

## Lecture 9

# Electrostatic Nature of Intermolecular Forces

In Lecture 1 we have introduced the intermolecular van der Waals interaction, which has a power law of  $r^{-6}$ . In the following 2 lectures we will see how such relations are derived.

We have only 4 fundamental forces in nature: the gravity, the electromagnetism, the weak interactions and strong interactions. There are no magics about the intermolecular forces: they all stem from the electromagnetism. In particular, when magnetism can be ignored, the electrostatics and electrodynamics govern the intermolecular interactions.<sup>1</sup> In this lecture, we will introduce the fundamentals about the intermolecular forces, using the knowledge from electrostatics. The perspectives of this lecture are:

- Basic derivations of intermolecular interactions
- Understanding the power laws of different interactions
- Comparison between different interactions

### 9.1 Charge and dipole

In Lecture 8 we have briefly introduced the basic concepts about dipole moments in a dielectric medium. We will give a formal definition of the dipole moments here, which serves as an important recipe for the derivation of intermolecular interactions.

Assume a body  $\Omega$  with charge density distribution  $\rho(r)$  (containing both free and bound charges), where  $r$  is the position in a certain coordinate system. The geometry can be seen in Figure 9.1. The electrostatic potential  $\psi(x)$  in vacuum at position  $x$  is defined as:

$$\psi(x) = \frac{1}{4\pi\epsilon_0} \int_{\Omega} \frac{\rho(r)}{|r-x|} d^3r \quad (9.1)$$

We do not always need to evaluate the term  $|r-x|$ . For instance when we are modeling the interaction of two molecules separated by a large distance, it is often more desirable to isolate the parts with  $r$ , i.e. the molecular properties and the  $x$  part, i.e. the distance part.

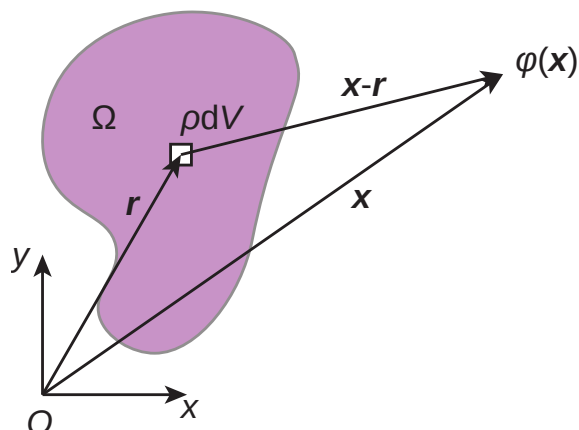


Figure 9.1: Additive calculation of Coulombic potential.

This is done by first moving the coordinate origin  $\mathbf{O}$  near the “center” of  $\Omega$ , and performing a Taylor expansion to  $1/|r - x|$  (see Figure 9.1):

$$\begin{aligned} \psi(x) &= \frac{1}{4\pi\epsilon_0} \int_{\Omega} \left[ \frac{1}{|\mathbf{O} - \mathbf{x}|} + r \nabla \frac{1}{|r - x|} \Big|_{r=0} + \dots \right] \rho(r) d^3r \\ &\approx \underbrace{\frac{1}{4\pi\epsilon_0} \int_{\Omega} \frac{\rho(r)}{|\mathbf{x}|} d^3r}_{\text{Monopole}} + \underbrace{\frac{1}{4\pi\epsilon_0} \int_{\Omega} \frac{\mathbf{r} \cdot \mathbf{x}}{|\mathbf{x}|^3} \rho(r) d^3r + \dots}_{\text{Dipole}} \end{aligned} \quad (9.2)$$

As can be seen, by isolating the  $r$  and  $x$  terms, we separate the electrostatic potential into two parts, namely the “Monopole” and “Dipole” contributions. As you may imagine, for higher order expansion terms, the contributions from “Quadrupole”, “Hexapole” also exist (as thus known as multipole expansion of charges<sup>2</sup>). Here we only study the monopole and dipole terms. From Equation 9.2, the definition for total charge  $q$  and dipole moment  $u$  of  $\Omega$  is naturally recovered:

$$q = \int_{\Omega} \rho(r) d^3r \quad (9.3)$$

$$u = \int_{\Omega} \mathbf{r} \rho(r) d^3r \quad (9.4)$$

And as you may observe,  $\psi_{\text{monopole}}(x) \propto |x|^{-1}$ , which is the Coulomb’s law, while  $\psi_{\text{dipole}}(x)$  is roughly proportional to  $|x|^{-2}$ . This means the dipoles behaves similar to the monopoles, while with a different power law of distance.

In systems where charges are localized on individual molecules, we can view the dipoles as two monopoles  $-q$  and  $+q$  separated by vector  $r$ , and the dipole moment  $u$  is defined as:

$$u = ql \quad (9.5)$$

pointing from  $-q$  to  $+q$  (see Figure 9.2 left). As an example, the dipole moment of water  $u_w$ , is the vector sum of the dipole moments of the O-H bonds  $u_{\text{OH}}$ .



Figure 9.2: The dipole. Left: the dipole moment  $u$  is defined pointing from  $-q$  to  $+q$ . Right: the dipole moment  $u_w$  of water, is the sum of the bond dipole moments  $u_{OH}$ .

The unit of dipole is  $C \cdot m$ . In chemistry the alternative unit Debye (D) is also used, where  $1 \text{ D} \approx 0.21 e \cdot \text{\AA}$ . Let's see some examples of dipole moments:

- The permanent  $u$  of water is ca. 1.85 D.
- The Transient  $u$  of a Bohr-atom is 2.54 D.

As can be seen, there are two types of dipoles in the system. A permanent dipole exists in a **polar** molecule, such as water and ethanol, that electron cloud does not distribute uniformly in the molecule. On the other hand, in a **non-polar** molecule, a transient dipole moment exists pointing from electron to the nucleus which changes over time. The time-averaged dipole moment of a non-polar molecule without external field is always 0.

## 9.2 The electric polarizability

As discussed in Lecture 8, the dipole moment of a dielectric medium changes when an electric field is applied. Such process is called electric **polarization** and the dipoles created are called **induced-dipole moments**. The strength of polarization of an individual molecule is defined as the **polarizability**, usually named as  $\alpha$  and defined as:

$$\alpha = \frac{|u|}{|E|} \quad (9.6)$$

The unit of polarizability is  $F \cdot m^2$ . It is also alternatively expressed in **polarizability volume**  $\alpha/(4\pi\epsilon_0)$ , with the unit of  $m^3$ .

Depending the origin of the polarization, the polarizability of a material can be divided into electronic and dipolar polarizabilities. They are defined as:

### 1. Electronic polarizability $\alpha_0$

The electronic polarizability  $\alpha_0$  characterizes how much an electron can be displaced under an electric field. Consider a Bohr hydrogen atom model, that an electron orbits a proton with a orbital radius of  $r_B$  (Figure 9.3). The strength of the electric field that binds the electron is electric field that binds the charges is  $|E| = e/(4\pi\epsilon_0 r_B^2)$ , plug this into Equation 9.6, we have:

$$\alpha_0 = \frac{|u|}{|E|} = 4\pi\epsilon_0 r_B^3 \quad (9.7)$$

We can see that  $\alpha_0$  has a real meaning: the characteristic volume the electron cloud. The electronic polarizability is ubiquitous (i.e. independent of the polarity of the molecule) and independent of temperature.

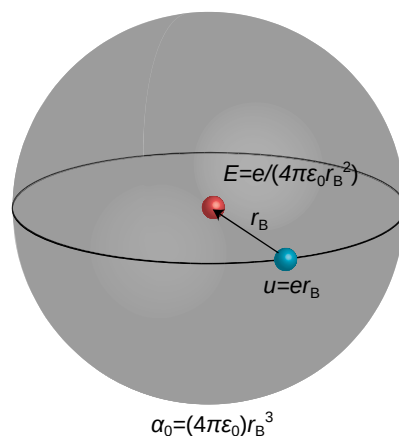


Figure 9.3: Polarizability of a Bohr atom with radius  $r_B$ . The polarizability is proportional to its volume.

## 2. Dipolar polarizability $\alpha_{\text{dip}}$

Unlike the electronic polarizability which is independent of the polarity of the molecule, the dipolar polarizability  $\alpha_{\text{dip}}$  comes from polar molecules. For an ensemble of polar molecules at thermal equilibrium, the net dipole moment is zero. However under external electric field, the individual dipole moments tend to align along the E-field lines, and creates a net induced dipole moment.

We will use a simple statistic mechanics approach to see the origin of such polarizability. The energy of a dipole moment  $u$  in an external field  $E$  depends on the angle  $\theta$  between them:<sup>3</sup>

$$w_{u-E}(\theta) = -u \cdot E = -uE \cos(\theta) \quad (9.8)$$

where  $u$  and  $E$  are the modules of  $u$  and  $E$ , respectively. This means, if a dipole can freely rotate, when placing an external field  $\mathbf{E}$ , it is possible to **align** the dipole due to minimization of energy (Figure 9.4). At finite temperature  $T$ , the average dipole  $\hat{u}$  can be calculated using Boltzmann statistics

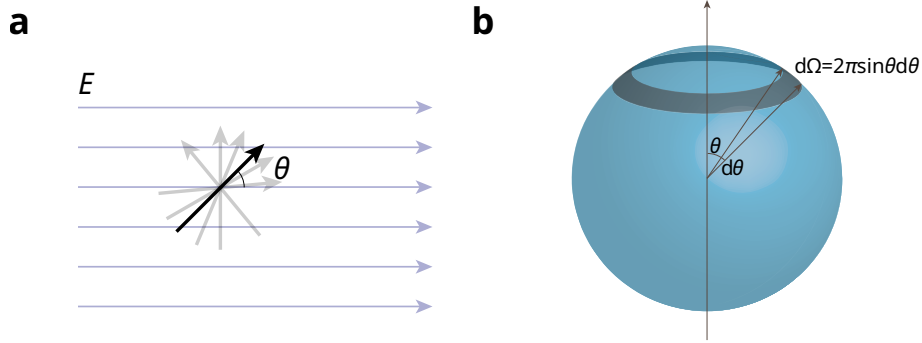


Figure 9.4: (a) Free-rotating dipole  $\mathbf{u}$  in a uniform electric field  $\mathbf{E}$ . (b) Scheme for angle dependent integral.

$$\begin{aligned}
 \hat{u} &= \frac{\int_{\theta=0}^{\theta=\pi} u \cos(\theta) \exp\left(-\frac{uE \cos(\theta)}{k_B T}\right) d\Omega}{\int_{\theta=0}^{\theta=\pi} \exp\left(-\frac{uE \cos(\theta)}{k_B T}\right) d\Omega} \\
 &= \frac{\int_0^\pi u \cos(\theta) \exp\left(\frac{uE \cos(\theta)}{k_B T}\right) (2\pi \sin(\theta)) d\theta}{\int_0^\pi \exp\left(\frac{uE \cos(\theta)}{k_B T}\right) (2\pi \sin(\theta)) d\theta}
 \end{aligned} \tag{9.9}$$

Let  $\cos(\theta) = y$ ,  $\frac{uE}{k_B T} = \beta$ , we have:

$$\begin{aligned}
 \hat{u} &= u \frac{\int_{-1}^1 y \exp(\beta y) dy}{\int_{-1}^1 \exp(\beta y) dy} \\
 &= u \left[ \frac{e^{\beta y} (\beta y - 1)}{\beta^2} \Big|_{-1}^1 \right] / \left[ \frac{e^{\beta y}}{\beta} \Big|_{-1}^1 \right] \\
 &= u \left[ \frac{e^\beta + e^{-\beta}}{e^\beta - e^{-\beta}} - \frac{1}{\beta} \right] \\
 &= u \left[ \coth(\beta) - \frac{1}{\beta} \right]
 \end{aligned} \tag{9.10}$$

Finally we define  $L(\beta) = \coth(\beta) - \frac{1}{\beta}$  (which is known as the Langevin function), we plot the behavior of  $L(\beta)$  as function of  $\beta$  in Fig 9.5. As can be seen,  $L(\beta)$  is approximated by

$\beta/3$  when  $\beta \ll 1$ . Therefore, we can estimate the polar polarizability as:

$$\begin{aligned}\alpha_{\text{dip}} &= \frac{uL(\beta)}{E} \\ &\approx \frac{1}{3} \frac{u\beta}{E} \\ &\approx \frac{1}{3} \frac{u^2}{k_B T}\end{aligned}\quad (9.11)$$

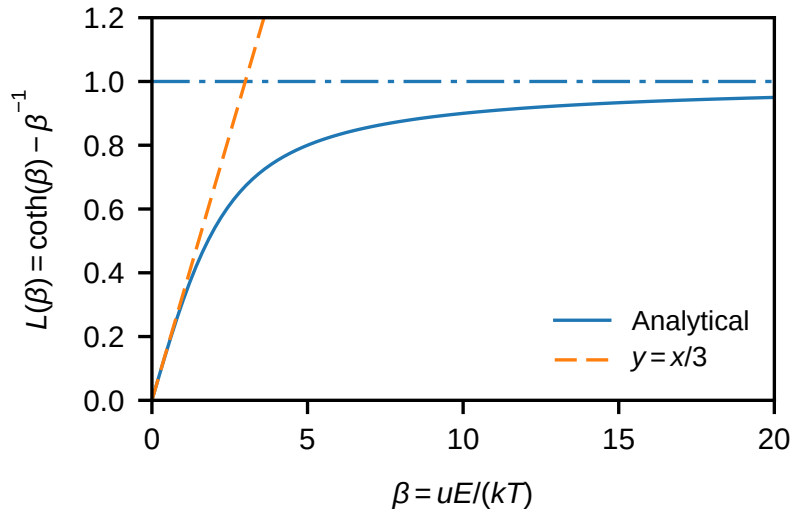


Figure 9.5:  $L(\beta)$  as function of  $\beta$ . When  $\beta \ll 1$ , it is close to  $L(\beta) = \beta/3$

In summary, the polarizability of a freely rotating molecule under moderate field, is a sum of the electronic and dipolar polarizabilities:

$$\alpha = \alpha_0 + \alpha_{\text{dip}} = \alpha_0 + \frac{u^2}{3k_B T} \quad (9.12)$$

Finally, we give a short introduction about the relation between the electric polarizability  $\alpha$  and the relative permittivity  $\epsilon_r$  discussed in Lecture 8. The displacement field  $D$  is related to the electric field  $E$  via:

$$\begin{aligned}D &= \epsilon_r \epsilon_0 E \\ &= \epsilon_0 E + P\end{aligned}\quad (9.13)$$

where  $P$  is the **polarization density** of a given domain and defined as  $P = \partial u / \partial V$ . The  $E$  and  $P$  can be regarded as the contribution from free and bound charges, respectively. We can use the definition of electric polarizability to replace  $u$  in the polarization density. Note that in the presence of other molecules, the electric field that polarizes the molecule is different from the external field in Equation 9.12 due to the so-called “local field effect”.<sup>4</sup> After

considering the local field effect, the *microscopic* quantity  $\alpha$  is related to the macroscopic quantity  $\epsilon_r$  for a molecular solid with:<sup>5</sup>

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{N\alpha}{3\epsilon_0} \quad (9.14)$$

where  $N$  is the number of molecules per unit volume. This relation is known as the Clausius-Mossotti equation and is very handy to calculate relative permittivities of simple liquids.

### 9.3 Interplay between the charge components

The charge, dipole and induced dipole are the essential components that we need for completing the theory of intermolecular interactions. We will discuss all possible mutual interaction approaches, which are summarized in Table 9.1. For each type of interaction  $w_{AB}$ , A and B can be charge ( $q$ ), dipole ( $u$ ) or electric polarizability ( $\alpha$ ).

Table 9.1: Examples of  $w_{AB}$  for every possible interaction type.

A	B	Example of $w_{AB}$
$q$	$q$	Formation energy of ionic crystals
$q$	$u$	Solvation energy of ion in water
$q$	$\alpha$	Anion/cation - $\pi$ interaction energy
$u$	$u$	Surface tension of polar solvent (non H-bond)
$u$	$\alpha$	Surface tension between non-polar/polar solvents
$\alpha$	$\alpha$	London dispersion energy of noble gases

#### 9.3.1 Charge-charge interaction

This is the well-known Coulombic interaction between charges:

$$w_{qq}(r) = -\frac{q^2}{4\pi\epsilon_0\epsilon_r r} \quad (9.15)$$

*Power law:*  $r^{-1}$

Let's see 2 examples:

1.  $\text{Na}^+ - \text{Cl}^-$  in vacuum.  $r = 2.76 \text{ \AA}$ .  $w = -8.4 \times 10^{-19} \text{ J} \approx -200 k_B T$
2.  $\text{Na}^+ - \text{Cl}^-$  in water,  $\epsilon_w = 78$ ,  $w \approx -2.6 k_B T$ .

The above examples show that ionic materials tend to dissolve in highly polar solvent (high  $\epsilon_r$ ) like water. (This does not explain the  $K_{sp}$  difference of ionic crystals, though, which is also related with the hydration energy). Another interesting example of the charge-charge interaction: the formation energy of ionic crystals. In the fcc lattice of 1:1 ionic

crystal such as NaCl, if the distance between cation-anion is  $r$ , the total lattice energy is given by:

$$w_{\text{fcc}} = -\frac{e^2}{4\pi\epsilon_0} \left[ \frac{6}{r} - \frac{12}{\sqrt{2}r} + \frac{8}{\sqrt{3}r} - \frac{6}{\sqrt{4}r} + \frac{24}{\sqrt{5}r} + \dots \right] \quad (9.16)$$

$$= -1.748 \frac{e^2}{4\pi\epsilon_0 r}$$

The constant 1.748 is called the **Madelung constant**.<sup>6</sup> The total formation energy of an *infinite* lattice is comparable with individual ion pairs, which is quite amazing.

### 9.3.2 Charge-dipole interaction

Due to the angle dependent of dipole in an external field as shown in Figure 9.5, all interactions involving dipoles needs to consider the angle-dependent and angle-averaged energies.

#### Angle-dependent

According to Equation 9.8, the interaction potential can be calculated by the electric field generated by the charge  $E(r) = q/(4\pi\epsilon_0\epsilon_r r^2)$  (Figure 9.6):

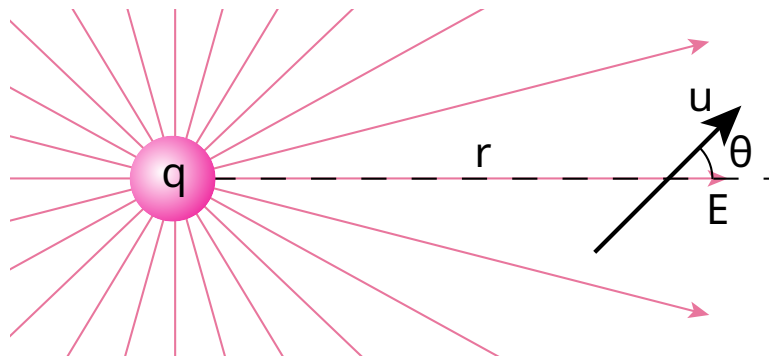


Figure 9.6: Geometry of the charge-dipole interaction

$$w_{qu}(r, \theta) = -uE \cos(\theta) = -\frac{qu \cos(\theta)}{4\pi\epsilon_0\epsilon_r r^2} \quad (9.17)$$

*Power law:  $r^{-2}$*

As can be seen, the interaction energy is lowest if  $\theta = 0$ , i.e. the dipole and the electric field align. This energy is still considerable for highly polar molecules, for instance:

- $\text{Na}^+ - \text{H}_2\text{O}$  in vacuum,  $r = 2.35 \text{ \AA}$ ,  $w(r, \theta = 0) = -40 k_B T$ . This will drop below  $1 k_B T$  if it is in aqueous



**Angle-averaged**

Let's use the Boltzmann statistics again:

$$\hat{w}_{qu}(r) = \frac{\int_0^\pi w_{qu}(r, \theta) \exp\left(-\frac{w_{qu}(\theta, r)}{k_B T}\right) (2\pi \sin(\theta)) d\theta}{\int_0^\pi \exp\left(-\frac{w_{qu}(\theta, r)}{k_B T}\right) (2\pi \sin(\theta)) d\theta} \quad (9.18)$$

Replace  $w_{qu}(r, 0) = \beta k_B T$  (the definition of  $\beta$  see Equation 9.10), it leads to the final result:

$$\hat{w}_{qu}(r) = -k_B T \beta L(\beta) \quad (9.19)$$

again, when  $\beta \ll 1$ , we can use the approximation  $L(\beta) = \beta/3$ :

$$\hat{w}_{qu}(r) \approx -\frac{k_B T}{3} \beta^2 = -\frac{1}{3} \frac{q^2 u^2}{(4\pi\epsilon_0\epsilon_r)^2 r^4 k_B T} \quad (9.20)$$

this gives the **internal energy** of the system. In fact, when aligning the dipole, the entropy effect comes into play, and the **free energy** is only half of the internal energy (i.e., the factor 1/3 should be replaced by 1/6).

*Power law:  $r^{-4}$ . Also note this energy is  $T$ -dependent.*

**9.3.3 Dipole-dipole****Angle-dependent**

The dipole-dipole interaction is even more complex, as it involves 3 angles. Assume an axis passing through the center of both dipoles,  $\theta_1$  and  $\theta_2$  are the angles between the dipole and the axis, while  $\phi$  is the angle between the two dipoles when looking from the direction of the axis (Figure 9.7).

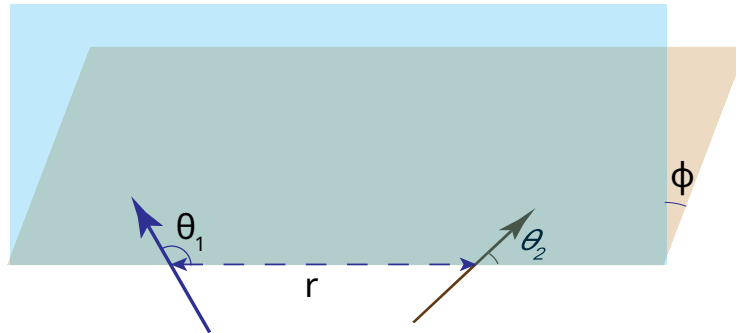


Figure 9.7: Geometry for dipole-dipole interaction.

The interaction energy is given by:

$$w_{uu}(r, \theta_1, \theta_2, \phi) = -\frac{u_1 u_2}{4\pi\epsilon_0\epsilon_r r^3} [2 \cos(\theta_1) \cos(\theta_2) - \sin(\theta_1) \sin(\theta_2) \cos(\phi)] \quad (9.21)$$

*Power law:  $r^{-3}$*

Let's compare some cases when  $\phi = 0$ , i.e. the 2 dipoles are in the same plane. Assume  $w_0 = -\frac{u_1 u_2}{4\pi\epsilon_0\epsilon_r r^3}$

- $\theta_1 = \pi/2, \theta_2 = \pi/2, w = -w_0$
- $\theta_1 = \pi/2, \theta_2 = -\pi/2, w = w_0$
- $\theta_1 = 0, \theta_2 = 0, w = 2w_0$
- $\theta_1 = 0, \theta_2 = \pi, w = -2w_0$

In other words, the configuration with lowest energy is when the dipoles are aligned “head-to-tail”.

### Angle-averaged

Use the Boltzmann statistics we find that (when  $|w_{uu}| \ll k_B T$ ):

$$\hat{w}_{uu}(r) \approx -\frac{2u_1^2 u_2^2}{3(4\pi\epsilon_0\epsilon_r)^2 k_B T r^6} \quad (9.22)$$

and the free energy is half the value.

*Power law:  $r^{-6}$*

Here we find the first  $r^{-6}$  term that contributes to the total vdW interaction. Historically it is known as the **Keesom energy**.

The Keesom energy is much weaker than the charge-charge or charge-dipole interactions:

- $u = 1.85 \text{ D (vacuum)}, r = 3 \text{ \AA}, \epsilon_r = 1, w \approx -6.2 k_B T$  (can we still use the approximation here?)
- $u = 1.85 \text{ D (water)}, r = 3 \text{ \AA}, \epsilon_r = 78, w \approx -0.001 k_B T$

### 9.3.4 Charge-induced dipole interaction

The interaction of charge and induced dipole also follows the rules of dipole-field interaction. The **internal energy** is given by:

$$\begin{aligned}
w_{q\alpha}(r) &= -u_{\text{ind}}E(r) = -\alpha E^2 \\
&= -\frac{q^2\alpha}{(4\pi\epsilon_0\epsilon_r)^2 r^4} \\
&= -\frac{q^2(\alpha_0 + \frac{u^2}{3k_B T})}{(4\pi\epsilon_0\epsilon_r)^2 r^4}
\end{aligned} \tag{9.23}$$

again, the free energy is half the value, since entropy effect is involved in “creating” the dipole. Let’s see an example of the strength of such interaction:

- Monovalent ion ( $\text{Li}^+$ ,  $\text{Na}^+$ , etc) in EtOH,  $u = 1.7$  D,  $\epsilon_r = 24$   
 $\alpha_0/(4\pi\epsilon_0) = 5.1 \times 10^{-30}$  m<sup>3</sup>,  $r = 3$  Å,  $w_{q\alpha} = -0.338 k_B T$ .
- The charge-dipole interaction under the same condition:  $w_{qu} = -0.138 k_B T$ .

Power law:  $r^{-4}$ .

### 9.3.5 Dipole-induced dipole interaction

#### Angle-dependent

The dipole-induced dipole interaction can be derived by replacing the  $E(r)$  by the field generated by a dipole  $E(r, \theta) = \frac{u\sqrt{1+3\cos^2(\theta)}}{4\pi\epsilon_0\epsilon_r r^3}$ :

$$w_{u\alpha}(r, \theta) = -\frac{u_1^2(\alpha_{02} + \frac{u_2^2}{3k_B T})(1+3\cos^2(\theta))}{(4\pi\epsilon_0\epsilon_r)^2 r^6} \tag{9.24}$$

Power law:  $r^{-6}$  Again, the free energy is half of the value here.

#### Angle-averaged

We perform the Boltzmann statistics again:

$$\hat{w}(r) = -\frac{2u_1^2(\alpha_{02} + \frac{u_2^2}{3k_B T})}{(4\pi\epsilon_0\epsilon_r)^2 r^6} \tag{9.25}$$

/Power law:  $r^{-6}$ . This is the second  $r^{-6}$  term which is called the **Debye energy**.

### 9.3.6 Induced dipole-induced dipole interaction

The induced dipole-induced dipole interaction seems a bit strange. What’s inducing the dipole from nowhere? Before diving into this question, let’s first see some mathematical tricks:

We recognize, that in the previous equations with power laws, the following rule seems valid for polarization-dependent interactions:

- $q$ : associate with  $r^{-1}$
- $u$ : associate with  $r^{-3}$
- $\alpha$ : associate with  $r^{-3}$

How about unifying the equations into one? Consider 2 molecules with permanent charge  $q_i$ , dipole moment  $u_i$  and electronic polarizability  $\alpha_{0,i}$ , and the following equation:

$$w = - \prod_{i=1}^2 \frac{1}{(4\pi\epsilon_0\epsilon_r)^2} \left[ \frac{q_i^2}{\sqrt{6k_B T r}} + \frac{\sqrt{2}u_i^2}{\sqrt{3k_B T r^3}} + \frac{\sqrt{6k_B T}\alpha_{0,i}}{r^3} \right] \quad (9.26)$$

Apart from the Coulombic terms involving  $q_1q_2$ , we recognize several familiar terms in the final product (as average internal energy, for free energy add 1/2 to each of them):

- charge-dipole

$$w_{qu} = - \frac{q_1^2 u_2^2 + q_2^2 u_1^2}{3k_B T (4\pi\epsilon_0\epsilon_r)^2 r^4} \quad (9.27)$$

- dipole-dipole (Keesom energy)

$$w_{uu} = - \frac{2u_1^2 u_2^2}{3k_B T (4\pi\epsilon_0\epsilon_r)^2 r^6} \quad (9.28)$$

- charge-electronic polarizability

$$w_{q\alpha_0} = - \frac{q_1^2 \alpha_{02} + q_2^2 \alpha_{01}}{(4\pi\epsilon_0\epsilon_r)^2 r^4} \quad (9.29)$$

- dipole-electronic polarizability (Debye energy)

$$w_{q\alpha_0} = - \frac{2(u_1^2 \alpha_{02} + u_2^2 \alpha_{01})}{(4\pi\epsilon_0\epsilon_r)^2 r^6} \quad (9.30)$$

Naturally, a final part containing both the electronic polarizability will occur:

$$w_{\alpha_0\alpha_0} = - \frac{6k_B T \alpha_{01} \alpha_{02}}{(4\pi\epsilon_0\epsilon_r)^2 r^6} \quad (9.31)$$

This is part of the actual dispersion energy, and we will discuss about it in Lecture 10.

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