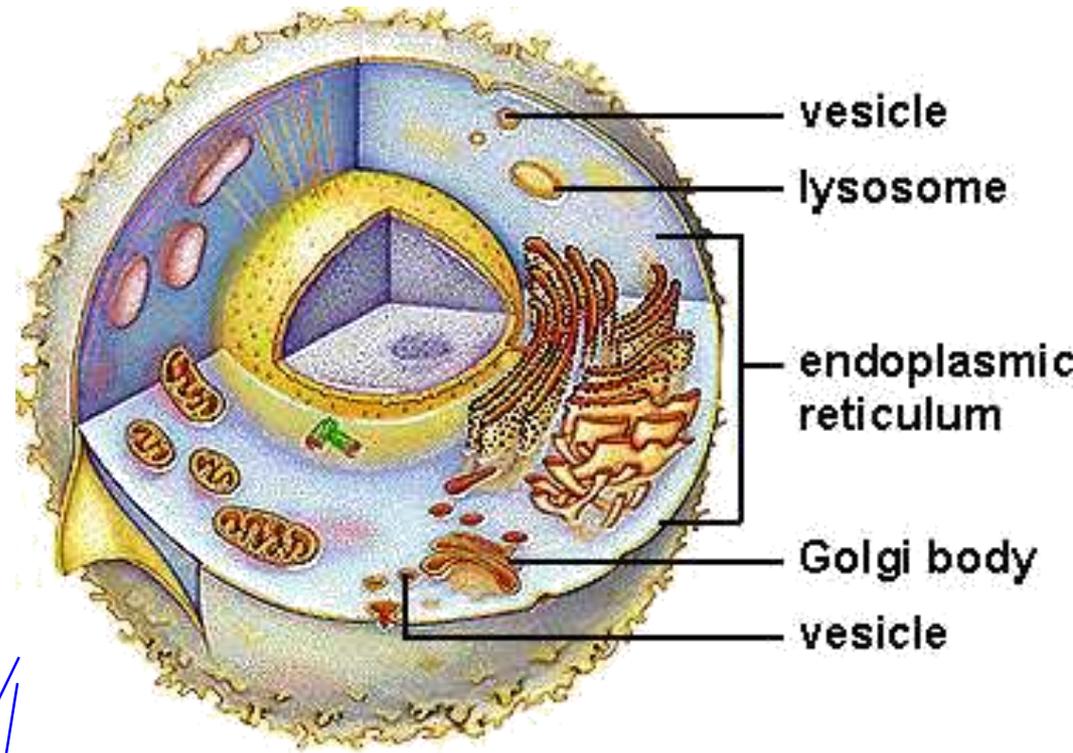
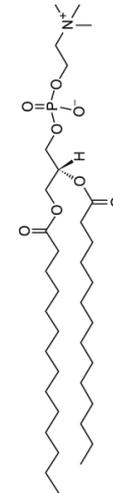
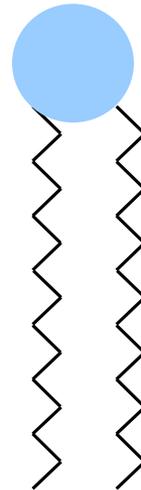
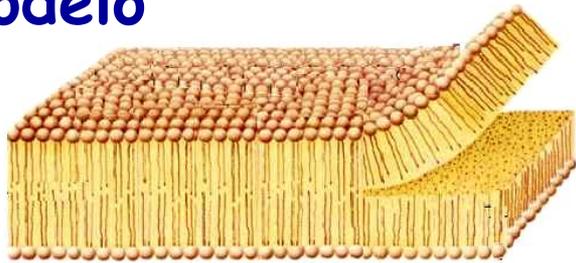


# uma célula



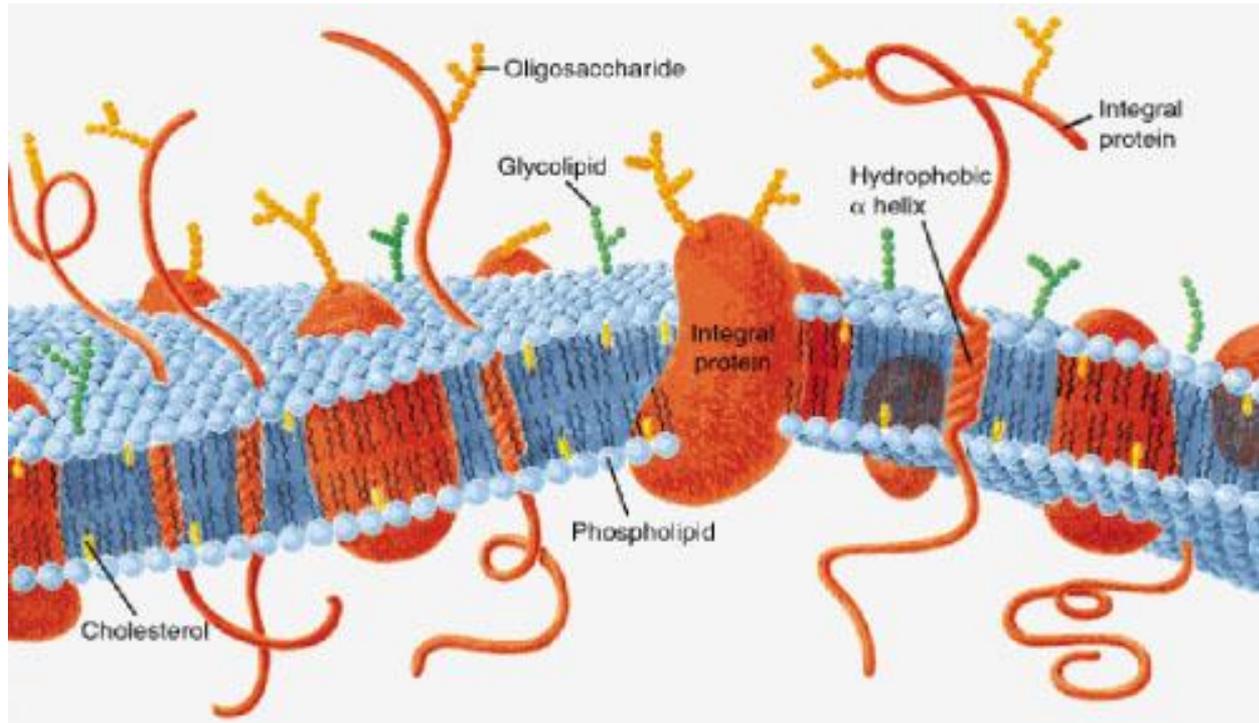
membrana celular

modelo



# lipídio

# Diagrama esquemático de uma membrana celular



*(Voet, Voet, 1990)*

Compartimentalização: separação entre interior e exterior

Seletividade: transporte seletivo através da membrana

Comunicação: transdução de sinais

# Anfifílicos

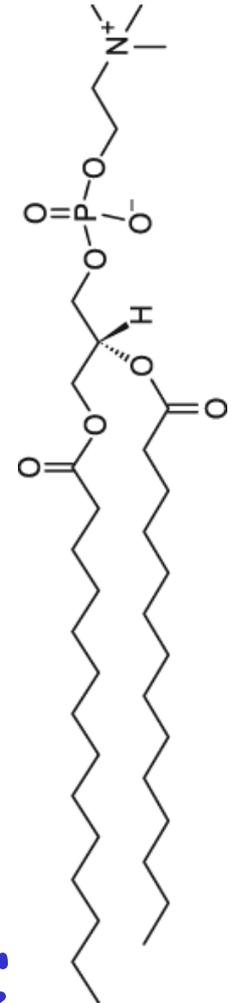
anfifílico: parte polar e parte apolar

αμφις (amphis): ambos

φιλία (philia): amor, amizade

## Lipídios:

“do material biológico, o que é solúvel em clorofórmio, e, portanto, não é solúvel em  $H_2O$ ”



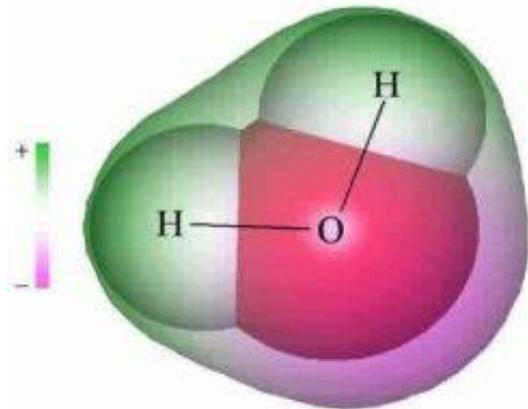
**DMPC**

dimiristoil fosfatidil colina

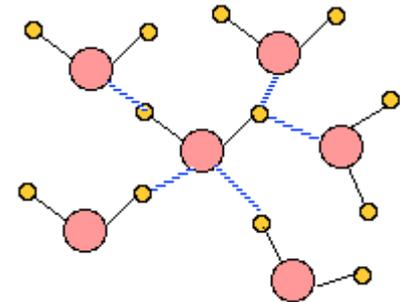
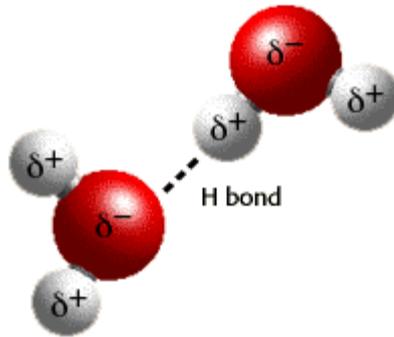
# H<sub>2</sub>O

55% em peso do corpo de uma pessoa adulta

molécula polar  
 $\rho = 1.834 \text{ D}$



Ligações de hidrogênio

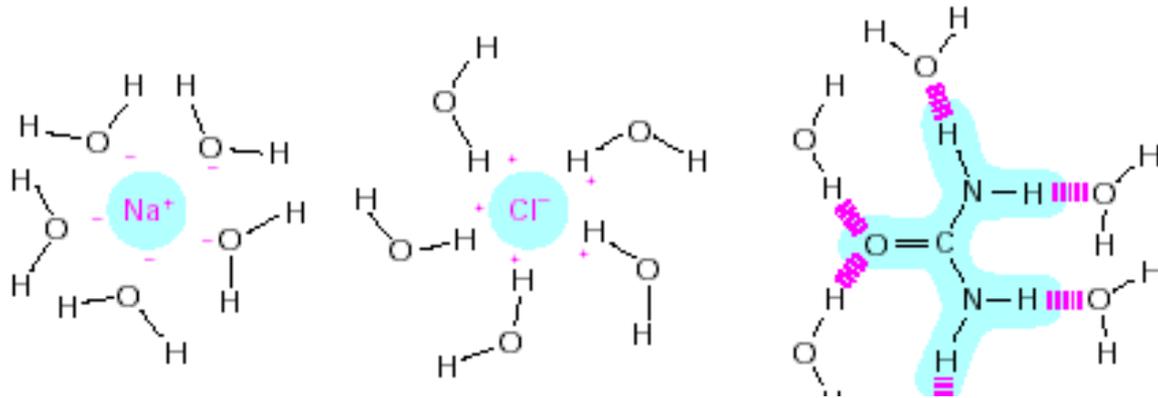


gelo  $\sim 4$  H-bonds/molécula  
líquido  $\sim 2$  H-bonds/moléculas (dinâmicas)

Muitos estudos ainda em andamento... p. ex., Vera Henriques

# Grupos hidrofóbicos ou hidrofílicos:

**hidrofílicos:** capazes de formar ligações com a  $H_2O$



## hidrofóbicos

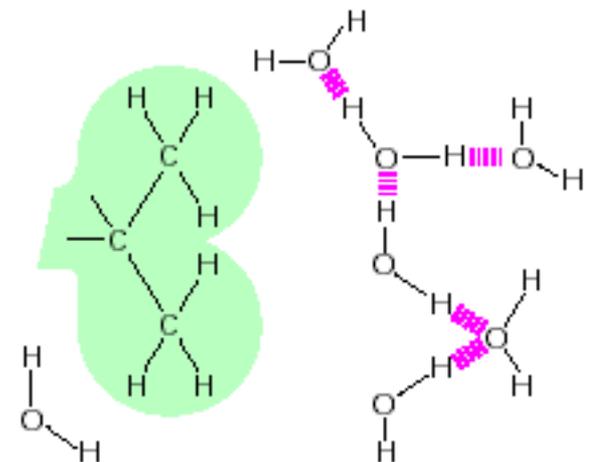
Etano ( $C_2H_6$ ) do benzeno para  $H_2O$ :

$$\Delta S_{tr} = -83.7 \text{ J/mol K}$$

$$\Delta H_{tr} = -9.4 \text{ kJ/mol}$$

$$\Delta G = \Delta H - T \Delta S$$

$$(T = 298 \text{ K}) \quad \Delta G_{tr} = + 15.5 \text{ kJ/mol}$$



Etano ( $C_2H_6$ ) do benzeno para  $H_2O$ :

$$\Delta S_{tr} = -83.7 \text{ J/mol K}$$

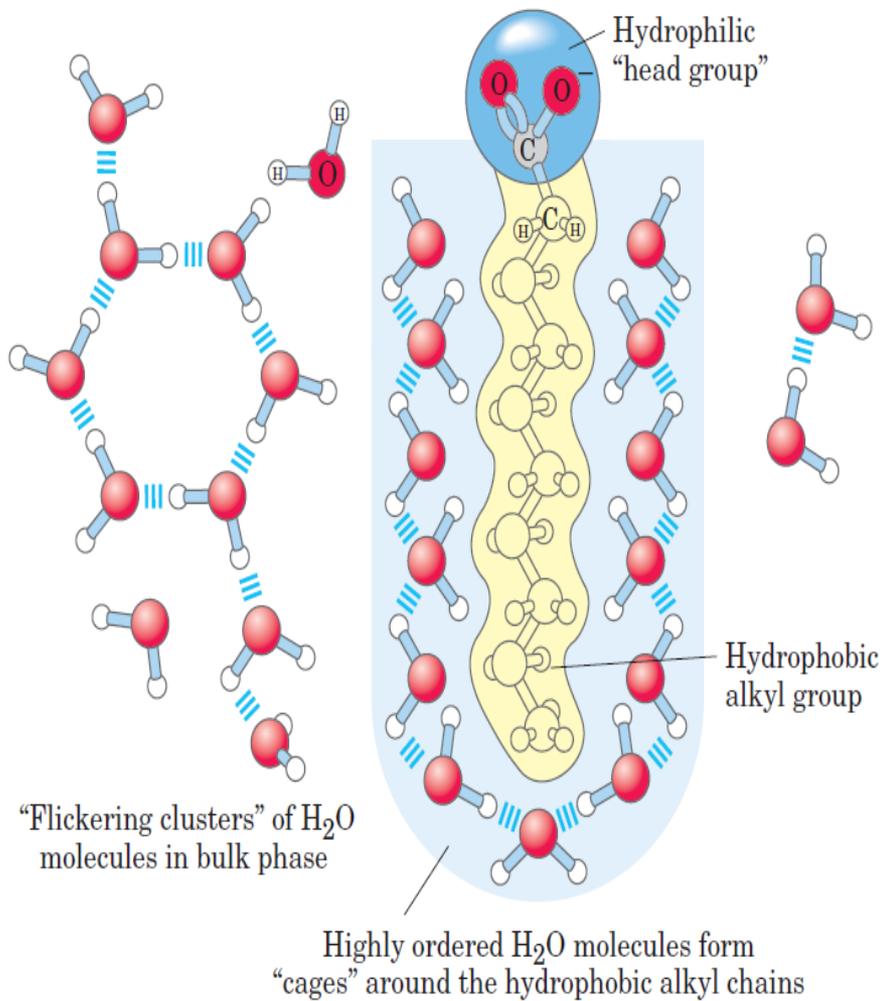
$$\Delta H_{tr} = -9.4 \text{ kJ/mol}$$

$$\Delta G = \Delta H - T \Delta S$$

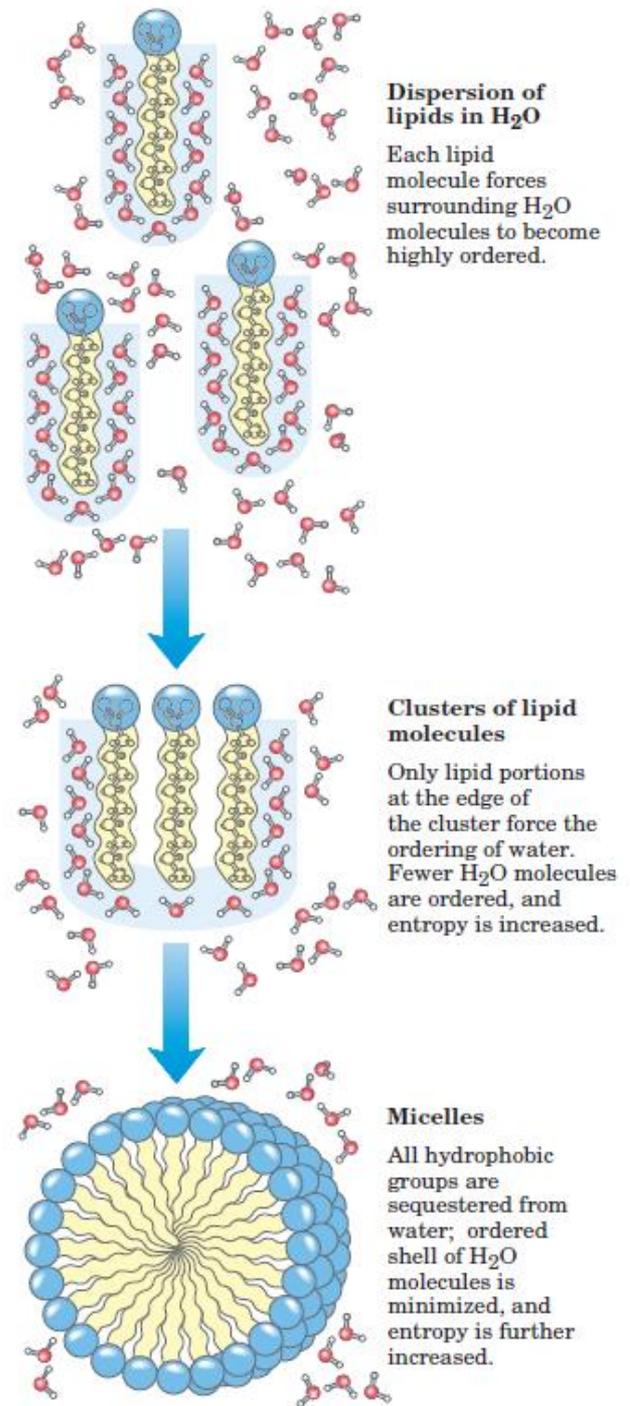
$$(T = 298 \text{ K}) \quad \Delta G_{tr} = + 15.5 \text{ kJ/mol}$$

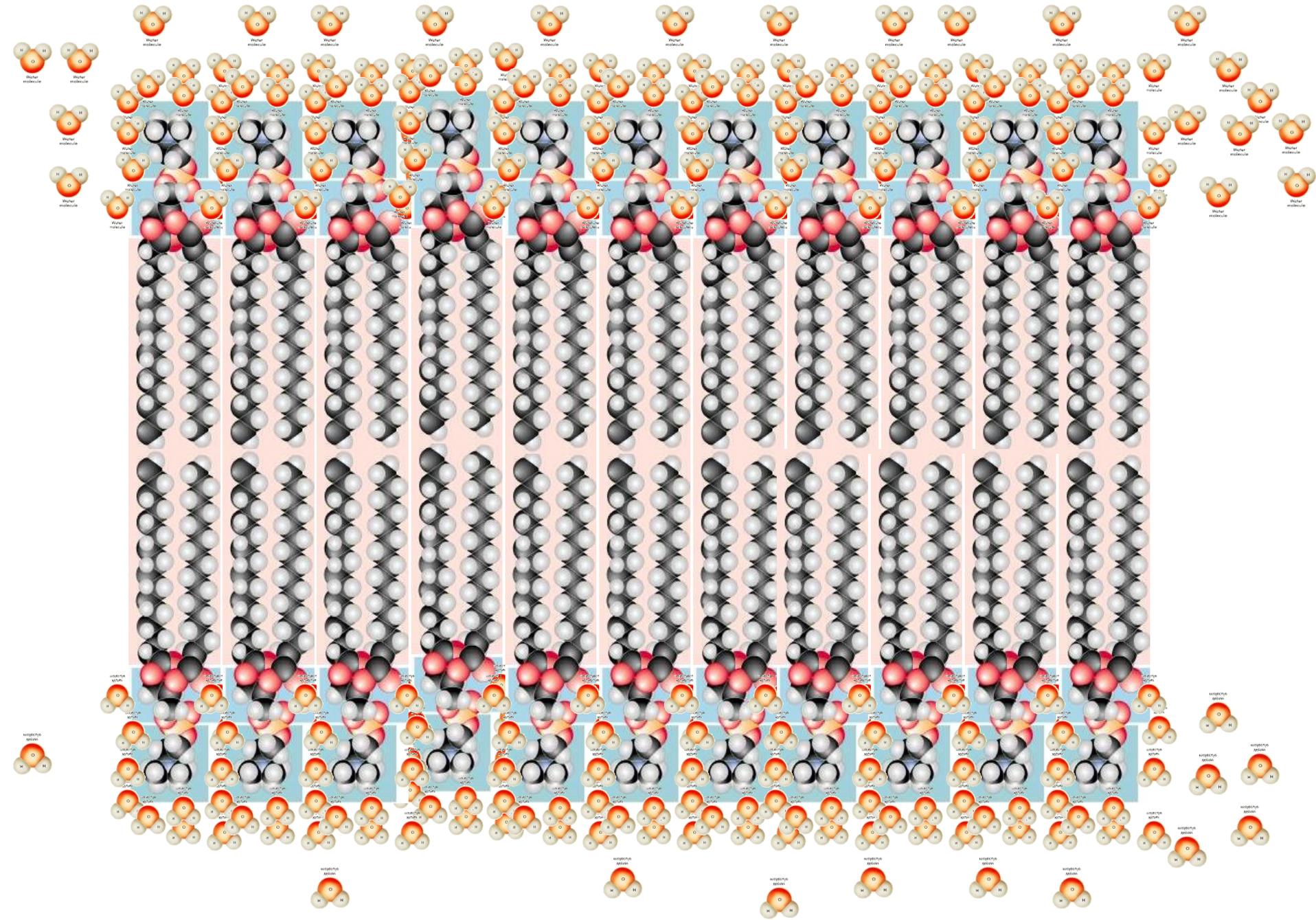
Grande diminuição da entropia é principalmente relacionada à organização das moléculas de  $H_2O$  em volta do grupo "hidrofóbico": forma um tipo de "gaiola".

Isto é, o contato entre  $H_2O$  e o grupo hidrofóbico é menos favorável do que o contato entre duas moléculas de  $H_2O$ .

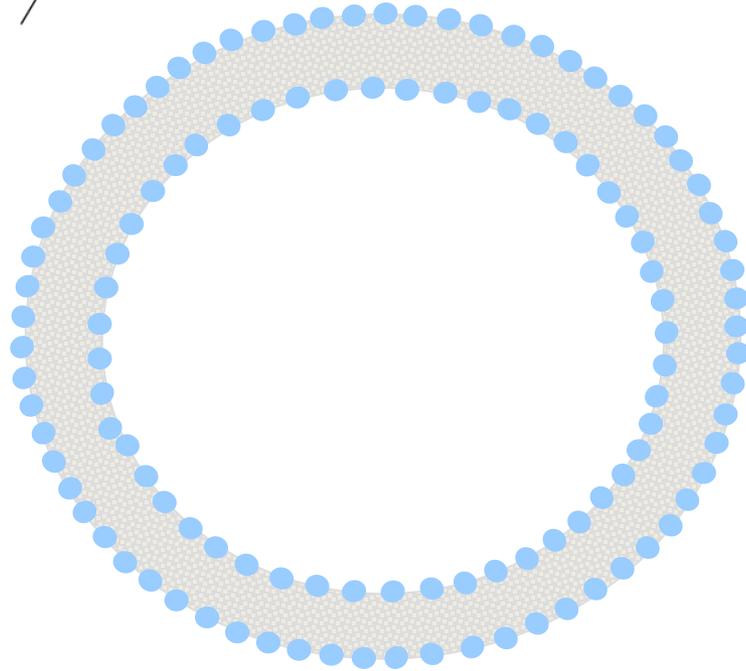
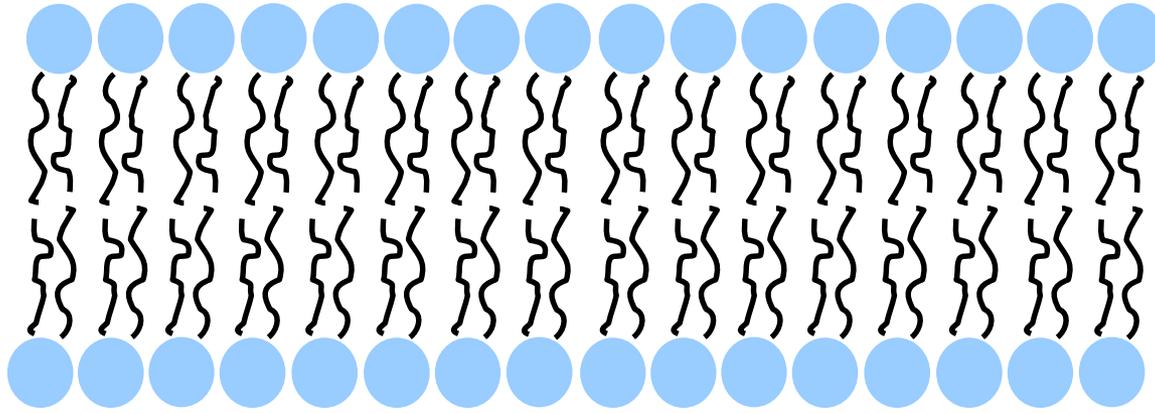
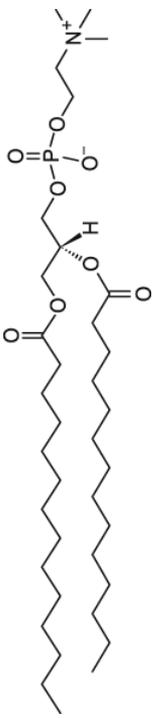


(Lehninger Principles of Biochemistry)

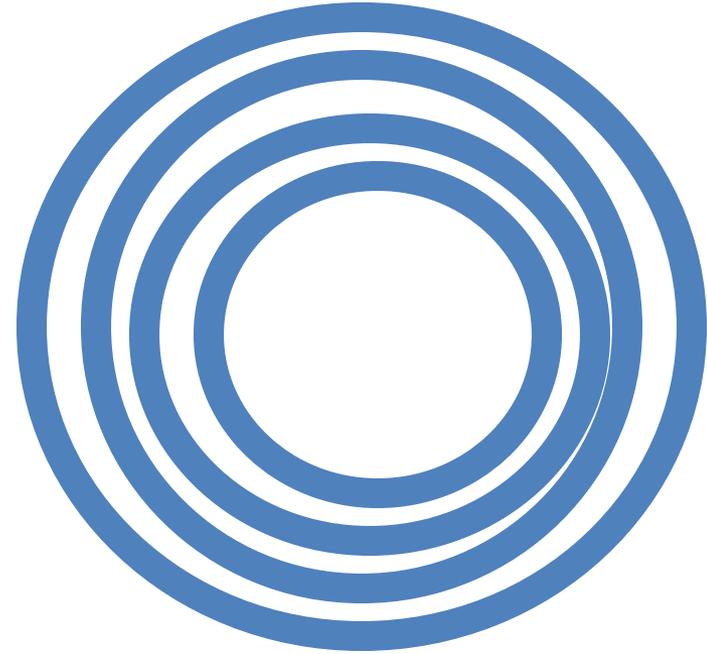




# Modelos de membranas biológicas



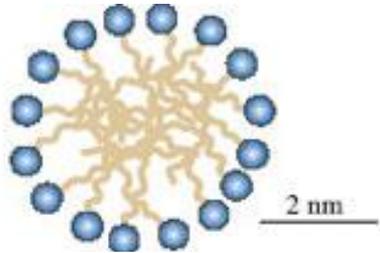
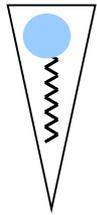
vesículas unilamelares



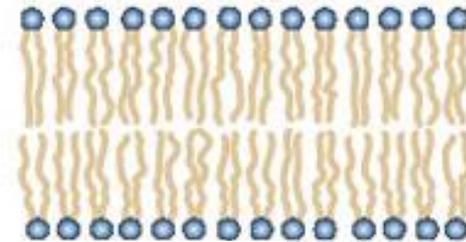
vesículas multilamelares

# Lipídios podem também formar outras estruturas em solução aquosa...

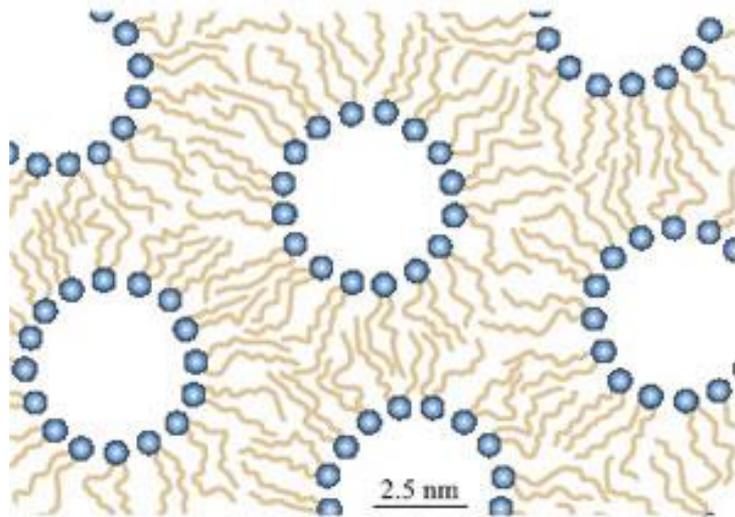
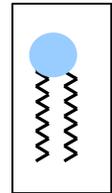
dependendo de sua estrutura e da solução



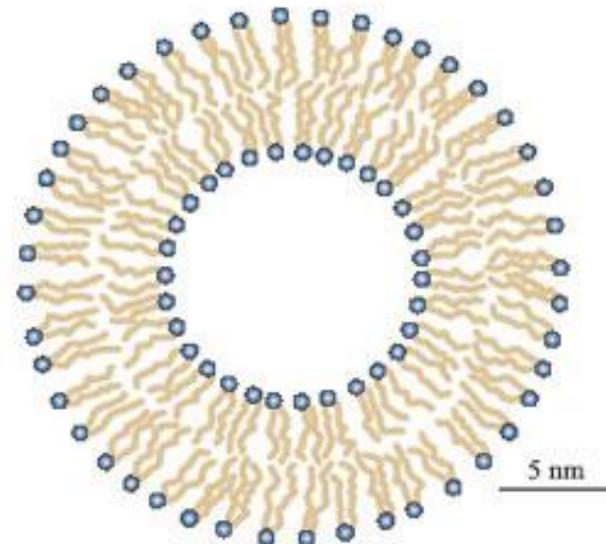
micela:



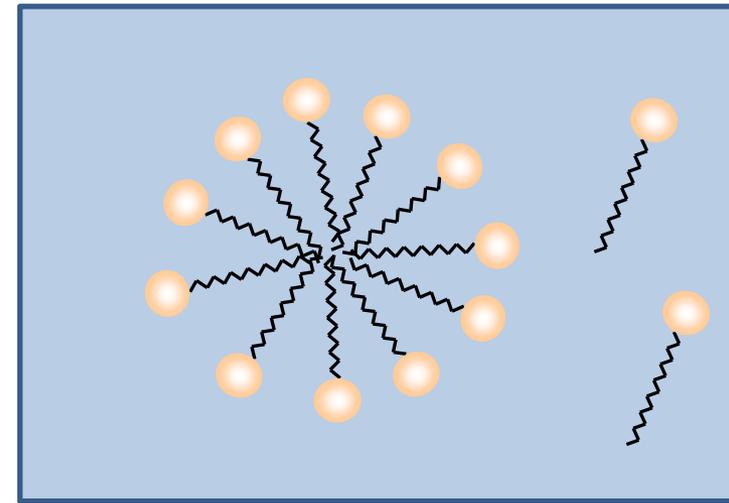
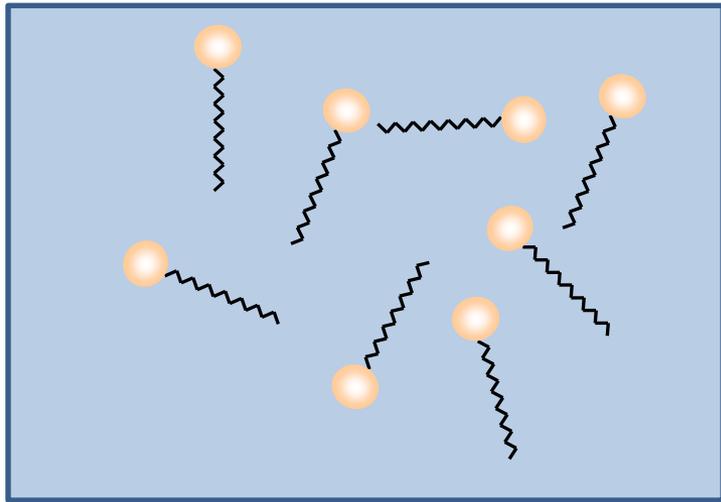
bicamada



micela invertida



vesícula ou lipossomo



**CMC**

**Concentração Micelar Crítica**

Para micelas, ou bicamadas, ou ...

Força atrativa de van der Waals entre as cadeias

Força repulsiva entre as cabeças polares

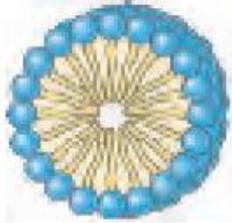
Efeito entrópico

**Micelas: um equilíbrio dinâmico**

# E como os Lipídios se organizam?



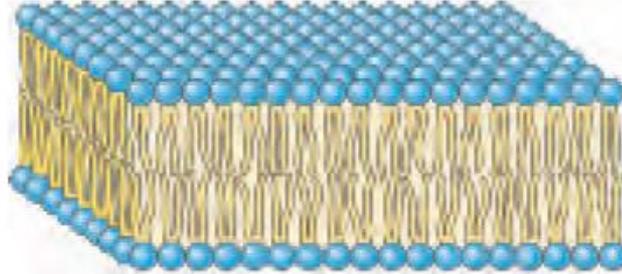
Individual units are wedge-shaped (cross section of head greater than that of side chain)



(a) Micelle

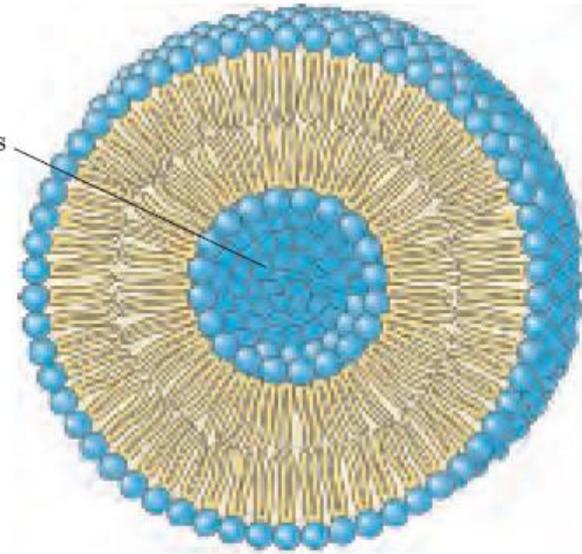


Individual units are cylindrical (cross section of head equals that of side chain)

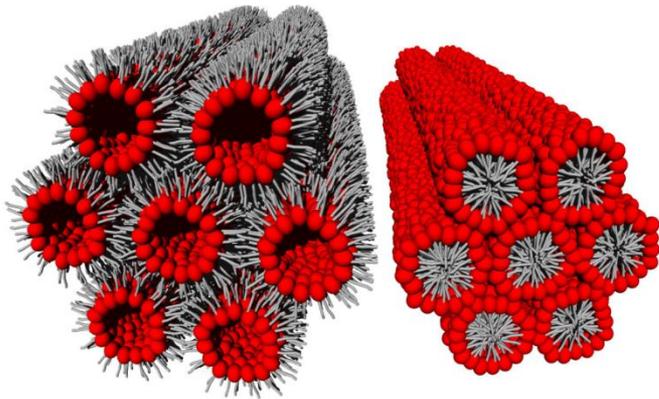


(b) Bilayer

Aqueous cavity



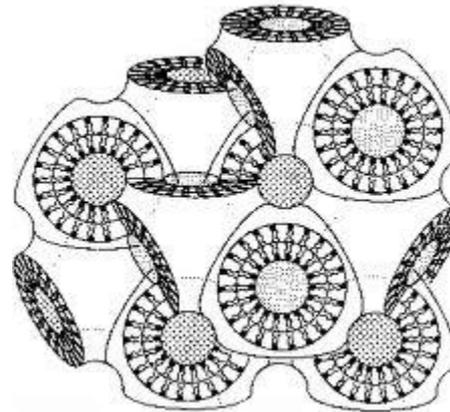
(c) Liposome



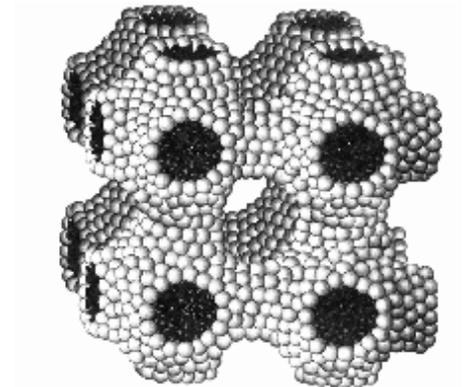
$H_{II}$

$H_I$

fases hexagonais



fases cúbicas



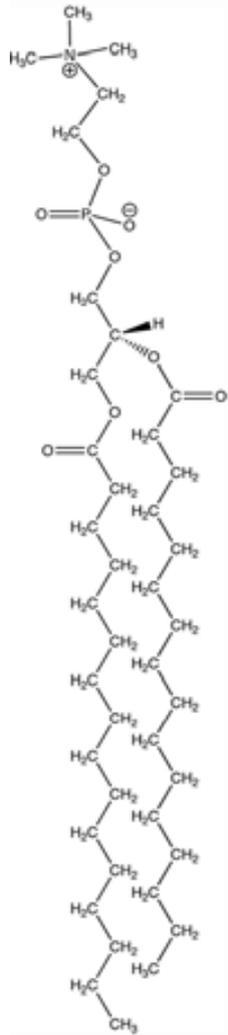
# Composição das membranas biológicas

cabeça polar

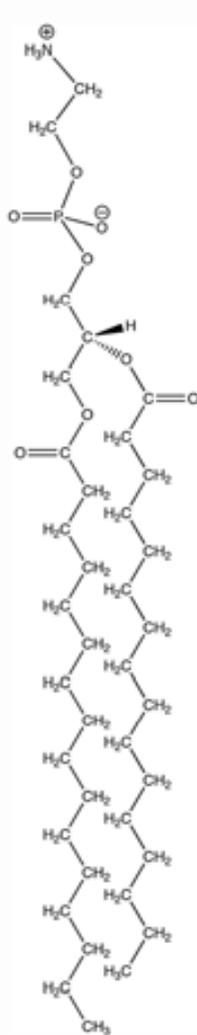


cadeia  
hidrocarbônica  
apolar

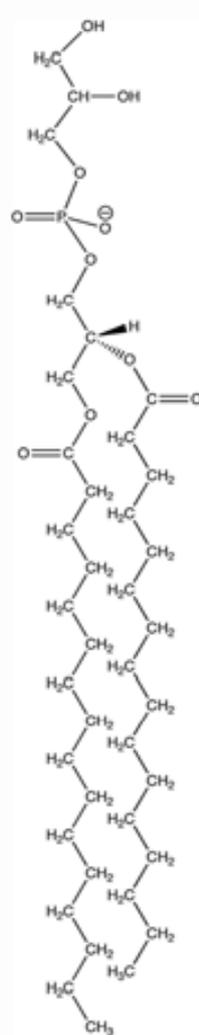
# Diferentes cabeças polares



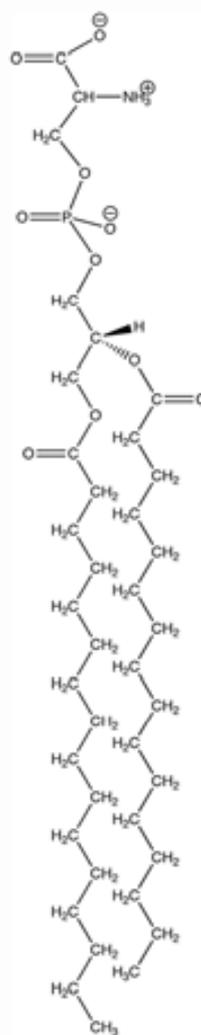
**DPPC**



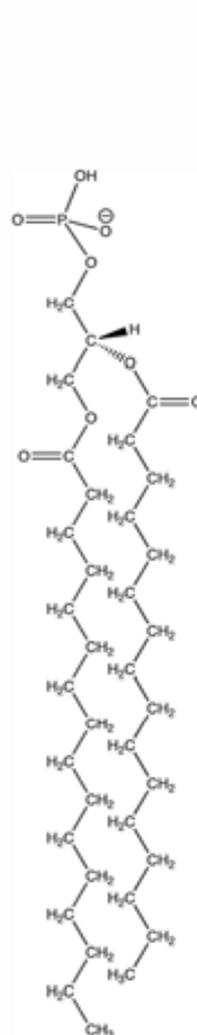
**DPPE**



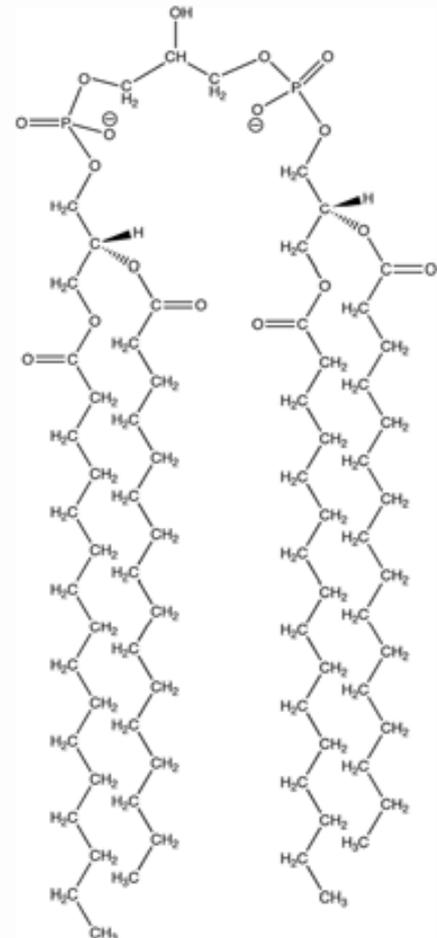
**DPPG**



**DPSP**

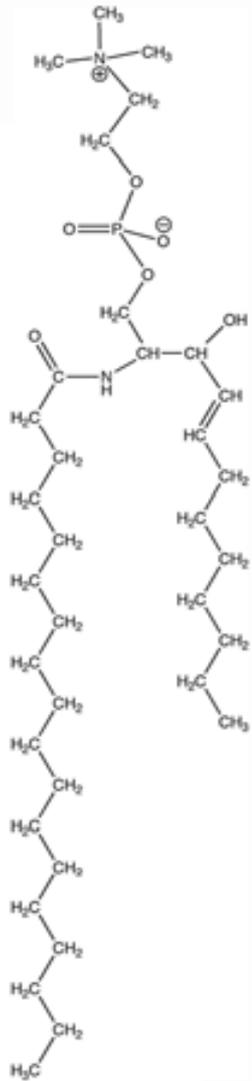


**DPPA**

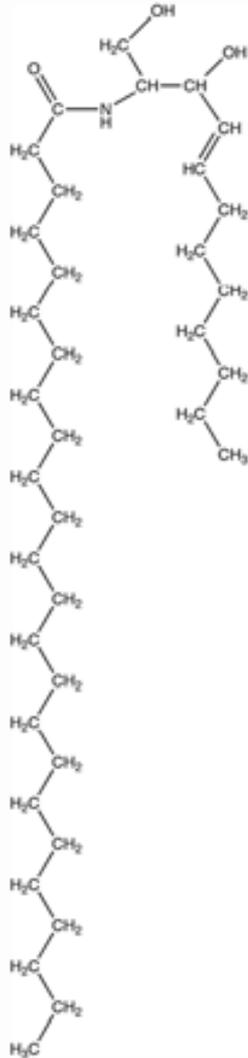


**cardiolipin**

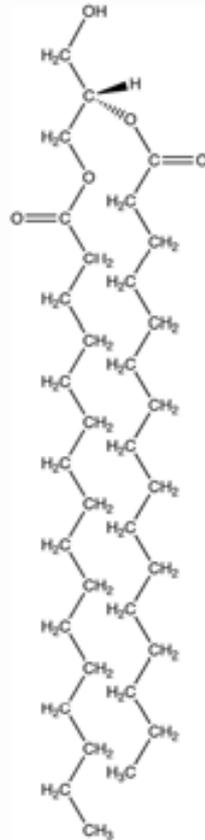
# Continuando...



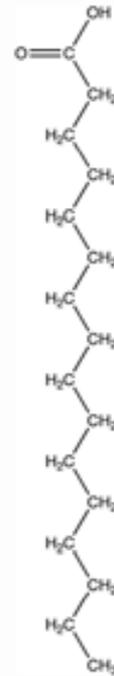
**sphingomyelin**



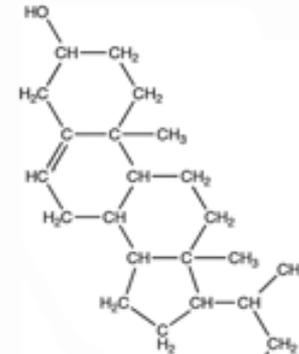
**ceramide**



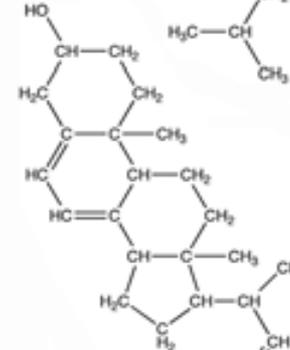
**DPG**



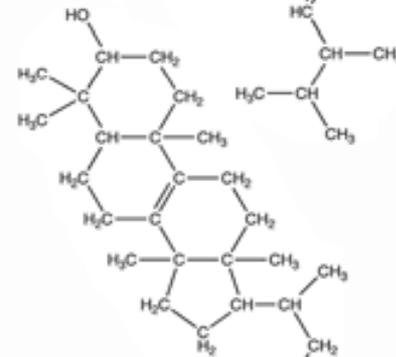
**PA**



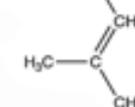
**cholesterol**



**ergosterol**



**lanosterol**

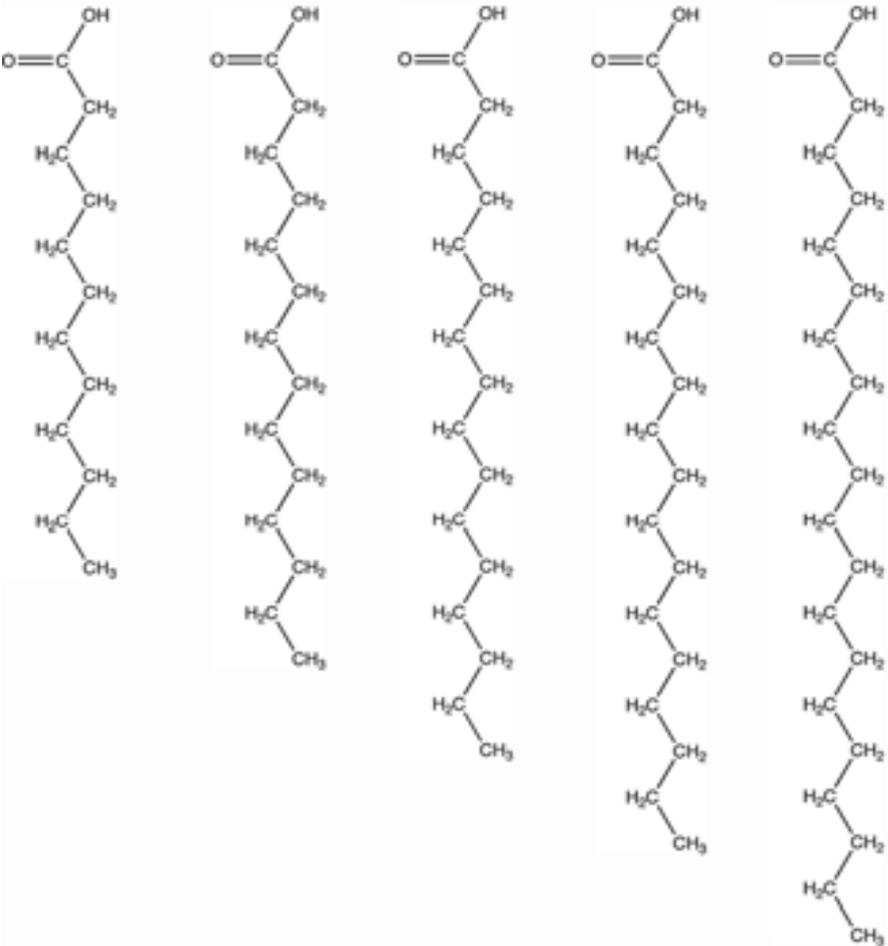


**Tab. 3.1** Head group composition of the membranes of some mammalian liver cells, erythrocytes, and nerve cells in weight percent. Adapted from Jamieson and Robinson (1977). Abbreviations: PC = phosphatidylcholines, PE = phosphatidylethanolamines, PS = phosphatidylserines, PI = phosphatidylinositols, SM = sphingomyelin, CL = cardiolipin.

Membrane	PC	PE	PS	PI	SM	CL	Glycolipid	Cholesterol	Others
Erythrocyte (human)	20	18	7	3	18	–	3	20	11
Plasma (rat liver)	18	12	7	3	12	–	8	19	21
ER	48	19	4	8	5	–	tr	6	10
Golgi	25	9	3	5	7	–	0	8	43
Lysosome	23	13	–	6	23	≈ 5	–	14	16
Nuclear membrane	44	17	4	6	3	1	tr	10	15
Mitochondria	38	29	0	3	0	14	tr	3	13
Neurons	48	21	5	7	4	–	3	11	1
Myelin	11	17	9	1	8	–	20	28	6

# Diferentes cadeias hidrocarbônicas

## saturadas



**lauric**

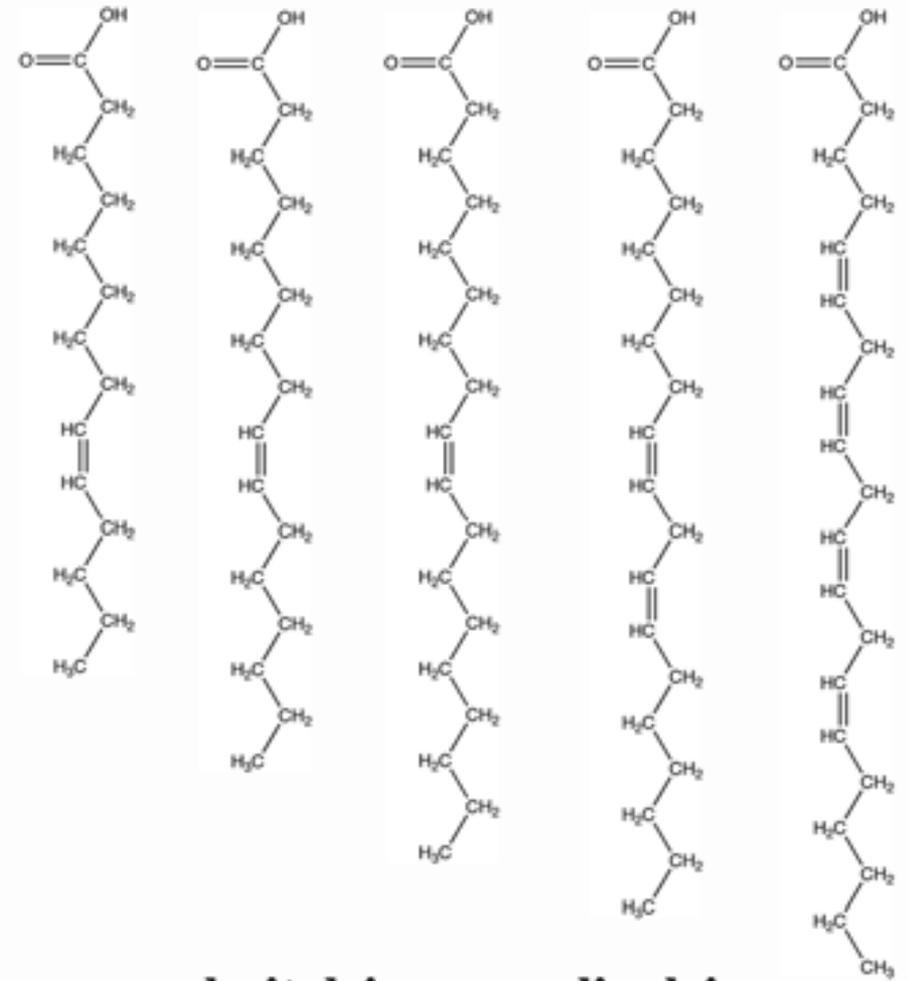
**myristic**

**palmitic**

**stearic**

**arachidic**

## insaturadas



**palmitoleic**

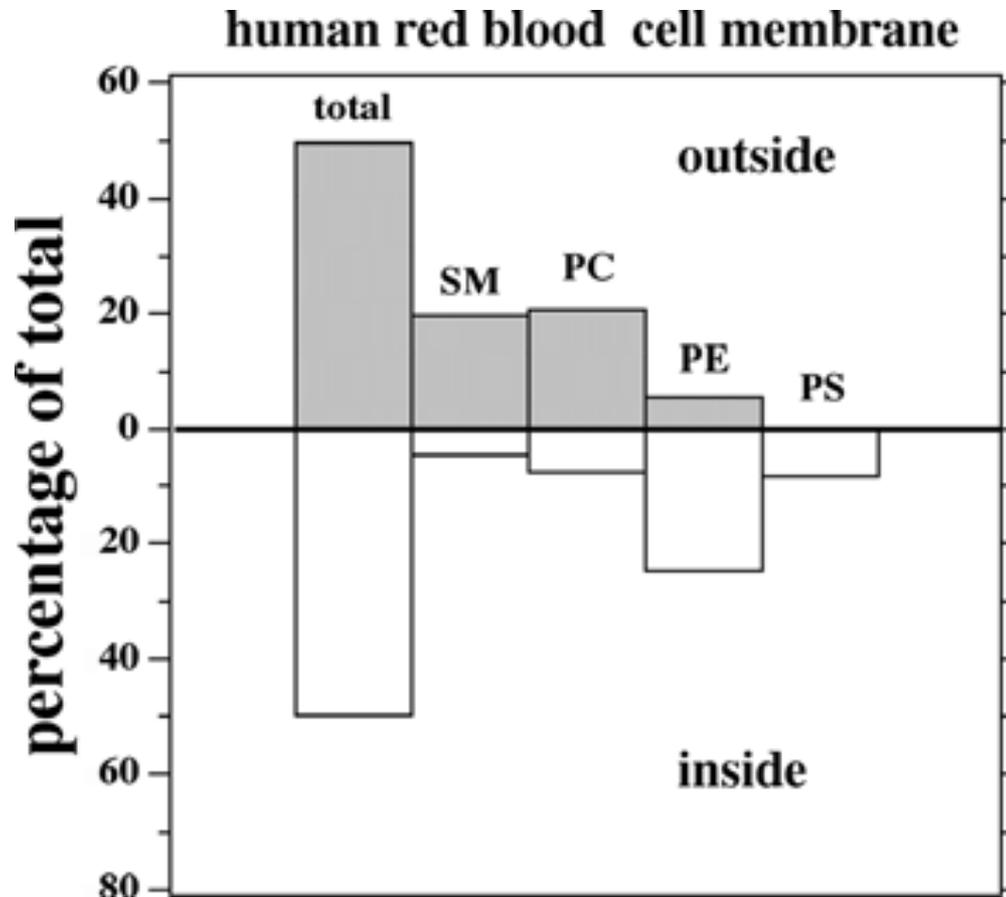
**oleic**

**linoleic**

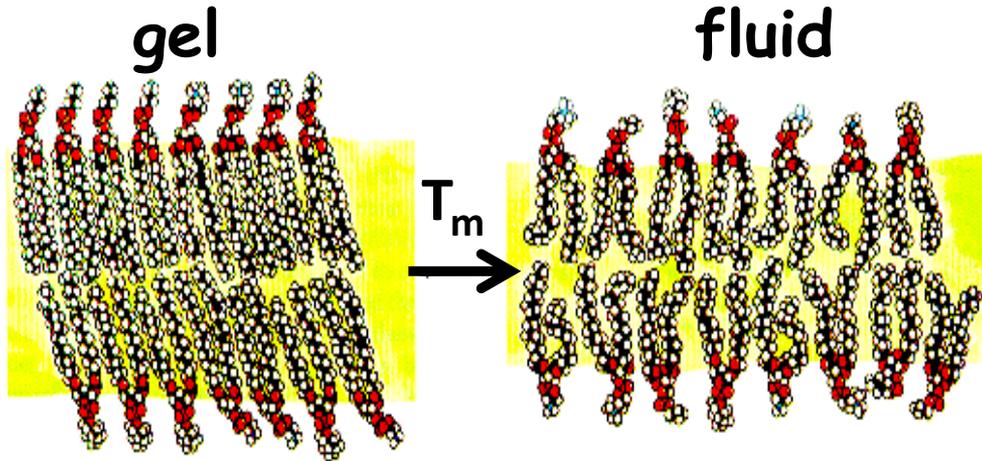
**arachidonic**

**myristoleic**

# Assimetria dos lipídios em membranas biológicas



# Bicamadas lipídicas: transição de fase principal

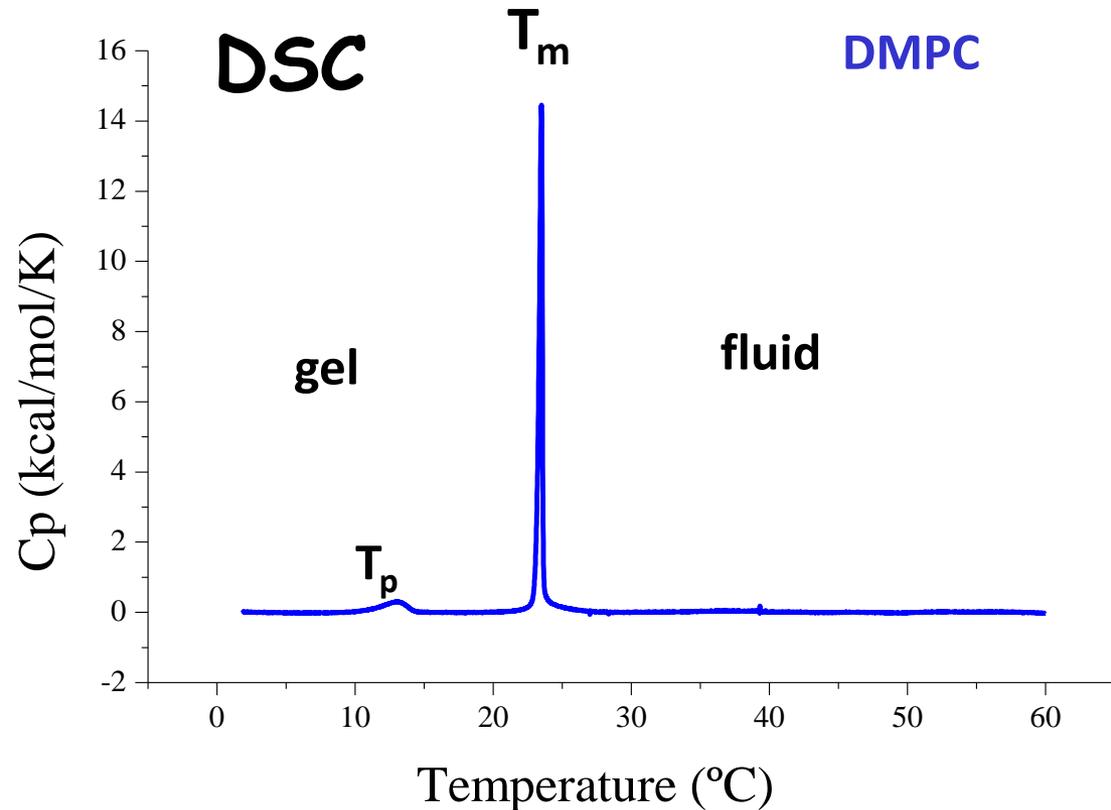


Apresentada pela maioria dos fosfolipídios saturados

(Voet and Voet, 1990)

Capacidade térmica ( $C_p$ )

transição ordem/desordem (1a ordem)



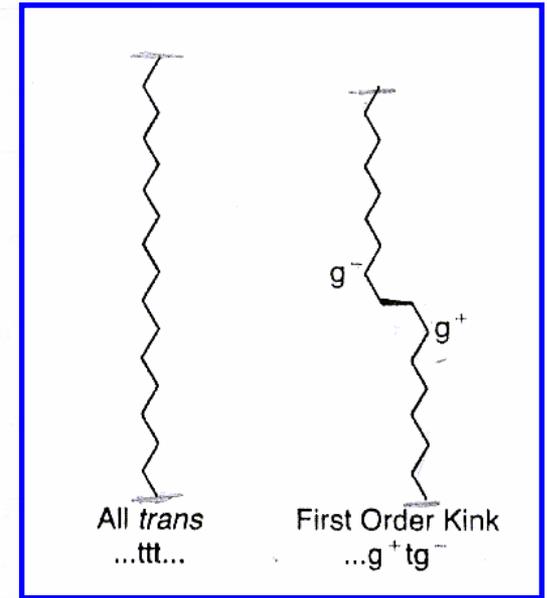
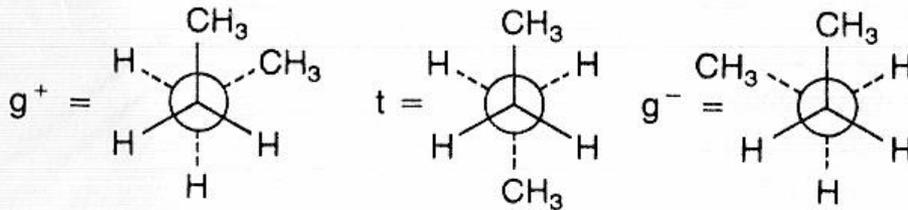
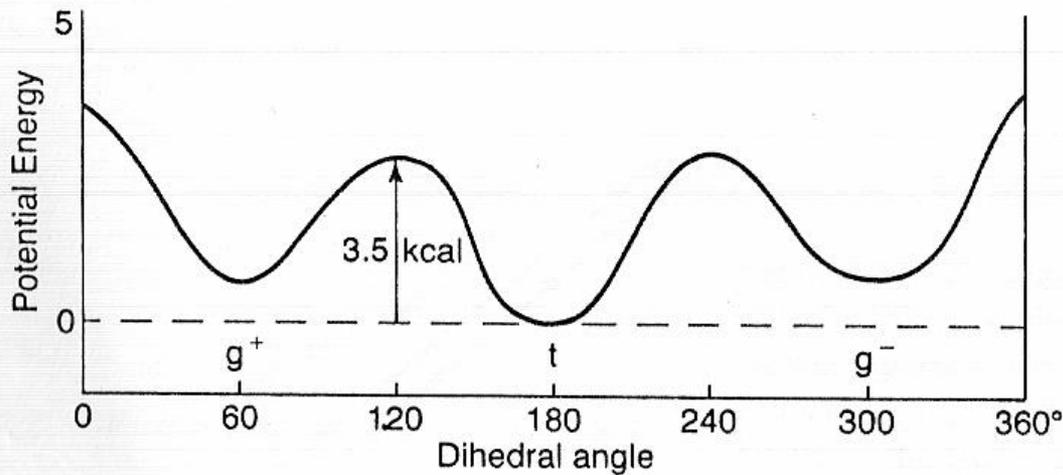
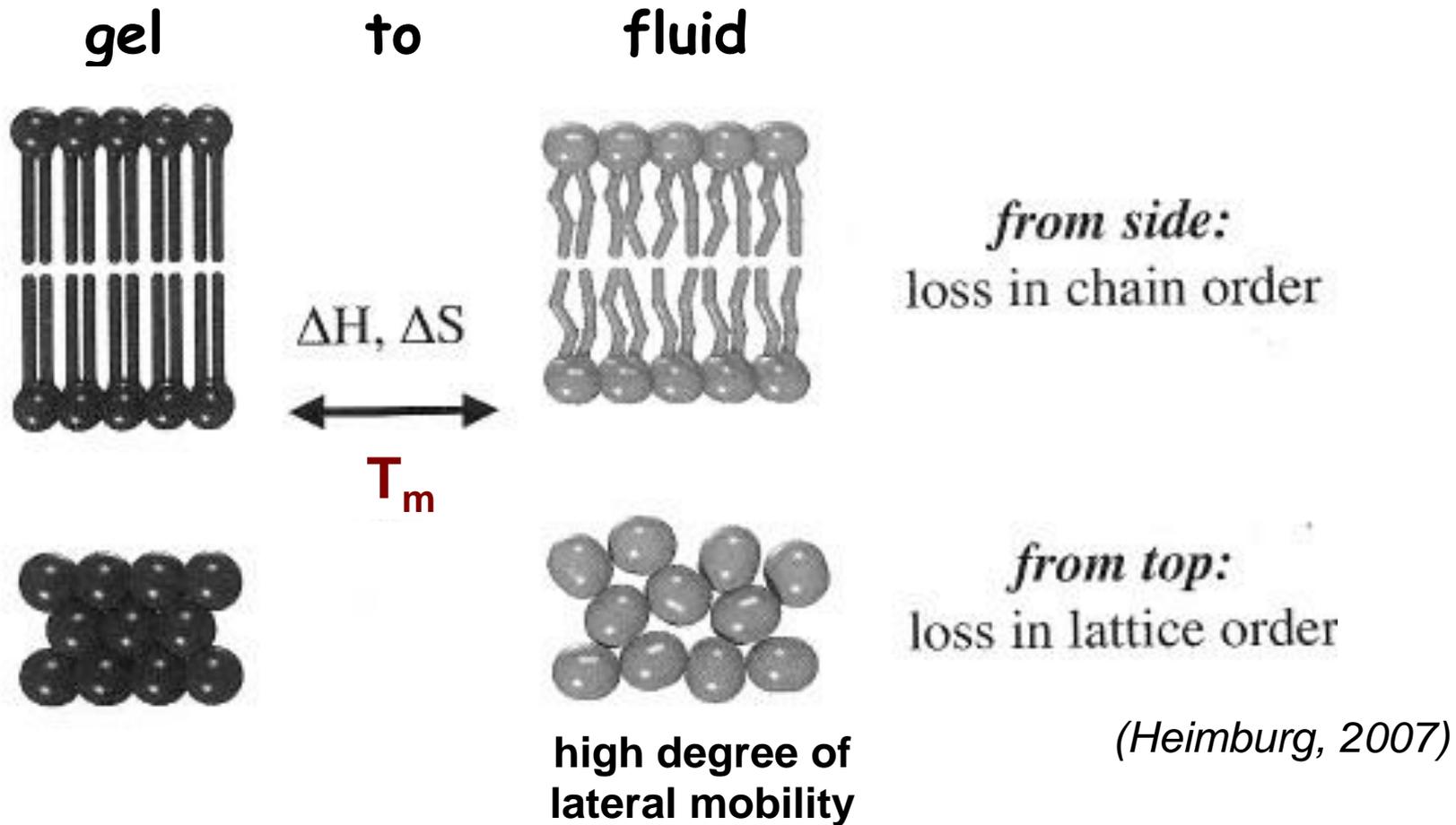


Figure 2.10. Potential energy curve for rotation about a carbon-carbon bond in an alkane. Below is the Newman projection diagram of the minimum energy *gauche* and *trans* conformations of butane:  $g^+$ ,  $g^-$ , and  $t$ . Adapted from ref. 535.

gel: maioria das ligações C-C trans

fluida: muitas ligações C-C gauche

# Transição de fase principal

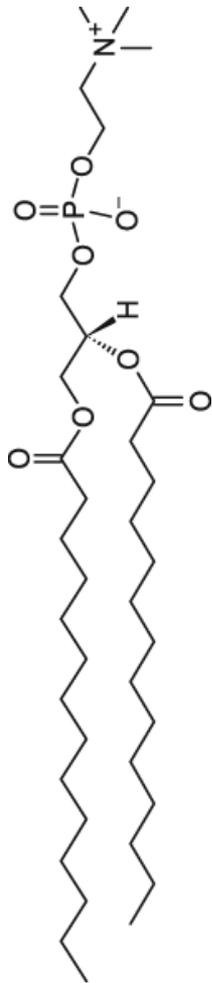


Transição de 1a ordem: ordem/desordem

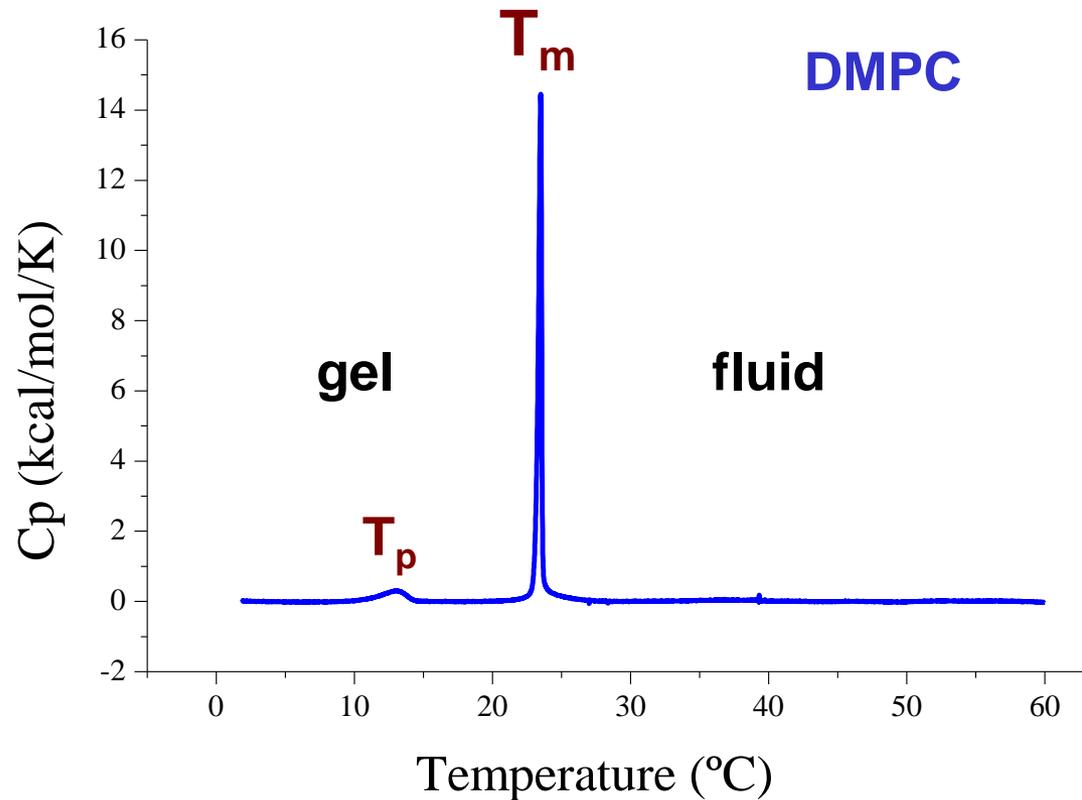
# Lipid bilayer main phase transition

DMPC

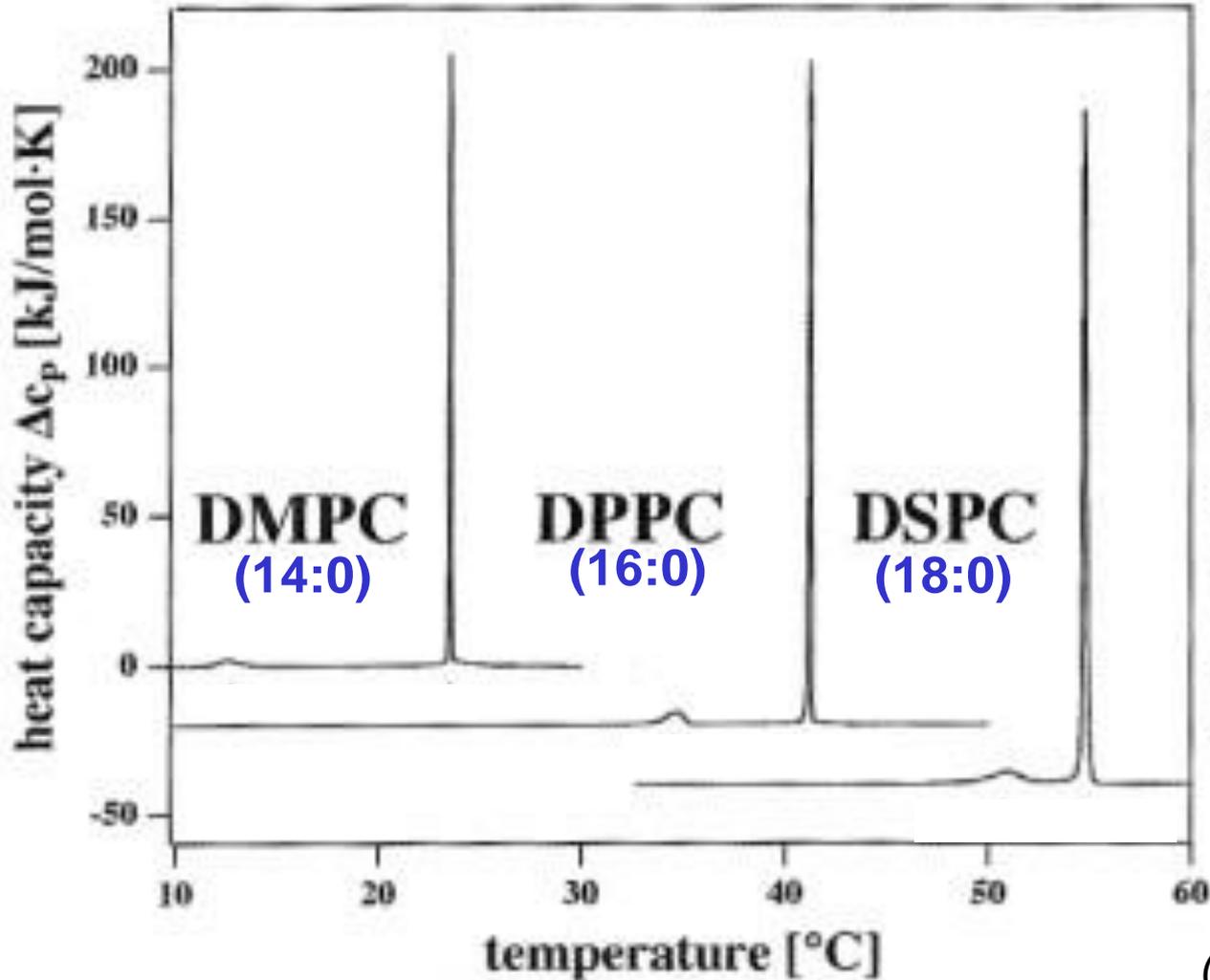
Differential scanning calorimetry (DSC)



Heat Capacity ( $C_p$ )



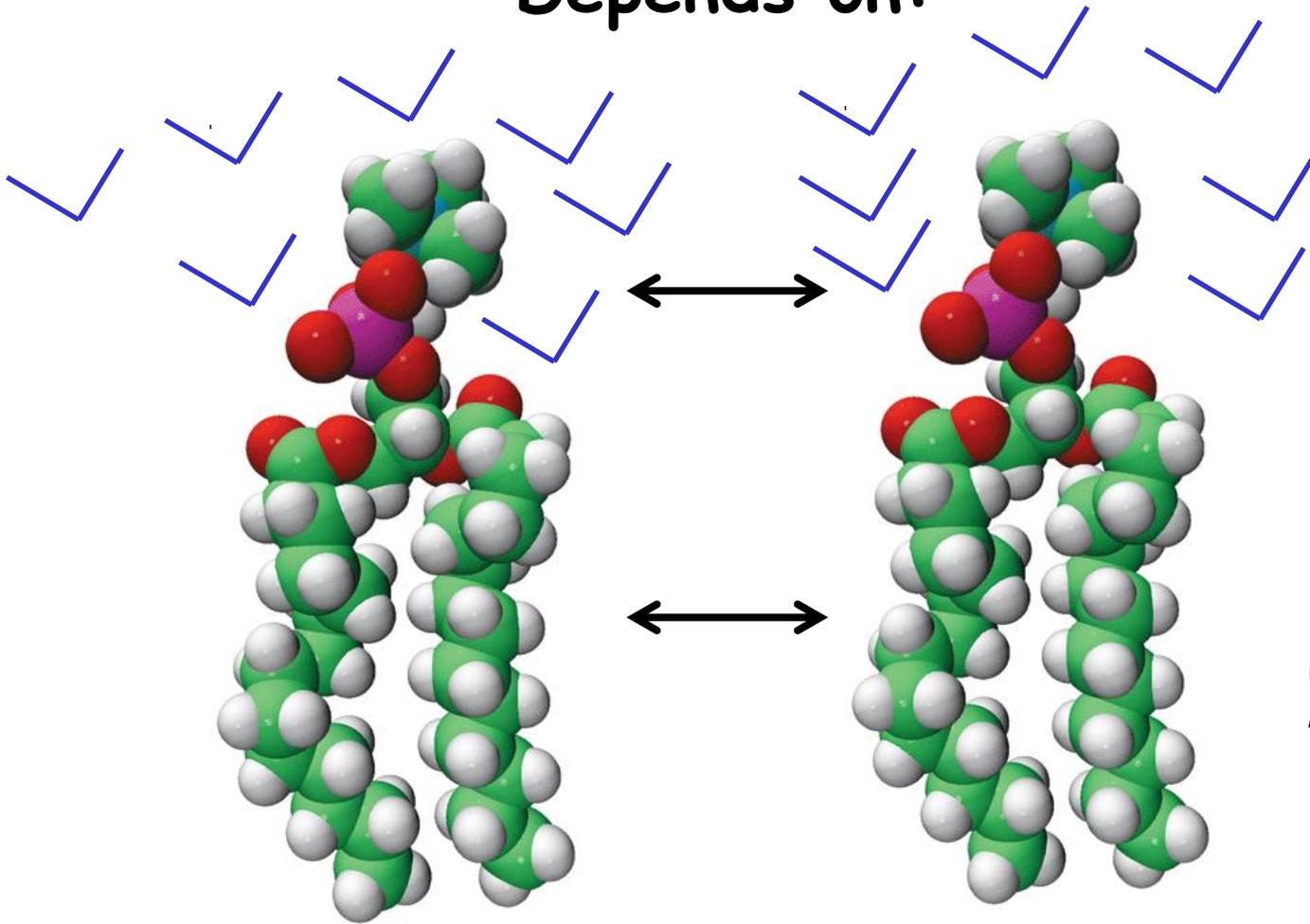
# Gel-fluid transition of lipid bilayers



(Heimburg, 2007)

$T_m$  is highly dependent on chain length

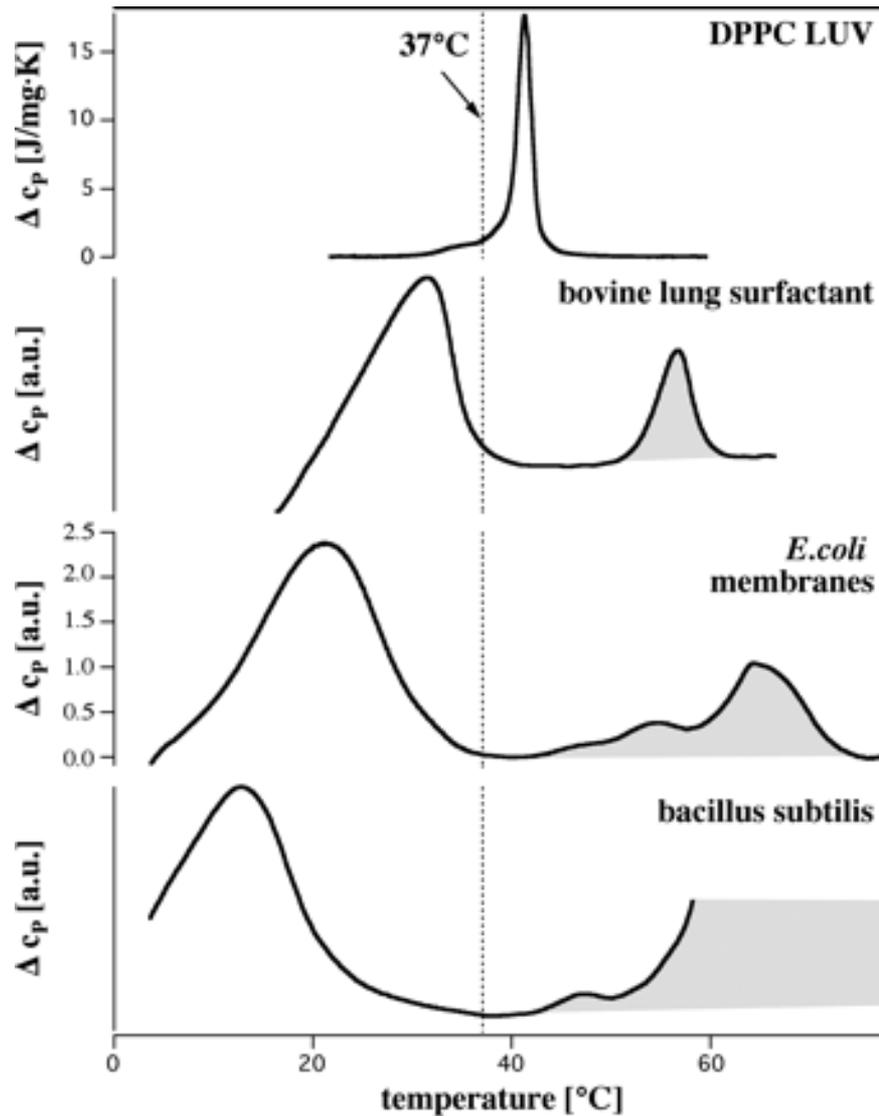
Depends on:



*(DMPC in Avanti  
Polar Lipids site)*

It is also related with bilayer curvature and  
bilayer/bilayer interaction

# Gel-fluid transition of biological membranes

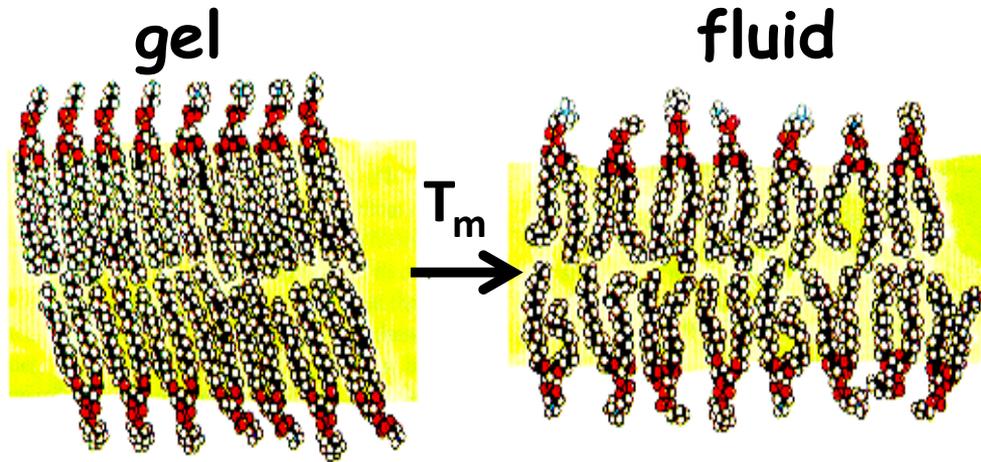


Mixture of different lipids

Possible presence of  
different lipid micro-  
domains

Very complicated systems!

# Propriedades das bicamadas lipídicas



$$\text{cmc} \sim 10^{-10} \text{ M}$$

coeficiente de difusão lateral

$$D_{\text{gel}} \sim 10^{-10} \text{ nm}^2/\text{ns}$$

$$D_{\text{fluid}} \sim 10^{-3} \text{ nm}^2/\text{ns}$$

área por cabeça polar  $\sim 0.6 \text{ nm}^2$

10s

1ms

“flip flop rate”  $\sim 1\text{-}10 \text{ h}$

**bicamada lipídica fluida: bem estável, mas muito maleável e dinâmica**