



Lecture 2

“Intro. To Crystal Structure of Biomaterial” “Atomic Bonding in Solid”

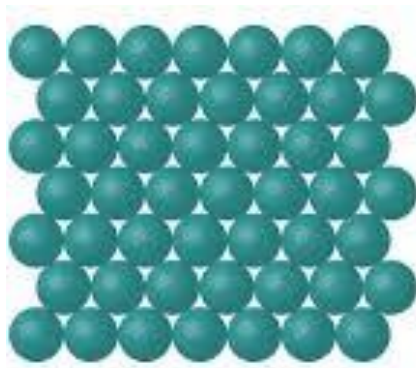
2.1. Introduction:

Some of the important properties of solid materials depend on geometric atomic arrangements and also the interactions that exist among constituent atoms or molecules. This lecture considers several fundamental and important concepts namely, atomic structure, and the various types of primary and secondary interatomic bonds that hold together the atoms that compose a solid.

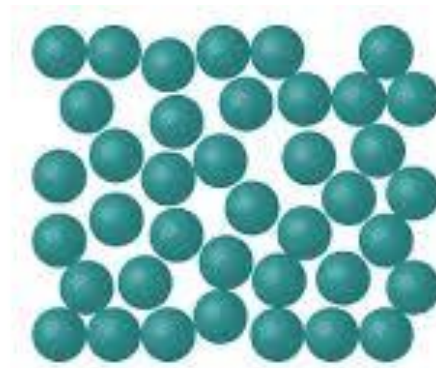
2.2. Structure of Materials:

Based on their **crystal structures**, solid materials can be classified into the following categories:

1. Crystalline solids
2. Amorphous solids



Crystalline



Amorphous

However, crystalline solids can be further classified into molecular, ionic, metallic, and covalent solids. A brief introduction to the classification of solids is provided in this article.

What are Crystalline Solids?

The solids featuring **highly ordered arrangements** of their particles (atoms, ions, and molecules) in microscopic structures are called crystalline solids.

These ordered microscopic structures make up a crystal lattice that accounts for the structure of the solid at any given point. Examples of crystalline solids include salt (sodium chloride), diamond, and sodium nitrate.

What are Amorphous Solids?

The solids in which the particles are **not arranged in any specific order** or the solids that lack the overall order of a crystal lattice are called amorphous solids.

The term ‘**amorphous**’, when broken down into its Greek roots, can be roughly translated to “**without form**”. Many polymers are amorphous solids. Other examples of such solids include glass, gels, and nanostructured materials.

An Ideal crystal is defined as an atomic arrangement that has infinite translational symmetry in all three dimensions, whereas such a definite definition is not possible for an ideal amorphous solid (a solid).

2.3 Atomic Bonding

At a high level of classification, materials can be divided into two classes: natural and synthetic. At a more fundamental level, materials can be separated into different general categories based on their molecular structure and the type of bonding between their atoms. Since the latter plays a primary role in determining the properties of a biomaterial, it is important to first gain an understanding of the different types of bonds.

Three different types of primary or chemical bonds are found in solids (ionic, covalent, and metallic). For each type, the bonding necessarily involves the valence electrons; furthermore, the nature of the bond depends on the electron structures of the constituent atoms.

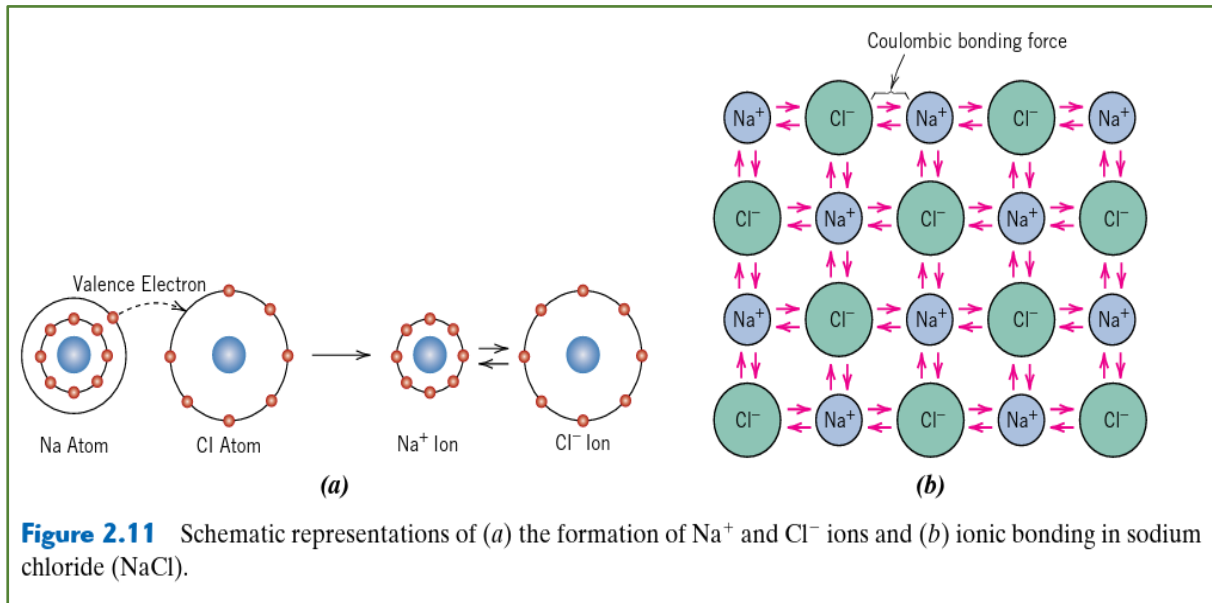
In general, each of these three types of bonding arises from the tendency of the atoms to assume stable electron structures, like those of inert gases, by completely filling the outermost electron shell. Secondary or physical forces and energies are also found in many solid materials; they are weaker than the primary ones but nonetheless influence the physical properties of some materials.

2.3.1 Primary Interatomic Bonds:

Primary bonds involve sharing or donating electrons between atoms to form a more stable electron configuration. All elements except inert gases have an unfilled valence shell. For example, sodium has a nucleus containing 11 protons and orbiting shells containing 11 electrons. The outer shell has one valence electron. Primary bonding occurs when electrons are lost or gained so that the outer shell is filled. For example, if a sodium atom loses its valence electron, it is left with a full outer shell of electrons and if a chlorine atom, which has only seven electrons in the outer shell, gains an electron, its outer shell is then full.

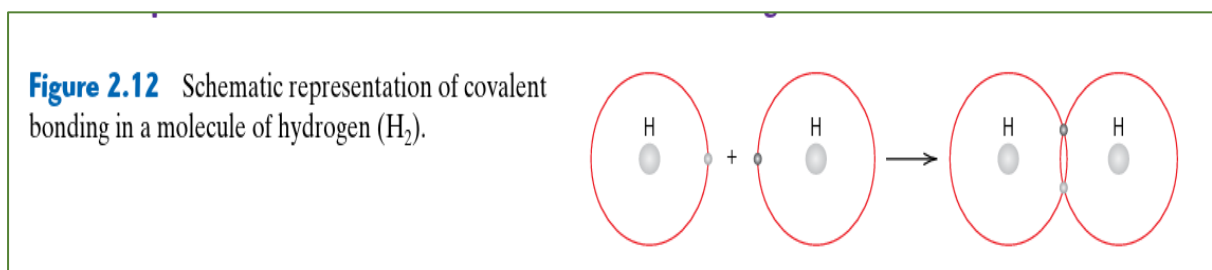
2.3.1.1 Ionic Bonding:

In Ionic Bonding, one atom gives out one valence electron and another accepts that electron. The ones that lose electrons become Cations and the ones that gain them become Anions. The elements (or correspondingly their atoms) that have a tendency to become Cations are called "electropositive" and those who have a tendency to become Anions are called "electronegative". The best example of such bonding in materials is NaCl (Sodium Chloride or rock salt). See sketch for NaCl.



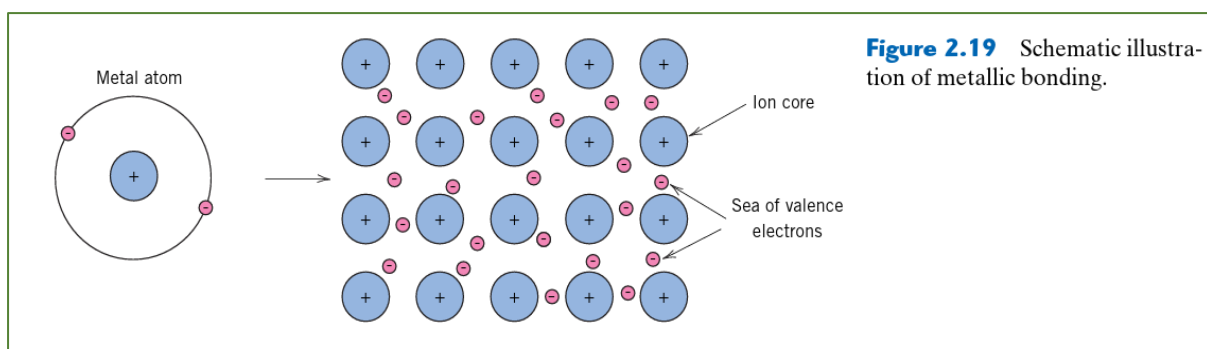
2.3.1.2. Covalent Bonding:

A second bonding type, covalent bonding, is found in materials whose atoms have small differences in electronegativity—that is, that lie near one another in the periodic table. For these materials, stable electron configurations are assumed by the sharing of electrons between adjacent atoms. Two covalently bonded atoms will each contribute at least one electron to the bond, and the shared electrons may be considered to belong to both atoms. Covalent bonding is schematically illustrated in Figure 2.12 for a molecule of hydrogen (H₂). The hydrogen atom has a single 1s electron. Each of the atoms can acquire a helium electron configuration (two 1s valence electrons) when they share their single electron (right side of Figure 2.12). Furthermore, there is an overlapping of electron orbitals in the region between the two bonding atoms. In addition, the covalent bond is directional—that is, it is between specific atoms and may exist only in the direction between one atom and another that participates in the electron sharing.



2.3.1.3. Metallic Bonding:

Metallic bonding, the final primary bonding type, is found in metals and their alloys (e.g., Al, Cu, Ag, Pd, etc.), these valence electrons are not bound to any particular atom in the solid, the atoms share their valence electrons not only or necessarily with neighboring atoms but rather with all the atoms in the matter. This is facilitated by the electrons forming a sea or cloud that engulfs the rest of the atom (i.e., the positively charged nucleus with its remaining non-valence electrons).



2.3.2. Secondary bonds:

Van der Waals and hydrogen bonds are physical bonds, that are weak in comparison to the primary or chemical bonds; bonding energies range between about 4 and 30 kJ/mol. Secondary bonding exists between virtually all atoms or molecules, but its presence may be obscured if any of the three primary bonding types are present.

Secondary bonding is evidenced for the inert gases, which have stable electron structures. In addition, secondary (or intermolecular) bonds are possible between atoms or groups of atoms, which themselves are joined together by primary (or intramolecular) ionic or covalent bonds.

2.3.2.1. Hydrogen Bonds:

Hydrogen bonds are relatively stronger than Van der Waal's force but compared to primary bonds they are weak. Bonds between hydrogen atoms and atoms of the most electronegative elements (N, O, F) are called hydrogen bonds. It is based

on the fact that hydrogen being the smallest atom provides very little repulsion when interacting with highly electronegative atoms in other molecules and thus succeeds in forming partial bonds with them. This makes hydrogen bonds strong but weaker compared to primary bonds since the interactions here are permanent dipole interactions.

2.3.2.2. Van der Waal's Forces:

Secondary bonds are bonds of a different kind to the primary ones. They are weaker in nature and are broadly classified as Van der Waal's forces and hydrogen bonds. These bonds are due to temporary atomic or molecular dipoles.

Van der Waal's bond is formed due to temporary dipoles. A temporary dipole is formed in a symmetric molecule but fluctuations of charges give rise to partial dipole moments for only a few moments. This can be seen in atoms of inert gases. For instance, a molecule of methane has one carbon atom and four hydrogen atoms joined together by single covalent bonds between the carbon and the hydrogen atoms. Methane is a symmetric molecule but when it is solidified, the bonds between the molecules are of weak Van der Waal's forces.

Figure 2.20 Schematic illustration of van der Waals bonding between two dipoles.

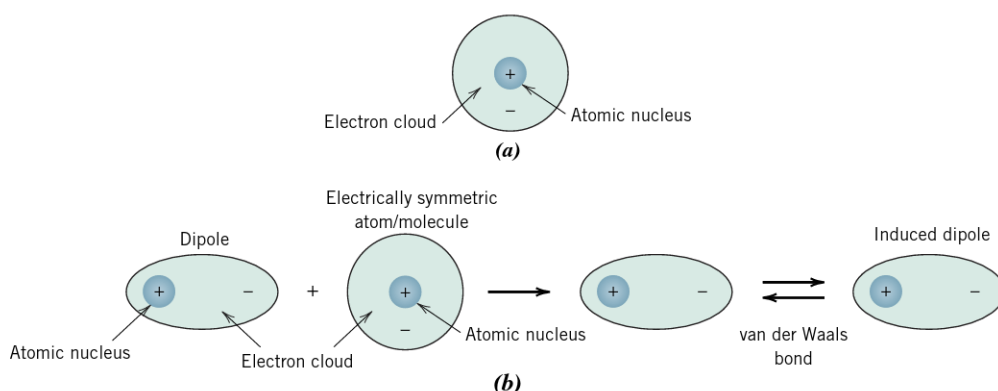
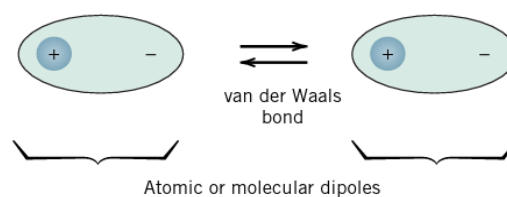
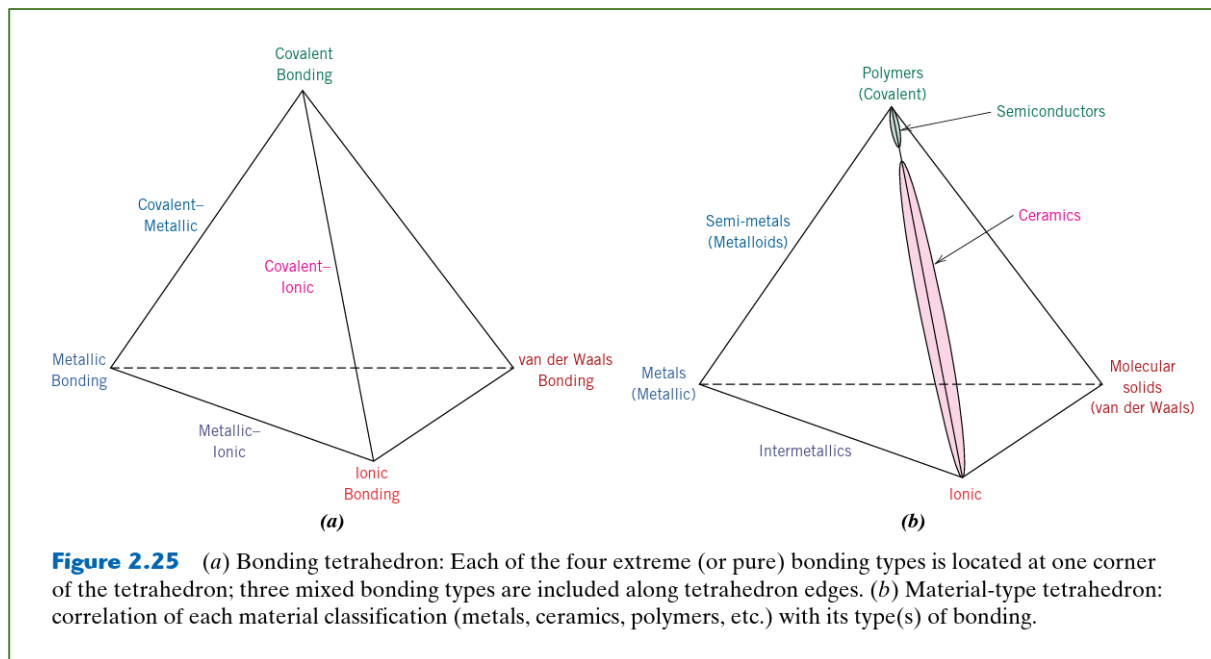


Figure 2.21 Schematic representations of (a) an electrically symmetric atom and (b) how an electric dipole induces an electrically symmetric atom/molecule to become a dipole—also the van der Waals bond between the dipoles.

Mixed Bonding:

Sometimes it is illustrative to represent the four bonding types - ionic, covalent, metallic, and van der Waals - on what is called a bonding tetrahedron - a three dimensional tetrahedron with one of these “extreme” types located at each vertex, as shown in Figure 2.25a. Furthermore, we should point out that for many real materials, the atomic bonds are mixtures of two or more of these extremes (i.e., mixed bonds). Three mixed-bond types covalent–ionic, covalent–metallic, and metallic–ionic are also included on the edges of this tetrahedron; some correlations between bonding type and material classification namely, ionic bonding (ceramics), covalent bonding (polymers), metallic bonding (metals), and van der Waals bonding (molecular solids).



Summary: Correlations between bonding type and material class were noted:

Polymers (covalent)

Metals (metallic)

Ceramics (ionic / mixed ionic–covalent)

Molecular solids (van der Waals)

Semi-metals (mixed covalent–metallic)

Intermetallics (mixed metallic–ionic)