

Chem 431A-L26

admin: TODAY:in class quiz#9

Online quiz chapt 7 deadline

Monday will be online

Quiz deadline for Chapt 10

Today: review membrane structure transitions

Cholesterol's role in the membrane.

Thermodynamics of membrane transport

1) One feature of **lipid bilayers** that helps to maintain the asymmetric distribution of lipids within it is the relatively slow way in which glycerophospholipid molecules can "flip" from one side of the bilayer to the other in the absence of enzymatic action. This flipping is called transverse diffusion and is a process that can be enhanced by a class of enzyme called **translocases**.

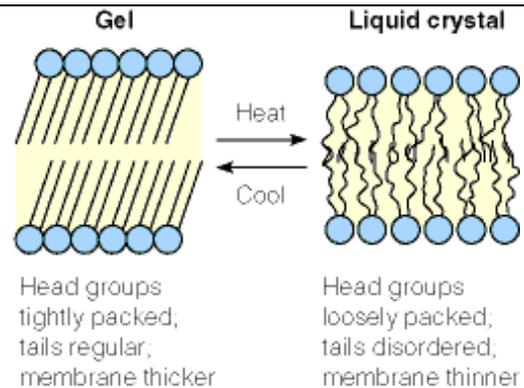
2) Two other features of **membrane** structure illustrate its asymmetry. First, carbohydrates are always attached on the outside surface of the cell. Second, **membrane** protein orientation (flipping) does not occur, so that proteins always maintain the same polarity.

### Role of cholesterol.

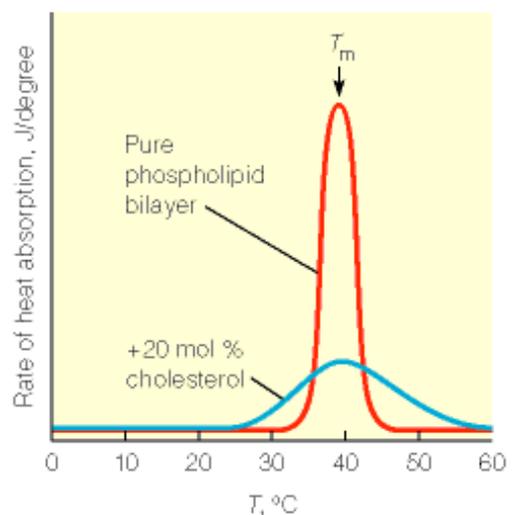
#### 3) melting transition of the membranes

As expected, the fluidity of membranes is temperature dependent. There is a transition temperature for a lipid bilayer below which it takes on a gel like behavior and loses its fluidity.  $T_m$ . It becomes a liquid crystal. Thicker when it is "solidified" than when it is melted. Show picture. Explain why it is so: the HC tails line up or are disordered depending on the state.

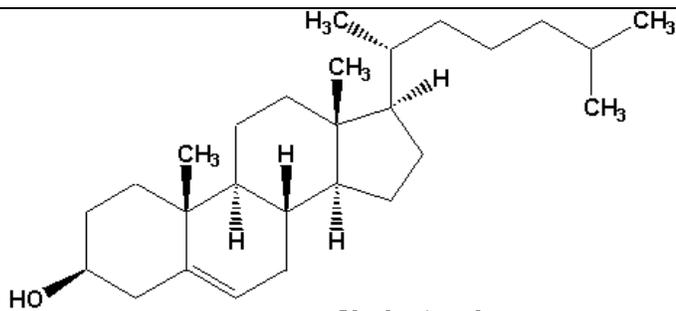
4) Recall the melting points of the various fa's. length of the fa's imp: the longer the higher the  $T_m$ . Unsaturation also imp: the unsatd fa's have lower  $T_m$ 's due to the "disruptive" effect of the kinks to the ordered "interdigitation" of the tails. the cell membranes also adjust their unsaturated fa composition to lower their  $T_m$  and cope with cold conditions. If they didn't, it would seriously impede the role of the cell m.  $T_m$  for cell m. are about 19-40°C, Esp. cold blooded animals modify their cell m. fa composition. Bacteria don't have unsatd fa's. Instead, they adjust their fa's by increasing the "branching" of the tails.



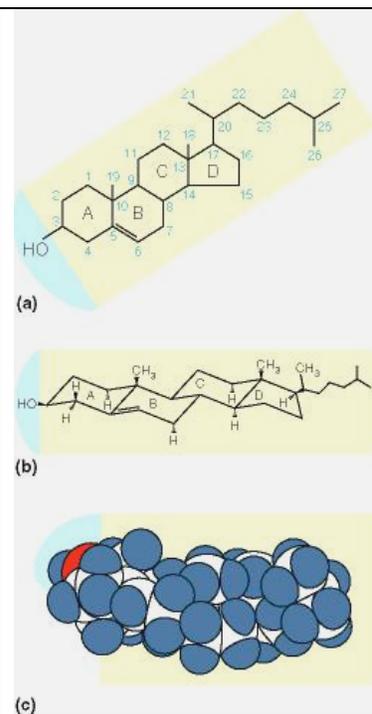
(a) Transition



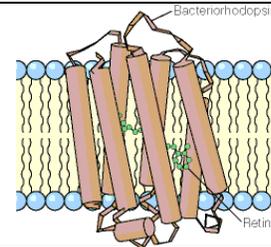
(b) Transition with and without cholesterol

**Cholesterol**

Role of cholesterol. Give structure of cholesterol: 4 fused rings which are in the “chair config” and thus somewhat rigid and planar and definitely bulky. Slightly amphiphatic with -OH in the 3 position while the rest is very Hphobic. (it is found in animal cell m's and is much more rigid than other cell m lipids.). Cholesterol is a major example of the lipids called “steroids”. Steroids are mostly found in eukaryotic organisms. Based on 4 fused rings: A, B, C, D. cholesterol is most abundant steroid in animals. Plants have very little cholesterol in general.



How does cholesterol act? By giving “plasticity” to the membrane. It blurs the  $T_m$ . Show graph of  $\Delta H$  vs  $T$  for a typical melting of a crystal. The  $\Delta H$  vs  $T$  for the melting of a membrane highly saturated vs highly unsaturated. Vs cholesterol rich m. -characteristics of membrane proteins.



### Thermodynamics of Transport Across Membranes

Like other processes, the Gibbs free energy change determines the direction in which a transport process occurs. The free energy change associated with movement of compound(s) across a biological membrane is a function of 1) the relative concentration of the material on both sides of the membrane, 2) the change in charge brought about by the movement of ionic compound(s) across the membrane, and 3) other energy releasing processes coupled to the transfer, such as hydrolysis of ATP. The Gibbs free energy for a transfer process of compound C from outside the membrane to inside

the membrane is given by

$$\Delta G = RT \ln(C_{in}/C_{out}) + \Delta G'$$

where  $\Delta G'$  depends on the particular transport process as follows:

$\Delta G' = 0$  for a diffusion-based process;

$\Delta G' = ZF\Delta\Psi$  for processes where net charge differences occur.  $F$  is the Faraday constant (96.5 kJ/mol/V),  $\Delta\Psi$  is the membrane potential in volts, and  $Z$  is the charge of the ion; and

$\Delta G' = \Delta G$  process for processes coupled to the transport.