

## Notes 10/19

Friday, October 19, 2007  
10:04 AM



Notes 1019

Audio recording started: 10:04 AM Friday, October 19, 2007

# Lipids: Properties Lipoproteins

Oct. 18, 2007

## Lecture Slides

- Some instructors charge you \$\$ for their notes
- Making digital lectures (Powerpoint) and loading them online takes *a lot* more effort for me and I don't get paid more for doing it
- The department does not supply most lecturers with a laptop
- I very much appreciate your patience with me

## Quick Review of Lipids

- Energy Storage
  - Triacylglycerols
    - Glycerol parent linked to three fatty acids
      - Fatty acids are saturated or unsaturated
- Membrane Lipids
  - Glycerophospholipids
    - Glycerol parent linked to two fatty acids and a polar phosphoryl head group
  - Sphingolipids
    - Ceramide parent linked to R-group
      - Sphingomyelin's R = PC or PE
      - Cerebroside's R = monosaccharide
      - Ganglioside's R = oligosaccharide
- Steroids
  - Cyclopentanoperhydrophenanthrene parent

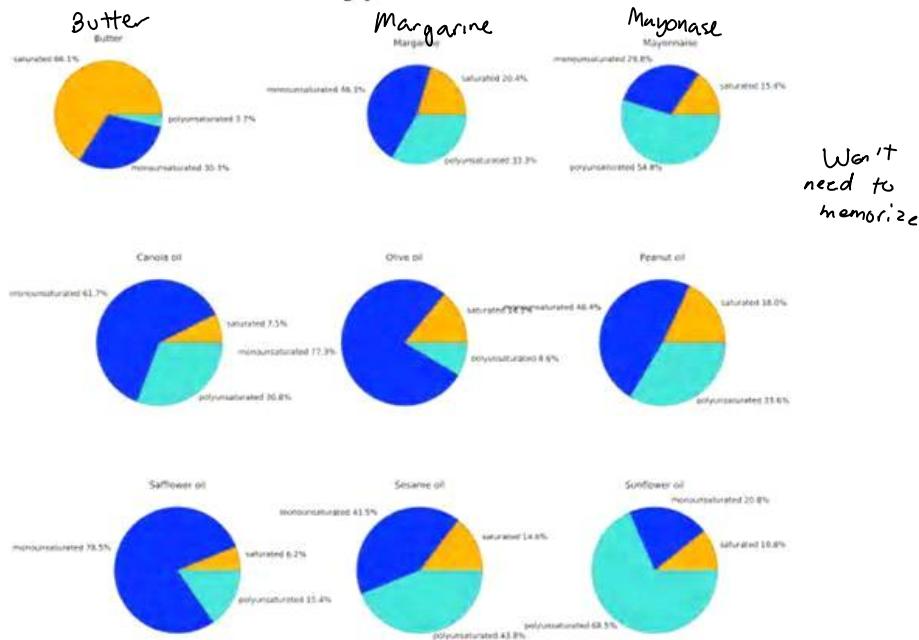
PC- phosphatidyl choline  
PE- phosphatidyl ethanolamine

## Sources of fats

- **Monounsaturated Fats**
  - Avocados
  - Canola oil
  - flaxseed oil
  - grapeseed oil
  - Olive oil
  - Peanut oil and other nuts
  - Sesame oil
- **Saturated Fats**
  - Fats from animals:
    - beef, veal, lamb, pork, lard, poultry fat, butter, cream, milk, cheeses (All of these contain dietary cholesterol as well)
  - Foods from plants:
    - coconut, coconut oil, palm oil and palm kernel oil, and cocoa butter.



## Relative amounts of types of fat in selected foods



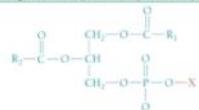
Source: Gebhardt SE, Thomas PG (2002). Nutritive Value of Foods. United States Department of Agriculture, Agricultural Research Service. Home and Garden Bulletin 72.

## Trans-fatty acids

- Unsaturated fatty acids can be "cis" and "trans."
- We won't study any particular examples of trans-fatty acids but they do exist in nature
- Trans-fatty acids (TFA) are found in small amounts in various animal products such as beef, pork, lamb, dairy products
- TFA are also formed during the process of hydrogenation
- making margarine, shortening, cooking oils and the foods made from them are a major source of TFA in the American diet.
- <http://www.bantransfats.com/>

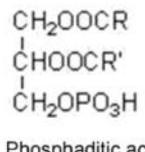
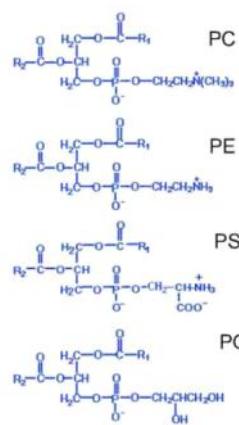


### Common Classes of Glycerophospholipids (Oct. 17, slide 23)



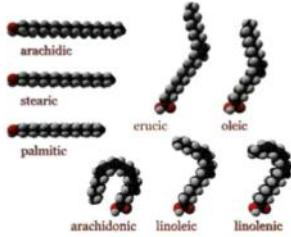
Name of X—OH	Formula of —X	Name of Phospholipid
Water	—H	Phosphatidic acid
Ethanolamine	—CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> <sup>+</sup>	Phosphatidylethanolamine
Choline	—CH <sub>2</sub> CH <sub>2</sub> N(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup>	Phosphatidylcholine (lecithin)
Serine	—CH <sub>2</sub> CH(NH <sub>2</sub> )COO <sup>—</sup> H	Phosphatidylserine
Glycerol	—CH <sub>2</sub> CH(OH)CH <sub>2</sub> OH	Phosphatidylglycerol

If this table isn't clear to you please look at the next slide...



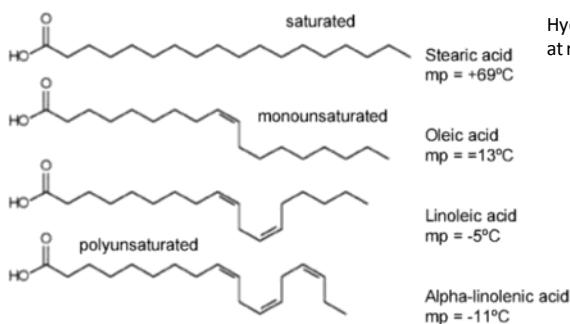
Be able to identify the R groups on these and name entire thing.

## Unsaturated fatty acids (Oct. 17, slide 18)



- Double-bond almost always cis configuration
- Rigid 30° bend restricts packing
- Reduced van der Waals interactions
- m.p. decreases with increasing unsaturation**
- Lard is solid, vegetable oil is liquid at R.T.

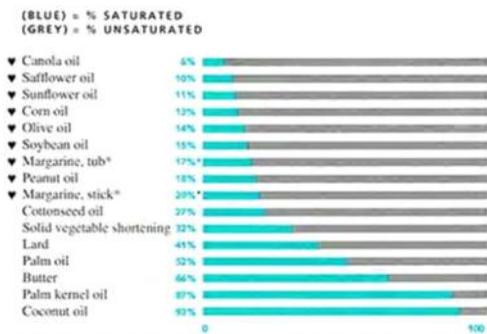
## m.p. decreases with increasing unsaturation



Hydrocarbon tail on stearic acid can pack more tightly and are therefore solid at room temp.

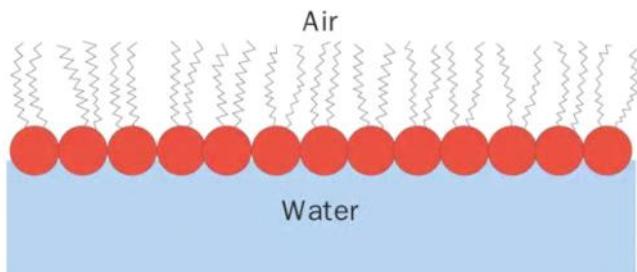
## The SatFat Graph

Use this handy graph to help you choose the products with the least amount of saturated fat.



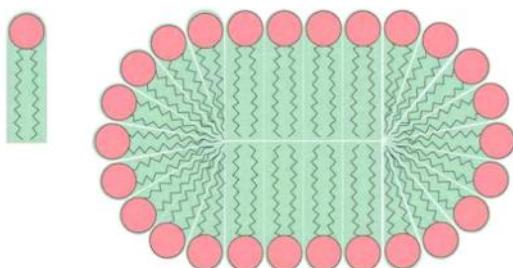
\*An average of margarines listing liquid oil as the first ingredient.

We are mostly water so our lipids must get along with water despite their differences

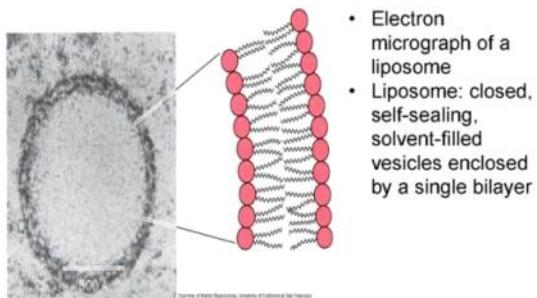


### Bilayer formation by phospholipids

(a) (b) Type of micelle



Glycerophospholipids and sphingolipids tend to form bilayers



- Electron micrograph of a liposome
- Liposome: closed, self-sealing, solvent-filled vesicles enclosed by a single bilayer

## Biological membranes are rich in lipids

Just understand that these members vary by organism

Lipid	Human Erythrocyte	Human Myelin	Beef Heart Mitochondria	<i>E. coli</i>
Phosphatidic acid	1.5	0.5	0	0
Phosphatidylcholine	19	10	39	0
Phosphatidylethanolamine	18	20	27	65
Phosphatidylglycerol	0	0	0	18
Phosphatidylinositol	1	1	7	0
Phosphatidylserine	8.5	8.5	0.5	0
Cardiolipin	0	0	22.5	12
Sphingomyelin	17.5	8.5	0	0
Glycolipids	10	26	0	0
Cholesterol	25	26	3	0

<sup>a</sup>The values given are weight percent of total lipid.

Source: Tanford, C., *The Hydrophobic Effect*, p. 109, Wiley (1980).

## Biological membranes have other biomolecules as well

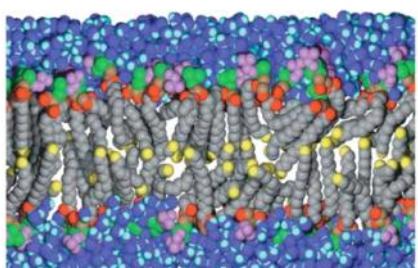
Membrane	Protein (%)	Lipid (%)	Carbohydrate (%)	Protein to Lipid Ratio
Plasma membranes:				
Mouse liver cells	46	54	2-4	0.85
Human erythrocyte	49	43	8	1.1
Amoeba	52	42	4	1.3
Rat liver nuclear membrane	59	35	2.0	1.6
Mitochondrial outer membrane	52	48	(2-4) <sup>a</sup>	1.1
Mitochondrial inner membrane	76	24	(1-2) <sup>a</sup>	3.2
Myelin	18	79	3	0.23
Gram-positive bacteria	75	25	(10) <sup>a</sup>	3.0
<i>Halobacterium</i> purple membrane	75	25		3.0

<sup>a</sup>Deduced from the analyses.

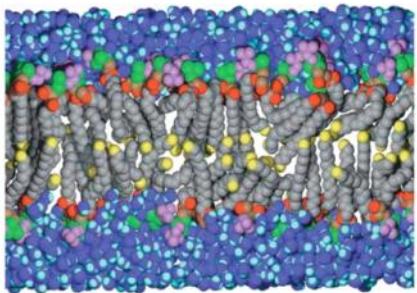
Source: Guidotti, G., *Annu. Rev. Biochem.* **41**, 732 (1972).

it much higher because  
it serves to insulate  
charge away from aq. solution

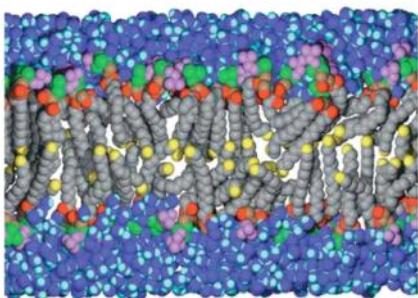
## Biological membranes are an exclusive party



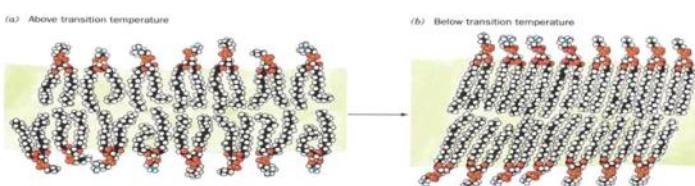
Biological membranes are an exclusive party



The secret into the party:  
You need to be “small” like  
water or in polar

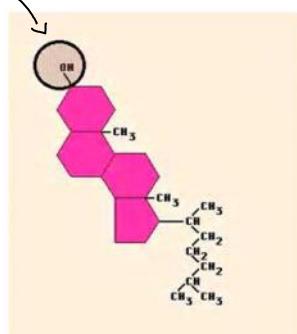


The party dies down on its own when its cold



- Structure of a lipid bilayer composed of PC and PE
- Bilayer fluidity varies with T
- It loses fluidity below a characteristic transition temperature
- Hydrocarbon chains become fully extended

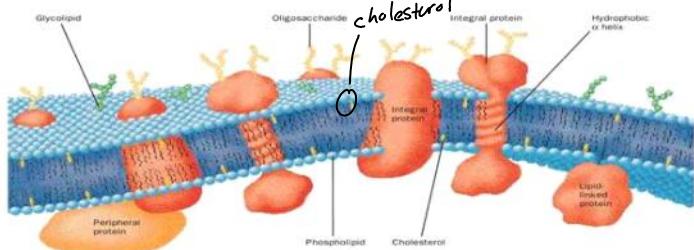
polar  
Cholesterol keeps things moving



It affects membrane fluidity

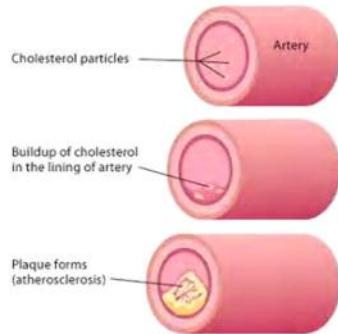
- weakly amphiphatic

Cholesterol can be good



- Cholesterol decreases membrane fluidity near the membrane surface due to its rigidity
- At high T cholesterol tends to reduce membrane fluidity, probably by interacting with the hydrocarbon tails of other lipids
- At low temperatures cholesterol helps prevent membranes from freezing and thus tends to maintain membrane fluidity

## Cholesterol can be bad...



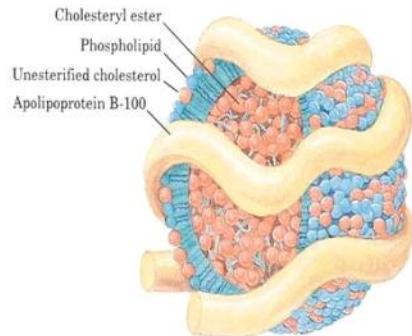
- ...to be continued

## Always designate a driver



- Lipids aren't very soluble in aqueous solutions
- How do they travel through the blood stream?
- Lipoprotein "taxis"

## Lipoproteins are globular micellelike particles



- nonpolar core of triacylglycerols and cholesterol esters
- surrounded by an amphiphilic coating of protein, phospholipid, and cholesterol

## Chapter 2 Problem #8

- Calculate the pH of:

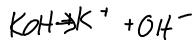
A. 0.1 M HCl  $pH = -\log(0.1) = 1$   $[H^+][OH^-] = 10^{-14}$

B. 0.1 M NaOH  $13$

C.  $3 \times 10^{-5}$  M HNO<sub>3</sub>

D.  $5 \times 10^{-10}$  M HClO<sub>4</sub>

E.  $2 \times 10^{-8}$  M KOH



$$[H^+][OH^-] = 10^{-14} M$$

$$[H^+] + [K^+] = [OH^-]$$

$$[H]([H^+] + [K^+]) = 10^{-14}$$

$$[H^+]^2 + 2 \times 10^{-8}[H^+] - 10^{-14} = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$