

Interactions between Atoms and Molecules

There are three aspects that are of particular importance for any interaction: Its strength, the distance over which it acts, and the environment through which it acts. Short range interactions, as summarized in Table 1, can be of following nature: ionic, covalent, metallic, or dipolar origin. Ionic, covalent, metallic and hydrogen bonds are so-called atomic forces that are important for forming strongly bonded condensed matter. These short range forces arise from the overlap of electron wave functions. Interactions of dipolar nature are classified further into strong hydrogen bonds and weak Van der Waals (VdW) interactions. They arise from dipole-dipole interactions. Both, hydrogen and VdW interactions can be responsible for cooperation and structuring in fluidic systems, but are also strong enough to build up condensed phases. Following is a description of these short range forces:

- A. **Ionic Bonds:** These are simple Coulombic forces, which are a result of electron transfer. For example in lithium fluoride, lithium transfers its 2s electron to the fluorine 2p state. Consequently the shells of the atoms are filled up, but the lithium has a net positive charge and the Fluorine has a net negative charge. These ions attract each other by Coulombic interaction which stabilizes the ionic crystal in the rock-salt structure.
- B. **Covalent Bond:** The standard example for a covalent bond is the hydrogen molecule. When the wave-function overlap is considerable, the electrons of the hydrogen atoms will be indistinguishable. The total energy will be decreased by the “exchange energy”, which causes the attractive force. The characteristic property of covalent bonds is a concentration of the electron charge density between two nuclei. The force is strongly directed and falls off within a few Ångstroms.
- C. **Metallic Bonds and Interaction:** The strong metallic bonds are only observed when the atoms are condensed in a crystal. They originate from the free valency electron sea which holds together the ionic core. A similar effect is observed when two metallic surfaces approach each other. The electron clouds have the tendency to spread out in order to minimize the surface energy. Thus a strong exponentially decreasing, attractive interaction is observed.
- D. **Dipole Interactions:**
 - D.1. **Hydrogen Bond Interaction:** Strong type of directional dipole-dipole interaction
 - D.2. **Van der Waals Interaction:** The relevance of VdW interactions goes beyond of building up matter (e.g., Van der Waals organic crystals (Naphthalene)). Because of their “medium” range interaction length of a few Ångstroms to hundreds of Ångstroms, VdW forces are significant in fluidic systems (e.g, colloidal fluids), and for adhesion between microscopic bodies. VdW forces can be divided into three groups:
 - o *Dipole-dipole force:* Molecules having permanent dipoles will interact by dipole-dipole interaction.
 - o *Dipole-induced dipole forces:* The field of a permanent dipole induces a dipole in a non-polar atom or molecule.
 - o *Dispersion force:* Due to charge fluctuations of the atoms there is an instantaneous displacement of the center of positive charge against the center of the negative charge. Thus at a certain moment a dipole exists and induces a dipole in another atom. Therefore non-polar atoms (e.g. neon) or molecules attract each other.

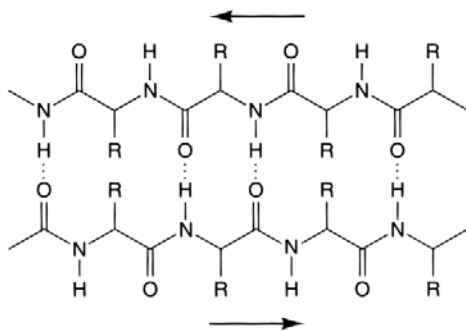
Table 1: Short Range Interaction Forces

Nature of Bond	Type of Force	Energy (kcal/mol)	Distance
Ionic bond	Coulombic force	180 (NaCl) 240 (LiF)	2.8 Å 2.0 Å
Covalent bond	Electrostatic force (wave function overlap)	170 (Diamond) 283 (SiC)	N/A
Metallic bond	free valency electron sea interaction (sometimes also partially covalent (e.g., Fe and W))	26 (Na) 96 (Fe) 210 (W)	4.3 Å 2.9 Å 3.1 Å
Hydrogen Bond	a strong type of directional dipole-dipole interaction	7 (HF)	
Van der Waals	(i) dipole-dipole force (ii) dipole-induced dipole force (iii) dispersion forces (charge fluctuation)	2.4 (CH ₄)	significant in the range of a few Å to hundreds of Å

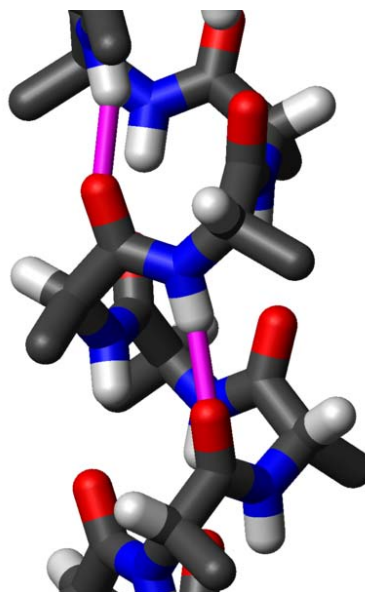
In comparison: Thermal Energy (Brownian Motion): 0.57 kcal/mol

(Unit conversion: 1 kJ/mol = 0.2388459 kcal/mol)

Hydrogen Bond



β-Sheet
with hydrogen bonding
between protein strands



α-Helix Structure

Every backbone N-H group donates a hydrogen bond to the backbone C=O group of the amino acid four residues earlier

Van der Waals Interactions for Point Interactions

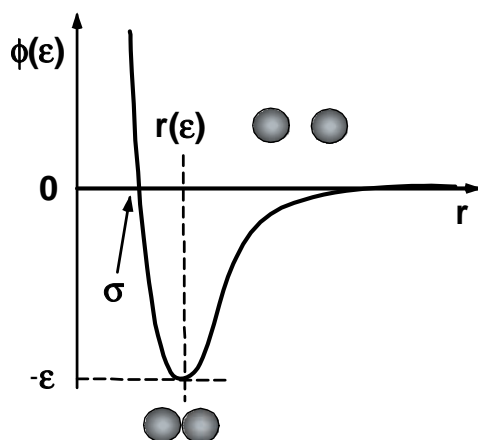
The attractive VdW pair potential between point particles (i.e., atoms or small nonpolar spherical molecule) is proportional to $1/r^6$, where r is the distance between the point particles. The widely used semi-empirical potential to describe VdW interactions is the Lennard-Jones (LJ) potential, referred to as the 6-12 potential because of its $(1/r)^6$ and $(1/r)^{12}$ distance r dependence of the attractive interaction and repulsive component, respectively. While the 6-potential is derived from point particle dipole-dipole interaction, the 12-potential is based on pure empiricism. The LJ potential is provided in the following two equivalent forms as function of the particle-particle distance r :

$$\phi(r) = -\frac{C_{vdw}}{r^6} + \frac{C_{rep}}{r^{12}} = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] \quad (1a)$$

where

$$\sigma = \left(\frac{C_{rep}}{C_{vdw}}\right)^{\frac{1}{6}}; \quad \epsilon = \frac{C_{vdw}^2}{4C_{rep}} \quad (1b)$$

C_{vdw} and C_{rep} are characteristic constants. $C = C_{vdw}$ is called the VdW interaction parameter. The empirical constant ϵ represents the characteristic energy of interaction between the molecules (the maximum energy of attraction between a pair of molecules). σ , a characteristic diameter of the molecule (also called the *collision diameter*), is the distance between two atoms (or molecules) for $\phi(r) = 0$. The LJ potential is depicted below.



Lennard Jones (6-12) potential (empirical Van der Waals Potential between two atoms or nonpolar molecules).

LJ parameters, ϵ and σ

Substance	σ (Å)	ϵ/k
H ₂ (<i>light element</i>)	2.915	38.0
Ar (<i>noble gas</i>)	3.418	124
<i>Polyatomic Substances</i>		
Air	3.617	97.0
N ₂	3.681	91.5
<i>Hydrocarbons</i>		
CH ₄	3.822	137
n-C ₆ -H ₁₄	5.909	413

$k = 1.380 \times 10^{-16}$ erg molecule⁻¹ K⁻¹ (Boltzmann's constant)