# Lecture Outline: Atomic Structure

- ☐ Electronic Structure of the Atom
- ☐ Periodic Table
- ☐ Types of Atomic Bonding, primary/secondary bonds
- ☐ Coordination and next neighbors
- ☐ Binding Energy, Interatomic Spacing, & their dependence on temperature
- ☐ Properties from Bonding
- ☐ Summary Bonding/Properties of Material Classes

Bohr's Atom model

orbital electrons:
n = principal
quantum number
n=3   **2   1**
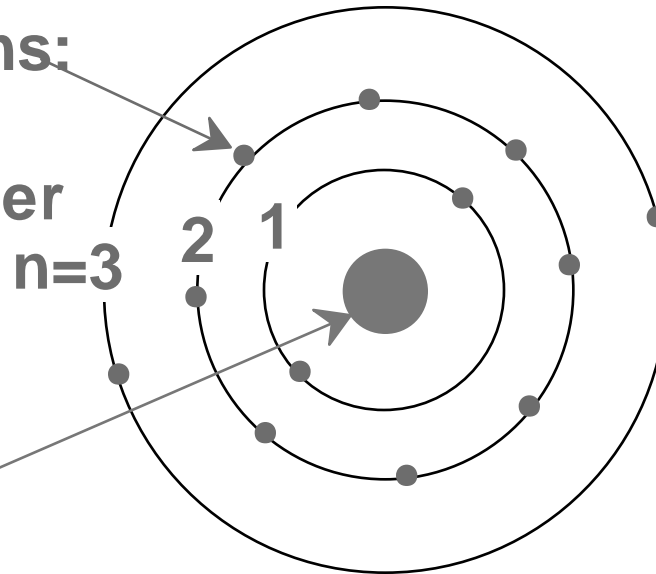
Nucleus: Z = # protons

= 1 for hydrogen to 94 for plutonium
N = # neutrons

Atomic mass A ˜ Z + N,
since nucleons are about 1840 times heavier than electrons

Quantum mechanics delivers better model

- Schrödinger equation time dependent

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial^2\Psi}{\partial z^2}\right)+U\Psi=i\hbar\frac{\partial\Psi}{\partial t}$$

- In atom stationary states, time independent Schrödinger equation

$$\Psi(x,y,z,t)^2 \quad \text{Probability density}$$

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{2m}{\hbar^2}(E-U)\psi=0$$

- Solving this equation for Coulomb potential

$$\psi(x,y,z)^2 \quad \text{Probability density}$$

$$U=-\frac{e^2}{4\pi\varepsilon_0 r}$$

Eigenvalues are discrete energy levels for electron

Square of eigenfunction gives probability density (where electron can be found)

There are 3 quantum numbers, n, l, m_l

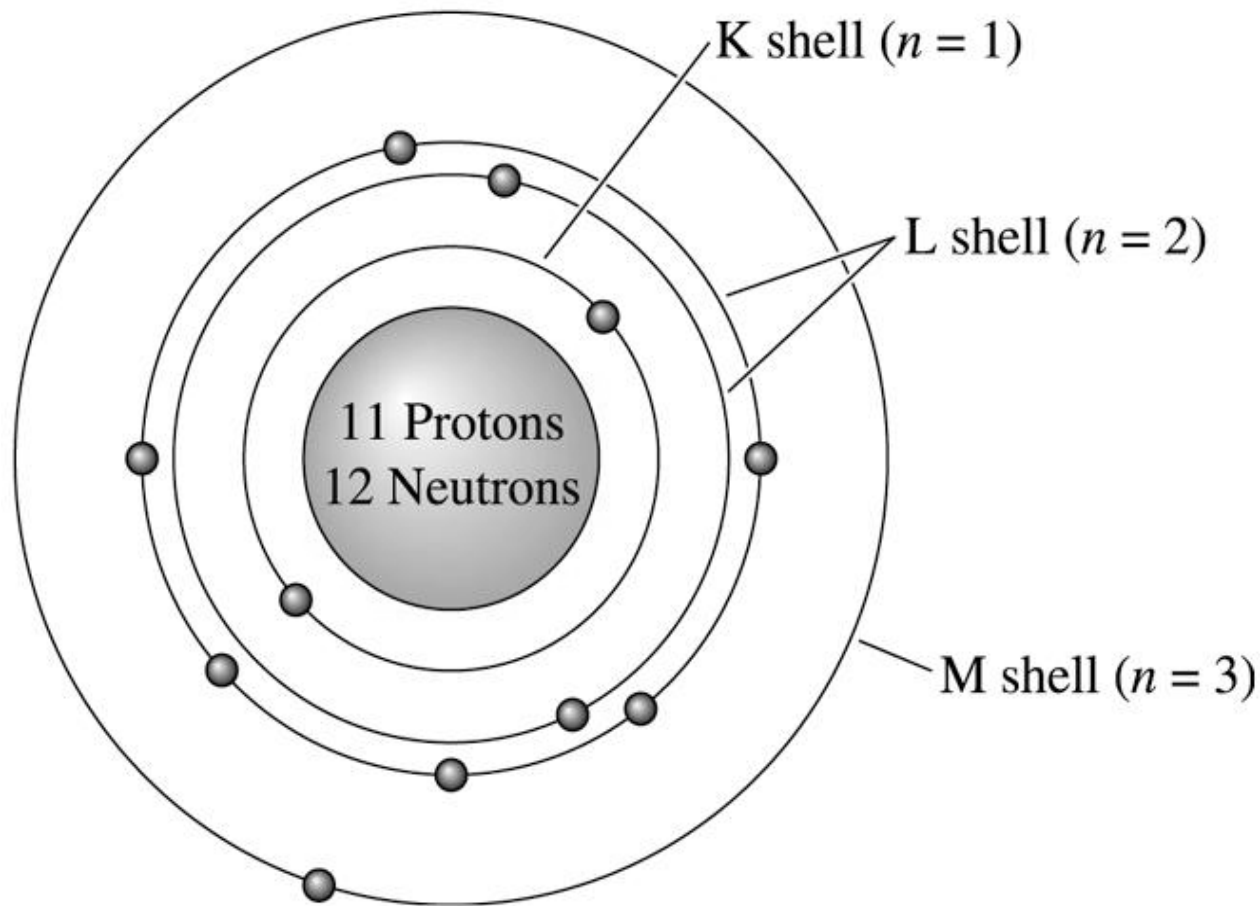n = 1, 2, 3, ...

l = 0, 1, 2, n-1

m_l = 0, 1, 2, $\pm l$

$$\hat{H}\psi_n = E_n\psi_n$$

$$E_n = -\frac{me^4}{32\pi^2\varepsilon_0^2\hbar^2}(\frac{1}{n^2})$$

$$\psi_{1,0,0} = \frac{1}{\sqrt{\pi}\,a_0^{3/2}}e^{-r/a_0}$$

n and l have special importance for orbitals, so a complementary nomenclature is used

There is one more quantum number: $m_s = \pm$ ½ called "spin up" or "spin down"

4

K shell ($n = 1$)

L shell ($n = 2$)

11 Protons
12 Neutrons

M shell ($n = 3$)

The atomic structure of sodium, atomic number 11, showing the electrons in the *K*, *L*, and *M* quantum shells

5

Pauli's exclusion principle:

if in the same system, no two electron can have the same set of quantum numbers; consequence in each of Schrödinger's orbitals, *we have a maximum of two electrons, one "spin up" the other "spin down" in each orbital*

TABLE 2-2 ■ *The pattern used to assign electrons to energy levels*

|	$l = 0$ (s)	$l = 1$ (p)	$l = 2$ (d)	$l = 3$ (f)	$l = 4$ (g)	$l = 5$ (h)
$n = 1$ (K)	2					
$n = 2$ (L)	2	6				
$n = 3$ (M)	2	6	10			
$n = 4$ (N)	2	6	10	14		
$n = 5$ (O)	2	6	10	14	18	
$n = 6$ (P)	2	6	10	14	18	22

Note: 2, 6, 10, 14, … refer to the number of electrons in the energy level.

$3s^1$ _____

electron 11 $n = 3, \; l = 0, \; m_l = 0, \quad m_s = +\frac{1}{2} \text{ or } -\frac{1}{2}$

$\begin{cases} \text{electron 10} & n = 2, \; l = 1, \; m_l = +1, \; m_s = -\frac{1}{2} \\ \text{electron 9} & n = 2, \; l = 1, \; m_l = +1, \; m_s = +\frac{1}{2} \end{cases}$

$2p^6$ _____

$\begin{cases} \text{electron 8} & n = 2, \; l = 1, \; m_l = 0, \quad m_s = -\frac{1}{2} \\ \text{electron 7} & n = 2, \; l = 1, \; m_l = 0, \quad m_s = +\frac{1}{2} \end{cases}$

$\begin{cases} \text{electron 6} & n = 2, \; l = 1, \; m_l = -1, \; m_s = -\frac{1}{2} \\ \text{electron 5} & n = 2, \; l = 1, \; m_l = -1, \; m_s = +\frac{1}{2} \end{cases}$

$2s^2$ _____

$\begin{cases} \text{electron 4} & n = 2, \; l = 0, \; m_l = 0, \quad m_s = -\frac{1}{2} \\ \text{electron 3} & n = 2, \; l = 0, \; m_l = 0, \quad m_s = +\frac{1}{2} \end{cases}$

$1s^2$ _____

$\begin{cases} \text{electron 2} & n = 1, \; l = 0, \; m_l = 0, \quad m_s = -\frac{1}{2} \\ \text{electron 1} & n = 1, \; l = 0, \; m_l = 0, \quad m_s = +\frac{1}{2} \end{cases}$

The complete set of quantum numbers for each of the 11 electrons in sodium

ELECTRON ENERGY STATES

Electrons **tend to occupy lowest available energy state**

Increasing energy →

n=4   4p   3d   4s

n=3   3p   3s

n=2   2p   2s

n=1   1s
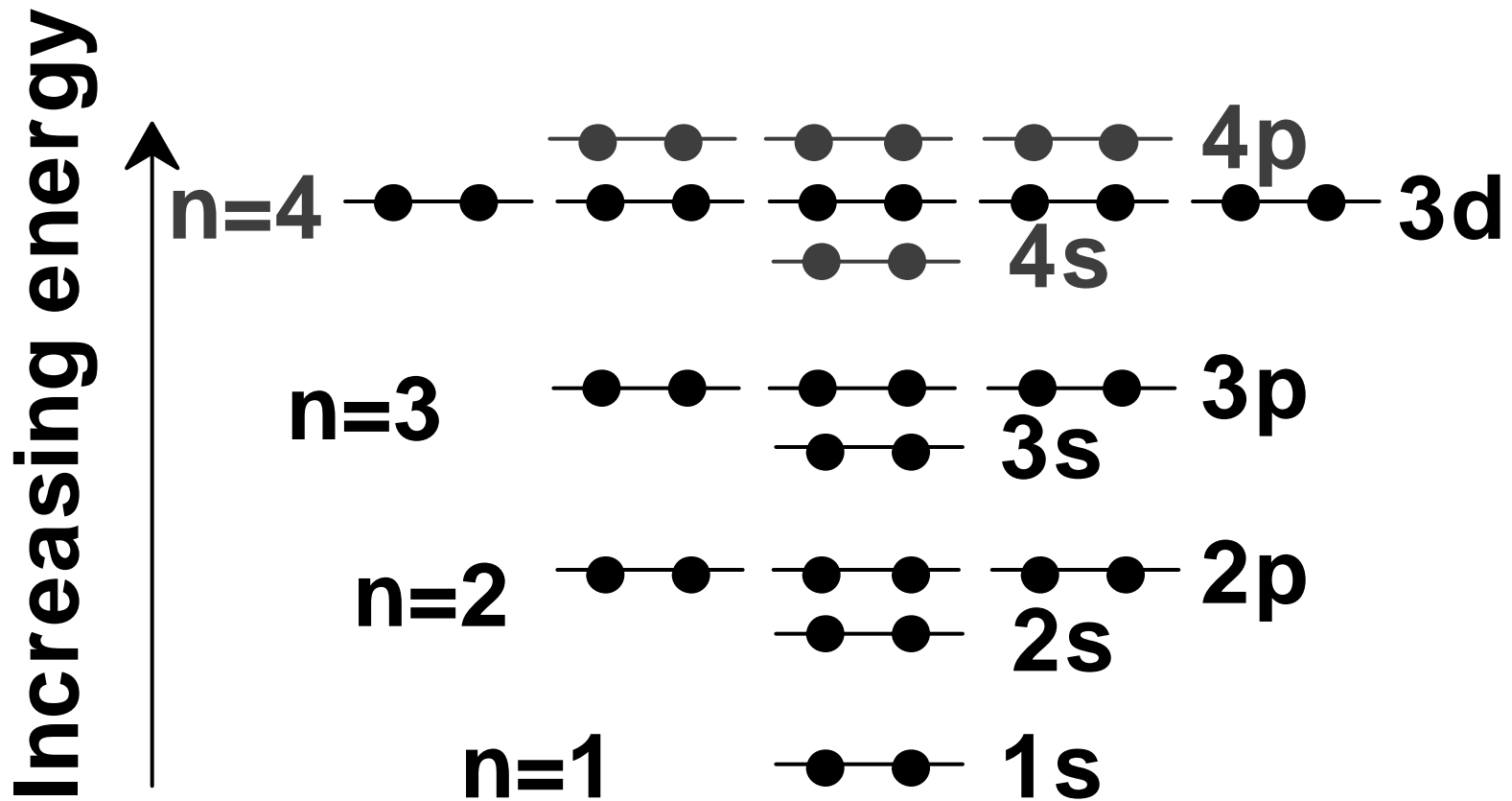
STABLE ELECTRON CONFIGURATIONS

- **have complete s and p subshells**
- **tend to be unreactive, inert gasses**

Z	Element	Configuration
2	He	$1s^2$
10	Ne	$1s^2 2s^2 2p^6$
18	Ar	$1s^2 2s^2 2p^6 3s^2 3p^6$
36	Kr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$

SURVEY OF ELEMENTS

- **Most elements: Electron configuration not stable.**

Element	Atomic #	Electron configuration	
Hydrogen	1	$1s^1$	
Helium	2	$1s^2$	(stable)
Lithium	3	$1s^2 2s^1$	
Beryllium	4	$1s^2 2s^2$	
Boron	5	$1s^2 2s^2 2p^1$	
Carbon	6	$1s^2 2s^2 2p^2$	
...		...	
Neon	10	$1s^2 2s^2 2p^6$	(stable)
Sodium	11	$1s^2 2s^2 2p^6 3s^1$	
Magnesium	12	$1s^2 2s^2 2p^6 3s^2$	
Aluminum	13	$1s^2 2s^2 2p^6 3s^2 3p^1$	
...		...	
Argon	18	$1s^2 2s^2 2p^6 3s^2 3p^6$	(stable)
...	...	...	
Krypton	36	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4^6$	(stable)

- **Why? Valence (outer) shell usually not filled completely.**

THE PERIODIC TABLE

- **Columns: Similar Valence Structure**

give up 1e

give up 2e

give up 3e

accept 1e

inert gases

| Metal |
| Nonmetal |
| Intermediate |

Key
29 → Atomic number
Cu → Symbol
63.54 → Atomic weight

Electropositive elements:
Readily give up electrons
to become + ions.

Electronegative elements:
Readily acquire electrons
to become - ions.

11

Comments Periodic Table

- ☐ III-V semiconductor is a semiconductor that is based on group IIIA and VA elements (e.g. GaAs).
- ☐ II-VI semiconductor is a semiconductor that is based on group IIB and VIA elements (e.g. CdSe).
- ☐ Transition elements are the elements whose electronic configurations are such that their inner "d" and "f" levels begin to fill up.
- ☐ Electropositive element is an element whose atoms want to participate in chemical interactions by donating electrons and are therefore highly reactive.
- ☐ Electronegative element is an element whose atoms want to participate in chemical interactions by accepting electrons and are therefore also highly reactive.

Electronegativity: relative measure of ability of an atom to attract electrons to form an anion, in HCl Cl is more electronegative than H and, therefore, attracts the electron more
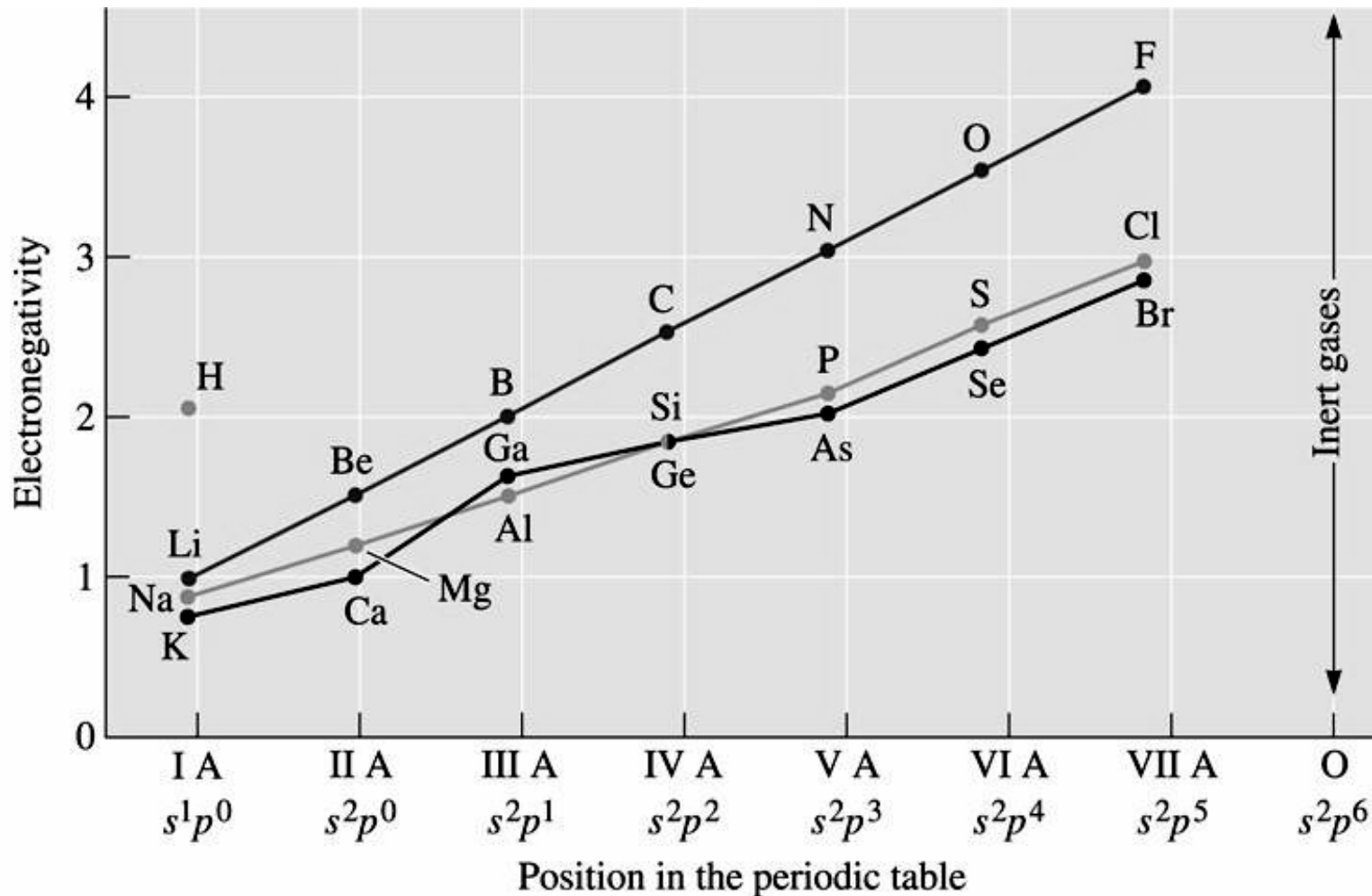
ELECTRONEGATIVITY

- **Ranges from 0.7 to 4.0,**
  - **Large values: tendency to acquire electrons.**

IA																	O
H **2.1**	IIA											IIIA	IVA	VA	VIA	VIIA	**He** **-**
Li **1.0**	**Be** **1.5**											5 B 2.0	6 C 2.5	7 N 3.0	8 O 3.5	**F** **4.0**	**Ne** **-**
Na **0.9**	**Mg** **1.2**	IIIB	IVB	VB	VIB	VIIB		VIII		IB	IIB	13 Al 1.5	14 Si 1.8	15 P 2.1	16 S 2.5	**Cl** **3.0**	**Ar** **-**
K **0.8**	**Ca** **1.0**	21 Sc 1.3	**Ti** **1.5**	23 V 1.6	**Cr** **1.6**	25 Mn 1.5	**Fe** **1.8**	27 Co 1.8	**Ni** **1.8**	29 Cu 1.9	**Zn** **1.8**	31 Ga 1.6	32 Ge 1.8	**As** **2.0**	34 Se 2.4	**Br** **2.8**	**Kr** **-**
Rb **0.8**	**Sr** **1.0**	39 Y 1.2	40 Zr 1.4	41 Nb 1.6	42 Mo 1.8	43 Tc 1.9	44 Ru 2.2	45 Rh 2.2	46 Pd 2.2	47 Ag 1.9	48 Cd 1.7	49 In 1.7	50 Sn 1.8	51 Sb 1.9	52 Te 2.1	**I** **2.5**	**Xe** **-**
Cs **0.7**	**Ba** **0.9**	57-71 La-Lu 1.1-1.2	72 Hf 1.3	73 Ta 1.5	74 W 1.7	75 Re 1.9	76 Os 2.2	77 Ir 2.2	78 Pt 2.2	79 Au 2.4	80 Hg 1.9	81 Tl 1.8	82 Pb 1.8	83 Bi 1.9	84 Po 2.0	**At** **2.2**	**Rn** **-**
Fr **0.7**	**Ra** **0.9**	89-102 Ac-No 1.1-1.7															

← **Smaller electronegativity**   **Larger electronegativity** →

13

The electronegativities of selected elements relative to the position of the elements in the periodic table

14

Atomic Bonding

4 basic types: Metallic bond, Covalent bond, Ionic bond, van der Waals bond

first 3 are primary bonds $^{eV}/_{atom}$, real compounds frequently have a mixture of these basic types

Secondary bonds/Van der Waals bonds: < 0.1 $^{eV}/_{atom}$, due to dipol-dipol interactions between atoms or molecules

Several physical properties can be explained on the basis of atomic bonds. As covalent bonds are highly directional, we will have large anisotropy for such crystals

e.g. Ductility refers to the ability of materials to be stretched or bent without breaking, we have it mainly for metals because metal bonds are both non-directional and non-polar

Coordination of atoms, nearest neighbors, next nearest neighbors determine many physical properties as well

Coordination of atoms, molecules, nearest neighbors

Atoms or ions are modeled as hard spheres that cannot penetrate each other, two (or many) of them come together to form a molecule (or crystal)

Geometry of 3D atomic arrangement then determines the number of nearest neighbors, **coordination number**

For different kinds of bonds and different compounds and crystals, we have different bond lengths. This is accounted for by sets of different radii of hard spheres that represent ionic, covalent and metallic bonds.

A **primary bond crystal**, however large, may be considered to be one large molecule,

H ○ 0.046 He ● 0.05

H⁻
0.208

Li
0.157

Be
0.113

Li⁺
0.060

Be²⁺
0.031

B 0.097 C 0.077 N 0.071 O 0.060 F 0.071 Ne 0.160

O²⁻ 0.140 F⁻ 0.136

Na
0.192

Mg
0.160

Na⁺
0.095

Mg²⁺
0.065

Al 0.143 Si 0.117 P 0.110 S 0.104 Cl 0.099 Ar 0.192

S²⁻ 0.184 Cl⁻ 0.181

K
0.238

Ca
0.197

Sc
0.160

K⁺
0.133

Ca²⁺
0.099

Ti 0.147 V 0.136 Cr 0.128 Mn 0.118 Fe 0.124 Co 0.125 Ni 0.125 Cu 0.128 Zn 0.137 Ga 0.135 Ge 0.139 As 0.125 Se 0.116 Br 0.119 Kr 0.197

Se²⁻ 0.198 Br⁻ 0.195

Rb
0.251

Sr
0.215

Y
0.181

Rb⁺
0.148

Sr²⁺
0.113

Zr 0.160 Nb 0.147 Mo 0.140 Tc 0.127 Ru 0.125 Rh 0.134 Pd 0.137 Ag 0.144 Cd 0.148 In 0.144 Sn 0.158 Sb 0.138 Te 0.143 I 0.136 Xe 0.218

Te²⁻ 0.221 I⁻ 0.216

Cs
0.270

Ba
0.217

Lu
0.173

Cs⁺
0.169

Ba²⁺
0.135

Hf 0.144 Ta 0.143 W 0.141 Re 0.138 Os 0.135 Ir 0.135 Pt 0.139 Au 0.144 Hg 0.155 Tl 0.171 Pb 0.175 Bi 0.182

Po At Rn

FIGURE 2.6 Relative sizes of some atoms and ions. Values are given in nanometers for the radii of the atoms and ions. Metallic radii are given for atoms where applicable. (*Adapted from F. M. Miller, "Chemistry: Structure and Dynamics," McGraw-Hill, 1984, p. 176.*)

Ratio of radii = 1   Ratio of radii = 0.75
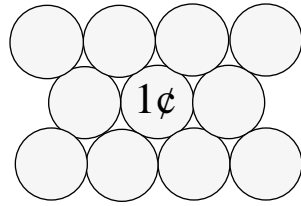
Nearest neighbors = 6   Nearest neighbors = 4
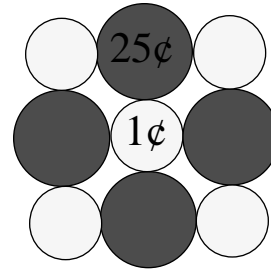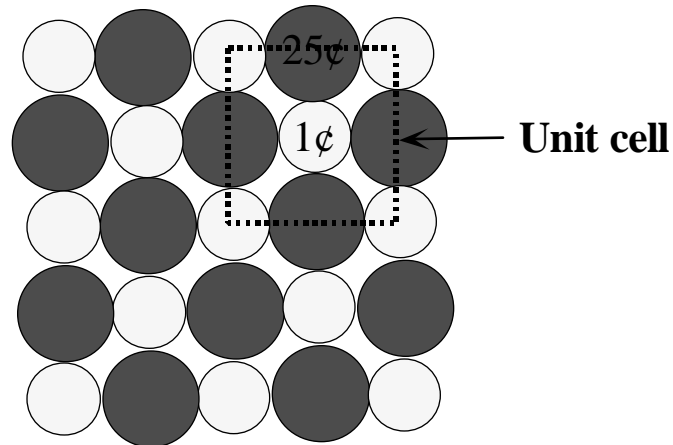
A two-dimensional crystal of pennies and quarters

Fig. 1.35: Packing of coins on a table top to build a two dimensional crystal.

$R = 1.0$
$r = 0.2$

CN = 1 possible   CN = 2 possible   CN = 3 maximum   CN = 4 unstable
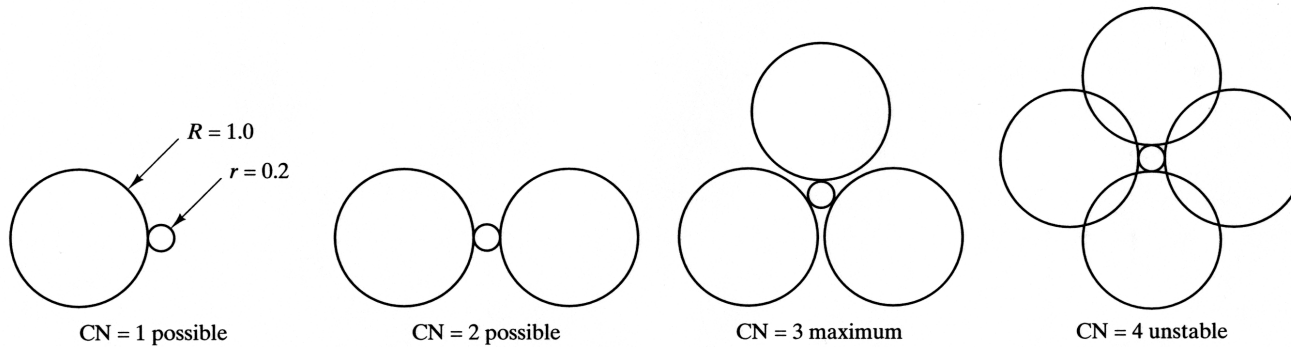
Figure 2-11   *The largest number of ions of radius R that can coordinate an atom of radius r is 3 when the radius ratio, r/R = 0.2. (Note: The instability for CN = 4 can be reduced but* not *eliminated by allowing a three-dimensional, rather than a coplanar, stacking of the larger ions.)*

$$\cos 30° = 0.866 = \frac{R}{r+R} \rightarrow \frac{r}{R} = 0.155$$

$30°$
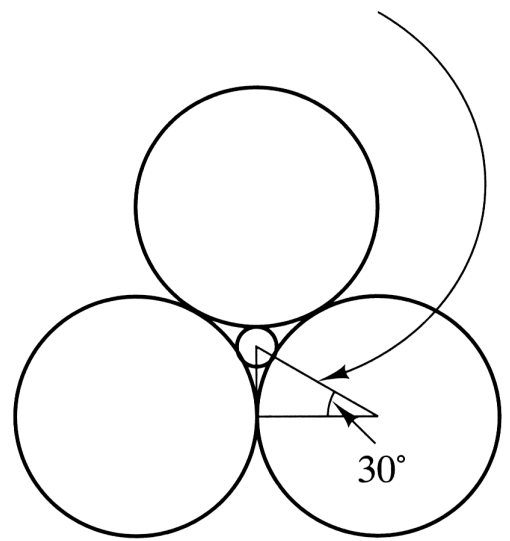
Figure 2-12   *The minimum radius ratio, r/R, that can produce threefold coordination is 0.155.*

Coordination number	Critical (r/R) value	(r/R) Stability range	Geometry
2	0	$0 < r/R < 0.155$	Always possible
3	0.155	$0.155 \leq r/R < 0.225$	
4	0.225	$0.225 \leq r/R < 0.414$	
6	0.414	$0.414 \leq r/R < 0.732$	
8	0.732	$0.732 \leq r/R < 1$	
12	1	$r/R = 1$	

19

IONIC BONDING

- **Occurs between + and - ions.**
- **Requires electron transfer.**
- **Large difference in electronegativity required.**
- **Example: NaCl**

**Na (metal)
unstable**

**Cl (nonmetal)
unstable**

electron

**Na (cation)
stable**

+

-

**Cl (anion)
stable**

**Coulombic
Attraction**
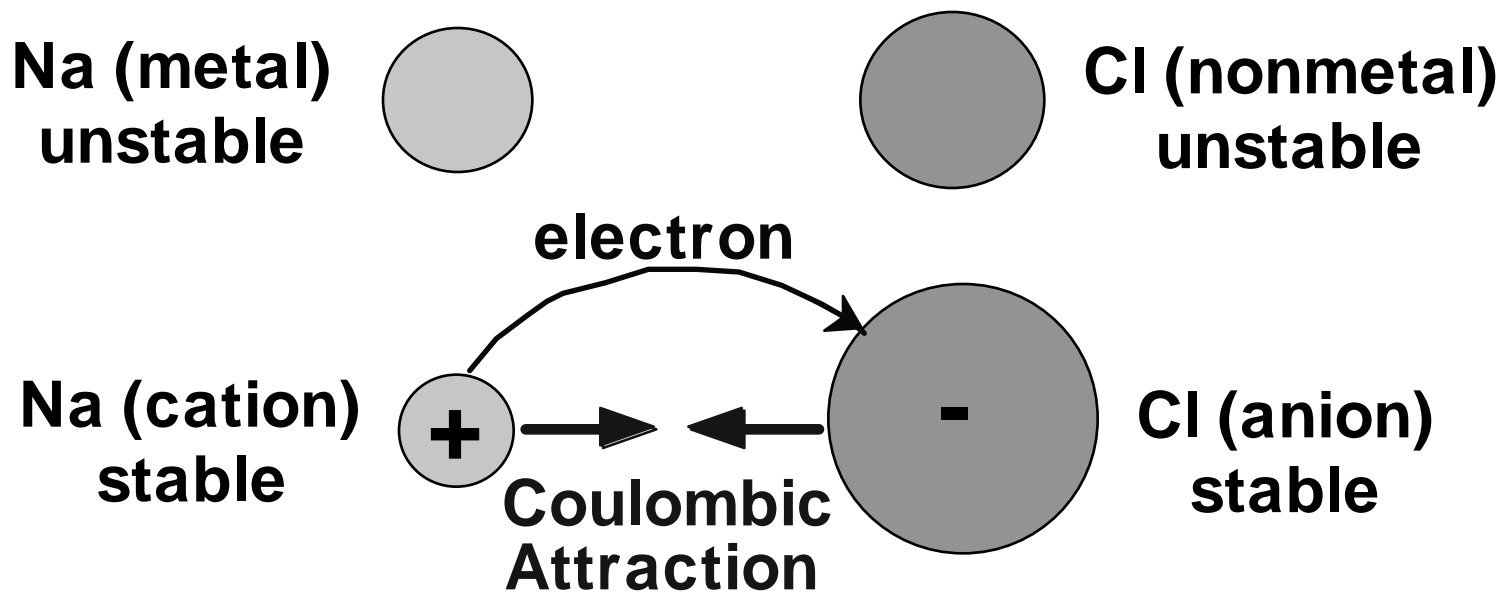
In a bit more detail, also a crystal is formed easily

Na atom   Cl atom Na^+ ion Cl^- ion
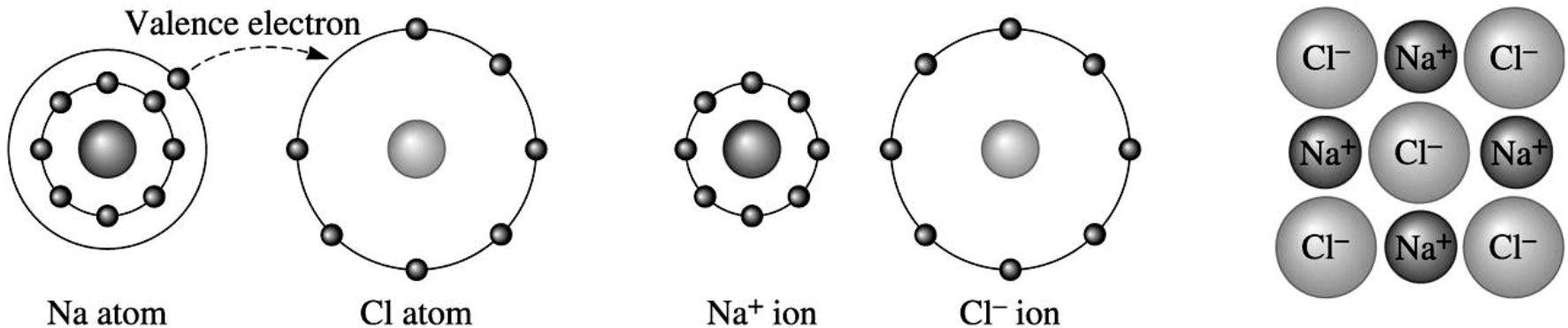
An ionic bond is created between two unlike atoms with very different electronegativities. When sodium donates its valence electron to chlorine, each becomes an ion; Coulomb attraction occurs, and the ionic bond is formed

$$\vec{F} = \frac{|Z_1 Z_2| e^2}{4 \pi e_0 r^2}$$

As bond is non directional, coordination in crystal is high, 3D arrangements are determined by geometry
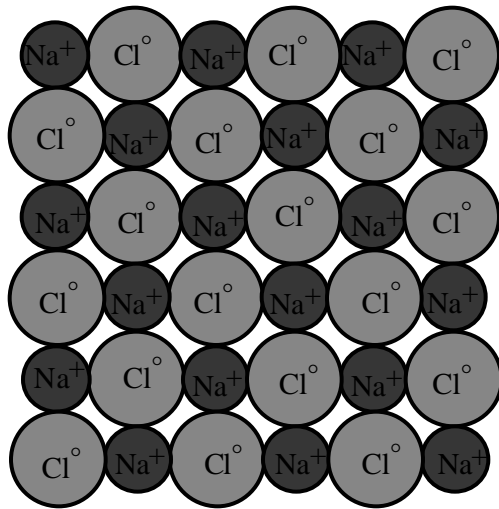
(a)
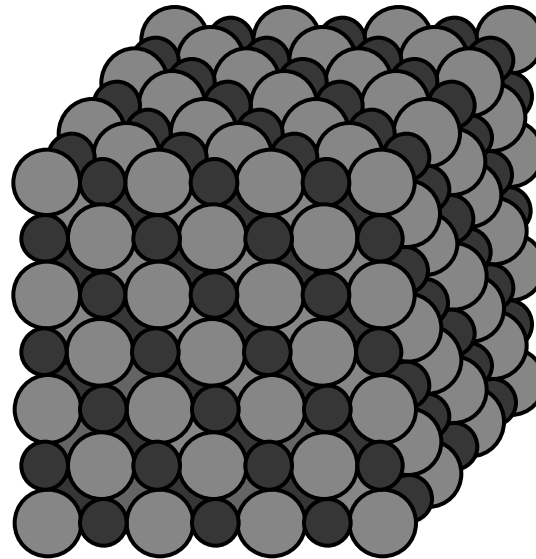
(b)

This crystal consist of Na+ and Cl- ions, not NaCl molecules, so it may be considered to be one large molecule itself

Fig. 1.9: (a) A schematic illustration of a cross section from solid NaCl. NaCl solid is made of Cl $^-$ and Na$^+$ ions arranged alternatingly so that the oppositely charged ions are closest to each other and attract each other. There are also repulsive forces between the like-ions. In equilibrium the net force acting on any ion is zero. (b) Solid NaCl.
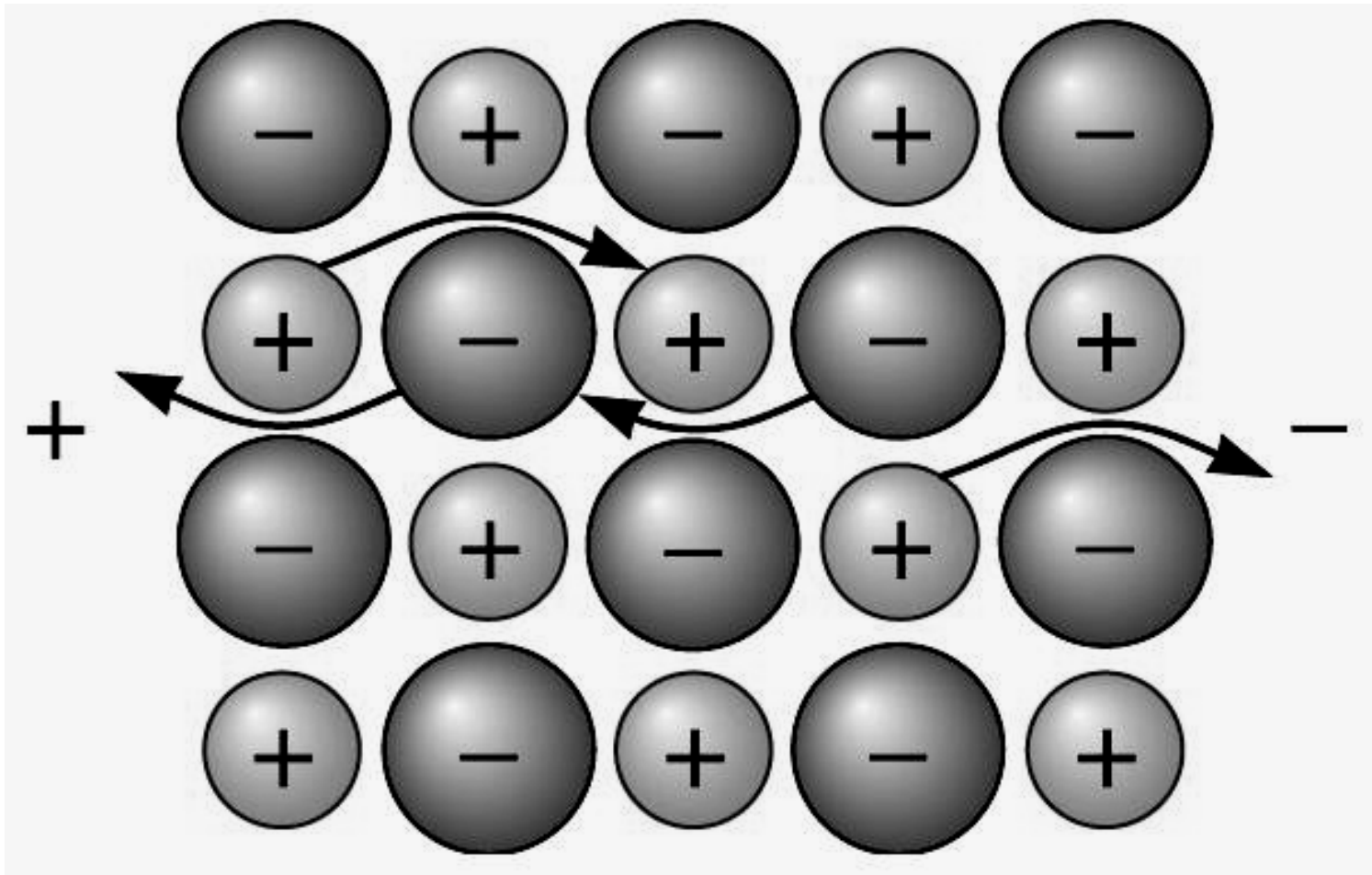
When voltage is applied to an ionic material, entire ions must move to cause a current to flow. Ion movement is slow and the electrical conductivity is, therefore, poor.

23

EXAMPLES: IONIC BONDING

- **Predominant bonding in Ceramics**

NaCl
MgO
CaF$_2$
CsCl

IA																	0
H 2.1	IIA											IIIA	IVA	VA	VIA	VIIA	He -
Li 1.0	Be 1.5											5 B 2.0	6 C 2.5	7 N 3.0	O 3.5	F 4.0	Ne -
Na 0.9	Mg 1.2	IIIB	IVB	VB	VIB	VIIB		VIII			IB	IIB	13 Al 1.5	14 Si 1.8	15 P 2.1	16 S 2.5	Cl 3.0	Ar -
K 0.8	Ca 1.0	21 Sc 1.3	Ti 1.5	23 V 1.6	Cr 1.6	25 Mn 1.5	Fe 1.8	27 Co 1.8	Ni 1.8	29 Cu 1.9	Zn 1.8	31 Ga 1.6	32 Ge 1.8	As 2.0	34 Se 2.4	Br 2.8	Kr -
Rb 0.8	Sr 1.0	39 Y 1.2	40 Zr 1.4	41 Nb 1.6	42 Mo 1.8	43 Tc 1.9	44 Ru 2.2	45 Rh 2.2	46 Pd 2.2	47 Ag 1.9	48 Cd 1.7	49 In 1.7	50 Sn 1.8	51 Sb 1.9	52 Te 2.1	I 2.5	Xe -
Cs 0.7	Ba 0.9	57-71 La-Lu 1.1-1.2	72 Hf 1.3	73 Ta 1.5	74 W 1.7	75 Re 1.9	76 Os 2.2	77 Ir 2.2	78 Pt 2.2	79 Au 2.4	80 Hg 1.9	81 Tl 1.8	82 Pb 1.9	83 Bi 1.9	84 Po 2.0	At 2.2	Rn -
Fr 0.7	Ra 0.9	89-102 Ac-No 1.1-1.7															

← Give up electrons

Acquire electrons →

COVALENT BONDING

- **Requires shared electrons**
- **Example: CH$_4$**

  **C: has 4 valence e,
       needs 4 more**

  **H: has 1 valence e,
       needs 1 more**

**Electronegativities
are comparable,
so electrons are shared.**

CH$_4$
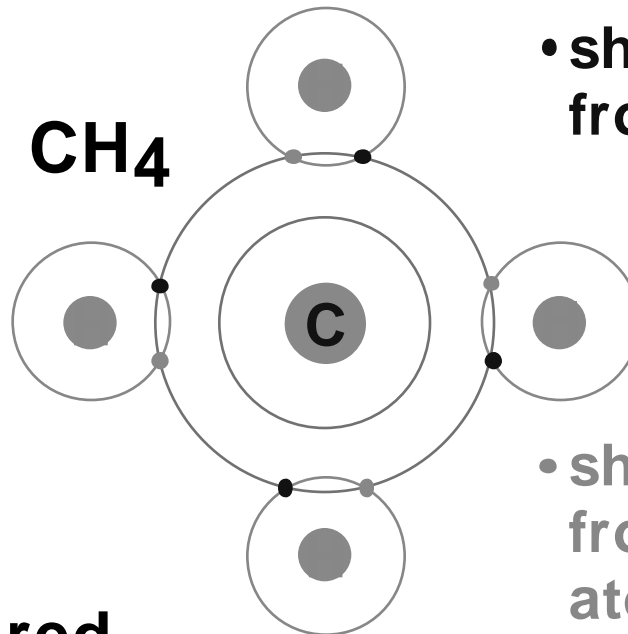
- **shared electrons
  from carbon atom**

- **shared electrons
  from hydrogen
  atoms**

Quantum mechanics prescribes directionality of
the orbitals, covalent bonds, must, therefore, be
highly directional, physical properties must be
highly anisotrope

25

Silicon atom
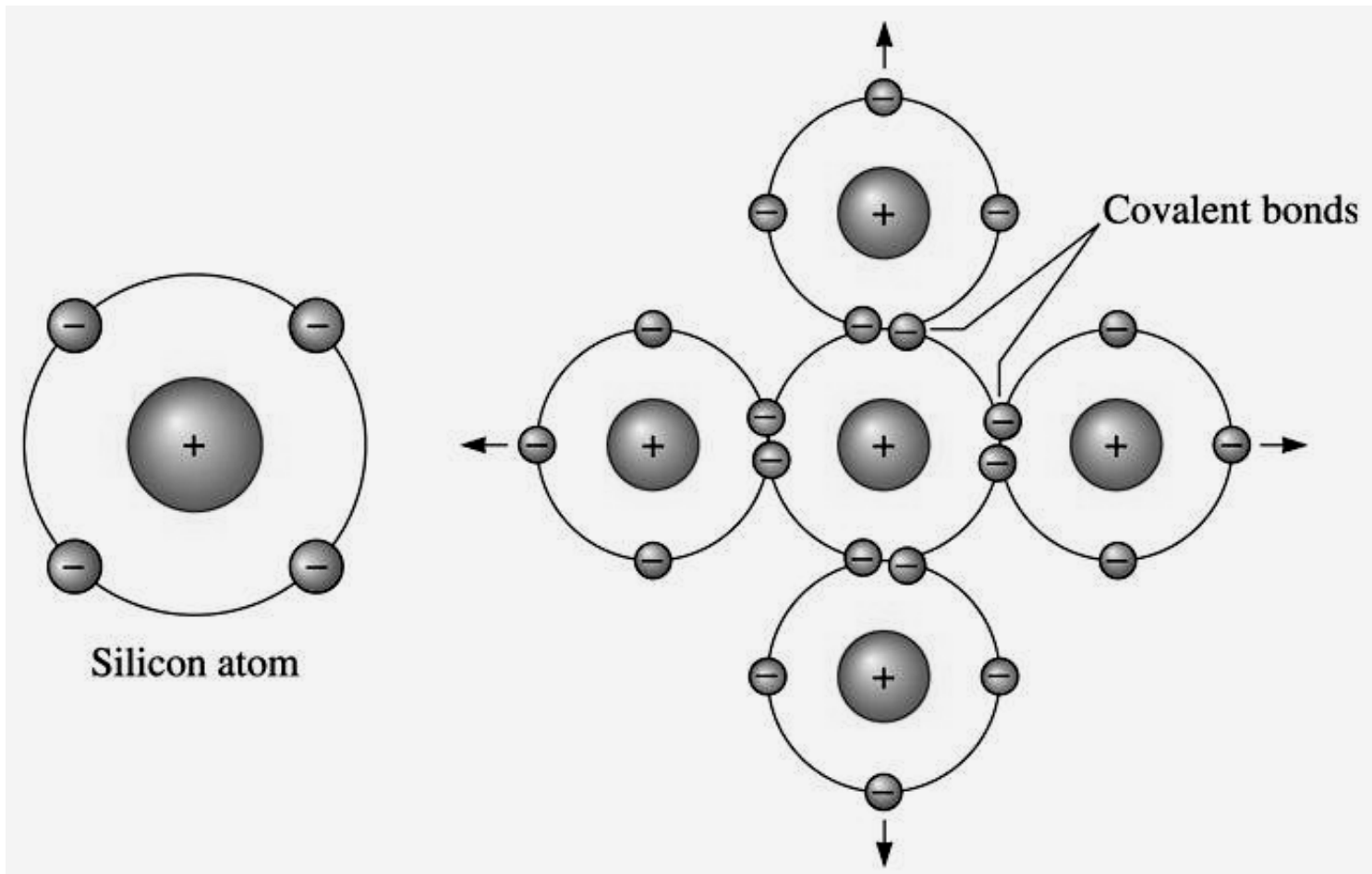
Covalent bonds

Covalent bonding requires that electrons be shared between atoms in such a way that each atom has its outer *sp* orbital filled. In silicon, with a valence of four, four covalent bonds must be formed

26

coordination in covalently bound crystals tends to be low
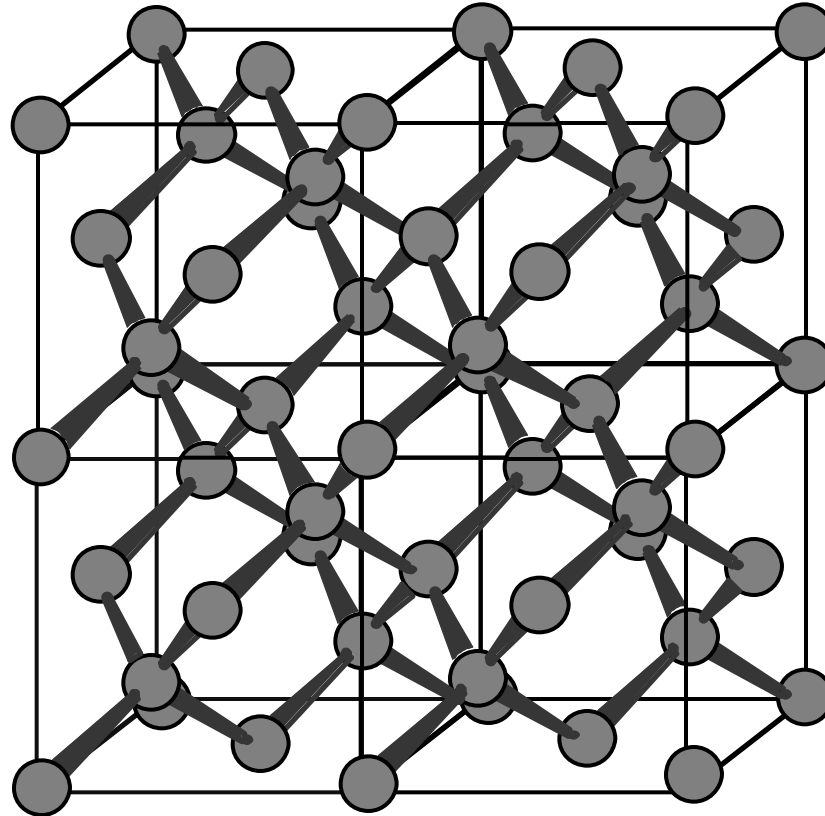
Fig. 1.6: The diamond crystal is a covalently bonded network of carbon atoms. Each carbon atom is bonded covalently to four neighbors forming a regular three dimensional pattern of atoms which constitutes the diamond crystal.

27
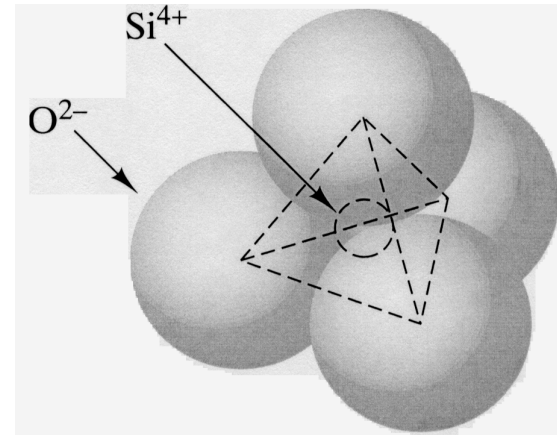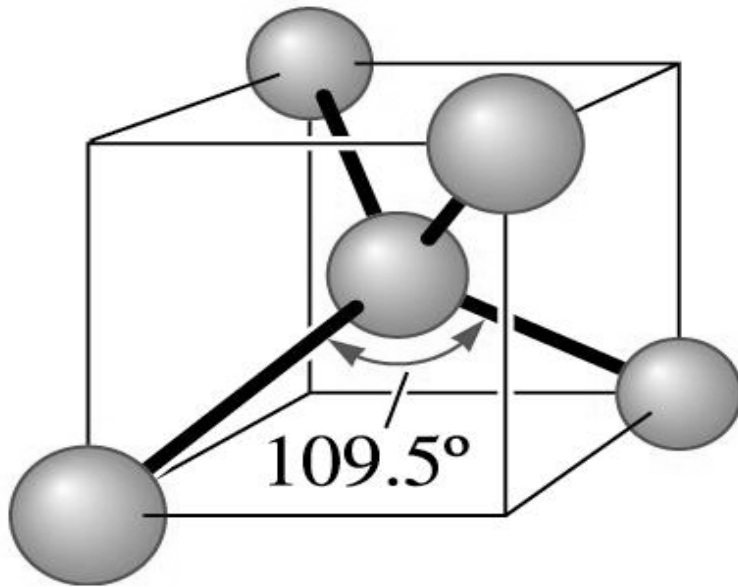
Figure 2-17 *The SiO$_4^{4-}$ tetrahedron represented as a cluster of ions. In fact, the Si—O bond exhibits both ionic and covalent character.*

Covalent bonds are directional! In crystalline silicon, perfect tetrahedra are formed, with angles of 109.5° between each covalent bond. If crystalline, we can only have a perfect tetrahedron for atoms with exactly the same electronegativity, i.e. Si atoms.

In SiO$_2$ glass, SiO$_4$ tetrahera can be "close to perfect" as long range order is missing, in fact that bond is partly ionic / partly covalent

EXAMPLES: COVALENT BONDING

H₂O · **H₂** · **C(diamond)** · **SiC** · Column IVA · **F₂** · **Cl₂** · **GaAs**

IA																	0
H 2.1	IIA											IIIA	IVA	VA	VIA	VIIA	He -
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 2.0	F 4.0	Ne -
Na 0.9	Mg 1.2	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar -
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.8	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr -
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe -
Cs 0.7	Ba 0.9	La-Lu 1.1-1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn -
Fr 0.7	Ra 0.9	Ac-No 1.1-1.7															

Molecules of nonmetals, Molecules containing metals & nonmetals,

Elemental solids (right half side of Periodic Table)

Compound solids (about column IV A), semiconductors, GaAs

29
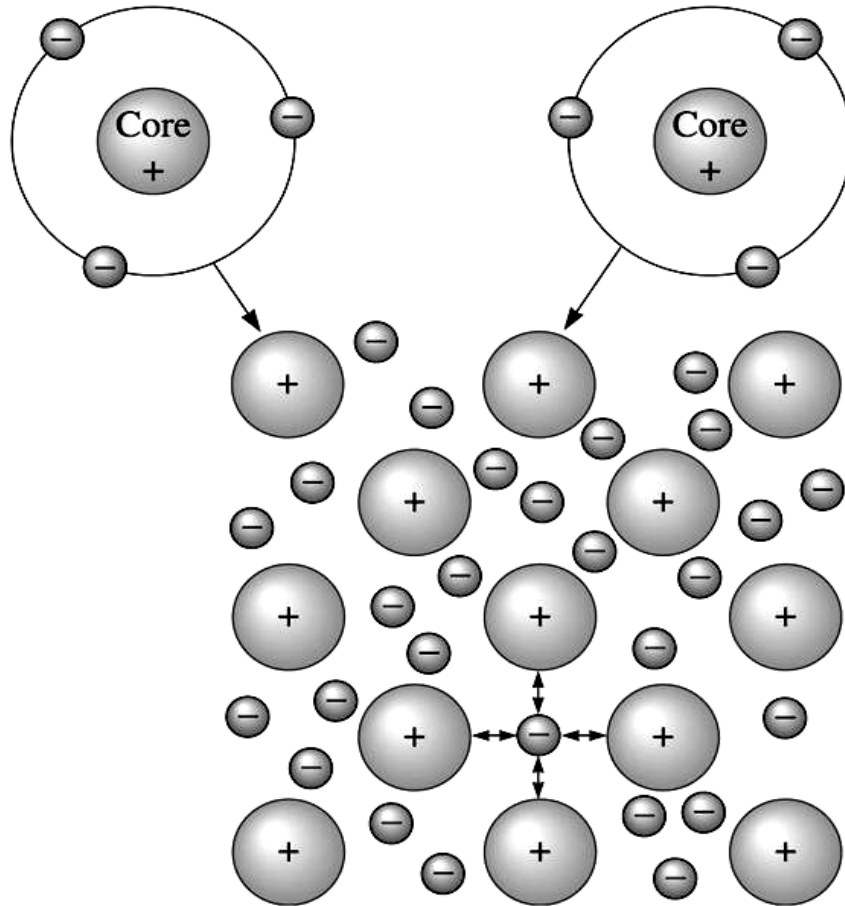
METALLIC BONDING

metallic bond forms when atoms give up their valence electrons, 1, 2 or 3 from each atom, which then form an electron sea. The positively charged atom cores are bonded by mutual attraction to the negatively charged electrons. As the bond is not polar, metals are ductile

• **Primary bond for metals and their alloys,**

there are exceptions, the intermetallics

As bond is nondirectional, coordination in a crystal is high

Positive metal ion cores

Free valence electrons forming an electron gas
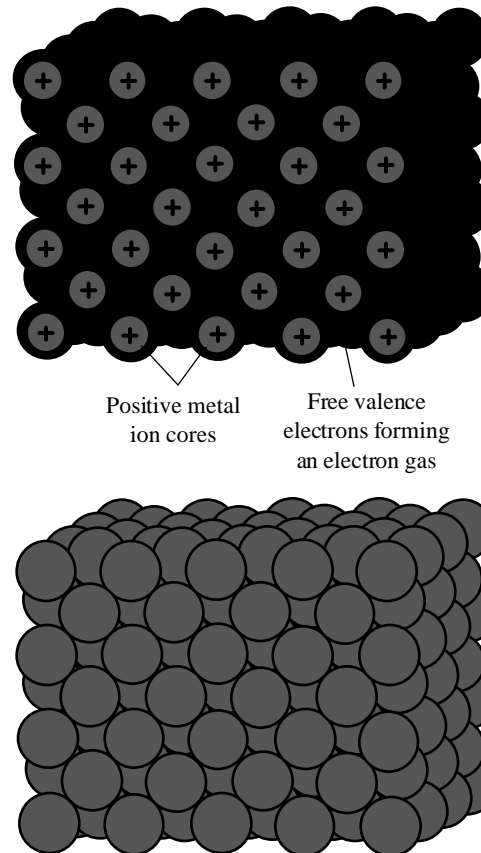
Fig. 1.7: In metallic bonding the valence electrons from the metal atoms form a "cloud of electrons" which fills the space between the metal ions and "glues" the ions together through the coulombic attraction between the electron gas and positive metal ions.
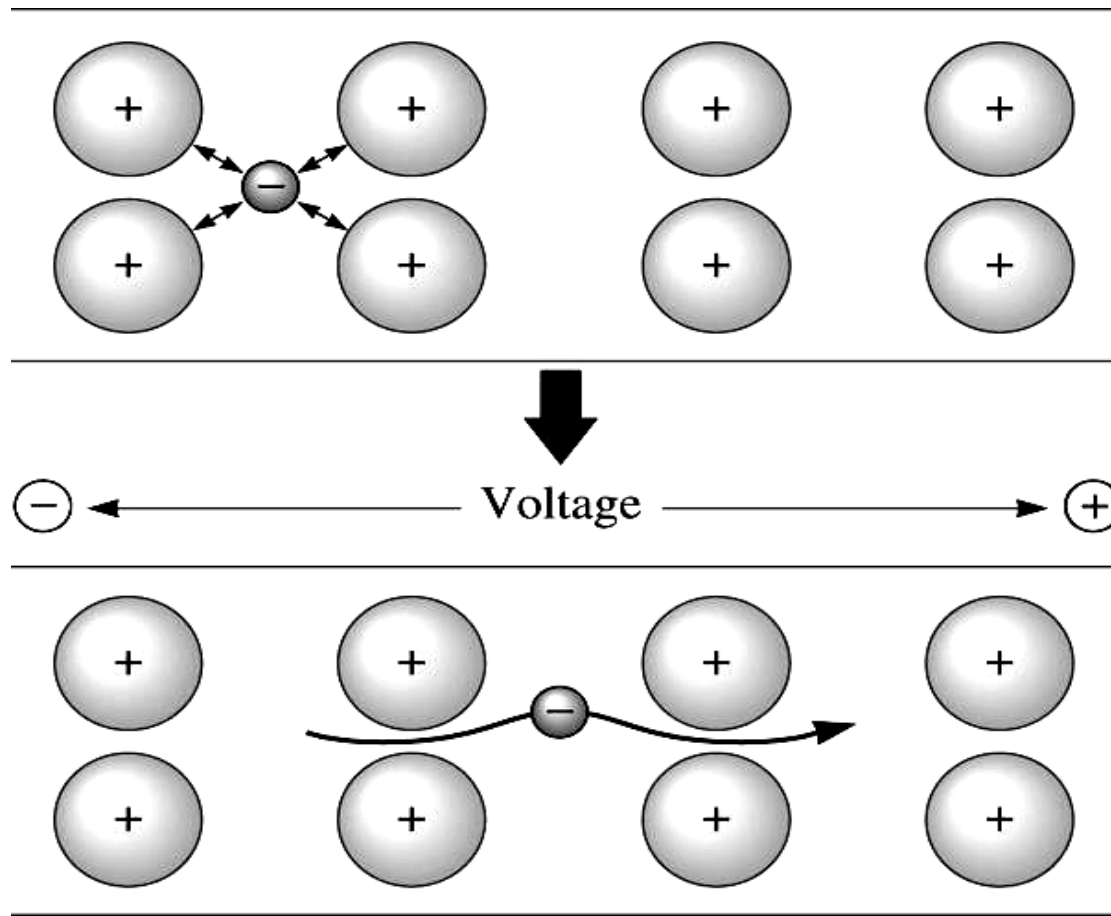
When voltage is applied to a metal, the electrons in the electron sea can easily move and carry a current, if there are different metal atoms in between, i.e. point defects, or other crystal defects, the current is impeded, so conductivity will be high but strongly depended of perfection of crystal

32

"Light blue" elements are metals, "Grey elements" are non-metals, "Dark blue" elements are kind of in between, clearly Si and Ge are non-metals, Sn is also a semiconductor below ~ 13 °C

33

SECONDARY BONDING

Arises from interaction between dipoles

- **Fluctuating dipoles**

asymmetric electron clouds

+ − secondary bonding

ex: liquid H_2

$H_2 \rightarrow \leftarrow H_2$

H H secondary bonding H H
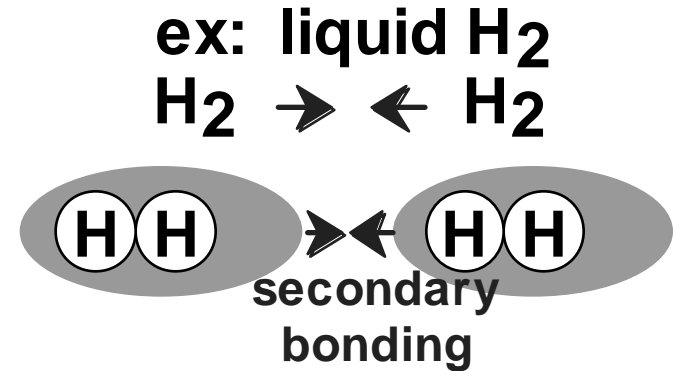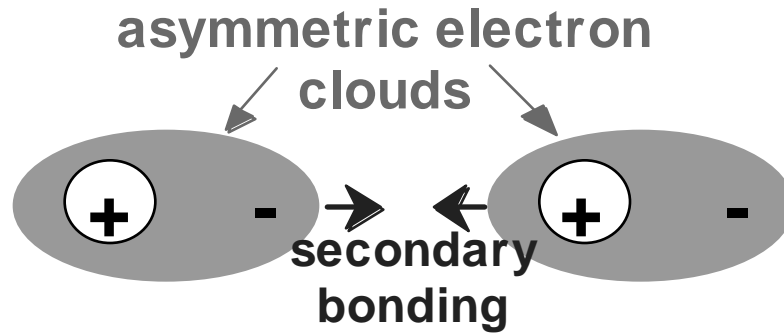
- **Permanent dipoles-molecule induced**

- general case: + − secondary bonding + −

- liquid HCl: H Cl secondary bonding H Cl

- polymer
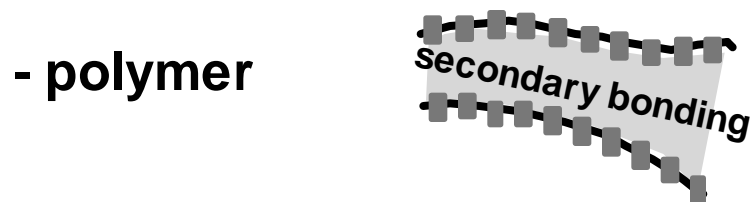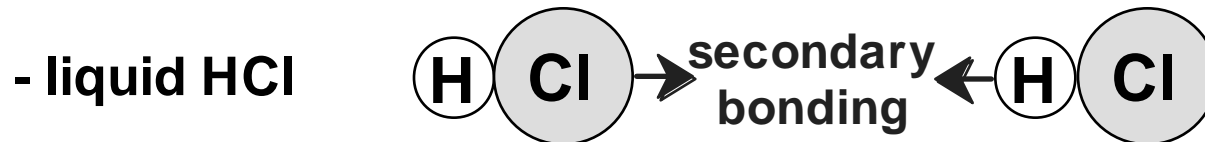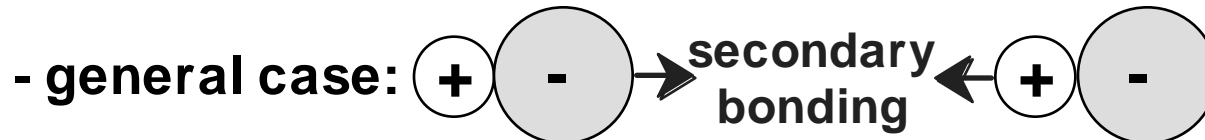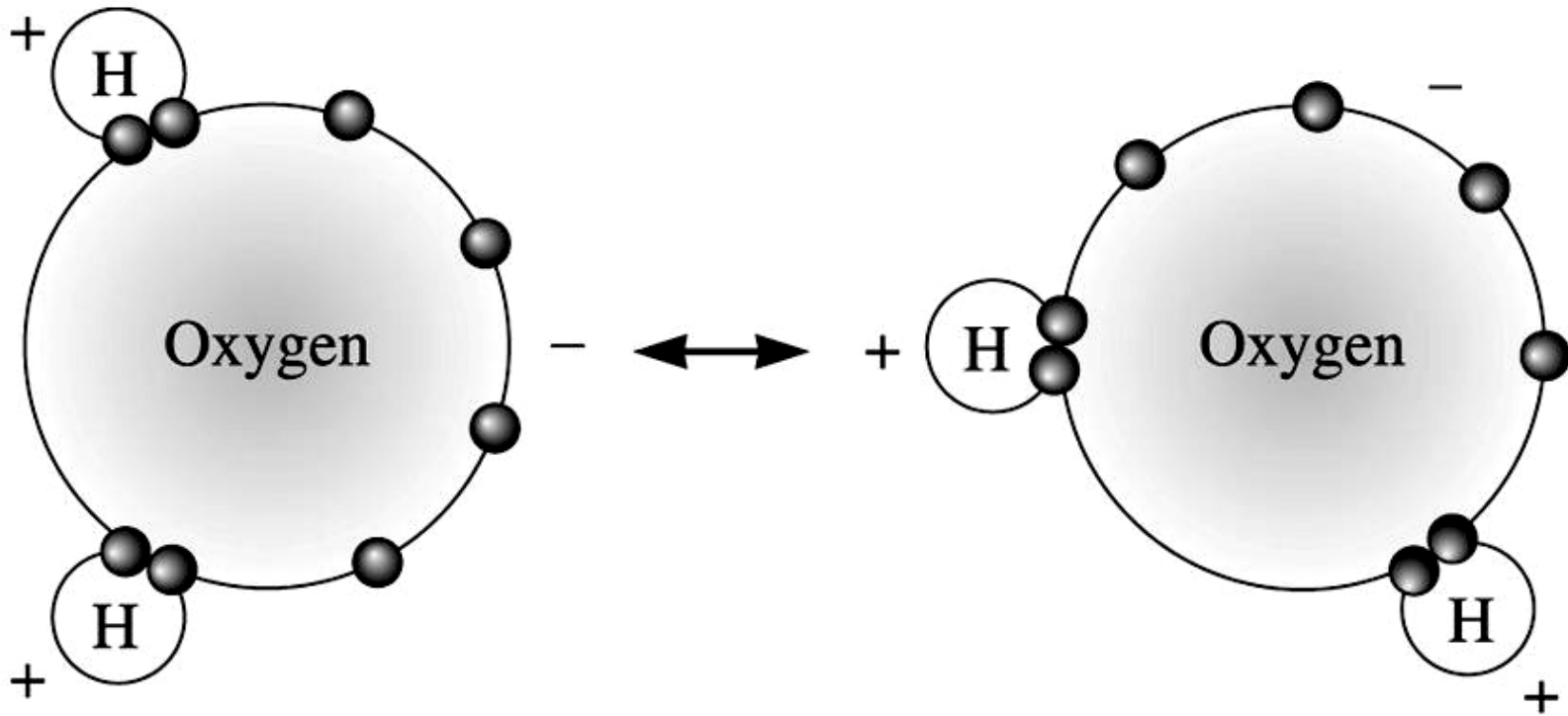
secondary bonding

Secondary bonds are formed as a result of polarization of molecules or groups of atoms. In water, electrons in the oxygen tend to concentrate away from the hydrogen. The resulting charge difference permits the molecule to be weakly bonded to other water molecules. These hydrogen bonds are crucial to many physical and chemical properties of H_2O
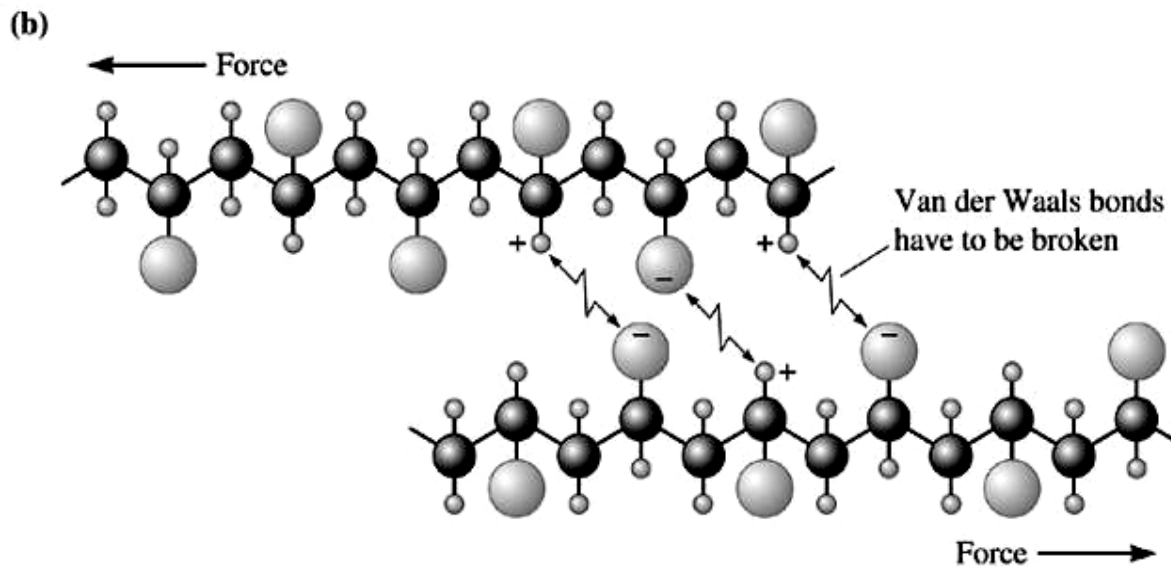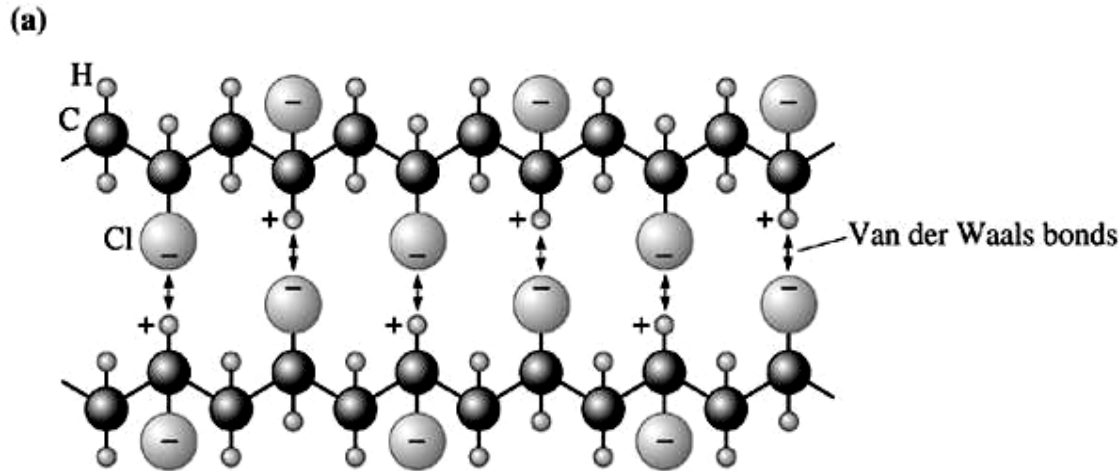
(a) **In polyvinyl chloride (PVC), the chlorine atoms attached to the polymer chain have a negative charge and the hydrogen atoms are positively charged. The chains are weakly bonded by van der Waals bonds. This additional bonding makes PVC stiffer,**

(b) **When a force is applied to the polymer, the week van der Waals bonds are broken and the chains slide easily past one another**

Binding Energy, Interatomic Spacing, & Physical Properties

☐ Interatomic spacing is equilibrium spacing between the centers of two atoms (at a particular temperature), equilibrium is lowest energy state, attractive and repulsive forces are balanced

☐ Binding (bond) energy is energy required to separate two atoms from their equilibrium spacing to an infinite distance apart, $E = mc^2$, so each time two atoms bound to each other, some mass is converted into energy, …

☐ Modulus of elasticity, Young's modulus, is slope of the stress-strain curve in elastic region (macroscopic), can be derived from slope of force versus distance curve at interatomic spacing (microscopic)

☐ Coefficient of thermal expansion and melting temperature can also be explained from binding energy curve
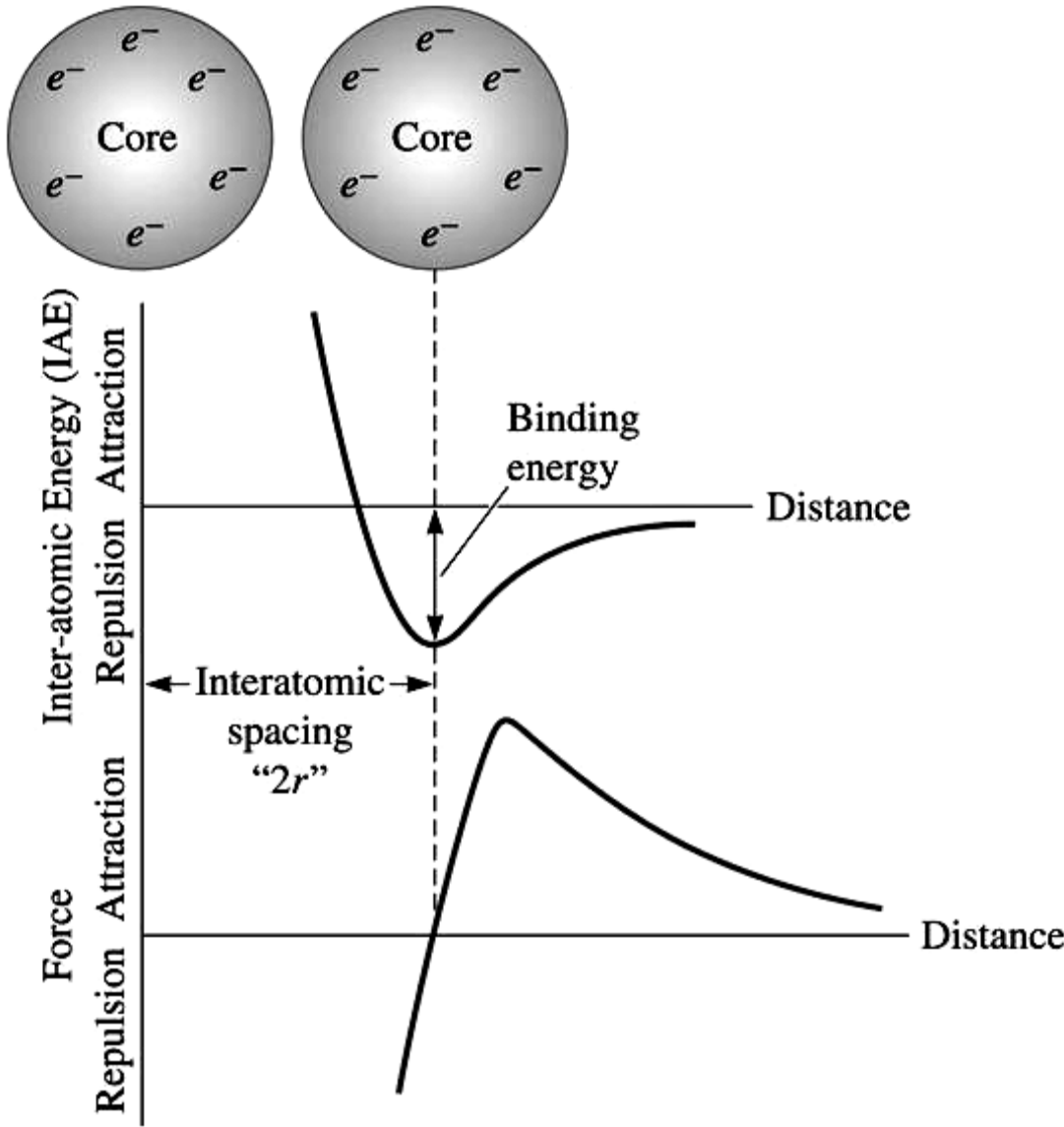
Atoms or ions are separated by equilibrium spacing that corresponds to the minimum inter-atomic energy for a pair of atoms or ions (or when zero force is acting to repel or attract the atoms or ions, force balance)

If there is external influences, e.g. load, temperature change, equilibrium spacing will change
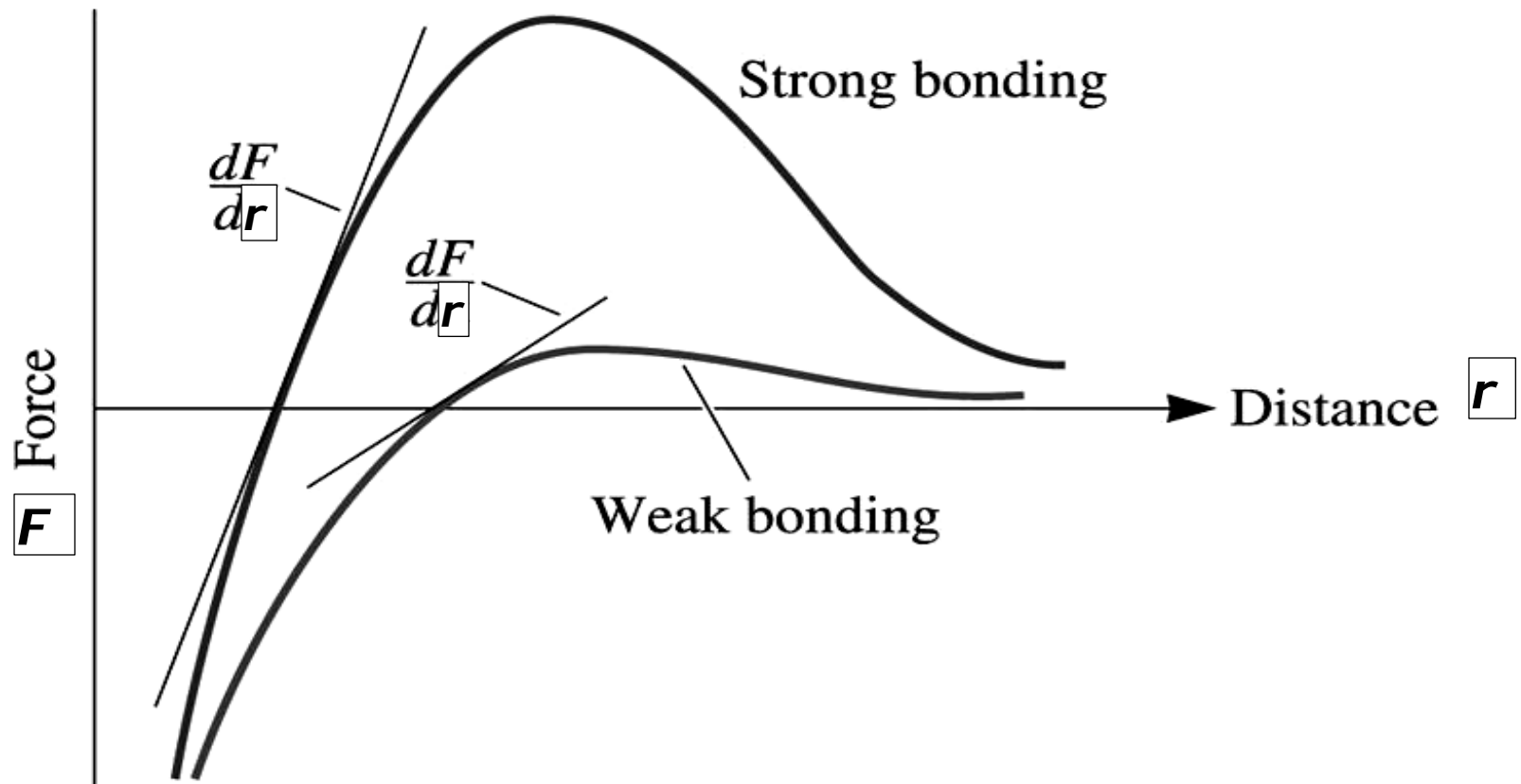
38

In more detail

$$\frac{\partial U}{\partial x} = F$$
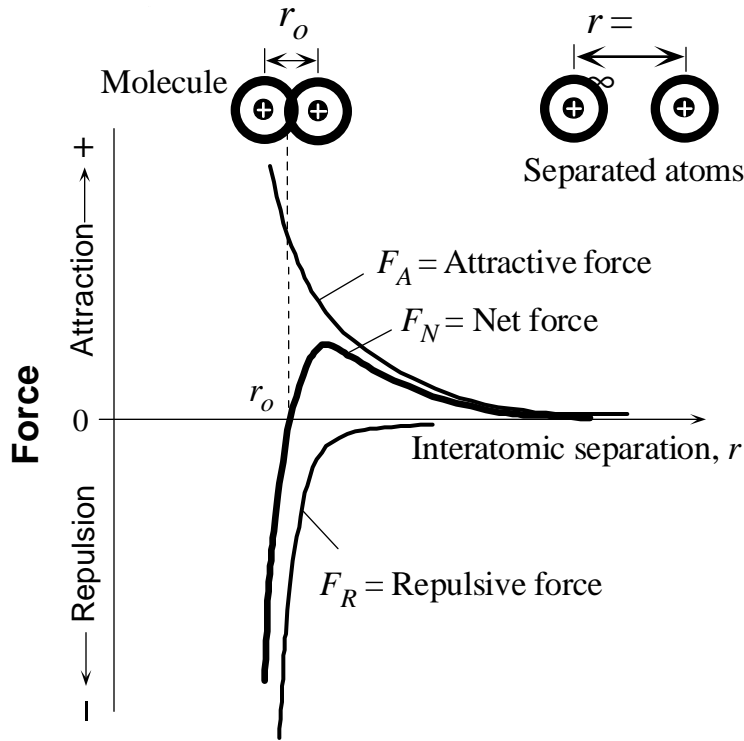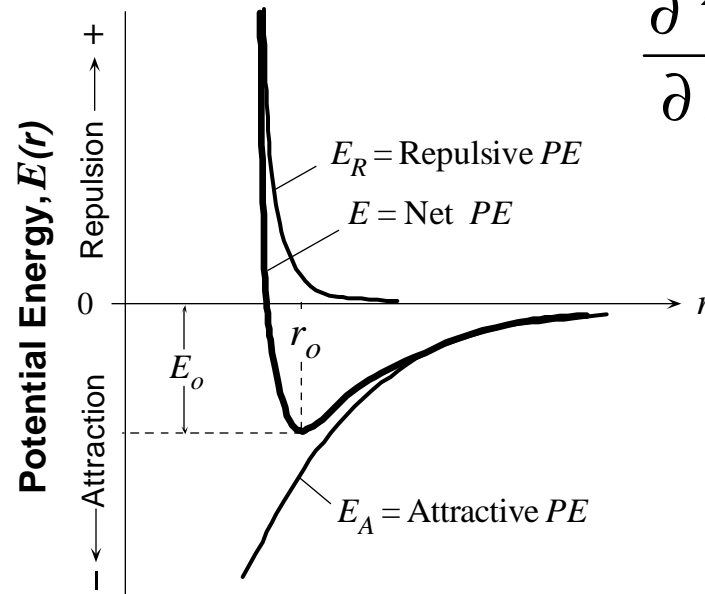
$$\frac{\partial^2 U}{\partial x^2} = \frac{\partial F}{\partial x}$$

(a) Force vs r (b) Potential energy vs r

Fig. 1.3: (a) Force vs interatomic separation and (b) Potential energy vs interatomic separation.

PROPERTIES FROM BONDING: E

force-distance curve **F=F(r)** for two materials, showing the relationship between atomic bonding and the modulus of elasticity (Young's modulus), a steep slope at equilibrium position x_0 (or r_0) gives a high modulus
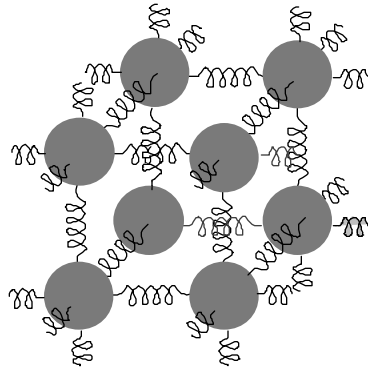
(a)

(b)

$Y \propto dF_N/dr$

dF_N

dr

r_o
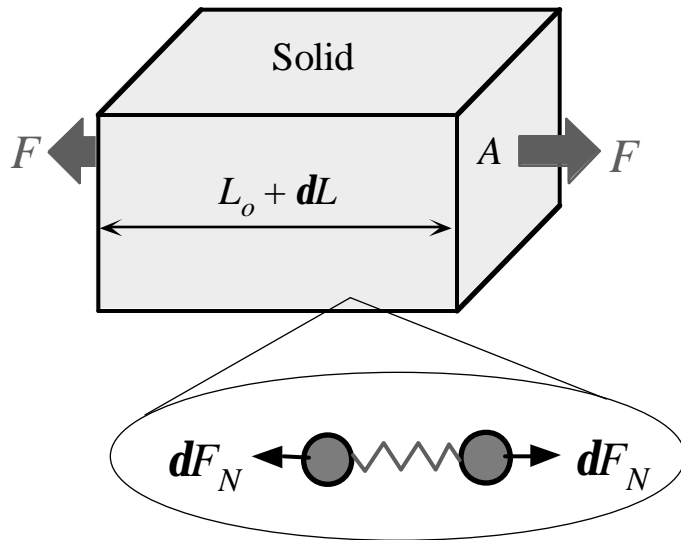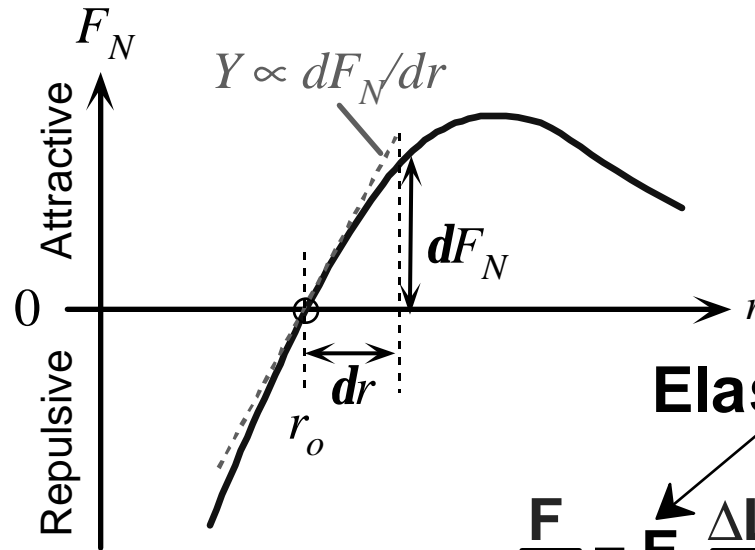
Elastic modulus

$$\frac{F}{A_o} = E\frac{\Delta L}{L_o}$$

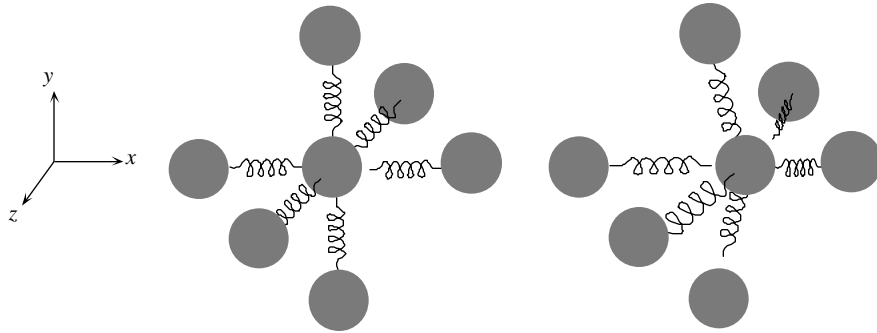Fig. 1.14: (a) Applied forces F strech the solid elastically from L_O to dL. The force is divided amongst chains of atoms that make the solid. Each chain carriers a force dF_N. (b) In equilibrium, the applied force is balanced by the net force dF_N between the atoms as a result of their increased separation.

Energy

unstretched length
r_o

smaller Elastic Modulus

larger Elastic Modulus

PROPERTIES FROM BONDING: α

(a)

length, L_O

unheated, T_1

ΔL

heated, T_2

coeff. thermal expansion

$$\frac{\Delta L}{L_O} = \alpha (T_2 - T_1)$$

(b)

Energy

r_O

r

larger α

smaller α
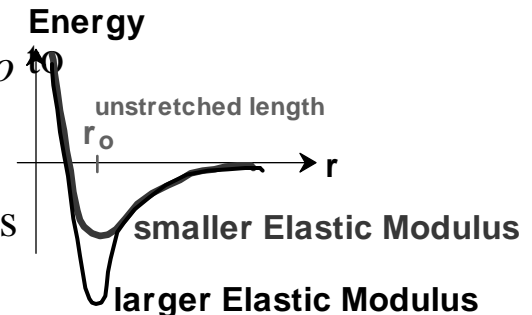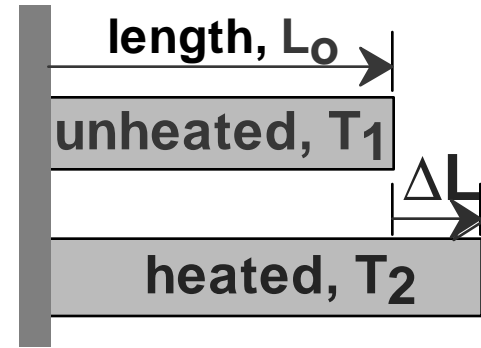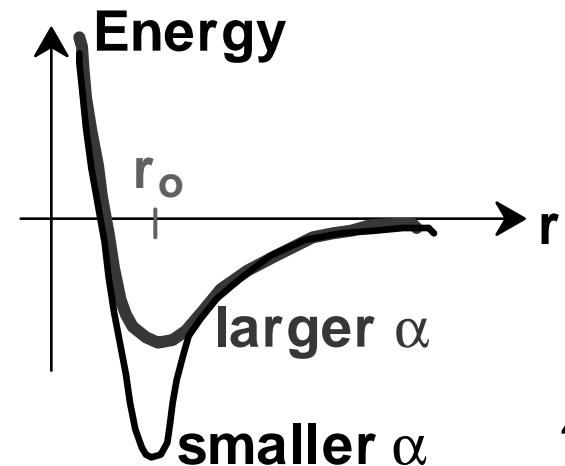
Fig. 1.17 (a) The ball-and-spring model of solids in which the springs represent the interatomic bonds. Each ball (atom) is linked to its neighbors by springs. Atomic vibrations in a solid involve 3 dimensions. (b) An atom vibrating about its equilibrium position stretches and compresses its springs to the neighbors and has both kinetic and potential energy.
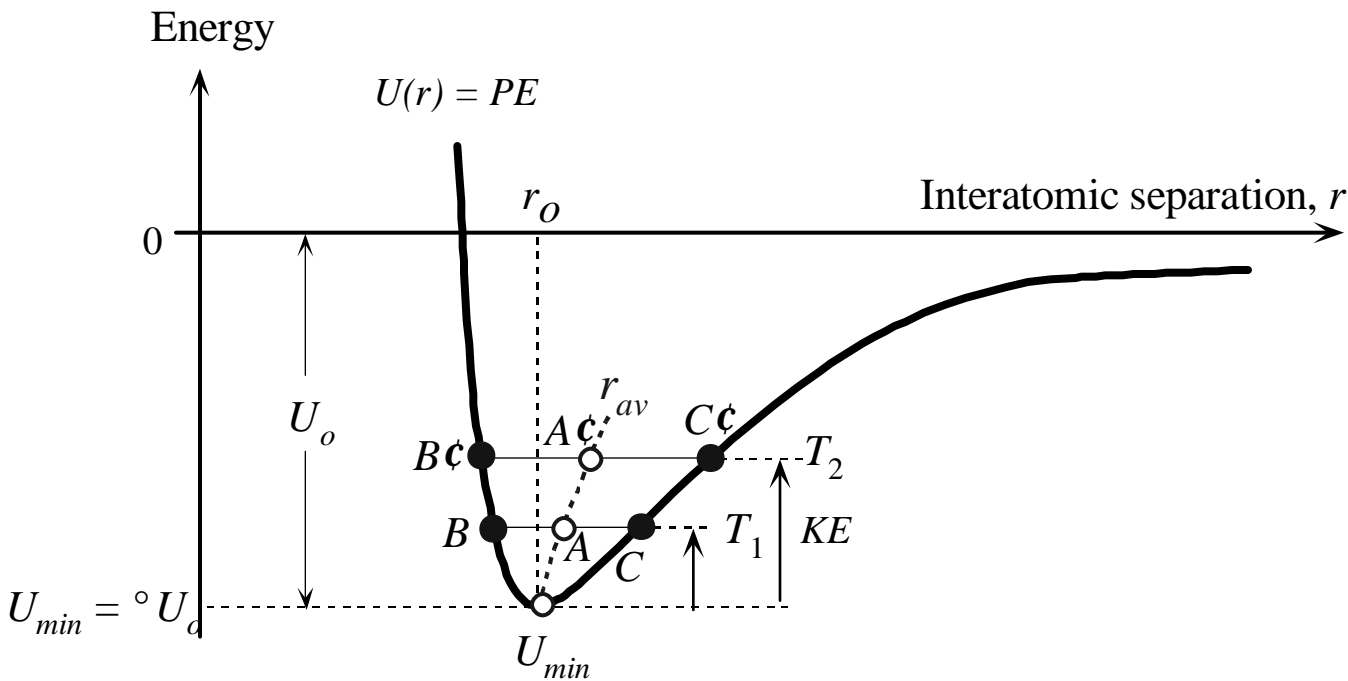
42

Fig. 1.18: The potential energy *PE* curve has a minimum when the atoms in the solid attain the interatomic separation at $r = r_O$. Due to thermal energy, the atoms will be vibrating and will have vibrational kinetic energy. At $T = T_1$, the atoms will be vibrating in such a way that the bond will be stretched and compressed by an amount corresponding to the *KE* of the atoms. A pair of atoms will be vibrating between *B* and *C*. Their average separation will be at *A* and greater than r_O.

Deeper potential energy wells, which one has for more heavily bond atoms, **tend to be more symmetric, coefficient of thermal expansion is, therefore, smaller** as equilibrium position does not change so much with temperature

WARNING: only over a limited temperature range will there be linear relationship
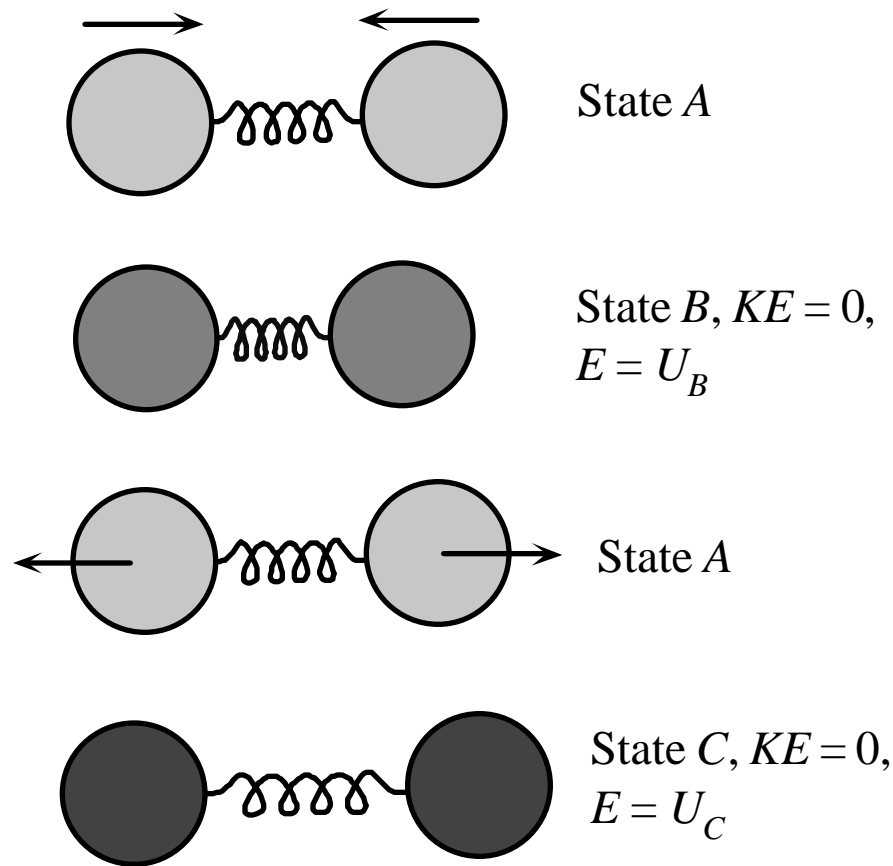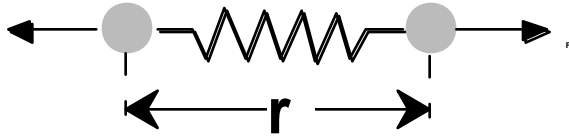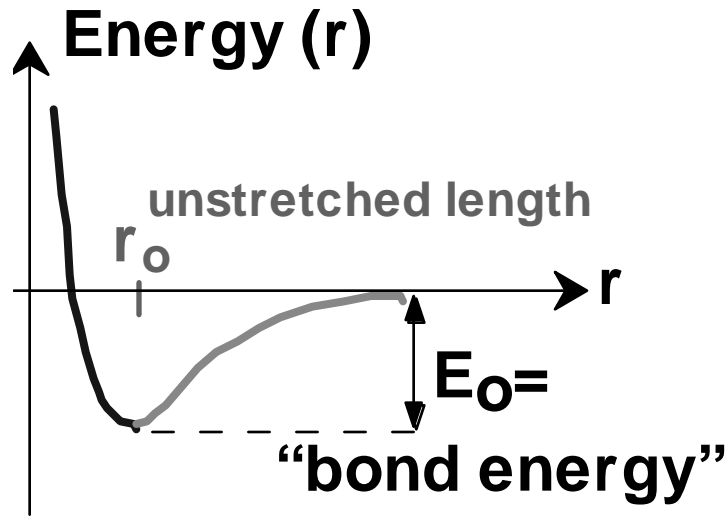
$$\frac{\Delta x}{x_0} = a(T - T_0)$$

43

Fig. 1.19: Vibrations of atoms in the solid. We consider, for simplicity a pair of atoms. Total energy is $E = PE + KE$ and this is constant for a pair of vibrating atoms executing simple harmonic motion. At B and C, KE is zero (atoms are stationary and about to reverse direction of oscillation) and PE is maximum.
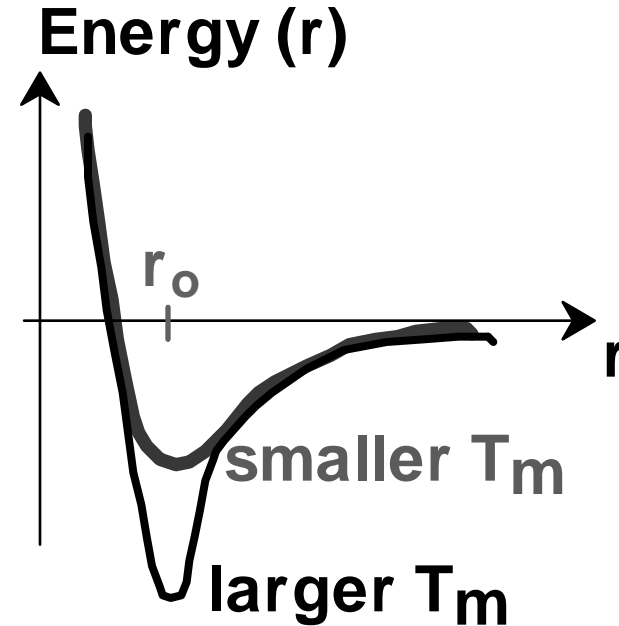
PROPERTIES FROM BONDING: T_M

- **Bond length, r**

- **Bond energy, E_o**

Energy (r)

unstretched length

r_o

$E_O=$

"bond energy"

- **Melting Temperature, T_m**

Energy (r)

r_o

r

smaller T_m

larger T_m

T_m is larger if E_o is larger.

45

SUMMARY: BONDING

Type	Bond Energy	Comments
Ionic	Large!	Nondirectional (ceramics)
Covalent	Variable large-Diamond small-Bismuth	Directional (semiconductors, ceramics polymer chains)
Metallic	Variable large-Tungsten small-Mercury	Nondirectional (metals)
Secondary	smallest	Directional inter-chain (polymer) inter-molecular

Material classes and atomic bonds

Ceramics,

(Ionic & covalent bonding):

Large bond energy
large T_m
large E
small α

Semiconductors
(covalent bonding)

Variable bond energy
Large to moderate T_m
large to moderate E
Small to moderate α

Metals **(Metallic bonding):**

Variable bond energy
moderate T_m
moderate E
moderate α

Polymers **(Covalent & Secondary):**
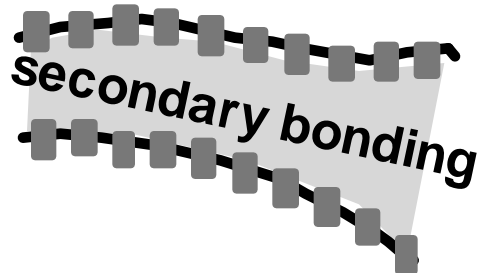
secondary bonding

Highly anisotropic Properties
Secondary bonding dominates
small T
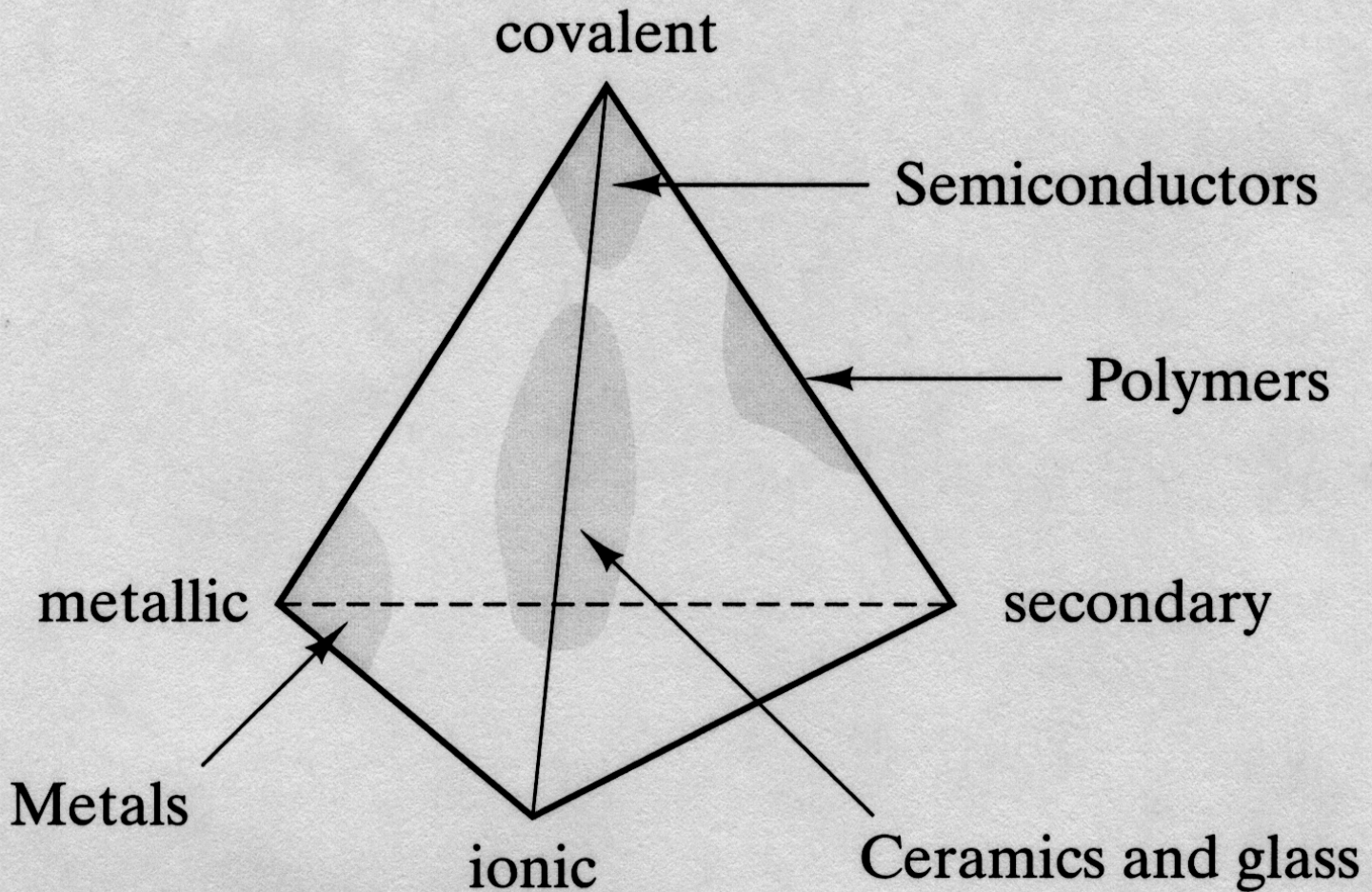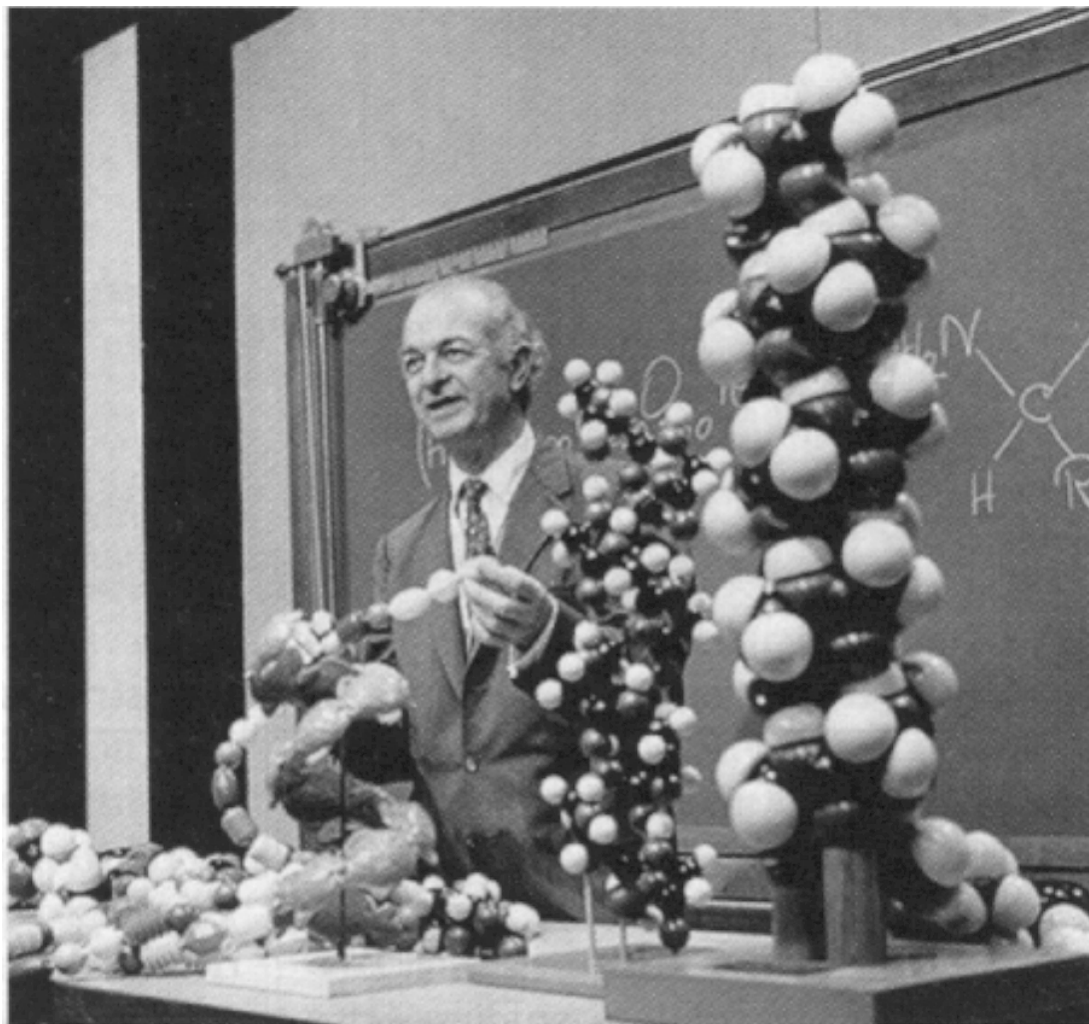**small E**
large α

47

Figure 2-24 *Tetrahedron representing the relative contribution of different bond types to the four fundamental categories of engineering materials (the three structural types plus semiconductors).*

MULTITALENTED Pauling, photographed in about 1960, teaches with molecular models. In the foreground is a model of the α-helix structure he proposed for proteins, another of his great achievements.

Perhaps Portland (Oregon)'s most famous son, what do you think ?

He got both a Nobel prize for chemistry and a Nobel prize for peace !

(and studied at OSU in Corvallis)