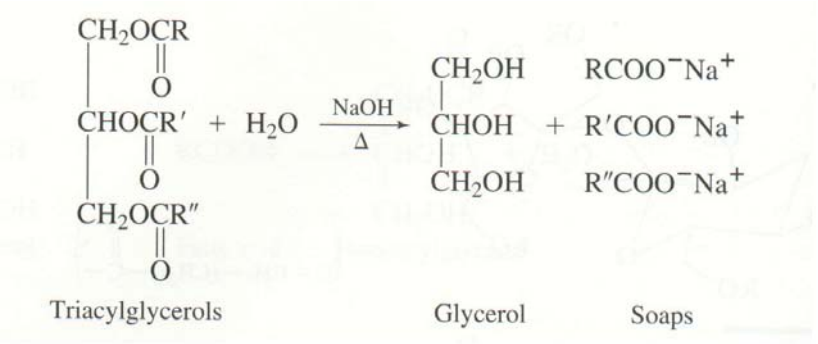
Lipids and Membranes

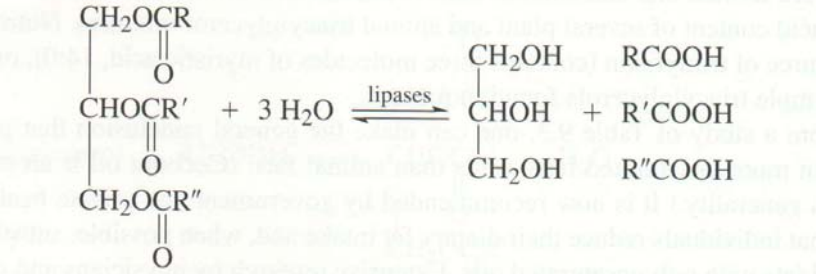
Lipids

- Lipids are hydrophobic or amphiphilic
  - insoluble in water
  - soluble in organic solvents
  - soluble in lipids
- Lipids are used as
  - energy storage molecules
  - structural components of membranes
  - protective molecules
  - hormones and signal transduction molecules
  - photosynthetic pigments

Lipids

- Lipids belong to several classes
  - nomenclature based upon soap making
- Saponifiable lipids
  - ester linked fatty acid(s) and polar head group
  - triacylglycerols
  - phosphoacylglycerols
  - sphingolipids
  - glycolipids





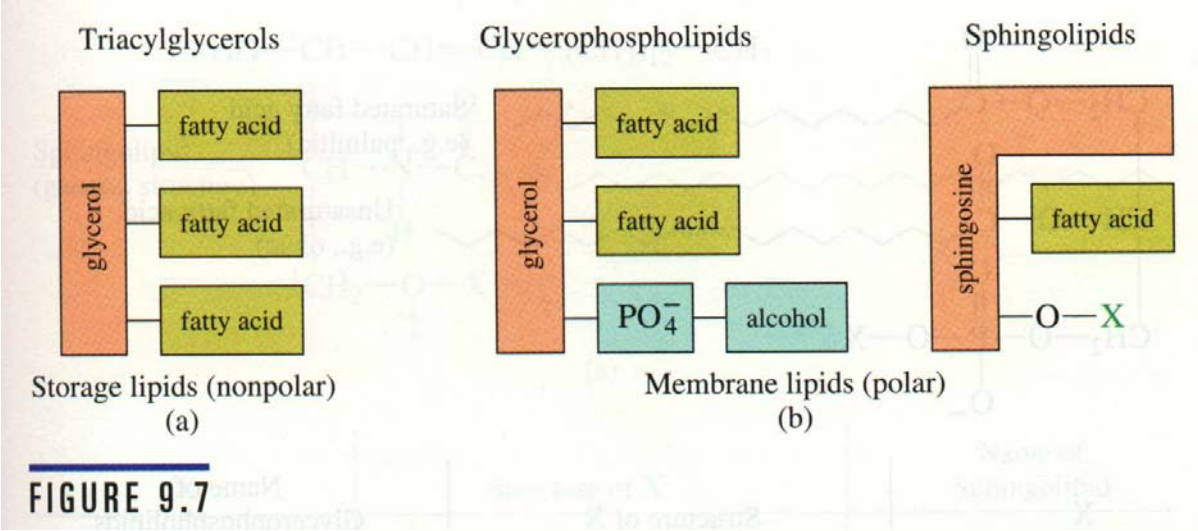


FIGURE 9.7

Fatty Acids

- Fatty acids are long chain carboxylic acids
  - 12 to 20 carbon atoms (linear chain)
  - no hydrogen bonding functional groups
    - causes fatty acids to be involved in hydrophobic interactions
  - often have double bonds (usually *cis*)
    - can be unsaturated or polyunsaturated fatty acids

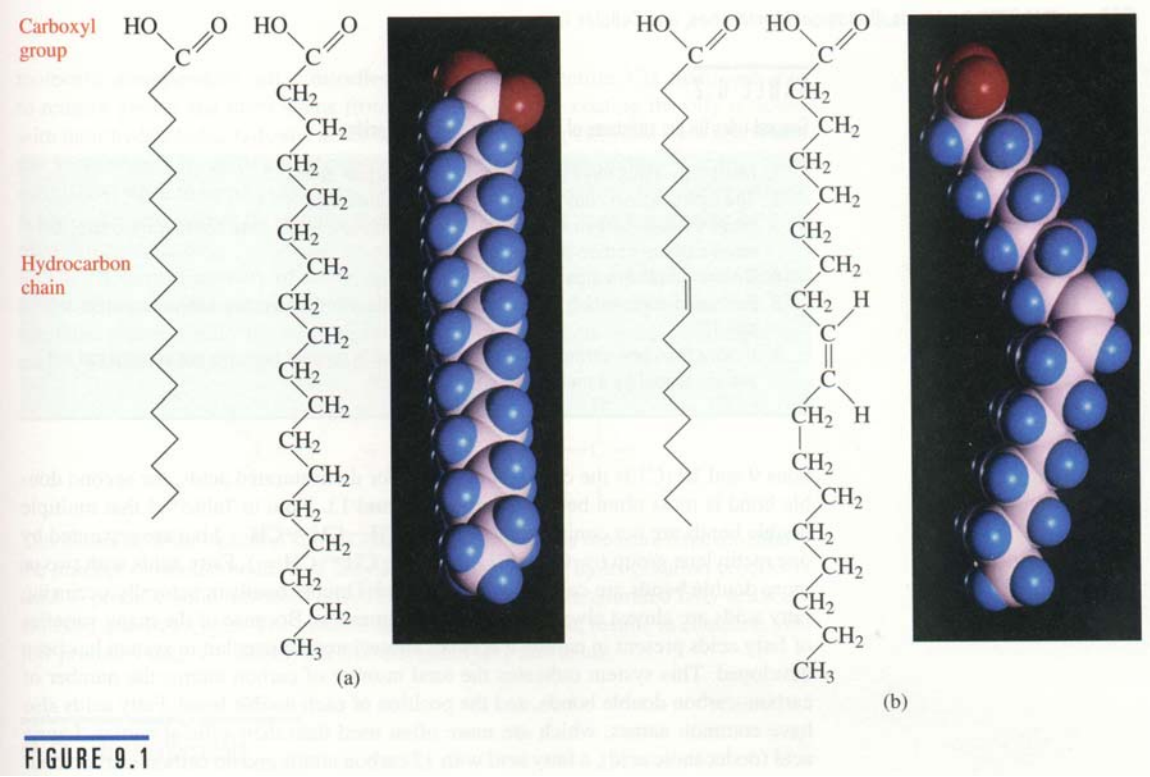


FIGURE 9.1

Fatty Acids

- Lipids can contain many different fatty acids

TABLE 9.1

Structures and names of common, naturally occurring fatty acids

Number of Carbons[a]	Common Name	Systemic Name	Abbreviated Symbol[b]	Structure
12	Lauric acid	*n*-Dodecanoic acid	12:0	$CH_3(CH_2)_{10}COOH$
14	Myristic acid	*n*-Tetradecanoic acid	14:0	$CH_3(CH_2)_{12}COOH$
16	Palmitic acid	*n*-Hexadecanoic acid	16:0	$CH_3(CH_2)_{14}COOH$
16	Palmitoleic acid	*n*-Hexadecenoic acid	$16:1^{\Delta 9}$	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$
18	Stearic acid	*n*-Octadecanoic acid	18:0	$CH_3(CH_2)_{16}COOH$
18	Oleic acid	*n*-Octadecenoic acid	$18:1^{\Delta 9}$	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$
18	Linoleic acid	—	$18:2^{\Delta 9,12}$	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$
18	Linolenic acid	—	$18:3^{\Delta 9,12,15}$	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$
20	Arachidonic acid	—	$20:4^{\Delta 5,8,11,14}$	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_3COOH$

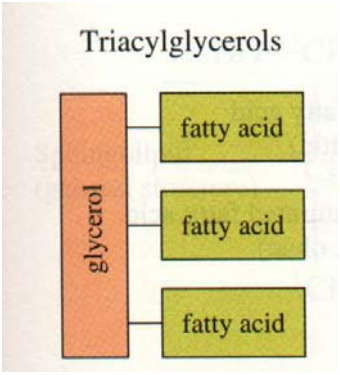
[a]Note that all have an even number of carbons.

[b]Indicates the number of carbon atoms and the position of the carbon–carbon double bonds.

- Fatty acid chain length and degree of unsaturation influence the melting point of lipids that contain them

Lipids

- Triacylglycerols are made up from 3 fatty acids ester linked to glycerol



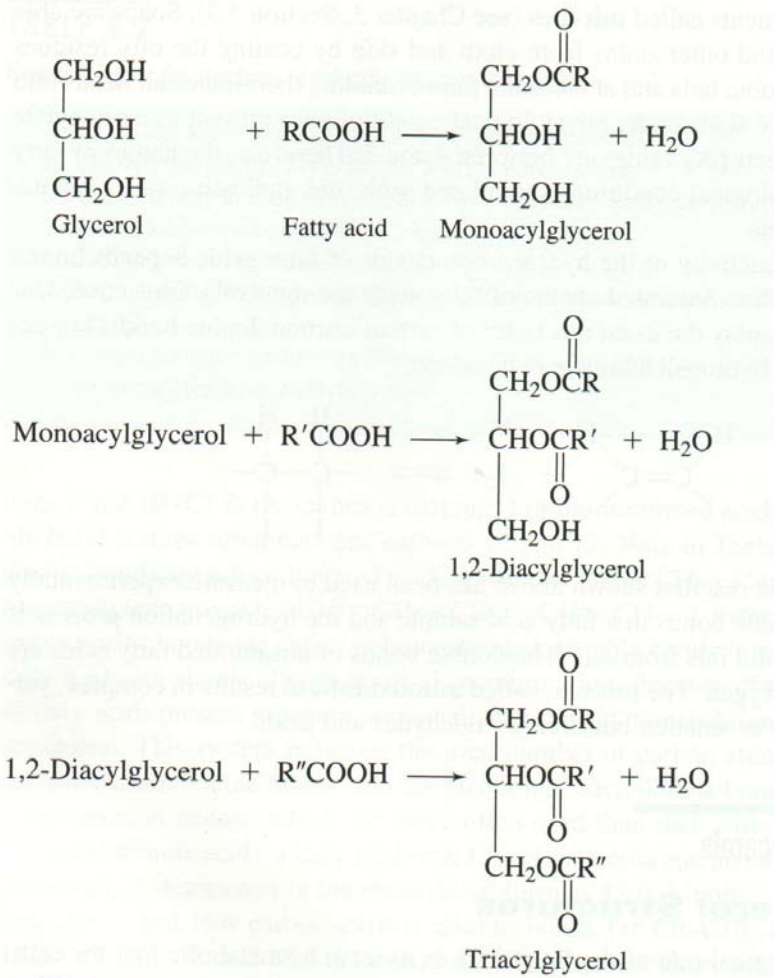


FIGURE 9.2

Lipids

- triacylglycerols are storage lipids
  - fats and oils
  - melting point depends upon esterified fatty acids

TABLE 9.3

Fatty acid content of common oils and fats. The fatty acids are present in triacylglycerol form

	Fatty Acids[a]				
	Saturated				Unsaturated
Source	C_4–C_{12}	C_{14}	C_{16}	C_{18}	$C_{16} + C_{18}$
Canola oil	—	—	5	1	94
Olive oil	2	2	13	3	80
Butter	10	11	29	10	40
Beef fat	2	2	29	21	46
Coconut oil	60	18	11	2	8
Corn oil	—	2	10	3	85
Palm oil	—	2	40	6	52
Nutmeg oil	7	90	3	—	—

[a]The numbers represent percentage of each fatty acid.

- triacylglycerols are non-polar and a rich source of energy
  - more highly reduced than carbohydrates
  - not hydrated

- Hydrogenation of oils is used to produce solid triacylglycerols
  - hydrogenation leads to the reduction (saturation) of *cis*-double bonds
- Hydrogenation can also produce *trans*-fatty acids as by-products

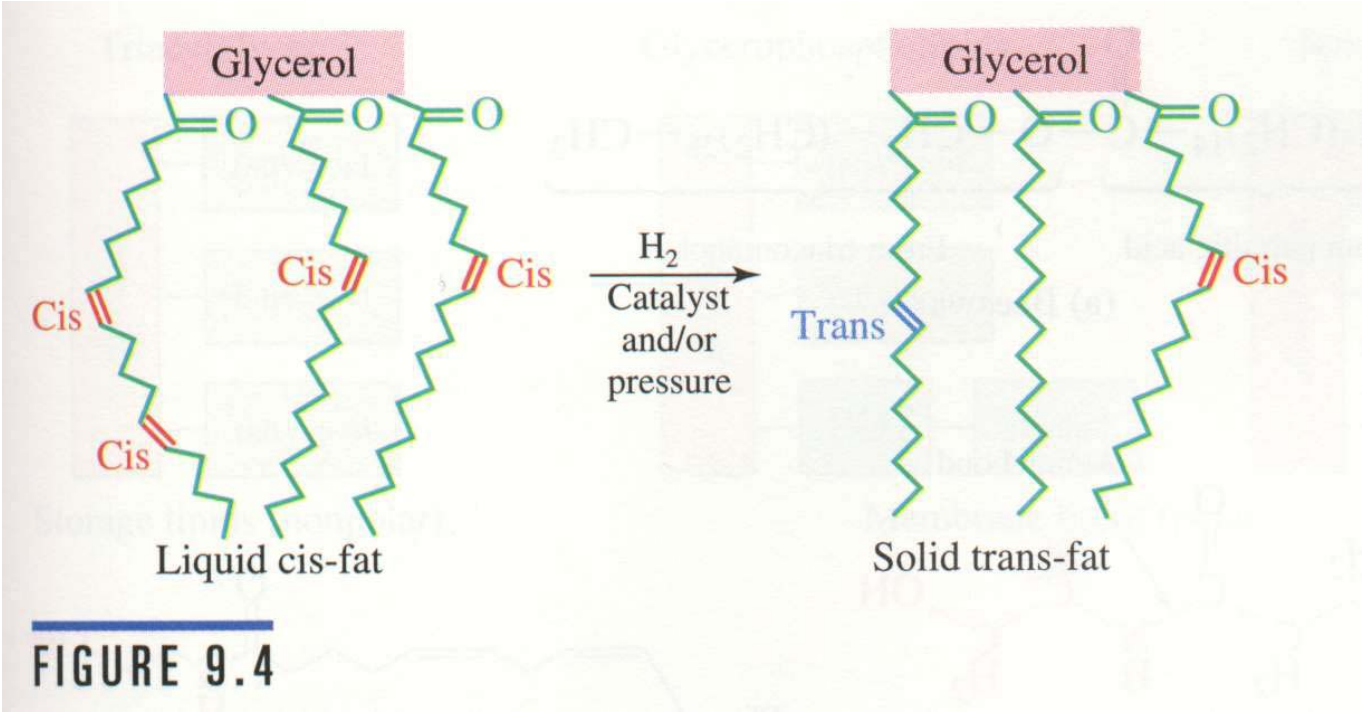
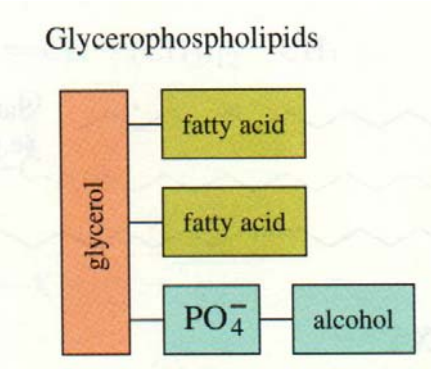


FIGURE 9.4

Lipids

- Phosphoacylglycerols (phosphoglycerides) are membrane lipids that are based upon the core structure of phosphatidic acid
  - glycerol esterfied to 2 fatty acids plus phosphoric acid
- The phosphate residue of a phosphoacylglycerol is further esterified to a hydrophilic head group substituent
- phophoglycerides are amphiphilic



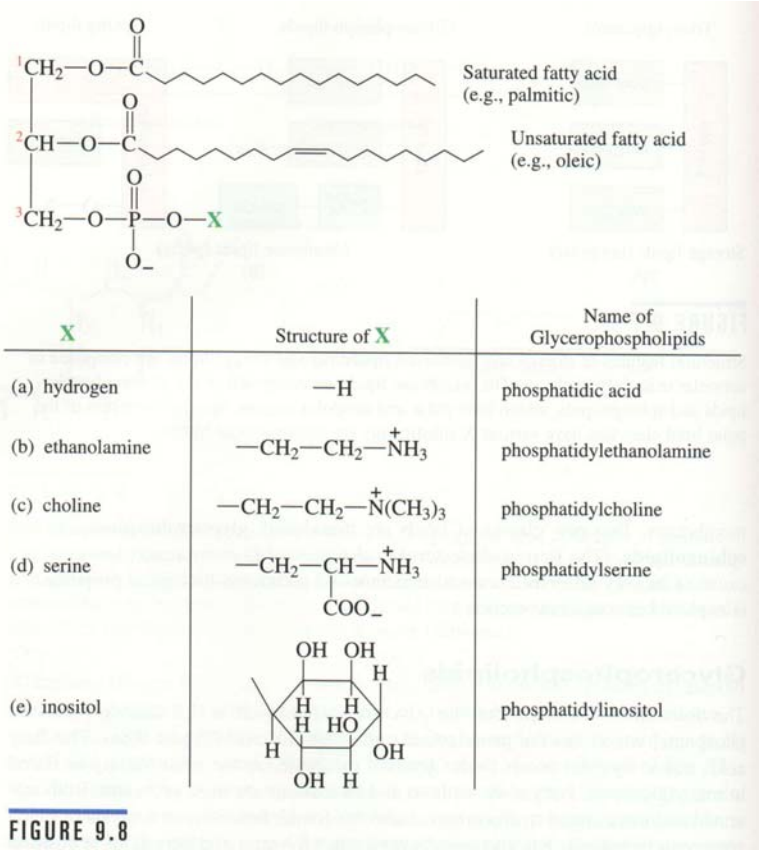
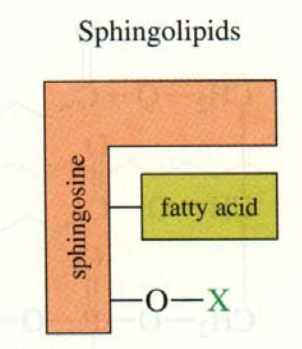


FIGURE 9.8

Lipids

- Sphingolipids are membrane lipids that are based upon the core structure of sphingosine, a long chain amino alcohol
- sphingosine is linked with a fatty acid (amide linked) to give ceramide
- The hydroxyl residue of a ceramide is further esterified to a hydrophilic head group substituent
- sphingolipids are amphiphilic
- sphingomyelin is similar in character to phosphoacylglycerols
  - major lipid of myelin sheath
- Tay-Sachs disease
  - defect in glycolipid degradation



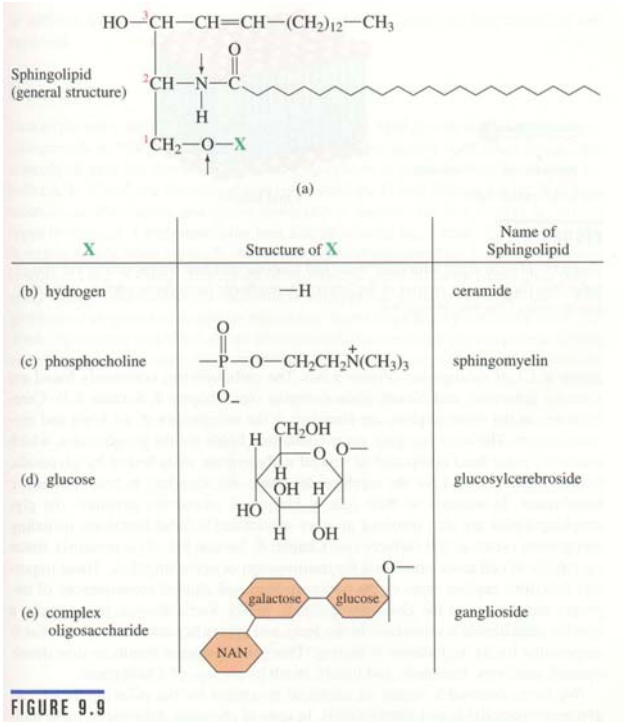
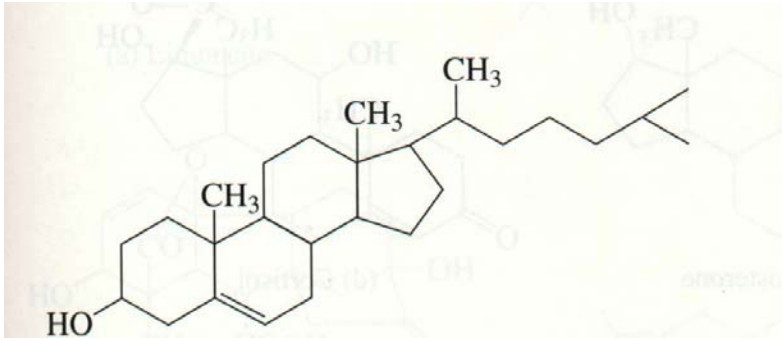


FIGURE 9.9

Lipids

- Non-saponifiable lipids
  - no ester linkage
- Sterols are non-saponifiable lipids
- cholesterol is a common membrane lipid
  - very hydrophobic
  - hydrophilic group is the OH group
- Many sterols are hormones
  - testerosterone
  - progesterone
  - estrogen



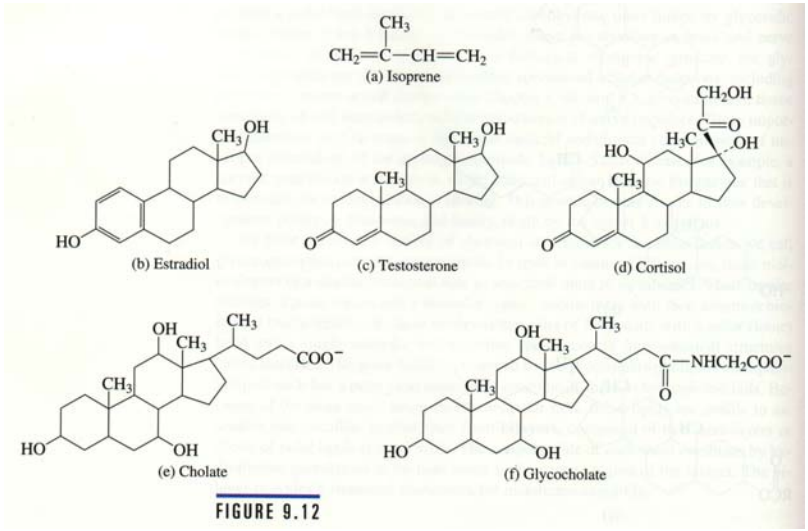


FIGURE 9.12

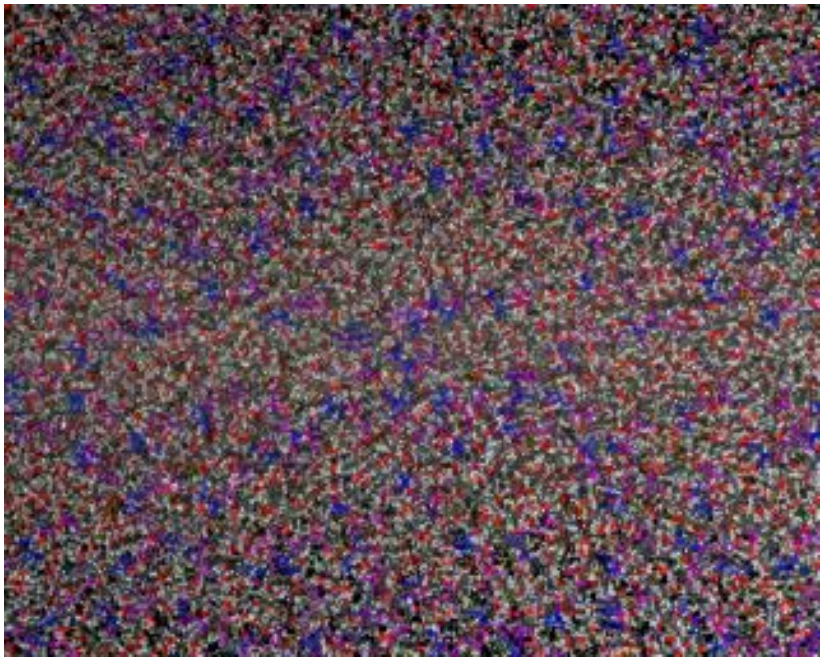
Membranes

- Fluid mosaic model of membrane structure
  - a *mosaic* of lipid and proteins
  - the membrane is *fluid* in its functional state

- Membrane function
  - separate cytoplasm from environment
    - provide selective barrier to uptake
  - provide system for uptake of compounds
    - nutrient transporters
  - mediate interactions with environment
    - receptors
  - provide environment for catalysis
    - electron transport chains

Membranes

- Membranes surround all cells and organelles
  - 2 membranes surround chloroplasts and mitochondria
- Membrane are based upon lipid bilayers
  - lipid fatty acid chains interact via hydrophobic interactions
  - fatty acid chains face inward
  - polar head groups hydrogen bond with water
  - polar head groups face outward



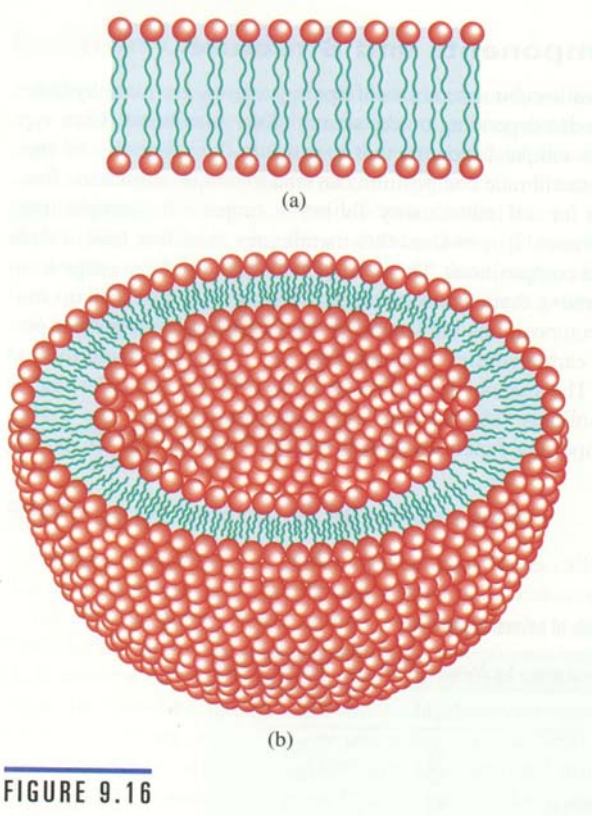
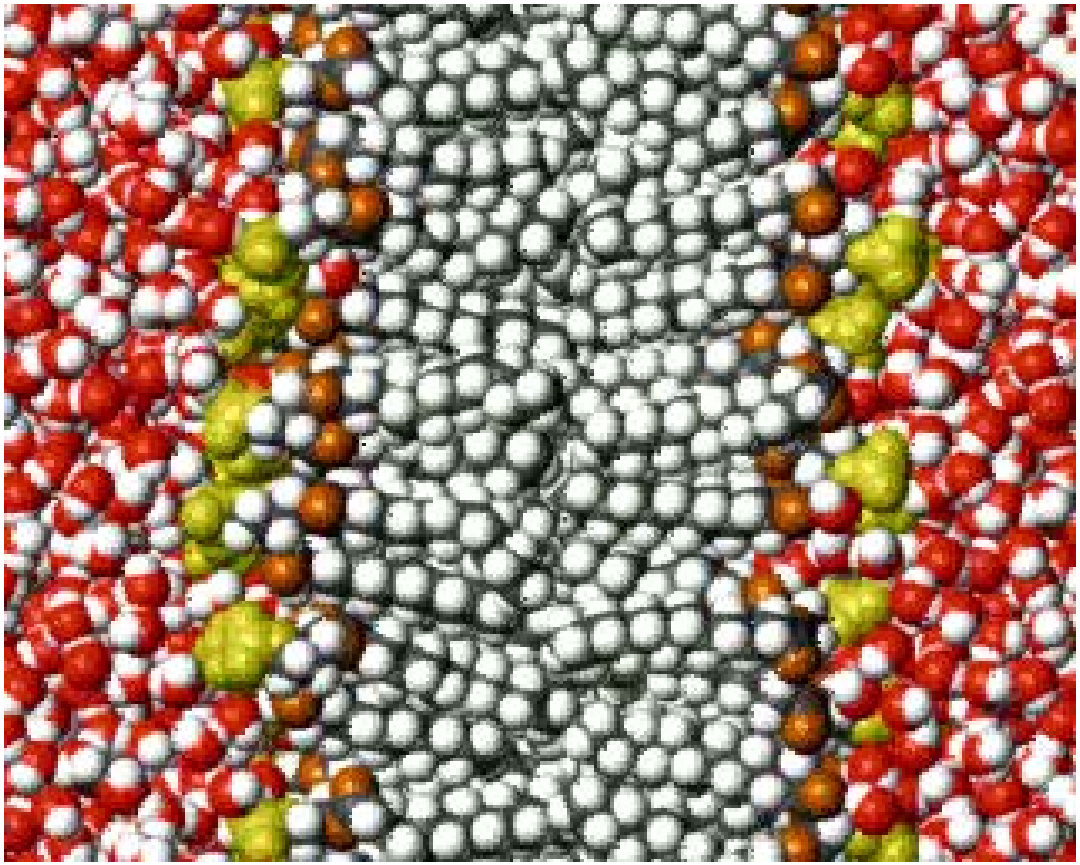


FIGURE 9.16

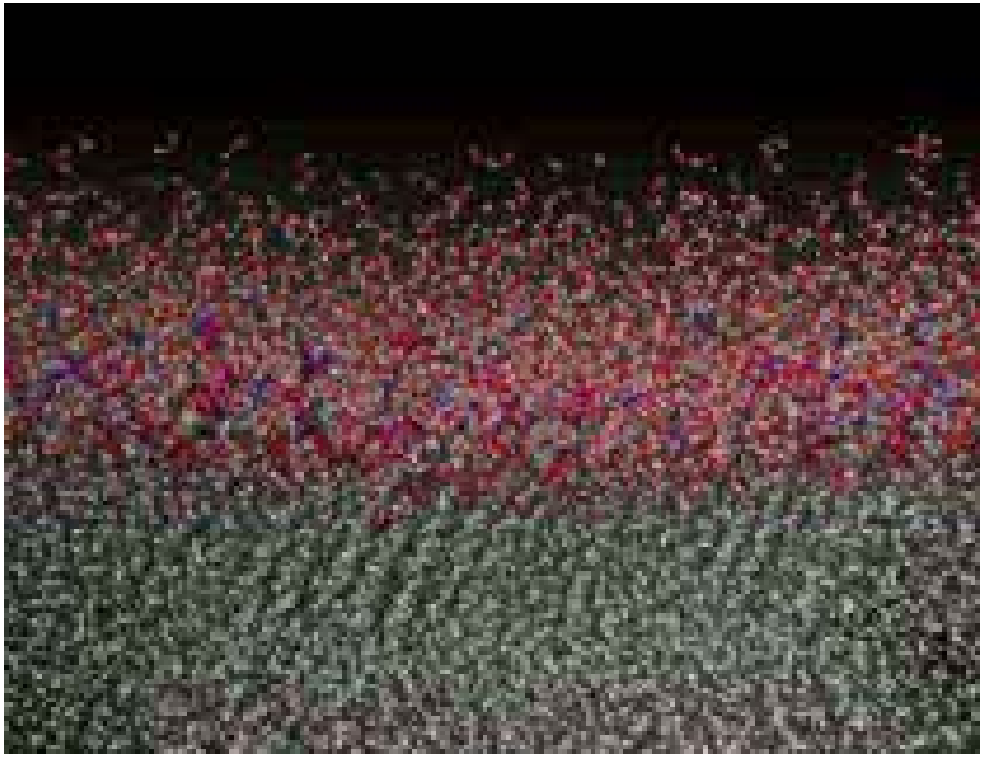
Membranes

- Membranes are fluid bilayers
  - solid membranes do not function normally
- many factors influence melting temperature
  - fatty acid chain length, fatty acid saturation level



Membranes

- Membranes are fluid bilayers
  - lipids with saturated fatty acids in membrane lead to rigidity
    - close packing of linear fatty acid chains give lipids containing these fatty acids higher melting points
  - lipids with unsaturated fatty acids in membrane are more fluid
    - fatty acid side chains cannot pack tightly so lipids containing these fatty acids have lower melting points



Membranes

- Membrane are comprised of proteins embedded in a fluid bilayer
  - integral membrane proteins
  - peripheral membrane proteins

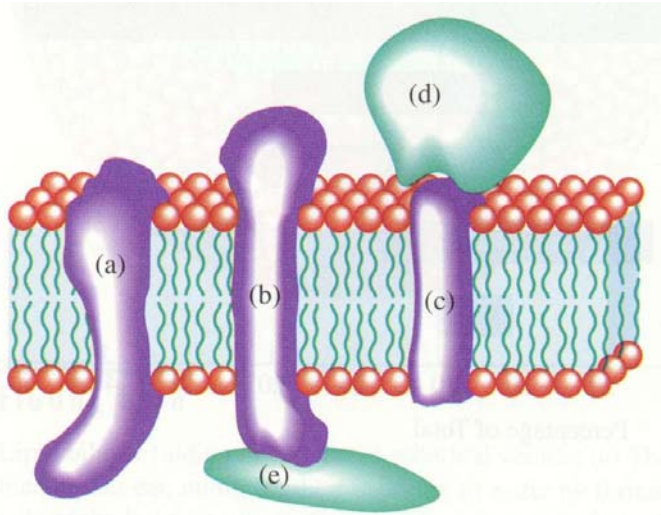


FIGURE 9.18

- Integral membrane proteins
  - hydrophobic amino acid residues interact with fatty acid chains in hydrophobic core of membrane
  - removed from membrane with detergents such as SDS
- Peripheral membrane proteins
  - interact weakly with membranes lipid headgroups or integral membrane proteins by hydrogen bonding or electrostatic interactions
  - removed from membrane with mild agents such as salts

Membranes

- Integral membrane proteins have various topologies
  - anchored via membrane-spanning alpha helices
  - completely embedded in membrane
    - may form pores required in transport proteins such as ion channels

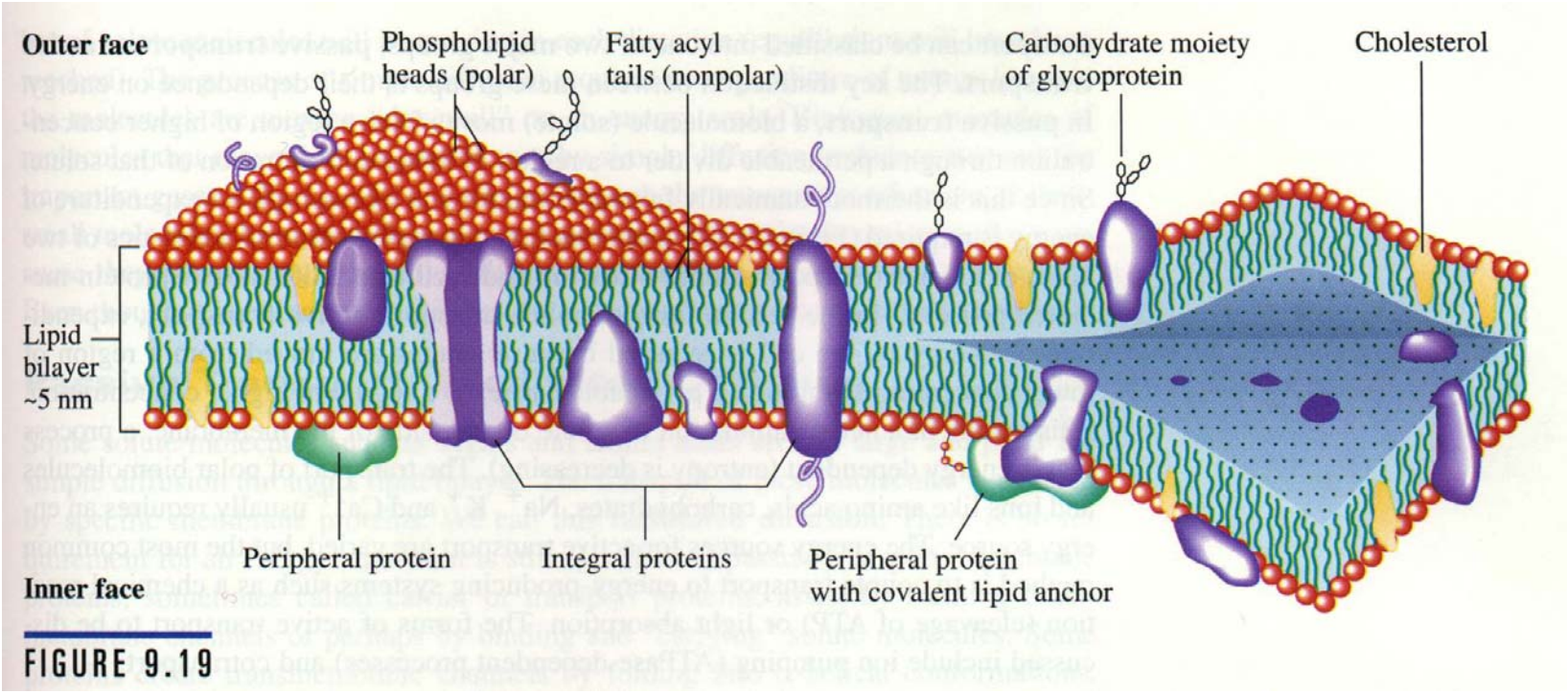


FIGURE 9.19