

Intermolecular Interactions

Reading

Jacob Israelachvili's *Intermolecular and Surface Forces* is an excellent text.

Fundamental forces

Gravity

Electromagnetic (Coulomb)

Weak

Strong

The electromagnetic force is by far the most important in chemistry.

We will discuss many types of interactions between molecules, but they are all fundamentally Coulomb 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.

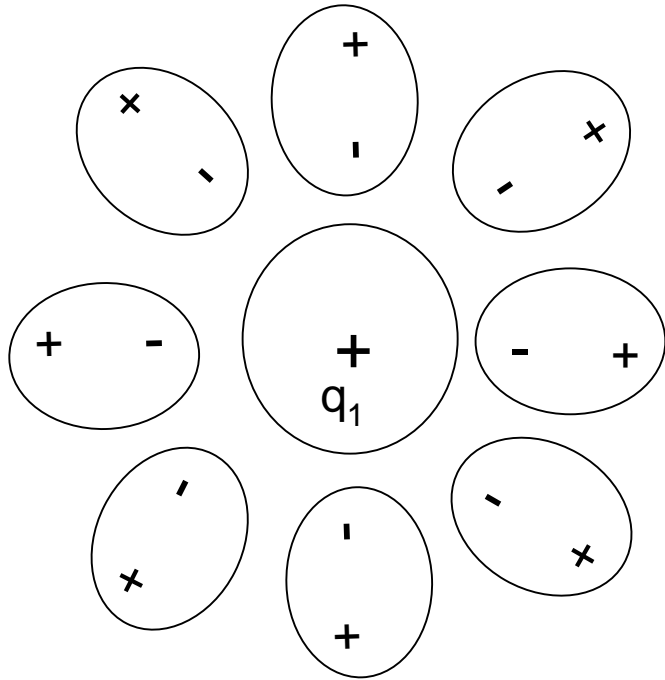
Charge-charge



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

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

Charge-charge interaction in a dielectric



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

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

ϵ = dielectric constant

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

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

Dielectric constants

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

Compound			ϵ	Compound			ϵ
<i>Hydrogen bonding</i>				<i>Polymers</i>			
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 ₂ O	78.5		<i>Glasses</i>			
	D ₂ O	77.9		Fused quartz SiO ₂			3.8
Formic acid	HCOOH (at 16°C)	58.5		Soda glass			7.0
Ethylene				Borosilicate glass			4.5
glycol	C ₂ H ₄ (OH) ₂	40.7		<i>Crystalline solids</i>			
Methanol	CH ₃ OH	32.6		Diamond (carbon)			5.7
Ethanol	C ₂ H ₅ OH	24.3		Quartz SiO ₂			4.5
<i>n</i> -Propanol	C ₃ H ₇ OH	20.2		Micas			5.4–7.0
Ammonia	NH ₃	16.9		Sodium chloride NaCl			6.0
Acetic acid	CH ₃ COOH	6.2		Alumina Al ₂ O ₃			8.5
<i>Non-hydrogen bonding</i>				<i>Miscellaneous</i>			
Acetone	(CH ₃) ₂ CO	20.7		Paraffin (liquid)			2.2
Chloroform	CHCl ₃	4.8		Paraffin wax (solid)			2.2
Benzene	C ₆ H ₆	2.3		Silicone oil			2.8
Carbon				Liquid helium (2–3 K)			1.055
tetrachloride	CCl ₄	2.2		Water (liquid at 0°C)			87.9
Cyclohexane	C ₆ H ₁₂	2.0		Water (ice at 0°C)			91.6–106.4
Dodecane	C ₁₂ H ₂₆	2.0		Air (dry)			1.00054
Hexane	C ₆ H ₁₄	1.9					

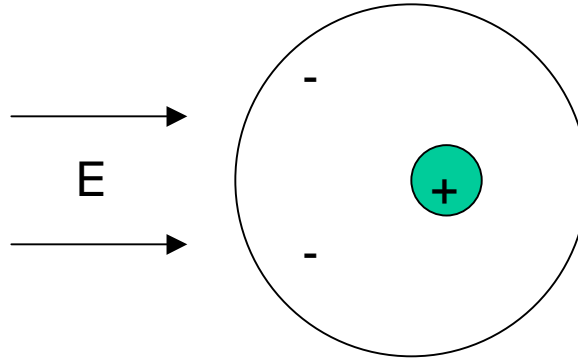
^a The dielectric constant is a measure of the extent of reduction of electric fields and consequently of the reduced strengths of electrostatic interactions in a medium.

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*

Induced dipoles

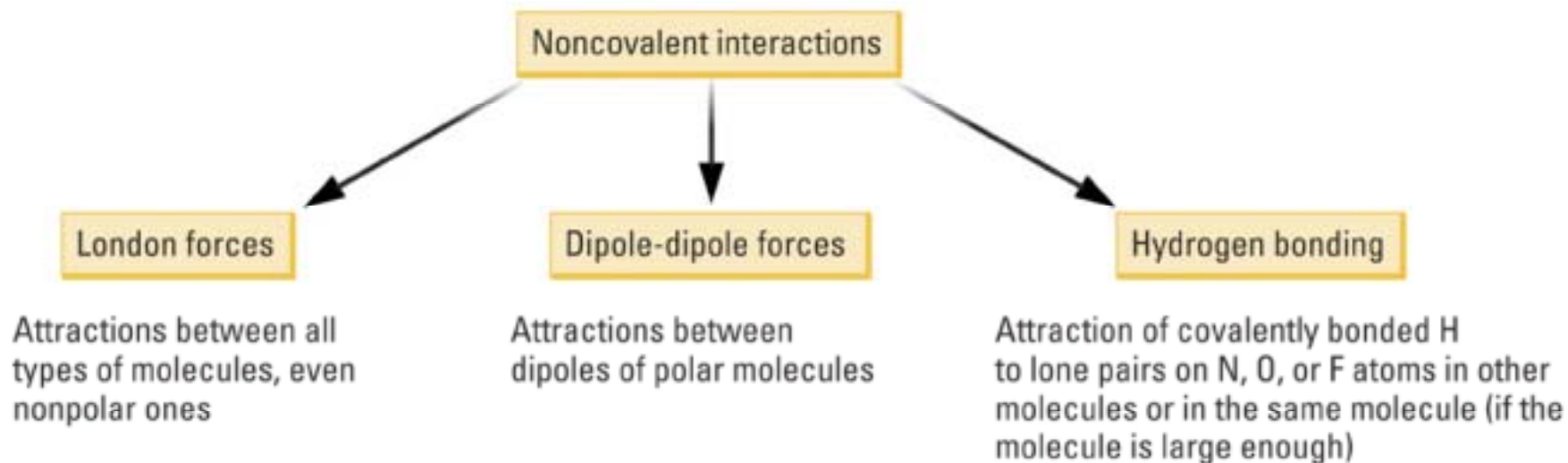


An electric field can pull the electron cloud of a molecule away from the nucleus, creating a dipole moment. The induced dipole is given by

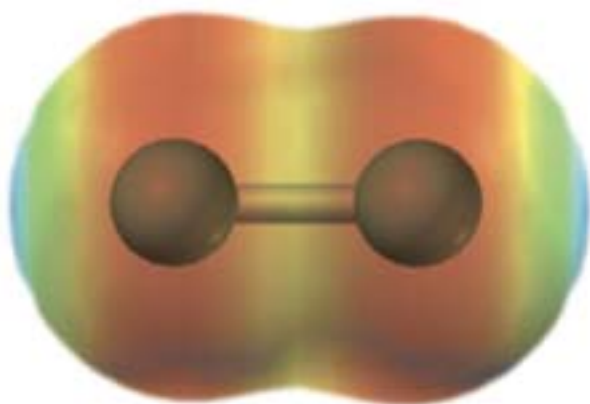
$$\mu_{\text{induced}} = \alpha E,$$

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

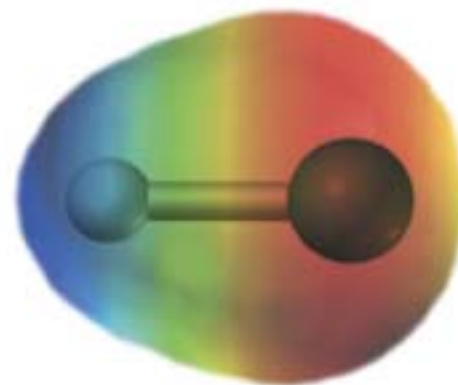
Types of Intermolecular Forces



Molecular Polarity

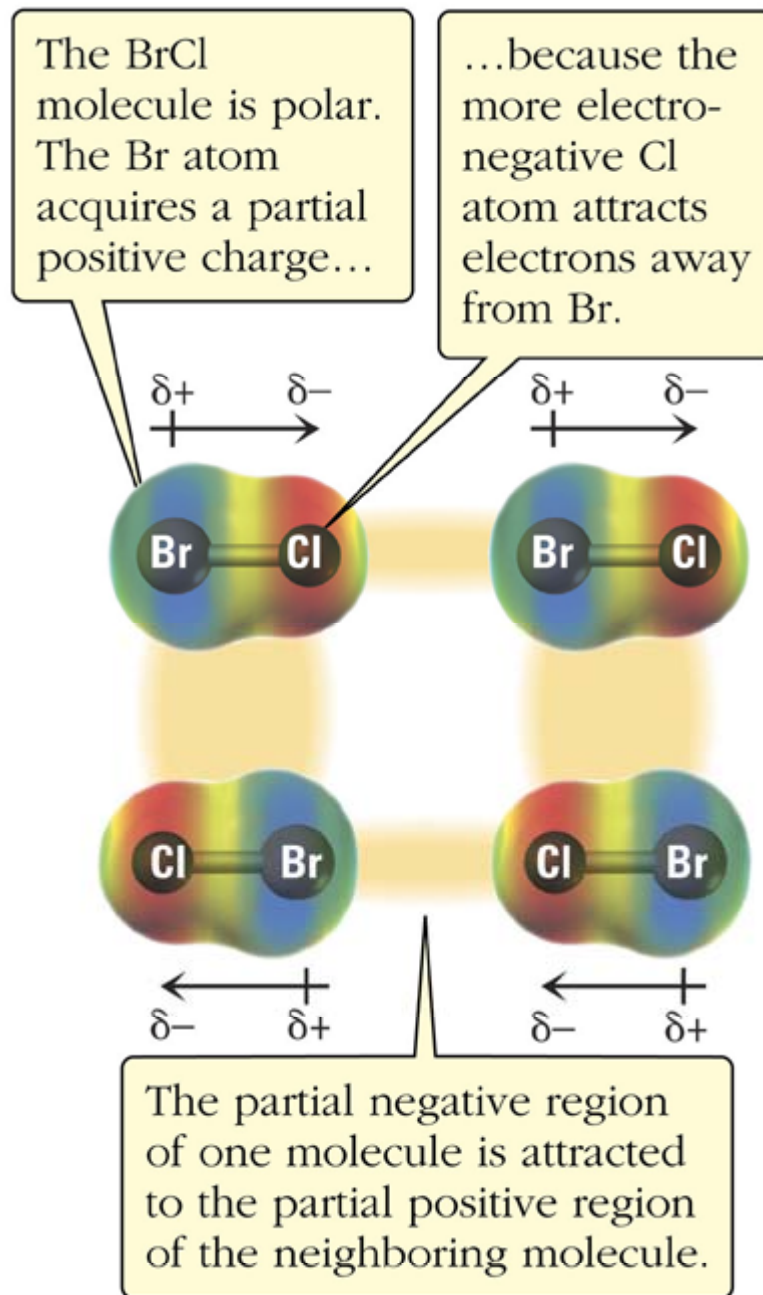


Nonpolar
molecule, Cl₂



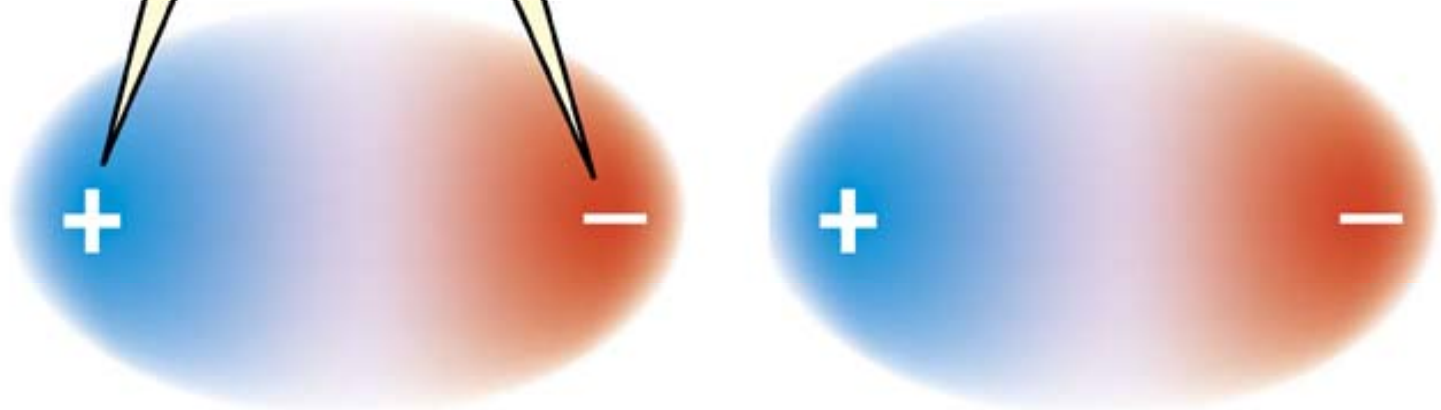
Polar molecule,
HCl

Dipole-Dipole Attractions



London Forces

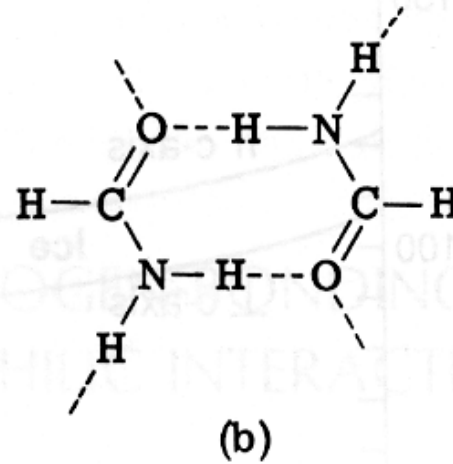
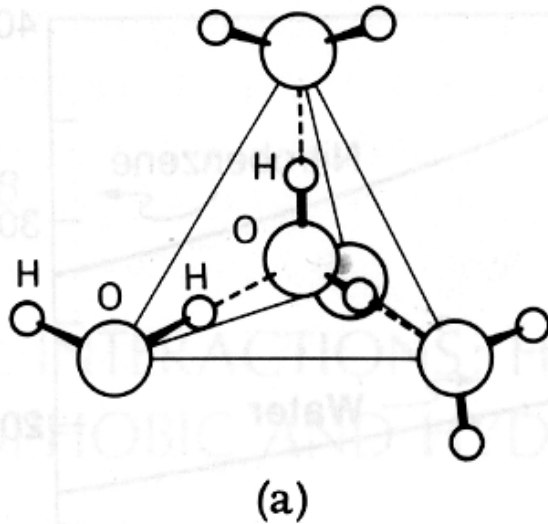
These are temporary partial charges.



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.

Hydrogen bonding



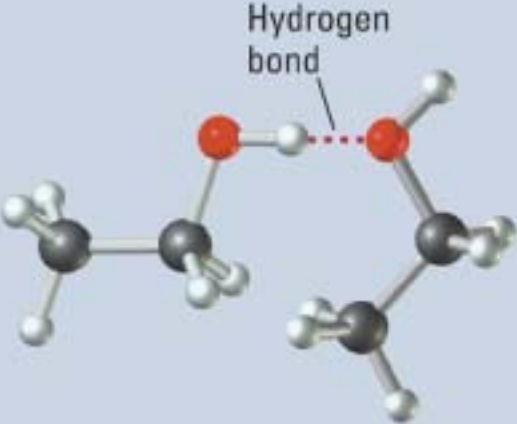
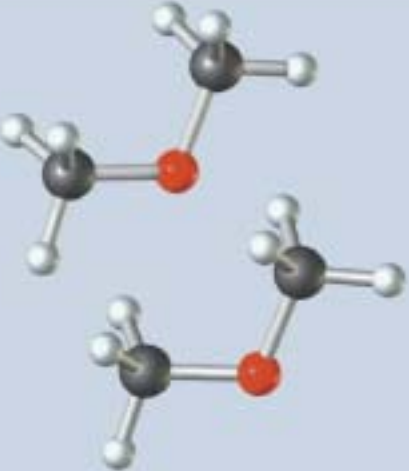
Bond strength

10-40 kJ/mole

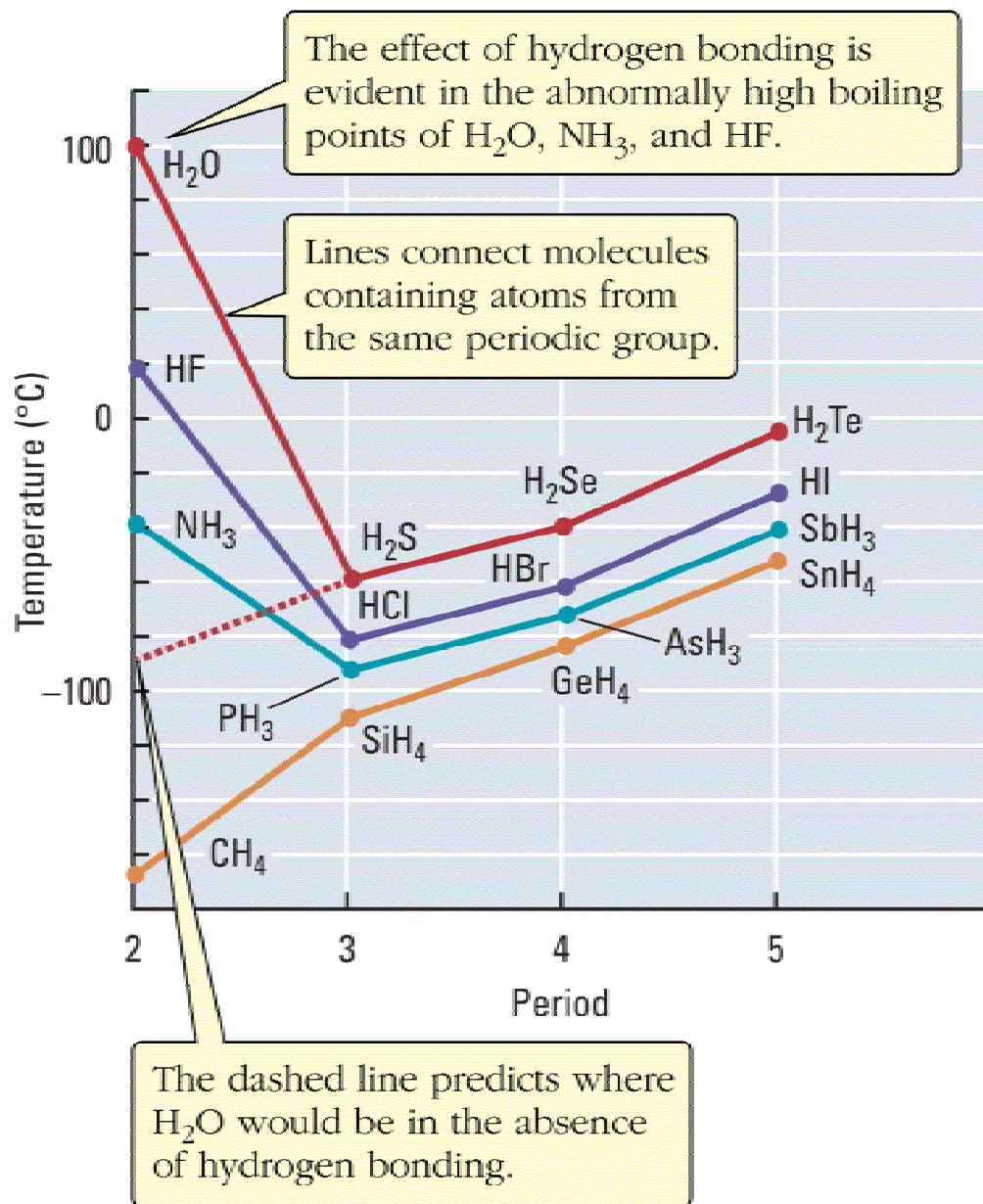
($kT = 2.5$ kJ/mole)

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.

Hydrogen Bonding in Ethanol

Molecular model	 <p>ethanol $\text{CH}_3\text{CH}_2\text{OH}$</p>	 <p>dimethyl ether CH_3OCH_3</p>
Dipole moment, D	1.69	1.30
Melting point, °C	-114.1	-141.5
Boiling point, °C	78.29	-24.8

Hydrogen-Containing Binary Compound Boiling Points



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.

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

Molecule		Molecular weight	Dipole moment (D)	Boiling point (°C)
Ethane	CH ₃ CH ₃	30	0	-89
Formaldehyde	HCHO	30	2.3	-21
Methanol	CH ₃ OH	32	1.7	64
<i>n</i> -Butane	CH ₃ CH ₂ CH ₂ CH ₃	58	0	-0.5
Acetone	CH ₃ COCH ₃	58	3.0	56.5
Acetic acid	CH ₃ COOH	60	1.5	118
<i>n</i> -Hexane	CH ₃ (CH ₂) ₄ CH ₃	86	0	69
Ethyl propyl ether	C ₅ H ₁₂ O	88	1.2	64
1-Pentanol	C ₅ H 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.

Mixing

Mixing is thermodynamically favorable if $\Delta G = \Delta H - T\Delta S$ is negative.

Entropy usually favors mixing since there are more ways to arrange molecules that are mixed.

Polar molecules dissolve polar molecules and nonpolar molecules dissolve nonpolar molecules because the new intermolecular interactions have similar enthalpy to the ones that are replaced.

Dislike molecules tend not to mix because the interactions between polar and nonpolar molecules aren't as strong as those between polar molecules.

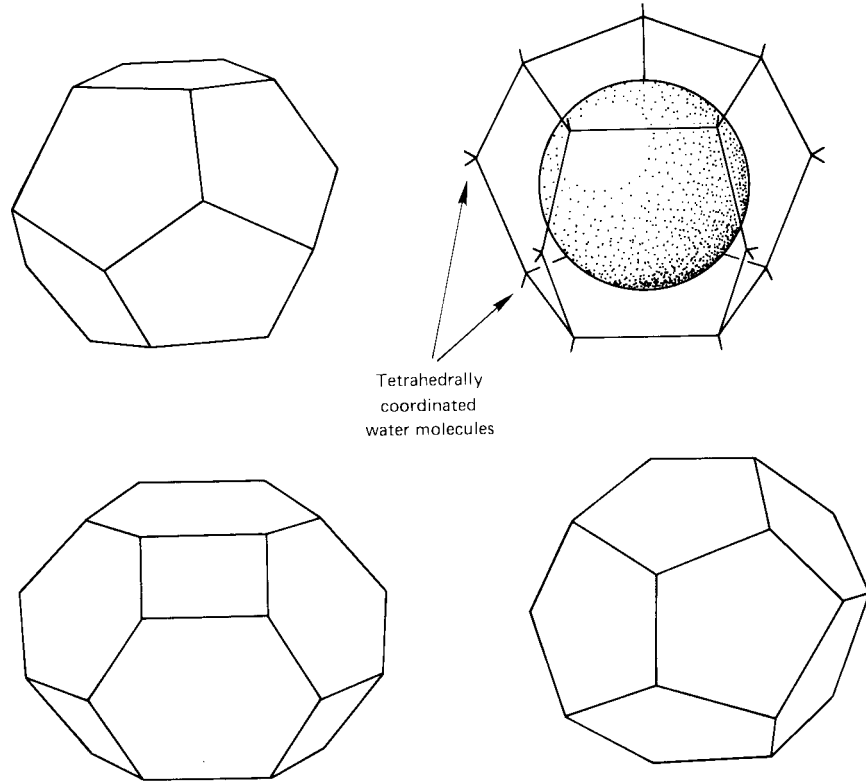
Consequence of low entropy of mixing

The heat of mixing for a monomer in a solvent is similar to the heat of mixing for the corresponding polymer. Since the entropy of mixing is much less for the polymer, polymers are less soluble.

When two polymers are mixed, the enthalpy change is usually positive or only slightly negative. Since the entropy of mixing is small, most polymers do not mix with each other.

The hydrophobic effect

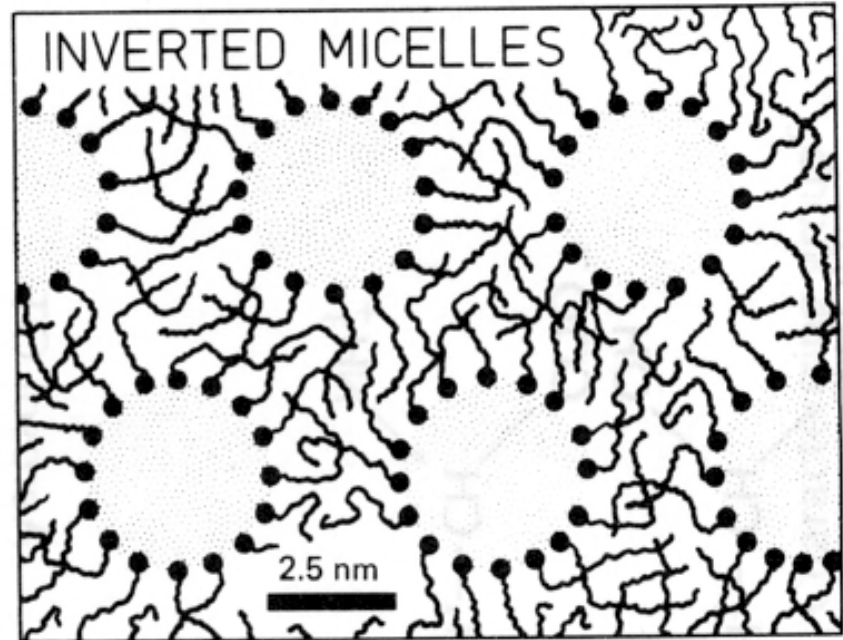
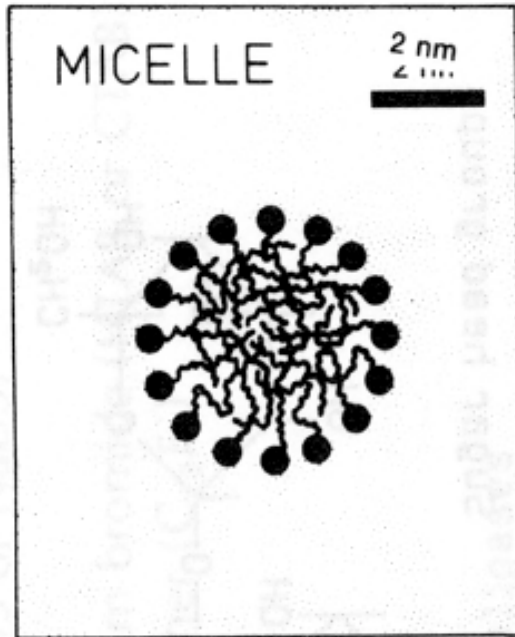
Water molecules can form a hydrogen bond network around almost anything, but doing so decreases entropy.



The hydrophobic effect is proportional to the surface area of the hydrophobic molecule.

Entropy decreases upon mixing in this case.

What are the intermolecular interactions in these systems?



The dark circles are charged.

Why do these structures form?

Interactions in Micellar Solution

- Charge-charge interactions between head groups
- Charge-dipole interactions.
- H-bonds between H_2O .
- Hydrophobic effect on hydrocarbon in H_2O .
- Charge-induced dipole interactions.
- Dipole-induced dipole interaction.
- van der Waals force in hydrocarbon.
- Dissolution of counter ion and its attraction with head groups.