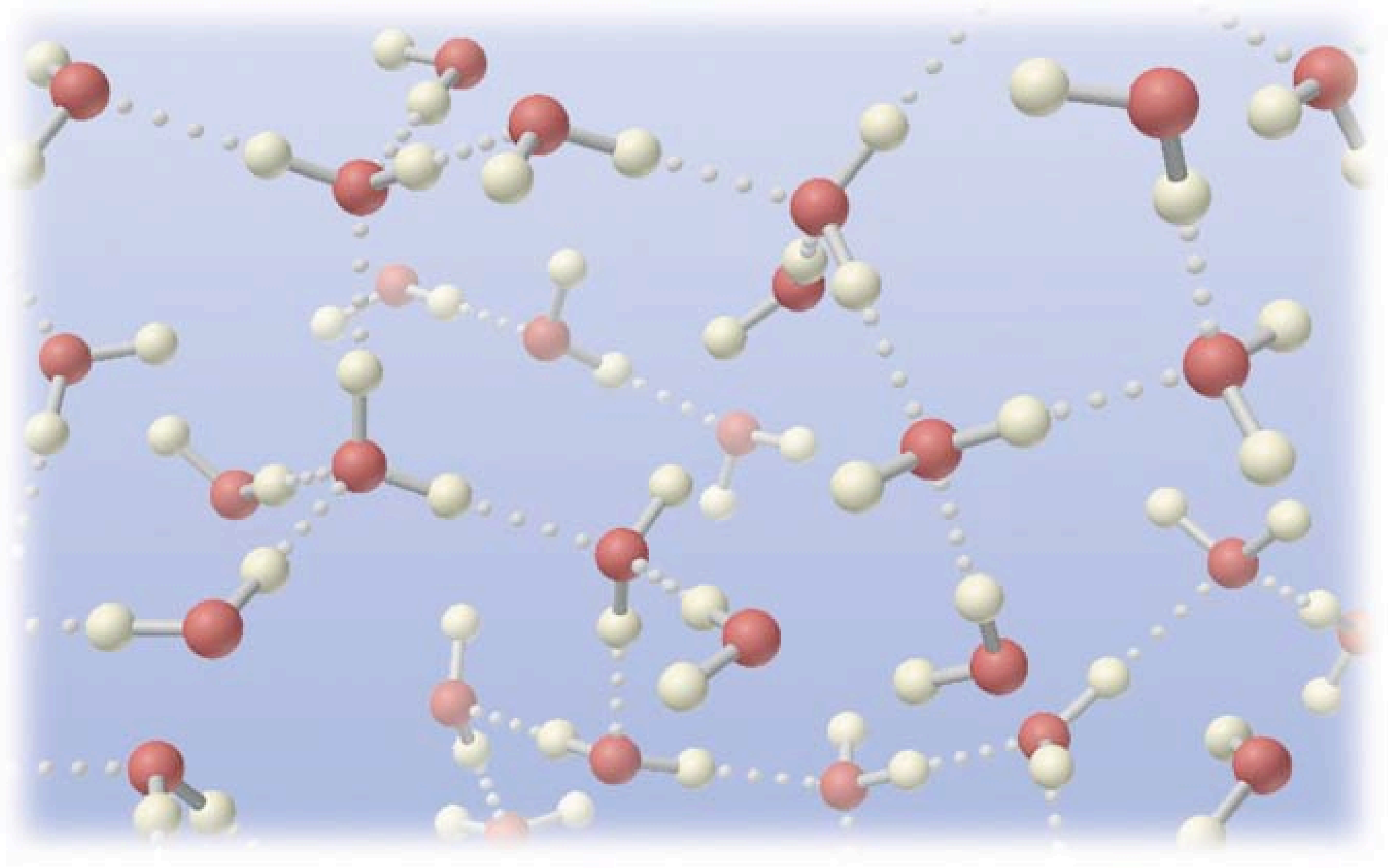
Water



H_2O

Liquid, solid, and vapor coexist in the same environment

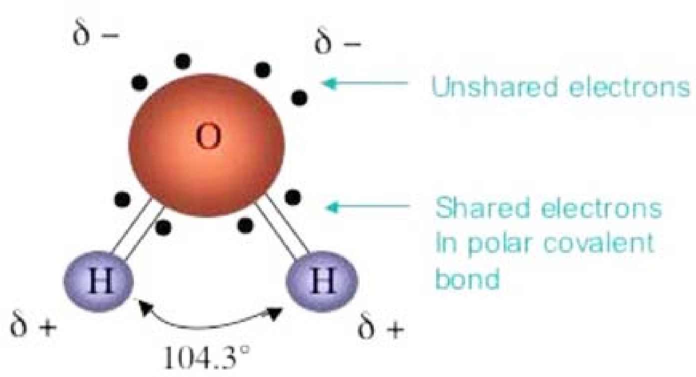
WATER MOLECULES FORM HYDROGEN BONDS

Water is a fundamental requirement for life, so it is important to understand the structural and chemical properties of water.

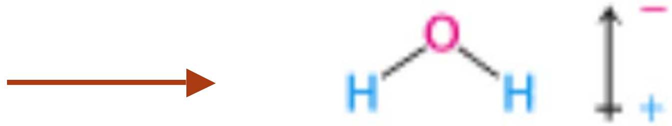
Most biological molecules are surrounded by water, and even their molecular structure is in part governed by how their component groups interact with water.

Water plays a role in how biological molecules assemble to form larger structures or undergo chemical transformation. In fact, water itself—or its H^+ and OH^- constituents—participates directly in many biochemical processes.

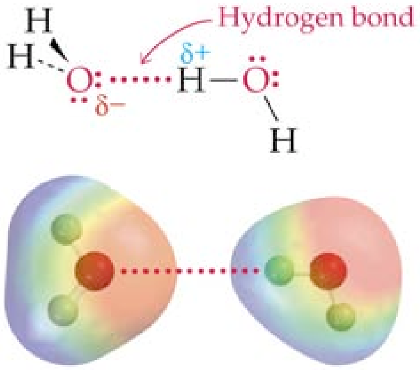
Structure of water molecule

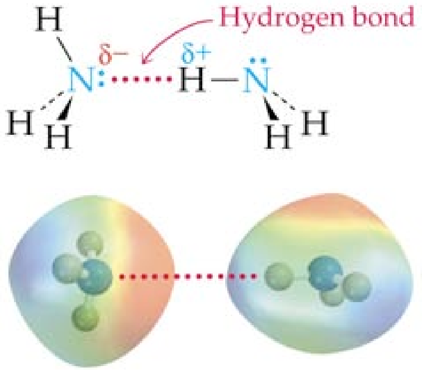


The central O atom forms covalent bonds with two H atoms, leaving two unshared pairs of electrons. The molecule has approximately tetrahedral geometry, with the O atom at the center of the tetrahedron, the H atoms at two of the four corners, and electrons at the other two corners. The electrical charge is therefore *polarized*: Water is a highly ***polar molecule***.



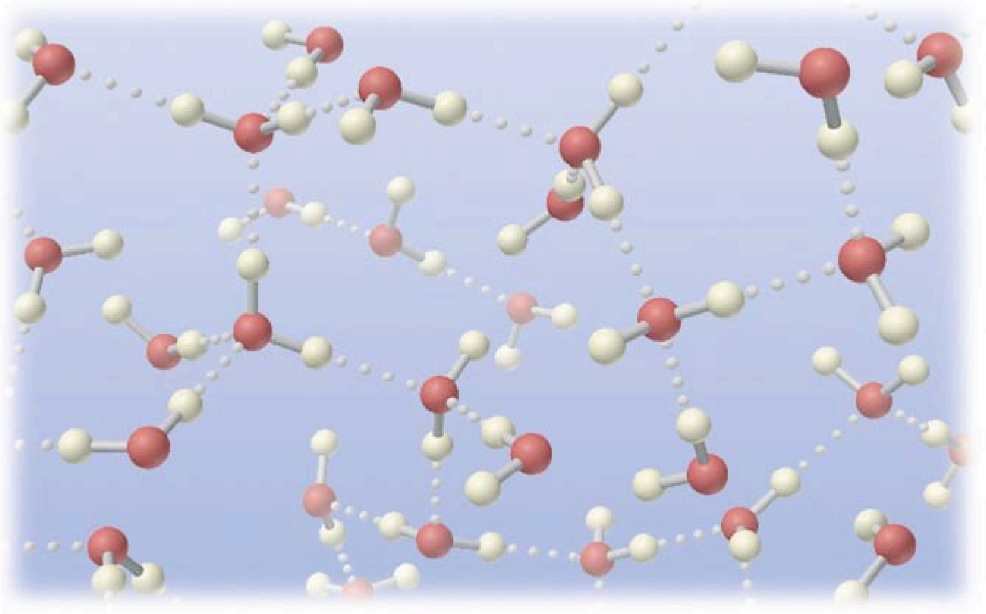
Water: Hydrogen-bonding network





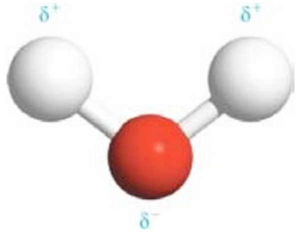
Hydrogen bonds are found between molecules of water and molecules of ammonia. They are defined as the attractive interaction between a hydrogen atom bonded to a very electronegative atom (O, N, or F) and an unshared electron pair on another electronegative atom.

Liquid water contains a vast three-dimensional network of hydrogen bonds resulting from the attraction between positively polarized hydrogens and electron pairs on negatively polarized oxygens. Each oxygen can form two hydrogen bonds, represented by dotted lines.

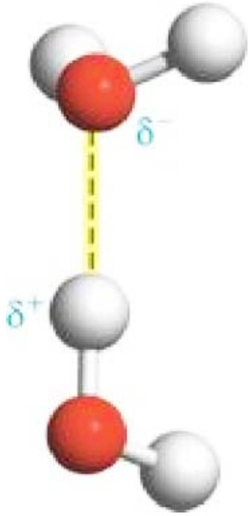


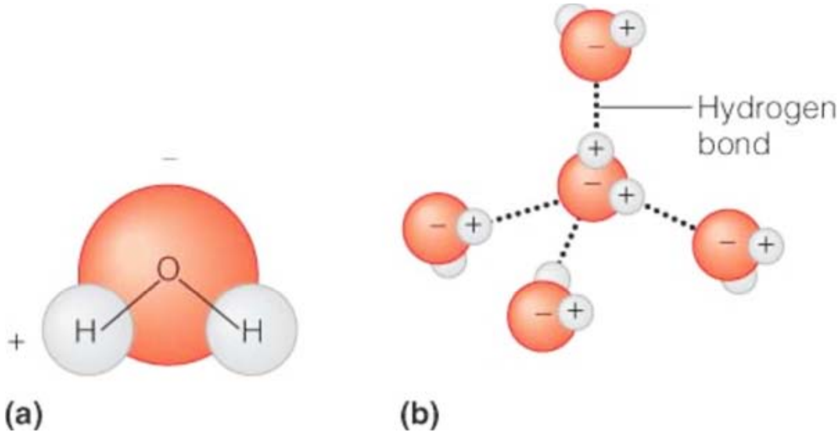
Hydrogen bonding cont’d

As a result of this electronic arrangement, *the water molecule is* ***polar;*** that is, it has an uneven distribution of charge. The oxygen atom bears a partial negative charge (indicated by the symbol δ⁻), and each hydrogen atom bears a partial positive charge (indicated by the symbol δ⁺). ***This polarity is the key to many of water's unique physical properties.***



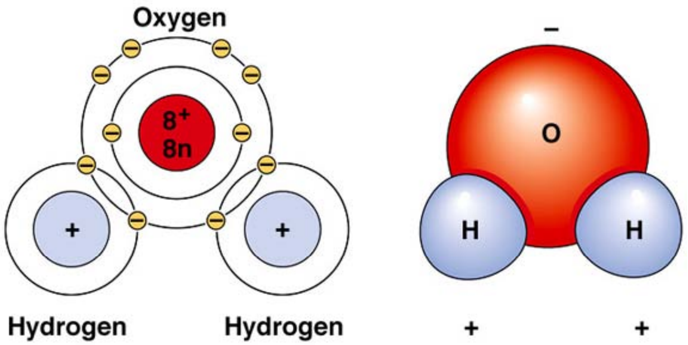
Neighboring water molecules tend to orient themselves so that each partially positive hydrogen is aligned with a partially negative oxygen. This interaction, shaded yellow here, is known as a **hydrogen bond.**
Nearly all the unique properties of water arise from water’s H-bond capabilities.

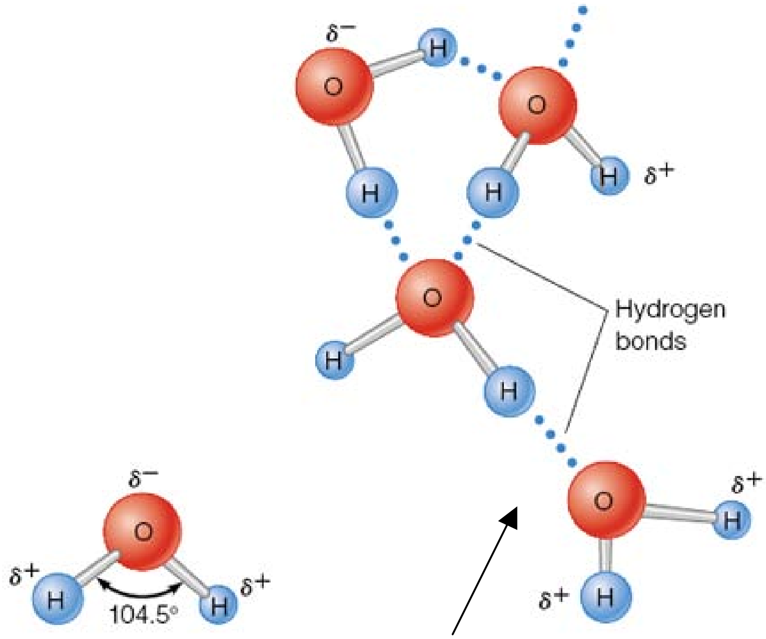




Hydrogen bond formation in water. (a) In a water molecule, the electrons of the hydrogen atoms are strongly attracted to the oxygen atom. Therefore, the part of the water molecule containing the oxygen atom has a slightly negative charge, and the part containing hydrogen atoms has a slightly positive charge. **(b)** In a hydrogen bond between water molecules, the hydrogen of one water molecule is attracted to the oxygen of another water molecule.

H bonding: Summary (a little more technical)





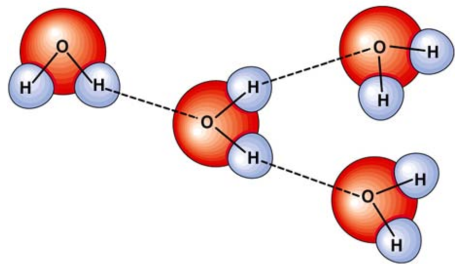
(a) Polarity of water molecule

(b) Hydrogen bonding between water molecules

Hydrogen Bonding Between Water Molecules.

(a) The water molecule is polar because it has an asymmetric charge distribution. The two hydrogen atoms are bonded to the oxygen at an angle of 104.5°. The oxygen atom bears a partial negative charge (the Greek letter delta stands for "partial") and is thus the electronegative portion of the molecule. The two hydrogen atoms are electropositive; their end of the molecule has a partial positive charge

(b) The extensive association of water molecules with one another in either the liquid or the solid state is due to hydrogen bonds (dotted lines) between the electronegative oxygen atom of one water molecule and the electropositive hydrogen atoms of adjacent molecules. In ice, the resulting crystal lattice is regular and complete; every oxygen is hydrogen-bonded to hydrogens of two adjacent molecules. In liquid water, some of the structure is disrupted, allowing the molecules to "pack" a little more tightly.



All the following properties can be understood in terms of water's hydrogen-bonding network

Water moderates high and low temperatures

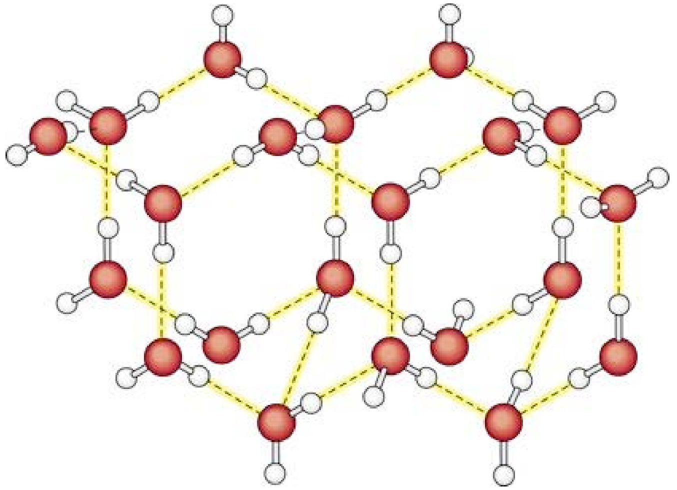
Water also moderates the effects of high temperatures because it takes a great deal of heat energy (539 calories per gram) to convert liquid water to water vapor. This is the *heat of* ***vaporization.*** This, too, is due to the polar nature of water molecules and the hydrogen bonds that interconnect them. For a water molecule to evaporate, it must absorb sufficient energy to make it move quickly enough to break all the hydrogen bonds that hold it to nearby water molecules. Only the fastest-moving water molecules, carrying the most energy, can break their hydrogen bonds and escape into the air as water vapor. The remaining liquid is cooled by the loss of these high-energy molecules.

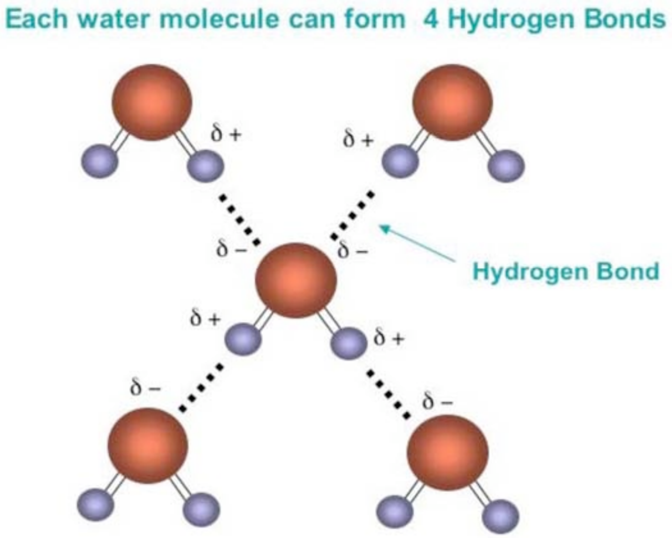
It takes a lot of energy to heat water

The energy required to heat a gram of a substance by 1°C is called its ***specific heat***. Because of its polar nature and hydrogen bonding, water has a very high specific heat, and therefore water moderates temperature changes. When heat enters a watery system such as a lake or a living cell, much of the heat energy initially goes into breaking hydrogen bonds rather than speeding up individual molecules. Thus, it requires more energy to heat water than to heat most other substances by the same amount.

Water Forms an Unusual Solid: Ice

Each water molecule can potentially participate in four hydrogen bonds, since it has two hydrogen atoms to "donate" to a hydrogen bond and two pairs of unshared electrons that can "accept" a hydrogen bond. In ice, a crystalline form of water, each water molecule does indeed form hydrogen bonds with four other water molecules.This regular, lattice-like structure breaks down to some extent when the ice melts.

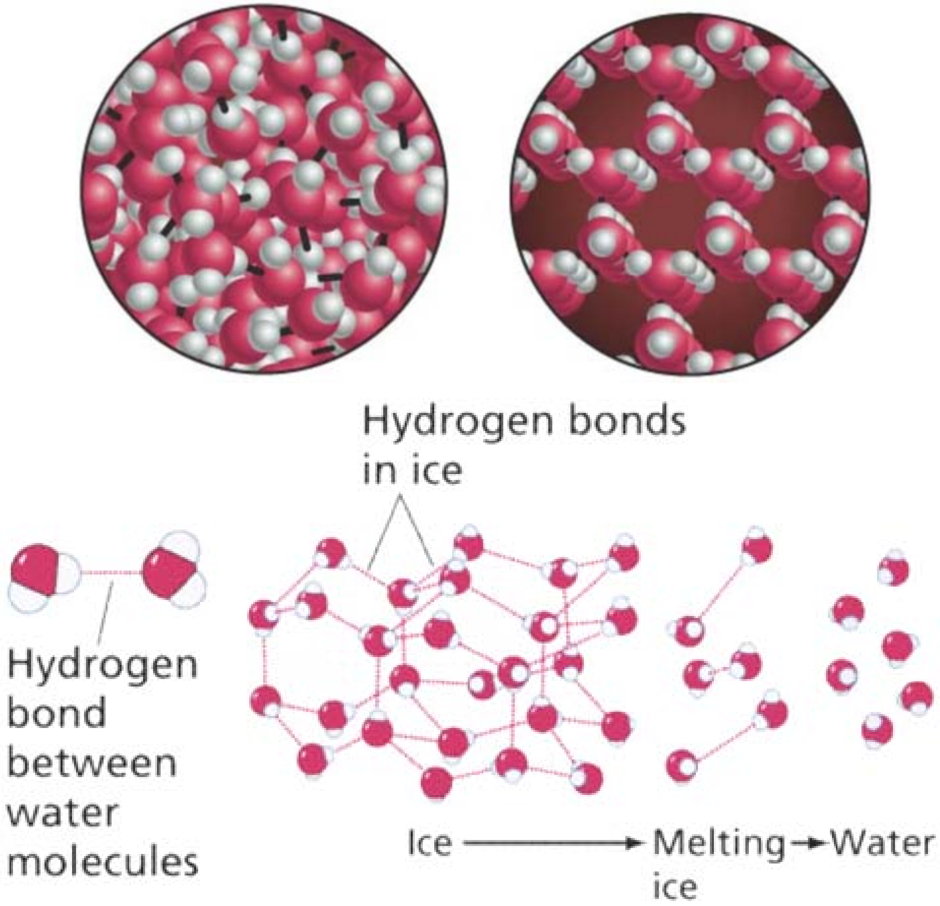




ICE:Each water molecule acts as a donor for two hydrogen bonds and an acceptor for two hydrogen bonds, thereby interacting with four other water molecules in the crystal. (Only two layers of water molecules are shown here.)

In liquid water, each molecule still can form hydrogen bonds with up to four other water molecules, but each bond has a lifetime of only about 10^{-12} s. As a result, *the structure of water is continually flickering as water molecules rotate, bend, and reorient themselves.*

More on water and ice

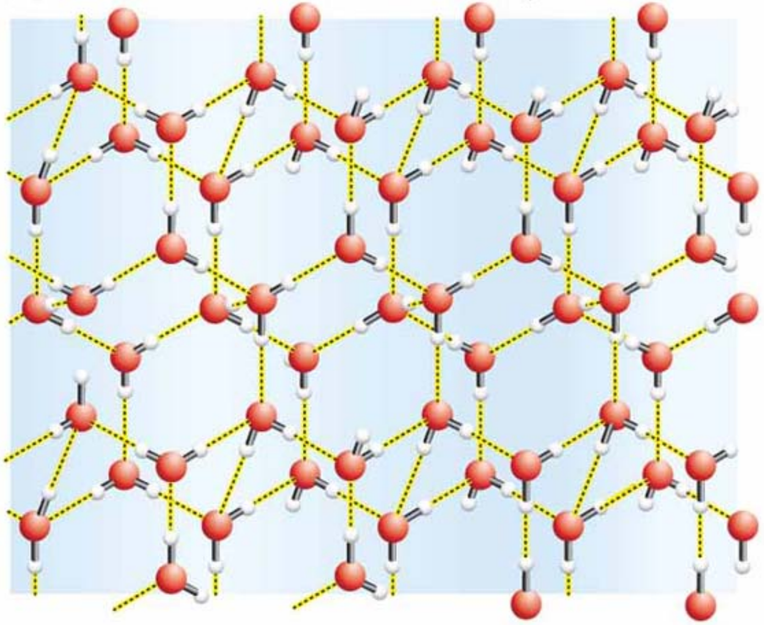


Water can exist in three forms at the same temperatures at which noncovalent interactions are efficient.

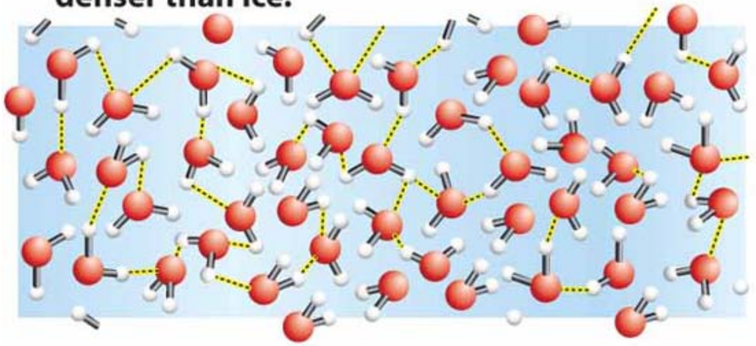
Most liquids become denser when they solidify, so the solid sinks. Ice is unique because it is less dense than liquid water. The regular arrangement of water molecules in ice crystals keeps them farther apart than they are in the liquid phase, where they jumble more closely together; thus, ***ice is less dense than water.***

When a pond or lake starts to freeze in winter, the ice floats on top, forming an insulating layer that delays the freezing of the rest of the water.. If ice were to sink, ponds, lakes, and oceans would freeze solid from the bottom up during the winter: How would such an ocean ever unfreeze?

(a) In ice, water molecules form a crystal lattice.



(b) In liquid water, no lattice forms, so liquid water is denser than ice.



One more illustration of how the different rigidity of the H-bonding network in ice and water is responsible for one of its most important properties: ice floats.

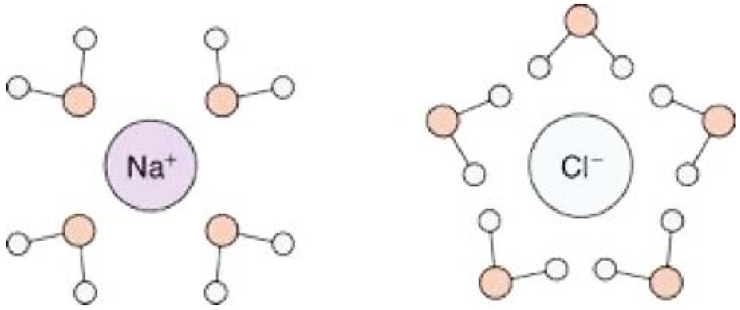
Cohesion, surface tension, boiling temperature

Because of its ability to form hydrogen bonds, water is highly cohesive. This accounts for its high surface tension, which allows certain insects to walk on water.

The cohesiveness of water molecules also explains why water remains a liquid whereas similar molecules such as CH_4 and H_2S are gases at room temperature (25°C).

Water dissolves many compounds

The ability of the water molecule to form hydrogen bonds and participate in other electrostatic interactions explains why water is an effective solvent for a wide variety of compounds. The polar nature of the water molecule allows it to associate with ions (for example, the Na^+ and Cl^- ions from the salt NaCl) by aligning its partial charges accordingly. Because the interactions between the polar water molecules and the ions are stronger than the attractive forces between the Na^+ and Cl^- ions, the salt dissolves



Biological molecules that bear polar or ionic groups are also readily solubilized, in this case because their groups can form hydrogen bonds with the water molecules. **These substances are called *hydrophilic*.**

Micelles, Lipid Bilayers, Vesicles: Water's hydrophobic effect

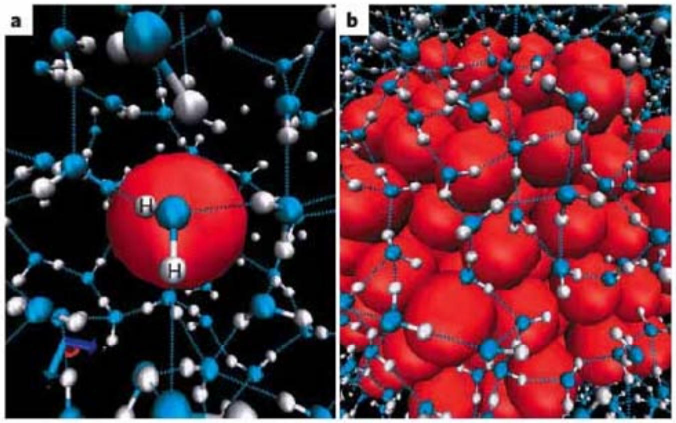
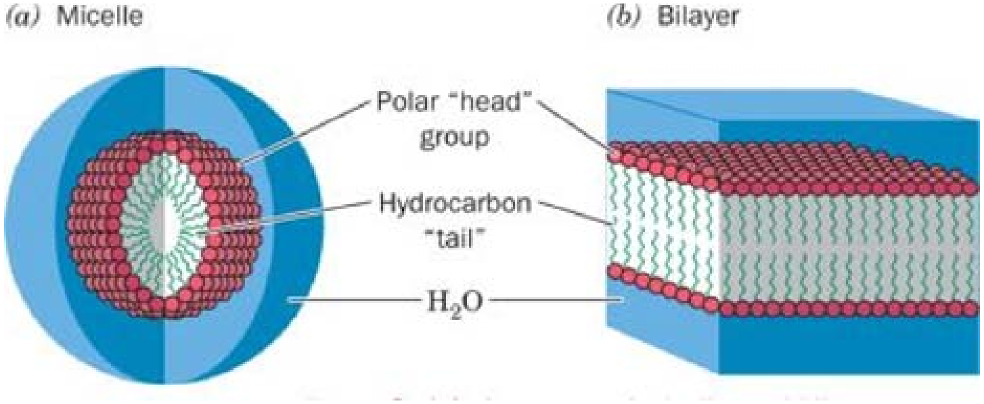
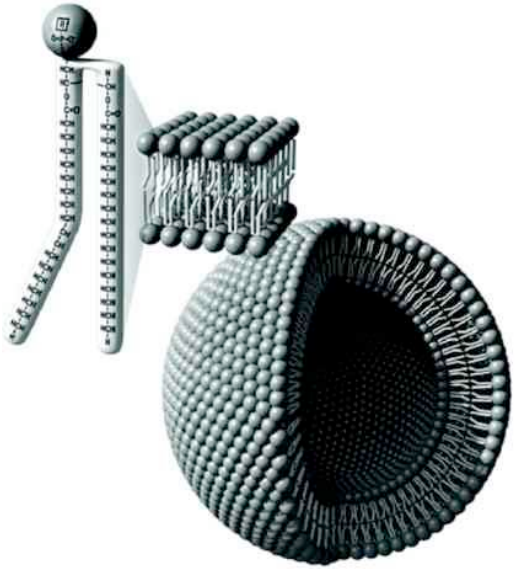
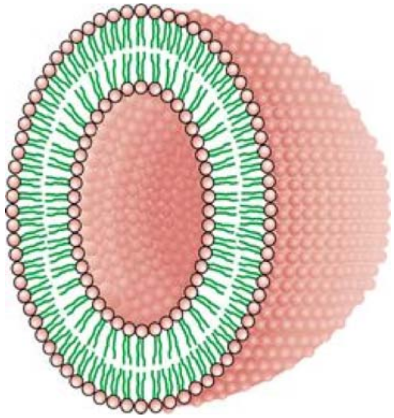


Figure 1 | Configurations of liquid water molecules near hydrophobic cavities in molecular-dynamics simulations. The blue and white particles represent the oxygen (O) and hydrogen (H) atoms, respectively, of the water molecules. The dashed lines indicate hydrogen bonds (that is, O-H···O



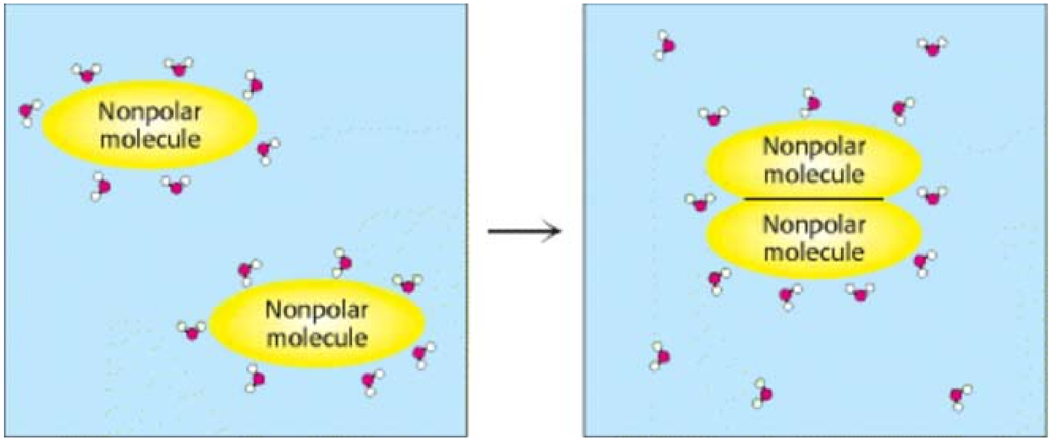




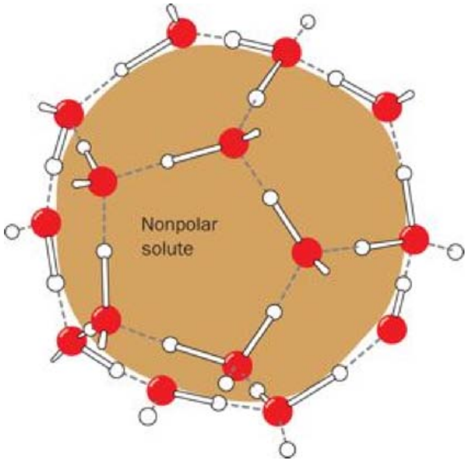
Vesicle = folded up bilayer

The Hydrophobic Effect

The exclusion of nonpolar substances from an aqueous solution is known as the ***hydrophobic effect.*** It is a powerful force in biochemical systems, even though it is not a bond or attractive interaction in the conventional sense.



The Hydrophobic Effect. The aggregation of nonpolar groups in water leads to an increase in entropy owing to the release of water molecules into bulk water.

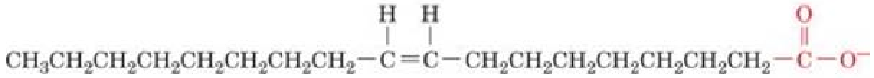


The hydrophobic effect governs the structures and functions of many biological molecules. For example, the polypeptide chain of a protein folds into a globular mass so that its hydrophobic groups are in the interior, away from the solvent, and its polar groups are on the exterior, where they can interact with water. Similarly, the structure of the lipid membrane that surrounds all cells is maintained by the hydrophobic effect acting on the lipids.

Amphiphilic molecules form membrane structures

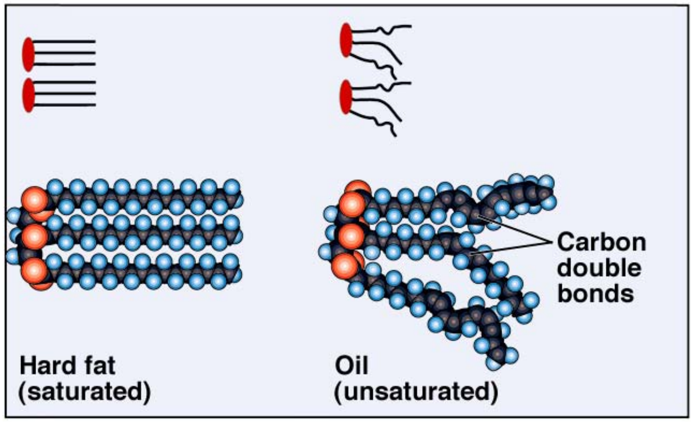
$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O^-$$

Palmitate ($C_{15}H_{31}COO^-$)



$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2{-}\overset{\overset{\displaystyle H}{|}}{C}{=}\overset{\overset{\displaystyle H}{|}}{C}{-}CH_2CH_2CH_2CH_2CH_2CH_2CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O^-$$

Oleate ($C_{17}H_{33}COO^-$)



The hydrocarbon “tail” of the molecule (blue or black) is ***nonpolar*** while its carboxylate “head” (red) is strongly ***polar***.

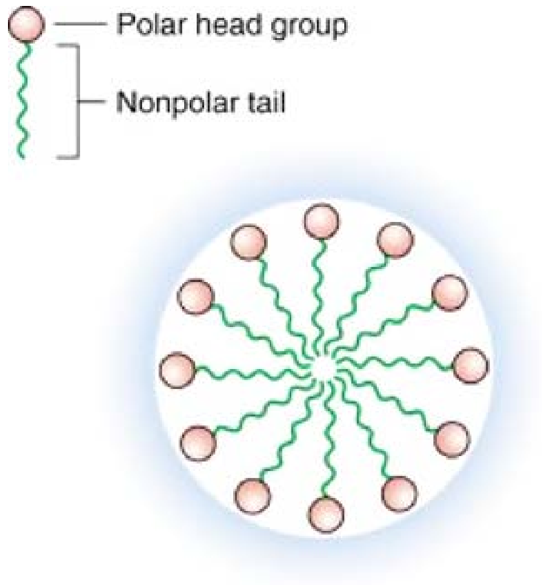
Molecules such as this one, which have both hydrophobic and hydrophilic portions, are said to be **amphi-philic** or **amphipathic.**

What happens when amphiphilic molecules are added to water? In general, *the polar groups of amphiphiles orient themselves toward the solvent molecules and are therefore hydrated, while the nonpolar groups tend to aggregate due to the hydrophobic effect.*

As a result, the amphiphiles may form a spherical **micelle,** a particle with a solvated surface and a hydrophobic core.

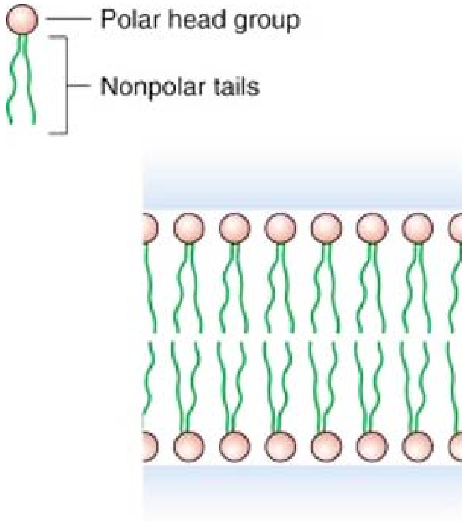
Hydrophobic effect forms micelles, bilayers

micelle



A micelle formed by amphiphilic molecules. The hydrophobic tails of the molecules aggregate, out of contact with water, due to the hydrophobic effect. The polar head groups are exposed to and can interact with the solvent water molecules.

bilayer



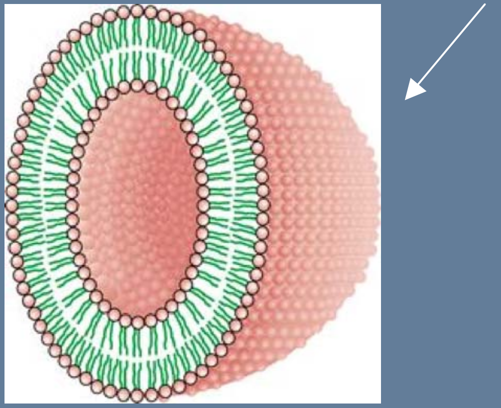
The amphiphilic lipid molecules form **two** layers so that their **polar head groups are exposed to the solvent while their hydrophobic tails are sequestered in the interior of the bilayer, away from water**. One-tailed lipids tend to form micelles and two-tailed lipids tend to form bilayers.

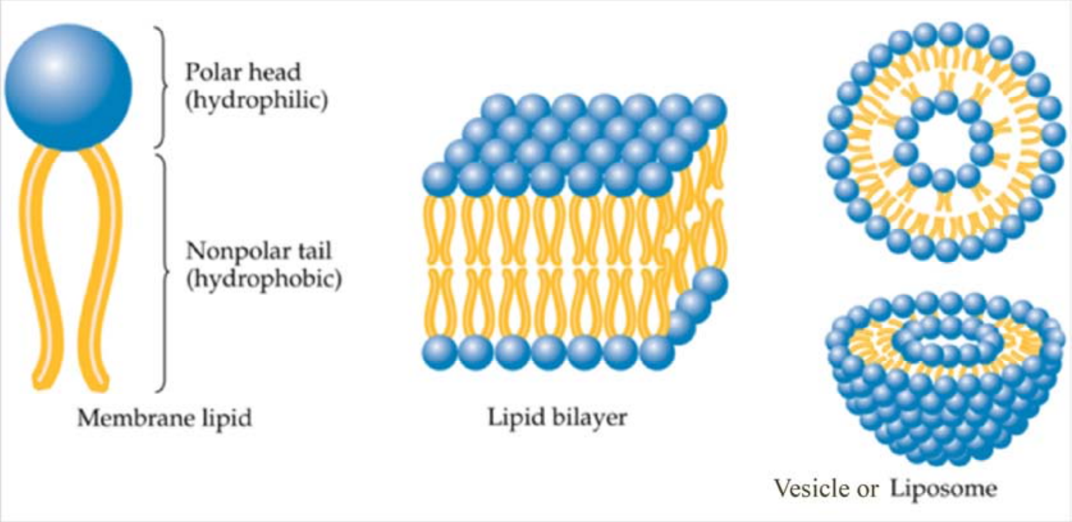
Bilayer, vesicle

A bilayer may close up to form a *vesicle*

To eliminate its solvent-exposed edges, a lipid bilayer tends to close up to form a **vesicle,** shown cut in half:

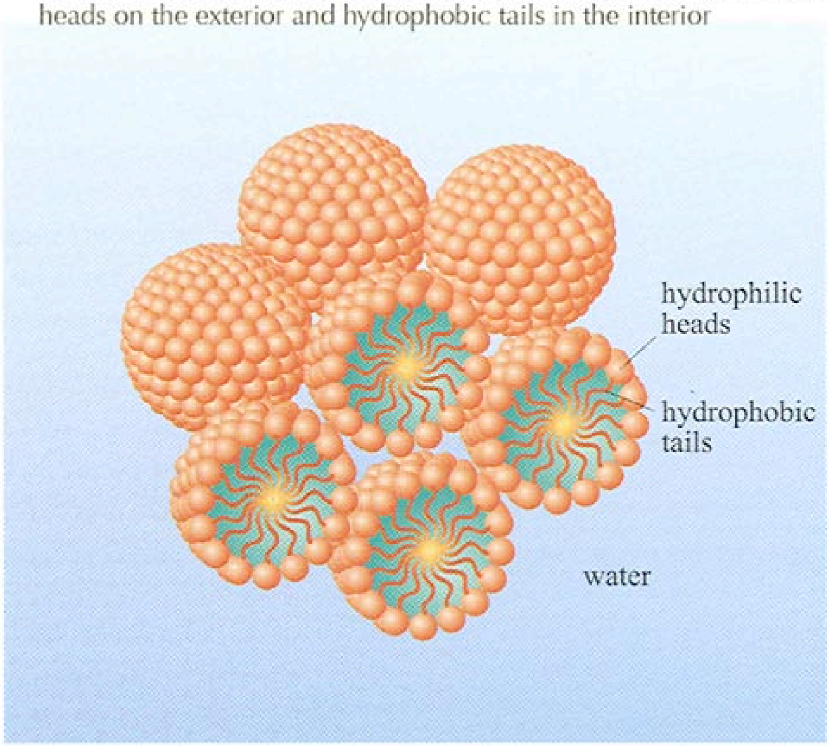
Many of the subcellular compartments (organelles) in eukaryotic cells are really just more elaborate versions of the lipid vesicle shown here.





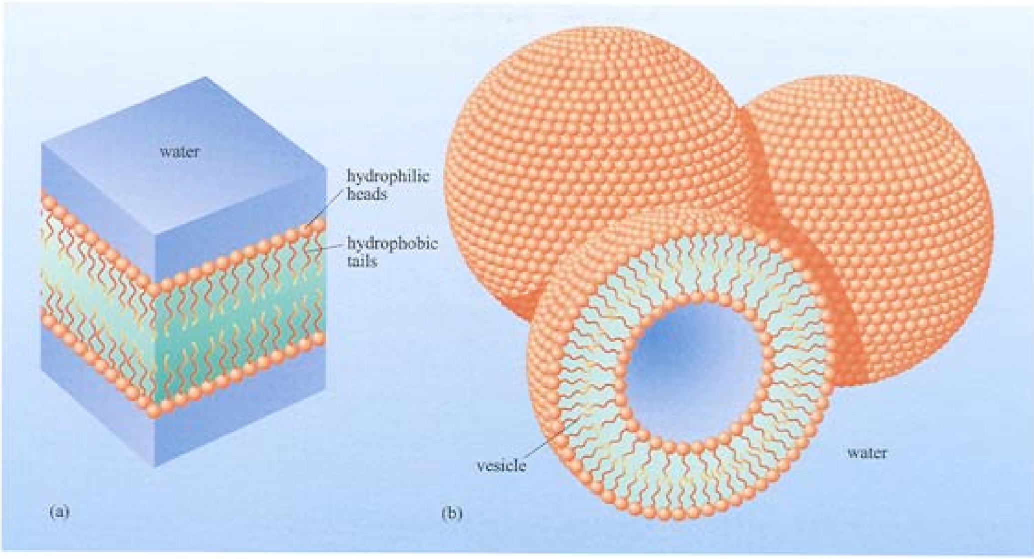
Review: **micelle, bilayer, vesicle**

Cluster of lipid micell: spherical collection of lipids with hydrophilic heads on the exterior and hydrophobic tails in the interior



Cluster of micelles

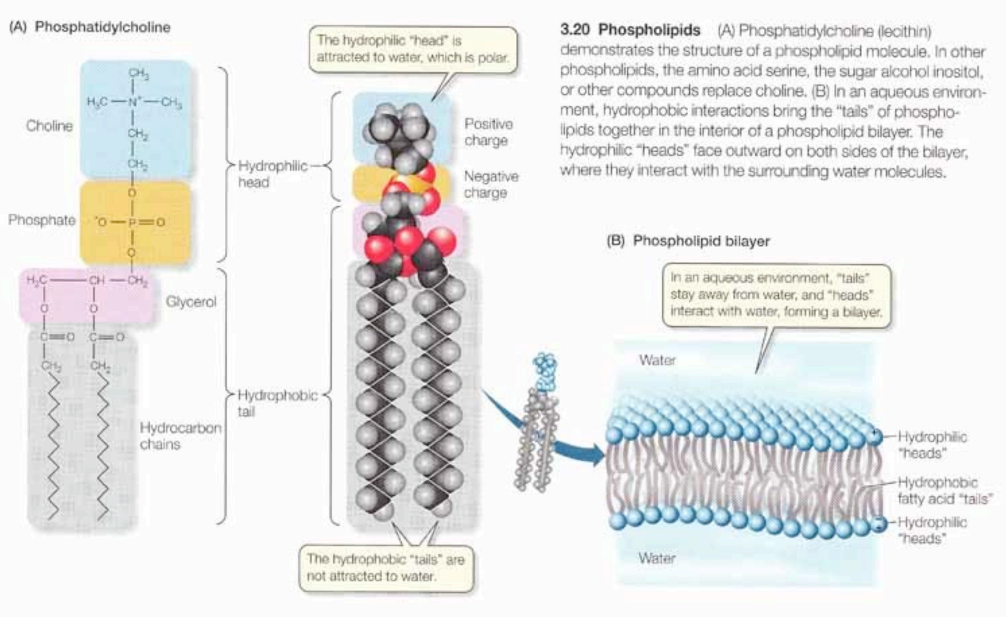
Fold the *bilayer* into a *vesicle* -- they can cluster too.



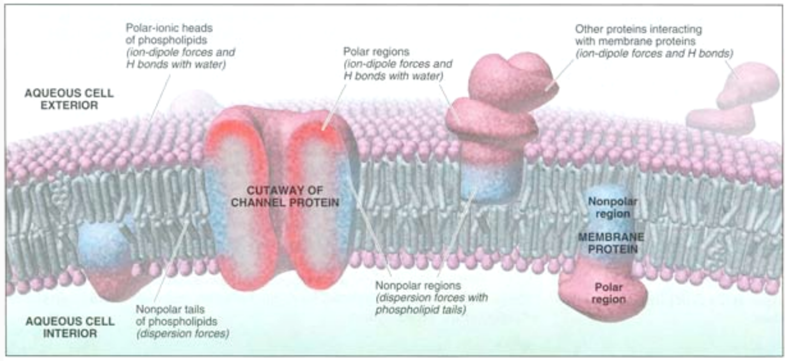
Think: Why did membranes use bilayer membranes instead of the fancier vesicles? Imagine large bilayer sheet, and think about where the chemical activity could take place, compare with a giant vesicle.

Modern life: membranes have acquired a huge amount of complexity.

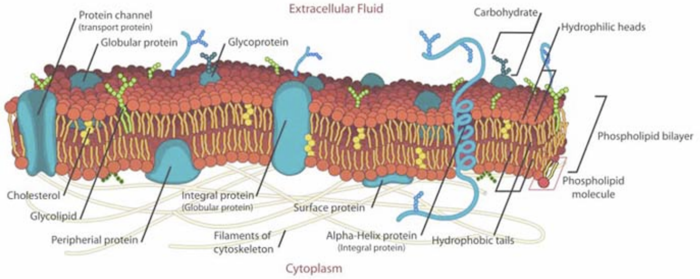
Living organisms have phosholipid bilayer membranes

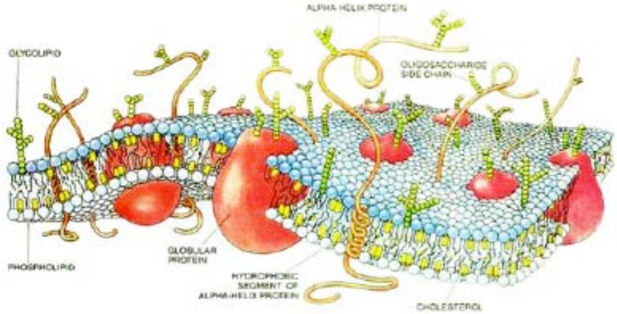


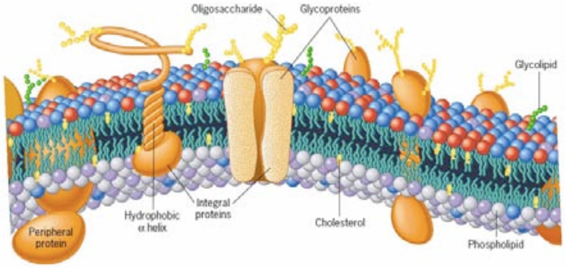
3.20 Phospholipids (A) Phosphatidylcholine (lecithin) demonstrates the structure of a phospholipid molecule. In other phospholipids, the amino acid serine, the sugar alcohol inositol, or other compounds replace choline. (B) In an aqueous environment, hydrophobic interactions bring the "tails" of phospholipids together in the interior of a phospholipid bilayer. The hydrophilic "heads" face outward on both sides of the bilayer, where they interact with the surrounding water molecules.



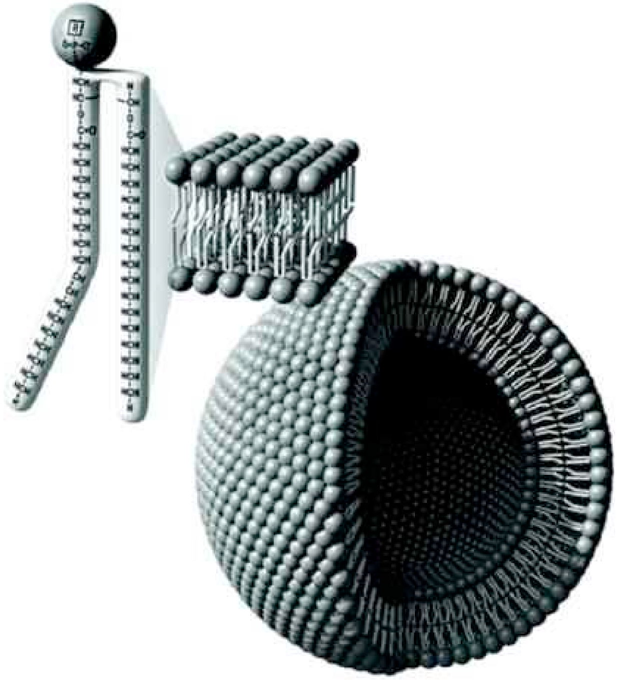
A modern lipid bilayer: Extremely complex



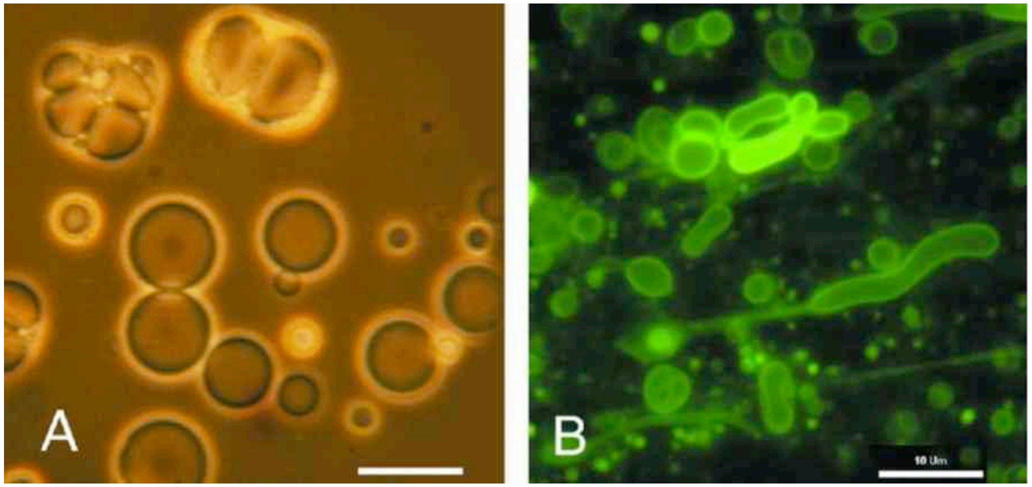




Because of hydrophobic effect, compartmentalization (encapsulation) into membrane structures is easy, *may have been the first step in origin of life. Usually called the "**lipid world**."*



The self-assembly of amphiphiles occurs when molecules with both hydrophilic and hydrophobic regions arrange themselves into a minimum energy configuration, such as a spherical phospholipid bilayer vesicle

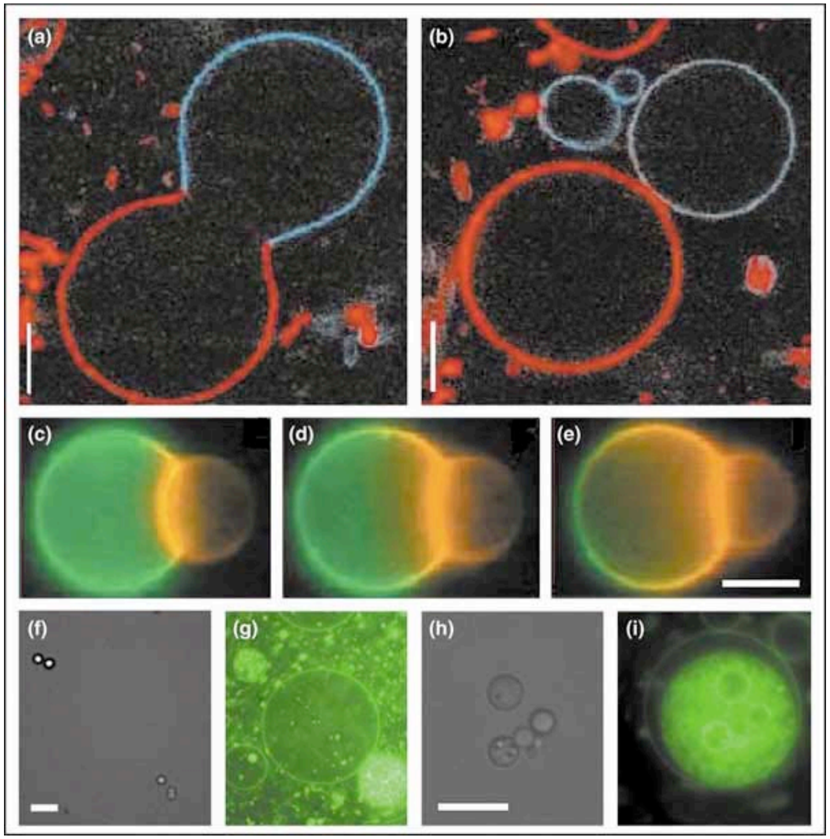


Primitive membrane structures.

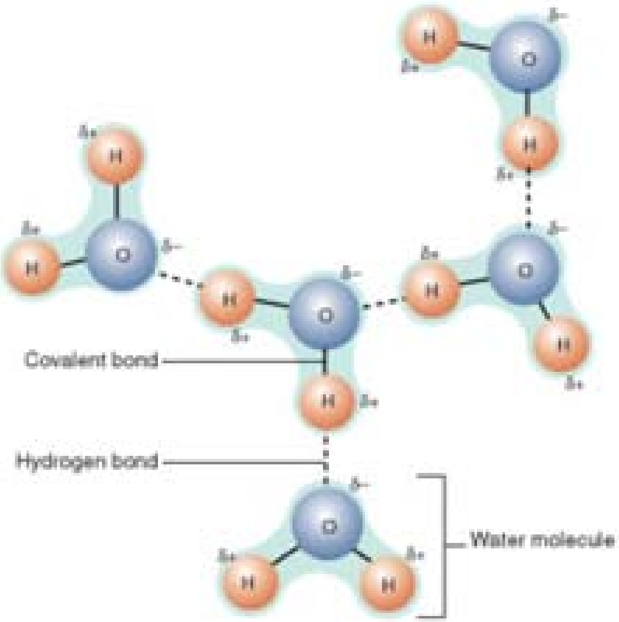
A: Amphiphilic compounds from the Murchison meteorite form membranous vesicles when exposed to dilute aqueous salt solutions at pH > 7.0.

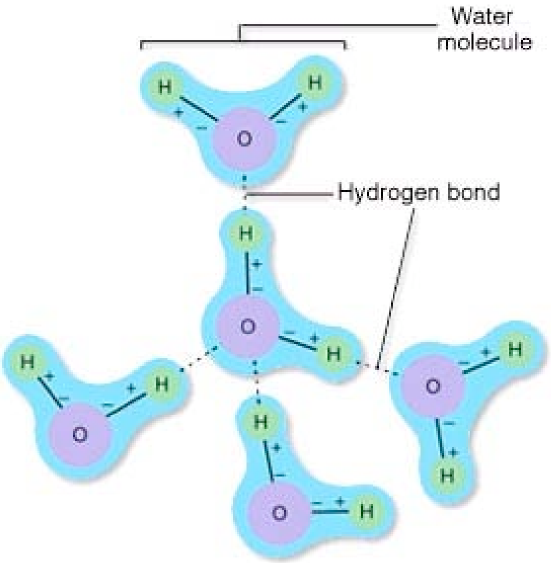
B: Monocarboxylic acids in pure form also self-assemble into membranous vesicles

Self-replicating vesicles



(Hanczyc, M. M. & Szostak, J. W. (2004) “Replicating vesicles as models of primitive cell growth and division” Curr. Opin. Chem. Biol. 8, 660.





Hydrogen Bonds in an Ice Crystal