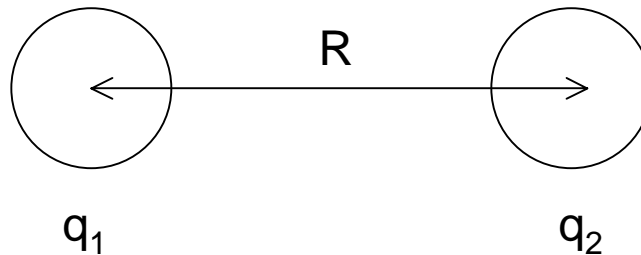# Chemical Bonds and Intermolecular Interactions

Intermolecular interactions

Intermolecular interactions are also called non-covalent interactions. Molecules that are connected by intermolecular interactions are also said to have physical bonds.
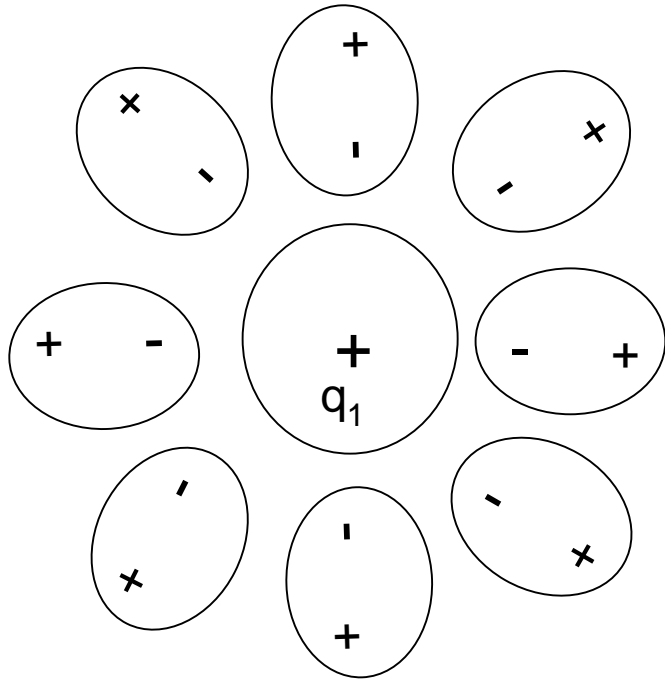
1. Charge-charge

In a vacuum, the force between the charges is $F = \dfrac{q_1 q_2}{R^2}$

and the potential energy is $V(R) = \dfrac{q_1 q_2}{R}$

Charge-charge interaction in a dielectric

The electric field from an ion is screened in a medium because the field aligns dipoles.

$$E = \frac{q_1}{\varepsilon R^2}$$

ε = dielectric constant

The potential energy of two charge molecules in a medium with dielectric constant ε is

$$V = \frac{q_1 q_2}{\varepsilon R}$$

Dielectric constants

TABLE 3.2 Static dielectric constants[a] ε of some common liquids and solids at 25°C

| Compound		ε	Compound	ε
Hydrogen bonding			*Polymers*	
Methyl			Nylon	3.7–4.2
formamide	$HCONHCH_3$	182.4	Fluorocarbons	2.1–3.6
Formamide	$HCONH_2$	109.5	Polycarbonate	3.0
Hydrogen			Polystyrene	2.4
fluoride	HF (at 0°C)	84	PTFE	2.0
Water	H_2O	78.5		
	D_2O	77.9	*Glasses*	
Formic acid	HCOOH (at 16°C)	58.5	Fused quartz SiO_2	3.8
Ethylene			Soda glass	7.0
glycol	$C_2H_4(OH)_2$	40.7	Borosilicate glass	4.5
Methanol	CH_3OH	32.6		
Ethanol	C_2H_5OH	24.3	*Crystalline solids*	
n-Propanol	C_3H_7OH	20.2	Diamond (carbon)	5.7
Ammonia	NH_3	16.9	Quartz SiO_2	4.5
Acetic acid	CH_3COOH	6.2	Micas	5.4–7.0
			Sodium chloride NaCl	6.0
			Alumina Al_2O_3	8.5
Non-hydrogen bonding				
Acetone	$(CH_3)_2CO$	20.7	*Miscellaneous*	
Chloroform	$CHCl_3$	4.8	Paraffin (liquid)	2.2
Benzene	C_6H_6	2.3	Paraffin wax (solid)	2.2
Carbon			Silicone oil	2.8
tetrachloride	CCl_4	2.2	Liquid helium (2–3 K)	1.055
Cyclohexane	C_6H_{12}	2.0	Water (liquid at 0°C)	87.9
Dodecane	$C_{12}H_{26}$	2.0	Water (ice at 0°C)	91.6–106.4
Hexane	C_6H_{14}	1.9	Air (dry)	1.00054

[a] The dielectric constant is a measure of the extent of reduction of electric fields and consequently of the reduced strengths of electrostatic interactions in a medium.

Polar molecules like formamide and water have very high dielectric constants because they have strong dipole moments and are good at screening electric fields.

Salts can dissolve in polar solvents because the Coulomb attraction is substantially reduced.

Israelachvili
*Intermolecular and Surface Forces*

Screening by ions
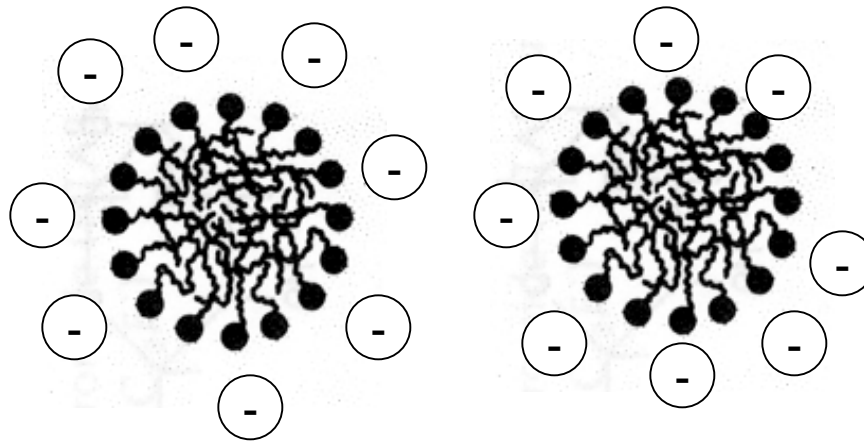
The headgroups are positively charged in this case.

In real materials, ions always have counterions. The counter ions will screen the field from the ions. Consequently, the field does not simply go as $1/R^2$. Determining the electrostatic potential involves solving some differential equations to determine where the counterions will be and what the total potential is from all of the charges in the system.

The charge-charge interaction between two charged molecules or particles can be weakened by adding salt.
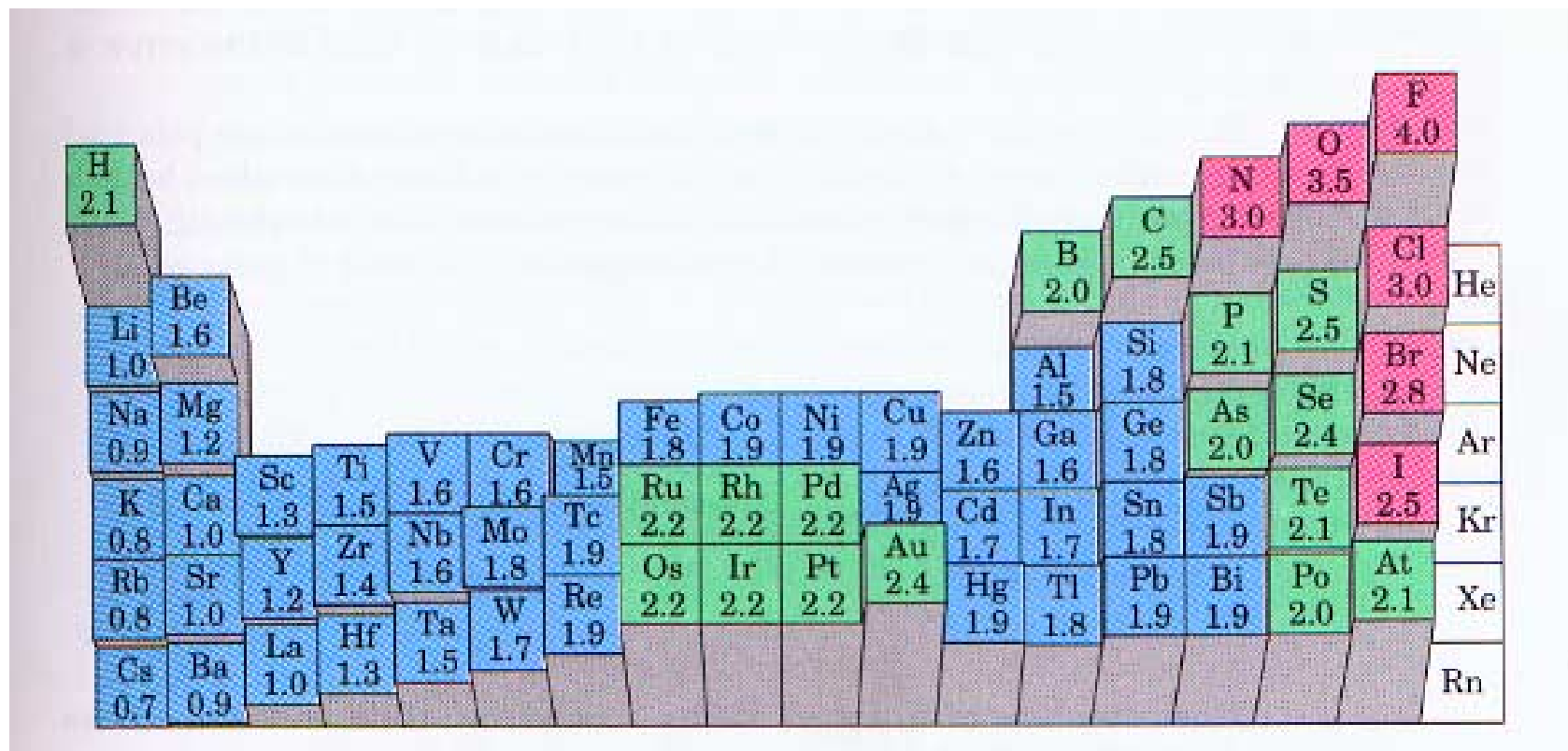
2. Charge-dipole interactions

q_2

-

q_2

R

d

+

+

q_1

$\mu = q_2 d$

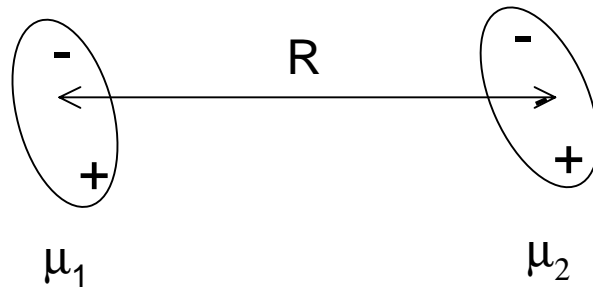$$V = \frac{-q_1 \mu \cos\theta}{\varepsilon R^2}$$

N^+

O

H   H
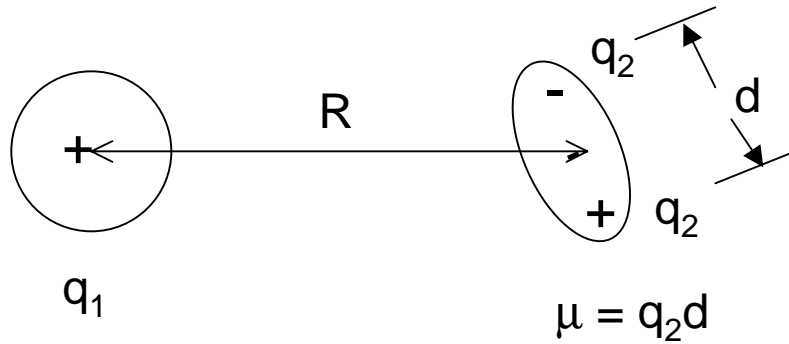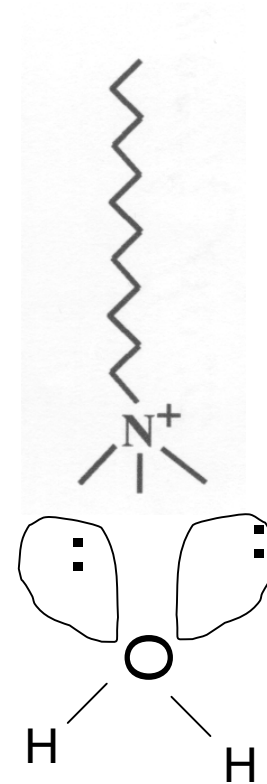
Electronegativity of the elements

Electronegativity measures the ability of an element to attract electrons in a covalent bond.

McMurry, *Organic Chemistry*

3. Dipole-dipole interactions

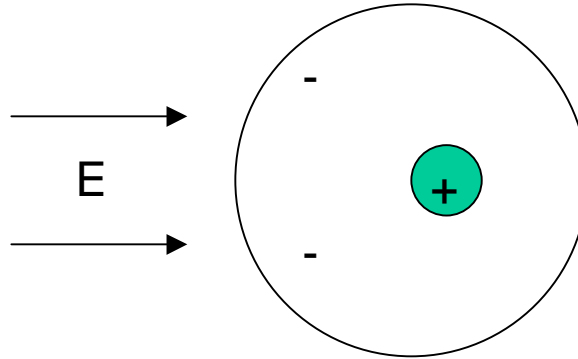$$V \propto \frac{\mu_1 \mu_2}{\varepsilon R^3}$$

Hydrogen bonding

(a)

(b)
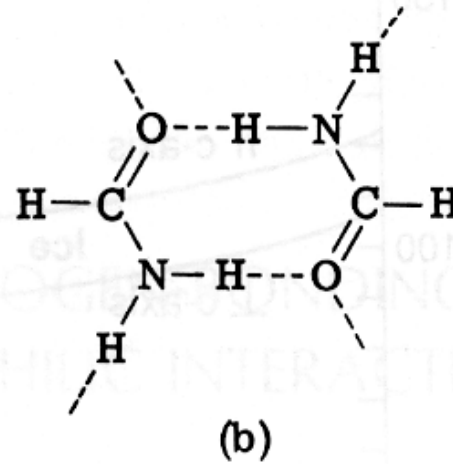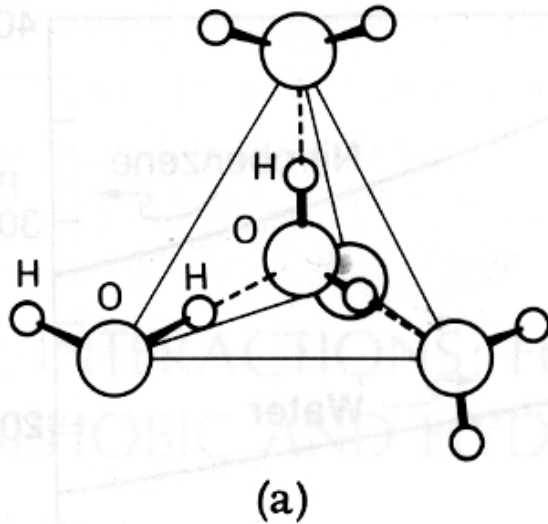
Bond strength

10-40 kJ/mole

(kT= 2.5 kJ/mole)

Hydrogen bonds form when H is bonded to O,N, F or Cl. There can be quite strong because hydrogen atoms are so small. The sole electron on the proton can be pulled significantly towards the electronegative element.

Jacob Israelachvili, *Intermolecular and Surface Forces* (1992).

Induced dipoles

An electric field can pull the electron cloud of a molecule away from the nucleus, creating a dipole moment. The induced dipole is given by

$$\mu_{induced} = \alpha E,$$

where α is the polarizability and E is the electric field.

Polarizability (in units of $4\pi\varepsilon_0 \text{Å}^3$)

Atoms and molecules

He	0.20	NH_3	2.3	$CH_2{=}CH_2$	4.3
H_2	0.81	CH_4	2.6	C_2H_6	4.5
H_2O	1.48	HCl	2.6	Cl_2	4.6
O_2	1.60	CO_2	2.6	$CHCl_3$	8.2
Ar	1.63	CH_3OH	3.2	C_6H_6	10.3
CO	1.95	Xe	4.0	CCl_4	10.5

Bond polarizabilities

Aliphatic	C—C	0.48		C—O	0.60
Aromatic	C⋯C	1.07		C=O	1.36
	C=C	1.65		N—H	0.74
Aliphatic	C—H	0.65		C—Cl	2.60
	O—H	0.73		C—Br	3.75

Molecular groups

C—O—H	1.28	CH_2	1.84
C—O—C	1.13	Si—O—Si	1.39
C—NH_2	2.03	Si—OH	1.60

Jacob Israelachvili, *Intermolecular and Surface Forces* (1992) p. 69.

Factors that determine polarizability

• Loosely held electrons are more polarizable than tightly held ones. For this reason, the valence electrons account for almost all of the polarizability of an atom.

•Polarizability tends to be proportional to the volume of a molecule.

For CH_4, $\alpha = 2.6$ For CCl_4, $\alpha = 10.5$

• π electrons are more polarizable than σ electrons.

• Interactions with nanoobjects like carbon nanotubes and metal nanocrystals can be very strong since the free electrons make these objects extremely polarizable.
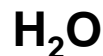
Examples of calculating molecular polarizabilities

CH$_2$=CH$_2$
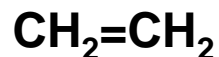
4(C-H) + 1(C-C)
4(0.65) + 1(1.65) = 4.25   Actual = 4.3

H$_2$O

2(OH) = 2(0.73) = 1.46   Actual = 1.48

CHCl$_3$

1(CH) + 3(C-Cl)
1(0.65) + 3(2.60) = 8.45   Actual = 8.2

Benzene (C$_6$H$_6$)
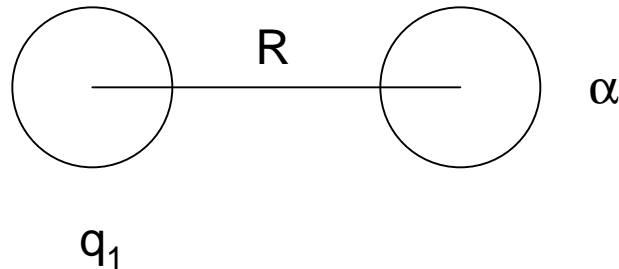
6(C--C) + 6(C-H)
6(1.07) + 6(0.65) = 10.3   Actual = 10.3

Adding up the polarizabilities of the bonds works pretty well. It breaks down for large conjugated molecules with highly delocalized electrons.

4. Charge-induced dipole interactions

The induced dipole moment on the right molecule is

$$\mu_{ind} = \alpha E = \frac{\alpha q_1}{\varepsilon R^2}$$

Previously, we showed that the potential energy for a charge-dipole interaction is
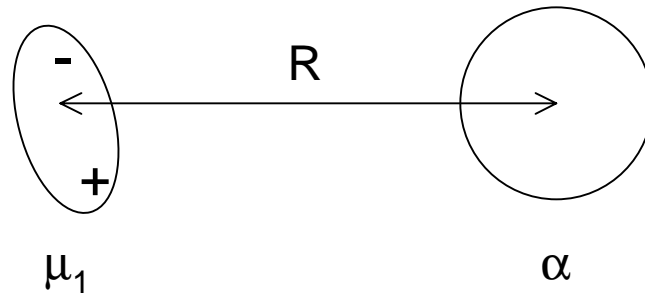
$$V = \frac{-q_1 \mu \cos\theta}{\varepsilon R^2}$$

In this case, $\cos\theta = 0$, so

$$V = \frac{q\mu_{ind}}{\varepsilon R^2} = \frac{-\alpha q^2}{\varepsilon^2 R^4}$$

A more careful calculation that takes into account the energy needed to form the dipole, shows that the potential energy is half of that shown above.
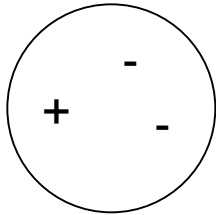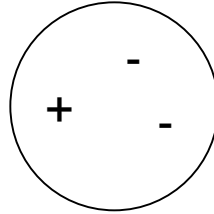
5. Dipole-induced dipole interaction

Example: water-oil

$$V = -\frac{\mu^2\alpha}{2\varepsilon^2 R^6}\left(3\cos^2 + 1\right)$$

6. Instantaneous dipole-induced dipole (van der Waal's) interaction

$$\mu_1^{inst}$$

$$E = \frac{\mu_1^{inst}}{R^3}$$

$$\mu_2^{ind} = \alpha E = \frac{\alpha\mu_1^{inst}}{R^3}$$

$$V = \frac{\mu_1\mu_2}{R^3} = \frac{\mu_1^{inst}(\alpha\mu_1^{inst})}{R^6}$$

van der Waal's bonds between two atoms are weak, but the total van der Waal's interaction between large and/or highly polarizable molecules can be significant.

Strength of the intermolecular interactions

For the smallest molecules (diatomic ones), we covered the interactions in order from strongest to weakest.

1. charge-charge
2. charge-dipole
3. dipole-dipole
4. charge induced dipole
5. dipole-induced dipole
6. instantaneous dipole-induced dipole (van der Waal's)

As the size of a molecule increased, the charge and dipole moment tend not to increase, so van der Waal's can become the most important interaction.

Hydrogen bonds, which are a special case, are almost as strong as charge-charge bonds.

Boiling points: a measure of intermolecular bond strength

Substance	T_B at 1 Atm (K)	Main interaction
Neon	27	Van der Waal's Interaction
Nitrogen	77	Van der Waal's Interaction
Methane (CH_4)	112	Van der Waal's Interaction
HCl	118	Weak hydrogen bonding
Ammonia (NH_3)	140	Hydrogen bonding
HF	293	Hydrogen bonding
Benzene(C_6H_6)	353	Van der Waal's Interaction
Water	373	Hydrogen bonding
Sodium	1156	Metallic bonding
Carbon	4470	Covalent bonds

Comparison of alkanes with no dipole, a dipole and H-Bonding

Molecule		Molecular weight	Dipole moment (D)	Boiling point (°C)
Ethane	CH_3CH_3	30	0	−89
Formaldehyde	HCHO	30	2.3	−21
Methanol	CH_3OH	32	1.7	64
n-Butane	$CH_3CH_2CH_2CH_3$	58	0	−0.5
Acetone	CH_3COCH_3	58	3.0	56.5
Acetic acid	CH_3COOH	60	1.5	118
n-Hexane	$CH_3(CH_2)_4CH_3$	86	0	69
Ethyl propyl ether	$C_5H_{12}O$	88	1.2	64
1-Pentanol	$C_5H_{11}OH$	88	1.7	137

[a] In order to make comparisons meaningful, molecules have been put into three groups of similar molecular weights and size. Within each group the first molecule is non-polar and interacts purely via dispersion forces, the second is polar and the third also interacts via H-bonds.

In large molecules, the van der Waal's interactions add up and become significant.

Jacob Israelachvili, *Intermolecular and Surface Forces* (1992).