

3.091 – Introduction to Solid State Chemistry

Lecture Notes No. 5a

ELASTIC BEHAVIOR OF SOLIDS

1. INTRODUCTION

Crystals are held together by interatomic or intermolecular bonds. The bonds can be covalent, ionic, or even secondary bonds. Covalent bonding examples include the sp^3 bonding that occurs in crystals like diamond or in single crystal silicon. Ionic bonding occurs in crystals like that of sodium chloride. Secondary bonding, such as hydrogen bonding, is primarily responsible for crystal formation in molecular crystals. An example of a molecular crystal is sucrose or common table sugar. These bonds establish an equilibrium length and can be thought of as “springs”. The atoms and molecules of a crystal vibrate about their equilibrium positions just as a mass on a spring can oscillate around its equilibrium position.

2. THE HARMONIC POTENTIAL AND THE EQUILIBRIUM BOND LENGTH

A mass on a spring is shown in Figure 1. The spring is characterized by a spring constant, k , which relates the spring force imposed on the mass, m , to the displacement from the equilibrium position. The relationship is provided by Hooke's Law, where the force, F , is given by

$$F = -k(x - x_0) = -k\Delta x$$

where Δx is the displacement from the equilibrium position of the mass. The equilibrium position is the position of no net force imposed by the spring. Displacing the mass from its equilibrium position requires work be performed. The result is that the potential energy of the mass is raised. The potential energy as a function of position for the mass on the spring is known as the Harmonic Potential and is given by

$$U - U_0 = \frac{1}{2}k(\Delta x)^2$$

These concepts are reviewed in a screen cast module ([Harmonic potential](#)).

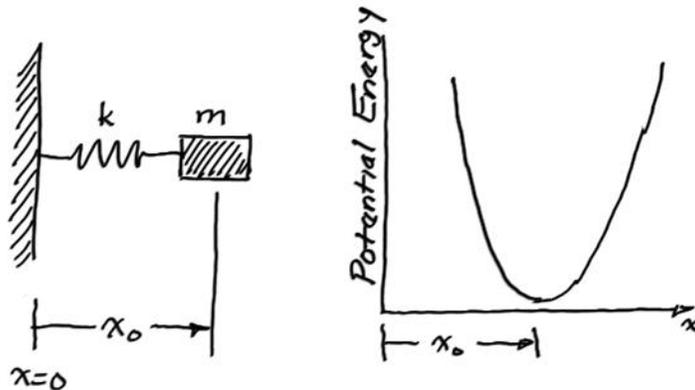


Figure 1: A mass on a spring and the Harmonic Potential.

Figure 2 compares the potential energy of an individual bond with the Harmonic Potential. The potential energy curve of a bond is anharmonic but closely approaches the Harmonic Potential at small displacements from the equilibrium position. Thus, an individual bond can be approximated as a spring and its associated spring constant. Stronger bonds have a larger spring constant than bonds that are weaker. This is equivalent to saying that a stronger bond requires more energy to stretch than a weaker bond.

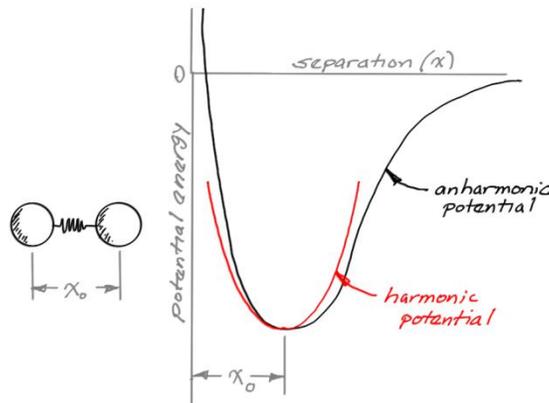


Figure 2: The anharmonic potential of an individual bond and the comparison to the harmonic potential near the equilibrium bond distance.

3. ELASTIC DEFORMATION OF A CRYSTAL

A crystal can be thought of an array of atoms or molecules with nearest neighbors interacting via bonds. A cubic structure is shown in Figure 3 with the bonds between nearest neighbors being represented as springs. If one were to try and stretch or compress the crystal, many bonds of the crystal would have to deform slightly. Crystals formed from stronger bonds would presumably be more difficult to deform.

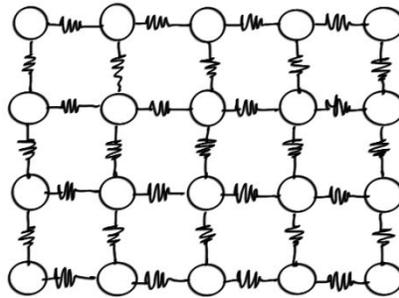


Figure 3: A cubic crystal with an array of atoms bonded to nearest neighbors. The bonds are represented as springs.

Let's consider the deformation of a real material as shown in Figure 4. In this Figure, a stress, σ , is applied in the directions shown so as to stretch the material along the x-axis. The stress is just the force per unit area applied to the ends of the material. The total force, F , is just the product of the stress and the area, A , over which it is applied. The material is observed to lengthen in the x-direction so that its new dimension is x which equals $x_0 + \partial x$. The differential ∂x is small and is a positive quantity. Also shown in Figure 4 is a change in dimension in a direction perpendicular to the applied stress. You have seen this phenomenon when you stretch a rubber band. The rubber band gets longer but it also gets thinner. This will be explained below, but for now realize that the new y-dimension is $y = y_0 + \partial y$ where ∂y is a negative quantity.

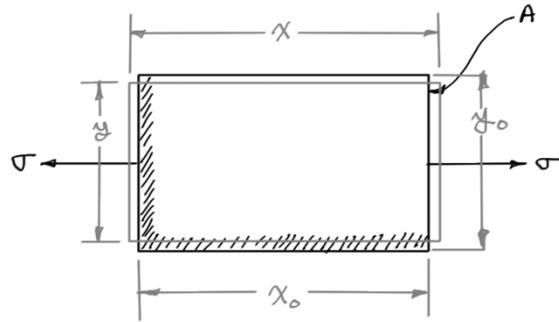


Figure 4: Small elastic deformation of a material causes it to deform in multiple directions.

We define the strain, ϵ_x , that the object undergoes as

$$\epsilon_x = \frac{x - x_0}{x_0}$$

If the difference between x and x_0 is very small, ∂x , then we have the differential strain, $\partial \epsilon_x$ is equal to $\partial x/x_0$.

It is probably not surprising to you that stretching a crystal like that shown in Figure 3 requires the stretching of the bonds that make up the crystal. If these bonds are approximated as springs then the entire crystal should be approximated by something like Hooke's Law. Indeed, real materials do behave like Hooke's law at least for small deformations. This behavior is shown in Figure 5. Strain is the result of an applied stress. The strain is linearly dependent on the magnitude of the stress. This relationship is given by

$$\sigma = E\epsilon$$

where E is a material property known as Young's modulus. Strain has no units, so inspection of the equation above shows you that the Young's modulus has the same units as stress (force per unit area). [\[See screencast on Elastic behavior and Young's modulus\]](#)

Materials that behave as shown in Figure 5 are said to be “elastic”. If a stress is applied then a strain is created. Elastic materials return to their original dimension when the stress is removed. All solids have the property that they are elastic if the strain is sufficiently small.

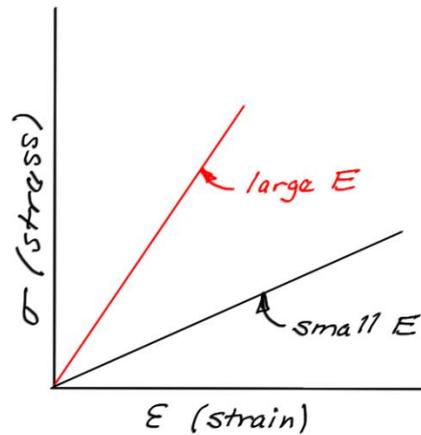


Figure 5: The stress-strain curve for small displacements. All solids at small enough displacements exhibit elastic behavior. The elastic behavior for materials with small and large Young’s modulus is shown in the graph.

4. YOUNG'S MODULUS AND BONDING

The Young's modulus is directly related to the strength of the bonds that make up the crystal. Shown below is a table of the Young's modulus for one column in the periodic table. The Young's modulus decreases by two orders of magnitude as one moves from carbon to lead. This is a direct result of the bond energy also decreasing from carbon to lead.

	$E(\text{GPa})$	Bond energy (kJ/mole)	Bond Length (\AA)
C	1200	346	1.54
Si	169	222	2.33
Ge	138	188	2.41
Sn	65	99	3.26
Pb	16	30	3.4

The bonds that are stretched or bent in a crystal depend on which direction you are applying the stress. As a simple example, consider single crystal silicon as shown in Figure 6. Pulling or compressing the crystal in the $[110]$ direction will be different than along the principle axis $[100]$. The $[110]$ direction of the silicon crystal is the direction of highest linear density of atoms. Thus, it is not surprising that the Young's modulus in the $[110]$ direction is 169 GPa while that in the $[100]$ direction is only 130 GPa. [\[See the screen cast on Young's Modulus and crystal direction.\]](#)

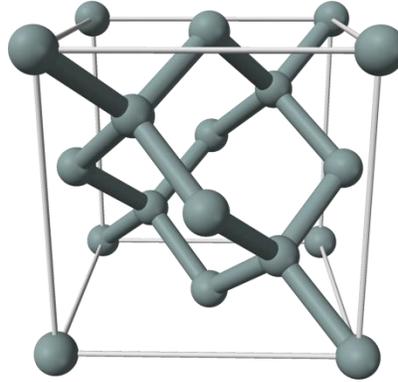


Figure 6: The unit cell of silicon is a diamond lattice. The silicon atoms are arranged on an FCC lattice with four additional silicon atoms placed on half the tetrahedral sites of the FCC lattice. This gives eight atoms per unit cell. Each of the atoms in the structure has four nearest neighbors in a tetrahedral arrangement. The silicon-silicon bonds are pointed in the tetrahedral directions to reflect the sp^3 bonding.

5. POISSON'S RATIO AND BONDING

Elastic strain in one direction causes a strain in a perpendicular direction as described above. The amount of strain in the perpendicular direction is a property of the material. Indeed, it is a function of the nature of bonds in the solid as well as the crystal structure. Consider the case described in Figure 4 in the limits of very small strains. The differential strain in the x-direction is given by

$$\partial \epsilon_x = \frac{\partial x}{x}$$

where $\partial \epsilon_x$ is a positive quantity for the tensile stress applied in the x-direction. The strain in the y-direction is given by

$$\partial \epsilon_y = \frac{\partial y}{y}$$

where ∂y is a negative quantity.

The material property that describes the amount of strain that appears in the perpendicular direction to the applied stress is Poisson's ratio, ν . Poisson's ratio is given by

$$\nu = -\frac{\partial \epsilon_y}{\partial \epsilon_x}$$

Most materials have a Poisson's ratio with magnitude in the range $0 < \nu < 0.5$ with the most common being near 0.3. [\[See screencast on Poisson's ratio\]](#)

Bonding and crystal structure determine the magnitude of the Poisson's ratio for a material. Crystal structure also determines how ν varies with crystallographic direction. Consider the cubic crystal shown in Figure 7. A stress is applied in the $[110]$ direction in this crystal. The crystal will elongate in the $[110]$ direction by stretching and bending bonds. In order to do so, however, the dimensions in the $[\bar{1}10]$ direction have to contract. The crystal has lost its perfect cubic symmetry and has become very slightly monoclinic.

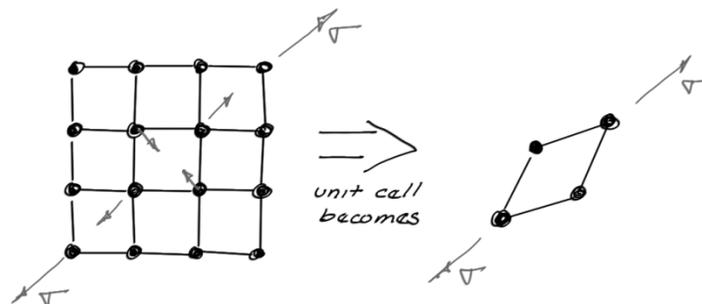


Figure 7: A cubic crystal stretched in the $[110]$ direction by an applied stress. Bonds bend and stretch to accommodate the strain. A contraction occurs in the perpendicular direction.

6. STRAIN ENERGY

Energy is stored in a material when it is strained. This energy storage is very similar to what happens when a spring is stretched. Work must be done to extend the lengths of the spring. This energy is the potential energy of the spring. The same is true of solids.

As solids are stretch or compressed, the work performed is stored as potential energy in the solid. We call this energy “strain energy”. The strain energy per unit volume of material, E_V , describes how much energy is stored and is given by

$$E_V = \frac{1}{2} \sigma \epsilon$$

[See screencast on strain energy and the origin of this equation] The equation above says that the larger the stress required to achieve a given strain, the more energy will be stored. Materials with higher Young’s modulus require larger stress to obtain a given amount of strain.

Strain energy can be quite large even for small strains if the Young’s modulus of the material is large. Consider stretching single crystal silicon in the [110] direction by 1% ($\epsilon = 0.01$). The Young’s modulus in this direction is 169 GPa. The stress required to achieve the 1% strain can be easily calculated ($\sigma = E\epsilon$) to be 1.69×10^9 Pa.

Substitution in the equation above yields the strain energy of 8.45×10^6 J/m³ or 8.45 J/cc. This energy can be compared to the energy required to heat the silicon. The heat capacity of silicon is 1.64 J/(cc-K). This means that if this strain energy were suddenly turned into heat, the silicon temperature would rise by 5K (=8.45/1.64).