

3.2: Intermolecular Forces

In Chapter III.1 we investigated interactions between bonded molecules, and to model the configurational energy of a macromolecule we introduced an empirical potential energy function for the covalent bonding potential energy, the angular potential energy, and the torsional potential energy. We now discuss interactions between atoms that are not directly bonded together, called non-bonding interactions. These give rise to two common types of intermolecular interactions: electrostatic interactions between charged molecules, and van der Waals (dispersion) interactions. The Coulomb interaction between charges plays an important role in the assembly of biological structures. Other important types of intermolecular forces are the dipole-dipole interaction between polar molecules and the dipole-induced-dipole between a polar molecule and a non-polar molecule with a given polarizability. The formation of biological complexes, secondary structure, and protein/ligand complexes is governed by the energetic contributions of each of these types of interactions.

Learning Objectives

- Be able to sketch and label the attractive and repulsive Coulomb potential between ions.
- Be able to sketch and label the Lennard Jones potential for dispersion interactions.
- Know how the different potential energy terms for the Coulomb, van der Waals, dipole, and induced dipole scale with the interatomic distance. Know which of these potentials is considered long-ranged.
- Be able to compute the potential energy between two ions given the interatomic distance or vice versa.
- Be able to predict how the addition of counter ions or salts in aqueous solvent screens the Coulombic interaction

The Coulomb potential between ions

The potential energy acting between two charged species in a vacuum, as shown in **Figure III.2.A**, depends on the separation distance between the ions, r , and the charge on the ions z_A and z_B :

$$V = \frac{z_A z_B}{4\pi\epsilon_0 r} \quad (3.2.1)$$

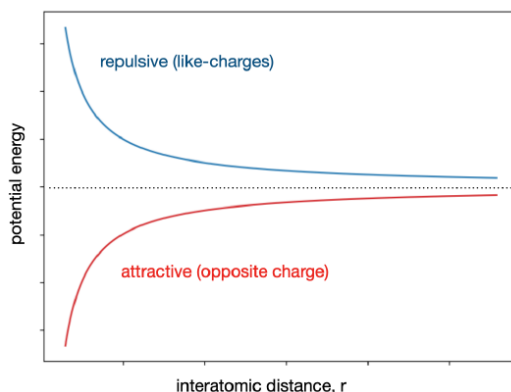


Figure III.2.A. The Coulomb potential energy given by Equation 3.2.1 describes the electrostatic interactions between ions. The potential energy is attractive between ions of opposite charge and repulsive between ions of the same charge.

Notice that the potential energy from Equation 3.2.1 is positive (repulsive) for like-charges and negative (attractive) for opposite-charges. The constant ϵ_0 is the **vacuum permittivity** as is $\epsilon_0 = 8.854187816 \times 10^{-12} \text{ J C}^2 \text{ m}^{-1}$. Equation 3.2.1 is known as the **Coulomb interaction** because the force acting between two ions attract or repel each other according to **Coulomb's law**:

$$F = -\frac{z_A z_B}{4\pi\epsilon_0 r^2} \quad (3.2.2)$$

Equations 3.2.1 and 3.2.2 describe the interactions between charged species in a vacuum. For atoms that are not in a vacuum, we need to take account of the fact that the solvent or surrounding molecules lie between the two interacting ions and mediate the strength of this interaction. For example, in aqueous solvent, the bare ions are surrounded by water molecules which weakens the interaction between ions as shown in **Figure III.2.B**.

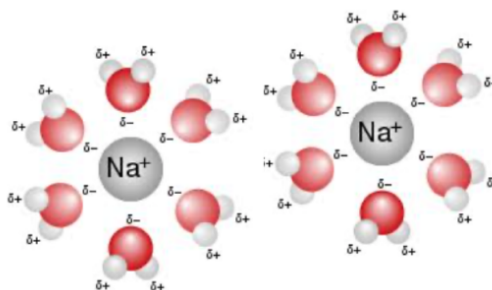


Figure III.2.B. The Coulomb potential energy between bare charges is screened in solution as the water molecules form a solvation shell around the ions.

To account for the solvent, the permittivity of the medium is expressed as the vacuum permittivity times the **relative permittivity** ϵ_r . For ions in a medium the Coulomb interaction becomes

$$V = \frac{z_A z_B}{4\pi\epsilon_0\epsilon_r r} \quad (3.2.3)$$

Table III.2.a reports the relative permittivity ϵ_r for different solvents. Note that highly polar solvents like water ($\epsilon_r = 78$) can have a large effect on the strength of the Coulomb interaction.

Table III.2.a. Relative dielectric strength of some common solvents

| Solvent | relative dielectric constant, ϵ_r |
|-------------|--------------------------------------------|
| Acetic acid | 6 |
| Methanol | 33 |
| Formic acid | 58 |
| Water | 78 |

Ion-dipole and dipole-dipole interactions

Polar molecules have a net dipole moment μ . In the presence of an ion, there will be an ion-dipole interaction resulting from an attractive interaction between the ion and one end of the dipole moment, and a repulsive interaction between the ion and the other end of the dipole moment. In general, the strength of the interaction will depend on the orientation between the dipole moment and the ion as shown in Figure X. The interaction potential in a vacuum is given by

$$V = -\frac{\mu_A z_B \cos \theta}{4\pi\epsilon_0 r^2} \quad (3.2.4)$$

where θ is the angle that measures the alignment between the dipole moment and the ion (shown in Figure X). Notice that if z_B is positive, the lowest energy occurs when $\theta = 0$ (and $\cos \theta = 1$) because the positive ion will be closest to the negative end of the dipole moment.

For the interaction between two polar molecules, **dipole-dipole** interaction will depend on the orientation of the two polar molecules and will be *attractive* when the two dipole moments are aligned tail to tip because oppositely charged ends of the molecule attract (see Figure X). The dipole dipole interaction between two molecules in a vacuum is

$$V = \frac{\mu_A \mu_B (1 - 3 \cos^2 \theta)}{4\pi\epsilon_0 r^3} \quad (3.2.5)$$

Note that this potential energy decrease more rapidly as function of distance ($1/r^3$) than Equation 3.2.4.

From Equation 3.2.5, we see that the *attractive* dipole-dipole is strongest (most negative) when $\theta = 0$ or $\theta = 180^\circ$ (and $1 - 3 \cos^2 \theta = -2$). This corresponds to the case when the dipole moments of the two polar molecules are perfectly aligned as in Figure X. In this case, the dipole-dipole interaction energy is

$$V = -\frac{2\mu_A \mu_B}{4\pi\epsilon_0 r^3} \quad (3.2.6)$$

It should be emphasized that Equation 3.2.6 is the dipole-dipole attractive potential energy if the molecules have a fixed orientation in which the dipole moments are perfectly aligned as shown in Figure X.

In macroscopic systems, where molecules are free to rotate, the average dipole-dipole interaction energy represents the average orientation of the dipole moments. When molecules are free to rotate, the dipole-dipole interaction energy is

$$V = -\frac{2}{3} \frac{\mu_A^2 \mu_B^2}{(4\pi\epsilon_0)^2 r^6} \frac{1}{k_B T} \quad (3.2.7)$$

The exact form of Equation 3.2.7 is not important to us here, but it is important to notice that the distance dependence on the average interaction energy between polar molecules scales as the inverse *sixth* power of the interatomic distance. (which turns out to be the same as the van der Waals interaction)

Key Result

The average interaction energy between polar molecules scales as $V \propto \frac{1}{r^6}$ where r is the distance between atoms.

Induced-dipole interactions and dispersion interactions

dipole-induced-dipole interaction energy

$$V = -\frac{\mu_A^2 \alpha_B}{\pi \epsilon_0 r^6} \quad (3.2.8)$$

scales as $1/r^6$ (same scaling as average dipole-dipole interaction).

dispersion interaction energy

$$V = -\frac{3}{2} \frac{\alpha_A \alpha_B}{r^6} \frac{I_A I_B}{I_A + I_B} \quad (3.2.9)$$

where I_A and I_B are the ionization energies of the two molecules and α_A and α_B are the polarizabilities. scales as $1/r^6$ (same scaling as average dipole-dipole interaction and dipole-induced-dipole interaction).

In general, we can summarize all the non-Coulomb interactions (average dipole-dipole interaction, dipole-induced-dipole, and dispersion interaction) as scaling as $1/r^6$. These potentials are often lumped together in a single attractive “van der Waals” term

$$V = -\frac{A}{r^6} \quad (3.2.10)$$

where A is a parameter that depends on the identity of the atoms and molecules and the types of interactions present between them. Equation 3.2.10 will be used in the remainder of this book to describe attractive van der Waals type interactions.

Key Result

The van der Waals attractive energy is represented as a contribution from three different types of interactions: average dipole-dipole, dipole-induced-dipole, and dispersion interactions. The potential energy is written as $V = -\frac{A}{r^6}$ such that the van der Waals attractive energy scales as the inverse separation distance to the sixth power and A is a coefficient that depends on the identity of the atoms and molecules.

The Lennard-Jones (12,6) potential

$$V = \frac{B}{r^n} \quad (3.2.11)$$

where B is another parameter, and n is an integer (typically set to 12). For the case where $n = 12$, the potential energy is a balance between short-ranged repulsion ($1/r^{12}$) and van der Waals attractions at larger distances ($1/r^6$). The sum of the repulsive and van der Waals attractive interaction can be expressed by the **Lennard-Jones potential**

$$V = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (3.2.12)$$

where ϵ is a parameter with units of energy that characterizes the depth of the attractive minima and σ is a parameter with units of distance that parameterizes the range of the potential. Figure X shows a comparison of the Lennard-Jones potential with the Born-Oppenheimer potential energy surface between two argon atoms.

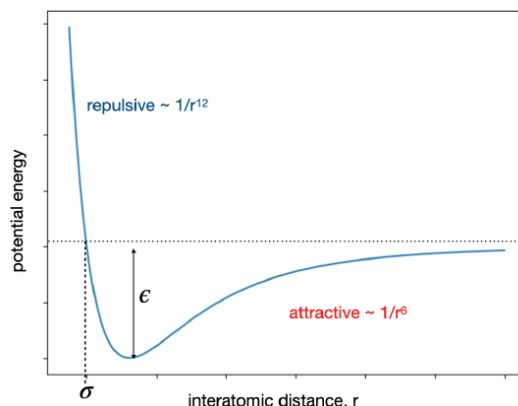


Figure III.2.?. The form of the Lennard-Jones potential given by Equation 3.2.12 is a common potential to describe both the attractive van der Waals interaction that scales as $\sim 1/r^6$, along with a short-ranged repulsive interaction that scales as $\sim 1/r^{12}$. The Lennard-Jones potential is parameterized by the value of ϵ , which defines the well depth, and the value of σ which is the interparticle distance at which the potential energy is zero.

The Lennard-Jones potential is a good approximation for the interaction energy between two non-charged species. Table X presents the values of the parameters ϵ and σ for some atoms and molecules.

Hydrogen Bonds

$$V = \frac{E}{r^{12}} - \frac{E}{r^{10}} \quad (3.2.13)$$

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