction term goes 1/r and is thus much less local than the attractive term of the Lennard-Jones potential:

$$U(R) = \sum_{j'} \lambda e^{-R/\rho} - \sum_j \pm \frac{1}{p_{ij}} \frac{q^2}{R} \qquad [18]$$

Where the first summation is only over the nearest neighbors and the 2nd summation is over all atom pairs in the crystal. We can simplify this expression by introducing z for the number of nearest neighbors and introducing the Madelung constant α for the summation over p_{ij}, i.e.

$$\alpha = \sum_j \frac{\pm}{p_{ij}} \qquad [19]$$

Resulting in:

$$U_{tot}(R) = \frac{1}{2}N\left(z\lambda e^{-R/\rho} - \alpha\frac{q^2}{R}\right)$$ [20]

Notice that the Madelung constant only depends on the geometry of the lattice and is independent of the ionic radius or ionic charge. The Madelung constants for different crystal structures are given in the text on page 65:

α_{NaCl}=1.747565, α_{CsCl}=1.762675, α_{ZnS}=1.63806 (zinc blende), α_{ZnS} (Wurtzite, 4 of the 8 tetrahedral voids occupied by S)=1.64132, α_{CaF2} (fluorite, all tetrahedral voids occupied by F), [21]

One can find the cohesive energy similarly as in the case of the Van der Waals solid, i.e. set the derivative of equation [20] equal to zero to find the lattice parameter and then replace the repulsive term in equation [21] with $\rho\alpha q^2/R_o^2$. This results in a cohesive energy equal to:

$$U_{tot} = -\frac{N\alpha q^2}{R_o}\left(1 - \frac{\rho}{R_o}\right)$$ [22]

We also discussed other bonds, i.e. covalent, metal and hydrogen bonds, qualitatively.

In the 2nd part of the chapter we discussed elastic strains, based on Hooke's laws but now in 3D including shearing strains and stresses beyond the conventional normal strains and stresses. Although the explanation the introduction to the strain and stress lingo in Kittel is very Engineering like, I think it is important we all have a good understanding of terminology. Distortion of the lattice is defined in terms of the distortion of the original orthogonal coordinate system, $\hat{x}, \hat{y}, \hat{z}$ in a new coordinate system $\vec{x}', \vec{y}', \vec{z}'$:

$$\vec{x}' = (1 + \varepsilon_{xx})\hat{x} + \varepsilon_{xy}\hat{y} + \varepsilon_{xz}\hat{z}$$
$$\vec{y}' = \varepsilon_{yx}\hat{x} + (1 + \varepsilon_{yy})\hat{y} + \varepsilon_{yz}\hat{z}$$ [23]
$$\vec{z}' = \varepsilon_{zx}\hat{x} + \varepsilon_{zy}\hat{y} + (1 + \varepsilon_{zz})\hat{z}$$

Where $\varepsilon_{\alpha\beta}$ define the deformation. Note that ε_{xx}, ε_{yy}, and ε_{zz} are the fractional changes of length of $\hat{x}, \hat{y}, \hat{z}$. So imagine that you draw the unit vectors of a right handed coordinate system on you undeformed object, then you will deform the object and determine the exact coordinates of the unit vectors after deformation. We learned that the effect of the deformation described by [23] on the position of an atom originally at $\vec{r} = x\hat{x} + y\hat{y} + z\hat{z}$ is given by the displacement vector:

$$\vec{R} = \vec{r}' - \vec{r} = x(\vec{x}' - \hat{x}) + y(\vec{y}' - \hat{y}) + z(\vec{z}' - \hat{z})$$ [24]

Or in terms of the ε deformation parameters:

$$\vec{R}(\vec{r}) = \left(x\varepsilon_{xx} + y\varepsilon_{yx} + z\varepsilon_{zx}\right)\hat{x} + \left(x\varepsilon_{xy} + y\varepsilon_{yy} + z\varepsilon_{zy}\right)\hat{y} + \left(x\varepsilon_{xx} + y\varepsilon_{yz} + z\varepsilon_{zz}\right)\hat{z}$$
$$\vec{R}(\vec{r}) = u(\vec{r})\hat{x} + v(\vec{r})\hat{y} + w(\vec{r})\hat{z}$$

[25]

So the relation between displacement u,v,w and deformation parameter is:

$$\varepsilon_{xx} = \frac{\partial u}{\partial x} \qquad \varepsilon_{yx} = \frac{\partial u}{\partial y} \qquad \varepsilon_{zx} = \frac{\partial u}{\partial z}$$

$$\varepsilon_{xy} = \frac{\partial v}{\partial x} \qquad \varepsilon_{yy} = \frac{\partial v}{\partial y} \qquad \varepsilon_{zy} = \frac{\partial v}{\partial z}$$

$$\varepsilon_{xx} = \frac{\partial w}{\partial x} \qquad \varepsilon_{yz} = \frac{\partial w}{\partial y} \qquad \varepsilon_{zz} = \frac{\partial w}{\partial z}$$

[26]

We can now use the definition of normal strain and shear strain to find relations between the strain and the displacement functions, u, v, and w. Normal strain in x, y, and z, i.e. ex, ey, and ez, are defined as the change in length in x, y, and z direction. Look to the figure below and notice that after deformation the x-coordinate of B changes with $\partial u / \partial x$ and use the relations of equations [26]:

$$e_{xx} = \frac{\partial u}{\partial x} = \varepsilon_{xx}$$

$$e_{yy} = \frac{\partial v}{\partial y} = \varepsilon_{yy}$$

$$e_{zz} = \frac{\partial w}{\partial z} = \varepsilon_{zz}$$

[27]

Shearing strains e_{xy} is defined as the change in angle, i.e. $\alpha+\beta$ for the figure below. From the figure below we see that:
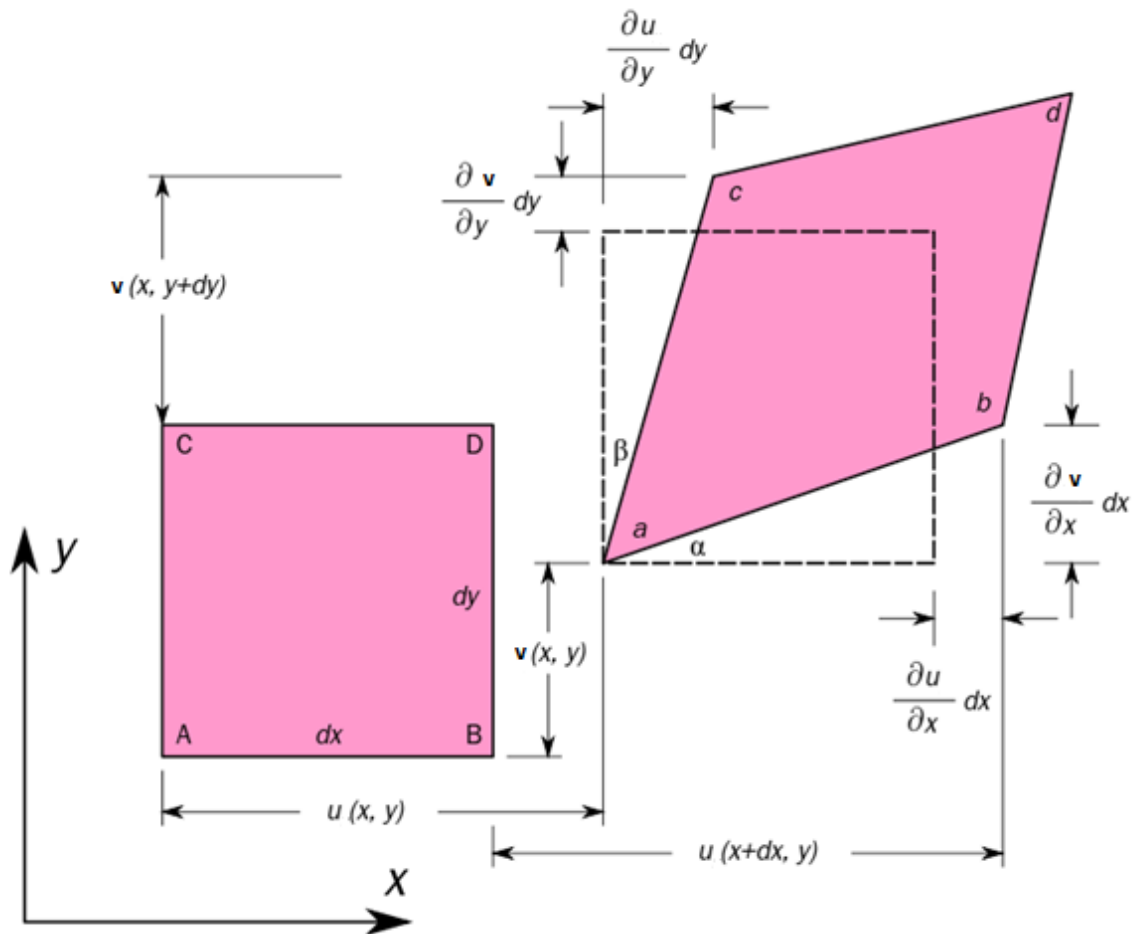
$$e_{xy} \approx \alpha + \beta \approx \tan(\alpha) + \tan(\beta) = \frac{\dfrac{\partial v}{\partial x}}{1 + \dfrac{\partial u}{\partial x}} + \frac{\dfrac{\partial u}{\partial y}}{1 + \dfrac{\partial v}{\partial y}} \approx \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} = \varepsilon_{yx} + \varepsilon_{xy}$$

[28]

Similarly for the other directions we find:

$$e_{yz} \approx \frac{\partial v}{\partial z} + \frac{\partial w}{\partial y} = \varepsilon_{zy} + \varepsilon_{yz}$$

$$e_{zx} \approx \frac{\partial u}{\partial z} + \frac{\partial w}{\partial z} = \varepsilon_{zx} + \varepsilon_{xz}$$

[29]

So we see conclude from this that for the shear strains:

$$e_{\alpha\beta} = e_{\beta\alpha}$$

[30]

We defined the dilation δ as the fractional increase of volume and found for it:

$$\delta = e_{xx} + e_{yy} + e_{zz}$$

So summarizing there are only 6 independent strain components: i.e. e_{xx}, e_{yy}, e_{zz}, e_{xy}, e_{yz}, and e_{zx}.

We introduced the stress components, X_x, X_y, X_z, Y_x, Y_y, Y_z, Z_x, Z_y, Z_z where the capital indicates the direction of the force and the subscript indicates the normal to the plane to which the force is applied. So X_x, Y_y, and Z_z are normal stresses, and the others are shear stresses. We saw that because of equilibrium the sum of the torques should be zero which led to the following equalities:

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

So there is only 6 independent stress components in a material. The relation between the 6 strain components and the 6 stress components can be described by a 6x6 matrix. See equations (37) and (38)

in the text book. The elements of the S-matrix are referred to as elastic compliance constants, and the elements of the C-matrix are referred to as the elastic stiffness constants or moduli of elasticity. Note that the C-matrix is the 3D equivalent of the spring constant. Although the C-matrix has 36 components, its off-diagonal components are symmetric and $C_{\alpha\beta}=C_{\beta\alpha}$. We realized this from the fact that the elastic potential energy of the total crystal consists of all possible terms of $0.5C_{\alpha\beta}e_{\alpha}e_{\beta}$ terms. So the negative derivative of the potential energy will have similar terms in e_{α} and e_{β}. So there are only (36-6)/2+6=21 independent elastic stiffness constants for an arbitrary material.

We expect that for materials that have symmetry because of the crystal structure, the total number of independent elastic stiffness constants is considerable lower. Kittel derives the case for cubic crystals. He shows on page 78 that because the four three-fold rotation axis in the [111] direction the number of independent elastic stiffness constants is less just three, i.e. C11, C12, and C44. The total elastic stiffness matrix for a cubic crystal is given by:

$$\begin{pmatrix} X_x \\ Y_y \\ Z_z \\ Y_z \\ Z_x \\ X_y \end{pmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{bmatrix} = \begin{pmatrix} e_{xx} \\ e_{yy} \\ e_{zz} \\ e_{yz} \\ e_{zx} \\ e_{xy} \end{pmatrix} \qquad [31]$$

Note that Kittel does not present the situations for the isotropic case of for materials that have a crystal structure with a lower symmetry. A summary for the different crystal structures discussed in chapter 1 is displayed on the next page. In general only the triclinic crystal structure has 21 independent stiffness constants. An isotropic sample has only two independent elastic stiffness constants.

The energy density of a cubic crystal that is compressed equally in all three dimensions i.e. exx=eyy=ezz=0.33δ where d is the dialation is given by:
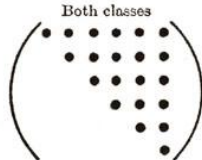
$$U = \frac{1}{6}\left(C_{11} + 2C_{12}\right)\delta^2 = \frac{1}{2}B\delta^2 \qquad [32]$$

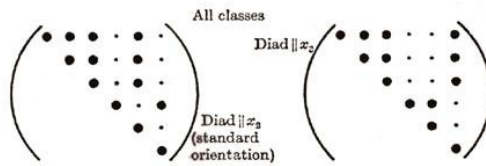Where B is often referred to as the bulk modulus.

KEY TO NOTATION

- zero component
- non-zero component
- equal components
- components numerically equal, but opposite in sign

For s ⊙   twice the numerical equal of the heavy dot component to which it is joined

For c ⊙   the numerical equal of the heavy dot component to which it is joined

For s X $2(s_{11}-s_{12})$

For c X $\frac{1}{2}(c_{11}-c_{12})$

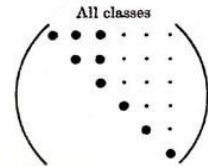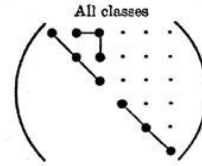All the matrices are symmetrical about the leading diagonal.

TRICLINIC (21)

Both classes
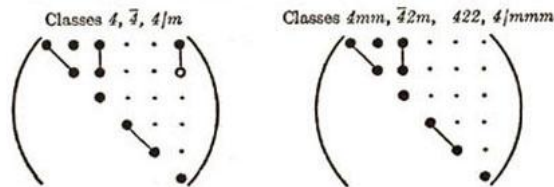
MONOCLINIC (13)

All classes

Diad $\parallel x_2$

Diad $\parallel x_3$ (standard orientation)

ORTHORHOMBIC (9)   CUBIC (3)

All classes   All classes

(7)   TETRAGONAL   (6)

Classes 4, $\bar{4}$, $4/m$ Classes $4mm$, $\bar{4}2m$, 422, $4/mmm$

(7)   TRIGONAL   (6)

Classes 3, $\bar{3}$ Classes 32, $\bar{3}m$, $3m$
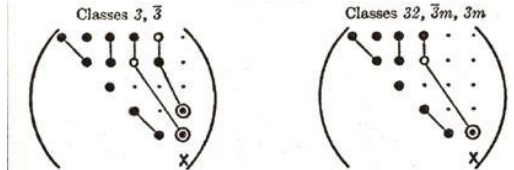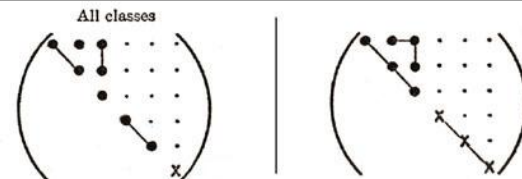
HEXAGONAL (5)   ISOTROPIC (2)

All classes

In the third part of chapter 3 we discussed the elastic wave propagation in cubic crystals. We used a cubic crystal system as that simplified the wave-equations. We started off by assuming a certain polarization and then applying Newton's 2nd law to a cubic segment of the material. For a polarization in the u-direction we have to consider all stresses in the x-direction, i.e. X_x, X_y, and X_z:

$$\rho\frac{\partial^2 u}{\partial t^2} = \frac{\partial X_x}{\partial x} + \frac{\partial X_Y}{\partial y} + \frac{\partial X_z}{\partial z}$$ [33]

Using the stiffness matrix, i.e. equation [31], gives us the following wave-equation:

$$\rho\frac{\partial^2 u}{\partial t^2} = C_{11}\frac{\partial e_{xx}}{\partial x} + C_{12}\left(\frac{\partial e_{yy}}{\partial x} + \frac{\partial e_{zz}}{\partial x}\right) + C_{44}\left(\frac{\partial e_{xy}}{\partial y} + \frac{\partial e_{zx}}{\partial z}\right)$$ [34]

Now using the strain displacement relation of equations 27 and 29 gives:

$$\rho\frac{\partial^2 u}{\partial t^2} = C_{11}\frac{\partial^2 u}{\partial x^2} + C_{44}\left(\frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2}\right) + (C_{12} + C_{44})\left(\frac{\partial^2 v}{\partial x\partial y} + \frac{\partial^2 w}{\partial x\partial z}\right)$$ [35]

We derived similar equations for waves polarized in the v and w directions, i.e.

$$\rho\frac{\partial^2 v}{\partial t^2} = C_{11}\frac{\partial^2 v}{\partial y^2} + C_{44}\left(\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial z^2}\right) + (C_{12} + C_{44})\left(\frac{\partial^2 u}{\partial x\partial y} + \frac{\partial^2 w}{\partial y\partial z}\right)$$ [36]

And

$$\rho\frac{\partial^2 u}{\partial t^2} = C_{11}\frac{\partial^2 w}{\partial y^2} + C_{44}\left(\frac{\partial^2 w}{\partial x^2} + \frac{\partial^2 w}{\partial y^2}\right) + (C_{12} + C_{44})\left(\frac{\partial^2 u}{\partial x\partial z} + \frac{\partial^2 v}{\partial y\partial z}\right)$$ [37]

We used those wave-equations and a plane wave trial solutions on page 82 and 83 to derive the dispersion relation of waves with different polarizations traveling in different directions in the crystal. We found that for longitudinal waves propagating in the [100] direction the wave velocity is given by:

$$v_s = v\lambda = \sqrt{\frac{C_{11}}{\rho}}$$ [38]

For the transverse wave the velocity is given by:

$$v_s = \sqrt{\frac{C_{44}}{\rho}}$$ [39]

In both cases the speed is proportional to the square root of a component of the elastic stiffness matrix and the density of the material. We concluded in class that it is not possible to determine the complete elastic stiffness matrix from sound wave measurements in the [001] direction of a cubic crystal. We also calculated the dispersion for waves propagating in the [110] direction of the crystal and learned that from speed measurements of the longitudinal wave, the transverse wave polarized perpendicular to the (100) plane, and the transverse wave polarized parallel to the (100) plane, one could determine all three elastic stiffness constants provided the density of the material is known.