

Chapter 2 Crystal binding and elastic constants

I. Chemical bonds

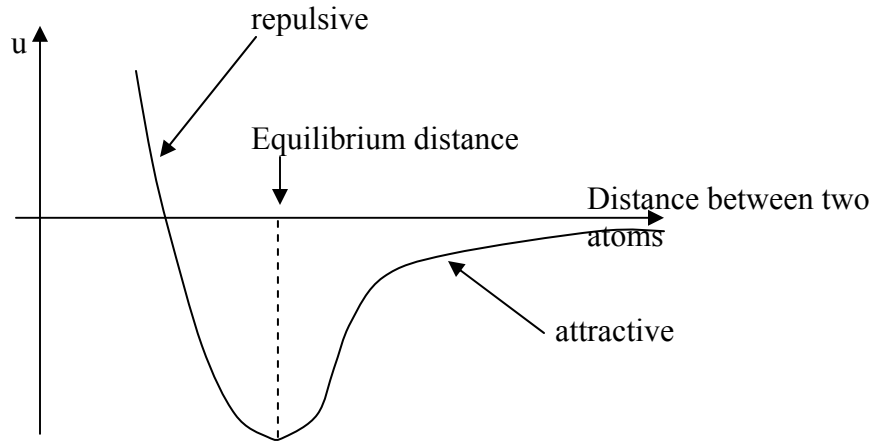
- There are two major types of chemical bonds (bonding between atoms to form a molecule: (i) ionic bond, and (ii) covalent bond.
- Ionization energy (first) is the energy required to move an electron from a neutral isolated atom to form an ion with one positive charge.
- Electron affinity is the amount of energy absorbed when an electron is added to a neutral isolated atom to form an ion with one negative charge. It has a negative value if energy is released. Most elements have a negative electron affinity. This means they do not require energy to gain an electron; instead, they release energy. Atoms more attracted to extra electrons have a more negative electron affinity. Only elements that have a positive affinity are the atoms with a complete shell (e.g. group 2 and the inert gases).
- Electronegativity is the average of the first ionization energy and the electron affinity. It is the measure of the ability of an atom or molecule to attract electrons in the context of a chemical bond. In Pauling scale, F (the most electronegative element) is given an electronegativity value of 3.98 and Li (the least electronegative element) is given an electronegativity value of 0.98.

		Electronegativity																	
Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
Period																			
1	H 2.20																	He	
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne	
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar	
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00	
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.6	
6	Cs 0.79	Ba 0.89	Lu 1.27	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 2.33	Bi 2.02	Po 2.0	At 2.2	Rn	
7	Fr 0.7	Ra 0.9	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo	

5. Bonding between two atoms:
 Large difference in electronegativity \Rightarrow Ionic bonding
 e.g. Na – Cl (difference in electronegativity = $3.16 - 0.93 = 2.23$)
 Moderate difference in electronegativity \Rightarrow polar covalent bonding
 e.g. H – O (difference in electronegativity = $3.44 - 2.2 = 1.24$)
 Small difference in electronegativity \Rightarrow covalent bonding
 e.g. C – O (difference in electronegativity = $3.44 - 2.55 = 0.89$)
 O – O (difference in electronegativity = 0)

II. Crystal bindings

1. Electrons and electrostatic forces play an important role in binding atoms together to form a solid (crystal).
2. All materials solidify at low enough temperatures. The only exception is helium. Helium only liquefies at low temperatures under ambient pressure. Two factors for this to occur: (i) helium atom is very light (hence high ground state energy and high zero point oscillation if it solidify), and (ii) helium atom is inert (i.e. electrons occupy a complete shell). Helium can be solidified, but only under high pressure (higher than 27 atm. Ref: Phys. Rev. 82, 263–264 (1951)).
3. There must be some bindings to hold atoms together to form a solid. Common types of crystal bindings:
 - (i) Ionic bonding
 - (ii) Covalent bonding
 - (iii) Metallic bonding
 - (iv) Hydrogen bonding
 - (v) Van der Waals interaction
4. Cohesive energy u of a solid is the energy required to disassemble the solid into its constituent part (e.g. atoms of the chemical elements out of which the solid is composed).
5. For a stable, the cohesive energy has an attractive term when the inter atomic distance is large (so that the crystal can be formed), and a repulsive term when the inter atom distance is short (so the crystal will not collapse).



6. The equilibrium distance between two atoms is given by

$$\left. \frac{\partial u}{\partial r} \right|_{r=r_0} = 0$$

III. Ionic bonding

1. When the difference in electronegativity between two different types of is large, electrons will be transferred from the low electronegative atom to the high electronegative atom. The low electronegative atom will become a positive *ion* and the high electronegative atom will become a negative ion (e.g. $\text{Na} + \text{Cl} \rightarrow \text{Na}^+ + \text{Cl}^-$). These ions will attract each other by electrostatic force to form a solid.

2. The repulsive force is due to the Pauli exclusion principle – this prevents the crystal from collapsing.

3. The attractive force is due to the Coulomb attraction between the ions.

4. If U_{ij} is the interacting energy between ions i and j ,

$$U_{ij} = \lambda \exp(-r_{ij}/\rho) \pm \frac{q^2}{4\pi\epsilon_0 r_{ij}}$$

where $\pm q$ are the charges of the ions, and $\lambda \exp(-r_{ij}/\rho)$ is the repulsive potential with λ and ρ as empirical constants, which can be determined from lattice parameter and compressibility.

5. The repulsive potential is really short range, hence it is effective only for nearest neighbors. The Coulomb attraction, however, is *long range* and it will extend indefinitely. If R is the nearest neighbor distance, and we write $r_{ij} = p_{ij} R$, then we have

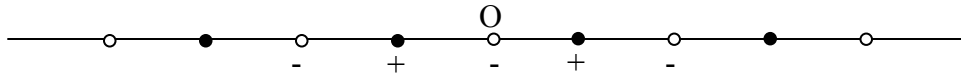
$$U_{ij} = \begin{cases} \lambda e^{-R/\rho} - \frac{1}{4\pi\epsilon_0} \frac{q^2}{R} & \text{(nearest neighbors)} \\ \pm \frac{1}{4\pi\epsilon_0} \frac{q^2}{R p_{ij}} & \text{(otherwise)} \end{cases}$$

6. If the total number of ions is N and the number of nearest neighbors is z . Total energy of the whole crystal U_{tot} :

$$\begin{aligned}
 U_{\text{tot}} &= N \times \text{potential energy corresponds to one single ion} \\
 &= N \sum_{j \neq 0} U_{0j} \\
 &= N \left[z\lambda e^{-R/\rho} + \sum_{j \neq 0} \pm \frac{1}{4\pi\epsilon_0} \frac{q^2}{Rp_{0j}} \right] \\
 &= N \left[z\lambda e^{-R/\rho} + \frac{q^2}{4\pi\epsilon_0 R} \sum_{j \neq 0} \pm \frac{1}{p_{0j}} \right] \\
 &= N \left[z\lambda e^{-R/\rho} - \frac{q^2 \alpha}{4\pi\epsilon_0 R} \right]
 \end{aligned}$$

where $\alpha = \sum_{j \neq 0} \mp \frac{1}{p_{0j}}$ is the Madelung constant.

7. The Madelung has to be positive for an attractive potential. It depends on the crystal structure only. For example, for a one dimensional linear lattices,



$$\begin{aligned}
 \alpha &= \sum_{j \neq 0} \mp \frac{1}{p_{0j}} = (\dots + \frac{1}{3} - \frac{1}{2} + \frac{1}{1} + \frac{1}{1} - \frac{1}{2} + \frac{1}{3} + \dots) \\
 &= 2(1 - \frac{1}{2} + \frac{1}{3} + \dots) \\
 &= 2 \ln 2
 \end{aligned}$$

$$\text{because } \ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} + \dots$$

8. However, mathematically, the series is *divergent*. This is because the Coulomb force is a long range force and it is not decaying fast enough to ensure a convergent series. One direct way to overcome this problem is to break up the terms and rearrange the summation so that each cell remains neutral in charge.

α for NaCl structure is 1.7476.

IV. Covalent bonds

1. When the electronegativity between two atoms is small, the two atoms can form covalent bond by sharing a pair of electrons (one from each atom).

2. Most atoms can form more than one covalent bond. For example, C has four outer electrons ($2s^2p^2$ or more correctly $2sp^3$) and hence it can form 4 covalent bonds.

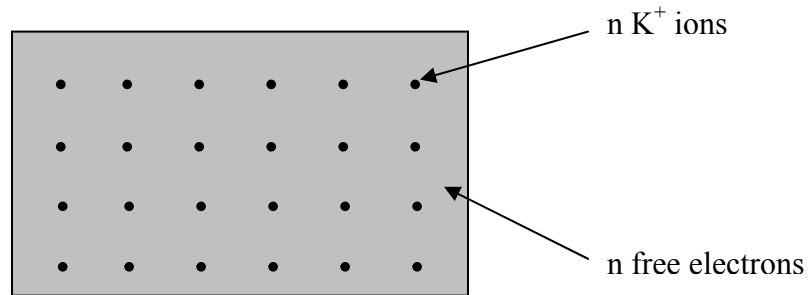
3. A crystal can be formed with one atom forming covalent bonds with several other atoms.

4. Covalent bond is highly directional and the bonds will repel from each other. So a crystal can be formed even the structure has a low filling factor. For example, carbon and silicon can have diamond structure, with atoms joined to four nearest neighbors at tetrahedral angles slowing only four nearest neighbors. Diamond structure has a filling factor of 0.34 compared with 0.74 of close-pack structure.

5. Very often atoms form molecules by forming molecules. These neutral molecules have no charge for ionic bonding with other molecules, and they do not have the extra electron to form covalent bonding with other molecules. They need other types of crystal bonding to form a solid: Van der Waals interaction, metallic bonding, and hydrogen bonding.

V. Metallic bonding

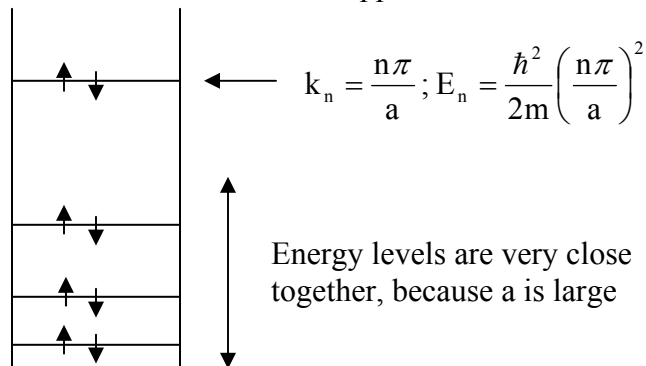
1. Atoms bounded by “free electrons”. Good example is alkali metals (Li, K, Na etc.



2. One can view the metallic bond as a total delocalization of electrons from covalent bond. The total Coulomb potential is negative:

$$U^{\text{Coul}} = \underbrace{U^{\text{e-e}}}_{\text{positive}} + \underbrace{U^{\text{e-i}}}_{\text{negative}} + \underbrace{U^{\text{i-i}}}_{\text{positive}} < 0$$

3. The attractive potential is balanced by the kinetic energy (i.e. repulsive term) of the electrons. One can view these as electrons trapped in a box formed by the solid:

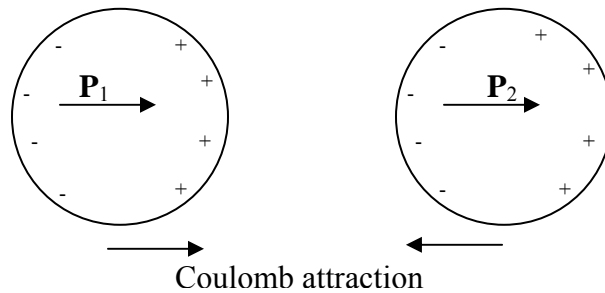


As α decreases (when the crystal is “collapsing”), E_n (the kinetic energy of the electrons) increases and this prevents the crystal from collapsing.

4. It is not necessary for metals to have metallic bonding. For example, many transition metals show covalent properties.

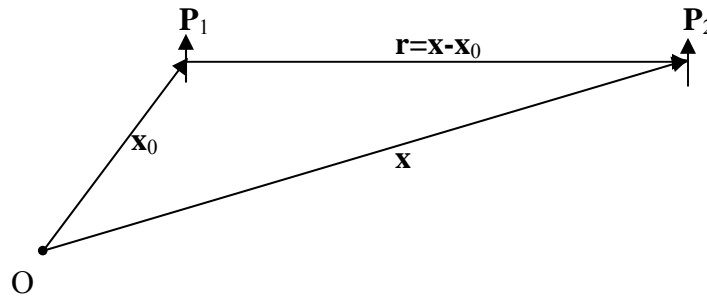
VI. Van der Waals interaction

1. Coulomb attraction can occur between two neutral spheres, as long as they have some “internal charges” so that the neutral spheres can be polarized:



2. Suppose there is a dipole moment of \mathbf{P}_1 at the first sphere. This will produce a dipole at the second sphere.

3.



$$\text{Electric field at point } \bar{r} \text{ due to a dipole} = E(\bar{x}) = \frac{3\hat{n}(\bar{p} \cdot \hat{n}) - \bar{p}}{4\pi\epsilon_0 |\bar{x} - \bar{x}_0|^3} \quad (\text{Jackson 3rd edition p.147})$$

\hat{n} is a unit vector along $\bar{x} - \bar{x}_0$ direction.

For simplicity, let us assume $\bar{x} - \bar{x}_0$ is perpendicular to \bar{p}_1 (and eventually \bar{p}_2) as shown in above figure.

$$\text{Electric field at } \bar{p}_2 \text{ due to } \bar{p}_1 \text{ is } \bar{E} = \frac{-\bar{p}_1}{4\pi\epsilon_0 r^3} \quad \text{where } \bar{r} = \bar{x} - \bar{x}_0$$

If the polarizability of the second sphere is α , we have a relationship between \bar{p}_1 and \bar{p}_2 :

$$\bar{p}_2 = \alpha E = \frac{-\alpha\bar{p}_1}{4\pi\epsilon_0 r^3}$$

The potential energy two interacting dipoles is given as :

$$\Phi = \frac{\bar{p}_1 \cdot \bar{p}_2 - 3(\hat{n} \cdot \bar{p}_1)(\hat{n} \cdot \bar{p}_2)}{4\pi\epsilon_0 |\bar{x} - \bar{x}_0|^3} \quad (\text{Jackson 3rd edition, p.151})$$

Therefore the potential energy between \bar{p}_1 and \bar{p}_2 is :

$$\Phi_{\text{att}}(r) = \frac{\bar{p}_1 \cdot \bar{p}_2}{4\pi\epsilon_0 r^3} = \frac{\bar{p}_1}{4\pi\epsilon_0 r^3} \cdot -\alpha\bar{p}_1 = -\frac{\alpha p_1^2}{4\pi\epsilon_0} \frac{1}{r^6} = -\frac{A}{r^6}$$

This is the attractive potential between two neutral molecules.

4. Repulsive potential is due to Pauli exclusion principle. It is customary to use power law to describe the repulsive potential:

$$\Phi_{\text{rep}}(r) = \frac{B}{r^{12}}$$

5. The total potential between two molecules can then be written as:

$$\begin{aligned} \Phi(r) &= \Phi_{\text{att}}(r) + \Phi_{\text{rep}}(r) = -\frac{A}{r^6} + \frac{B}{r^{12}} \\ &= 4\epsilon \left[-\left(\frac{\sigma}{r}\right)^6 + \left(\frac{\sigma}{r}\right)^{12} \right] \end{aligned}$$

where $4\epsilon\sigma^6 = A$ and $4\epsilon\sigma^{12} = B$.

6. The total potential energy of the solid is

$$U = \sum_{i \neq j} \Phi(\bar{r}_{ij}) = \frac{N}{2} \sum_{j \neq 0} \Phi(\bar{r}_{0j}) = \frac{N}{2} \sum_{\bar{r} \neq 0} \Phi(\bar{r}) \quad (\bar{r} = \bar{r}_{0j})$$

Potential energy per particle is:

$$u = \frac{U}{N} = \frac{1}{2} \sum_{\bar{r} \neq 0} \Phi(r) = \frac{1}{2} \sum_{\bar{r} \neq 0} 4\epsilon \left[-\left(\frac{\sigma}{r}\right)^6 + \left(\frac{\sigma}{r}\right)^{12} \right]$$

Let $r = pR$ where $R =$ nearest neighbor distance

$$\begin{aligned} \therefore u &= \frac{1}{2} \sum_{\bar{r} \neq 0} 4\epsilon \left[-\frac{1}{p^6} \left(\frac{\sigma}{R}\right)^6 + \frac{1}{p^{12}} \left(\frac{\sigma}{R}\right)^{12} \right] \\ &= 2\epsilon \left[-\underbrace{\sum_{\bar{r} \neq 0} \frac{1}{p^6} \left(\frac{\sigma}{R}\right)^6}_{A_6} + \underbrace{\sum_{\bar{r} \neq 0} \frac{1}{p^{12}} \left(\frac{\sigma}{R}\right)^{12}}_{A_{12}} \right] \\ &= 2\epsilon \left[-A_6 \left(\frac{\sigma}{R}\right)^6 + A_{12} \left(\frac{\sigma}{R}\right)^{12} \right] \end{aligned}$$

7. A_6 and A_{12} depend on the crystal structure *only*. For fcc (structure of inert gas), $A_6 = 14.15$ and $A_{12} = 12.13$.

8. The nearest neighbor distance is determined by minimizing u :

$$\begin{aligned} \frac{\partial u}{\partial R} = 0 &\Rightarrow 2\varepsilon \left[-A_6 \frac{\partial}{\partial R} \left(\frac{\sigma}{R} \right)^6 + A_{12} \frac{\partial}{\partial R} \left(\frac{\sigma}{R} \right)^{12} \right] = 0 \\ &\Rightarrow 2\varepsilon \left[-6A_6 \frac{\sigma^5}{R^6} + 12A_{12} \frac{\sigma^{11}}{R^{12}} \right] = 0 \\ &\Rightarrow -6A_6 + 12A_{12} \frac{\sigma^6}{R^6} = 0 \\ &\Rightarrow \frac{R^6}{\sigma^6} = \frac{2A_{12}}{A_6} \\ &\Rightarrow R = \left(\frac{2A_{12}}{A_6} \right)^{\frac{1}{6}} \sigma \\ &= 1.09017 \sigma \quad \text{for fcc.} \end{aligned}$$

9. Larger molecule \Rightarrow stronger Van der Waals force
 \Rightarrow higher melting point.

For example:

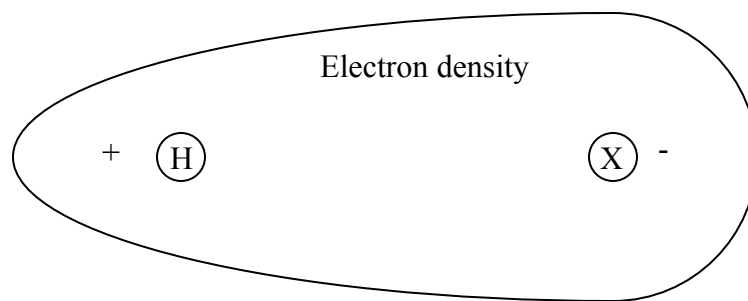
He Ne Ar Kr Xe Rn

————— \longrightarrow Increasing melting point

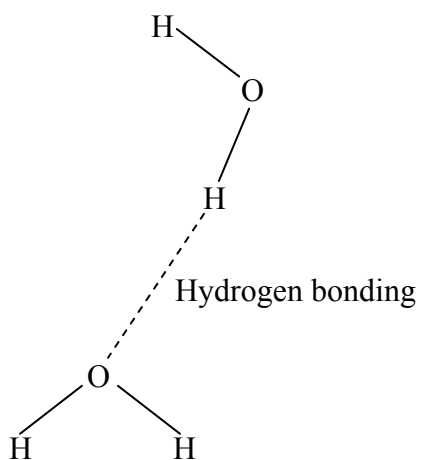
This is also true for many organic molecules.

VII. Hydrogen bonding

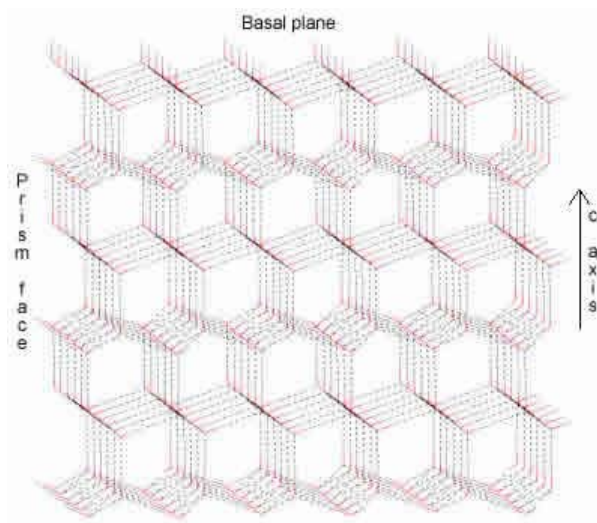
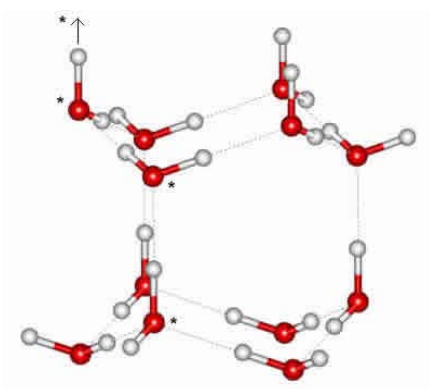
1. Hydrogen ion is just a proton (10^{-13} cm in radius), 10^{-5} times smaller than any other ions.
2. First ionization energy of atomic hydrogen is very high (13.6 eV) because the outset electron is in the first shell without any shielding. It is highly unlikely for hydrogen to form ionic bonding.
3. The complete shell of hydrogen atom is 2 electrons and a hydrogen atom has only one electron. It can form only one covalent bond and it does not have sufficient bond to bind the whole crystal together with covalent bond.
4. However, the covalent bond between hydrogen and the other atom (e.g. oxygen) can often be polarized, when the electronegativity between these two atoms has a moderate difference. When this happen:



5. These polarized molecules will “stick” to each other by Coulomb attraction. This is possible because the hydrogen size is very small. For example, for water:



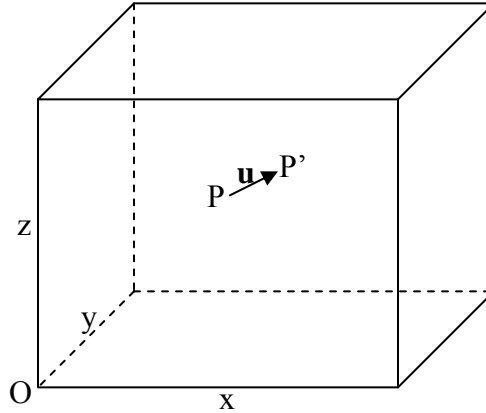
Ice structure:



VIII. Strains

1. Strain is the change in length of an object in direction i ($i=x,y,z$) per unit undistorted length in direction j ($j=x,y,z$). i and j are not necessary the same, so strain is actually a 3x3 second rank tensor.

2.



Let the origin be fixed as the sample is deformed. Let the coordinates of point P before the deformation be (x, y, z) . This point moves to point P' at $(x+u_x, y+u_y, z+u_z)$ as the sample is deformed. $\mathbf{u} = (u_x, u_y, u_z)$ is the displacement vector of P . The displacement is a cumulative effect of other points. In other words, if O is fixed in the process, the displacement will be “proportional” to the distance from the origin:

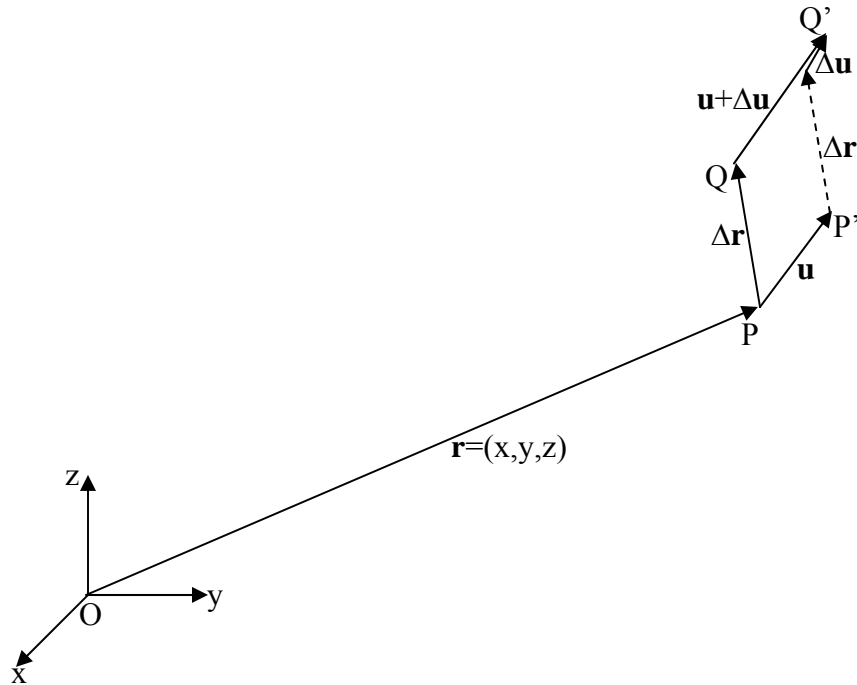
$$\varepsilon_{ij} = \frac{\partial u_i}{\partial x_j} = \text{constant} \quad (\text{for homogeneous/linear system})$$

For another point Q with an original displacement $(\Delta x, \Delta y, \Delta z)$ from point P , its (Q') displacement from point P' after the deformation will be given by

$$\Delta u_x = \frac{\partial u_x}{\partial x} \Delta x + \frac{\partial u_x}{\partial y} \Delta y + \frac{\partial u_x}{\partial z} \Delta z = \varepsilon_{xx} \Delta x + \varepsilon_{xy} \Delta y + \varepsilon_{xz} \Delta z$$

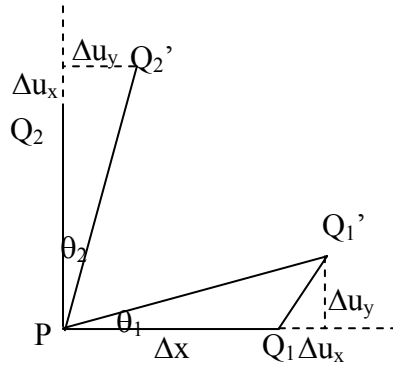
$$\Delta u_y = \frac{\partial u_y}{\partial x} \Delta x + \frac{\partial u_y}{\partial y} \Delta y + \frac{\partial u_y}{\partial z} \Delta z = \varepsilon_{yx} \Delta x + \varepsilon_{yy} \Delta y + \varepsilon_{yz} \Delta z$$

$$\Delta u_z = \frac{\partial u_z}{\partial x} \Delta x + \frac{\partial u_z}{\partial y} \Delta y + \frac{\partial u_z}{\partial z} \Delta z = \varepsilon_{zx} \Delta x + \varepsilon_{zy} \Delta y + \varepsilon_{zz} \Delta z$$



3. Meaning of ϵ_{ij} :

Let us consider a particular case when PQ_1 is along (say) x-axis and PQ_2 is along the y-axis, with P at the origin. After the deformation:



For PQ_1 , $\Delta y = \Delta z = 0$

$$\therefore \Delta u_x = \frac{\partial u_x}{\partial x} \Delta x = \epsilon_{xx} \Delta x \Rightarrow \epsilon_{xx} = \text{extension per unit length along the x - direction.}$$

$$\Delta u_y = \frac{\partial u_y}{\partial x} \Delta x = \epsilon_{yx} \Delta x$$

$$\theta_1 \approx \tan \theta_1 = \frac{\Delta u_y}{\Delta x + \Delta u_x} \approx \frac{\Delta u_y}{\Delta x} = \epsilon_{yx}$$

Similarly, for PQ_2 , $\Delta x = \Delta z = 0$

$$\therefore \Delta u_x = \frac{\partial u_x}{\partial y} \Delta y = \varepsilon_{xy} \Delta x$$

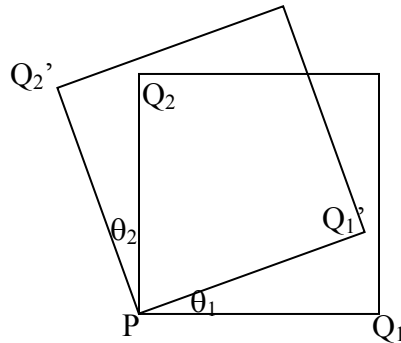
$$\Delta u_y = \frac{\partial u_y}{\partial y} \Delta y = \varepsilon_{yy} \Delta x \Rightarrow \varepsilon_{yy} = \text{extension per unit length along the } y \text{- direction}$$

$$\theta_2 \approx \tan \theta_2 = \frac{\Delta u_x}{\Delta y + \Delta u_y} \approx \frac{\Delta u_x}{\Delta y} = \varepsilon_{xy}$$

In summary, ε_{ij} = the angle between a line along the x_i direction and the x_i axis, if $i \neq j$. ε_{ii} = extension per unit length along the x_i direction.

4. Problem of ε_{ij} :

Now consider the rotation of a sample along the z-axis:



This will give a matrix of ε as:

$$\varepsilon_{ij} = \begin{pmatrix} 0 & -\theta & 0 \\ \theta & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

This has no physical sense because a rotation will not produce any deformation of the solid.

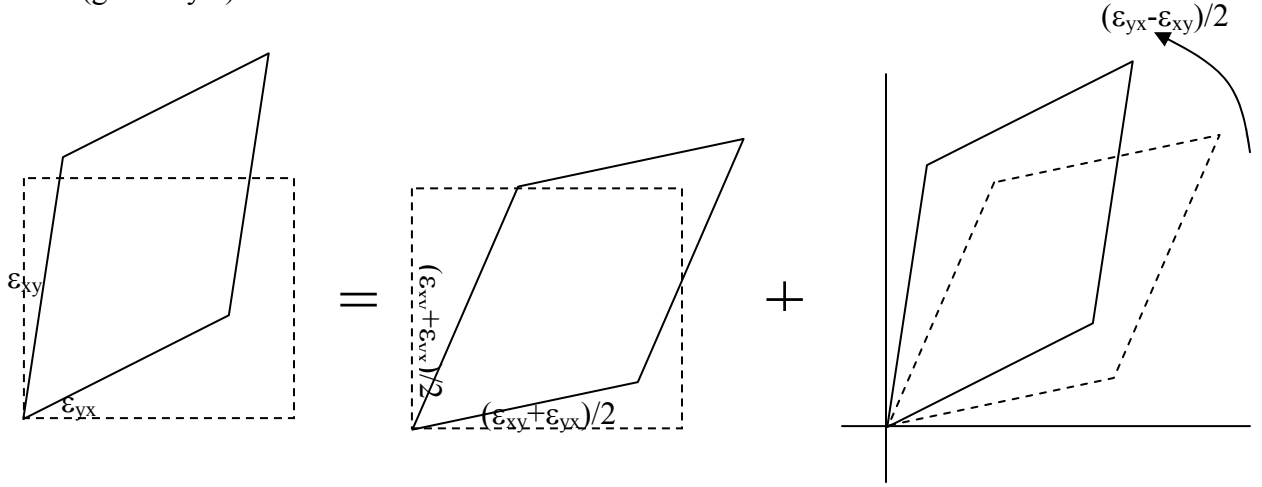
5. To ensure a rotational motion will yield a zero matrix, we need to define the *strain* e_{ij} as:

$$e_{ij} = \frac{\varepsilon_{ij} + \varepsilon_{ji}}{2}$$

6. Obviously, $e_{ij} = e_{ji}$. There are only 6 independent strain components, they are: e_{xx} , e_{yy} , e_{zz} , e_{xy} , e_{xz} , and e_{yz} .

7. Physical interpretation of the strain components:

We can “decompose” any re-configuration (given by ε) into a rotation and a real strain (given by e):



e_{ii} are the extensions per unit length parallel to the x_i axis. e_{ij} ($i \neq j$) measure the *tensor shear strain*: if two line elements are drawn parallel to the x_i and x_j axes in the undeformed body, the angle between them after deformation is $\pi/2 - 2e_{ij}$. Note particularly that the tensor shear strain e_{ij} is *one-half* of the change in angle between the two elements.

7. *Dilation* δ is defined as the fractional change in volume. Consider a sample of unit dimension ($V=1$), with unit vectors $\mathbf{x}, \mathbf{y}, \mathbf{z}$ along the three side of the cube. Under strain, these will become new axis $\mathbf{x}', \mathbf{y}', \mathbf{z}'$.

$$\left. \begin{aligned} \Delta u_x &= \varepsilon_{xx} \Delta x + \varepsilon_{xy} \Delta y + \varepsilon_{xz} \Delta z \\ \Delta u_y &= \varepsilon_{yx} \Delta x + \varepsilon_{yy} \Delta y + \varepsilon_{yz} \Delta z \\ \Delta u_z &= \varepsilon_{zx} \Delta x + \varepsilon_{zy} \Delta y + \varepsilon_{zz} \Delta z \end{aligned} \right\} \Rightarrow \begin{cases} \bar{x}' = (1 + \varepsilon_{xx})\bar{x} + \varepsilon_{yx}\bar{y} + \varepsilon_{zx}\hat{z} \\ \bar{y}' = \varepsilon_{xy}\bar{x} + (1 + \varepsilon_{yy})\bar{y} + \varepsilon_{zy}\hat{z} \\ \bar{z}' = \varepsilon_{xz}\bar{x} + \varepsilon_{yz}\bar{y} + (1 + \varepsilon_{zz})\hat{z} \end{cases}$$

$$\therefore V' = \bar{x}' \cdot (\bar{y}' \times \bar{z}') = \begin{vmatrix} 1 + \varepsilon_{xx} & \varepsilon_{yx} & \varepsilon_{zx} \\ \varepsilon_{xy} & 1 + \varepsilon_{yy} & \varepsilon_{zy} \\ \varepsilon_{xz} & \varepsilon_{yz} & 1 + \varepsilon_{zz} \end{vmatrix}$$

$$= (1 + \varepsilon_{xx}) \begin{vmatrix} 1 + \varepsilon_{yy} & \varepsilon_{zy} \\ \varepsilon_{yz} & 1 + \varepsilon_{zz} \end{vmatrix} - \varepsilon_{yx} \begin{vmatrix} \varepsilon_{xy} & \varepsilon_{zy} \\ \varepsilon_{xz} & 1 + \varepsilon_{zz} \end{vmatrix} + \varepsilon_{zx} \begin{vmatrix} \varepsilon_{xy} & 1 + \varepsilon_{yy} \\ \varepsilon_{xz} & \varepsilon_{yz} \end{vmatrix}$$

$$= (1 + \varepsilon_{xx})(1 + \varepsilon_{yy})(1 + \varepsilon_{zz}) - (1 + \varepsilon_{xx})\varepsilon_{zy}\varepsilon_{yz} - \varepsilon_{yx}\varepsilon_{xy}(1 + \varepsilon_{zz})$$

$$+ \varepsilon_{yx}\varepsilon_{zy}\varepsilon_{xz} + \varepsilon_{zx}\varepsilon_{xy}\varepsilon_{yz} - \varepsilon_{zx}(1 + \varepsilon_{yy})\varepsilon_{xz}$$

$$\approx (1 + \varepsilon_{yy} + \varepsilon_{yy} + \varepsilon_{zz} + \varepsilon_{xx}\varepsilon_{yy} + \varepsilon_{yy}\varepsilon_{zz} + \varepsilon_{yy}\varepsilon_{zz}) - \varepsilon_{zy}\varepsilon_{yz} - \varepsilon_{yx}\varepsilon_{xy} - \varepsilon_{zx}\varepsilon_{xz}$$

$$\approx 1 + \varepsilon_{yy} + \varepsilon_{yy} + \varepsilon_{zz} = 1 + e_{yy} + e_{yy} + e_{zz}$$

In other words, the *first order* contribution to volume change when a material is under strain is the diagonal elements of the strain matrix.

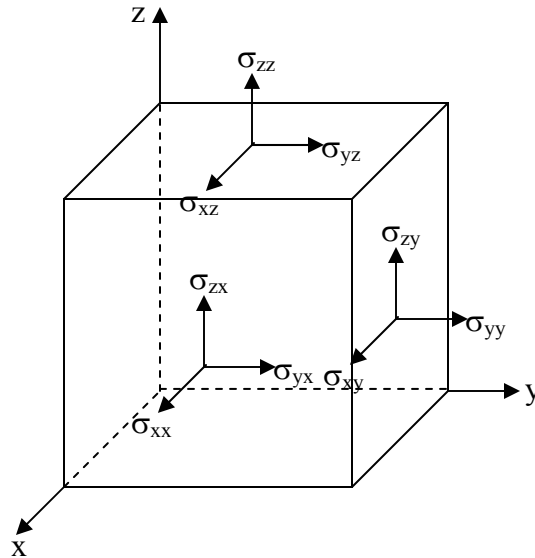
Now,

$$V' = \begin{vmatrix} 1 + \varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\ \varepsilon_{yx} & 1 + \varepsilon_{yy} & \varepsilon_{yz} \\ \varepsilon_{zx} & \varepsilon_{zy} & 1 + \varepsilon_{zz} \end{vmatrix} \approx 1 + e_{xx} + e_{yy} + e_{zz}$$

$$\therefore \delta = \frac{V' - V}{V} = e_{xx} + e_{yy} + e_{zz} = \text{Tr}(e)$$

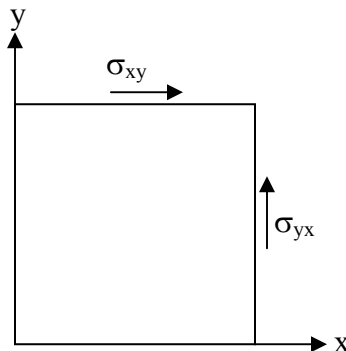
IX. Stress

1. Stress is the force component acting on a unit area in the solid.
2. Stress σ_{ij} is the i -component of the force acting on the surface perpendicular to the j -axis:



Note that in the textbook (Kittel 8th edition, σ_{ij} is written as I_j . For example, σ_{xy} here is the same as X_y in the textbook.

3. σ_{ij} is known as shear stress if $i \neq j$.
4. For equilibrium, there should be no torque acting on the sample.



For net torque equals to zero, we require $\sigma_{xy} = \sigma_{yx}$. In general, we have $\sigma_{ij} = \sigma_{ji}$. Like the case of strain, we have 6 independent stress components, they are: σ_{xx} , σ_{yy} , σ_{zz} , σ_{xy} , σ_{xz} , and σ_{yz} .

X. Hooke's Law – Elastic compliance and stiffness constants

1. Since we have 6 independent e and 6 independent S , we will redefine their indices as follow:

$$e_i: \quad e_1 = e_{xx}, e_2 = e_{yy}, e_3 = e_{zz}, e_4 = e_{yz}, e_5 = e_{zx}, e_6 = e_{xy}.$$

$$\sigma_i: \quad \sigma_1 = \sigma_{xx}, \sigma_2 = \sigma_{yy}, \sigma_3 = \sigma_{zz}, \sigma_4 = \sigma_{yz}, \sigma_5 = \sigma_{zx}, \sigma_6 = \sigma_{xy}.$$

2. Hooke's law states that for sufficient small deformations the strain is directly proportional to the stress. The strain components are linear functions of the stress components:

$$e_i = \sum_j S_{ij} \sigma_j$$

S_{ij} is a six by six matrix. In matrix notation:

$$\mathbf{e} = \mathbf{S} \boldsymbol{\sigma}$$

3. \mathbf{S} is called the elastic compliance. $\mathbf{C} = \mathbf{S}^{-1}$ (inverse matrix of \mathbf{S}) is called the elastic stiffness (similar to the spring constant k in the common Hooke's law):

$$\boldsymbol{\sigma} = \mathbf{C} \mathbf{e}$$

4. Energy stored in a spring is given by $U = kx^2/2$. For a solid, we first calculate the work done (per unit volume) due to a small strain:

$$\begin{aligned} dU = dW &= \sum_i \sigma_i de_i \\ &= \sum_{i,j} C_{ij} e_j de_i \end{aligned}$$

Integrating with respect to de_i :

$$\text{Energy density } U = \frac{1}{2} \sum_{i,j} C_{ij} e_j e_i$$

5. Mathematically we require:

$$\frac{\partial^2 U}{\partial e_i \partial e_j} = \frac{\partial^2 U}{\partial e_j \partial e_i} \Rightarrow C_{ij} = C_{ji}$$

In other words, \mathbf{C} is a symmetric matrix with $C_{ij} = C_{ji}$. It has only $(36-6)/2 + 6 = 21$ independent elements.

6. From this energy density, Hooke's Law can be "derived":

$$\frac{\partial U}{\partial e_i} = \frac{1}{2} \frac{\partial}{\partial e_i} \sum_{ij} C_{ij} e_i e_j = \frac{1}{2} \sum_i (C_{ij} + C_{ji}) e_i = \sum_i C_{ji} e_i$$

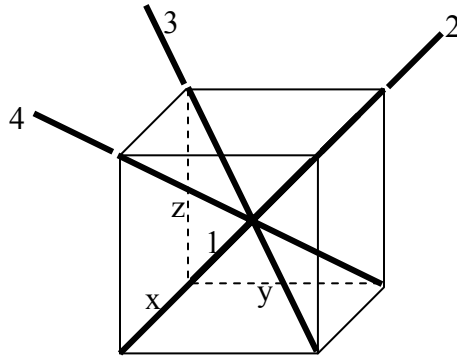
7. The *bulk modulus* B is defined as:

$$B = -\frac{1}{V} \frac{dp}{dV} \Rightarrow U = \frac{1}{2} B \delta^2$$

and the compressibility K is defined as $K=1/B$.

XI. Cubic crystals

1. A cubic system has four three fold symmetry axes along the diagonal.



Rotation along these four axes by 120° counterclockwise corresponds to transforming the x, y, and z according to the following schemes:

Axix 1: $x \rightarrow y \rightarrow z \rightarrow x$

Axix 2: $-x \rightarrow z \rightarrow y \rightarrow -x$

Axix 3: $-x \rightarrow z \rightarrow -y \rightarrow -x$ (or $x \rightarrow -z \rightarrow y \rightarrow x$)

Axix 4: $x \rightarrow z \rightarrow -y \rightarrow x$

(One simple way to imagine the above schemes is to ask which axes $(\pm x, \pm y, \pm z)$ are surrounding the axis of rotation and then permute these $(\pm x, \pm y, \pm z)$ axes. Note that there is a mistake in text (Kittel 8th edition that $-x \rightarrow z \rightarrow y \rightarrow -x$ and $-x \rightarrow y \rightarrow z \rightarrow -x$ actually represent the same axis of rotation (axis 2 in above figure, one in anticlockwise direction and the other in clockwise (or 240° anticlockwise) direction.)

2. Considering rotation of 120° in both clockwise and anticlockwise directions, along all four axes of rotation. These operations mean we can permute x, y, and z in any way, and add positive and negative signs to any of x, y, and x.

3. Changing the sign of x, y, and z will affect the stress and strain in the following way (as an example):

$$e_{x(-y)} = -e_{xy} \quad \sigma_{x(-y)} = -\sigma_{xy}$$

4. Energy density $U = \frac{1}{2} \sum_{i,j} C_{ij} e_j e_i$

U has to remain invariant under above operations, and the most general form that can reserve this invariant is:

$$U = \frac{1}{2} C_{11} (e_{xx}^2 + e_{yy}^2 + e_{zz}^2) + \frac{1}{2} C_{44} (e_{xy}^2 + e_{yz}^2 + e_{zx}^2) + C_{12} (e_{xx} e_{yy} + e_{yy} e_{zz} + e_{zz} e_{xx})$$

In other words, the 21 independent C_{ij} is reduced to only 3 under cubic symmetry. Hooke's Law for cubic system:

$$\begin{pmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{yz} \\ \sigma_{zx} \\ \sigma_{xy} \end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{pmatrix} \begin{pmatrix} e_{xx} \\ e_{yy} \\ e_{zz} \\ e_{yz} \\ e_{zx} \\ e_{xy} \end{pmatrix}$$

5. Consider a sound wave traveling along the x-axis of a cubic sample. The wave can be longitudinal or transverse. The longitudinal wave involves strain ϵ_{ii} and hence the velocity is given by

$$v_{\text{long}} = \sqrt{\frac{C_{11}}{\rho}}$$

Shear strain is involved in the longitudinal wave, so the transverse wave speed is given by

$$v_{\text{trans}} = \sqrt{\frac{C_{44}}{\rho}}$$

Appendix: Ice structure

See “<http://www.lsbu.ac.uk/water/ice1h.html>”, or ice_structure.pdf in this folder.

