

Module 2 : Molecular Structure

Lecture 10 : Non-covalent interactions 1: Intermolecular Forces

Objectives

In this Lecture you will learn the following

- Bonding beyond covalent bonding.
- Different types of intermolecular forces.
- Intermolecular forces.
- Hydrogen bonding in different systems.

10.1 Introduction

Covalent bonding in molecules such as H_2 , N_2 or CH_4 is characterized by a nearly "complete" sharing of valence electrons between adjacent nuclei and even the nuclei beyond the adjacent ones, as in the case of butadiene and benzene. This is a predominant form of bonding which really gives the "structures" to molecules. There are other forms of "bonding" in which features that are complementary to covalent bonding dominate in the description of the bonding process.

In ionic bonding (such as in the NaCl lattice), the ions are held together in periodic arrays and the major attractive force is the electrostatic attraction between the ions. In addition to the electrostatic attraction between the ions, there is a repulsive force between the ions, in addition to the electrostatic repulsion between the ions, there is a repulsion between the electronic clouds of the ions. Hydrogen bonding is another common bonding process wherein a hydrogen atom is normally shared between two electronegative atoms. The distances for hydrogen bonds are in the range of 1.5 to 2.5 \AA while the distances in covalent bonds are in the range of 0.7 to 2 \AA . The distances between adjacent ions in an ionic crystal are generally determined by the sizes of ions and can vary between 1 and 5 \AA .

At low temperatures even "nonreactive" species such as rare gas atoms condense to form liquids and solids and this is due to the existence of intermolecular forces. Solids formed by Ar, CH_4 or benzene are referred to as molecular solids. In these solids, the molecularity of the constituent species is intact and the molecules are held together by weak intermolecular forces. The strength of intermolecular forces is typically 0 to 3 kcal/mol, the strength of hydrogen bonds is between 3 to 8 kcal/mol while the strength of ionic and covalent bonding is in the range of 25 to 250 kcal/mol. In the present and the next lecture, we shall study the nature and consequences of intermolecular forces.

Among the intermolecular forces the most universal one is the dispersion force. The dispersion force exists between all molecules even when they do not possess any charge or dipole moment. It arises from a correlated motion of electrons between two molecular entities. Although the average dipole moment (defined as the charge separation multiplied by the distance separating the charges; this will be elaborated in the next section) of a neutral molecule is zero, the instantaneous dipole moment (the vector sum of the dipole moments due to the individual electrons, with the nuclei taken as the origin) is not zero. The instantaneous dipole moment of a molecule can influence the polarization cloud of a neighbouring molecule and be influenced by the instantaneous dipole moment of the adjacent molecule. This is the mechanism of dispersion interaction.

10.2 Dispersion Forces

The instantaneous dipole moment of one molecule executes a correlated motion (it is like two dancers dancing at tandem) with the instantaneous dipole moment of the neighbouring molecule. The dispersion energy U_{disp} is distance (r_{ij}) dependent and is always attractive. A calculation on a simple model gives

$$U_{\text{disp}} = -1.5 \left[\frac{h\nu_i\nu_j}{\nu_i + \nu_j} \right] \frac{\alpha_i\alpha_j}{r_{ij}^6} \quad (10.1)$$

Here ν_i and ν_j are the characteristic frequencies of molecules i and j and are almost equal to the frequency of the electronic transition from the lowest energy level in these molecules. The polarizabilities (polarizability measures the extent of distortion of an electron cloud by an external electric field) of molecules i and j are α_i and α_j . This attractive dispersive force between molecules is also known as the van der Waals force. The above formula is valid at large separations r_{ij} . At short distances, there is always the Pauli repulsion between molecules. Although the form of this repulsion is exponential, power law repulsion forms such as r^{-12} or r^{-10} are commonly used. One of the most commonly used form for intermolecular forces is the Lennard-Jones potential $U_{\text{LJ}}(r)$ whose form is given by

$$U_{\text{LJ}}(r) = 4 \varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (10.2)$$

This is also called a 6-12 potential because of the r^{-6} and r^{-12} terms appearing in it. The attractive term $(\sigma/r)^6$ incorporates the asymptotic dispersion interaction. The contact distance between the molecules is given by σ and ε is the depth of the potential. The values of parameters σ and ε for some systems are given in Table 10.1

System	$(\varepsilon / k_B) / \text{K}$	$\sigma / \text{\AA}$
Ar-Ar	145	3.8
Kr-Kr	201	3.6
Xe-Xe	288	3.9
Na-Ar	72	3.8
Li-Xe	175	3.8
CH ₄ -CH ₄	145	4.2

Table 10.1 The parameters for the Lennard-Jones potentials for some systems.

These potentials are empirical, i.e., the values of the parameters are obtained by fitting the potential to the experimental data such as virial coefficients. The virial coefficients quantify the departure of the equation of state of a real system from the ideal gas behaviour. The first correction to the ideal gas behaviour is given by

the second virial coefficient (B) defined through

$$PV / nRT = 1 + (n / V) B + \dots \quad (10.3)$$

The value of B is related to intermolecular potential [$u(r)$] through

$$B = - 2 \pi N_A \int_0^{\infty} [1 - e^{-U(r) / k_B T}] r^2 dr \quad (10.4)$$

where N_A is the Avogadro number. The values of ϵ and σ in Table 10.1 are obtained by fitting these parameters to the virial coefficient data. This is a typical example of how microscopic characteristics of molecules determine the macroscopic thermodynamic behaviour of gases and liquids.

The other common models for intermolecular potentials are the hard sphere potential, $U_{HS}(r)$ and the square well potential, $U_{SW}(r)$ defined by

$$\begin{aligned} U_{HS}(r) &= 0 \text{ if } r > \sigma \\ &= \infty \text{ if } r \leq \sigma \end{aligned} \quad (10.5)$$

$$\begin{aligned} U_{SW}(r) &= \infty \text{ if } r \leq \sigma \\ &= -\epsilon \text{ if } \sigma < r \leq \sigma + \delta \\ &= 0 \text{ if } r > \sigma + \delta \end{aligned} \quad (10.6)$$

The three potentials are shown in Fig 10.1

Fig 10.1 (a) The Lennard Jones potential, (b) The hard sphere potential and (c) The square well potential.

10.3 Electrostatic forces between molecules.

The ion-ion interactions which vary as $1/r$ will be considered in the lectures on the solid state. In the present section, we will consider the ion-dipole, dipole-dipole, ion-induced dipole and the dipole-induced dipole interactions. The induced-dipole induced-dipole case, which is the same as the dispersion or van der Waals force has already been discussed in the previous section.

If q_i are the charges (inclusive of sign) in a molecule (or any other general object), the dipole moment vector \vec{M} is defined by

$$\vec{M} = \sum_i q_i \vec{r}_i \quad (10.7)$$

Here \vec{r}_i is the vector from the center of mass to the location of charge. If the charge density is not discrete, but continuous and defined by a spatial charge density $\rho(x,y,z)$ where $\rho(x,y,z)$ is charge per unit volume at the location (x,y,z) , the dipole moment is defined by

$$\vec{M} = \int \vec{r}(x,y,z) \rho(x,y,z) dx dy dz \quad (10.8)$$

Dipole moment is a moment of first order in r (first power in r). Higher moments such as the quadrupole moment is defined by

$$Q_{xy} = \int \int \int xy \rho(x,y,z) dx dy dz \quad (10.9)$$

This is the xy component of the quadrupole moment. In a diatomic, out of the six components xx , xy , xz , yy , yz and zz only one is independent. With z axis as the molecular axis, the value of the quadrupole moment is given by

$$Q = \sum_i q_i (3z_i^2 - r_i^2) / e \quad (10.10)$$

The unit of M is Debye (D) or 10^{-18} esu.cm., the MKS unit is Cm. If e and $-e$ are separated by 1 \AA , then the dipole moment is 4.8×10^{-10} esu $\times 10^{-8}$ cm = 4.8×10^{-18} esu.cm = 4.8 D. The unit of quadrupole moment is area (cm^2). This is the rationale for dividing by e (the electronic charge) in eq. (10.10)

In a uniform electric field (\vec{E}) a molecule gets polarized due to the distortion of its charge distribution. This distortion can be measured by the induced dipole moment (to be distinguished from the permanent dipole moment) which is defined as

$$\vec{M} = \alpha \vec{E} \quad (10.11)$$

where $\alpha(x,y,z)$ is the polarizability. For small fields, α is independent of \vec{E} . Since the charge distribution in molecules is different in different directions (such as along a bond, perpendicular to a bond, etc), the value of α depends on the direction of the field as well as the direction in which we are considering the polarization. Therefore, we have two subscripts for α i.e., α_{xx} , α_{xy} and so on. The first subscript of α is taken as the direction of \vec{M} and the second subscript, the direction of \vec{E} . The unit of α is volume. The value of \vec{M} , Q and α for a few systems are given in Table 10.2

Atom / Molecule	Dipole Moment (Debyes)	Quadrupole Moment (10^{-16} cm^2)	Polarizability (10^{-24} cm^3)
H	0	0	0.6668
Xe	0	0	4.04

H ₂	0	0.616	0.819
O ₂	0	- 0.4	1.60
CO	0.112	- 2.0	1.98
HCl	1.109	3.7	2.63
NH ₃	1.47	1.51	2.22
H ₂ O	1.86	2.6, - 1.9, - 0.1	1.48

Table 10.2 Values of dipole moments, quadrupole moments and polarizabilities for a few systems.

The three values of the quadrupole moments of water refer to Q_{xx} , Q_{yy} and Q_{zz} , with the molecule placed in the xz plane and the z axis being the molecular axis

The ion-induced dipole (id) interaction is given by

$$U_{\text{ion-id}}(r) = - \alpha q_i^2 / 2r^4 \quad (10.12)$$

Here q_i is the ionic charge. The separation of a ion from the other species which is polarized (whose polarizability is given by α) is denoted by r . This interaction is attractive because a +ve ion pulls the negative charge density (induced by it) towards itself.

Fig 10.2 Ion-induced-dipole and dipole-dipole interactions.

The interaction between two dipoles with magnitudes μ_i and μ_j separated by \vec{r}_{ij} is given by

$$U_{dd} = \mu_i \mu_j / r_{ij}^3 [- \cos \theta_i \cos \theta_j + \sin \theta_i \sin \theta_j \cos (\varphi_i - \varphi_j)] \quad (10.13)$$

The angle between the dipole vector and \vec{r}_{ij} is measured by θ . The angles φ_i and φ_j measure the angles of the projections of the dipoles in a plane perpendicular to the plane of the paper. We see from the formula that if the dipoles oppose one another, the interaction energy is positive and the interaction is negative or attractive if they are aligned in the same direction.

A dipole polarizes a neighbouring charge distribution. If the dipole is at an angle θ_i with respect to r_{ij} separating the dipole and another entity (that is polarized) and α_j is the polarizability of that entity, then the dipole induced dipole (d-id) interaction is given by

$$U_{d-id}(r_{ij}) = - \alpha_j \mu_i^2 (3 \cos^2 \theta_i + 1) / 2r_{ij}^6 \quad (10.14)$$

All the above interactions diminish with increasing distance. A sketch of the magnitude of these interactions as a function of distance is given in fig. 10.4

Figure 10.3 Magnitudes of various intermolecular interactions as a function of the intermolecular separation.

As we have already noted, the dispersion interaction is always present. The other induced electrostatic interactions that we discussed in this section depend on the presence of a charge or a dipole moment on one of the species.

10.4 Hydrogen bonding

When an electronegative atom B (such as F,N,O,S,...) approaches (to short distances of about $2\overset{\circ}{\text{A}}$) a hydrogen atom which is bound to another electronegative atom A, then the A - H distance increases to some extent allowing for the A - H...B interaction. This is the well known hydrogen bond which is present in several molecular systems and has a role to play in various processes from the strengths of fibers, genetic coding and even in human memory.

The changes in boiling points among closely related systems such as Ne, Ar, Kr or dipolar molecules with similar dipole moments can be generally explained in terms of changes in polarizability or changes in dipole moments. Ethanol and ethylene oxide have dipole moments 1.7D and 1.9 D but ethanol boils at 352K while ethylene oxide boils at 284K. Ethylene oxide should have had a higher boiling point if the dipole moments were solely responsible for changes in boiling points. Extensive hydrogen bonding in ethanol is responsible for the higher energy (through higher temperature) required to separate ethanol molecules at the surface of the liquid from the bulk.

The strength of hydrogen bond is greater than dispersive interactions but lower than covalent bond dissociation energies. The magnitudes are in the range of 3 to 10 kcal/mol and hence the name "bond". The

hydrogen bond length (B...H) in B...H-A is in the range of 1.5 to $2.5\overset{\circ}{\text{A}}$. Examples of hydrogen bonding in HF, water, acetic acid dimer, salicylic acid (intramolecular hydrogen bond), polyamide fiber and DNA are shown in figure 10.4.

Figure 10.4 (a) and (b): Some examples of hydrogen bonds.

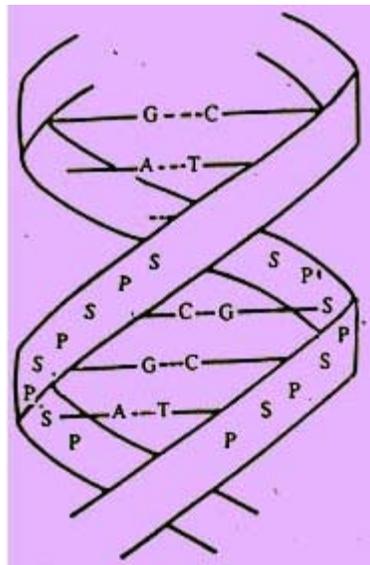


Figure 10.4 (c), (d), (e), and (f) Some examples of hydrogen bonds.

10.5 Problems

- 10.1) What are the values of bond angles and dipole moments in H_2O , H_2S and H_2Se ? How can you rationalise these?
- 10.2) Among C - F, C - Cl, C-Br and C - I which are stronger bonds? Can you rationalise the relative ordering of their bond strengths?
- 10.3) What is the dipole moment of a system wherein a charge of $+2e$ is separated from a charge of $-2e$ by 2 \AA ?
- 10.4) If two molecules of the kind mentioned in problem (3) above are separated from each other by 5 \AA (this is the center to center separation between the two dipoles) what is the interaction energy between them when they are aligned a) in parallel, b) in antiparallel configuration, c) perpendicular to each other and d) at 45° with respect to each other? Keep the distance between the centers fixed in a) to d) .
- 10.5) Q (of eq. 10.10) multiplied by the molecular diameter can be expressed in the units of cm^3 . Is this the same as polarizability?
- 10.6) All molecules do not have a nonzero dipole moment. What is the corresponding statement for molecular quadrupole moments? Do all entities have a non - zero polarizability?
- 10.7) Four charges, $+e$, $-e$, $+e$ and $-e$ are located at the corners of a square of sides 1 \AA . What is the quadrupole moment of this square?
- 10.8) An ion of $+ve$ charge is separated from a polarizable sphere of polarizability 10^{-24} cm^3 by 7 \AA . What is the interaction energy between them? (use eq 10.10). If the ion is removed and a dipole is placed in its position, what should be the strength of the dipole that gives the above value of ion - induced dipole energy?

Recap

In this Lecture you have learnt the following

Summary

In the present lecture we outlined various types of interactions other than the common covalent interactions. Among charged or dipolar species, different interactions such as ion-ion, ion-dipole, dipole-dipole, ion induced dipole,... prevail and the formulae for these have been given. Dispersion interactions exist between any pair of entities and at large distances, they fall off as r^{-6} . Hydrogen bonding is a short range interaction, occurring when a hydrogen atom is sandwiched or shared between two electronegative atoms.

Recent work shows that the requirement of two electronegative atoms is not required and molecules such as methane and benzene also participate in hydrogen bonding. Interactions other than covalent and ionic are much weaker and fall off rapidly with distance. Sketches of various intermolecular forces have been given in the lecture. These non-covalent interactions play a central role in the formation of solids and liquids and a good understanding of these can assist greatly in obtaining materials with specifically designed properties.