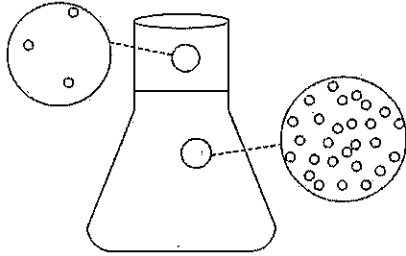


# LIQUIDS

Liquids exhibit many characteristics that help us understand their nature. They have low compressibility, lack rigidity, and have high density when compared with gases. Comparing liquids to gases using kinetic molecular theory helps us to understand the liquid state. According to KMT, gases are composed of molecules or single atoms that are in constant random motion throughout mostly empty space, they are compressible, and gas is fluid because individual molecules move relatively easily to one another.



Liquids are also fluid, however they are relatively incompressible compared to gases. According to KMT, the molecules of a liquid are also in constant random motion but are more tightly packed, so there is much less free space. Because the molecules can move relative to one another, a liquid can flow, but the lack of empty space explains why a liquid is nearly incompressible and more dense.

Recall that gases normally follow closely the ideal gas law,  $PV = nRT$ . The simplicity of this equation is the result of the nearly negligible forces of interaction between molecules and the nearly negligible molecular size compared with the total volume of gas. No such simple equations exist for the liquid state. Neither the size of the particles or the forces of attraction can be neglected in liquids. **In fact, the properties of liquids depend of the forces of attraction.**

# Intermolecular Forces

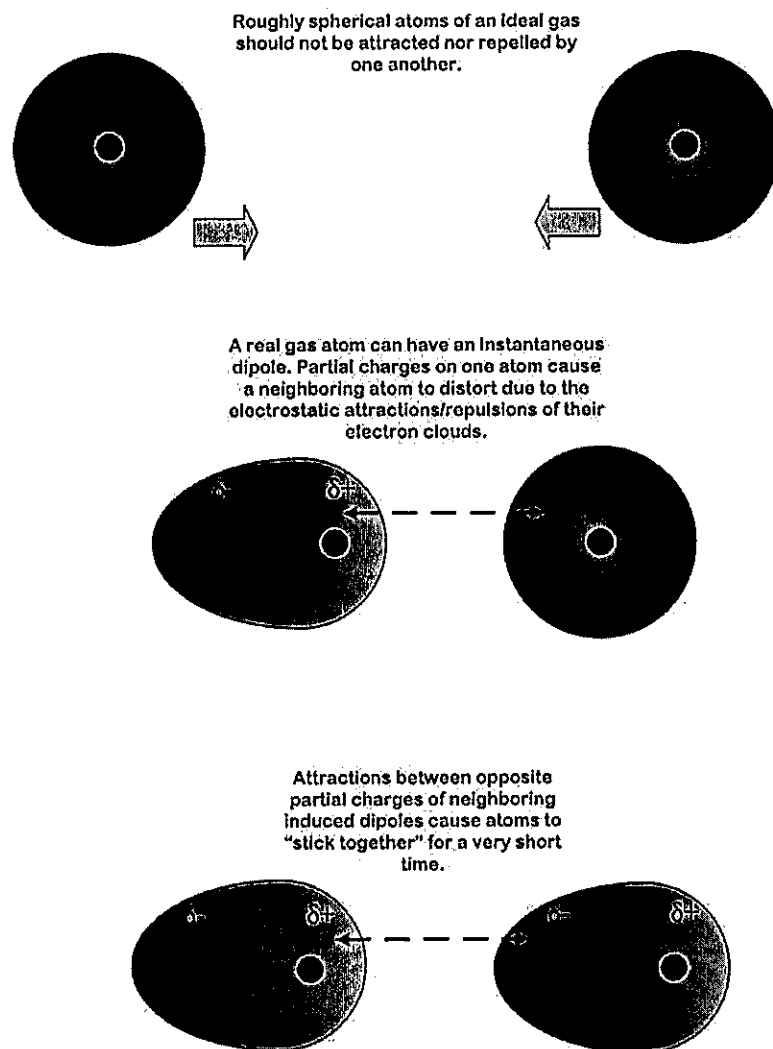
Gaseous atoms and molecules are never truly ideal because they all interact with other gas particles. Weak attractions between **separate** gas particles are known as **intermolecular forces (IMF)** or van der Waals forces after the chemist who proposed the correction to the ideal gas law that accounts for these forces. Conversely, the covalent bonds within a molecule are known as **intramolecular forces**.

IMFs are important in understanding the properties of liquids. There are three types of IMFs that may occur in pure substances: London Dispersion forces, dipole-dipole attractions, and hydrogen bonds.

## London Dispersion Forces

The weakest of the intermolecular attractions are induced dipole forces, also called London dispersion forces after Fritz London, who proposed these weak forces in 1930, or simply dispersion forces.

Any atom or molecule has a surrounding electron cloud. The electron cloud is roughly spherical, but, due to the Heisenberg Uncertainty Principle and the quantum nature of the atom, the electrons spend part of the time unevenly distributed in



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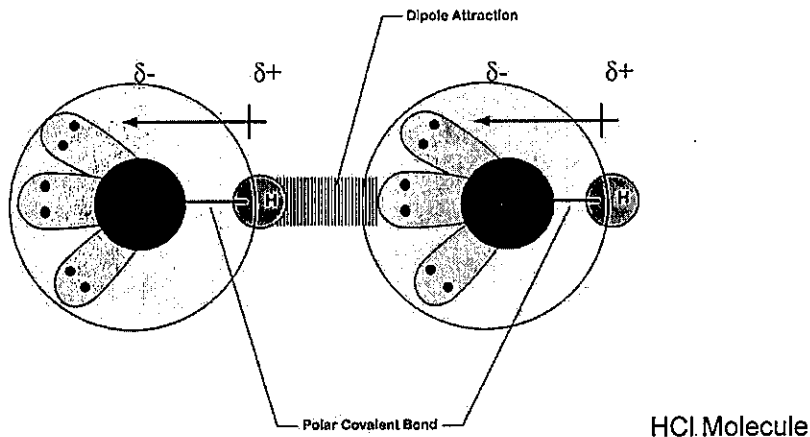
the cloud. Because of this atoms will have brief moments where a partial negative charge,  $\delta^-$ , and a partial positive charge,  $\delta^+$  exists. This “lopsided” state is called an instantaneous dipole, which can either attract or repel neighboring atoms.

If the atoms are close together, the attractive and repulsive forces of an instantaneous dipole can distort the electron cloud of a neighboring atom. This distortion is known as an **induced dipole**, that causes the opposite partial charges to attract one another.

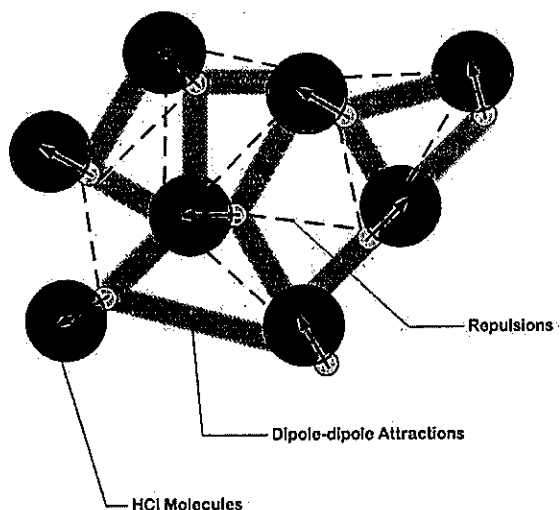
The larger the atom or molecule the better its electron cloud can distort. This is because the electrons are farther from the positive nucleus and so are held less strongly. The dispersion forces are also stronger if the particle is an already lopsided molecule.

ALL atoms and molecules exhibit London Dispersion Forces.

## Dipole-dipole Forces



Polar molecules also have a permanent dipole, which gives them an uneven distribution of electron density due to non-bonding pairs of electrons and/or polar covalent bonds. The molecule HCl has both a polar covalent bond and three non-bonding electron pairs. Partial opposite charges attract one another, as they do in induced dipole attractions. Since the partial charges are permanent and the dipoles stronger, dipole-dipole forces are stronger than induced dipole forces. Polar molecules have induced dipole forces AND dipole-dipole forces.



Dipole-dipole attractions occur over longer distances than induced dipole attractions, so they take place among larger groups of molecules. Molecules will tend to move so as to maximize attractions and minimize repulsions. Also, dipole-dipole attractions are stronger if the molecule is highly polar.

## **Hydrogen Bonding**

Hydrogen bonds are a special type of dipole-dipole attraction that occurs only between the hydrogen atom and nitrogen, oxygen or fluorine. This type of IMF is exceptionally short, polar, and strong. Note that these attractions are NOT bonds as the name implies; they are particularly strong van der Waals forces.

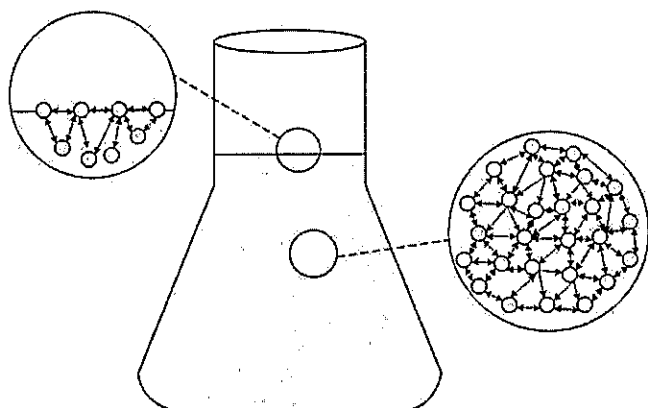
Hydrogen bonds are important in biological molecules such as proteins and DNA.

# Properties of Liquids

## Fluidity

A liquid has a definite volume (not compressible) but not a definite shape. Like a gas, a liquid takes the shape of its container. Unlike a gas, the volume of a liquid doesn't change much as pressure increases. We can explain the properties of a liquid using kinetic molecular theory. A liquid is similar to an ideal gas because the molecules that make up the liquid are moving enough to prevent the substance from having a fixed shape. A liquid is different from an ideal gas because the molecules that make up the liquid are so close together that they resist changes in volume even at high pressure due to the presence of IMFs.

Particles in the bulk of the liquid are pulled in all directions by intermolecular forces. Particles on the surface are pulled from below but not from above. This unbalanced force is the surface tension.



## Surface Tension

The surface tension is the force required to increase the surface area of a liquid. This force can be thought of as an elastic 'skin' stretched over the surface of a liquid. Liquids form spherical droplets because a sphere is the shape with the least surface area per unit volume. The liquid will roll itself into a droplet so as to stretch the skin as little as possible. Surface tension is caused by unbalanced IMF. Most molecules in the liquid are attracted to neighbors on all sides. The molecules on the surface, however, are attracted to molecules below but not above. This results in a net force pulling the surface molecules inward.

**Cohesive forces** are the attractions between a particle and others of the *same* kind, such as the hydrogen bonds among a collection of water molecules. **Adhesive forces** are attractions between a particle and others of a *different* kind, such as the attraction of a water molecule to the glass of its container. These take place at surfaces and interfaces.

Surface tension and adhesive force cause a liquid to form a meniscus in a glass test tube. A liquid with strong cohesive forces, such as water, tries to roll itself into a ball to minimize surface tension. But water is also attracted to the walls of the test tube by adhesive dipole-dipole forces. The best compromise is to form a concave surface.

Liquid mercury will form a meniscus that is convex, because it is non-polar. It has induced dipole adhesive forces, but it does not form strong intermolecular attractions with the glass. Thus, it is more attracted to itself than the walls of a glass container.

So, how can you predict if a liquid will have strong or weak adhesive forces? In general, the adhesive forces will be strong if the liquid has the same types and strengths of intermolecular attractions for the container as its cohesive forces. Glass is silicon dioxide, a polar compound capable of fairly strong dipole-dipole attractions. So is water. Mercury, on the other hand, is not polar. It is composed of individual mercury atoms loosely bound by metallic bonds. Its only adhesive force is induced dipole and the metallic bonds themselves. Water sticks to the glass because it forms dipole-dipole attractions to the glass that are similar to those that it forms with itself. The mercury, in contrast, is not attracted to the glass at all.

### **Capillary Action**

Capillary rise is a phenomenon related to surface tension. When a small diameter glass tube, or capillary, is placed upright in water, a column of liquid rises in the tube (It defies gravity!). This capillary rise can be explained in the following way: Water molecules happen to be attracted to glass (adhesion). Because of this attraction a thin film of water starts to move up the inside of the glass capillary. But in order to reduce the surface area of this film, the water level begins to rise also. The final water level is a balance between the surface tension and the energy required to lift the water against the pull of gravity.

## Viscosity

Viscosity is the amount of resistance to flow that a particular liquid has. In other words, viscosity is a measure of how thick or sticky a liquid is. The higher the viscosity, the harder the liquid is to pour. Liquids with the strongest intermolecular attractions will have the highest viscosity. As the temperature of a liquid increases, the viscosity decreases. At higher temperatures, the particles of the liquid have higher kinetic energy to overcome their intermolecular attractions. This is why hot maple syrup pours faster than cold maple syrup.

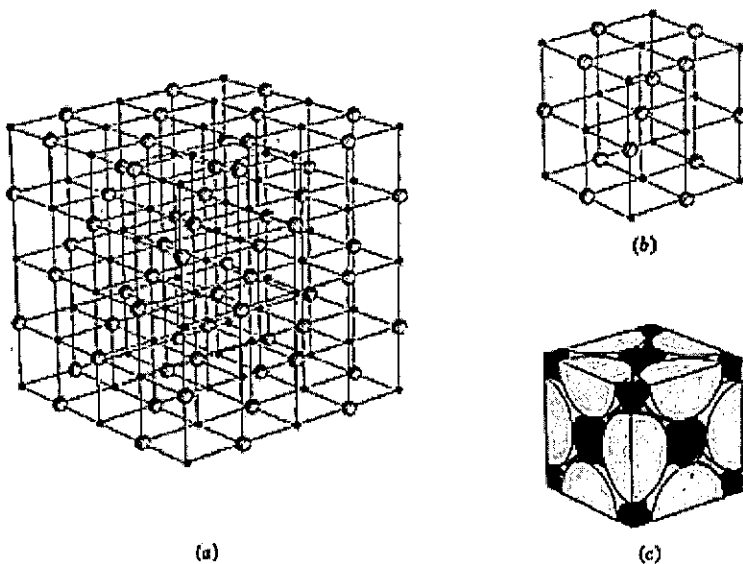
## Boiling Points

When a substance boils (goes from the liquid state to the gaseous state) the molecules go from being very close together as a liquid to being separated at a distance as a gas. If the molecules are attracted to each other, it will be much more difficult to separate them; thus the boiling point should go up. Therefore, the factors such as polarity and molecular weight that lead to stronger IMFs tend to also lead to higher boiling points.

# HONORS CHEMISTRY – SOLID STATE

## Two types of solids in broadest terms: CRYSTALLINE SOLIDS and AMORPHOUS SOLIDS

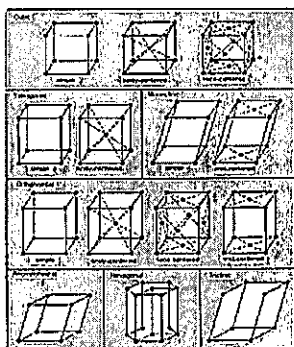
Crystals are made of **unit cells**. A unit cell is the "smallest unit that the crystal can be divided into." Like Lego blocks that assemble to make a castle, each individual block is a unit cell.



The crystal lattice and unit cell of a crystal of sodium chloride. Sodium ions,  $\text{Na}^+$ , are the smaller spheres, Chloride ions,  $\text{Cl}^-$ , are the larger spheres.

(a) Overall crystal lattice; (b) unit cell; (c) unit cell, showing division of spheres.

Basic Unit Cell Shapes:



The shape of the unit cell reflects the shape of the overall crystal.





# Solids

## Key

crystalline solid  
crystal  
amorphous solid

melting  
melting point  
supercooled liquid

crystal structure  
unit cell

The common expression "solid as a rock" suggests something that is hard or unyielding and has a definite shape and volume. In this section, you will examine the properties of solids and compare them with those of liquids and gases. The properties of solids are explained in terms of the kinetic-molecular theory, as are the other states of matter.

## ● MAIN IDEA

### The particles in a solid hold relatively fixed positions.

The particles of a solid are more closely packed than those of a liquid or gas. Intermolecular forces between particles are thus much more effective in solids. All interparticle attractions, such as dipole-dipole attractions, London dispersion forces, and hydrogen bonding, exert stronger effects in solids than in the corresponding liquids or gases. Attractive forces tend to hold the particles of a solid in relatively fixed positions, with only vibrational movement around fixed points. Because the motions of the particles are restricted in this way, solids are more ordered than liquids and are much more ordered than gases. The importance of order and disorder in physical and chemical changes will be discussed in the chapter "Reaction Energy." Compare the physical appearance and molecular arrangement of the substances in Figure 3.1 in solid, liquid, and gas form.

The particles in a solid hold relatively fixed positions.

Crystal particles are arranged in a three-dimensional lattice.

The particles in amorphous solids are not arranged in a regular pattern.

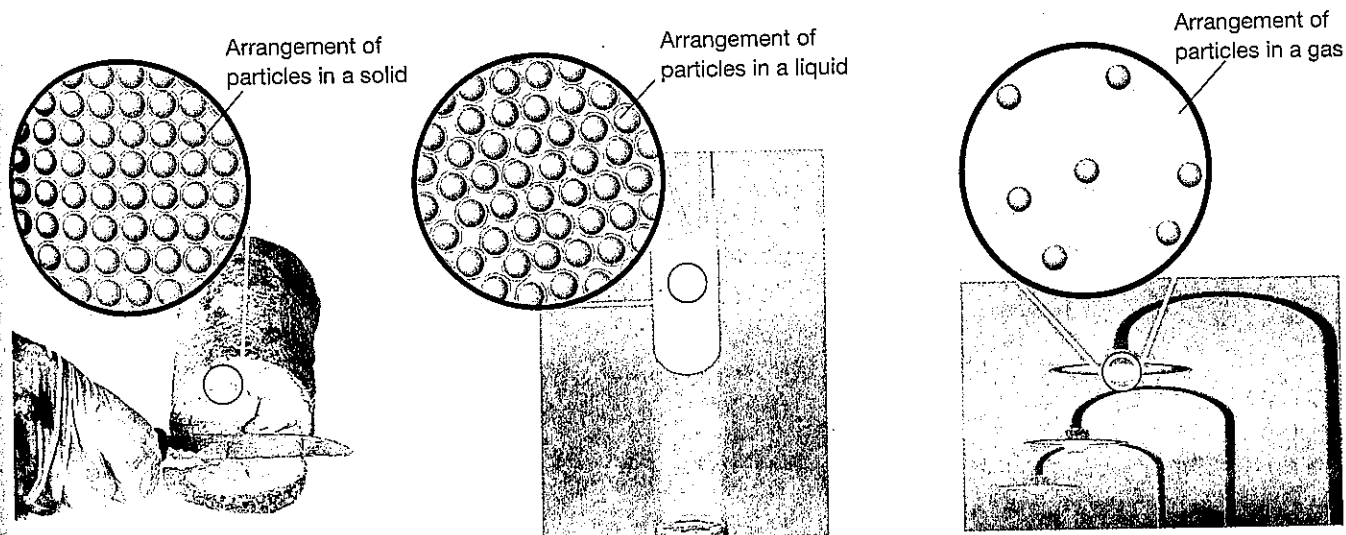
## ✓ CRITICAL THINKING

**Analyze** Analyze the pictures below, and describe in detail what each picture is showing.

FIGURE 3.1

## States of Matter

Particles of substances in three different states are shown.



There are two types of solids: crystalline solids and amorphous solids. Most solids are crystalline solids—they consist of crystals. A crystal is a substance in which the particles are arranged in an orderly, geometric, repeating pattern. Noncrystalline solids, including glass and plastics, are called amorphous solids. An amorphous solid is one in which the particles are arranged randomly. The two types of solids will be discussed in more detail later in this section.

### Definite Shape and Volume

Unlike liquids and gases, solids can maintain a definite shape without a container. In addition, crystalline solids are geometrically regular. Even the fragments of a shattered crystalline solid have distinct geometric shapes that reflect their internal structure. Amorphous solids maintain a definite shape, but they do not have the distinct geometric shapes of crystalline solids. For example, glass can be molded into any shape. If glass is shattered, the fragments can have a variety of irregular shapes.

The volume of a solid changes only slightly with a change in temperature or pressure. Solids have definite volume because their particles are packed closely together. There is very little empty space into which the particles can be compressed. Crystalline solids generally do not flow, because their particles are held in relatively fixed positions.

### Definite Melting Point

Melting is the physical change of a solid to a liquid by the addition of energy as heat. The temperature at which a solid becomes a liquid is its melting point. At this temperature, the kinetic energies of the particles within the solid overcome the attractive forces holding them together. The particles can then break out of their positions in crystalline solids, which have definite melting points. In contrast, amorphous solids, such as glass and plastics, have no definite melting point. They have the ability to flow over a range of temperatures. Therefore, amorphous solids are sometimes classified as **supercooled liquids**, which are substances that retain certain liquid properties even at temperatures at which they appear to be solid. These properties exist because the particles in amorphous solids are arranged randomly, much like the particles in a liquid. Unlike the particles in a true liquid, however, the particles in amorphous solids are not constantly changing their positions.

### High Density and Incompressibility

In general, substances are most dense in the solid state. Solids tend to be slightly denser than liquids and much denser than gases. The higher density results from the fact that the particles of a solid are more closely packed than those of a liquid or a gas. Solid hydrogen is the least dense solid; its density is about 1/320 that of the densest element, osmium, Os.

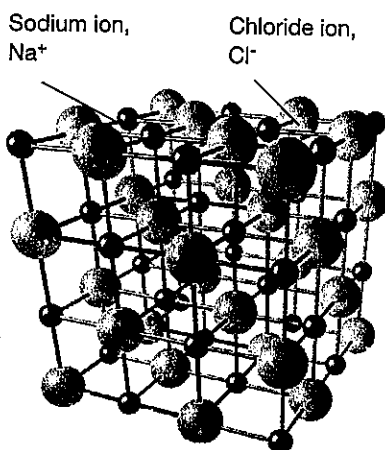
Solids are generally less compressible than liquids. For practical purposes, solids can be considered incompressible. Some solids, such as wood and cork, may *seem* compressible, but they are not. They contain pores that are filled with air. When subjected to intense pressure, the pores are compressed, not the solid matter in the wood or cork itself.

FIGURE 3.2

### Crystal Lattice of Sodium Chloride



(a) This is a scanning electron micrograph (SEM) of sodium chloride crystals.



(b) The crystal structure of sodium chloride is made up of individual unit cells represented regularly in three dimensions. Here, one unit cell is outlined in red.

### Low Rate of Diffusion

If a zinc plate and a copper plate are clamped together for a long time, a few atoms of each metal will diffuse into the other. This observation shows that diffusion does occur in solids. The rate of diffusion is millions of times faster in liquids than in solids, however.

#### ● MAIN IDEA

### Crystal particles are arranged in a three-dimensional lattice.

Crystalline solids exist either as single crystals or as groups of crystals fused together. The total three-dimensional arrangement of particles of a crystal is called a **crystal structure**. The arrangement of particles in the crystal can be represented by a coordinate system called a **lattice**. The smallest portion of a crystal lattice that shows the three-dimensional pattern of the entire lattice is called a **unit cell**. Each crystal lattice contains many unit cells packed together. Figure 3.2 (on the previous page) shows the relationship between a crystal lattice and its unit cell. A crystal and its unit cells can have any one of seven types of symmetry. This fact enables scientists to classify crystals by their shape. Diagrams and examples of each type of crystal symmetry are shown in Figure 3.3.

### The particles in amorphous solids are not arranged in a regular pattern.

The word *amorphous* comes from the Greek for "without shape." Unlike the atoms that form crystals, the atoms that make up amorphous solids, such as glasses and plastics, are not arranged in a regular pattern.

Glasses are made by cooling certain molten materials in a way that prevents them from crystallizing. The properties that result make glasses suitable for many uses, including windows, light bulbs, transformer cores, and optical fibers that carry telephone conversations.

Plastics, another type of amorphous solid, are easily molded at high temperatures and pressures. They are used in many structural materials.

Other, more recently created amorphous solids have been placed in many important applications. Amorphous semiconductors are used in electronic devices, including solar cells, copiers, laser printers, and flat-panel displays for computer monitors and television screens.