

Chapter Outline

- **Review of Atomic Structure**
Electrons, protons, neutrons, quantum mechanics of atoms, electron states, the periodic Table
- **Atomic Bonding in Solids**
Bonding energies and forces
- **Primary Interatomic Bonding**
Ionic
Covalent
Metallic
- **Secondary Bonding**
Three types of dipole-dipole bonds
- **Molecules and molecular solids**

Understanding of interatomic bonding is the first step towards understanding/explaining materials properties

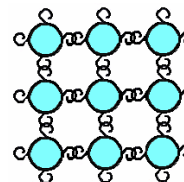
Nature of Interatomic Bonding

Why the individual atoms coalesce into larger structures and take on the characteristics and properties of many different materials?

People were trying to answer this question for well over two millennia, since the time of the atomic hypothesis of Democritus, 440 B.C.* Roman poet Lucretius (95-55 B.C.) wrote in *De Rerum Natura* (On the Nature of Things):

“What seems to us the hardened and condensed
Must be of atoms among themselves more hooked,
Be held compacted deep within, as it were
By branch-like atoms- of which sort the chief
Are diamond stones, despisers of all blows,
And stalwart flint and strength of solid iron...”

John Dalton (1766-1844) found the evidence of those "hooks" in his quantitative chemical measurements, making the foundation of modern atomic theory of matter.



* the idea that everything is made of distinct atoms has been a subject of skeptical discussions as recently as the beginning of the twentieth century, before Einstein's observation of Brownian motion in 1905 and Max von Laue's observation of the diffraction of X-rays by crystals in 1912 provided strong support for the atomistic theory.

Structure of atoms: Brief review

The bonding mechanisms between atoms are closely related to the structure of the atoms themselves.

Atoms = nucleus (protons and neutrons) + electrons

Charges:

Electrons and protons have negative and positive charges of the same magnitude, 1.6×10^{-19} Coulombs.

Neutrons are electrically neutral.

Masses:

Protons and Neutrons have the same mass, 1.67×10^{-27} kg.

Mass of an electron is much smaller, 9.11×10^{-31} kg and can be neglected in calculation of atomic mass.

The atomic mass (A) = mass of protons + mass of neutrons

protons gives chemical identification of the element

protons = atomic number (Z)

neutrons defines isotope number

Atomic mass units. Atomic weight.

The atomic mass unit (amu) is often used to express atomic weight. 1 amu is defined as 1/12 of the atomic mass of the most common isotope of carbon atom that has 6 protons (Z=6) and six neutrons (N=6).

$$M_{\text{proton}} \approx M_{\text{neutron}} = 1.66 \times 10^{-24} \text{ g} = 1 \text{ amu.}$$

The atomic mass of the ^{12}C atom is 12 amu.

The atomic weight of an element = weighted average of the atomic masses of the atoms naturally occurring isotopes. Atomic weight of carbon is 12.011 amu.

The atomic weight is often specified in mass per mole.

A mole is the amount of matter that has a mass in grams equal to the atomic mass in amu of the atoms (A mole of carbon has a mass of 12 grams).

The number of atoms in a mole is called **the Avogadro number**, $N_{\text{av}} = 6.023 \times 10^{23}$.

1 amu/atom = 1 gram/mol

Example:

Atomic weight of iron = 55.85 amu/atom = 55.85 g/mol

Some simple calculations

The number of atoms per cm^3 , n , for material of density d (g/cm^3) and atomic mass M (g/mol):

$$n = N_{\text{av}} \times d / M$$

Graphite (carbon): $d = 2.3 \text{ g}/\text{cm}^3$, $M = 12 \text{ g}/\text{mol}$
 $n = 6 \times 10^{23} \text{ atoms}/\text{mol} \times 2.3 \text{ g}/\text{cm}^3 / 12 \text{ g}/\text{mol} = 11.5 \times 10^{22} \text{ atoms}/\text{cm}^3$

Diamond (carbon): $d = 3.5 \text{ g}/\text{cm}^3$, $M = 12 \text{ g}/\text{mol}$
 $n = 6 \times 10^{23} \text{ atoms}/\text{mol} \times 3.5 \text{ g}/\text{cm}^3 / 12 \text{ g}/\text{mol} = 17.5 \times 10^{22} \text{ atoms}/\text{cm}^3$

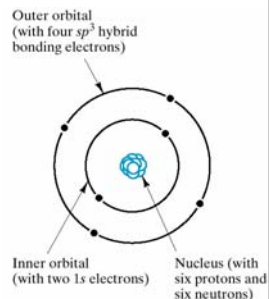
Water (H_2O) $d = 1 \text{ g}/\text{cm}^3$, $M = 18 \text{ g}/\text{mol}$
 $n = 6 \times 10^{23} \text{ molecules}/\text{mol} \times 1 \text{ g}/\text{cm}^3 / 18 \text{ g}/\text{mol} = 3.3 \times 10^{22} \text{ molecules}/\text{cm}^3$

For material with $n = 6 \times 10^{22} \text{ atoms}/\text{cm}^3$ we can calculate mean distance between atoms $L = (1/n)^{1/3} = 0.25 \text{ nm}$.

☐ the scale of atomic structures in solids – a fraction of 1 nm or a few Å.

Electrons in Atoms (I)

The electrons form a cloud around the nucleus, of radius of 0.05 – 2 nm.



This picture looks like a mini planetary system. But quantum mechanics tells us that this analogy is not correct:

Electrons move not in circular orbits, but in 'fuzzy' orbits. Actually, we cannot tell how it moves, but only can say what is the probability of finding it at some distance from the nucleus.

Only certain "orbits" or shells of electron probability densities are allowed. The shells are identified by a **principal quantum number n**, which can be related to the size of the shell, $n = 1$ is the smallest; $n = 2, 3 \dots$ are larger.

The **second quantum number l**, defines subshells within each shell. **Two more quantum numbers** characterize states within the subshells.

Electrons in Atoms (II)

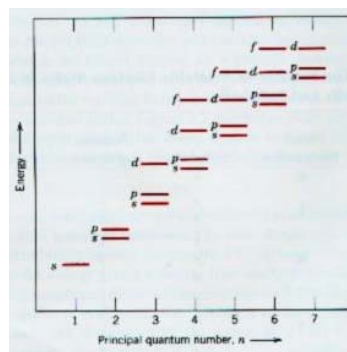
- The quantum numbers arise from solution of Schrodinger's equation
- Pauli Exclusion Principle: only one electron can have a given set of the four quantum numbers.

The number of available states in electron shells & subshells

Principal Q. N., n	Subshells	Number of States	Number of Electrons	
			Per Subshell	Per Shell
1 (l=0) <i>K-shell</i>	s	1	2	2
2 (l=0) <i>L-shell</i>	s	1	2	8
2 (l=1)	p	3	6	
3 (l=0)	s	1	2	18
3 (l=1) <i>M-shell</i>	p	3	6	
3 (l=2)	d	5	10	
4 (l=0)	s	1	2	32
4 (l=1) <i>N-shell</i>	p	3	6	
4 (l=2)	d	5	10	
4 (l=3)	f	7	14	

Each "orbit" or shell can accommodate only a maximum number of electrons, which is determined by quantum mechanics. In brief, the most inner *K-shell* can accommodate only two electrons, called *s-electrons*; the next *L-shell* two *s-electrons* and six *p-electrons*; the *M-shell* can host two *s-electrons*, six *p-electrons*, and ten *d-electrons*; and so on.

Electrons in Atoms (III)



Subshells by energy: $1s, 2s, 2p, 3s, 3p, 4s, 3d, 4s, 4p, 5s, 4d, 5p, 6s, 4f, \dots$

- Electrons that occupy the outermost filled shell – **the valence electrons** – they are responsible for bonding.
- Electrons fill quantum levels in order of increasing energy (only n, ℓ make a significant difference).

Examples: Argon, $Z = 18$: $1s^2 2s^2 2p^6 3s^2 3p^6$
 Iron, $Z = 26$: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$

Electrons in Atoms (IV)

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 4p ⁶ (stable)

Electron configurations where all states within valence electron shell are filled are stable → unreactive inert or noble gas.

Periodic Table

The first accepted periodic table of elements was published in 1869 by Mendeleev. In the same year, a German chemist Lothar Meyer independently published a very similar table, but his contribution is generally ignored.

All elements in the periodic table have been classified according to the electron configuration.



Draft of the periodic table, Mendeleev, 1869

Periodic Table

IA	IIA	VIII										IB	IIB	IIIA	IIIA	IVA	VA	VIA	VIA	VIA	0																						
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36								
H	He	B	C	N	O	F	Ne	Na	Mg	Al	Si	P	S	Cl	Ar	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr										
Li	Be	B	C	N	O	F	Ne	Na	Mg	Al	Si	P	S	Cl	Ar	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr										
Na	Mg	Al	Si	P	S	Cl	Ar	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe								
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe								
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn								
Fr	Ra	Ac-Actin	Rf	Db	Sg	Bh	Hs	Mt	Ds									Fr	Ra	Ac-Actin	Rf	Db	Sg	Bh	Hs	Mt	Ds																

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

Elements in the same column (Elemental Group) share similar properties. Group number indicates the number of electrons available for bonding.

- 0: Inert gases (He, Ne, Ar...) have filled subshells: chem. inactive
- IA: Alkali metals (Li, Na, K...) have one electron in outermost occupied s subshell - eager to give up electron - chem. active
- VIIA: Halogens (F, Br, Cl...) missing one electron in outermost occupied p shell - want to gain electron - chem. active

Periodic Table - Electronegativity

IA	IIA	VIII										IB	IIB	IIIA	IIIA	IVA	VA	VIA	VIA	VIA	0																						
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36								
H	He	B	C	N	O	F	Ne	Na	Mg	Al	Si	P	S	Cl	Ar	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr										
Li	Be	B	C	N	O	F	Ne	Na	Mg	Al	Si	P	S	Cl	Ar	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr										
Na	Mg	Al	Si	P	S	Cl	Ar	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr								
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe								
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn								
Fr	Ra	Ac-Actin	Rf	Db	Sg	Bh	Hs	Mt	Ds									Fr	Ra	Ac-Actin	Rf	Db	Sg	Bh	Hs	Mt	Ds																

Figure 2.7 from the textbook. The electronegativity values.

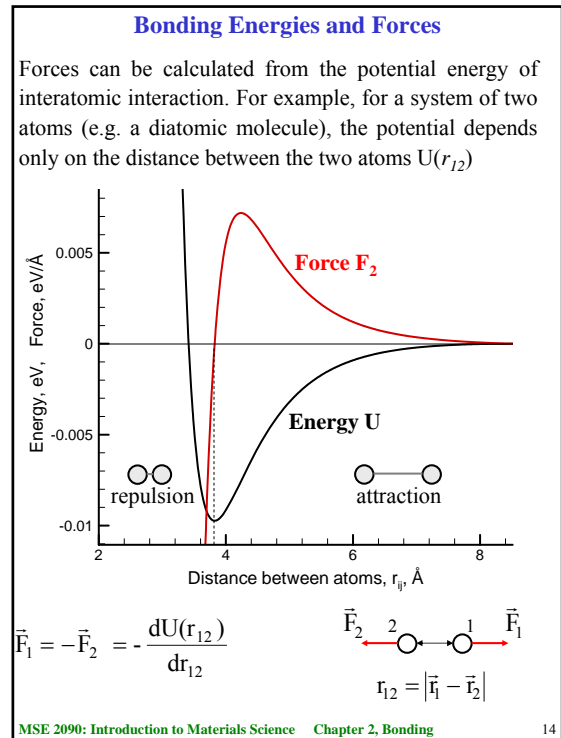
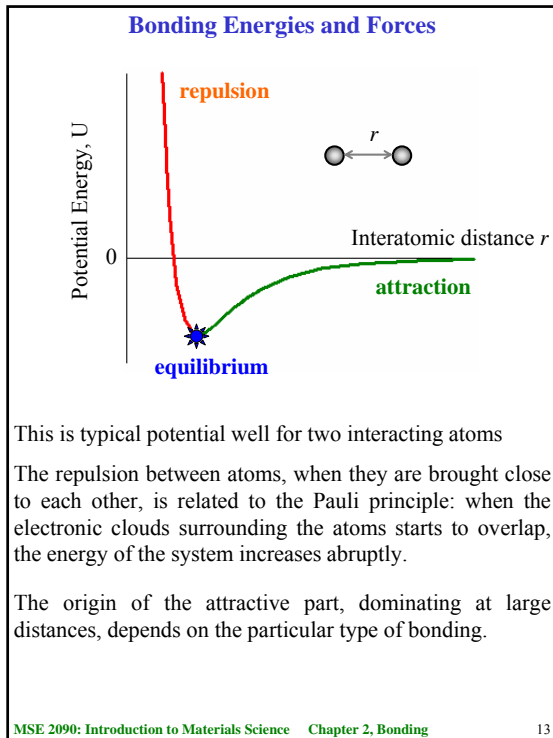
Electronegativity - a measure of how willing atoms are to accept electrons

Subshells with one electron → low electronegativity

Subshells with one missing electron → high electronegativity

Electronegativity increases from left to right

Metals are electropositive - they can give up their few valence electrons to become positively charged ions



The electron volt (eV) – energy unit convenient for description of atomic bonding

Electron volt - the energy lost / gained by an electron when it is taken through a potential difference of one volt.

$$E = q \times V$$

for $q = 1.6 \times 10^{-19}$ Coulombs and $V = 1$ volt

$$1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$$

Types of Bonding

The electronic structure of atoms defines the character of their interaction among each other. Filled outer shells result in a stable configuration as in noble inert gases. Atoms with incomplete outer shells strive to reach this noble gas configuration by sharing or transferring electrons among each other for maximal stability. Strong “primary” bonding results from the electron sharing or transfer.

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Types of Bonding

Primary bonding: e^- are transferred or shared
Strong (100-1000 KJ/mol or 1-10 eV/atom)

- Ionic: Strong Coulomb interaction among negative atoms (have an extra electron each) and positive atoms (lost an electron). Example - Na^+Cl^-
- Covalent: electrons are shared between the molecules, to saturate the valency. Example - H_2
- Metallic: the atoms are ionized, loosing some electrons from the valence band. Those electrons form a electron sea, which binds the charged nuclei in place

Secondary Bonding: no e^- transferred or shared
Interaction of atomic/molecular dipoles
Weak (< 100 KJ/mol or < 1 eV/atom)

- Fluctuating Induced Dipole (inert gases, H_2 , Cl_2 ...)
- Permanent dipole bonds (polar molecules - H_2O , HCl ...)
- Polar molecule-induced dipole bonds (a polar molecule induces a dipole in a nearby nonpolar atom/molecule)

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Ionic Bonding (I)

Ionic Bonding is typical for elements that are situated at the horizontal extremities of the periodic table.

Atoms from the left (metals) are ready to give up their valence electrons to the (non-metallic) atoms from the right that are happy to get one or a few electrons to acquire stable or noble gas electron configuration.

As a result of this transfer mutual ionization occurs: atom that gives up electron(s) becomes positively charged ion (**cation**), atom that accepts electron(s) becomes negatively charged ion (**anion**).

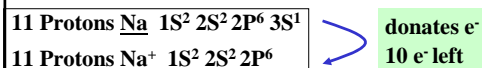
Formation of ionic bond:

- Mutual ionization occurs by electron transfer (remember electronegativity table)
 - Ion = charged atom
 - Anion = negatively charged atom
 - Cation = positively charged atom
- Ions are attracted by strong coulombic interaction
 - Oppositely charged atoms attract each other
 - An ionic bond is non-directional (ions may be attracted to one another in any direction)

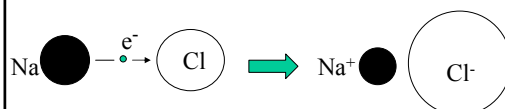
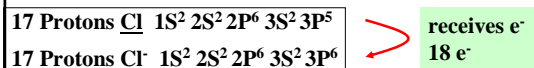
Ionic Bonding (II)

Example: table salt (NaCl)

Na has 11 electrons, 1 more than needed for a full outer shell (Neon)



Cl has 17 electron, 1 less than needed for a full outer shell (Argon)

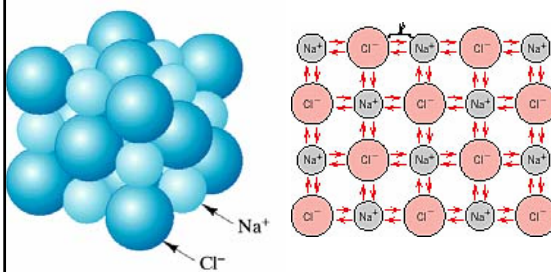


- Electron transfer reduces the energy of the system of atoms, that is, electron transfer is energetically favorable
- Note relative sizes of ions: Na shrinks and Cl expands

Ionic Bonding (III)

A strong electrostatic attraction between positively charged Na⁺ ions and negatively charged Cl⁻ atoms along with Na⁺ - Na⁺ and Cl⁻ - Cl⁻ repulsion result in the NaCl crystal structure which is arranged so that each sodium ion is surrounded by Cl⁻ ions and each Na⁺ ion is surrounded by Cl⁻ ions, see the figure on the left.

Any mechanical force that tries to disturb the electrical balance in an ionic crystal meets strong resistance: ionic materials are strong and brittle. In some special cases, however, significant plastic deformation can be observed, e.g. NaCl single crystals can be bent by hand in water.



Ionic bonds: very strong, nondirectional bonds

Ionic Bonding (IV)

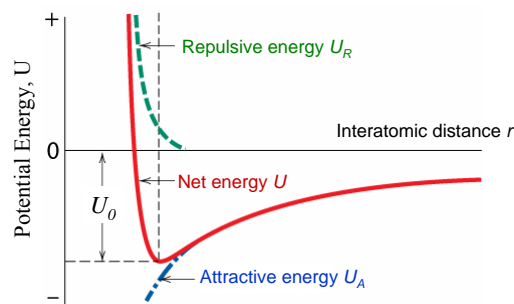
Attractive coulomb interaction between charges of opposite sign:

$$U_A = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r} = -\frac{A}{r}$$

Repulsion due to the overlap of electron clouds at close distances (Pauli principle of QM):

$$U_R = \frac{B}{r^n}$$

$$U = U_A + U_R = -\frac{A}{r} + \frac{B}{r^n}$$



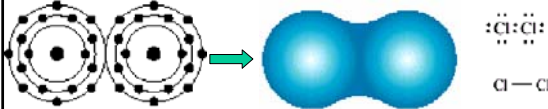
Covalent Bonding (I)

In covalent bonding, electrons are **shared** between the molecules, to saturate the valency. In this case the electrons are not transferred as in the ionic bonding, but they are localized between the neighboring ions and form **directional** bond between them. The ions repel each other, but are attracted to the electrons that spend most of the time in between the ions.

Formation of covalent bonds:

- Cooperative sharing of valence electrons
- Can be described by orbital overlap
- Covalent bonds are **HIGHLY directional**
- Bonds - in the direction of the greatest orbital overlap
- Covalent bond model: an atom can covalently bond with at most $8 - N^v$, $N^v = \text{number of valence electrons}$

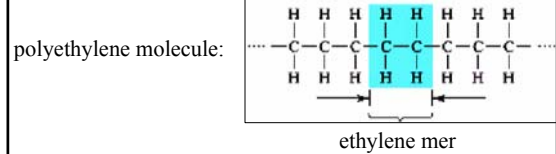
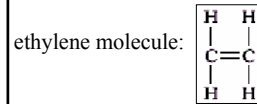
Example: Cl_2 molecule. $Z_{\text{Cl}} = 17$ ($1s^2 2s^2 2p^6 3s^2 3p^5$)
 $N^v = 7$, $8 - N^v = 1 \rightarrow$ can form only one covalent bond



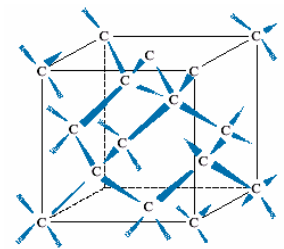
Covalent Bonding (II)

Example: Carbon materials. $Z_c = 6$ ($1s^2 2s^2 2p^2$)

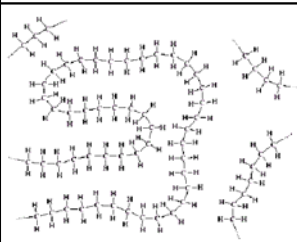
$N^v = 4$, $8 - N^v = 4 \rightarrow$ can form up to four covalent bonds



diamond:
 (each C atom has four covalent bonds with four other carbon atoms)

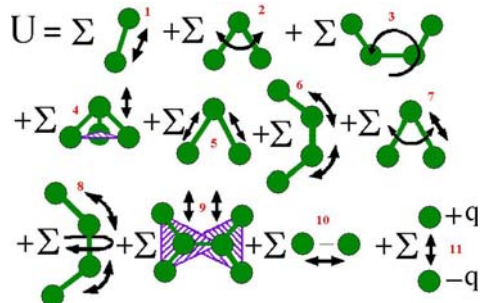


Covalent Bonding (III)



2-D schematic of the "spaghetti-like" structure of solid polyethylene

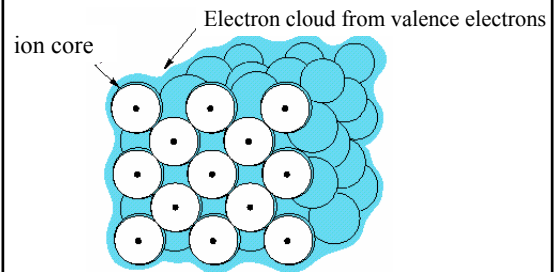
The potential energy of a system of covalently interacting atoms depend not only on the distances between atoms, but also on angles between bonds...



Metallic Bonding

Valence electrons are detached from atoms, and spread in an 'electron sea' that "glues" the positive ions together.

- A metallic bond is non-directional (bonds form in any direction) \rightarrow atoms pack closely



The "bonds" do not "break" when atoms are rearranged – metals can experience a significant degree of plastic deformation.

Examples of typical metallic bonding: Cu, Al, Au, Ag, etc. Transition metals (Fe, Ni, etc.) form mixed bonds that are comprising of metallic bonds and covalent bonds involving their 3d-electrons. As a result the transition metals are more brittle (less ductile) than Au or Cu.

Secondary Bonding (I)

Secondary = van der Waals = physical (as opposite to chemical bonding that involves e^- transfer) bonding results from interaction of atomic or molecular dipoles and is weak, ~ 0.1 eV/atom or ~ 10 kJ/mol.



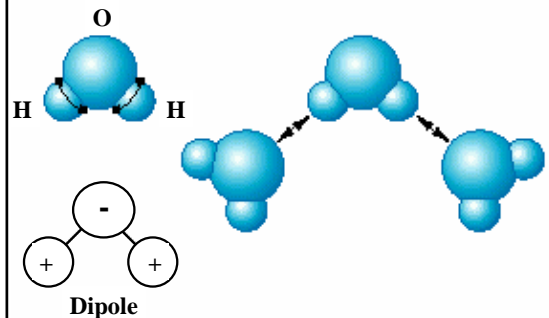
Permanent dipole moments exist in some molecules (called **polar molecules**) due to the asymmetrical arrangement of positively and negatively charged regions (HCl, H₂O). Bonds between adjacent polar molecules – **permanent dipole bonds** – are the **strongest among secondary bonds**.

Polar molecules can **induce** dipoles in adjacent non-polar molecules and bond is formed due to the **attraction between the permanent and induced dipoles**.

Even in electrically symmetric molecules/atoms an electric dipole can be created by fluctuations of electron density distribution. Fluctuating electric field in one atom A is felt by the electrons of an adjacent atom, and induce a dipole moment in this atom. **This bond due to fluctuating induced dipoles is the weakest (inert gases, H₂, Cl₂).**

Secondary Bonding (II)

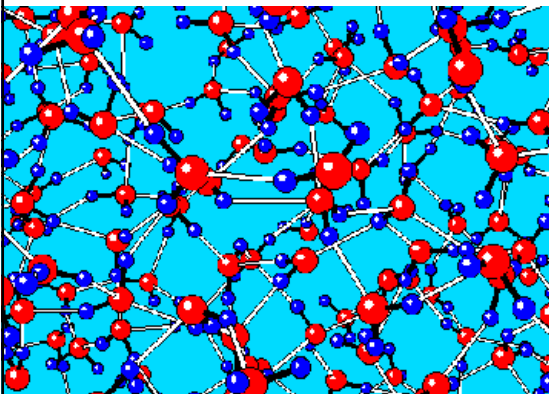
Example: hydrogen bond in water. The H end of the molecule is positively charged and can bond to the negative side of another H₂O molecule (the O side of the H₂O dipole)



“Hydrogen bond” – secondary bond formed between two **permanent dipoles** in adjacent water molecules.

Secondary Bonding (III)

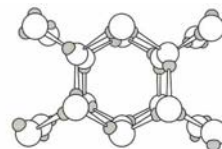
Hydrogen bonding in liquid water from a molecular-level simulation



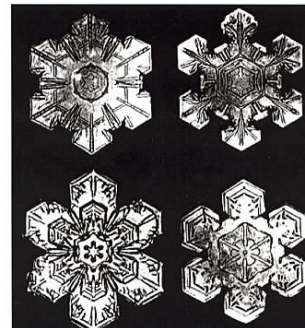
Molecules: Primary bonds inside, secondary bonds among each other

Secondary Bonding (IV)

The Crystal Structures of Ice



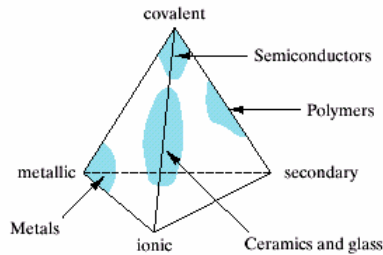
Hexagonal Symmetry of Ice Snowflakes



Figures by Paul R. Howell

Bonding in real materials

In many materials more than one type of bonding is involved (ionic and covalent in ceramics, covalent and secondary in polymers, covalent and ionic in semiconductors).



Examples of bonding in Materials:

- Metals: Metallic
- Ceramics: Ionic / Covalent
- Polymers: Covalent and Secondary
- Semiconductors: Covalent or Covalent / Ionic

Correlation between bonding energy and melting temperature

Table 2.3 Bonding Energies and Melting Temperatures for Various Substances

Bonding Type	Substance	Bonding Energy		Melting Temperature (°C)
		kJ/mol (kcal/mol)	eV/Atom, Ion, Molecule	
Ionic	NaCl	640 (153)	3.3	801
	MgO	1000 (239)	5.2	2800
Covalent	Si	450 (108)	4.7	1410
	C (diamond)	713 (170)	7.4	>3550
Metallic	Hg	68 (16)	0.7	-39
	Al	324 (77)	3.4	660
	Fe	406 (97)	4.2	1538
	W	849 (203)	8.8	3410
van der Waals	Ar	7.7 (1.8)	0.08	-189
	Cl ₂	31 (7.4)	0.32	-101
Hydrogen	NH ₃	35 (8.4)	0.36	-78
	H ₂ O	51 (12.2)	0.52	0

Summary

Make sure you understand language and concepts:

- Atomic mass unit (amu)
- Atomic number
- Atomic weight
- Bonding energy
- Coulombic force
- Covalent bond
- Dipole (electric)
- Electron state
- Electronegative
- Electropositive
- Hydrogen bond
- Ionic bond
- Metallic bond
- Mole
- Molecule
- Periodic table
- Polar molecule
- Primary bonding
- Secondary bonding
- Van der Waals bond
- Valence electron

Reading for next class:

Chapter 3: The structure of crystalline solids

Unit cells

Crystal structures

- Face-centered cubic
- Body-centered cubic
- Hexagonal close-packed

Density computations

Types of solids

- Single crystals
- Polycrystalline
- Amorphous

Optional reading (Parts that are not covered / not tested):

- 3.8–3.10 Crystallography
- 3.15 Anisotropy
- 3.16 Diffraction