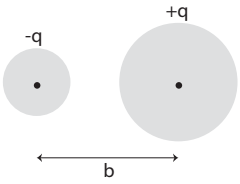
Bridging Length Scales - A constant reminder

#4: The nature of bonds and enthalpy of formation

(Polar nature of bonds (the dipole moment)

Molecules and crystals are often described qualitatively as being polar or non-polar. Being polar means that a single molecule has a net dipole moment. In a crystal it means that a large aggregate of atoms have a net dipole moment.

Therefore a molecule by itself may have a dipole moment but when in a crystal of a certain structure the dipole moments of individual bonds cancel leaving a net value of zero dipole moment.



Dipole Moment = b*2q= (distance between the charges)x(difference between the charges)

The units of a dipole moment are Debye

One D = 3.336×10^{-30} coulomb meters

Let us say that q= charge on one electron (1.6×10^{-19} C) then 1D corresponds to a spacing of 1 Angstrom.

Then one D corresponds to a distance of the bond, b, to be

d for water molecule

The **O-H Bond Lengths** In The **Water Molecule** (H_20)are 0.96 A, And The H-O-H Angle Is 104.5O.

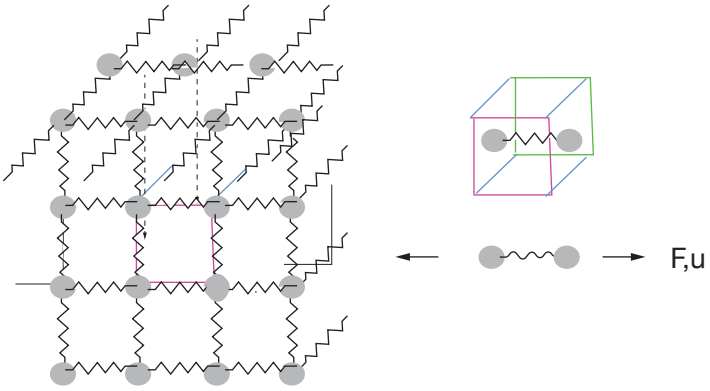
Questions?

•elastic constants are related to the bond strength - bond energy (the amount of work done to separate the bond)

•what other handbook property is related to the energy of a bond - work done to change the fundamental structure of the solid. One example is melting - heat of fusion. Another state is the vapor phase.. that is related to heat of boiling. The heat of boiling from the solid to the vapor state is the sum of the heat of melting and the heat of boiling.

We wish to consider mechanical analog of a change of state (solid to liquid or solid to vapor).

Force displacement curve for one bond



Z = 6 for the simple cubic structure

Z=8 for body centered cubic structure

Z= 12 for face centered cubic structure

edge length = a (lattice parameter)

Volume per atom = a^3 = OMEGA

bond length = $(OMEGA)^{1/3}$

cross section area per bond = $(OMEGA)^{2/3}$

stress ($\sigma = \frac{F}{\Omega^{2/3}}$)

strain ($\varepsilon = \frac{u}{\Omega^{1/3}}$

Energy per atom=energy per bond x Z/2

where Z is the number of nearest neighbors - called the coordination number.

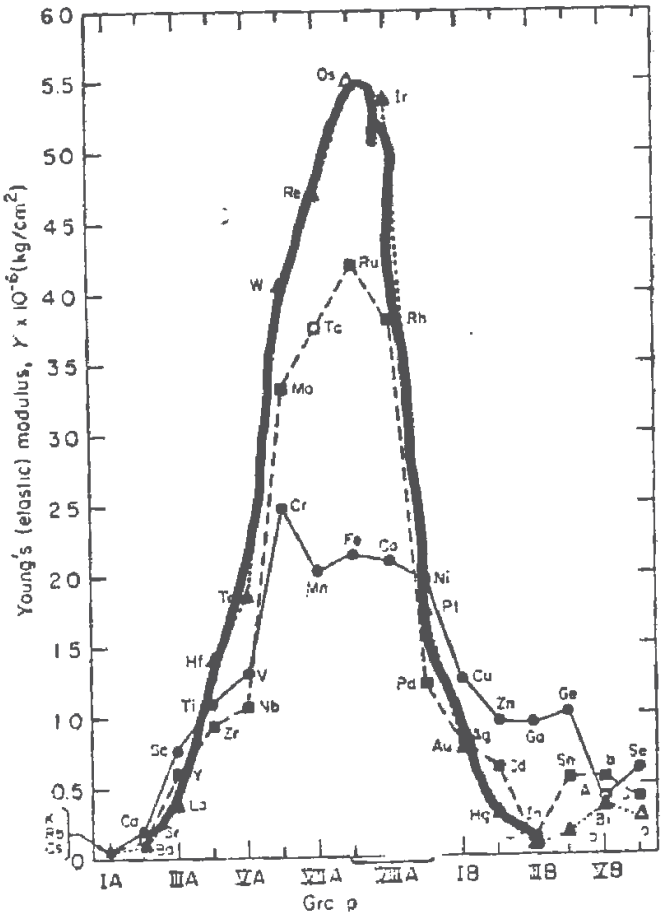
The Periodic Table from Pauling (The Chemical Bond)`

Ne 10	Na 11	Mg 12	Al 13	Si 14	P 15	S 16	Cl 17	Ar 18									
O	Ia	IIa	IIIa	IVa	Va	VIa	VIIa	VIII			Ib	IIb	IIIb	IVb	Vb	VIb	VIIb	VIIIb	0
Ar 18	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36	
Kr 36	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54	
Xe 54	Cs 55	Ba 56	La 57	*	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
Rn 86	Fr 87	Ra 88	Ac 89	**	Th 90	Pa 91	U 92												

* Rare-earth metals	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er	Tm 69	Yb 70	Lu 71
** Uraniu metals	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	E 99	Fm 100	Mv 101	No 102	Lw 103

FIG. 2-15.—The periodic system of the elements.

Youngs Modulus from Gerschneider



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Approximation for the Force Displacement Curve

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

Note that the equation given in the box in the previous page allows us to convert force into tensile stress, and the displacement into tensile strain.

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

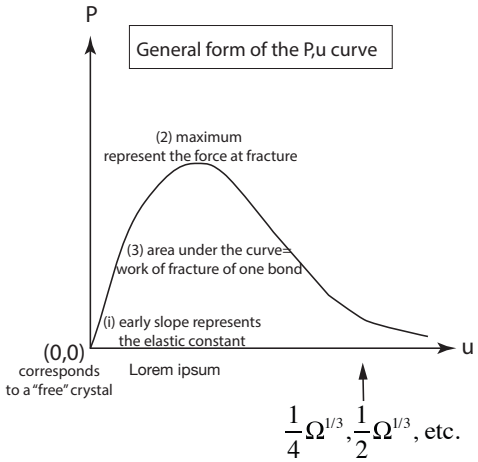
This requires the following assumptions

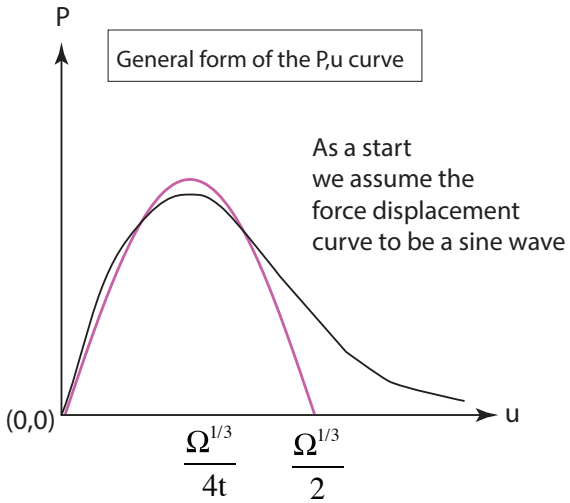
- How far do the atoms have to be stretched until they are totally separated?
- Where is the maximum in the force that is, where is the point of the onset of fracture?

There are two additional points to consider

The force displacement curve must be periodic

The u-axis in this curve should scale with a the lattice parameter, or the interatomic spacing, that is $\Omega^{1/3}$





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

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

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

$$\frac{F_o}{\Omega^{2/3}} = \sigma_{ideal} = \frac{E}{2\pi}$$ = (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.

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

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

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

Now consider the enthalpy of formation

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

now we have related the energy of formation to the elastic modulus

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

We have related two very two very different properties (handbook) that is the energy of formation, the elastic modulus and the molar volume to each other.