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PHYS3009: Force and Function at the Nanoscale
Week 22 – 9:00am Friday – 17 February 2023

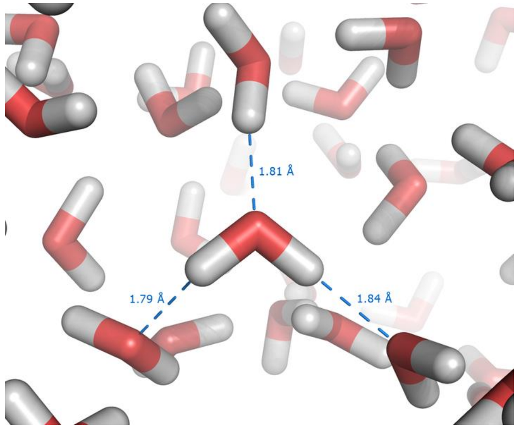
Hydrogen Bonds and Water

Force & function at the nanoscale

Water is odd stuff

Water is arguably the most important liquid on earth.

Without water it is doubtful that living organisms could have evolved.



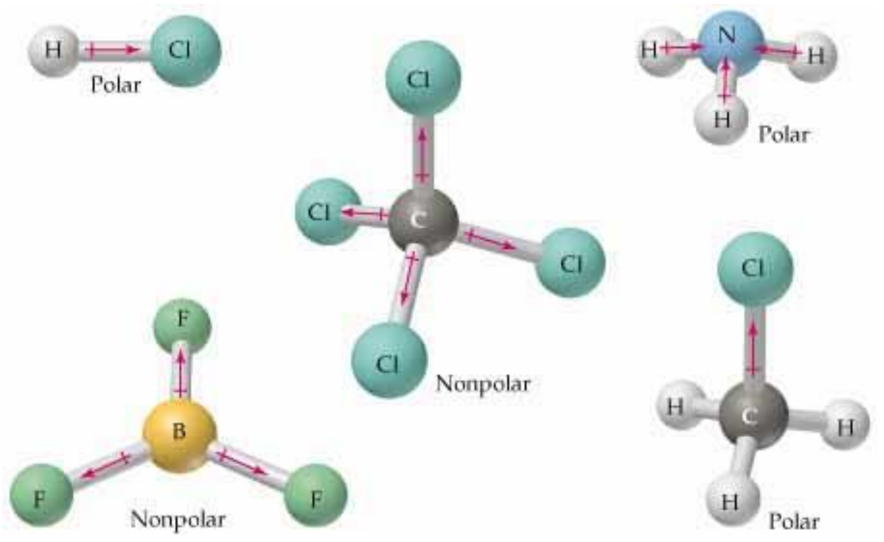
It has unusual properties:

- High melting and boiling points.
- High surface tension
- Expands upon freezing

These properties are due to the special nature of the interactions between water molecules.

Hydrogen Bonds

Atoms such as O, N, F and Cl are highly electronegative (they tend to pull electrons towards themselves).



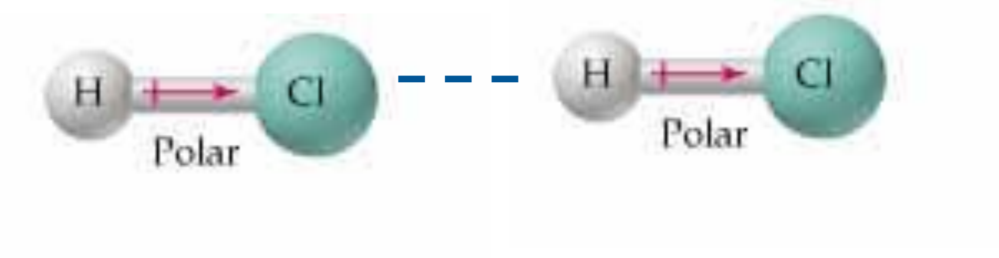
Covalent bonds with these atoms can be quite polar. Bonds between these atoms and hydrogen tend to have a greater polarity, but the molecule overall may be non-polar.

Dipolar interactions between bonds involving hydrogen are referred to as **hydrogen bonds**

Problem 6.1 Hydrogen Bonds

1. What kind of dipole is this HCl which forms a Hydrogen bond?

2. If a Hydrogen bond has a typical energy of $12k_BT$ is it:
   a. "Significant"?
   b. "Strong" or "Weak"?



How strong are hydrogen bonds?

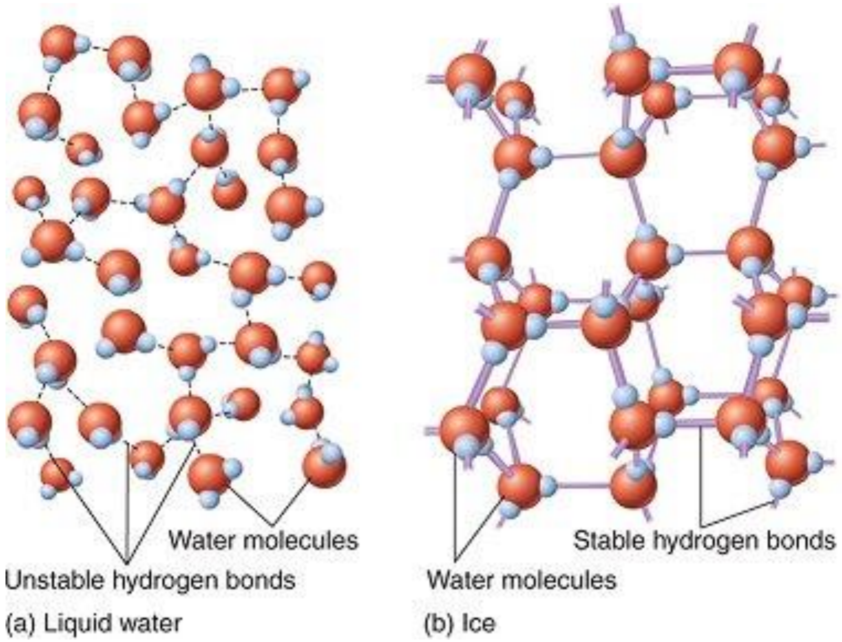
Interaction	Strength (k_BT)	Strength (eV)	Strength ($kJmol^{-1}$)
VdW / Dispersion	2	0.004-0.04	0.4-4
Hydrogen Bonds	4-16	0.1-0.4	10-40
Covalent Bonds	100	2-8	500
Ionic Bonds			

These values are very approximate but they give an idea of the typical size of numbers.

$1eV = 1.602x10^{-19}J$
$1\ mol = 6x10^{23}$
$1\ K_BT = 1.38x10^{-23} * 293 = 4.04x10^{-21}J$

The structure of ice

The **directional nature of hydrogen bonds** causes water molecules to pack into an open tetrahedral structure



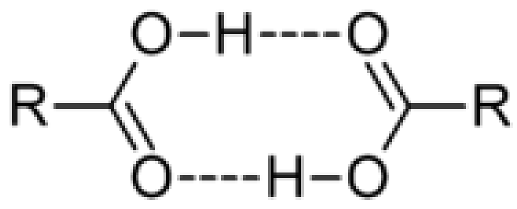
In doing so, the average number of nearest neighbour molecules decreases from ~5 in liquid to 4 in ice (resulting in a lower density)

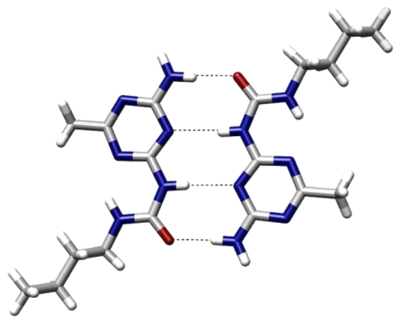
This is unusual as crystalline solids are usually more dense than the liquid because atoms/molecules become more closely spaced.

Hydrogen bonding in other molecules

Hydrogen bonds can be found in many types of molecules both synthesised and naturally occurring.

H-bonds are dipole-dipole interactions between specific functional groups. As such they have some directionality



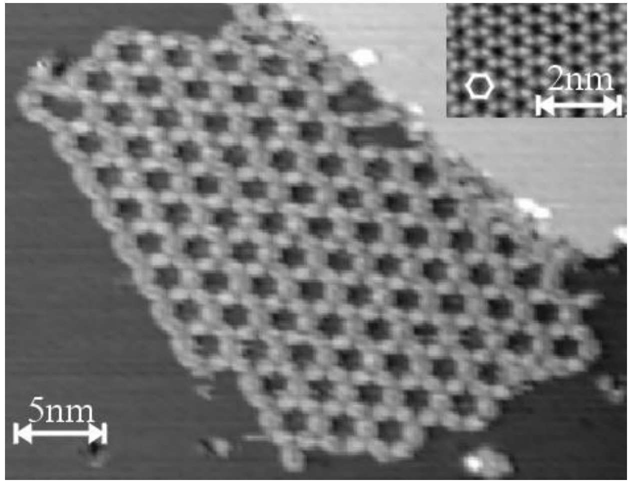


As such they can be used to direct how molecules “stick” to one another. The important factor is that thermal fluctuations can disrupt the bond occasionally, allowing molecules to find the lowest energy configuration.

Hydrogen bonding in nanoscience

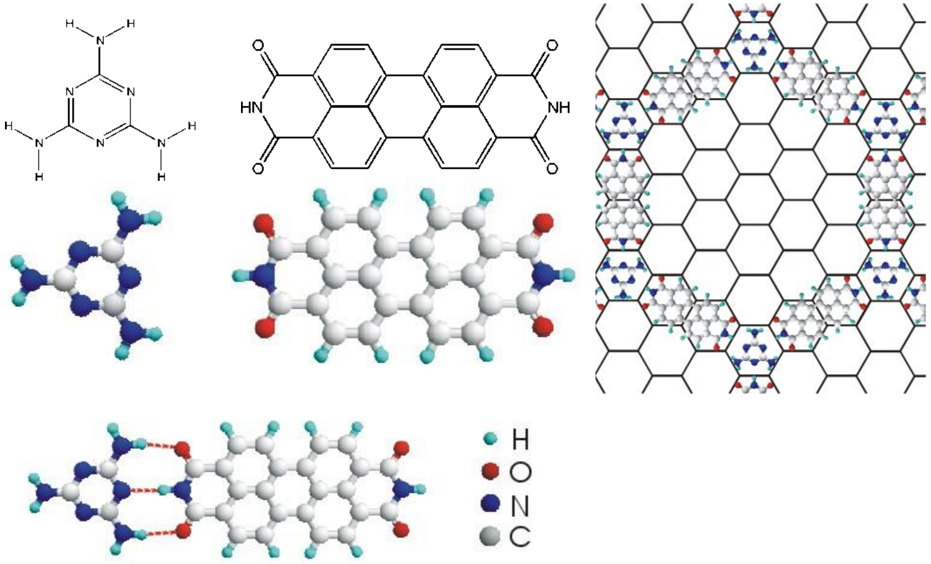
Molecules which form many H bonds with neighbours have higher dissociation energies and are thus more sticky

If the molecules are designed carefully, the directionality of H-bonds can be used to form supramolecular aggregates which self assemble in solution or on a surface



PTCDI + melamine network

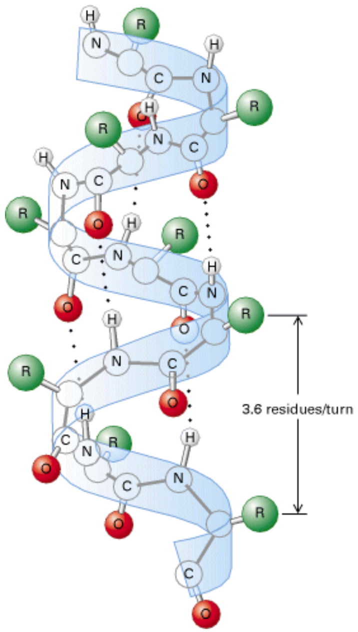
Courtesy of Peter Beton

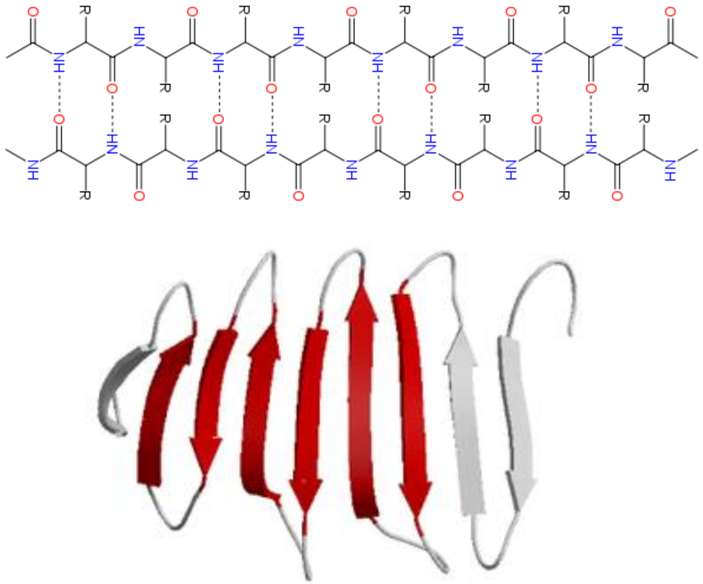


Hydrogen bonding in nature

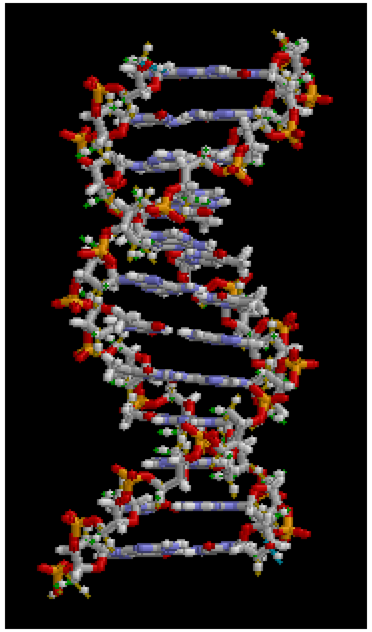
Biological molecules also exploit the directionality of H-bond formation to produce rigid structural elements that give these large molecules a well defined shape

Proteins (α-helices and β-sheets)





DNA
(Base pair bonding)



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The hydrophobic Interaction

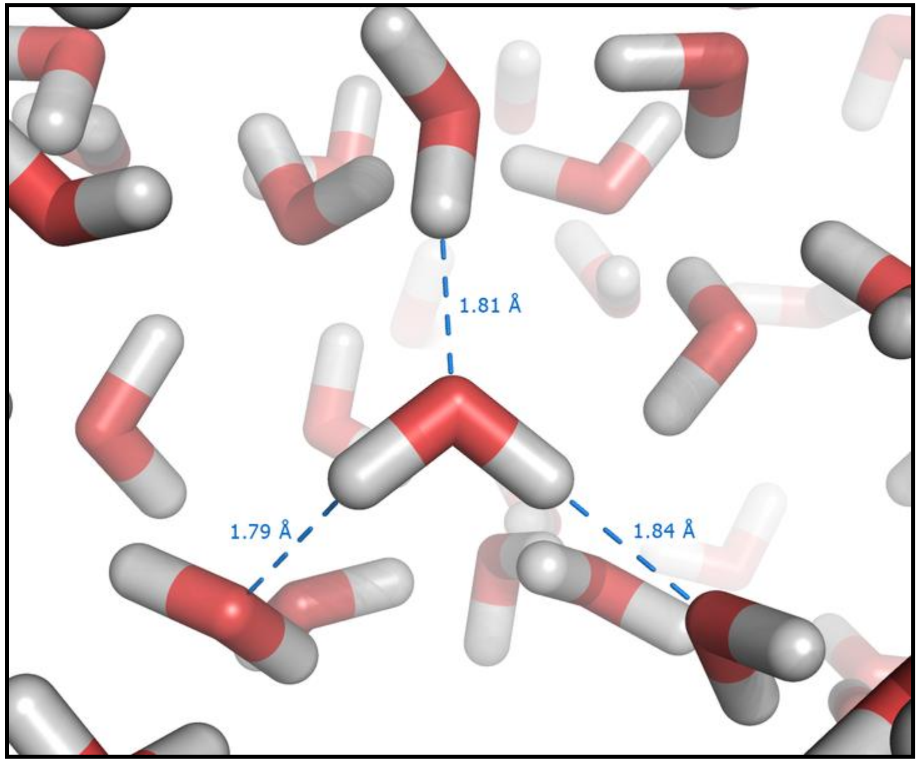
Force & function at the nanoscale

The structure of water

Whilst at room temperature water has some ordering, the molecules are free to spin, move.

In the absence of non-polar molecules there is consequently a large entropy (disorder).

This is a favourable state for the water molecules to be in (We'll return to why later in the course)

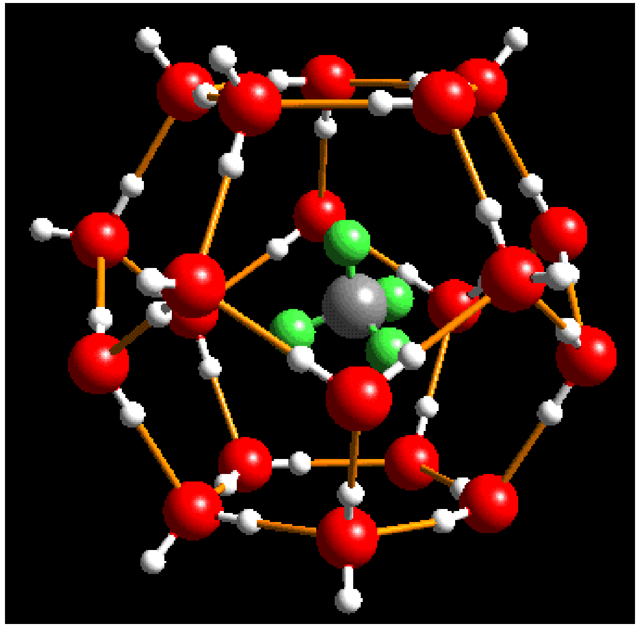


The interaction of water with non-polar molecules

Add some non-polar molecules to the water…

These cannot hydrogen bond with water and so to maximise the favourable interactions the water close to the molecule becomes more ordered (low entropy and therefore unfavourable).

Question: If I have multiple non-polar molecules in water what will happen?



This ordered water molecule structure maximises H-bonding and is called a Clathrate cage.

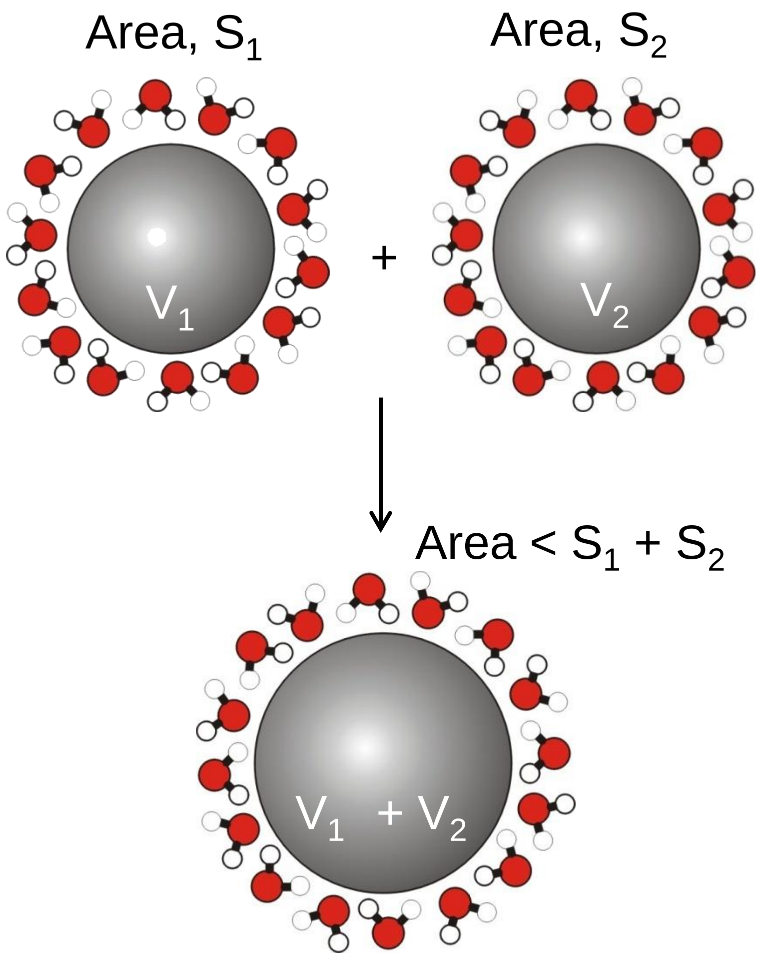
The hydrophobic effect

Consider 2 non-polar molecules with a layer of water around it that is “unhappy” because they are having to form an ordered structure.

If the two non-polar molecules are brought together then the area in contact with the water reduces.

Now some water molecules can go back to the bulk water with high disorder which is favourable.

As a result there is an effective driving force pushing the non-polar molecules together.



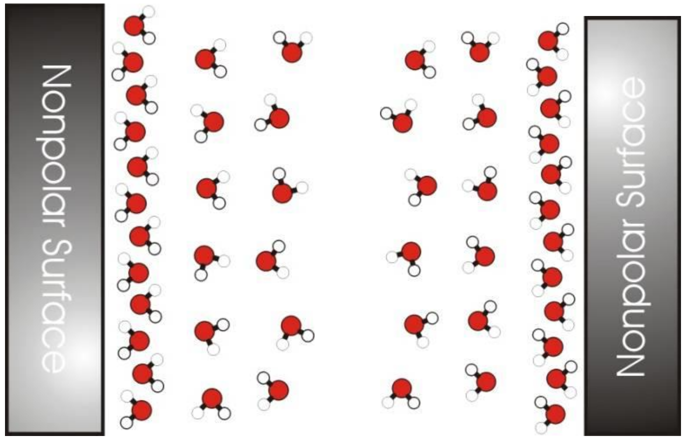
The hydrophobic effect is not the result of a direct interaction between nonpolar molecules but reorganisation of the liquid water to reduce entropy changes.

Hydrophobic interaction energy

There is no satisfactory theory to explain the details of the hydrophobic interaction.

This is because the interaction between two surfaces involves many layers of intervening molecules.

Measurements show that the interaction energy, U, decays exponentially with the separation between surfaces.



$$U = -2\gamma_1 S \exp\left(-\frac{D}{\lambda_0}\right)$$

where γ_1 is the interfacial energy* with water, S is the interfacial area and λ_o is the range of the interaction

λ_o ~1-2nm

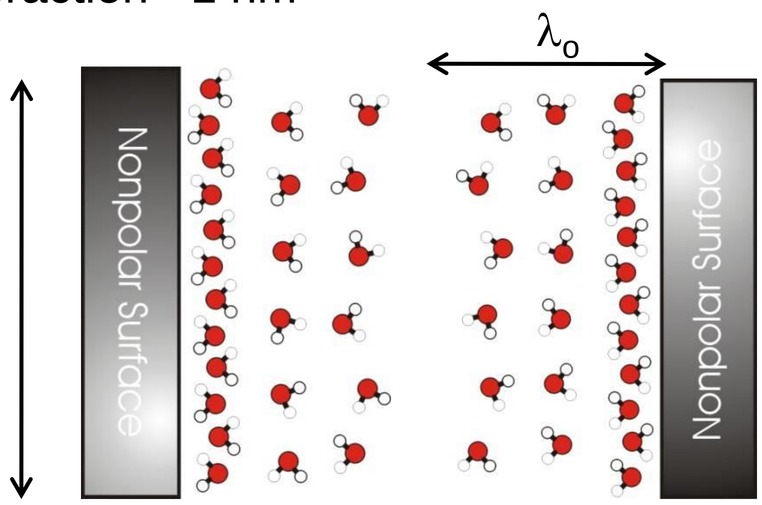
Problem 6.2 Hydrophobic pressure

Two non-polar surfaces are immersed in water. What is the pressure on the plates due to the hydrophobic interaction at D=10nm?

$$U = -2\gamma_1 S \exp\left(-\frac{D}{\lambda_0}\right)$$

γ_1 is the interfacial energy with water ($0.072 Jm^{-2}$), S is the interfacial area and λ_o is the range of the interaction ~1 nm

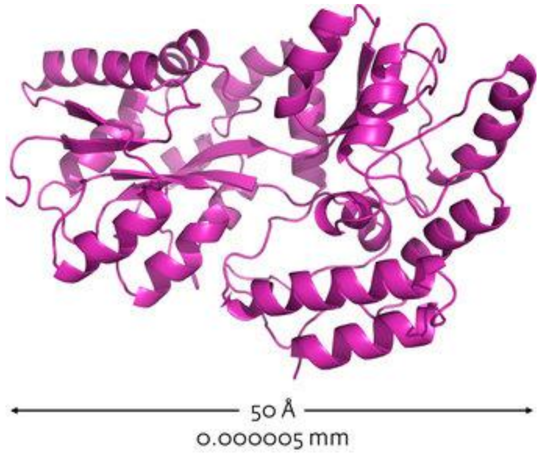
Area, S

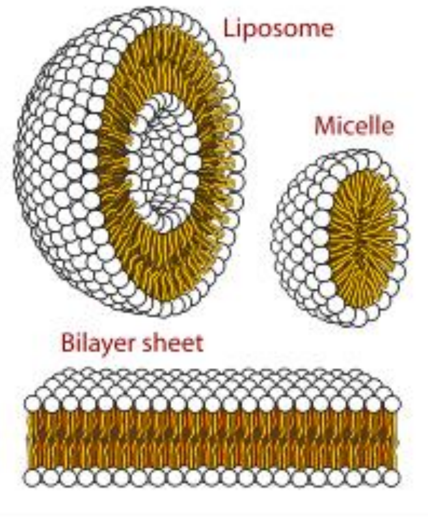


Hydrophobic interactions in nature

Hydrophobicity controls “Wetting” that is how liquids interact with surfaces (Next week)

The hydrophobic interaction is also used by protein molecules to ensure that different sections of the molecule fold up in a specific way. This is important because structure controls function.

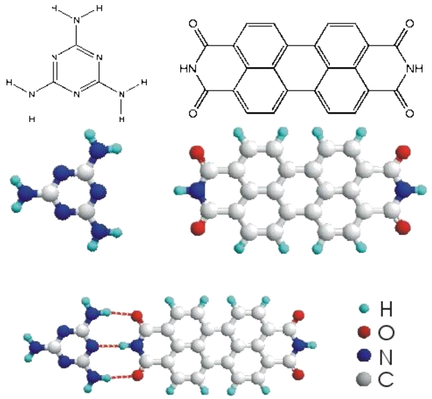




As you will see in future lectures, the hydrophobic force is also important in the formation of biological (cell) membranes

Summary of key concepts

Hydrogen bonds and hydrophobic interactions are attractive interactions. They are stronger than simple dispersion interactions (~4-30 $kJmol^{-1}$ vs ~1$kJmol^{-1}$)



They have more specificity than dispersion forces and are used in both nature and nanoscience to build structures

The hydrophobic effect arises due to changes in the entropy of water surrounding nonpolar molecules.

$$F = -\frac{2\gamma_1 S}{\lambda_0} \exp\left(-\frac{D}{\lambda_0}\right)$$