01E_Spring Model (Modulus and Energy Calculation)

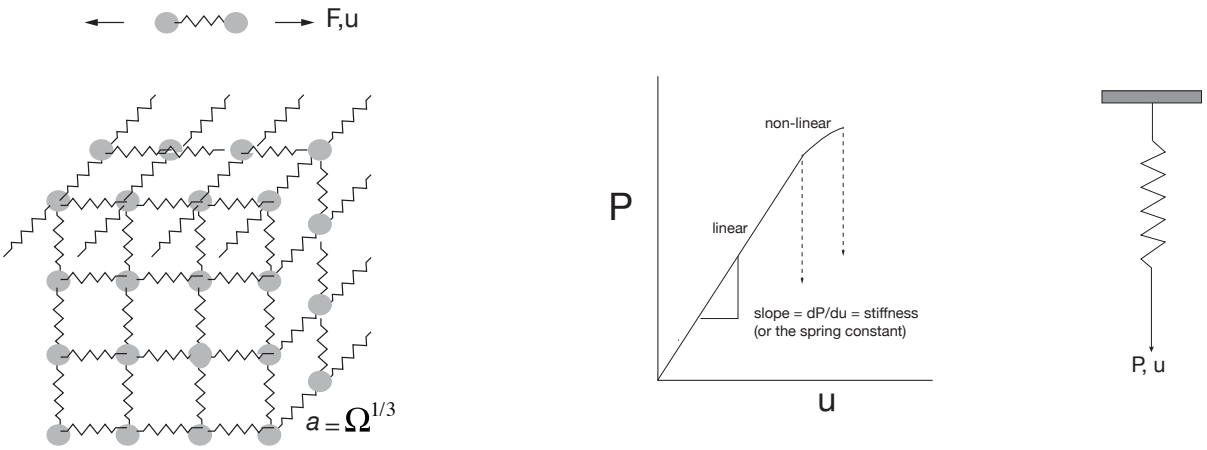
Topic:

•Relating the bulk modulus to density

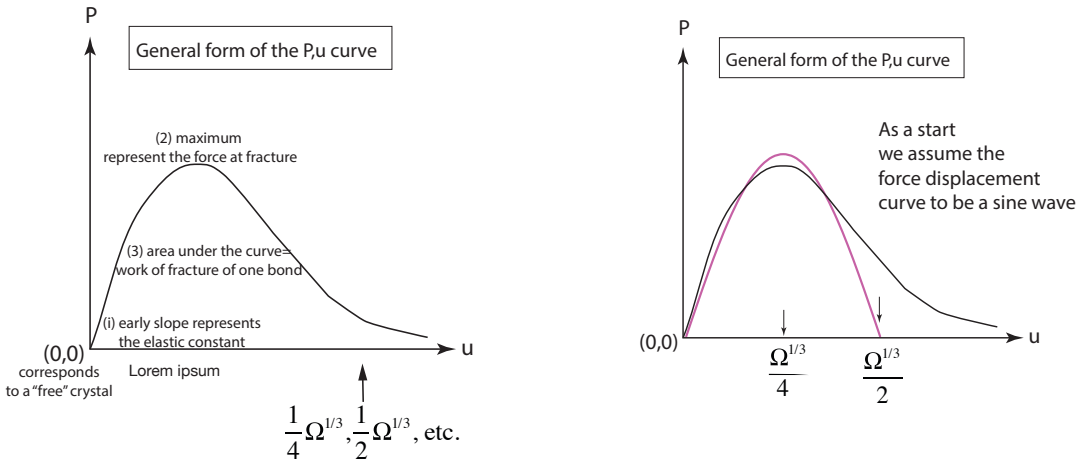
•Relating the bulk modulus to the energy of formation

Elastic Modulus, Stiffness and Compliance

Consider a simple spring model for bonds:



Approximation for the Force Displacement Curve



The length scale for "u" is related to the interatomic spacing, that is to $\Omega^{1/3}$

The force displacement curve has three attributes

- The slope at $u \to 0$, that is the slope at small displacements is the Elastic Modulus
- The maximum in the curve corresponds to the force required to "fracture" the bond
- The total area under the (P,u) curve is the work of fracture, or the energy of the bond measured mechanically

In order to relate the area under the curve to the enthalpy of formation (it can the heat of fusion or the heat of evaporation) it is necessary also to count the number of bond between nearest neighbors in the solid. The nearest neighbors are also called the coordination number, called by the symbol Z .

Noting that one bond is shared by two nearest neighbors the work in the fracture of the bond is also shared. Therefore only one half of the work belongs to one atom. Therefore if,

U_{Bond} = is the energy calculated from the force, displacement curve,

then the enthalpy of formation (again this may be the heat of fusion or the heat of evaporation) is given by

$$\Delta H_{per/atom} = \frac{U_{bond} Z}{2}$$

Therefore the enthalpy per mole (which is usually quoted in handbooks)

$$\Delta H_{mol} = \frac{U_{bond} Z N_A}{2}$$

where N_A is the Avogadro's number ($6.02*10^{23}$ atoms/molecules per mole)

Adjustable Parameters in the Force-Displacement Curve

Notes:

- How far do the atoms have to be stretched until they are totally separated?
- Where is the maximum in the force that is, where is the point of the onset of fracture?
- The u-axis in this curve should scale with a the lattice parameter, or the interatomic spacing, that is $\Omega^{1/3}$

Relating the force-displacement curve to the Young Modulus

The equation for the force displacement curve is

$$F = F_O \sin(\frac{2\pi u}{\Omega^{1/3}})$$

Early slope which gives the Youngs modulus

$$\left(\frac{dF}{du}\right)_{u\to 0} = \frac{2F_o\pi}{\Omega^{1/3}} \cos\left(\frac{2\pi u}{\Omega^{1/3}}\right)_{u\to 0} = \frac{2F_o\pi}{\Omega^{1/3}}$$

Convert above into the Youngs modulus

$$E = \frac{d\sigma}{d\varepsilon} = \frac{d(F/\Omega^{2/3)})}{d(u/\Omega^{1/3)})} = \frac{dF}{du}\frac{1}{\Omega^{1/3}} = \frac{2F_o\pi}{\Omega^{2/3}}$$

Calculation of the Maximum force or the Strain to Fracture (called the ideal strength_

$$\frac{F_o}{\Omega^{2/3}} = \sigma_{ideal} = \frac{E}{2\pi}$$ = (100/2*pi)% strain at fracture = 15% strain.

Fracture measurements of highly polished, ideal optical fibers give a maximum fracture strain of about this number.

Calculation of the Energy for Formation per Bond (and per mole)

$$\text{Work per bond} = \int_0^{onehalfwavelength} F_o \sin\left(\frac{2\pi u}{\Omega^{1/3}}\right) du$$

$$U_{bond} = F_o \frac{\Omega^{1/3}}{2\pi}\left[-\cos\left(\frac{2\pi u}{\Omega^{1/3}}\right)\right]_0^{halfwavelength}$$

$$= \frac{2F_0\Omega^{1/3}}{2\pi} = \frac{2\Omega^{1/3}}{2\pi}\frac{E\Omega^{2/3}}{2\pi} = \frac{E\Omega}{2\pi^2}$$

Now consider the enthalpy of formation

$$\Delta H = \frac{U_{bond} Z}{2} N_A \text{energy of formation per mole}$$

$$\Delta H = \frac{E V_{mole}}{4\pi^2} Z$$

now we have related the energy of formation to the elastic modulus. Actually, the Bulk modulus is a better quantity to analyzed since it is isotropic, and independent of the Poisson Ratio, which is not contained in the Spring Model.

Approximate relationship between the elastic modulus and density

The Elastic Modulus (the Youngs Modulus)

$$E = \frac{stress}{strain} = \frac{P/\Omega^{2/3}}{u/\Omega^{1/3}} = \frac{P}{u}\frac{1}{\Omega^{1/3}} \qquad (01A.1)$$

Note the units: stiffness has units of Nm^{-1}, therefore, E has units of Nm^{-2}.

Note that the elastic modulus depends on the bond lengths. If the atoms are more tightly packed then they would have a higher modulus. However, the modulus does not just depend on density but also on the strength of the bonds and upon the molecular weight as shown just below. is the stiffness of the bonds.

Recall that $\Omega = \frac{MolarVol}{N_A} = \frac{M_{wt}}{\rho N_A}$; Therefore $E = \frac{P}{u}\rho^{1/3}\left(\frac{N_A}{M_{wt}}\right)^{1/3}$. Therefore ,expect E to be related to $\rho^{1/3}$, at least very approximately. The lines for constant values of $\frac{E}{\rho^{1/3}}$ are drawn as straight lines in the map on the following page. They predict the correct trends between the modulus and the density The vertical shifts between them reflects the term

$\frac{P}{u}.\frac{1}{M_{wt}^{1/3}}$, that is elements with stronger bonding (higher values of $\frac{P}{u}$ and lower molecular weight move upwards). For example ceramics which are more strongly bonded and have lower molecular weight lie above metal such as copper and steels.