States of Matter

A Chem1 Reference Text

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1 Microscopic and macroscopic properties of matter

There are two contrasting views we can take of matter. At the most fundamental level is the *microscopic* view in which we regard matter as a collection of atoms and molecules. This is essential for understanding the chemical changes a substance is able to undergo, but it is not usually what we consider when we look at the material world in which we live. What we experience with our senses is the *macroscopic* view associated the *bulk* properties of matter such as its density, color, mechanical- and electrical properties. It is these properties that are generally of immediate practical interest, but a bit of reflection will convince you that the macroscopic properties must ultimately be governed by what happens at the atomic and molecular levels. A major purpose of this unit is to help you understand the connections between these two contrasting views.

What distinguishes solids, liquids, and gases– the so-called *states of matter*–, from each other? Let us begin at the microscopic level, by reviewing what we know about gases, the simplest state in which matter can exist. At ordinary pressures, the molecules of a gas are so far apart that intermolecular forces have an insignificant effect on the random thermal motions of the individual particles. As the temperature decreases and the pressure increases, intermolecular attractions become more important, and there will be an increasing tendency for molecules to form temporary clusters. These are so short-lived, however, that even under extreme conditions, gases cannot be said to possess "structure" in the usual sense.

The contrast at the microscopic level between solids, liquids and gases is most clearly seen in the simplified schematic views in Fig. 1. The molecular units of solids tend to be highly ordered, with each unit occupying a fixed position with respect to the others. In liquids, the molecules are able to slip around each other, introducing an element of disorder and creating some void spaces that decrease the density. Gases present a picture of almost total disorder, with practically no restrictions on where any one molecule can be.

Fig. 1 provides a simplified 2-dimensional microscopic view of the distinctions between the three states of matter.

1.1 Solids, liquids and gases: how to tell them apart

Having lived our lives in a world composed of solids, liquids, and gases, few of us ever have any difficulty deciding into which of these categories a given sample of matter falls. Our decision is most commonly based on purely visual cues: a gas is transparent and has no definite boundaries other than those that might be imposed by the walls of a confining vessel. Liquids and solids possess clearly delineated *phase boundaries* that give solids their definite shapes and whose light-reflecting properties enable us to distinguish one phase from another. Solids can have any conceivable shape, and their surfaces are usually too irregular to show specular (mirror-like) reflection of light. Liquids, on the other hand, are *mobile;* except

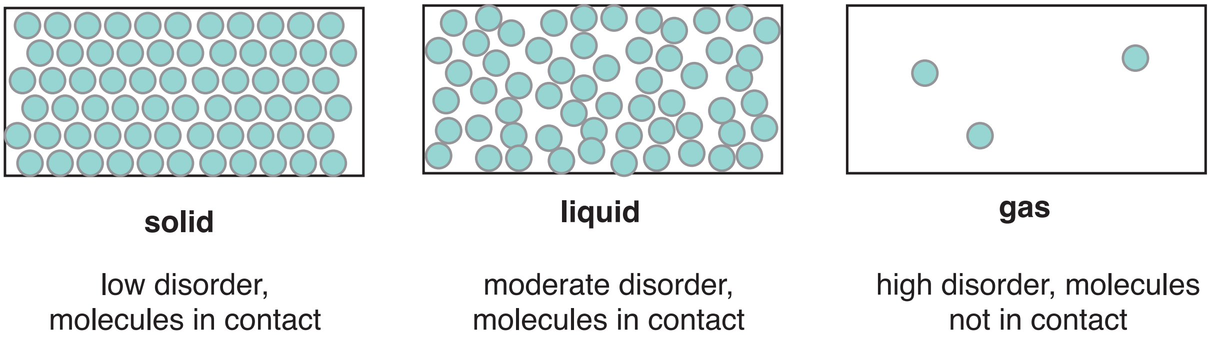


Figure 1: Schematic representations of the states of matter in terms of density and disorder.

property	*gas*	*liquid*	*solid*
density	small	large	large
thermal expansion coefficient	large ($= R \div P$)	small	small
cohesiveness	nil	small	large
surface tension	nil	medium	very large
viscosity	small	medium	very large
kinetic energy per molecule	large	small	smaller
disorder	very large	medium	small

Table 1: Relative magnitudes of some properties of the three states of matter

when suspended as droplets, liquids have no inherent shape of their own, but assume the shape of their container and show an approximately flat upper surface.

Our experience also tells us that these categories are quite distinct; a phase, which you will recall is a region of matter having uniform intensive properties, is either a gas, a liquid, or a solid. Thus the three states of matter are not simply three points on a continuum; when a solid melts to a liquid, it usually does so at a definite temperature, without apparently passing through any states that are intermediate between a solid and a liquid.

Although these common-sense perceptions are usually correct, they are not infallible, and in fact there are gases that are *not* transparent, there are solids such as glasses and many plastics that undergo a gradual transition from solid to liquid known as *softening*, and when subject to enough pressure, solids can exhibit something of the flow properties of liquids (glacial ice, for example).

A more scientific approach would be to compare the macroscopic physical properties of the three states of matter, but even here we run into difficulty. It is true, for example, that the *density* of a gas is usually about a thousandth of that of the liquid or solid at the same temperature and pressure; thus one gram of water vapor at 100 °C and 1 atm pressure occupies a volume of 1671 mL; when it condenses to liquid water at the same temperature, it occupies only 1.043 mL. It is this extreme contrast with the gaseous states that leads to the appellation "*condensed* states of matter" for liquids and solids. However, gases at very high pressures can have densities that exceed those of other solid and liquid substances, so density alone is not a sufficiently comprehensive criterion for distinguishing between the gaseous and condensed states of matter.

Problem Example 1

Compare the density of gaseous xenon (131 g/mol) at 100 atm and 0 °C with that of a hydrocarbon liquid for which $\rho = 0.104$ g/ml at the same temperature.

Similarly, the density of a solid is usually greater than that of the corresponding liquid at the same temperature and pressure, but not always: you have certainly seen ice floating on water.

Other physical properties, such as the *compressibility*, *surface tension*, and *viscosity*, are somewhat more useful for distinguishing between the different states of matter. Even these, however, provide no well-defined dividing lines between the various states.

Rather than try to develop a strict scheme for classifying the three states of matter, it will be more useful to simply present a few generalizations (Table 1, above.)

Some of these deal with macroscopic properties (that is, properties such as the density that relate to *bulk matter*), and others with microscopic properties that refer to the individual molecular units.

1.2 Equations of state

In our study of gases, we showed that the macroscopic properties of a gas (the pressure, volume, and temperature) are related through an equation of state, *and that for the limiting case of an ideal gas, this equation of state can be derived from the relatively small set of assumptions of the kinetic molecular theory.*

Is there a somewhat more elaborate theory that can predict the behavior of the other two principal states of matter, liquids and solids? Very simply, the answer is "no"; despite much effort, no one has yet been able to derive a general equation of state for liquids or solids. The best one can do is to construct models based on the imagined interplay of attractive and repulsive forces, and then test these models by computer simulation.

Nevertheless, the very factors that would seem to make an equation of state for liquids and solids impossibly complicated also give rise to new effects that are easily observed, and which ultimately define the distinguishing characteristics of the gaseous, liquid, and solid states of matter. In this unit, we will try to learn something about these distinctions, and how they are affected by the chemical constitution of a substance.

2 Condensed matter and structure

Even the most casual inspection of Fig. 1 shows that solids and liquids possess an important commonality that distinguishes them from gases: in solids and liquids, the molecules are in contact with their neighbors. As a consequence, these *condensed states of matter* possess much higher densities than gases.

2.1 Structure of liquids

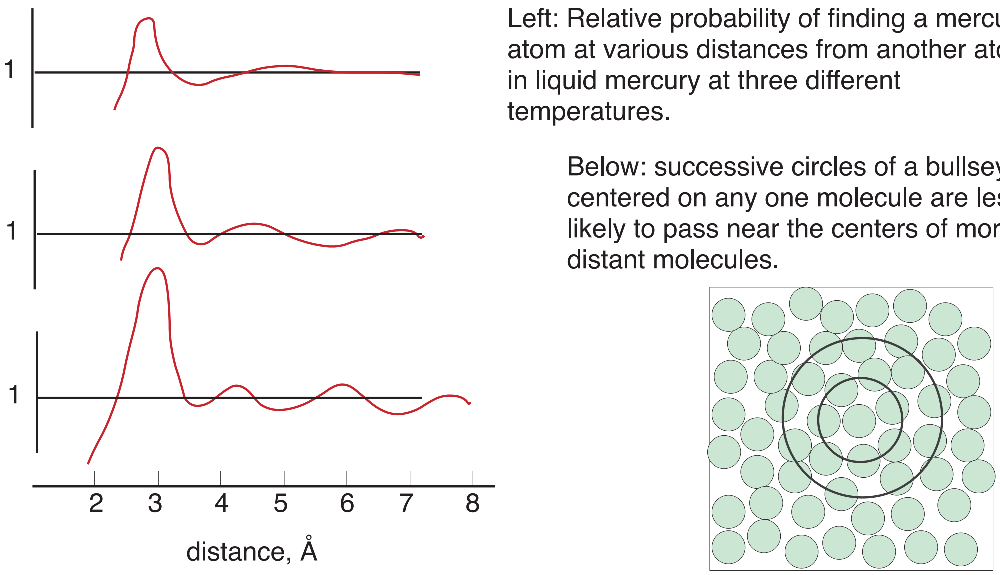
You can think of a simple liquid such as argon or methane as a collection of loosely-packed marbles that can assume various shapes. Although the overall arrangement of the individual molecular units is entirely random, there is a certain amount of short-range order: the presence of one molecule at a given spot means that the neighboring molecules must be at least as far away as the sum of the two radii, and this in turn affects the possible locations of more distant concentric shells of molecules.

An important consequence of the disordered arrangement of molecules in a liquid is the presence of void spaces. These, together with the increased kinetic energy of colliding molecules which helps push them apart, are responsible for the approximately 15-percent decrease in density that is observed when solids based on simple spherical molecules such as Ne and Hg melt into liquids. These void spaces are believed to be the key to the flow properties of liquids; the more "holes" there are in the liquid, the more easily the molecules can slip and slide over one another.

As the temperature rises, thermal motions of the molecules increase and the local structure begins to deteriorate, as shown in Fig. 2.

There is very little experimental information on the structure of liquids, other than the X-ray diffraction studies that yield plots such as in Fig. 2. It is very difficult to design experiments that yield the kind of information required to define the microscopic arrangement of molecules in the liquid state.

Many of our current ideas on the subject come from computer simulations based on hypothetical models. In a typical experiment, the paths of about 1000 molecules in a volume of space are calculated. The molecules are initially given random kinetic energies whose distribution is consistent with the Boltzmann distribution for a given temperature. The trajectories of all the molecules are followed as they change with time due to collisions and other interactions; these interactions must be calculated according to an assumed potential energy-vs.-distance function that is part of the particular model being investigated.



Left: Relative probability of finding a mercury atom at various distances from another atom in liquid mercury at three different temperatures.

Below: successive circles of a bullseye centered on any one molecule are less likely to pass near the centers of more distant molecules.

Figure 2: Short-range structure in liquids.

> *These computer experiments suggest that whatever structure simple liquids do possess is determined mainly by the repulsive forces between the molecules; the attractive forces act in a rather non-directional, general way to hold the liquid together. It is also found that if spherical molecules are packed together as closely as geometry allows (in which each molecule would be in contact with twelve nearest neighbors), the collection will have a long-range order characteristic of a solid until the density is decreased by about ten percent, at which point the molecules can slide around and move past one another, thus preserving only short-range order.*
>
> *In recent years, experimental studies based on ultra-short laser flashes have revealed that local structures in liquids have extremely short lifetimes, of the order of picoseconds to nanoseconds.*

The volume of a liquid, unlike that of a gas, is hardly affected at all by an increase in the pressure; we say that the *compressibility* $(\frac{1}{V}\frac{dV}{dP})$ is very small. The obvious interpretation of this fact is that the molecules of a liquid must be in "direct contact" with one another, so that any attempt to squeeze them even closer is strongly opposed by the repulsive forces between the electron clouds of neighboring molecules. This ability of a liquid to transmit a force is the basis of the hydraulically operated brake system in your car: the pressure of your foot on the brake pedal is instantly transmitted to the cylinders that operate mechanical brakes on each of the wheels.

2.2 Structure of water

Many liquids are composed of molecules that exert specific and often highly directional forces on each other. The most notable example of such a liquid is water, in which a hydrogen atom of one H_2O molecule is attracted to the oxygen atom of another molecule. This effect known as *hydrogen bonding;* hydrogen bonds are weaker than ordinary chemical bonds, so in liquid water they are continually being broken by thermal motions and then reformed in a slightly different configuration. Hydrogen bonding is responsible for the so-called *anomalous properties* of water that make it an unusual and unique substance.

The most energetically favorable configuration of H_2O molecules is one in which each molecule is hydrogen-bonded to three neighboring molecules. Owing to the thermal motions described above, this ideal is never achieved in the liquid, but when water freezes to ice, the molecules settle into exactly this

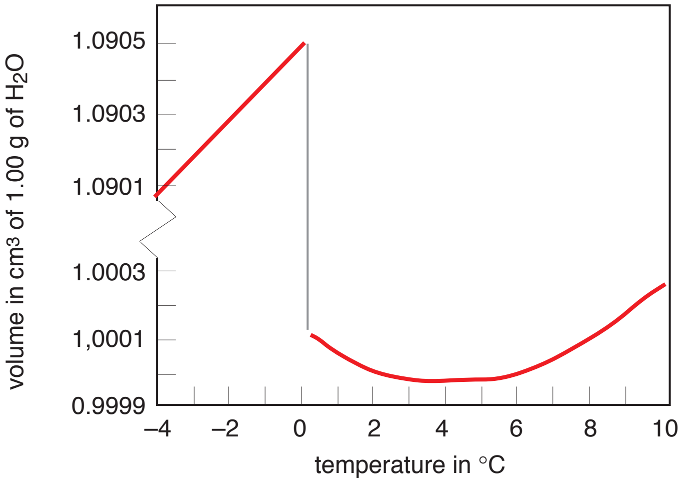


Figure 3: Specific volume of water as a function of temperature.

kind of an arrangement in the ice crystal. This arrangement requires that the molecules be somewhat farther apart then would otherwise be the case; as a consequence, ice, in which hydrogen bonding is at its maximum, has a more open structure, and thus a lower density than water.

When ice melts, the more vigorous thermal motion disrupts much of the hydrogen-bonded structure, allowing the molecules to pack more closely. Water is thus one of the very few substances whose solid form has a lower density than the liquid at the freezing point. Localized clusters of hydrogen bonds still remain, however; these are continually breaking and reforming as the thermal motions jiggle and shove the individual molecules. As the temperature of the water is raised above freezing, the extent and lifetimes of these clusters diminish, so the density of the water increases.

At higher temperatures, another effect, common to all substances, begins to dominate: as the temperature increases, so does the amplitude of thermal motions. This more vigorous jostling causes the average distance between the molecules to increase, reducing the density of the liquid; this is ordinary *thermal expansion*.

Because the two competing effects (hydrogen bonding at low temperatures and thermal expansion at higher temperatures) both lead to a decrease in density, it follows that there must be some temperature at which the density of water passes through a maximum. This temperature is 4 °C; this is the temperature

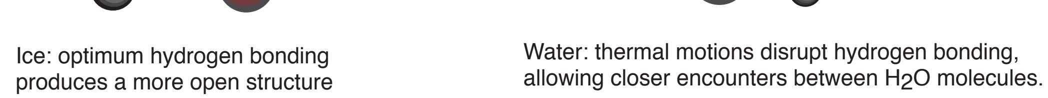


Figure 4: Schematic structures of ice and water.

of the water you will find at the bottom of an ice-covered lake in which this most dense of all water has displaced the colder water and pushed it nearer to the surface.

2.3 Structure of solids

The solid state, being the form of any substance that prevails at lower temperatures, is one in which thermal motion plays an even smaller role than in liquids. The thermal kinetic energy that the individual molecular units do have allows them to oscillate around a fixed center whose location is determined by the balance between local forces of attraction and repulsion due to neighboring units, but only very rarely will a molecule jump out of the fixed space alloted to it in the lattice. Thus solids, unlike liquids, exhibit cohesiveness and rigidity, and possess definite shapes.

Crystalline solids

In a solid comprised of identical molecular units, the most favored (lowest potential energy) locations occur at regular intervals in space. If each of these locations is actually occupied, the solid is known as a *perfect crystal*.

What really defines a crystalline solid is that its structure is composed of repeating *unit cells* each containing a small number of molecular units bearing a fixed geometric relation to one another. The resulting long-range order defines a three-dimensional geometric framework known as a *lattice*. A typical lattice arrangement is shown in Fig. 9.

Geometric theory shows that only fourteen different types of lattices are possible in three dimensions, and that just six different unit cell arrangements can generate these lattices. The regularity of the external faces of crystals, which in fact correspond to lattice planes, reflects the long-range order inherent in the underlying structure.

Perfection is no more attainable in a crystal than in anything else; real crystals contain *defects* of various kinds, such as lattice positions that are either vacant or occupied by impurities, or by abrupt displacements or dislocations of the lattice structure.

Amorphous solids

In some solids there is so much disorder that the substance cannot be considered crystalline at all; such a solid is said to be *amorphous*. Amorphous solids possess short-range order but are devoid of any organized structure over longer distances; in this respect they resemble liquids. However, their rigidity and cohesiveness allow them to retain a definite shape, so for most practical purposes they can be considered to be solids.

Glasses and most plastics are common examples of amorphous solids. Ordinary glass is composed mostly of SiO_2, which usually exists in nature in a crystalline form known as *quartz*. In the manufacture of glass, quartz (in the form of sand) is melted and allowed to cool. As the liquid SiO_2 cools, it becomes so viscous that the molecules are unable to move to the low potential energy positions they would occupy in the crystal lattice, so that the disorder present in the liquid gets "frozen into" the solid. In a sense, glass can be regarded as a supercooled liquid. Glasses are transparent because the distances over which disorder appears are small compared to the wavelength of visible light.

Plastics and natural materials such as rubber or cellulose are composed of very large molecules called *polymers*. Owing to their great length, these molecules tend to become entangled in the liquid state, and are unable to separate to form a crystal lattice on cooling. In general, it is very difficult to get such substances to form anything other than amorphous solids.

The melting of a crystalline compound corresponds to a sudden loss of long-range order; this is the fundamental reason that such solids exhibit definite melting points, and it is why there is no intermediate

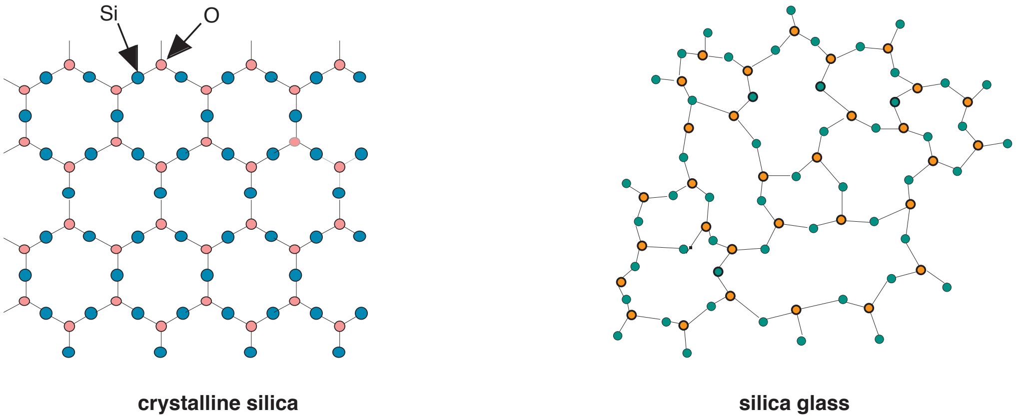


Figure 5: Schematic structures of crystalline and amorphous SiO_2.

form between the liquid and the solid states. In amorphous solids there is no long-range order, so there is no melting point in the usual sense. Such solids simply become less and less viscous as the temperature is raised. In some polymers (known as *thermoplastics*) there is a fairly definite *softening point* that is observed when the thermal kinetic energy becomes high enough to allow internal rotation to occur within the bonds of the individual polymer molecules, thus rendering them more flexible and deformable.

3 Physical interactions between molecular units

The very existence of condensed states of matter suggests that there are attractive forces acting between the basic molecular units of solids and liquids. The term *molecular unit* refers to the smallest structural unit– atom, ion, or molecule– that comprises the liquid or solid. The attractive forces that hold the unit itself together are always much stronger than those that bind one unit to another in the condensed phase.

3.1 Interactions between charged particles

Electrostatic attraction between oppositely-charged particles is the strongest of all the intermolecular forces. *Ionic solids* are held together by the coulombic forces between oppositely-charged ions which can be regarded as forming two inter-penetrating three-dimensional lattices. *Metals*, in their simplest conception, consist of positive ions held in a crystal lattice by mobile electrons which can move between the ions very much like a fluid.

Ionic solids, exemplified by salts such as NaCl or MgO, are familiar to most of us. They are typically hard, brittle, and have high melting points– all indicative of the strength of ion-ion attraction. When they do melt, these solids form conductive liquids, since the ions can now move freely in response to an imposed electric potential gradient.

The force F between two point charges of opposite sign is given by Coulomb's law

$$F = \frac{Q_1 Q_2 \alpha}{r^2} \tag{1}$$

When SI units are used, the charges Q are expressed in coulombs (C), the distance r in m, and the force in joules; $1\ \text{J} = 1\ \text{kg}\,\text{m}^2\text{s}^{-2}$. The proportionality constant α is needed to make the units come out right; it is known as the *permittivity*, and its value is 1.11265E-10 $\text{C}^2\text{J}^{-1}\text{m}^{-1}$. The sign of F determines whether the force will be attractive ($-$) or repulsive ($+$); notice that the latter is the case whenever the two Q's have the same sign. The above equation is an example of an *inverse square* law; the force falls off as the square of the distance. A similar law governs the manner in which the illumination falls off as you move away from a point light source; recall this the next time you walk away from a street light at night, and you will have some feeling for what an inverse square law means.

The stronger the attractive force acting between two particles, the greater the amount of work required to separate them. *Work* represents a flow of *energy*, so the foregoing statement is another way of saying that when two particles move in response to a force, their potential energy is lowered. This work, as you may recall if you have studied elementary mechanics, is found by integrating the force with respect to distance over the distance moved. Thus the energy that must be supplied in order to completely separate two oppositely-charged particles initially at a distance $r_\circ$ is given by

$$w = \int_{r_\circ}^{\infty} \frac{Q_1 Q_2 \alpha}{r_\circ^2} dr = \frac{Q_1 Q_2 \alpha}{r_\circ} \tag{2}$$

Problem Example 2

How much energy would be required to separate one mole of K^+ and Cl^- ions, if they behave as point charges that are 4.0 pm apart?

3.2 Interactions between charged and uncharged species

According to Eq 1, the electrostatic force between an ion and an uncharged particle having $Q = 0$ should be zero. Bear in mind, however, that this formula assumes that the two particles are *point charges* having zero radii. A real particle such as an atom or a molecule is made of a series of positively-charged nuclei and an equal number of electrons. Some of these electrons remain localized around individual nuclei, while others, mainly those involved in bonding, occupy a larger volume of space that may extend over several atoms. In a symmetrical species such as an atom of neon or a molecule of O_2 or of CCl_4, the centers of all the positive charges and negative charges coincide. However, in an unsymmetrical molecule such as CO or H_2O the centers of the opposite charges are slightly displaced.

This unbalance of charge is electrically equivalent to what is known in physics as an *electric dipole*. An idealized electric dipole consists of two point charges of magnitude $+q$ and $-q$ separated by a distance r. Even though the overall system is electrically neutral, the charge separation gives rise to an electrostatic effect whose strength is expressed by the *electric dipole moment* given by

$$\mu = qr \tag{3}$$

Electric dipoles possess both magnitude and direction, and are thus vectorial quantities; they are conventionally represented by arrows whose heads are at the negative end.

If a charge of magnitude equal to that of the electron (1.6022×10^{19} C) is displaced by 100 pm (1 Å), the magnitude of the dipole moment will be

$$\mu = (1.6022 \times 10^{19} \text{ C}) \times (10^{-10} \text{ cm}) = 1.6022 \times 10^{29} \text{ C m} = 4.8 \text{ D}$$

The unit $D = 3.336 \times 10^{30}$ C-m is known as the *debye*, named after the Dutch physicist Peter Debye who pioneered the study of electric dipoles in the 1920's. The value of this unit comes from its pre-SI unit definition as 10^{-18} esu-cm – that is, the displacement of unit electron charge (4.8×10^{10} esu) by 1 Å (10^{-8} cm).

Any chemical bond linking two atoms of different electronegativity will possess a *bond dipole moment*, as depicted by the arrows in Fig. 6. The magnitude of charge displacement over the distance between the nuclei is always much less than the equivalent of one electron charge; the symbols δ^+ and δ^- are commonly used to indicate the polarity.

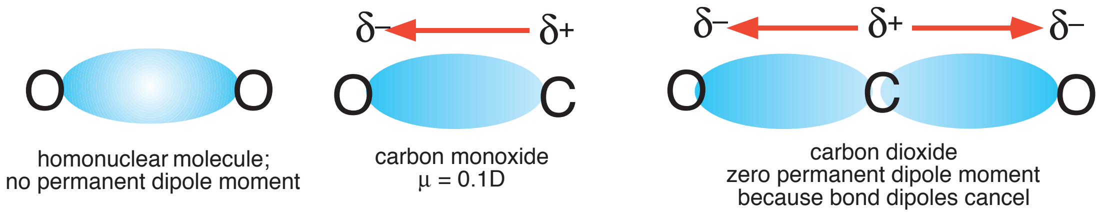


Figure 6: Bond dipoles and permanent dipole moments of molecules.

In a molecule that is composed of several atoms, the individual bond dipoles add vectorially to give a net *permanent dipole moment.* If the symmetry of the molecule is such that the bond dipole moments cancel out, then the molecule will not have a permanent dipole moment. Two examples of molecules that fall into this category are CO_2 (Fig. 6) and CH_4. If CO_2 were bent (like H_2O) it would have a permanent dipole moment.

When a polar substance (either in the gas phase or dissolved in a nonpolar solvent) is subjected to an external electric field, the molecules tend to align themselves with the field; the work required to bring about this alignment is drawn from the external circuit and manifests itself as an electrical capacitance. Measurement of this capacitance allows one to calculate the value of the dipole moment and provides a convenient way of distinguishing between different possible shapes of simple molecules.

In summary:

1. All bonds between atoms having different electronegativities (that is, between most dissimilar atoms) are *polar*, and possess bond dipole moments. The charge displacement amounts to much less than a unit electron charge, so a bond dipole is not the same as an ion pair.
2. The various bond dipoles add vectorially to give a resultant. If the latter is non-zero, the molecule possesses a *permanent dipole moment.* Such a molecule is said to be *polar.*
3. A polar molecule can still be electrically neutral. Likewise there are *non*polar *ions;* can you think of one?

3.3 Interactions of polar molecules

When an electric dipole is subjected to an external electric field, it will tend to orient itself so as to minimize the potential energy; that is, its negative end will tend to point toward the higher (more

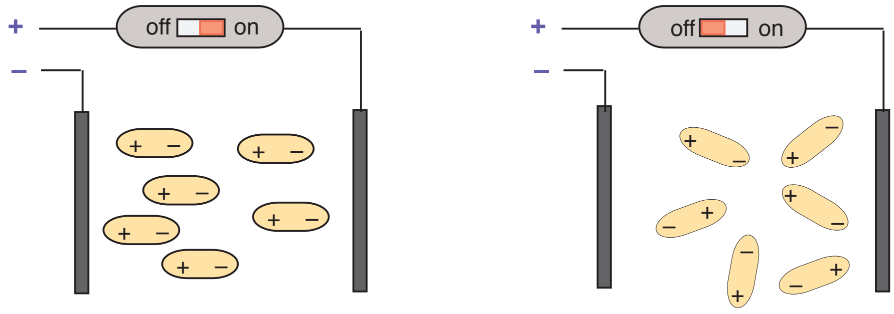


Figure 7: Alignment of polar molecules in an external electric field.

positive) electric potential. In liquids, thermal motions will act to disrupt this ordering, so the overall effect depends on the temperature. Although these effects can be brought about (and are frequently studied) by applying an external electric field to a sample9, the local fields due to nearby ions or dipoles in a substance play an important role in determining the physical properties of the substance, and it is in this context that dipolar interactions are of interest to us here. We will discuss each kind of interaction in order of decreasing strength.

Ion-Dipole interactions

A dipole that is close to a positive or negative ion will orient itself so that the end whose partial charge is opposite to the ion charge will point toward the ion. This kind of interaction is very important in aqueous solutions of ionic substances; H_2O is a highly polar molecule, so that in a solution of sodium chloride, for example, the Na^+ ions will be enveloped by a shell of water molecules with their oxygen-ends pointing toward these ions, while H_2O molecules surrounding the Cl^- ions will have their hydrogen ends directed inward. As a consequence of ion-dipole interactions, all ionic species in aqueous solution are *hydrated;* this is what is denoted by the suffix in formulas such as K^+*(aq)*, etc.

The strength of ion-dipole attraction depends on the magnitude of the dipole moment and on the *charge density* of the ion. This latter quantity is just the charge of the ion divided by its volume. Owing to their smaller sizes, positive ions tend to have larger charge densities than negative ions, and they should be more strongly hydrated in aqueous solution. The hydrogen ion, being nothing more than a bare proton of extremely small volume, has the highest charge density of any ion; it is for this reason that it exists entirely in its hydrated form H_3O^+ in water.

Dipole-dipole interactions

As two dipoles approach each other, they will tend to orient themselves so that their oppositely-charged ends are adjacent. Two such arrangements are possible: the dipoles can be side by side but pointing in opposite directions, or they can be end to end. It can be shown that the end-to-end arrangement gives a lower potential energy.

Dipole-dipole attraction is weaker than ion-dipole attraction, but it can still have significant effects if the dipole moments are large. The most important example of dipole-dipole attraction is *hydrogen bonding* which is discussed on page 15.

3.4 Interactions involving induced dipoles

Even if a molecule is electrically neutral and possesses no permanent dipole moment, it can still be affected by an external electric field. Because all atoms and molecules are composed of charged particles (nuclei and electrons), the electric field of a nearby ion will cause the centers of positive and negative charges to shift in opposite directions. This effect, which is called *polarisation*, results in the creation of a temporary, or *induced* dipole moment. The induced dipole then interacts with the species that produced it, resulting in a net attraction between the two particles.

The larger an atom or ion, the more loosely held are its outer electrons, and the more readily will the electron cloud by distorted by an external field. A quantity known as the *polarisability* expresses the magnitude of the temporary dipole that can be induced in it by a nearby charge.

Ion-induced dipole interactions The most significant induced dipole effects result from nearby ions, particularly cations (positive ions). Nearby ions can distort the electron clouds even in polar molecules, thus temporarily changing their dipole moments. The larger ions (especially negative ones such as SO_4^{2-} and ClO_4^- are highly polarisable, and the dipole moments induced in them by a cation can play a dominant role in compound formation.

substance	bp °C	molecular units	dominant type of interaction	equilibrium separation (pm)	attractive energy (kJ/mol)
sodium fluoride	990	Na^+ F^-	coulomb	18.8	657
sodium hydroxide	318	Na^+ OH^-	ion-dipole	21.4	90.4
water	100	H_2O	dipole-dipole	23.7	20.2
neon	−249	Ne	dispersion	33.0	0.26

Table 2: Intermolecular forces in different kinds of substances

Dipole-induced dipole interactions A permanent dipole can induce a temporary one in a species that is normally nonpolar, and thus produce a net attractive force between the two particles. This attraction is usually rather weak, but in a few cases it can lead to the formation of loosely-bound compounds. This effect explains the otherwise surprising observation that a wide variety of neutral molecules such as hydrocarbons, and even some of the noble gas elements, form stable *hydrate* compounds with water.

3.5 Dispersion or London forces

The fact that noble gas elements and completely non-polar molecules such as H_2 and N_2 can be condensed to liquids or solids tells us that there must be yet another source of attraction between particles that does not depend on the existence of permanent dipole moments in either particle.

To understand the origin of this effect, it is necessary to realize that when we say a molecule is "nonpolar", we really mean that the *time-averaged* dipole moment is zero. This is the same kind of averaging we do when we draw a picture of an orbital, which represents all the locations in space in which an electron can be found with a certain minimum probability. On a very short time scale, however, the electron must be increasingly localized; not even quantum mechanics allows it to be in more than one place at any given instant. As a consequence, there is no guarantee that the distribution of negative charge around the center of an atom will be perfectly symmetrical at every instant; every atom therefore has a weak, fluctuating dipole moment that is continually disappearing and reappearing in another direction. Although these extremely short-lived fluctuations quickly average out to zero, they can still induce new dipoles in a neighboring atom or molecule, which helps sustain the original dipole and gives rise to a weak attractive force known as the *dispersion* or *London* force (after F. London, who explained this effect in 1930).

Although dispersion forces are the weakest of all the intermolecular attractions, they are universally present. Moreover, they are *additive*; if two elongated molecules find themselves side by side, dispersion force attractions will exist all along the regions where the two molecules are close. This can produce quite strong attractions between large polymeric molecules.

3.6 Combinations of interactions: van der Waals forces

Although nonpolar molecules are by no means uncommon, most kinds of molecules possess permanent dipole moments, so liquids and solids composed of these species will be held together by a combination of dipole-dipole, dipole-induced dipole, and dispersion forces (Table 3). These weaker forces (that is, those not involving ions) are known collectively as *van der Waals* forces.

substance	bp °C	μ (debyes)	polarisability α	% dipole- induced dipole	% dipole-dipole	% dispersion
Ar	−186	0.0	1.6	0	0	100
CO	−190	0.1	2.0	0	0	100
HCl	−84	1.0	2.6	14.4	4.2	81.4
HBr	−67	0.8	3.6	3.3	2.2	94.5
HI	−35	0.4	5.4	0.1	0.4	99.5
NH_3	−33	1.5	2.6	44.6	5.4	50.0
H_2O	0	1.8	1.5	77.0	4.0	19.0
CH_3OH	65		63.4	14.4	22.2	

Table 3: Contributions to intermolecular forces in various substances

3.7 Variation of potential energy with distance

Intermolecular repulsion When two particles are very close, the attractive forces discussed above draw them even closer, since this reduces the potential energy. Obviously, however, there must be some limit to how close they can get; otherwise the two particles would simply coalesce into one. This implies the existence of a universal repulsive force between all matter, and that this repulsive force must increase more rapidly than the attraction as the distance between the particles decreases.

This repulsive force is the basis of the statement that “no two particles can occupy the same space at the same time”. As two atoms get very close, their electron clouds begins to interfere, producing an electrostatic repulsion that will counteract even the strong coulombic attraction of oppositely-charged ions.

The net force acting between two particles separated by a given distance is always a balance between the repulsive force and one or more of the attractive forces. A plot of the net potential energy as a function of distance (right side of Fig. 8) is known as a *Morse curve*, named after P.M. Morse who developed a mathematical description of this behavior in 1929.

The Morse curve shows how the potential energy of interaction varies with the distance between two particles. When the potential energy is below zero, there is a net attraction; when above zero, the particles repel each other. At large distances, shown on the right (corresponding to several molecular diameters), the potential energy approaches zero, meaning that the particles do not interact at all.

The opposing effects of attraction and repulsion lead to a potential energy minimum at a certain separation distance that is known as the *equilibrium* distance. This is the average distance that will be maintained by the two particles if there are no other forces acting on them, such as might arise from the presence of other particles nearby. The magnitude of the potential energy minimum in relation to the average thermal energy (given by RT, with $R = 8.314\ \mathrm{J\,K^{-1}\,mol}^{-1}$) determines whether the particles are likely to remain linked. At room temperature, the value of RT is about 2.5 kJ/mol, so unless the potential energy minimum is considerably in excess of this, the particles will soon break apart and quickly find new partners. If, on the other hand, the magnitude of the energy minimum is more negative than about −100 kJ/mol, then the binding between the two particles is so strong that we consider a *chemical bond* to exist between them.

In this section of the course, we will be concerned with the smaller potential energy dips produced by the attractive forces discussed in the preceding sections.

A general empirical expression for the interaction energy between two particles can be written as

$$E = Ar^{-n} + Br^{-m} \tag{4}$$

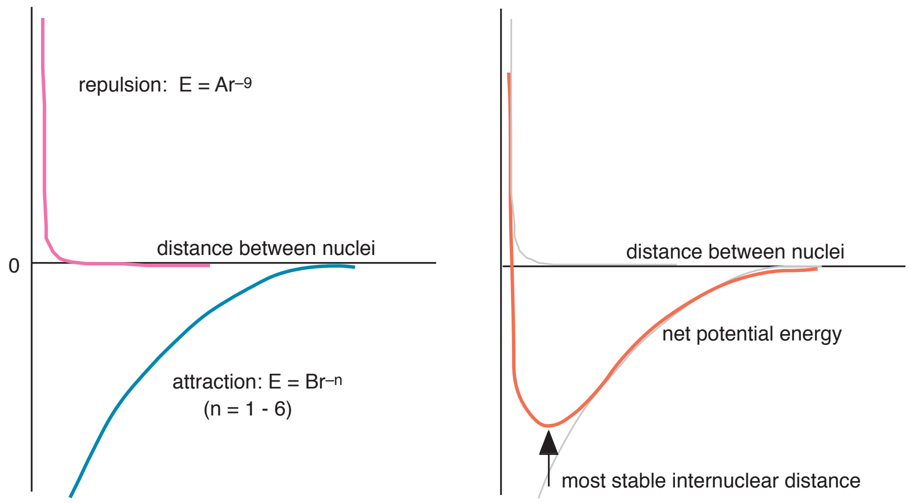


Figure 8: Potential energy as a function of distance between two particles.

types of units	dominant interaction	n	m
ions	coulomb	9	1
ion - polar molecule	ion-dipole	9	2
two polar molecules	dipole-dipole	9	3
ion - nonpolar molecule	ion-induced dipole	9	4
polar and nonpolar molecule	dipole-induced dipole	9	6
nonpolar molecules or atoms	dispersion	9	6

Table 4: Mie's equation exponent for various kinds of interactions

where A and B are proportionality constants and n and m are integers. Since the first term corresponds to repulsion, A is always positive, and n must be larger than m, reflecting the fact that repulsion always dominates at small separations.

4 Bonding within molecular units

Most molecular units are made up of two or more atoms or ions bound together by a relatively strong force which produces what we call a *chemical bond*. The various theories and models of chemical bonding are covered elsewhere in this course; our purpose here is to merely provide enough of an overview of the subject to help you understand how the different kinds of bonding lead to qualitatively different kinds of molecular units. These, in turn, form solids and liquids with quite distinctive physical properties.

All chemical bonding occurs as a result of electrons being simultaneously near two or more positively-charged nuclei, so as to counteract the repulsion that would normally exist between particles of like charge sign. It is convenient to classify chemical bonding into three major types, each giving rise to solids and liquids whose physical properties tend to be quite distinct. These bonding types are covalent, ionic, and metallic.

Covalent bonds form when a pair of valence (outer-shell) electrons are *shared* between two atoms. Although it is common practice to depict the shared electrons as being located between the two nuclei,

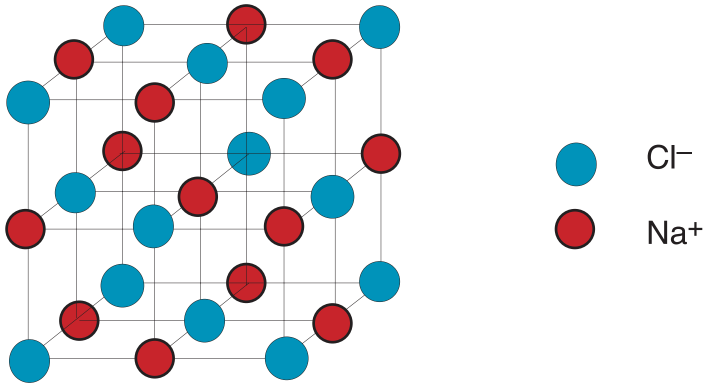


Figure 9: The sodium chloride crystal lattice.

a more correct interpretation is that the electrons occupy a charge cloud that flows into the region of each nucleus simultaneously by a quantum effect known as *tunneling.* For our purposes all that matters is that the electrons are simultaneously close to two nuclei, and this produces the bonding effect.

Covalent bonds vary greatly in strength; common values are 200-300 kJ/mol, but some are so weak (less than 100 kJ/mol) that they can hardly be called bonds at all. The strongest single-electron pair covalent bond (440 kJ/mol) is that in the very small H_2 molecule. Smaller atoms tend to form stronger covalent bonds than large ones. The main reason for this is that electrons shared with large atoms will be farther from the nuclei, reducing the net attractive force, which falls of as the inverse square of the distance. An important secondary effect arises from the greater numbers of electrons in the larger atom; these act to partially nullify, or *screen* the nuclear charge as "seen" by the shared electrons.

Except for bonds between identical atoms as in N_2, etc., nearly all covalent bonds possess a certain amount of *polar* character which gives rise to the bond dipole moments described in a preceding section. This polarity is due to unequal sharing of the bonding electrons, and increases as the electronegativity difference of the bonded atoms becomes greater.

In general, the covalent bonds linking the atoms in most molecules are so strong that the molecular unit retains its integrity in the solid, liquid, and gaseous states. The forces that act between the molecular units and which bind them into their liquid and solid forms all fall into the weak van der Waals category, and it very often happens that dispersion forces are the dominant interaction. Such compounds tend to have relatively low melting and boiling points, and possess the other properties characteristic of *molecular solids*, which are discussed further on.

Ionic bonding If the difference in electronegativity (as expressed on the common scale of 0-4) rises much above 1, the electron sharing is so unequal that for many practical purposes the compound can be regarded as consisting of a positive ion and a negative ion. Solids of this kind, exemplified by alkali-metal halides such as NaCl, are built up of two interpenetrating lattices of positive and negative ions. In contrast to what is found in covalent compounds, there are no discrete molecular units of "NaCl" in the solid; each ion is surrounded by six nearest neighbors of opposite charge, the whole arrangement being held together by a balance of forces extending in all directions. The resulting coulombic (ion-ion) attractions are quite strong, and the binding energy can be calculated by summing the interactions between one ion and its neighboring ions of like and unlike charge.

Even in the most highly ionic solids there is some electron sharing, so the idea of a "pure" ionic bond is an abstraction. In solids composed of larger ions (such as $CuCl_2$) and particularly of polyatomic ones ($SrClO_4$, NH_4CO_3), coulombic attraction tends to be much weaker, and ion-dipole and ion-induced dipole forces may dominate.

element	He	Ne	Ar	Kr	Xe
atomic number	2	20	18	36	54
boiling point (°K)	27	87	120	165	211
critical temperature (°K)	5	44	151	210	290
heat of vaporization (kJ/mol)	.08	1.76	6.51	59.0	12.6

Table 5: Properties of the noble gas elements

Metallic bonding In metals the valence electrons are free to wander throughout the solid, instead of being localized on one atom and shared with a neighboring one. The valence electrons behave very much like a mobile fluid in which the fixed lattice of atoms is immersed. This provides the ultimate in electron sharing, and creates a very strong binding effect in solids composed of elements that have the requisite number of electrons in their valence shells. The characteristsic physical properties of metals such as their ability to bend and deform without breaking, their high thermal and electrical conductivities and their metallic sheen are all due to the fluid-like behavior of the valence electrons.

5 The molecular units of chemical substances

With the general background presented above, we are now prepared to consider the various kinds of units that serve as the building blocks of matter, and to relate the properties of substances to the nature of these units and to the forces acting between them.

5.1 Molecular substances

By "molecule", we mean a discrete aggregate of atoms bound together sufficiently tightly (that is, by *directed covalent* forces) to allow it to retain its individuality when the substance is dissolved, melted, or vaporized. The two words emphasized in the preceding sentence are important; covalent bonding implies that the forces acting between atoms within the molecule are much greater than those acting between molecules, and the directional property of covalent bonding confers on each molecule a distinctive shape which affects a number of its properties.

Most compounds of carbon— and therefore, most chemical substances, fall into this category. Many simpler compounds of other elements also form molecules; H_2O, NH_3, CO_2, and PCl_5 are familiar examples. Some of the elements, such as H_2, O_2, O_3, P_4 and S_8 also fall into this category, as do the noble gas elements of Group 18, which can be thought of as "monatomic molecules".

Liquids and solids that are composed of molecules are held together by van der Waals forces, and many of their properties reflect this weak binding. Thus molecular solids tend to be soft or deformable, have low melting points, and are often sufficiently volatile to evaporate (sublime) directly into the gas phase; the latter property often gives such solids a distinctive odor. If you have ever worked with solid iodine in the laboratory, you will probably recall the sight and smell of its purple vapor.

Because dispersion forces and the other van der Waals forces increase with the number of atoms, larger molecules are generally less volatile, and have higher melting points, than do the smaller ones. Also, as one moves down a column in the periodic table, the outer electrons are more loosely bound to the nucleus, increasing the polarisability of the atom and thus its susceptibility to van der Waals-type interactions. This effect is particularly apparent in the progression of the boiling points of the noble gas elements (Table 5.

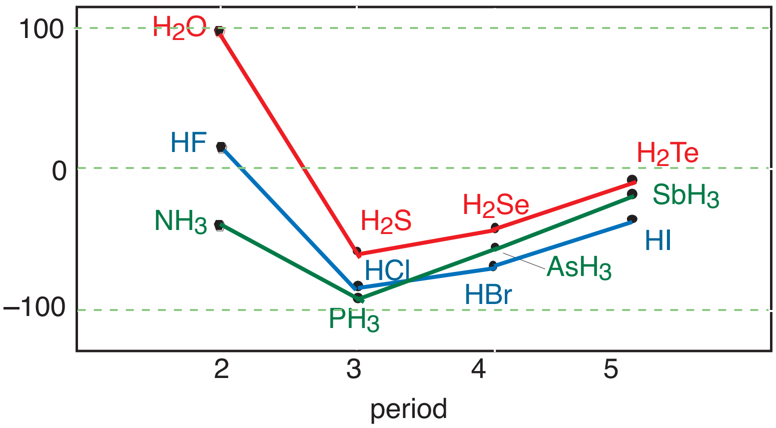


Figure 10: Boiling points of several series of binary hydrogen compounds.

5.2 Hydrogen bonding

According to the principles outlined in the preceding paragraph, we would expect the volatility of a series of similar substances to diminish as the molecular weight increases. Thus in the series of hydrogen compounds with Group 16 elements H_2O, H_2S, H_2Se, H_2Te, we might expect water to be the most volatile, with a normal boiling point of around 200 °K. It turns out, however, that water is the *least* volatile of the Group 16 halides (Fig. 10).

The high boiling point of water, along with all of its other "anomalous" properties, is attributed to an exceptionally strong dipole-dipole interaction that exists between molecules in which a hydrogen atom is attached to a highly electronegative atom such as fluorine, oxygen, or nitrogen. This is the basis of *hydrogen bonding* which was discussed in the section on liquids. The plots of Fig. 10 show very clearly how the effects of hydrogen bonding in several series of hydrogen-containing compounds are superimposed on those of the weaker van der Waals attractions that increase with molecular weight in the usual way.

The strength of a hydrogen bond (that is, the energy required to break it) is between 5 and 40 kJ/mol. This is much stronger than ordinary van der Waals attractions, but of course much weaker than an ordinary chemical bond.

Hydrogen bonding can be important in solids as well as in liquids. In ice, the H_2O molecules are oriented in such a way as to maximize the opportunities for hydrogen bonding and thus produce a lower potential energy. The molecular orientation required for optimum hydrogen bonding produces a more open and less dense structure than would be expected if the H_2O molecules simply packed together as closely as possible as they would in an ordinary liquid. Water is therefore one of the rare substances whose solid form is less dense than the liquid. The fact that the density of liquid water passes through a maximum at 4 °C suggests that at low temperatures the H_2O molecules begin to orient themselves into an ice-like arrangement while still in the liquid state (see Fig. 3 pm 6.)

Besides dominating the structure of water, hydrogen bonding plays a major role in the three-dimensional structure of biopolymers such as nucleic acids and proteins. In a protein, –NH_2 units (amino groups) bound to the carbon chain can hydrogen-bond with each other, holding the protein in a folded configuration that may be essential for its special function. Heating can disrupt these hydrogen bonds, allowing the chain to unfold and change its properties (Fig. 12.)

Intramolecular Hydrogen bonding can have a profound effect on the structures of large biomolecules such as proteins, which contain NH_2 and OH groups. In a raw egg, for example, the non-yolk part consists largely of the protein albumin. *Owing to intramolecular hydrogen bonding (in which hydrogen bonds extend between different parts of the same molecule), the albumin molecules are*

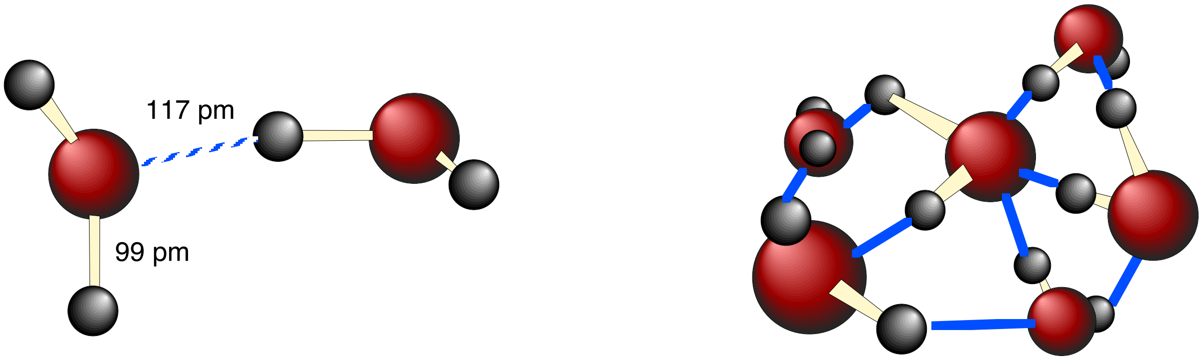


Figure 11: Hydrogen bonding in ice.

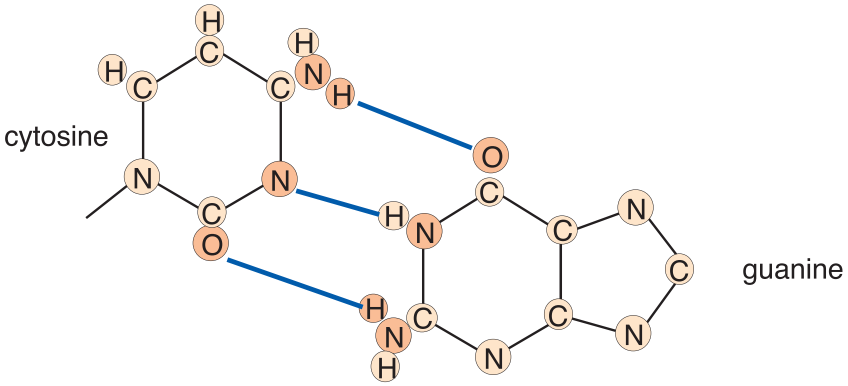
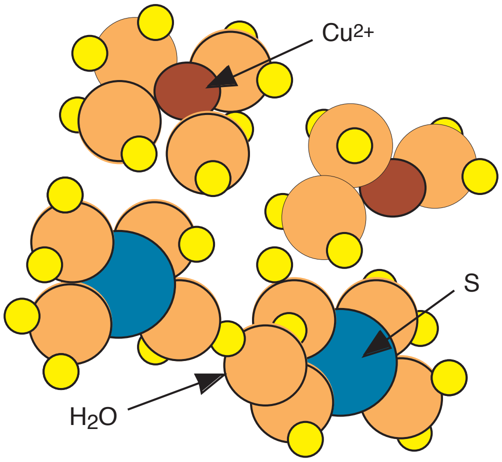


Figure 12: Hydrogen bonding between two base pairs in adjacent strands of DNA.



The copper(II) sulfate crystal is made up of repeating units containing two $CuSO_4 \cdot 5H_2O$ units. Each Cu^{2+} ion is octahedrally coordinated to six oxygen atoms, four on H_2O molecules and two on SO_4^{2-} ions, one of which belongs to the $CuSO_4$ unit immediately above (not shown here). The fifth water of hydration (the one labeled H_2O in the illustration) is hydrogen-bonded to the oxygen atoms of sulfate ions of the two adjacent $CuSO_4$ units.

Figure 13: Structure of solid copper(II) sulfate pentahydrate.

folded quite compactly and can easily move around in solution. However, if you boil an egg for a few minutes, the hydrogen bonds are disrupted by the thermal energy and the albumin molecules unfold and form a tangled mass that cannot flow at all.

5.3 Ionic substances

We have already discussed the nature of ionic bonding and the structure of ionic solids. The important point to understand is that the fundamental units of a substance such as common salt are a set of Na^+ ions and Cl^- ions arranged in a fixed geometry, and repeated in three dimensions to build up the crystal lattice (Fig. 9.) No discrete molecular units of NaCl exist; the formula only shows the stoichiometric ratio of the two kinds of ions in the compound.

Ionic solids are characterized by high melting points. This is especially true for solids composed of multiply-charged ions such as MgO. These solids also tend to be rather hard and brittle. *Hardness* reflects the *strength* with which the molecular units of a solid are bound together; in order to break an ionic crystal, you must break a large number of relatively strong coulombic attractions. The *brittleness* indicates that the binding is *directional*, in this case extending between discrete ion pairs. When a brittle substance is stressed, the bonds between its molecular units are unable to bend; there is no strain, or "give". This means that the stress tends to concentrate at one point, eventually breaking one bond, and then moving on to the next, thus propagating the crack throughout the object until it splits.

What happens to ionic solids when they melt or boil? Ionic liquids are electrically conductive, indicating that they still contain charged particles capable of independent motion. Thus the ions are still there, but without any long-range organization. There is evidence that they tend to pair up or form small short-lived aggregates. Ionic liquids have very high boiling points, and when they do vaporize, the resulting gas consists of molecules, not ions. Thus the molecular species NaCl and Na_2Cl_2 have been identified in the vapor from sodium chloride melts.

Hydrated ions and hydrates The interaction of ionic substances with water is particularly widespread and important in chemistry. Ion-dipole interaction (with the permanent dipole moment of H_2O) favors the formation of relatively strong links between H_2O molecules and ions. Many ionic crystals incorporate *waters of hydration* in this way, forming substances such as $CuSO_4 \cdot 5\,H_2O$ (Fig. 13 or $Na_2SO_4 \cdot 10\,H_2O$; such substances are known as *hydrates*.

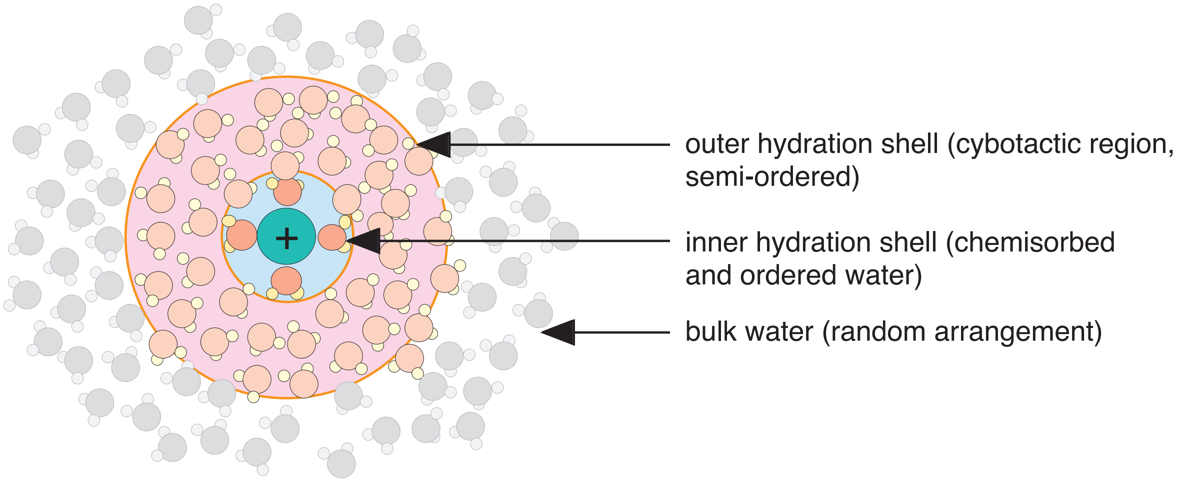


Figure 14: Structure of water in the region of a dissolved ion.

Many ionic solids are soluble in water; the species that result are not the free ions, but are *hydrated* ions that have water molecules bound to them through ion-dipole attraction (Fig. 14.) The charge sign of the ion determines whether the oxygen- or the hydrogen end of the water molecule is in contact with the ion. The number of water molecules in the *inner hydration shell* (the H_2O molecules that are directly "attached" to the ion) depends on the size and charge of the ion; very small ions have higher charge densities and bind the waters more tightly, but there may not be room enough for many water molecules to arrange themselves in a shall of small radius. The ordering of the waters in the inner hydration shell exerets some effect on the next several layers of water molecules which constitute the outer hydration shell or *cybotactic* region.

In many transition metal ions hydration is helped along by covalent bonding in which an electron pair on the the oxygen atom of water is shared with vacant *d* orbitals. The strong electric field created by the nearby water molecules interacts with the *d* orbitals of metal ion and re-groups them into levels whose energy difference often corresponds to the wavelength of visible light; this is why so many transition metal ions are colored in solution. Even the waters of hydration in crystals such as $CuSO_4 \cdot 5\,H_2O$ have this effect; this solid is blue, but anhydrous $CuSO_4$ is pale yellow.

5.4 Giant molecule compounds: catenated and covalent solids

Ionic solids are only one kind of infinite extended-lattice compound in which no distinct molecular units are evident. Many inorganic compounds exist only as solids in which the individual atoms are covalently bonded to each other in one, two, or three dimensions, forming chains, sheets, or networks. These substances are more generally known as *catenated solids* (catenation means "chaining together").

Covalent solids Three-dimensional covalently bonded catenation is the most extreme case, exemplified by diamond and silicon carbide. Each atom is covalently bonded to its nearest neighbors, so that the entire crystal is in effect one super-giant "molecule"– hence the appellation *covalent solid.* The extraordinarily strong binding forces that operate in all directions account for the extreme hardness of such substances; a diamond cannot be broken or abraded without cleaving large numbers of carbon-carbon bonds. Similarly, a covalent solid cannot "melt" in the usual sense, since the entire crystal is its own giant molecule. If a covalent solid is heated to a very high temperature it will eventually decompose into smaller units, perhaps into the elements, which will usually be gaseous under these conditions.

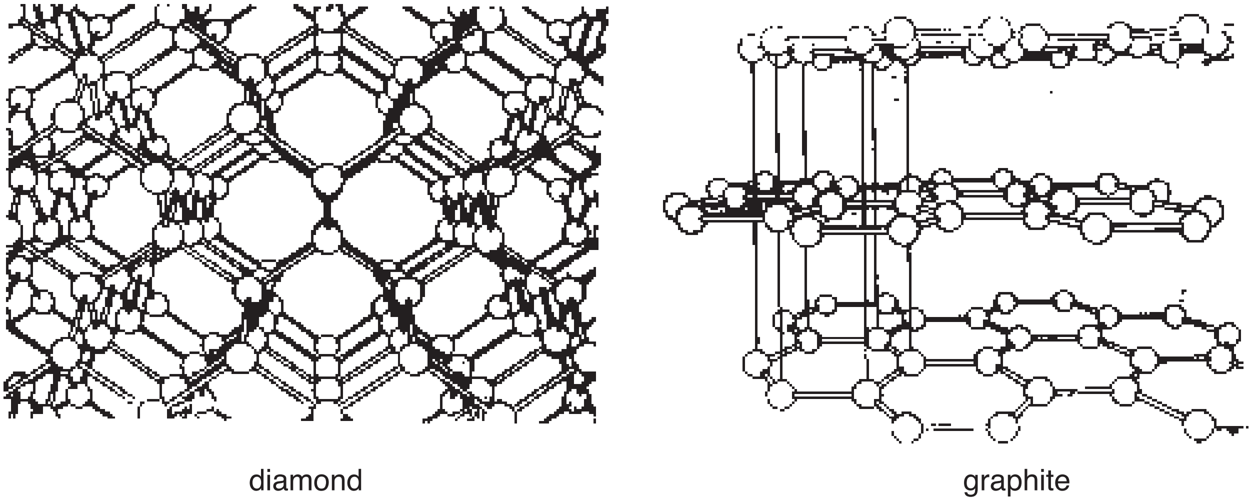
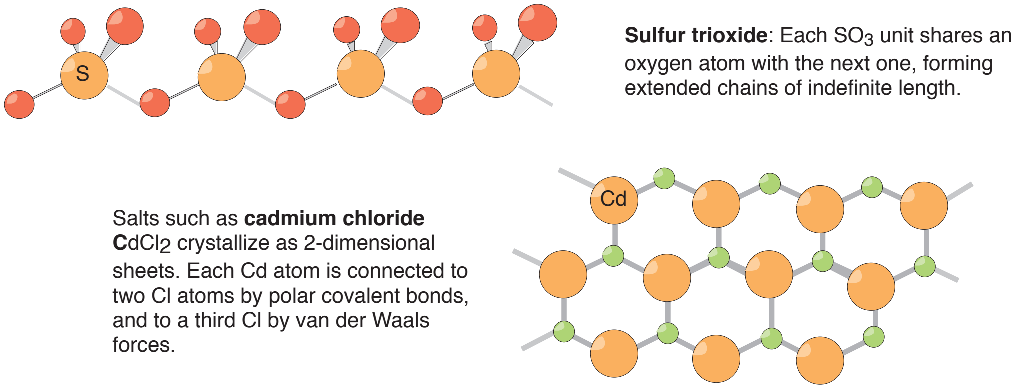


Figure 15: Structures of diamond and graphite.

Two-dimensional catenated compounds These substances, of which the graphite form of carbon is the best-known example, consist of stacked layers or sheets (right side of Fig. 15). The atoms within any one layer are covalently bound, so each layer is a kind of giant, flat molecule. In contrast to the strong binding within the two dimensions of each layer, adjacent layers are held together by weak van der Waals forces.

When these stacks are organized in a uniform way throughout the crystal, the physical properties of the solid are *anisotropic;* that is, they depend on the direction in which they are measured. In graphite, for example, both heat and electricity can flow much more easily in directions that lie in the plane parallel to the layers, rather than perpendicular to the layers. Similarly, graphite, which can be thought of as a "2-dimensional diamond" (Fig. 15), is soft and easily abraded if a mechanical force is applied in a direction that causes one layer to slide over another; this is why graphite makes a good solid lubricant and is the principal ingredient of "lead" pencils which depend on the ability of the loosely-bound carbon sheets to flake off when rubbed against a rough surface.

Many other very common substances form layered solids of this kind. For example, many common



Sulfur trioxide: Each SO_3 unit shares an oxygen atom with the next one, forming extended chains of indefinite length.

Salts such as **cadmium chloride** **C**dCl_2 crystallize as 2-dimensional sheets. Each Cd atom is connected to two Cl atoms by polar covalent bonds, and to a third Cl by van der Waals forces.

Figure 16: Typical solids based on 1- and 2-dimensional extended structures.

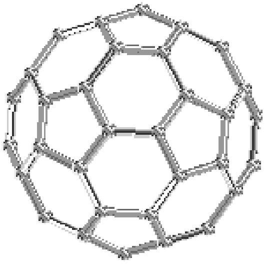


Figure 17: Buckminsterfullerene, C_{60}.

halides such as $CdCl_2$ (Fig. 16), NiI_2, and $ZnBr_2$ consist of sheets in which each metal atom is bonded to three neighboring halogen atoms, and each halogen is connected to six metal atoms; the M_3X_6 arrangement corresponds to the simplest formula MX_3.

Chain compounds Many substances form solids in which the atoms are grouped into long chains of indefinite length. One example is the solid form of sulfur trioxide SO_3, shown in the top part of]figrefextended. The atoms within a chain are covalently bound to each other, and van der Waals attractions hold adjacent chains together within the crystal, so that the overall structure appears to have three dimensions; this illustrates the difficulty one has in trying to establish rigid classifications of structures.

Fullerenes In the mid-1980's, compounds were discovered in which 20-70 carbon atoms are arranged in a hollow sphere. The most famous of these is C_{60} (Fig. 17), named *buckminsterfullerene* after the American engineer-architect and visionary Buckminster Fuller, who popularized the geodesic dome as a building structure. The hollow molecules (within which other atoms can sometimes be placed) resemble soccer balls in the alternating series of pentagonal and hexagonal carbon rings that make up their surfaces. These structures and others such as the more recently discovered carbon *nanotubes* possess interesting and unusual properties which have attracted intense research interest.

5.5 Metals

Approximately 70 percent of the elements are metals, and there are many compounds and mixtures that fall into this group. The familiar physical properties that distinguish a metallic substance from other kinds of matter are metallic *luster* (a result of very strong light absorption that nevertheless allows mirror-like reflection from surfaces), high electrical and thermal conductivity, and unusual mechanical properties such as ductility and malleability. All of these properties are a consequence of the mobility of the valence electrons which behave something like a fluid that fills the space between positive ions. Because the binding forces are spread out in every direction, the binding between any two atoms is weaker than in a covalent crystal, and the lack of directionality allows metallic solids to be deformed and bent without breaking. The very low mass of the electron fluid requires the use of quantum mechanics to thoroughly explain the unusual optical, thermal, and electrical properties of metals.

It is difficult to say what the basic "molecular units" are in metals; in many ways, they are similar to covalent solids in which the entire crystal is one large molecule. The wide differences between the melting points and hardnesses of different metals reflects differences in the number and nature of electrons able to participate in bonding.

Alloys An *alloy* is a metallic substance containing two or more elements. Alloys may be homogeneous mixtures (solid solutions), or they may be heterogeneous mixtures of several different solid phases. The study of how the properties of alloys are affected by their composition is an important part of metallurgical science.

Alloys may also exist as distinct *intermetallic compounds* such as Fe_3Zn_{21} or Al_9Co_2. Because of the lack of directed bonds in metals, it is relatively easy to insert a "foreign" atom into a lattice position that would normally be occupied by another kind of atom. Many intermetallic compounds therefore tend to be non-stoichiometric; for example, the solid known as γ-brass is ideally Cu_5Zn_8 (corresponding to $CuZn_{1.60}$), but its composition can vary from $CuZn_{1.58}$ to $CuZn_{1.65}$.

5.6 Other classes of substances

There are a number of other ways in which molecular units are joined into solids which do not quite fit into the headings given above.

Nonstoichiometric compounds

One of the most celebrated disputes in Chemistry was the one between the English chemist John Dalton, whose Law of Definite Composition mandated a fixed formula for every compound, and the French chemist Berthollet. Berthollet believed that the composition would depend on how the compound was prepared, and on its past history. The crude experimental techniques of the time initially favored Berthollet, but the Daltonian view was finally accepted.

We know now that both were right; a substance made up of definite molecules such as CO_2 or PCl_3 will always have a definite composition. Such substances are referred to as *Daltonides*. All other kinds of compounds are *Berthollides* and can have a variable composition, although very often over only a very narrow range, as in the case of most ionic solids and the brass alloy mentioned above. Many metal oxides and sulfides are Berthollides; for example, the stable form of the iron oxide we refer to as "FeO" contains fewer iron atoms than oxygen atoms. The iron atoms are mostly Fe(II) with a few of Fe(III); the ratio of Fe to O ranges from 0.84 to 0.94. The compound can be formally regarded as a mixture of Fe_2O_3 and Fe_3O_4.

High polymers

Polymers are distinct molecules that are constructed from large numbers of repeating units, or *monomers*. The more monomer units in the molecule, the higher the molecular weight; *high* polymers often have molecular weights in excess of 100,000.

The monomers may be identical (leading to *homo*polymers), or they may be of different kinds (*hetero*polymers). Naturally-occurring polymers include cellulose, chitin (the external skeletons of insects), and many gums, in which the monomeric units are sugars of various kinds. Proteins are polymers of amino acids, and natural rubber is a polymer of isoprene. Some of the more well known synthetic polymers are poly(ethylene), poly(tetrafluoroethylene) which is more commonly known as Teflon, poly(methylmethacrylate) (Plexiglas), and poly(vinyl chloride) ("vinyl", PVC).

Many natural polymers and virtually all synthetic ones are composed of molecules having a range of molecular weights, and so are never isolated as pure substances. The *molecular weight distribution* of a polymer expresses the relative contribution of each molecular weight to the overall mixture. The physical properties of polymers are strongly dependent on both its molecular structure and on the molecular weight distribution.

The extreme size of polymer molecules is responsible for some of the unique physical properties of polymeric substances. Even the very weak dispersion force attractions become very significant as they act between different parts of the extensive "surfaces" between neighboring molecules, or between the parts of a single folded molecule. Because these interactions are not very restricted in direction, many polymers, particularly those made synthetically, are quite flexible, or *plastic*.

> *Sometimes, when a solid polymer is not flexible enough for a particular application, a liquid lubricant, known as a* plasticizer, *is added. This is most commonly done with poly(vinyl chloride), or "vinyl", as is used in cheap raincoats and shower curtains, and in some upholstery materials; you can usually detect the presence of the plasticizer by its odor. Eventually the plasticizer will evaporate and the material will crack.*

Polymeric solids do not have sharp melting points; ordinary melting is prevented by the entanglement of the long chains. Instead of melting, these substances simply *soften* over a range of temperatures, gradually becoming more liquid-like as the temperature is raised. Part of this softening is believed to be associated with the increased stretching amplitude of the chemical bonds at higher temperatures, which allows them to undergo more deformation than can normally be accommodated.

Clathrates and inclusion compounds

There are a number of molecules and ionic compounds whose crystal structures are sufficiently open to permit the inclusion of some other molecule within their cage-like structure. These compounds are known as *clathrates*. The structure of ice is especially open, and it is not surprising that it should form clathrate-type hydrates with a variety of molecules, including dichlorine ($Cl_2 \cdot 8H_2O$), xenon ($Xe_4 \cdot 23H_2O$), and methane ($(CH_4)_4 \cdot 23H_2O$). These gas hydrates are stabilized mainly by dipole-induced dipole attraction, and tend to decompose when they are warmed. It has been proposed that compounds such as these could play an important role in the chemistry of many of the colder planets that are composed partly of frozen hydrogen-bonded substances such as water and ammonia.

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