

# **Biomaterials**

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Imprint          Springer New York, 2007

ISBN            9780387378800, 9780387378794

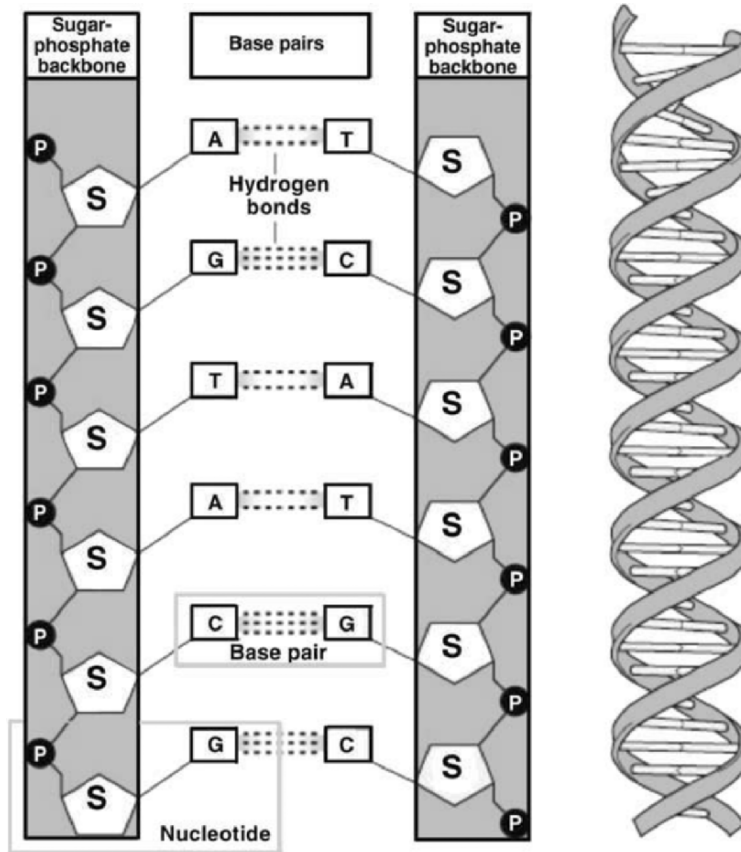
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# 2

## THE STRUCTURE OF SOLIDS



The structure of deoxyribonucleic acid (DNA) was discovered by James Watson and Francis Crick in 1953. DNA was determined to be a right-handed double helix based on x-ray crystallographic data provided to Watson and Crick by Maurice Wilkins and Rosalind Franklin. DNA is composed of repeating subunits called nucleotides. Nucleotides are further composed of a phosphate group, a sugar, and a nitrogenous base. Four different bases are commonly found in DNA: adenine (A), guanine (G), cytosine (C), and thymine (T). In their common structural configurations, A and T form two hydrogen bonds while C and G form three hydrogen bonds. Because of the specificity of base pairing, the two strands of DNA are said to be complementary. This characteristic makes DNA unique and capable of transmitting genetic information. Reprinted courtesy of the National Genomic Research Institute, National Institutes of Health.

The properties of a material are determined by its structure and chemical composition. Since chemical behavior depends ultimately upon the internal structural arrangement of the atoms, all material properties may be attributed to structure. Structure occurs on many levels of scale. These scales may be somewhat arbitrarily defined as the atomic or molecular (0.1–1 nm), nanoscale or ultrastructural (1 nm–1  $\mu$ m), microstructural (1  $\mu$ m–1 mm), and macrostructural (>1 mm). In pure elements, alloys, ceramics, and in polymers, the major structural features are on the atomic/molecular scale. Polycrystalline materials such as cast metals consist of grains that may be quite large; however, the boundaries between the grains are atomic scale features.

The first five sections of this chapter deal with the atomic/molecular structural aspects of materials. These sections constitute a review for those readers who have had some exposure to materials science. The final section deals with larger-scale structure associated with composite and cellular materials.

This and the next two chapters give a brief review on the background of the materials science and engineering mostly pertinent to the subsequent chapters. Any reader who cannot comprehend chapters 2–4 should review or study the basic materials science and engineering texts such as those given in the Bibliography.

## 2.1. ATOMIC BONDING

All solids are made up of atoms held together by the interaction of the outermost (*valence*) electrons. The valence electrons can move freely in the solid but can only exist in certain stable patterns within the confines of the solid. The nature of the patterns varies according to the *ionic*, *metallic*, or *covalent* bonding. In metallic bonds the electrons are *loosely* held to the ions, which makes the bond nondirectional. Therefore, in many metals it is easy for *plastic deformations* to occur (i.e., the ions can rearrange themselves permanently to the applied external forces). The ionic bonds are formed by exchanging electrons between metallic and non-metallic atoms. The metallic atoms, such as Na, donate electrons, becoming positive ions ( $\text{Na}^+$ ), while the nonmetallic atoms (e.g., Cl) receive electrons, becoming negative ions ( $\text{Cl}^-$ ). The valence electrons are much more likely to be found in the space around the negative ions than the positive ions, thus making the bonds very directional. The ionic solid structures are limited in their atomic arrangement due to the strong repulsive forces of like ions. Therefore, the positive ions are surrounded by negative ions, and vice versa. The covalent bonds are formed when atoms share the valence electrons to satisfy their partially filled electronic orbitals. The greater the overlap of the valence orbitals or shells, the stronger the bonds become, but bond strength is limited by the strong repulsive forces between nuclei. Covalent bonds are also highly directional and strong, as can be attested by diamond, which is the hardest material known.

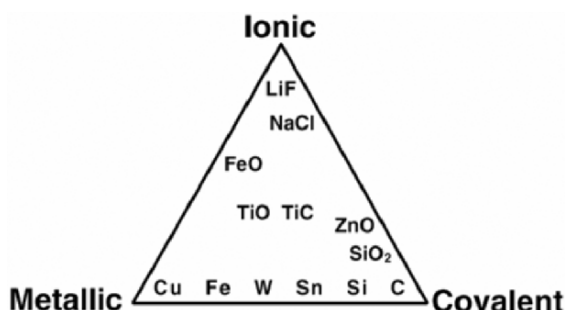
In addition to the primary bonds there are *secondary bonds*, which can be a major factor in contributing to material properties. Two major secondary bonds are the hydrogen and van der Waals bonds. The *hydrogen* bonds can arise when the hydrogen atom is covalently bonded to an electronegative atom so that it becomes a positive ion. The electrostatic force between them can be substantial since the hydrogen ion is quite small and can approach the negative ion very closely. The *van der Waals* forces arise when electrons are not distributed equally among ions that can form dipoles. The dipole–dipole interactions do not give rise to directional bonds and the effect is over a short distance. These bonds are much weaker than the hydrogen bonds, as given in Table 2-1.

**Table 2-1.** Strength of Different Chemical Bonds as Reflected in Their Heat of Vaporization

Bond type	Substance	Heat of vaporization (kJ/mol)
van der Waals	N <sub>2</sub>	13
Hydrogen	Phenol	31
	HF	47
Metallic	Na	180
	Fe	652
Ionic	NaCl	1062
	MgO	1880
Covalent	Diamond	1180
	SiO <sub>2</sub>	2810

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Although we have categorized the bonds as discussed above, the real materials may show some combination of bonding characteristics. For example, silicon atoms share electrons covalently but a fraction of the electrons can be freed and permit limited conductivity (semiconductivity). Thus silicon has covalent as well as some metallic bonding characteristics, as shown in Figure 2-1.

**Figure 2-1.** Some materials exhibit nearly ideal covalent, metallic, or ionic bonding, but most materials exhibit a hybrid of different bond types.

## 2.2. CRYSTAL STRUCTURE

### 2.2.1. Atoms of the Same Size

Crystals contain an orderly arrangement of atoms or molecules. A crystal need not be transparent. Diamond, salt crystals, and quartz are indeed transparent. Also, an ordinary piece of metal such as steel, aluminum, or brass contains many crystals in contact: it is polycrystalline. The crystals are ordinarily not visible since each one has nearly the same appearance. The poly-

crystalline nature of a metal can be revealed by etching the surface with an acid, which selectively dissolves the surface of crystals that have different orientations. Such etching may occur unintentionally in old brass door knobs and handles, in which the acid secreted by the hands of many people reveals the crystals, which can exceed 1 mm in size.

The arrangement of atoms in a crystal can be treated as an arrangement of hard spheres in view of their maintenance of characteristic equilibrium distances (bond length). Measurement of this distance is done by using x-rays, which have short wavelengths — of the order of one Angstrom ( $1 \text{ \AA} = 10^{-10} \text{ m}$ ), approaching the atomic radius. When the atoms are arranged in a regular array the structure can be represented by a *unit cell*, which has a characteristic dimension, the *lattice constant*,  $a$ , as shown in Figure 2-2. If this atomic structure is extended into three dimensions, the corresponding crystal structure will be cubic. This is a simple cubic space lattice, which is one of the three types of cubic crystals.

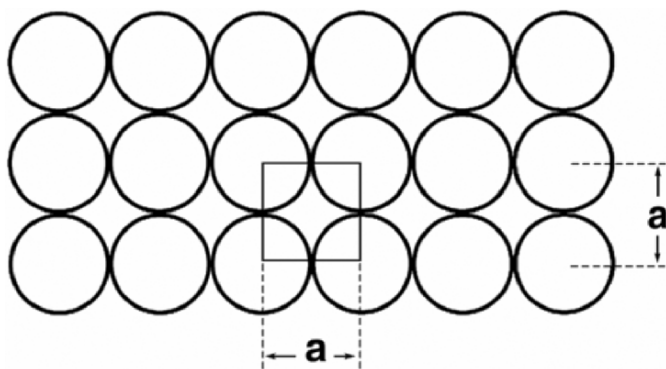


Figure 2-2. Stacking of hard balls (atoms) in simple cubic structure ( $a$  is the lattice spacing).

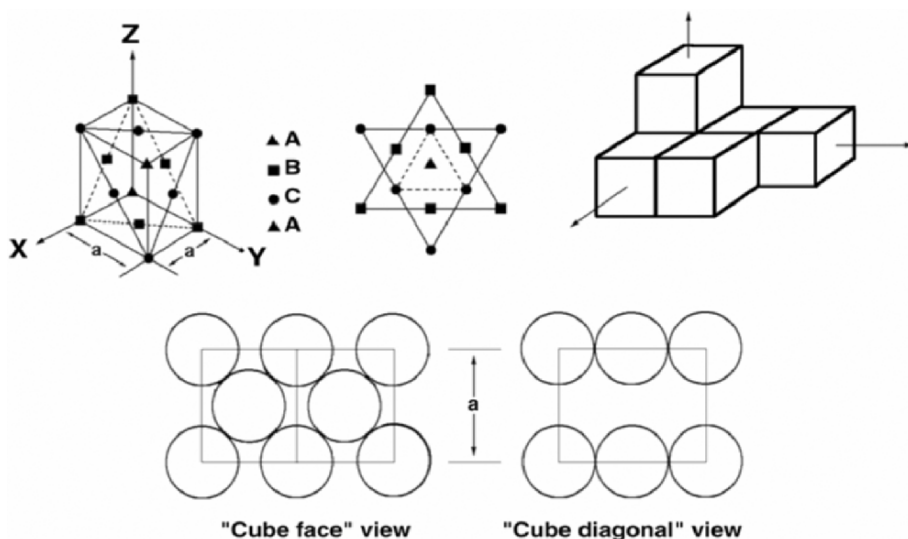
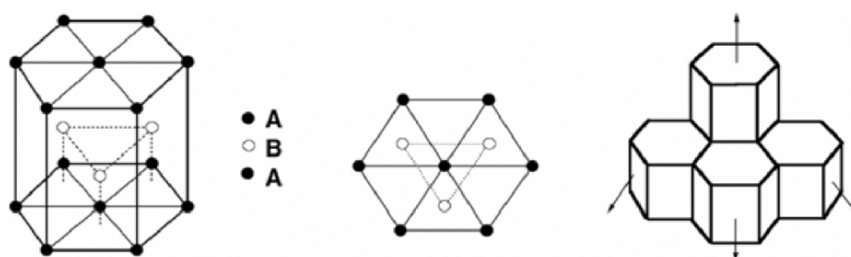
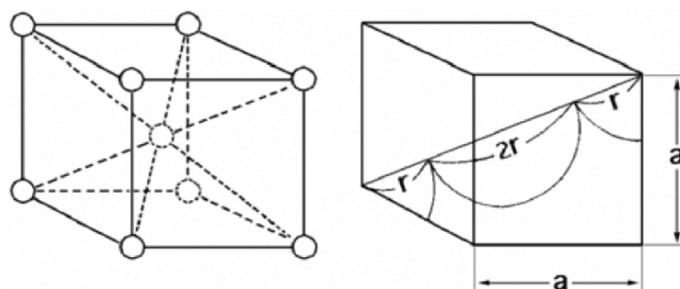


Figure 2-3. Face-centered cubic structure. Note the arrangement of atomic planes.

The *face-centered cubic* (fcc) structure is another cubic crystal, as shown in Figure 2-3. This structure is called *close packed* [actually, it should be called the *closest packed*] in three dimensions. Because each atom touches 12 neighbors [hence the *coordination number* ( $CN$ ) = 12] rather than six as in simple cubic, it results in a most efficiently packed structure. The *hexagonal close-packed* (hcp) structure is arranged by repeating layers of every other plane, that is, the atoms in the third layer occupy sites directly over the atoms in the first layer, as shown in Figure 2-4. This can be represented as ABAB..., while the fcc structure can be represented by three layers of planes ABCABC... Both hcp and fcc have the same packing efficiency (74%); both structures have the most efficient packed planes of atoms with the same coordination number.



**Figure 2-4.** Hexagonal close-packed structure. Compare the arrangement of atomic planes with fcc structure.



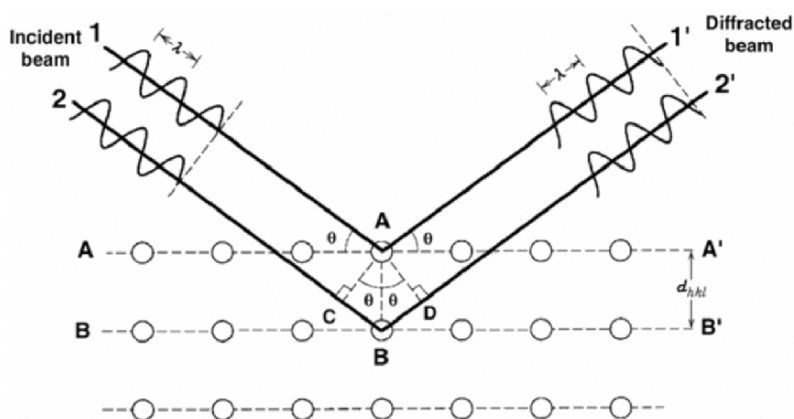
**Figure 2-5.** Body-centered cubic unit cell. Note that each unit cell has two atoms and  $4r = a/\sqrt{3}$ .

Another cubic structure is the body-centered cubic (bcc) structure, in which an atom is located in the center of the cube, as shown in Figure 2-5. This structure has a lower packing efficiency (68%) than the fcc structure. Other crystal structures include orthorhombic, in which the unit cell is a rectangular parallelepiped with unequal sides; hexagonal, with hexagonal prisms as unit cells; monoclinic, in which the unit cell is an oblique parallelepiped with one oblique angle and unequal sides; and triclinic, in which the unit cell has unequal sides and all oblique angles. Some examples of the crystal structures of real materials are presented in Table 2-2.

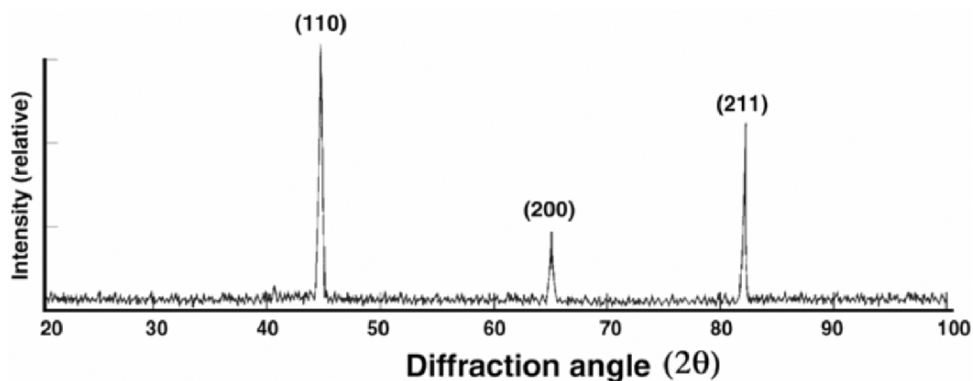
**Table 2-2.** Examples of Crystal Structures

Material	Crystal structure
Cr	bcc
Co	hcp (below 460°C) hcp (above 460°C)
Fe	bcc (below 912°C), ferrite ( $\alpha$ ) fcc (912–1394°C), austenite ( $\gamma$ ) bcc (above 1394°C), delta iron ( $\delta$ )
Mo	bcc
Ni	fcc
Ti	hcp (below 900°C) bcc (above 900°C)
Rock salt (NaCl)	fcc
Alumina ( $\text{Al}_2\text{O}_3$ )	hcp
Polyethylene	orthorhombic
Polyisoprene	orthorhombic

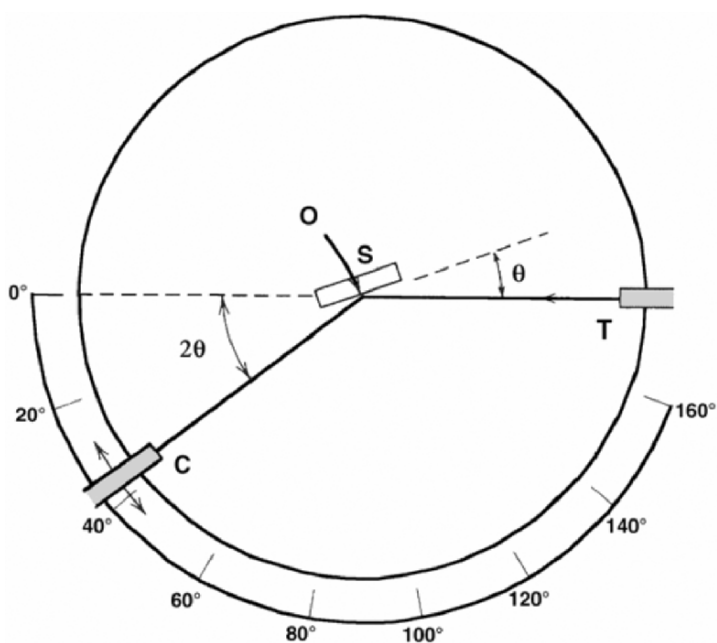
Determination of crystal structures is actually made by an x-ray instrument where monochromatic waves are diffracted from the planes of atoms, as shown in Figure 2-6. The diffracted x-rays are detected by film or recorded, as shown in Figure 2-7 for iron ( $\alpha$ -Fe). Figure 2-8 shows a schematic diagram of an x-ray diffractometer. The crystallographic directions and planes are expressed by Miller indices where  $(x,y,z)$  indicates the location of a point,  $[hkl]$  indicates the direction from  $(0,0,0)$  to  $(x,y,z)$  in whole numbers. For example,  $[111]$  indicates the direction from the origin to the point  $(1,1,1)$ , a diagonal direction. A family of directions is designated as  $\langle hkl \rangle$ . A crystallographic plane is designated by  $(hkl)$ , and a family of planes are designated by  $\{hkl\}$ .



**Figure 2-6.** X-ray diffraction by planes of atoms ( $AA'$  and  $BB'$ ).  $\lambda = BC + BD = 2AB \sin \theta = 2d_{hkl} \sin \theta$ . Modified with permission from Callister (2000). Copyright © 2000, Wiley.



**Figure 2-7.** X-ray diffraction pattern of polycrystalline  $\alpha$ -Fe. Reprinted with permission from Callister (2000). Copyright © 2000, Wiley.



**Figure 2-8.** Schematic diagram of an x-ray diffractometer; T: x-ray source; S: specimen; C: detector; and O: axis around which the specimen and detector rotate. Reprinted with permission from Callister (2000). Copyright © 2000, Wiley.

### Example 2.1

Iron (Fe) has a bcc structure at room temperature with atomic radius of  $1.24 \text{ \AA}$ . Calculate its density (atomic weight of Fe is  $55.85 \text{ g/mol}$ ).



**Answer**

From Figure 2-5,

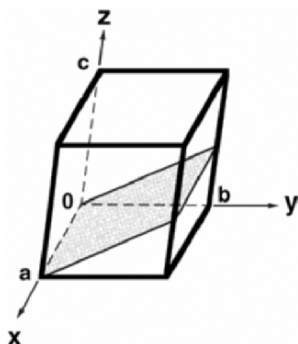
$$a = \frac{4r}{\sqrt{3}},$$

and the density ( $\rho$ ) is given by

$$\begin{aligned}\rho &= \frac{\text{weight/unit cell}}{\text{volume/unit cell}} \\ &= \frac{2 \text{ atoms/u.c.} \times 55.85 \text{ g/mol}}{(4 \times 1.24 / \sqrt{3} \times 10^{-24} \text{ cm})^3 / \text{u.c.} \times 6 \times 10^{23} \text{ atoms/mol}} \\ &= \underline{7.87 \text{ g/cm}^3}.\end{aligned}$$

**Example 2.2**

Determine the Miller indices for the plane shown:

**Answer**

Usually five steps are used to determine the Miller indices for a plane.

	$x$	$y$	$z$
Intercepts	$\infty$	$-b$	$c/2$
Intercepts in lattice spaces	$\infty$	$-1$	$1/2$
Reciprocal	$0$	$-1$	$2$
Reduction (not necessary)			
Enclosure		$(0\bar{1}2)$	

Note that the  $-1$  is expressed as  $\bar{1}$ .

**Example 2.3**

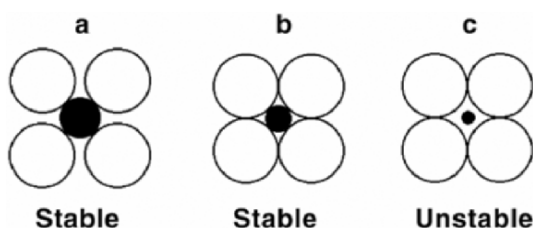
Determine the  $d_{110}$  of  $\alpha$ -Fe based on the diffraction pattern depicted in Figure 2-7. Fe has an atomic radius of 0.1241 nm (Appendix IV). The relationship between space  $d_{hkl}$  and lattice space  $a$  for a cubic unit cell is given as  $a = d_{hkl}(h^2 + k^2 + l^2)^{1/2}$ .

**Answer**

For a BCC unit cell,  $4r = \sqrt{3}a$ ,  $a = 0.1241 \times 4 / \sqrt{3} = 0.2866 \text{ nm}$ .

**2.2.2. Atoms of Different Size**

We seldom use pure materials for implants. Most of the materials used for implants are made of more than two elements. When two or more different sizes of atoms are mixed together in a solid, two factors must be considered: (1) the type of site and (2) the number of sites occupied. Consider the stability of the structure shown in Figure 2-9. In Figure 2-9a,b the interstitial atoms touch the larger atoms, and hence they are stable; but they are not stable in 2-9c. At some critical value the interstitial atom will fit the space between six atoms (only four atoms are shown in two dimensions), which will yield the maximum interaction between atoms and consequently the most stable structure results. Thus, at a certain radius ratio of the host and interstitial atoms the arrangement will be most stable. Figure 2-10 gives the maximum radius ratios for given coordination numbers. Note that these radius ratios are determined solely by geometric considerations.



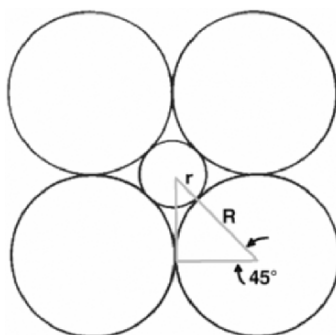
**Figure 2-9.** Possible arrangements of interstitial atoms as given in Figure 2-10. The critical radius for (b) is given by  $r + R = \sqrt{2}R$ ; hence  $r/R = 0.414$ .

**Example 2.4**

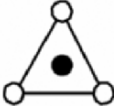
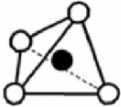
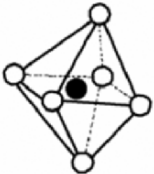
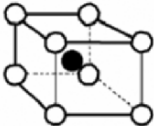

Calculate the minimum radius ratios for a coordination number of 6.

**Answer**

For coordination number 6, from Figure 2-10 looking down:



Two-dimensional representation of a structure with coordination number 6.

Structural geometry	Radius ratio	Coordination number
	0.155	3
	0.225	4
	0.414	6
	0.732	8
	1.0	12

**Figure 2-10.** Minimum radius ratios and coordination numbers.

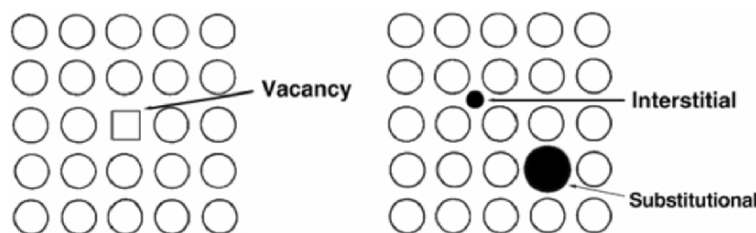
From the diagram,

$$\cos 45^\circ = \frac{R}{R+r}, \quad \frac{1}{\sqrt{2}} = \frac{R}{R+r},$$

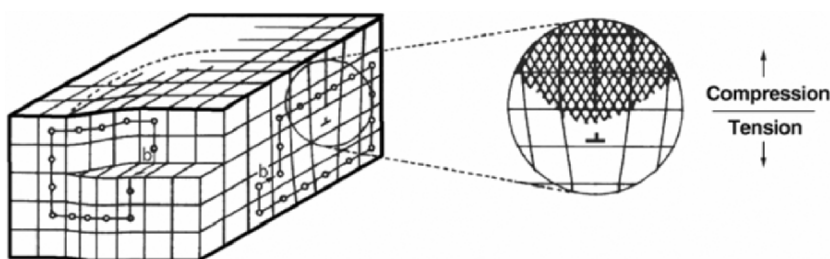
$$\sqrt{2}R = R+r, \quad \frac{r}{R} = \sqrt{2} - 1 = 0.414.$$

### 2.3. IMPERFECTIONS IN CRYSTALLINE STRUCTURES

Imperfections in crystalline solids are sometimes called defects, and they play a major role in determining their physical properties. Point defects commonly appear as lattice vacancies and substitutional or interstitial atoms, as shown in Figure 2-11. The interstitial or substitutional atoms are sometimes called alloying elements if placed intentionally, and impurities if they are unintentional.



**Figure 2-11.** Point defects in the form of vacancies and interstitials.



**Figure 2-12.** Line defects. The displacement is perpendicular to the edge dislocation but parallel to the screw dislocation (left-hand side). The unit length  $b$  has magnitude (one lattice space) and direction and is called a Burger's vector.

The line defects, called dislocations, are created when an extra plane of atoms is displaced or dislocated out of its regular lattice space registry (Figure 2-12). The line defects or dislocations will lower the strength of a solid crystal enormously since it takes much less energy to move or deform a whole plane of atoms one atomic distance at a time rather than all at once. This is analogous to moving a carpet or a heavy refrigerator on the floor. The carpet cannot be pulled easily if one tries to move it all at once, but if one folds it and propagates the fold until the fold reaches the other end, it can be moved without too much force. Similarly, the refrigerator can be moved easily if one puts one or two logs under it. However, if one uses too many logs (analogous to many dislocations), it becomes harder to move the refrigerator. Correspondingly, if a lot of dislocations are introduced in a solid the strength increases considerably. The reason is that the dislocations become entangled with each other, impeding their movement. The blacksmith practices this principle when he heats a horseshoe to red hot and hammers it. Hammering introduces dislocations. He has to repeat the heating and hammering process in order to increase the number of dislocations without breaking the horseshoe.

Planar defects exist at the grain boundaries. Grain boundaries are created when two or more crystals are mismatched at the boundaries. This occurs during crystallization. Within each grain all the atoms are in a lattice of one specific orientation. Other grains have the same crystal lattice but different orientations, creating a region of mismatch. The grain boundary is less dense than the bulk, hence most diffusion of gas or liquid takes place along the grain boundaries. Grain boundaries can be seen by polishing and subsequent etching of a "polycrystalline" material. This is due to the fact that the grain boundary atoms possess higher energy

than the bulk, resulting in a more chemically reactive site at the boundary. Figure 2-13 shows a polished surface of a metal implant. The size of grains plays an important role in determining the physical properties of a material. In general a fine-grained structure is stronger than a coarse one for a given material at a low recrystallization temperature since the former contains more grain boundaries, which in turn interfere with the movement of atoms during deformation, resulting in a stronger material.

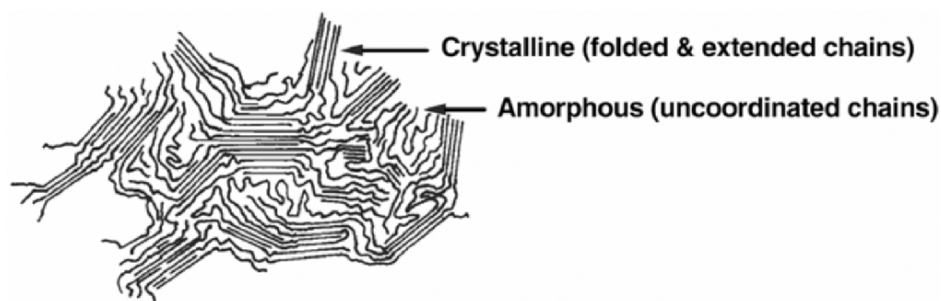


**Figure 2-13.** Midsection of a femoral component of a hip joint implant that show grains (Co–Cr alloy). Notice the size distribution along the stem and from the core to the surface.

## 2.4. LONG-CHAIN MOLECULAR COMPOUNDS (POLYMERS)

Polymers have very long-chain molecules that are formed by covalent bonding along the backbone chain. The long chains are held together either by secondary bonding forces — such as van der Waals and hydrogen bonds — or primary covalent bonding forces through crosslinks between chains. The long chains are very flexible and are easily tangled. In addition, each chain can have side groups, branches, and copolymeric chains or blocks that can also interfere with the long-range ordering of chains. For example, paraffin wax has the same chemical formula as polyethylene [ $(\text{CH}_2\text{CH}_2)_n$ ] but will crystallize almost completely because of its much shorter chain lengths. However, when the chains become extremely long [from 40 to 50 repeating units  $[-\text{CH}_2\text{CH}_2-]$  to several thousands as in linear polyethylene] they cannot be crystallized completely (up to 80–90% crystallization is possible). Also, branched polyethylene, in which side chains are attached to the main backbone chain at positions where a hydrogen atom normally occupies, will not crystallize easily due to the steric hindrance of side chains, resulting in a more noncrystalline structure. The partially crystallized structure is called semicrystalline which is the most commonly occurring structure for linear polymers. The semicrystalline

structure is represented by disordered noncrystalline regions and ordered crystalline regions, which may contain folded chains, as depicted in Figure 2-14.



**Figure 2-14.** Fringed (micelle) model of linear polymer with semicrystalline structure.

The degree of polymerization ( $DP$ ) is one of the most important parameters in determining polymer properties. It is defined as the average number of mers or repeating units per molecule, i.e., chain. Each chain may have a small or large number of mers depending on the condition of polymerization. In addition, the length of each chain may be different. Therefore, we deal with the average degree of polymerization or average molecular weight ( $MW$ ). The relationship between molecular weight and degree of polymerization can be expressed as

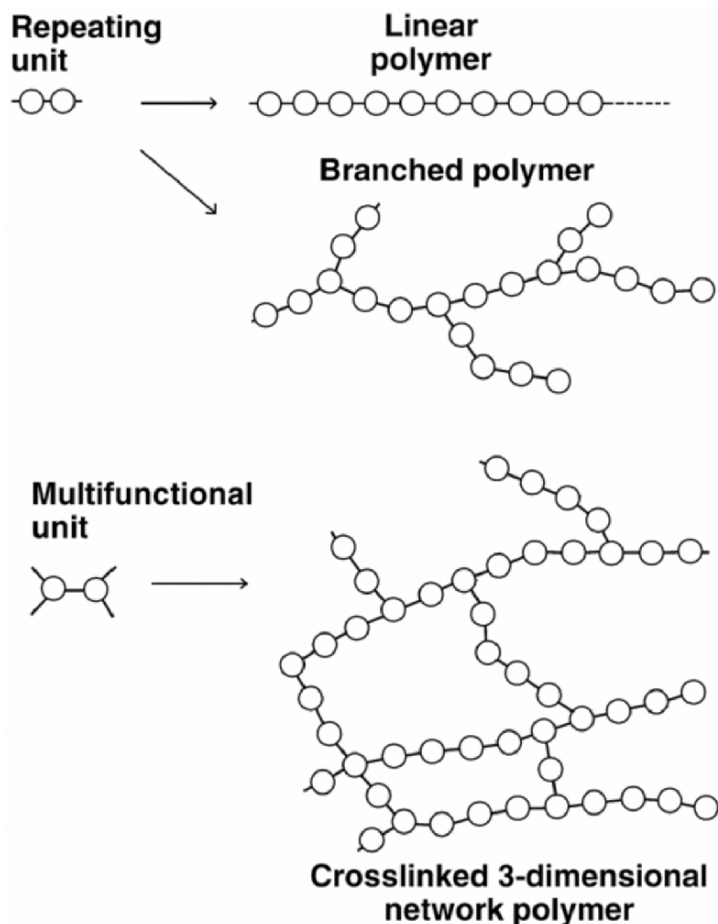
$$MW = DP \times MW \text{ of mer (or repeating unit)}, \quad (2-1)$$

The average molecular weight can be calculated according to the weight fraction ( $W_i$ ) in each molecular weight fraction ( $MW_i$ );

$$M_w = \frac{\sum W_i \cdot MW_i}{\sum W_i} = \sum W_i MW_i, \quad (2-2)$$

since  $\sum W_i = 1$ . This is the average molecular weight.

As the molecular chains become longer by the process of polymerization, their relative mobility decreases. Chain mobility is also related to the physical properties of the final polymer. Generally, the higher the molecular weight, the lesser the mobility of chains, which results in higher strength and greater thermal stability. The polymer chains can be arranged in three ways: linear, branched, and a crosslinked or three-dimensional network, as shown in Figure 2-15. Linear polymers such as polyvinyls, polyamides, and polyesters are much easier to crystallize than the crosslinked or branched polymers. However, they cannot be crystallized 100% as with metals. Instead they become semicrystalline polymers. The arrangement of chains in crystalline regions is believed to be a combination of folded and extended chains. The chain folds, which are seemingly more difficult to form, are necessary to explain observed single crystal structures in which the crystal thickness is too small to accommodate the length of the chain as determined by electron and x-ray diffraction studies. Figure 2-16 shows the two-dimensional representation of chain arrangements. The classical “fringed micelle” model (Figure 2-14) in which the amorphous and crystalline regions coexist has been modified to include chain folds in the crystalline regions.



**Figure 2-15.** Types of polymer chains.

Such crosslinked or three-dimensional network polymers as (poly)phenolformaldehyde cannot be crystallized at all and become noncrystalline, amorphous polymers.

Vinyl polymers have a repeating unit,  $-\text{CH}_2-\text{CHX}-$ , where X is a monovalent side group. There are three possible arrangements of side groups X: (1) atactic, (2) isotactic, and (3) syndiotactic, as shown in Figure 2-17. In atactic arrangements the side groups are randomly distributed, while in syndiotactic and isotactic arrangements they are either in alternating positions or on one side of the main chain. If side groups are small as in polyethylene ( $\text{X}=\text{H}$ ) and the chains are linear, the polymer crystallizes easily. However, if the side groups are large as in polyvinyl chloride ( $\text{X}=\text{Cl}$ ) and polystyrene ( $\text{X}=\text{C}_6\text{H}_5$ , benzene ring) and are randomly distributed along the chains (atactic), then a noncrystalline structure will be formed. The isotactic and syndiotactic polymers usually crystallize even when the side groups are large. Note that polyethylene does not have tacticity since it has symmetric side groups.

Copolymerization, in which two or more homopolymers (repeating units of one type throughout its structure) are chemically combined, always disrupts the regularity of polymer chains, thus promoting the formation of noncrystalline structure (Figure 2-18). Plasticizers

may be added to a polymer to achieve greater compliance. Plasticizers contain small molecules that facilitate the movement of the long-chain molecules of the polymer itself. Plasticizers also prevent crystallization by keeping the molecular chains separated from one another. This results in a noncrystalline version of a polymer that normally crystallizes. An example is celluloid, which is made of normally crystalline nitrocellulose plasticized with camphor. Plasticizers are also used to make rigid noncrystalline polymers like polyvinylchloride (PVC) into a more flexible solid (a good example is Tygon<sup>®</sup> tubing).

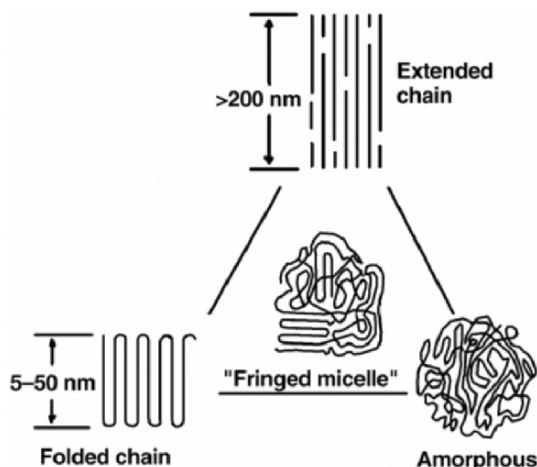


Figure 2-16. Two-dimensional representation of polymer solid.

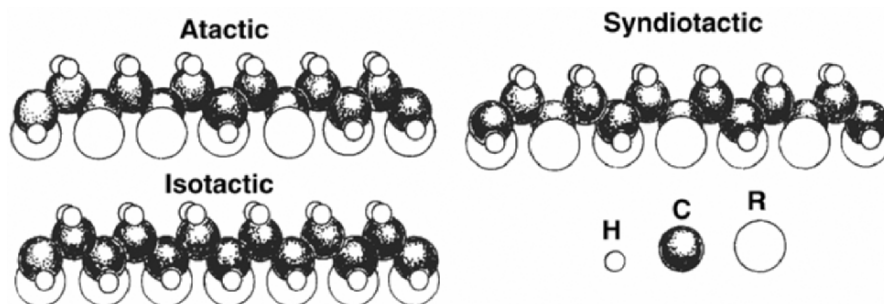
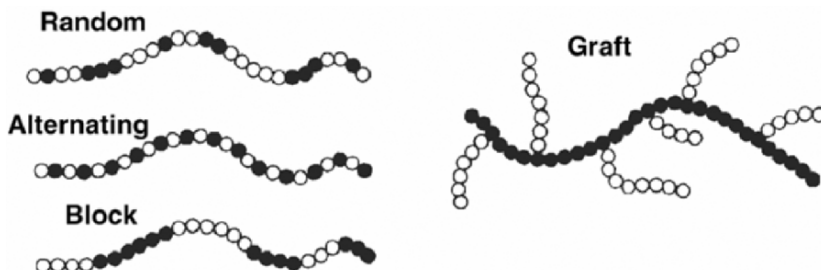


Figure 2-17. Tacticity of vinyl polymers.

Elastomers or rubbers are polymers that exhibit low stiffness and high stretchability at room temperature. They snap back to their original dimensions when the load is released. The elastomers are noncrystalline polymers that have an intermediate structure consisting of long-chain molecules in three-dimensional networks (see the next section for more details). The chains also have “kinks” or “bends” in them that straighten when a load is applied. For example, the chains of cis-polyisoprene (natural rubber) are bent at the double bond due to the methyl group interfering with the neighboring hydrogen in the repeating unit  $[-\text{CH}_2-\text{C}(\text{CH}_3)=\text{CH}-\text{CH}_2-]$ . If the methyl group is on the opposite side of the hydrogen, then it be-



comes trans-polyisoprene, which will crystallize due to the absence of the steric hindrance present in the cis form. The resulting polymer is a very rigid solid called gutta percha, which is not an elastomer.



**Figure 2-18.** Possible arrangements of copolymers.

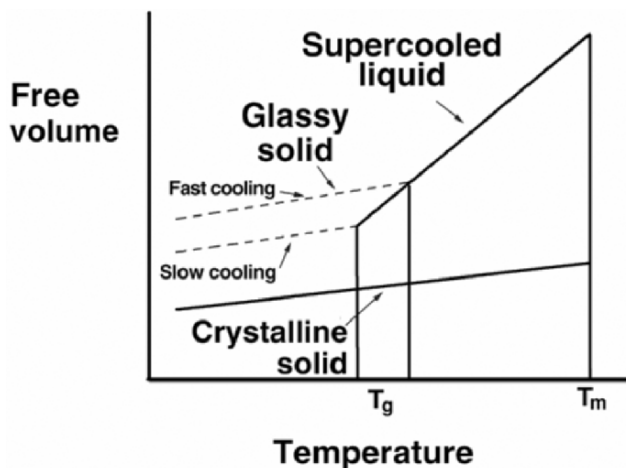
Below the glass transition temperature ( $T_g$ ; second-order transition temperature between viscous liquid and solid) natural rubber loses its compliance and becomes a glass-like material. Therefore, to be flexible, all elastomers should have  $T_g$  well below room temperature. What makes the elastomers not behave like liquids above  $T_g$  is in fact due to the crosslinks between chains that act as pinning points. Without crosslinks the polymer would deform permanently. An example is latex, which behaves as a viscous liquid. Latex can be crosslinked with sulfur (vulcanization) by breaking double bonds ( $C=C$ ) and forming  $C-S-S-C$  bonds between the chains. The more crosslinks are introduced, the more rigid the structure becomes. If all the chains are crosslinked together, the material will become a three-dimensional rigid polymer.

## 2.5. SUPERCOOLED AND NETWORK SOLIDS

Some solids such as window glass do not have a regular crystalline structure. Solids with such an atomic structure are called amorphous or noncrystalline materials. They are usually supercooled from the liquid state and thus retain a liquid-like molecular structure. Consequently, the density is always less than that of the crystalline state of the same material, indicating inclusion of some voids (free volume, Figure 2-19). Due to the metastable state of the structure, the amorphous material tends to slowly crystallize with time. The process may be so slow (as in window glass) that crystallization is never seen over humanly accessible time scales. Amorphous materials are also more brittle and less strong than their crystalline counterparts. It is very difficult to make metals amorphous since the metal atoms are extremely mobile in the liquid state, and crystallization to a solid is abrupt. However, one can make amorphous metal from liquid metal by cooling the melt sufficiently rapidly. This is done by splat cooling in which a thin layer of liquid is rapidly placed in contact with a highly heat-conductive metal plate at low temperature. This process causes the amorphous structure of the liquid to be preserved in the solid, since there is insufficient time for crystallization. Polymers can be easily made amorphous because of the relatively sluggish mobility of their molecules.

The network structure of a solid results in a three-dimensional, amorphous structure since the restrictions on the bonds and rigidity of subunits prevent them from crystallizing. Common

network structure materials are phenolformaldehyde (Bakelite®) polymer and silica ( $\text{SiO}_2$ ) glass, as shown in Figure 2-20. The network structure of phenolformaldehyde is formed by crosslinking through the phenol rings, while the Si–O tetrahedra are joined corner to corner via oxygen atoms. The three-dimensional network solids do not flow at high temperatures.



**Figure 2-19.** Change of volume versus temperature of a solid. The glass transition temperature ( $T_g$ ) depends on the rate of cooling; below  $T_g$  the material behaves as a solid like a window glass.

### Example 2.3

Calculate the free volume of 100 g of iodine supercooled from the liquid state, which has a density of  $4.8 \text{ g/cm}^3$ . Assume the density of amorphous iodine is  $4.3 \text{ g/cm}^3$  and the crystalline density is  $4.93 \text{ g/cm}^3$ .

### Answer

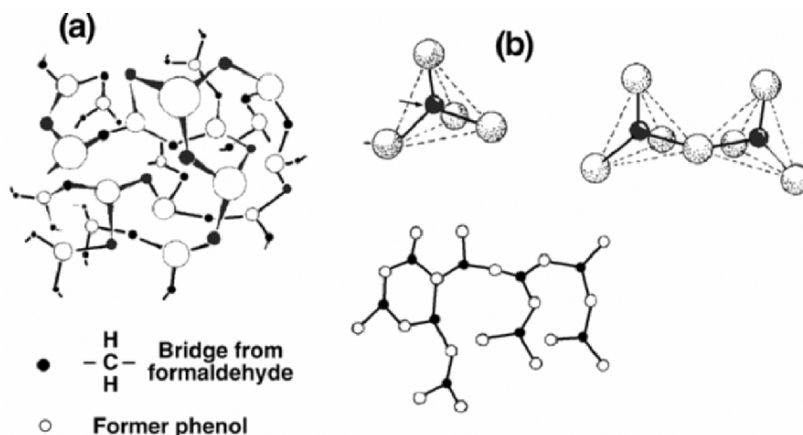
The fraction of supercooled iodine can be calculated by extrapolation. We consider the density to be proportional to crystallinity and calculate the slope of the line:

$$\frac{4.93 - 4.8}{4.93 - 4.3} = 0.21.$$

The weight of the supercooled liquid is  $0.21 \times 100 \text{ g} = 21 \text{ g}$ ; therefore, the total free volume is

$$\left( \frac{1}{4.3} \frac{\text{cm}^3}{\text{g}} - \frac{1}{4.93} \frac{\text{cm}^3}{\text{g}} \right) \times 21 \text{ g} = \underline{0.65 \text{ cm}^3}.$$

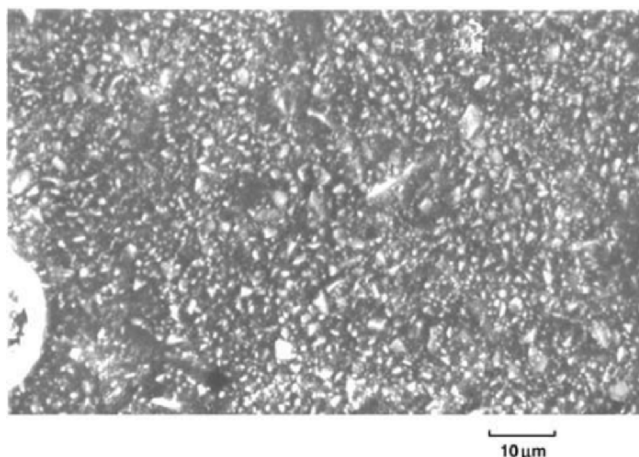
Upon complete crystallization, the volume of the iodine will decrease by  $0.65 \text{ cm}^3$ .



**Figure 2-20.** Network structure of noncrystalline solids: (a) phenolformaldehyde (Bakelite®); (b) silica glass structure. Subunit  $\text{SiO}_4$  is a tetrahedron with a silicon atom at its center.

## 2.6. COMPOSITE MATERIAL STRUCTURE

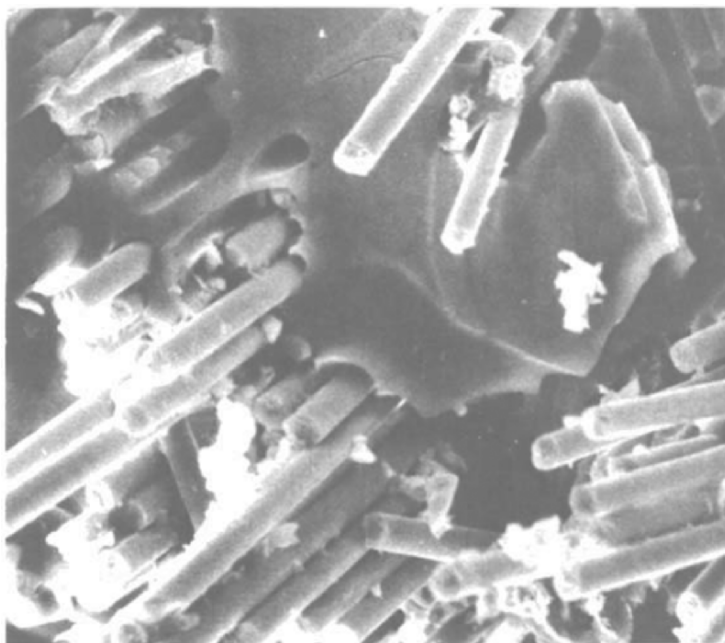
Composite materials are those which consist of two or more distinct parts. The term “composite” is usually reserved for those materials in which the distinct phases are separated on a scale larger than the atomic, and in which properties such as the elastic modulus are significantly altered in comparison with those of a homogeneous material. Accordingly, bone and fiberglass are viewed as composite materials, but alloys such as brass or metals such as steel with carbide particles are not. Although many engineering materials, including biomaterials, are not composites, virtually all natural biological materials are composites.



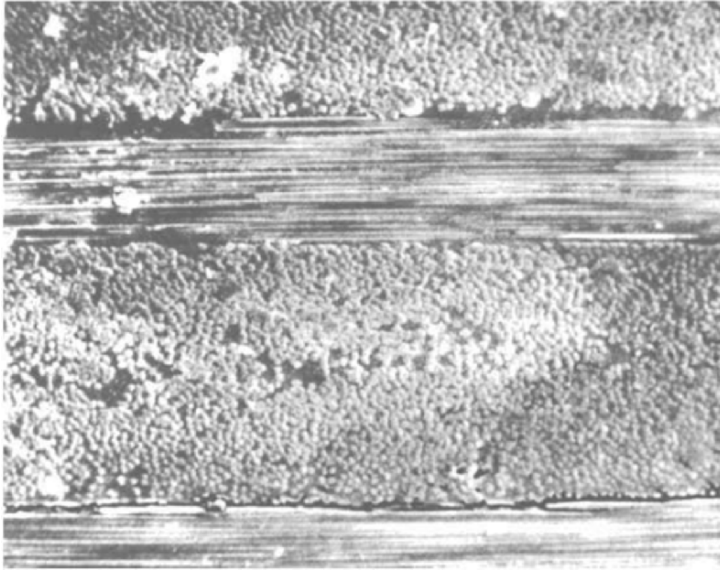
**Figure 2-21.** Dental composite. The particles are silica ( $\text{SiO}_2$ ) and the matrix is polymeric. Reprinted with permission from Boyer (1989). Courtesy of the author.

The properties of a composite material depend upon the shape of the heterogeneities (second-phase material), upon the volume fraction occupied by them, and upon the stiffness and integrity of the interface between constituents. The shape of the heterogeneities in a composite material is classified as follows. Possible inclusion shapes are the particle, with no long dimension; the fiber, with one long dimension; and the platelet or lamina, with two long dimensions. Cellular solids are those in which the “inclusions” are voids, filled with air or liquid. In the context of biomaterials, it is necessary to distinguish the above cells, which are structural, from biological cells, which occur only in living organisms.

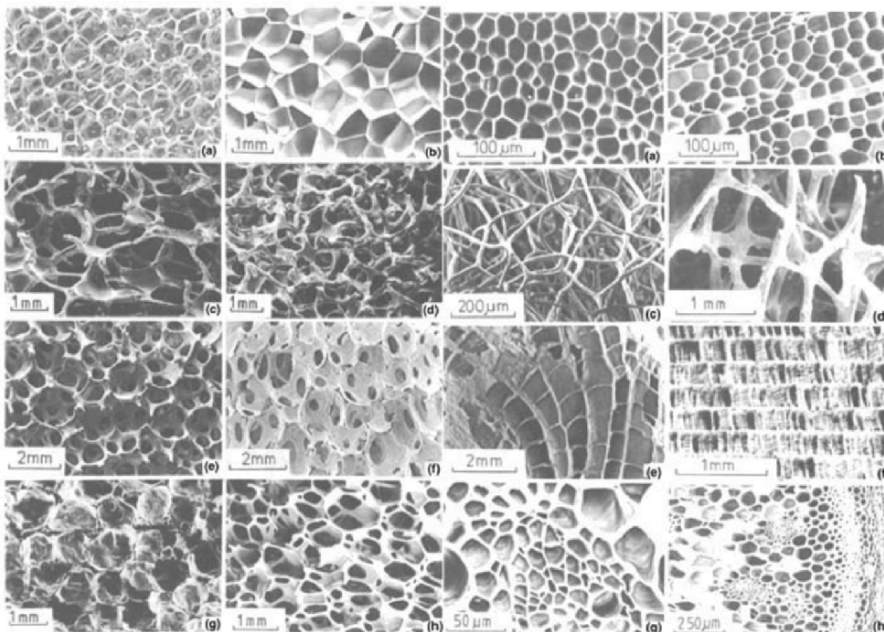
Examples of composite material structures are as follows. The dental composite filling material shown in Figure 2-21 has a particulate structure. This material is packed into the tooth cavity while still soft, and the resin is polymerized in situ. The silica particles serve to provide hardness and wear resistance superior to that of the resin alone. A typical fibrous solid is shown in Figure 2-22. The fibers serve to stiffen and strengthen the polymeric matrix. In this example, pullout of fibers during fracture absorbs mechanical energy, conferring toughness on the material. Fibers have been added to the polymeric parts of total joint replacement prostheses, in an attempt to improve the mechanical properties. Figure 2-23 shows a laminated structure in which each lamina is fibrous, while Figure 2-24 shows representative synthetic cellular materials.



**Figure 2-22.** Glass-fiber-epoxy composite: fracture surface showing fiber pullout. Reprinted with permission from Agarwal and Broutman (1980). Copyright © 1980, Wiley.



**Figure 2-23.** Structure of a cross-ply laminate. Reprinted with permission from Agarwal and Broutman (1980). Copyright © 1980, Wiley.



**Figure 2-24.** Synthetic (a) and natural (b) cellular materials. Reprinted with permission from Gibson and Ashby (1988). Copyright © 1988, Pergamon Press.

The properties of composite materials depend very much upon structure, as they do in homogeneous materials. Composites differ in that the engineer has considerable control over the larger-scale structure, and hence over the desired properties. The relevant structure–property relations will be developed in Chapter 8.

## PROBLEMS

- 2-1. Identify the type of bond (ionic or covalent) in the following compounds. (a) ammonia ( $\text{NH}_3$ ), (b) salt ( $\text{NaCl}$ ), (c) carbon tetrachloride ( $\text{CCl}_4$ ), (d) hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), (e) ozone ( $\text{O}_3$ ), (f) ethylene ( $\text{CH}_2=\text{CH}_2$ ), (g) water ( $\text{H}_2\text{O}$ ), (h) magnesium oxide ( $\text{MgO}$ ), and (i) diamond ( $\text{C}$ ).
- 2-2. Calculate the number of atoms present per  $\text{cm}^3$  for alumina ( $\text{Al}_2\text{O}_3$ ), which has a density of  $3.8 \text{ g/cm}^3$ .
- 2-3. Calculate the diameters of the smallest cations that have a 6- and 8-fold coordination with  $\text{O}^{2-}$  ions (see Table 6-1 and Figure 2-10).
- 2-4. Steel contains carbon, which forms iron carbide ( $\text{Fe}_3\text{C}$ ). Determine the weight percentage of carbon in  $\text{Fe}_3\text{C}$ .
- 2-5. A metal alloy of 92.5 w/o Ag and 7.5 w/o Cu is called sterling silver. Determine the atomic percentage of silver.
- 2-6. Titanium (Ti) is bcc above  $882^\circ\text{C}$ . The atomic radius increases 2% when the bcc structure changes to hcp during cooling. Determine the percentage volume change. Hint: there will be a change in the atomic packing factor.
- 2-7. The molecular weight of polymers can be either a number or weight average ( $M_n$  or  $M_w$ ) which are defined as

$$M_n = \frac{\sum (N_i M_i)}{\sum N_i} \quad \text{and} \quad M_w = \frac{\sum (W_i M_i)}{\sum W_i},$$

where  $N_i$  is the number of molecules with molecular weight  $M_i$ ,  $M_i$  is the molecular weight of the  $i$ th species, and  $W_i$  is the weight fraction of molecules of the  $i$ th species. Show that

$$M_n = \frac{1}{\sum (W_i / M_i)}.$$

- 2-8. Calculate the weight of an iron atom. The density of iron is  $7.87 \text{ g/cm}^3$ . Avogadro's number is  $6.02 \times 10^{23}$ . How many iron atoms are contained in a cubic centimeter?
- 2-9. A polyethylene is made of the following weight distributions (see chart).
  - a. Calculate  $M_n$ ,  $M_w$ , and  $M_w/M_n$  (polydispersity).
  - b. Plot  $W_i$  versus  $M_i$  and also  $M_w$  and  $M_n$  in the same plot.
  - c. Why is  $M_w$  always greater than  $M_n$ ?

$W_i$ (grams)	10	20	30	30	10
$M_i$ (kg/mol)	10	20	30	40	50

- 2-10. Ultrahigh-molecular-weight polyethylene is used to make the acetabular cup of a hip joint prosthesis. If the average molecular weight is 2.8 mg/mol,
- Calculate the number of repeating units (monomer,  $-\text{CH}_2-\text{CH}_2-$ ) in an average chain molecule.
  - Calculate the length of the stretched chain. Due to the tetrahedral structure of the carbon, a C–C–C bond will make an  $108^\circ$  angle, resulting in a 0.126-nm bond length projected horizontally even though the C–C bond length is 0.154 nm.
  - Calculate  $M_n$  if the polydispersity is 1.5.

## SYMBOLS/DEFINITIONS

### Greek letters

$\rho$ : Density, mass per unit volume.

### Latin letters

***a***: Lattice constant, which is the spacing of atoms in a crystal lattice. For example, in cubic crystal systems all the lattice constants are the same, i.e.,  $a = b = c$ , so that the atomic spacing is the same in each principal direction.

**bcc**: Body-centered cubic lattice; one atom is positioned in the center of the cubic unit cell.

**CN**: Coordination number; number of atoms touching an atom in the middle.

**fcc**: Face-centered cubic lattice; one atom is positioned in each face of the cubic unit cell.

**hcp**: Hexagonal close-packed lattice; twelve atoms surround and touch a central atom of the same species resulting in the hexagonal prism symmetry.

**$M_n$** : Average molecular weight of a polymer (number).

**$M_w$** : Average molecular weight of a polymer (weight).

**$r, R$** : Radius of an atom.

**$T_g$** : Glass transition temperature at which solidification without crystallization takes place from a viscous liquid.

### Words

**Composites**: Materials obtained by combining two or more materials at a scale larger than the atomic/molecular, e.g., nanoscale, microscale, or macroscale, taking advantage of salient features of each material. An example is (high-strength) fiber-reinforced epoxy resin.

**Copolymers**: Polymers made from two or more homopolymers; can be obtained by grafting, block, alternating, or random attachment of the other polymer segment.

**Covalent bonding**: Bonding of atoms or molecules by sharing valence electrons.

**Elastomers**: Rubbery materials. The restoring force comes from uncoiling or unkinking of coiled or kinked molecular chains. They can be highly stretched.

**Free volume**: The difference in volume occupied by the crystalline state (minimum) and non-crystalline state of a material for a given temperature and a pressure.

**Glass transition temperature ( $T_g$ )**: see  $T_g$ .

**Hydrogen bonding:** A secondary bonding through dipole interactions in which a hydrogen ion is one of the dipoles.

**Ionic bonding:** Bonding of atoms or molecules through electrostatic interaction of positive and negative ions.

**Imperfections:** Defects created in a perfect (crystalline) structure by vacancy, interstitial, and substitutional atoms by the introduction of an extra plane of atoms (dislocations) or by mismatching at the crystals during solidification (grain boundaries).

**Lattice constant:** The spacing of atoms in a crystal lattice. For example, in cubic crystal systems all the lattice constants are the same, i.e.,  $a = b = c$ , so that the atomic spacing is the same in each principal direction.

**Metallic bonding:** Bonding of atoms or molecules through loosely bound valence electrons around positive metal ions.

**Minimum radius ratio ( $r/R$ ):** Ratio between the radius of a smaller atom to be fitted into the space among the larger atom's radius based on geometric consideration.

**Packing efficiency:** The (atomic) volume per unit volume (or space).

**Plasticizer:** Substance made of small molecules, mixed with (amorphous) polymers to make the chains slide more easily past each other, making the polymer less rigid.

**Polycrystalline:** Structure of a material that is an aggregate of single crystals (grains).

**Semiconductivity:** Electrical conductivity of a material lies between that of a conductor and an insulator. There is an energy band gap of the order of 0.1 eV (Sn) to 6 eV (C, diamond), which governs the conductivity and its dependence on temperature.

**Semicrystalline solid:** Solid that contains both crystalline and noncrystalline regions; for example, in polymers due to their long-chain molecules.

**Steric hindrance:** Geometrical interference that restrains movement of molecular groups such as side chains and main chains of a polymer.

**Tacticity:** Arrangement of asymmetrical side groups along the backbone chain of polymers; groups could be distributed at random (atactic), on one side (isotactic), or alternating (syndiotactic).

**Unit cell:** Smallest repeating unit of a space lattice representing the whole crystal structure.

**Valence electrons:** Outermost (shell) electrons of an atom.

**van der Waals bonding:** Secondary bonding arising through the fluctuating dipole–dipole interactions.

**Vinyl polymers:** Thermoplastic linear polymers synthesized by free radical polymerization of vinyl monomers having a common structure of  $\text{CH}_2=\text{CHR}$ .

**Vulcanization:** Crosslinking of rubbers by sulfur.

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