Interatomic and intermolecular forces.

What will be covered?

1. Binding energy: basic concepts
2. Ionic bonding.
3. Chemical bonding.
   a. Primary bonds.
   b. Secondary bonds.

Why do we need to know this material?

Several important material properties are determined on the type and characteristic interatomic/interionic/intermolecular bonds:

1. Melting temperature is a function of the interatomic bonding energy. The higher this energy the higher the melting temperature.
2. The modulus of elasticity of a material is related to the shape of a materials force-atomic separation curve.
3. The strength of some polymeric materials are functions of the degree of secondary bonding between adjacent molecules.
4. Electrical conductivity is dependent on the type of interatomic bond. Metallic bonded materials are typically electrical conductors while those that are ionically or covalently bonded tend to be insulators.

The magnitude of the coefficient of thermal expansion is dependent upon the materials potential energy – atomic separation curve.

Binding energy: basic concepts.

Two atoms approaching to less than a few tens of angstroms (Å) exert forces on each other.

The net force can be thought of as a combination of an attractive and a repulsive term.

The dependence upon distance of the two forces is usually different, with repulsion dominating on very close approach.

This results in a maximum of the attractive forces at some intermediate distance as well as at a distance ($r_0$) at which the force is zero.

The relationship between the force and the potential energy, $U(r)$, is given by: $F(r) = \frac{dU(r)}{dr}$. 
In this convention, attractive forces are considered positive.

Based upon this relationship, the potential has a minimum at the same distance \( r_o \) at which the force is zero.

Values of \( r_o \) are generally on the order of a few angstroms.

At \( r_o \) the value of \( U(r) \) is termed the binding energy \( E_B \).

\( E_B \) ranges from 100 to 1500 kJ/mole for primary bonds and is of the order of 10 kJ/mole for secondary bonds.

The changes in interaction potential with distance can generally be described quite well by the following expression:

\[
U(r) = - \frac{a}{r^m} + \frac{b}{r^n}
\]

Here the coefficient \( a \) describes the attractive potential and \( b \) the repulsive potential.

The exponents \( m \) and \( n \) are characteristic of the type of binding and the electronic structure.

For the bonding of ions \( m = 1 \) while for covalent bonding \( m = 6 \). \( n \) is also called the Born constant and varies for different electronic configurations.

Note that binding occurs when \( m < n \); otherwise repulsion dominates.

The situation when \( m = 6 \) and \( n = 12 \) is termed the Lennard – Jones potential.

When the potential between two atoms has the general form shown in the energy-well figure, there is a good chance that stable aggregates of these atoms can be formed, and the atoms are said to be held together by chemical bonds.

Related to the shape of the potential energy well are the concepts of ionic and atomic radii.

In bonded structures the equilibrium distance of the the two bonding partners is considered the sum of their radii.
Several important factors can influence this distance:

Temperature: an increase in energy of thermal motion will increase the mean distance between atoms if the potential trough is asymmetrical. This leads to positive expansion coefficients.

 Ionic valence changes interatomic spacing.

Positively charged ions are smaller than the neutral atom whereas negatively charged ions are larger.

  e.g. Fe: 0.1241nm       Fe++: 0.04nm

Coordination number: the number of adjacent atoms can increase to the point of crowding:

  e.g.  Fe with CN = 8: 0.124nm  
       Fe with CN = 12: 0.127nm

There is a direct proportionality between $E_b$ and $T_m$. 
Specific description of ionic bonds.

Overview

Ionic bonding results from the strong electrostatic attraction between oppositely charged particles.

The ionizations of the originally electrically neutral atoms involved result from the transfer of valence electrons between the atom species involved.

One of these gives up its valence electrons and becomes a positively charged ion whereas the other accepts the transferred valence electrons and becomes a negatively charged ion.

The resulting coulombic attraction between the charged particles binds the two ions together.

Atoms most likely to participate in this mechanism may be identified by their positions in the periodic table relative to those of the noble gases.

Atoms with positions just preceding the noble gases tend to accept electrons; those just following tend to donate or to transfer their electrons.

The transfer if the valence electrons from the cation to the anion oppositely charges both species and causes both ions to have have highly spherical, noble gas-like electron configurations.

This is a major reason why classical electrostatics may be used to describe their bonding mechanism.

Mathematical development.

The energy of attraction between two isolated charged particles is given by Coulomb's law as:

\[ U_A = \frac{(Z_1 e)(-Z_2 e)}{4\pi \varepsilon_0 r} \]

where \( Z_1 \) and \( Z_2 \) are the respective numbers of charges on the positive and negative ions, \( e \) is the charge on the electron, \( 4\pi \varepsilon_0 \) is the dielectric constant of vacuum and \( r \) is the distance between the ions.
This expression can be simplified by using the relative dielectric constant of vacuum: $\varepsilon_r = 1$, so that:

$$U_A = -(Z_1)(Z_2)e^2/r$$

The minimization of the energy of attraction (i.e. the maximization of the negative $U_A$) between the ions requires that they be as close together as possible.

The electron clouds abut and start to overlap each other.

As the clouds begin their mutual penetration, the Pauli exclusion principle begins to take effect.

Since electrons with the same quantum numbers will be present in each cloud, the clouds will resist further penetration.

Hence, a mutual repulsion arises as expected based upon the Pauli exclusion principle.

Born has shown that the mutual repulsion energy between a pair of ions in a crystal is given by:

$$U_R = b/r^n$$

Where $b$ is a constant for a given ion pair and $n$ is known as the Born exponent or the repulsion exponent whose value depends on the electronic configuration.

<table>
<thead>
<tr>
<th>Noble Gas</th>
<th>Outer Core Configuration</th>
<th>Repulsion Exponent, $n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>1s$^2$</td>
<td>5</td>
</tr>
<tr>
<td>Ne</td>
<td>2s$^2$3p$^6$</td>
<td>7</td>
</tr>
<tr>
<td>Ar</td>
<td>3s$^2$3p$^6$</td>
<td>9</td>
</tr>
<tr>
<td>Kr</td>
<td>3d$^{10}$4s$^2$4p$^6$</td>
<td>10</td>
</tr>
<tr>
<td>Xe</td>
<td>4d$^{10}$5s$^2$5p$^6$</td>
<td>12</td>
</tr>
</tbody>
</table>

The total energy of bonding in terms of an isolated ion pair is thus the sum of the attractive and repulsive terms:

$$U_T(r) = \left[ -(Z_1)(Z_2)e^2/r \right] + b/r^n$$
The strong electrostatic attractions between ions in ionic crystals are both omnidirectional and long-range in nature.

This causes each ion of a given crystal sign to be attracted to every other ion of opposite sign in the crystal.

Since these attractive energies vary inversely with the distances between the ions, the more closely situated neighbors make larger contributions to this than do the more widely separated pairs.

The summation of all these contributions is a function of the crystal structure of the solid.

This is accounted for by modification of the above equation to include $\alpha_m$, the Madelung constant:

$$U_T(r) = \left[ -(Z_1)(Z_2)e^2 \alpha_m /r \right] + b/r^n$$

where $\alpha_m$ is proportional to $\sum_{j} \pm 1/|r_{ij}|$

The plus and minus sign refer to the attractions between both a positive and negative reference ion and all other ions in the crystal.

**Determination of the parameter $b$.**

At equilibrium, $U_T(r)$ will be a minimum and the variation of $U_T(r)$ with respect to $r$ will be zero so that, where $n$ is now a constant for a given ionic solid and $r = r_o$ is the equilibrium spacing,

$$dU_T(r)/dr = \left[ -(Z_1)(Z_2)e^2 \alpha_m/r_o^2 \right] - nb/r_o^{n+1} = 0$$

and

$$b = \left[ -(Z_1)(Z_2)e^2 \alpha_m/nr_o^{1-n} \right]$$

The Born exponent can be shown to vary inversely with the compressibility of the solid.

Incorporating this result,

$$U_T(r) = \left[ -(Z_1)(Z_2)e^2 \alpha_m/r_o \right] (1-1/n)$$
Note that the interionic distance \( r_o \) is the distance of closest approach of the ions of differing “sizes” treated as hard spheres and therefore represents the sum of the “radii” of both such spheres.

Since the radii of given ions will vary depending on factors that include lattice type and the nature of other ions in the lattices with the given ion, it is not the ionic radius.

The molar bonding energy is obtained from the above equation by multiplying both sides by Avagadro’s number, \( N_A \).

\[
U_{\text{mol}} = N_A \cdot U_i(r) = [-N_A(Z_1)(Z_2)e^2 \alpha_m/r_o] (1-1/n)
\]

Calculations based upon this relationship usually provide molar bonding energies that are slightly less than those determined experimentally. This results from the fact that the clouds that constitute the ions are not perfectly hard spheres; some mutual penetration appears to take place.

Some of the electrons in the interpenetrating clouds may be shared by both ions.

This is the equivalent of adding a small component of covalent bonding to the predominating ionic bonding.

![Diagram](image)

Indeed, it is probable that perfectly pure ionic bonding normally does not exist and that some small degree of covalency is present.
This may account for the aforementioned small differences between the experimental and calculated values of $U_{mol}$.

The minima in the potential energy curves determine the equilibrium interionic spacings, $r_o$; these are the primary determinants of the crystal lattices formed from the various paired ionic species.

The inflection points can be considered proportional to the minimum quantity of energy required to destroy the crystalline array (i.e. melting); these points occur when the second derivative of $U_T(r) = 0$.

Any externally added energies, or their derivative forces, equal to or larger than the inherent ones are thus expected to disrupt the crystalline array.

Also note that the slope of the force curve evaluated at $r = r_o$ is proportional to Young’s modulus ($E$) of the crystal.

$$\left[\frac{d^2U(r)}{Dr^2}\right]_{r=r_o} = CE$$ where $C$ is a constant.

In the absence of external forces, the crystal has an equilibrium spacing of $r_o$.

When an external force is applied, the interatomic spacing is altered.

Both biaxial extension and lateral contraction increase the lattice potential energy.

For small elastic extensions (contractions), $\Delta r$, the force increases linearly with $\Delta r/r_o$, i.e., the strain.

If the single crystal is extended along the [100], it is difficult to relate Young’s modulus in the [100] to the force or energy curves.

This is because there is an extension along the [100] but a lateral contraction along the [010] and [001].

This problem is avoided if the results of a hydrostatic state of stress are considered.

The crystal potential energy can be plotted versus the volume per atom, $\Omega$. 

\[ \text{...} \]
When a hydrostatic tensile stress is applied, the atomic volume is increased from $\Omega_o$ to $\Omega_o + \Delta \Omega$ and $U$ increases.

Now, $\sigma = F/A = -(\partial U/\partial \Omega)$.

In the vicinity of the equilibrium spacing ($r_o$) or volume ($\Omega_o$), both the $U - r$ and $U - \Omega$ relationships are quite symmetric; hence $\partial U/\partial \Omega$ increases linearly with $\Delta \Omega$ (i.e. $\Omega - \Omega_o$) around $\Omega = \Omega_o$ and so does $\sigma$. 
Therefore, the bulk modulus $K$ can be related to the change in atomic volume according to:

$$K = -\Omega_o \left( \frac{\partial U}{\partial \Omega} \right)_{\Omega} + \Omega_o \left( \frac{\partial^2 U}{\partial \Omega^2} \right)_{\Omega}$$

Since the derivative of the $U - \Omega$ curve increases linearly with increases in $\Omega$, $\partial U^2 / \partial \Omega^2$ is constant near $\Omega = \Omega_o$ and linear elasticity is observed.

At larger strain this is no longer true and linear elasticity is not found even though the elastic behavior still results from the stretching of primary atomic bonds.

While modulus values are related to bond energy, $U$, the bond energy in return depends on the equilibrium interatomic spacing and the nature of the chemical bonding force.

Based on these concepts, the properties of ionically bonded solids may be derived on the basis that the electrons involved are in very deep wells and consequently their bonding energies are expected to be high.

The electrons may be considered as being virtually immobile and as a result their electrical and thermal conductivities are anticipated to be very low, i.e. ionic solids would be expected to be insulators.

The deep wells and corresponding high bond strengths are manifested by deep and narrow energy versus distance curves.

These lead to the prediction of high modulii of elasticity, high melting points and low coefficients of thermal expansion.
General description of chemical bonds.

In general, a non-rigid classification scheme is utilized in which gradual transitions from one type to another are possible.

**Primary bonds**

Ionic
- Exchange of valence electrons
- Electrostatic (coulombic) attractive forces
- Non-directional nature
- Large bonding energies

Covalent
- Shared electrons between adjacent atoms
- Directional nature
- Wide range of bonding energies

Metallic
- Electron cloud / ion core
- Delocalized nature
- Wide range of bonding energies

**Secondary bonds**

Physical bonds that are weak relative to primary bonds and may be obscured by the presence of primary bonds.

Arise from atomic or molecular dipoles (electrostatic)

**Types**

**van der Waals**
- Induced dipole
- Instantaneous and temporary

**Polar**
- Permanent dipoles
- Depends on asymmetry of component atoms

**Hydrogen**
- Special case of polar bonding
- Occurs with covalent bonding of H to O, N and F
- Strength arises from presence of positively charged, unscreened bare proton
Importance

Accounts for properties of molecular substances ranging from diatomic molecules to polymers.

More detailed consideration of van der Waals interactions

Dipole – dipole bonds

When different atoms in a molecule carry equal and opposite charges, the molecule is described as polar and possesses a dipole moment ($\mu = qr$).

At large distance such a molecule acts as an electrically neutral system, but at molecular distances the separation becomes sufficiently small for an intermolecular attractive force to be generated.

Example: methyl chloride (CH$_3$Cl)

The magnitude of this interaction is given by:

$$
\Phi(r) = -\frac{2}{3} \left\{ \left[ \frac{\mu_1^2 \mu_2^2}{4\pi \varepsilon_0^2} \right] \left[ \frac{1}{r^6} \right] \left[ \frac{1}{kT} \right] \right\}
$$

where $\varepsilon_0$ is the permittivity of free space.

At $T$ increases, thermal agitation destroys the alignment of the dipoles.

Dipole induced dipole bonds

The presence of a polar molecule in the vicinity of another molecule (polar or non-polar) has the effect of polarizing the second molecule.

The induced dipole can then interact with the dipole moment of the first molecule.

The magnitude of the interaction depends on the size of the permanent dipole moment of the polar molecule and the polarizability $\alpha$ of the second molecule:
Since the induced dipole moment follows the direction of the inducing dipole, we do not need to take account of the effects of thermal motion.

Because the pair of molecules is unable to disorientate the induced moment from the direction of the inducing moment, the effect survives even when the polar molecule is rotating freely (at higher temperatures) in the vicinity of the polarizable molecule.

**Induced Dipole – induced dipole bonds.**

Fluctuation of electron clouds creates an instantaneous (time varying) dipole moment constantly changing in magnitude and direction.

This fluctuation generated a mutual polarization.

Example: methane (CH₄)

The magnitude of these dispersive forces is quite involved but a reasonable approximation is given by:

\[
\Phi(r) = -2 \left\{ \frac{\mu^2}{4\pi \varepsilon_o} \right\} \left\{ \frac{\alpha^2}{r^6} \right\}
\]

where \( \mu \) represents the ionization potential.

These dispersive forces account for the major portion of the intermolecular forces in nonpolar materials.

This interaction is critical when summed over large distance (i.e. molecular weight effects).
Total interactions.

The London formula also applies to the interactions between polarizable molecules so the total interaction energy between molecules is given by the sum of the above three equations.

All three energies are negative, implying a lowering of energy as the molecules approach; hence, they indicate the presence of attractive forces between the molecules.

Note that all three effects vary as $r^{-6}$

**General representation:**

Attraction:

$$\Phi(r) = -\frac{C_6}{r^6}$$

Repulsion:

$$\Phi(r) = \frac{C_n}{r^n} \quad \text{for various values of } n.$$

**Overall:**

When molecules are pushed together the nuclear and electronic repulsions begin to dominate the attractive forces.

The repulsive interactions rise very steeply with decreasing separation and so the intermolecular energy is expected to follow a sharply rising curve.