

## 7.6: Interaction Between Molecules

The properties observed for matter on the macroscopic level are determined by the properties of the constituent molecules and the interactions between them. The polar or non-polar character of a molecule will clearly be important in determining the nature of its interactions with other molecules. There will be relatively strong forces of attraction acting between molecules with large dipole moments. To a first approximation, the energy of interaction between dipolar molecules can be considered as completely electrostatic in origin, the negative end of one molecule attracting the positive end of another.

The presence of intermolecular forces accounts for the existence of solids and liquids. A molecule in a condensed phase is in a region of low potential energy, a potential well, as a result of the attractive forces which the neighboring molecules exert on it. By supplying energy in the form of heat, a molecule in a solid or liquid phase can acquire sufficient **kinetic energy** to overcome the **potential energy** of attraction and escape into the vapor phase. The vapor pressure (the pressure of the vapor in equilibrium with a solid or liquid at a given temperature) provides a measure of the tendency of a molecule in a condensed phase to escape into the vapor; the larger the vapor pressure, the greater the escaping tendency. The average kinetic energy of the molecule in the vapor is directly proportional to the absolute temperature. Thus the observation of a large vapor pressure at a low temperature implies that relatively little kinetic energy is required to overcome the potential interactions between the molecules in the condensed phase.

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The only potential interactions possible between non-polar, covalently bonded molecules are of the van der Waals' type as previously discussed for the interaction between two helium atoms at large internuclear separations. Molecules such as  $H_2$  and  $N_2$  have closed shell electronic structures in the same sense that helium does; all of the valence electrons are paired and no further chemical bonding may occur. The small polarizations of the charge densities induced by the long-range interactions of closed shell atoms or molecules result in only weak forces of attraction. The low boiling points (the temperature at which the vapor pressure above the liquid phase equals one atmosphere) observed for substances composed of molecules which can interact only through a van der Waals' type force are, therefore, understandable. Table 7.6.1 lists the normal boiling points for a number of representative compounds.

Table 7.6.1: Normal Boiling Points ( $^{\circ}K$ )

Substance	BP	Substance	BP
$H_2$	4.2	$NH_3$	240
$H_2O$	373	$NaCl$	1686
$N_2$	77.4	$LiF$	1949
$Ar$	87.4	$BeO$	4100

An argon atom is larger than a helium atom and its outer charge density is not bound as tightly as that in helium. (Recall that the ionization potential for argon is less than that for helium.) Consequently, the charge density of argon is more polarizable than that of helium and the forces of attraction between argon atoms and hence its normal boiling point are correspondingly greater. These same forces do, of course, operate in the gas phase as well and are the cause of the observed deviations from ideal gas behaviour.

The interactions between polar molecules such as  $HF$  and  $H_2O$  will be much larger and their normal boiling points greater than those observed for the non-polar molecules. When hydrogen is present at the positive end of a polar bond, the dipolar interactions are particularly strong and are given a special name, hydrogen-bonded interactions. The hydrogen bond increases in strength as the electronegativity of the atom to which the H is chemically bonded increases. (We noted previously that the dipole moment in the HA molecules increased as A was made more electronegative.) Liquid hydrogen fluoride consists of chains of molecules joined end to end; each hydrogen of one molecule is attracted to the fluorine of the next. In liquid water, each water molecule is hydrogen bonded to four other water molecules. This accounts for what appears to be an anomalously high boiling point for water when compared with the values observed for the neighboring hydride molecules  $NH_3$  and  $HF$ .

The condensed phases so far considered are called molecular solids or molecular liquids because the identity of the individual molecule is largely retained. As the forces between the molecules become larger, the point of view of regarding a solid as a collection of individual, interacting molecules becomes less satisfactory. In the limiting case of the strong interactions which exist between the ions in an ionic crystal, the concept of a discrete molecule in the solid phase ceases to exist. In solid  $KCl$ , for example, the potassium and chloride ions exist as separate entities; each potassium ion is in contact with six chloride ions, which in turn are each in contact with six potassium ions. Each ion attracts its six neighboring ions equally and thus the structure is symmetrical and therefore cubic; six ions of one sign occupy the centers of the faces of a regular cube with an ion of opposite sign at its center.

The number of nearest neighbors a given ion has in an ionic crystal is determined by the relative sizes of the positive and negative species. The  $Be^{+2}$  ion is considerably smaller than  $O^{2-}$  and the basic structure of  $BeO$  is tetrahedral, each ion surrounded by four ions of opposite charge. The strong electrostatic forces between the ions in a crystal are reflected in the high boiling points recorded in Table 7.6.1 for the ionic compounds.

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