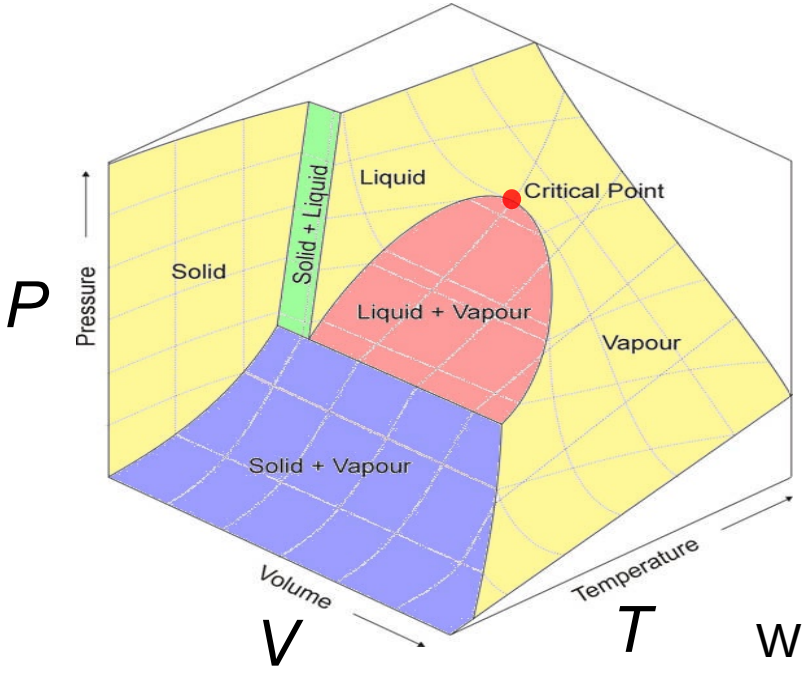
Transições de fase em modelos estatísticos simplificados

Prof. Mário N. Tamashiro

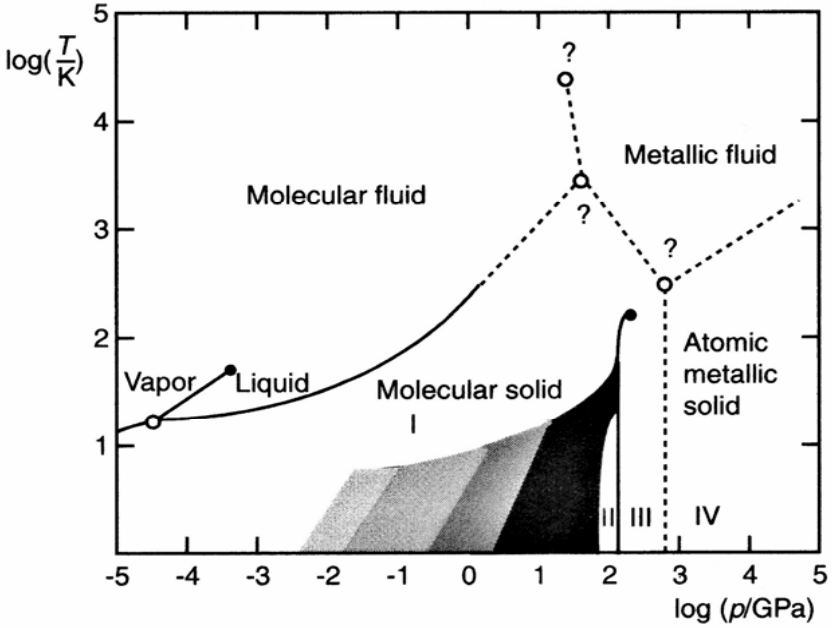
Por quê ocorrem transições de fase?

Segunda lei da termodinâmica: para um sistema isolado, $dS_{tot} \geq 0$ ⇨ convexidade dos potenciais termodinâmicos.
Violação das condições de estabilidade ⇨ transição de fase.
Transição descontínua ⇨ coexistência de fases.

Diagrama de fases típico de um fluido simples (homogêneo e isotrópico)

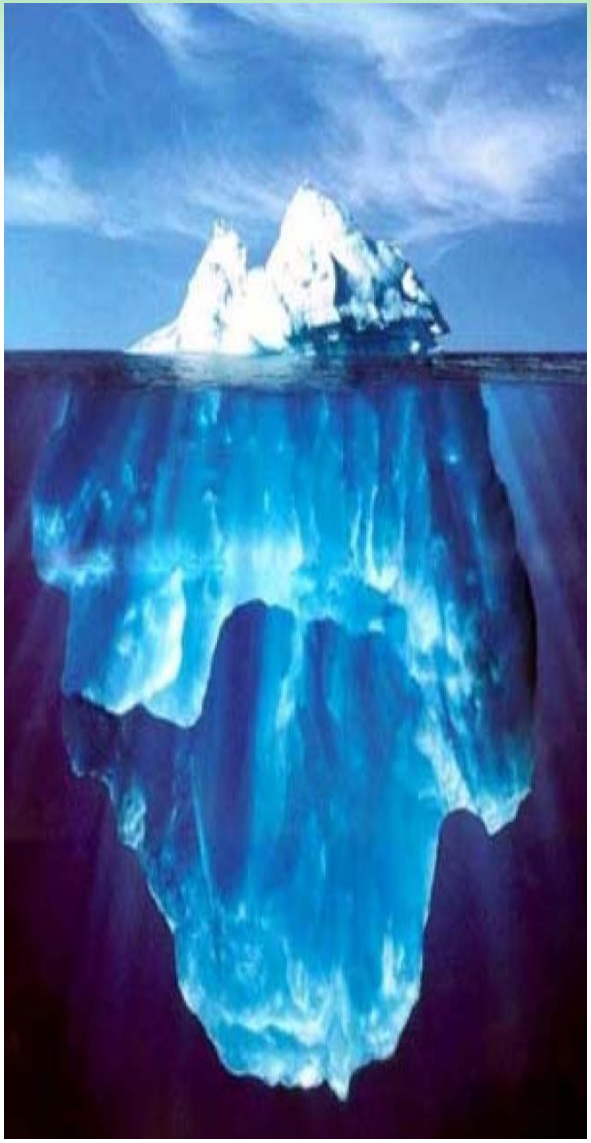


Exemplo: hidrogênio



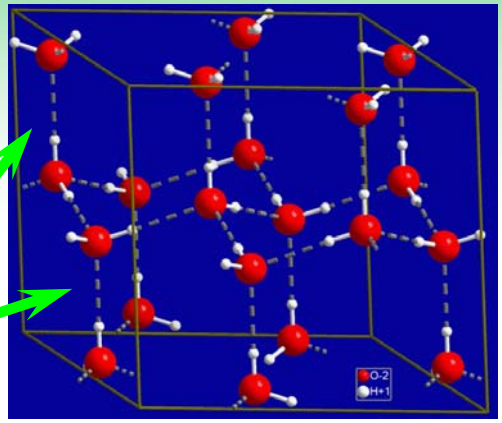
W. H. Holzapfel, *Rep. Prog. Phys.* **59**, 29 (1996)

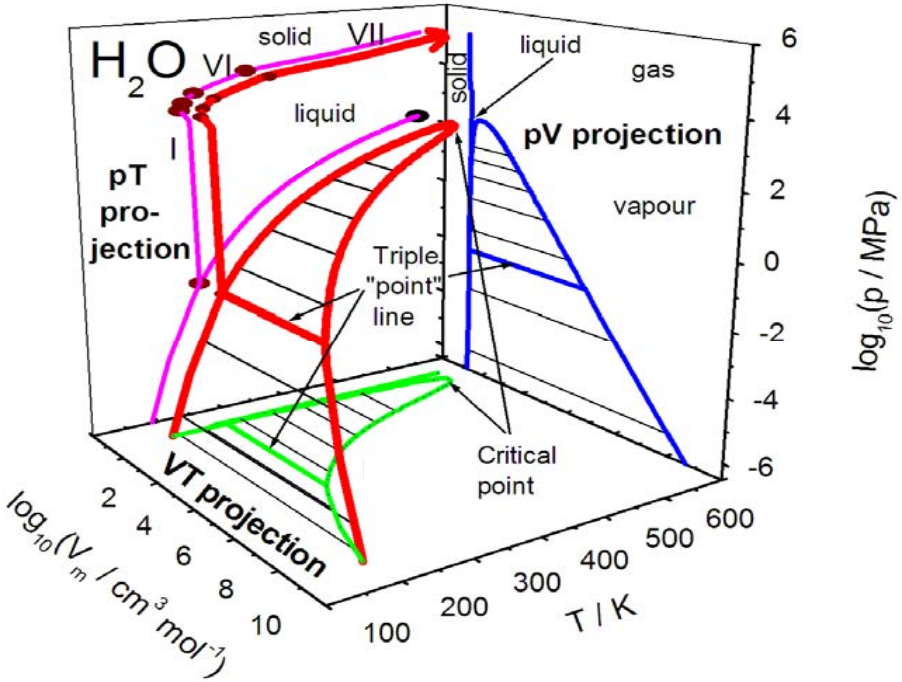
As transições da água pura são *'simples'*?



Estrutura tetraédrica do gelo comum I_h

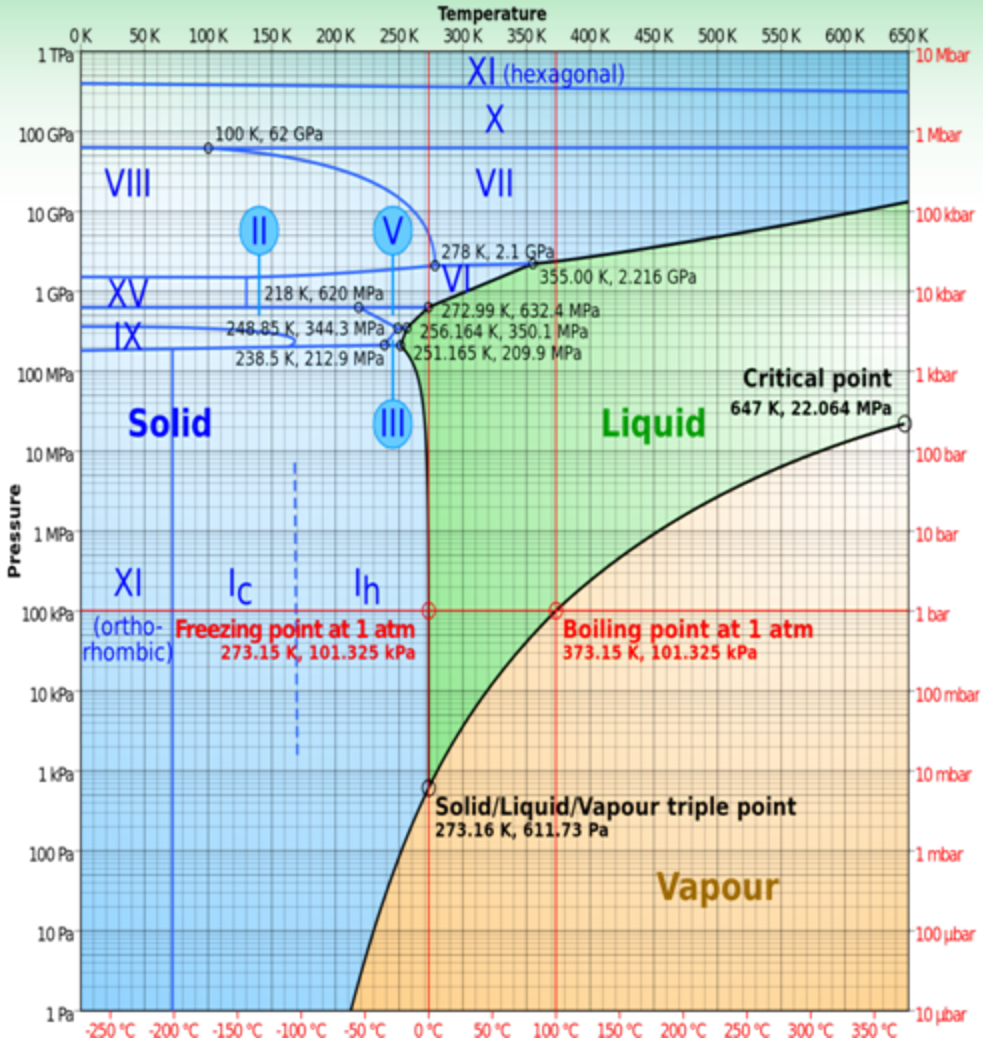
ligações (pontes) de hidrogênio



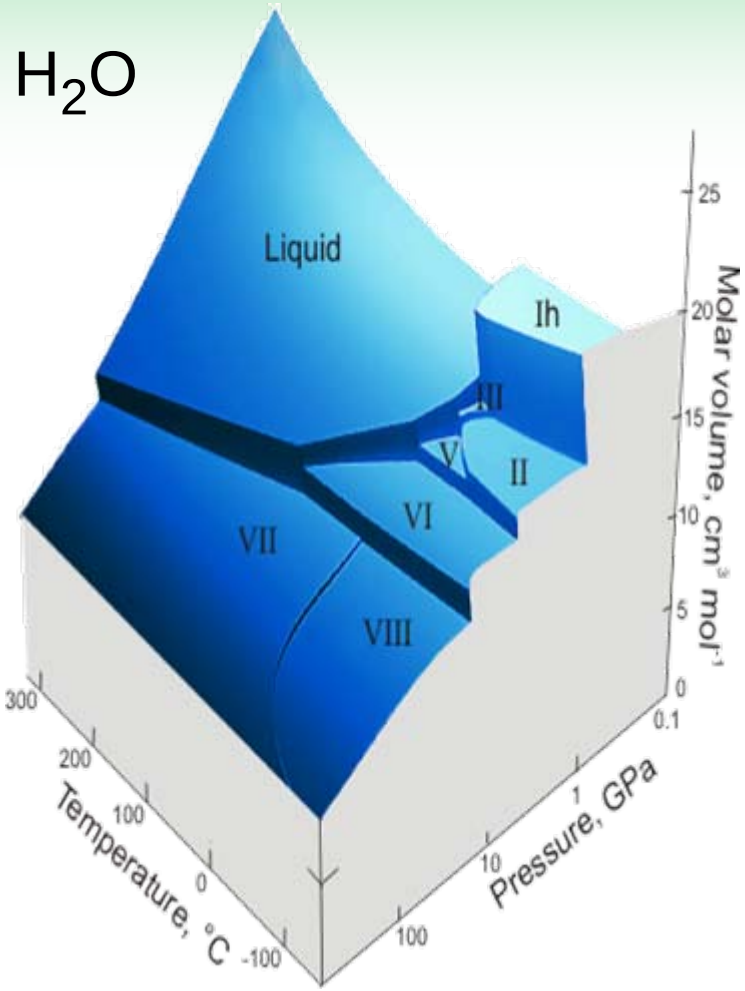


L. Glasser, *J. Chem. Educ.* **81**, 414 (2004)

15 fases sólidas distintas, algumas *metaestáveis.*



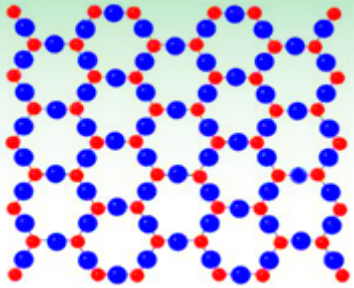
H_2O



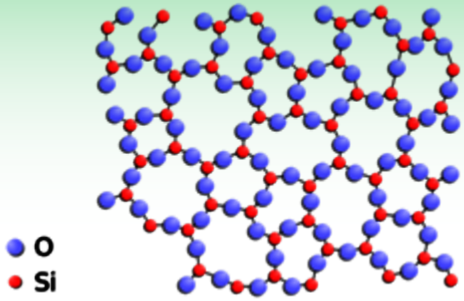
http://en.wikipedia.org/wiki/Ice#Phases http://www.lsbu.ac.uk/water/phase.html

Fases amorfas metaestáveis: LDA (low-density amorphous), HDA (high-density amorphous), VHDA (very high-density amorphous).

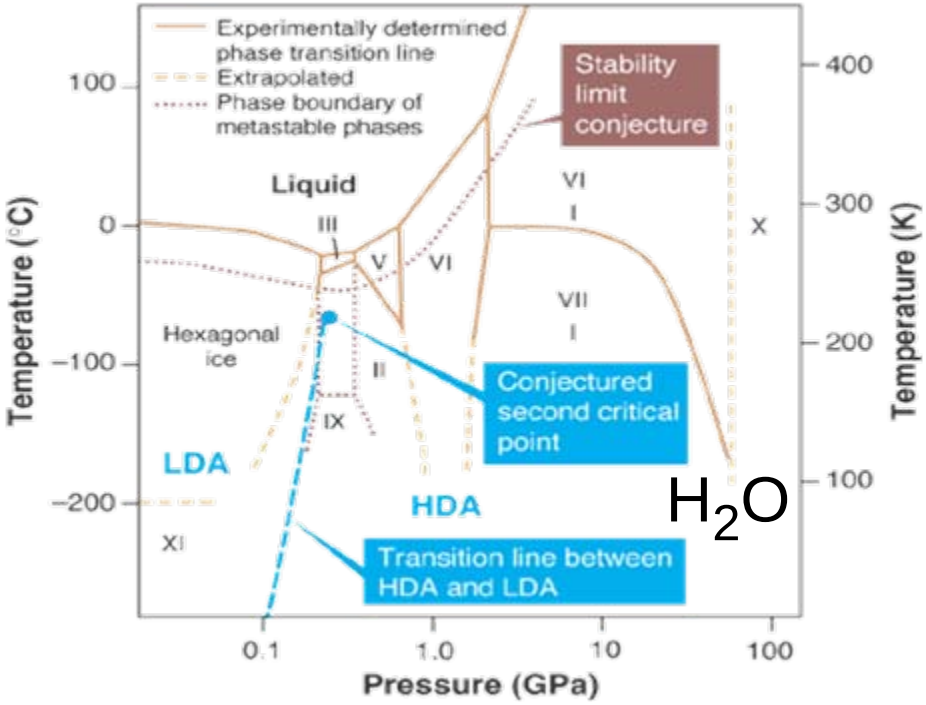
sílica cristalina (quartzo)



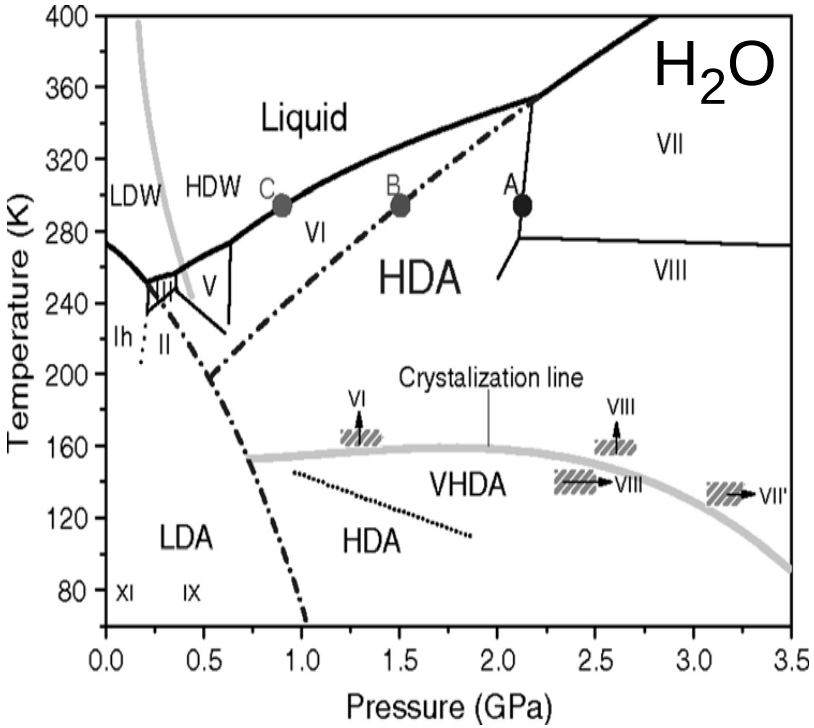
SiO_2



sílica amorfa (vidro)

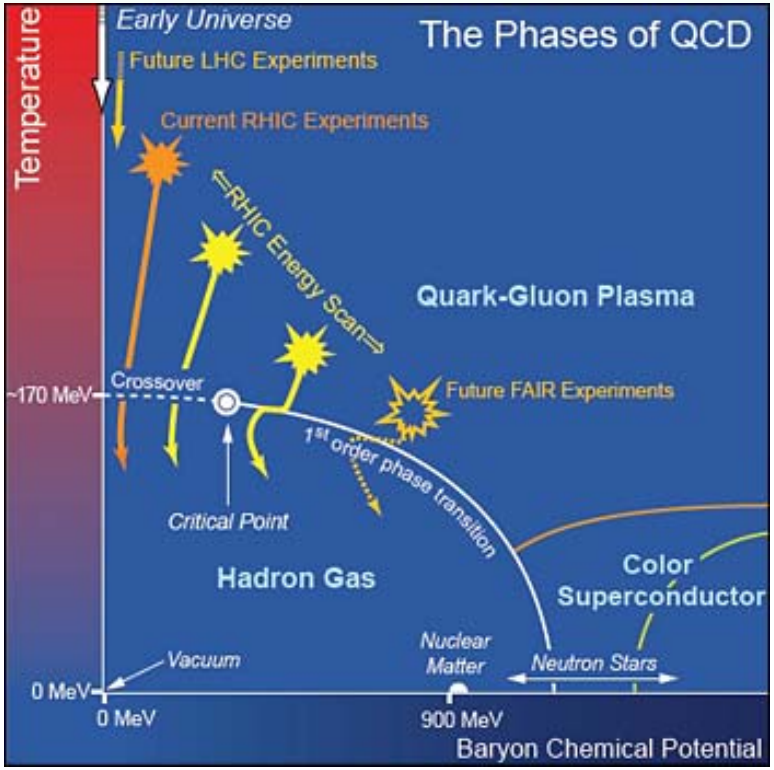


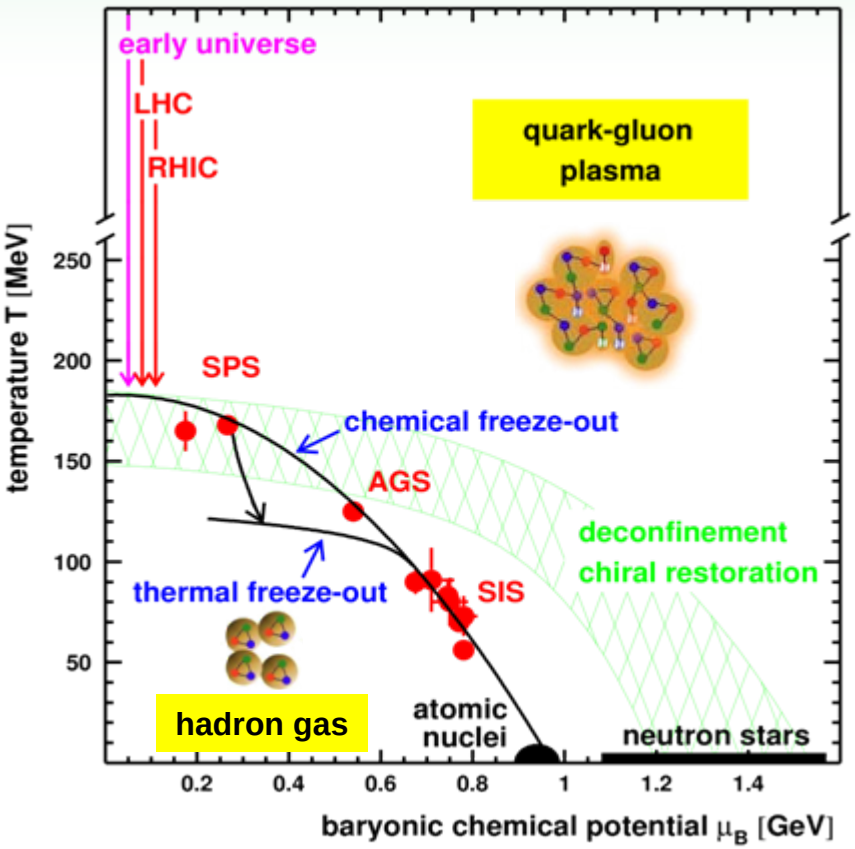
A. K. Soper, *Science* **297**, 1288 (2002)



J. Bai, X.-C. Zeng, *PNAS USA* **109**, 21240 (2012)

Transições de fase na cromodinâmica quântica (experimentos em aceleradores de partículas)

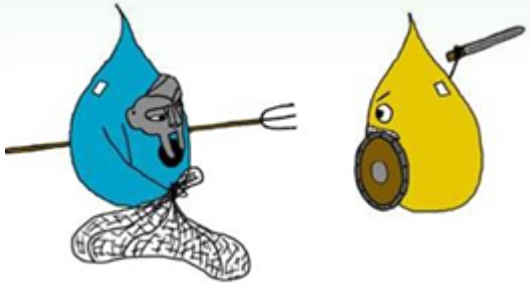




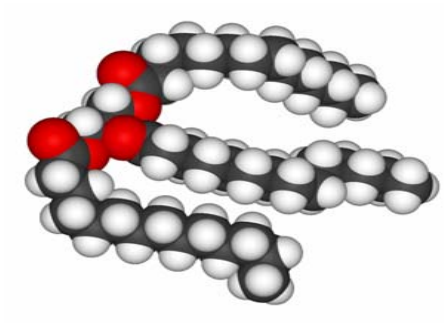
http://www.bnl.gov/newsroom/news.php?a=21870

M. Rho, *AIP Conf. Proc.* **556**, 160 (2001)

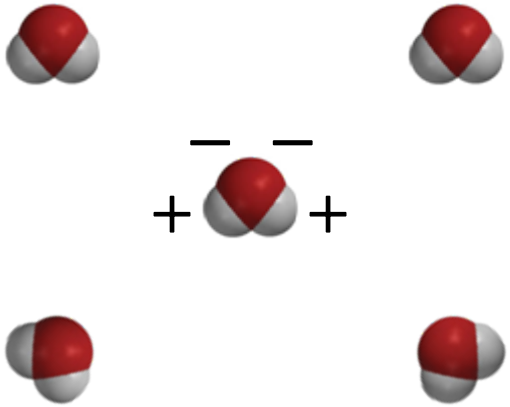
Sistema binário: água + óleo
(efeito hidrofóbico)



mistura bifásica

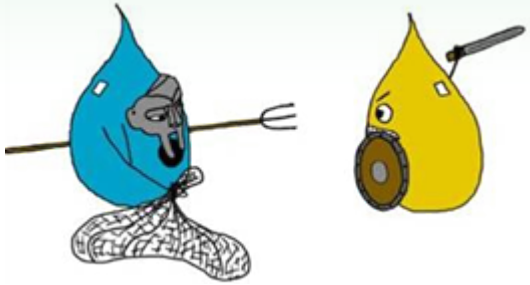


óleo é apolar

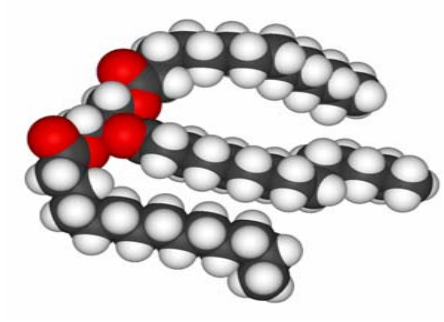


água é polar

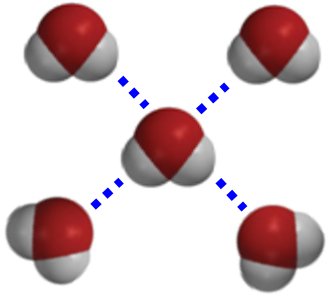
Sistema binário: água + óleo
(efeito hidrofóbico)



mistura bifásica



óleo é apolar

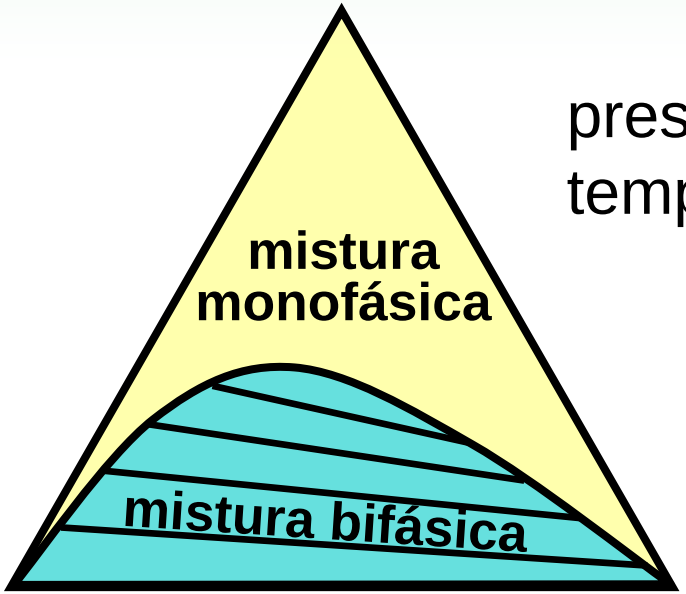


ligação (ponte) de hidrogênio

Efeito hidrofóbico na mitologia grega:

Atena x Poseidon

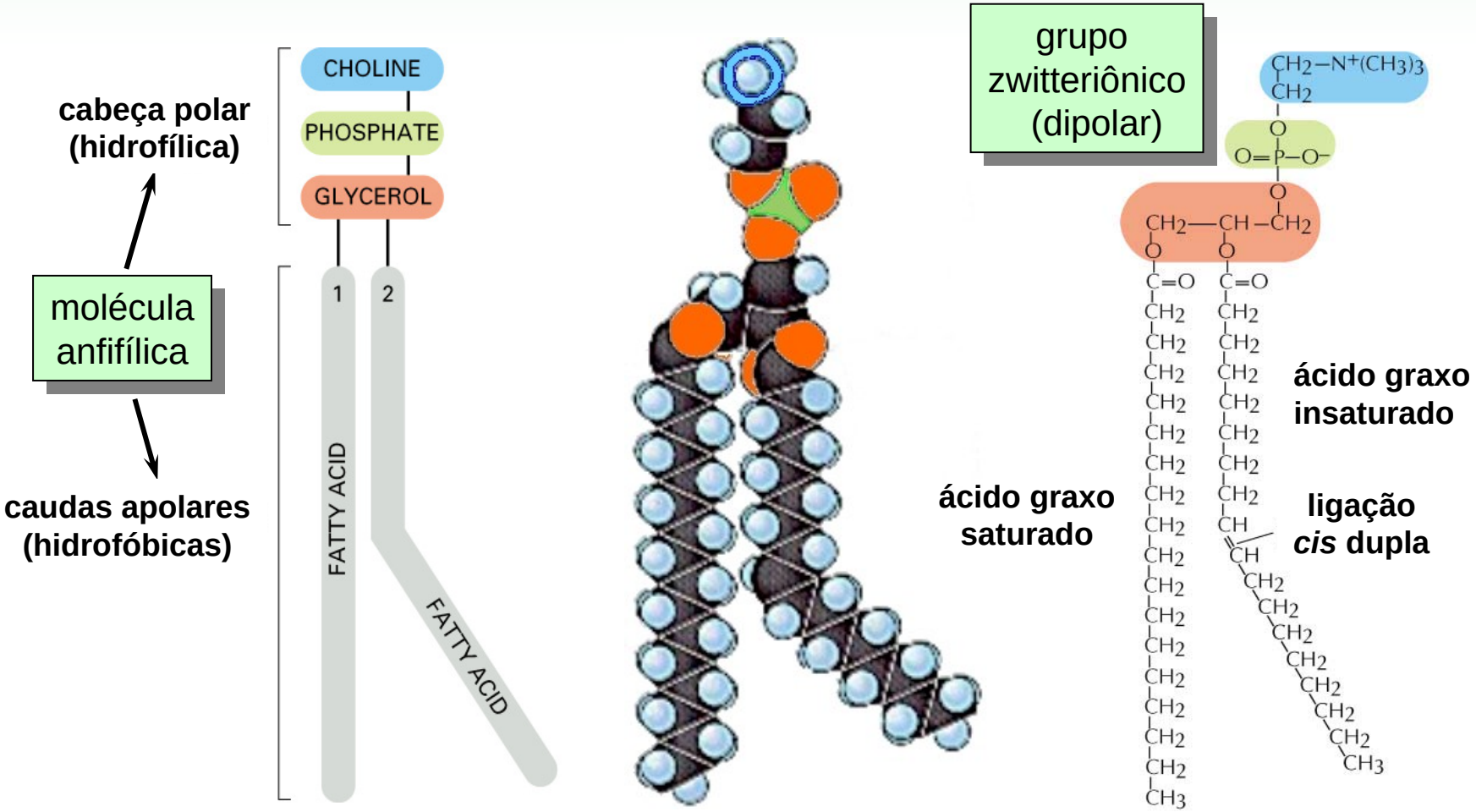
Sistema ternário: álcool + água + óleo



pressão *P* e temperatura *T* fixas

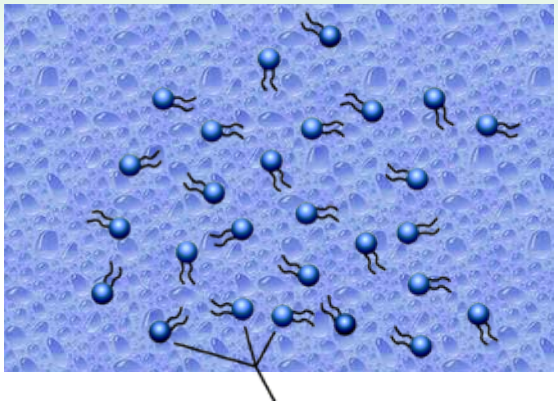
Estrutura química esquemática de um fosfolipídio típico

fosfatidil colina (PC); lecitina de gema de ovo (mistura de PCs)



Auto-organização de anfifílicos em solução

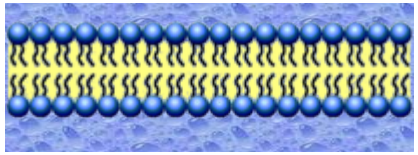
Moléculas anfifílicas formam estruturas supramoleculares em água



fosfolipídios livres em água

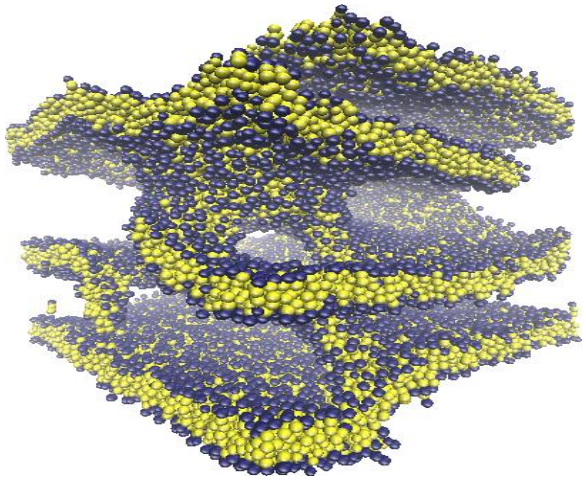
auto-organização

membrana planar
(bicamada, lamela)

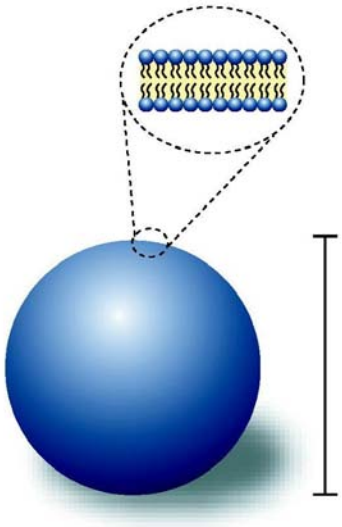


5 nm

caso especial de um
cristal líquido esmético



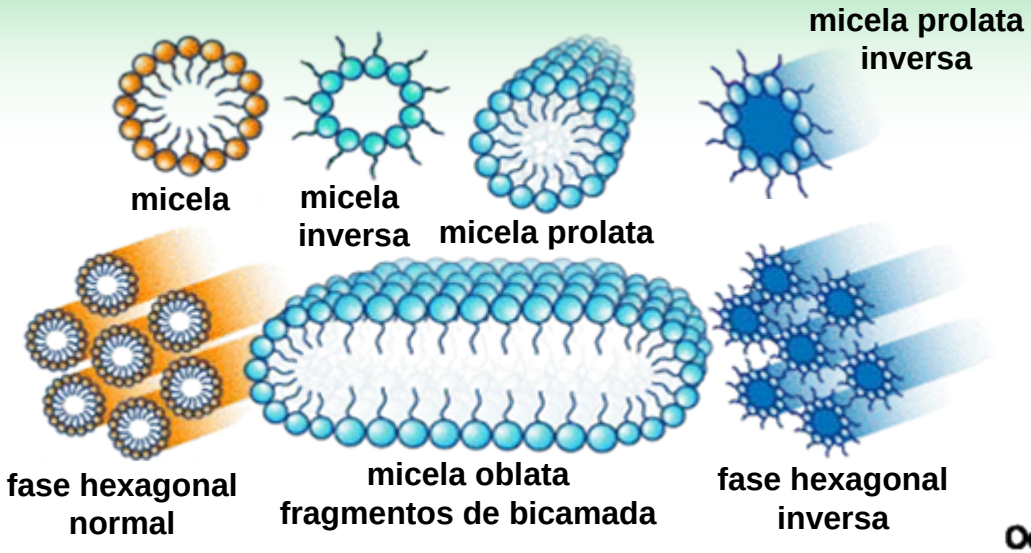
fase bicontínua (esponja)



5 µm - 100 µm

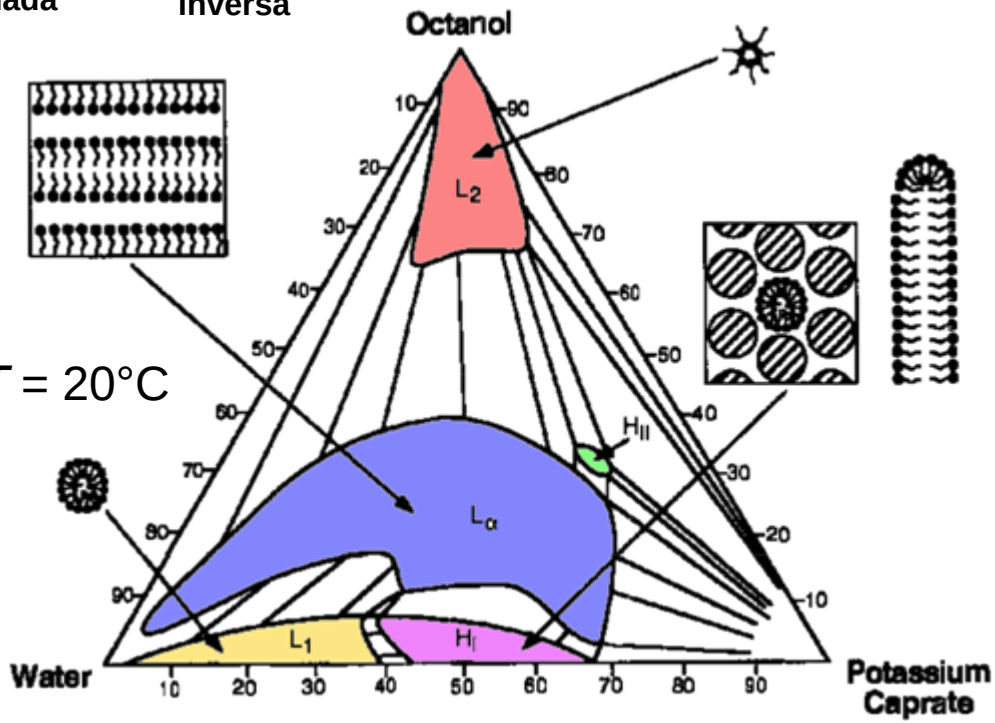
vesícula esférica unilamelar

Mesomorfismo de estruturas supramoleculares



estruturas micelares

Exemplo:
sistema ternário (água + octanol + decanoato de potássio), P = 1 atm, T = 20°C
B. Jönsson, H. Wennerström,
J. Phys. Chem. **91**, 338 (1987)



Escalas e níveis de modelagem teórica

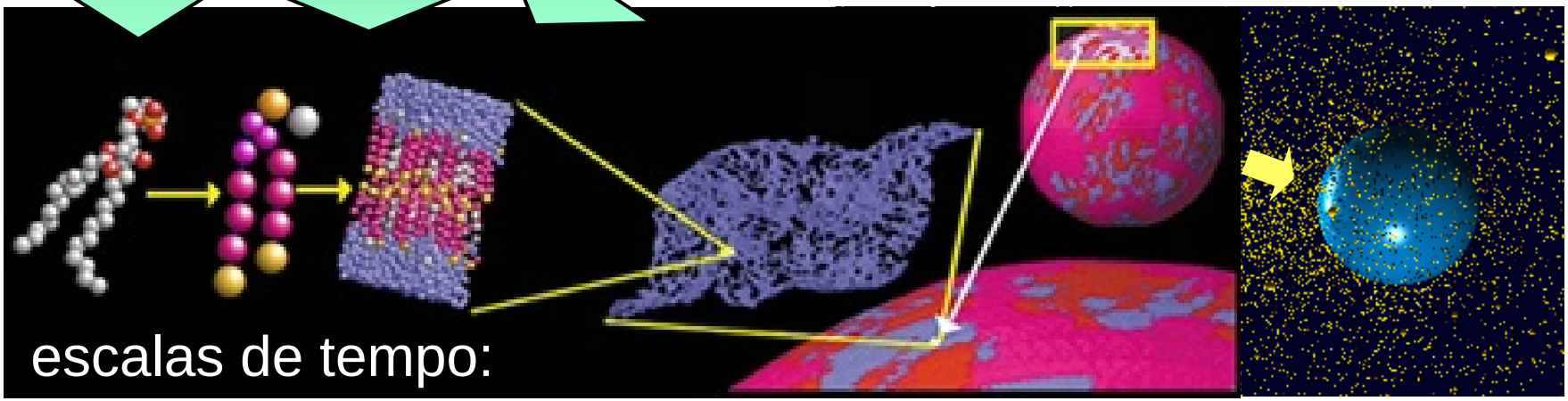
cálculos quânticos atomísticos *(ab-initio)*

dinâmica molecular clássica / simulações de Monte Carlo

modelos fenomenológicos contínuos *(coarse-grained)*

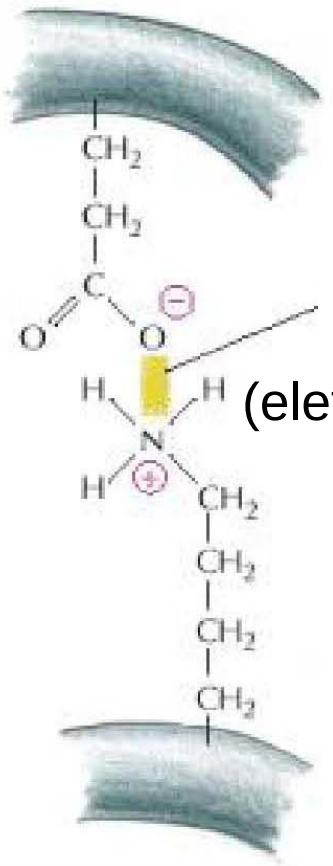
métodos semi-empíricos

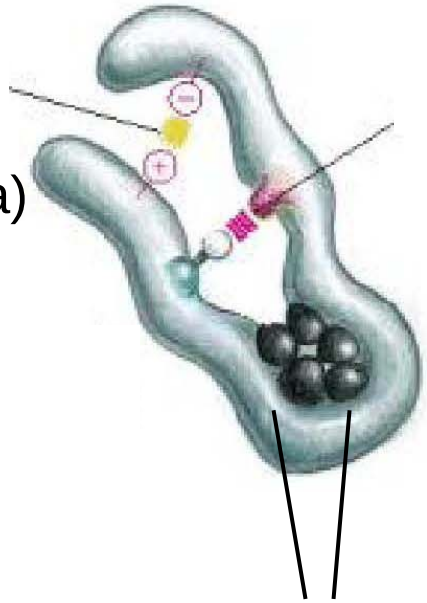
modelagem (físico-)estatística

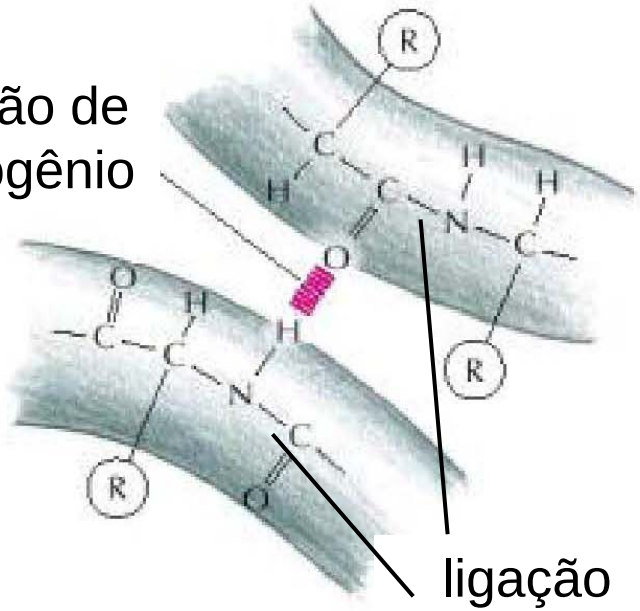


ps ns ms propriedades de equilíbrio

Interações (ligações) efetivas em / entre macromoléculas

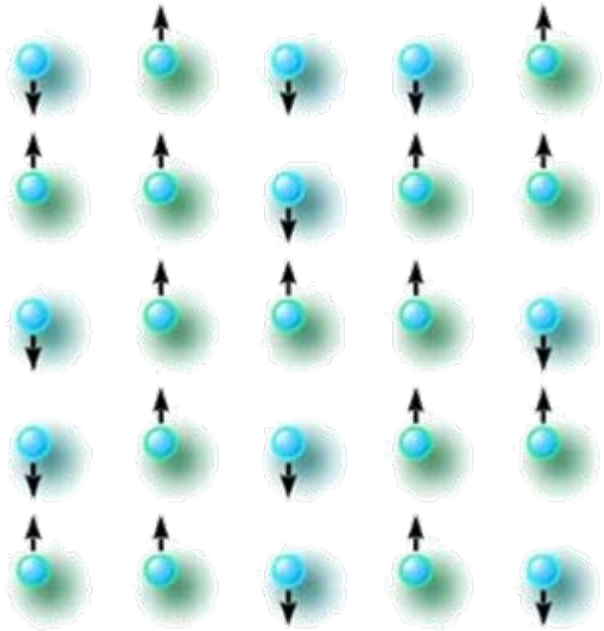




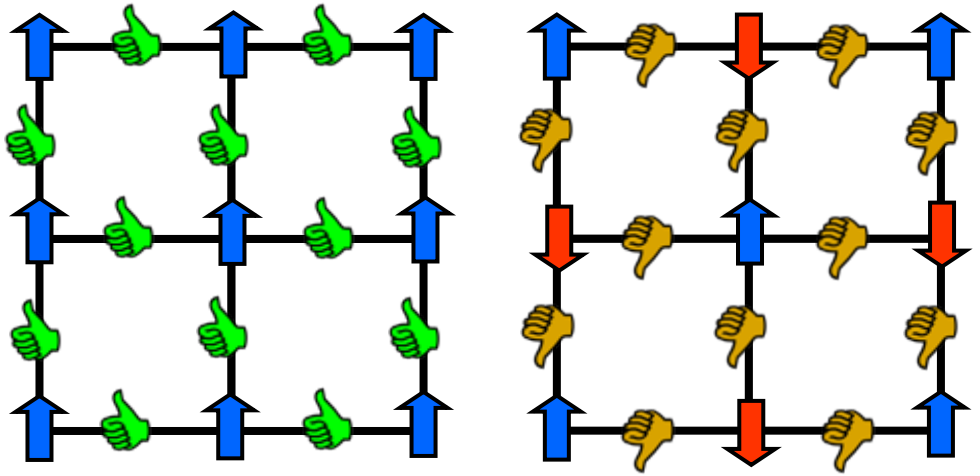


Modelo de (Lenz-) Ising

Modelo estatístico simplificado para transições de fase em materiais ferromagnéticos
Doutorado de Ernst Ising, *Zeit. Phys.* **31**, 253 (1925): não há transição de fase em 1-D
S. G. Brush, *Rev. Mod. Phys.* **39**, 883 (1967)



$$\mathcal{H}_{\text{eff}}(s) = -J \sum_{(i,j)} s_i s_j$$

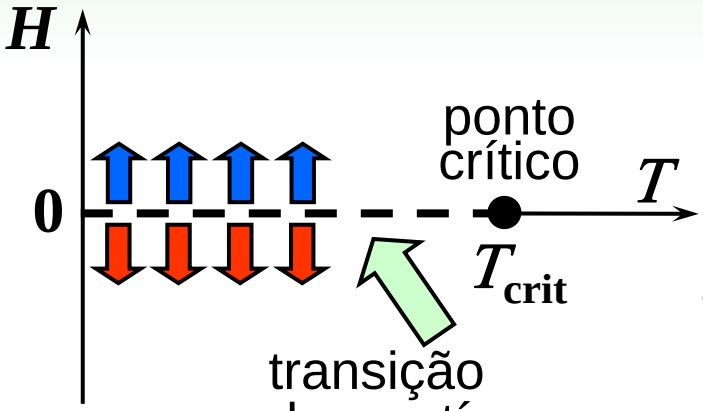


$= -J$ (ferro) $= +J$ (antiferro)

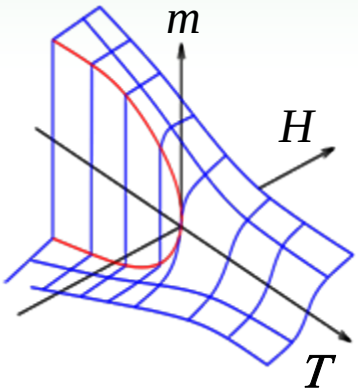
Solução exata: modelo de Ising 2-D

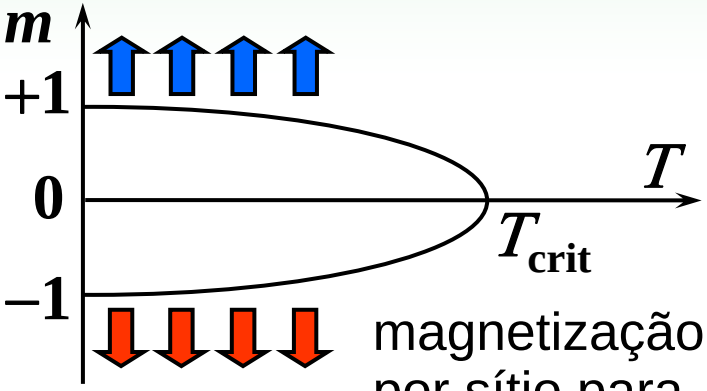
L. Onsager, *Phys. Rev.* **65**, 117 (1944): para $\boldsymbol{H = 0}$

C. N. Yang, *Phys. Rev.* **85**, 808 (1952): $\boldsymbol{m(H = 0)}$



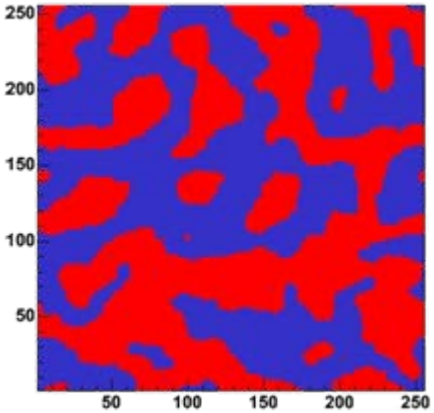
transição
descontínua,
1ª ordem $\boldsymbol{(H = 0)}$

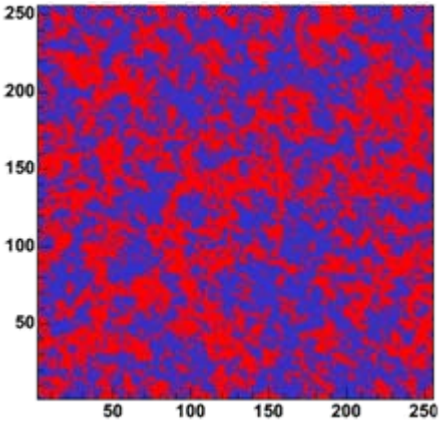




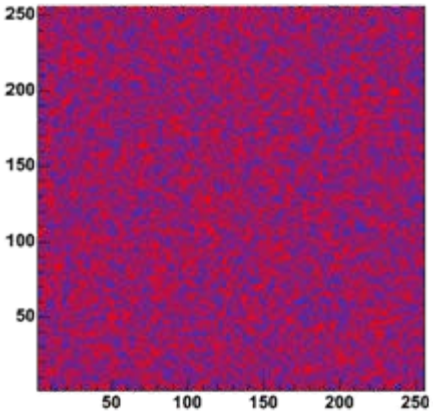
magnetização
por sítio para
$\boldsymbol{H = 0}$

fase ordenada
(baixas temperaturas)



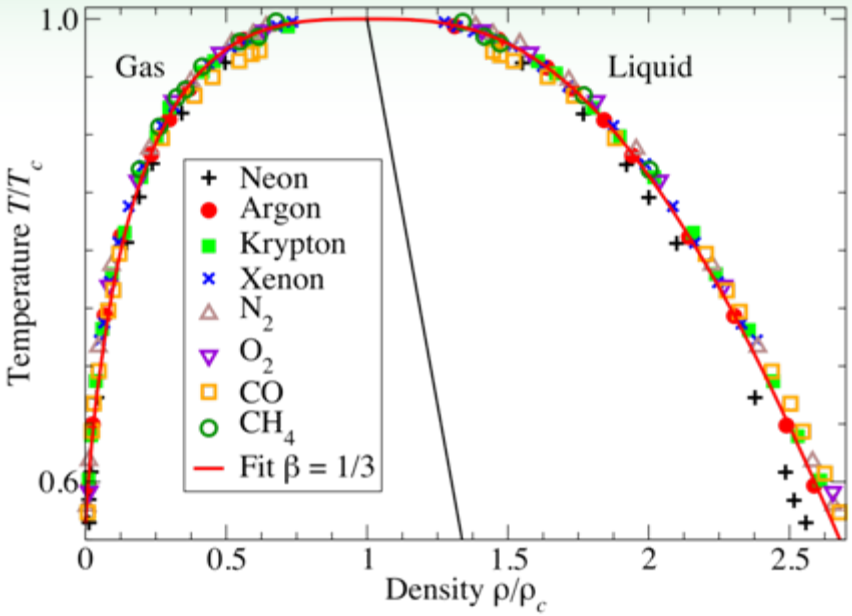


fase desordenada
(altas temperaturas)



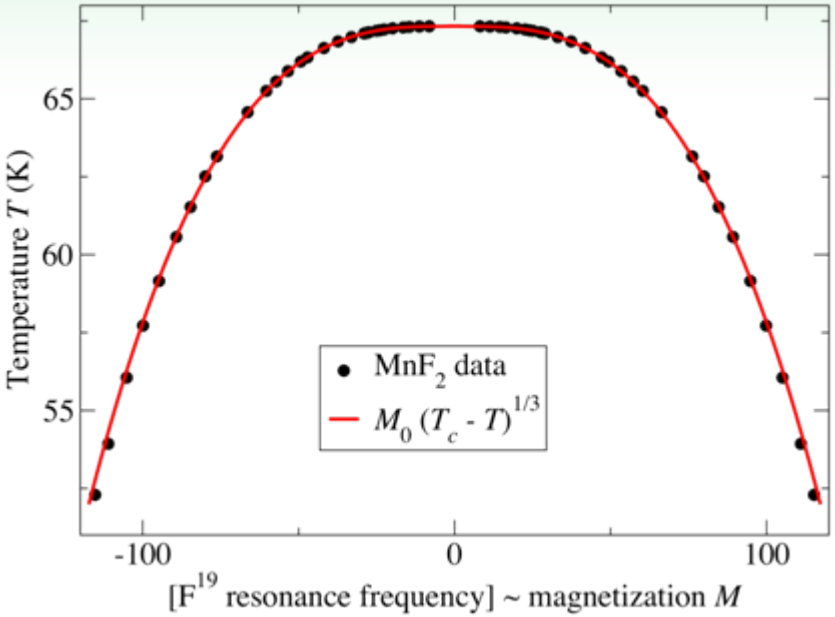
Universalidade do comportamento crítico

ponto crítico líquido-gás



Princípio dos estados correspondentes
E. A. Guggenheim,
J. Chem. Phys. **13**, 253 (1945)

transição crítica antiferro



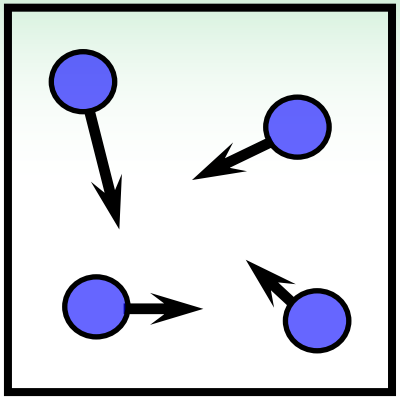
P. Heller, G. B. Benedek,
Phys. Rev. Lett. **8**, 428 (1962)

parâmetro de ordem ($\rho_L - \rho_G$ ou M) $\approx (1 - T/T_c)^{\beta}$, $\beta = 1/3$

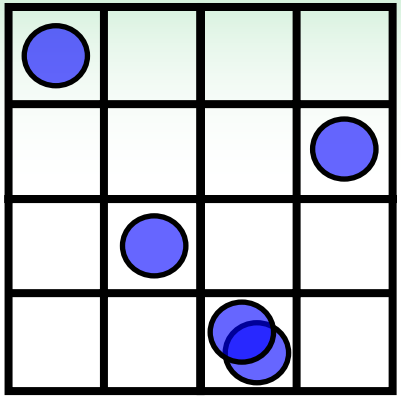
modelo de Ising 3-D: $\beta = 0{,}325 \pm 0{,}005$, 2-D: $\beta = 1/8$

Por quê também funciona para um gás?

partículas não-interagentes (gás ideal)



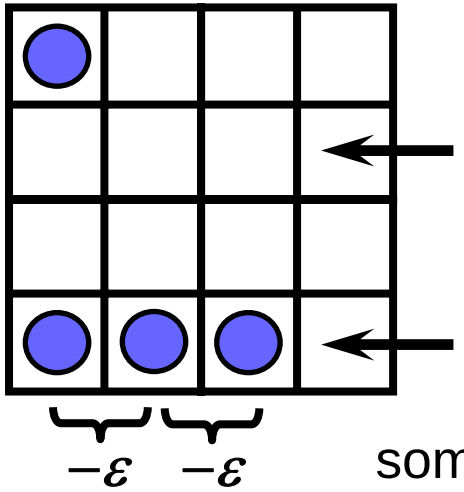
modelo mecânico
teoria cinética
N partículas,
volume V, pressão
P = força/área =
$N\langle m\boldsymbol{v}^2\rangle/3L^3 = Nk_BT/V$



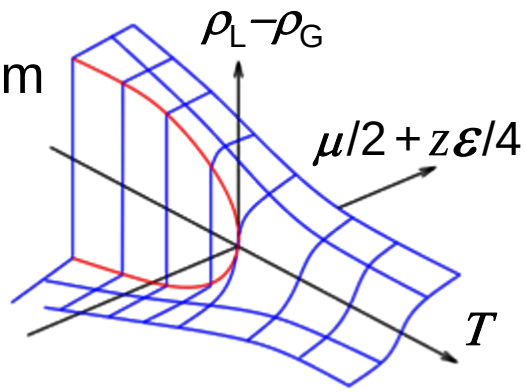
gás de rede
$S = k_B \ln(V^N/N!)$
$P/T = \partial S/\partial V$
$= Nk_B/V$
sem dinâmica,
só entropia

sem restrição

partículas interagentes (gás não-ideal)



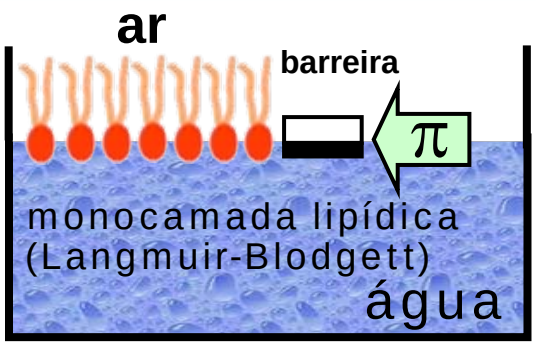
gás de rede mapeado no modelo de Ising
Aproximação de campo médio:
$U = -N^2\varepsilon/V$, $S = k_B \ln\{V!/[N!(V-N)!]\}$
$\Psi = U - TS - \mu N = -PV$
transição líquido-gás com
$\beta = 1/2$ (campo médio)



somente uma partícula por célula
(van der Waals) atração entre partículas vizinhas

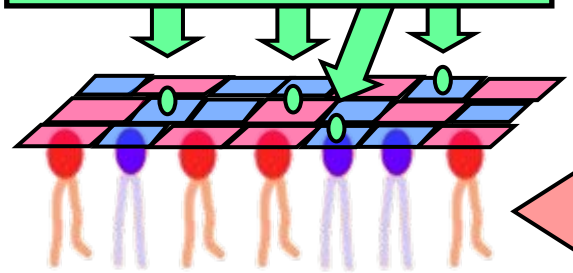
Transições de fase em lipídios carregados

Tese de doutorado de Renato G. R. Nunes (co-orientação IF-USP)
M. N. Tamashiro *et al*., *Phys. Rev. E* **84**, 031909 (2011)
V. B. Henriques *et al*., *Langmuir* **27**, 13130 (2011)



μ : potencial químico de contra-íons (controla a carga superficial da monocamada)

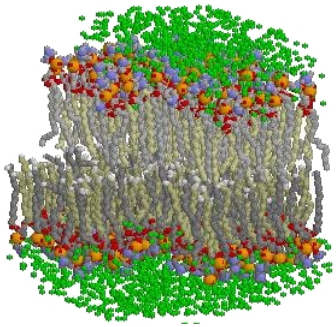
íons (cargas livres)

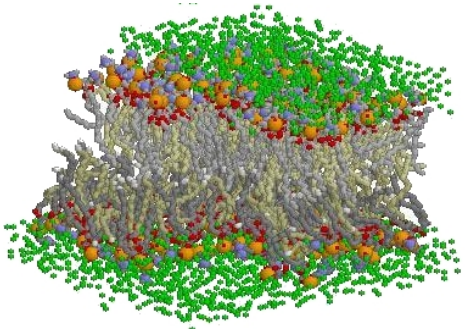


estado desordenado (fluido)

π : pressão lateral (controla a área total da monocamada)

estado ordenado (gel)

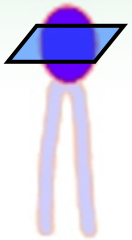




Ingredientes do modelo para lipídios neutros

Áreas por lipídio diferentes para cada um dos dois estados

gel: a_G



não-degenerado

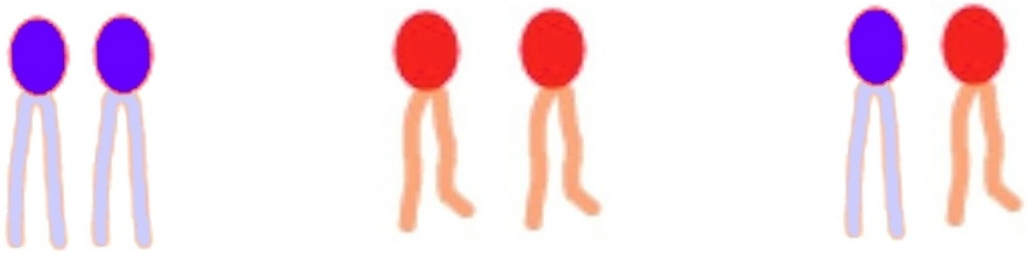
$(\Omega = 1)$

fluido: $a_F > a_G$

rotâmeros degenerados

$(\Omega > 1)$

Energia interna $U(\sigma)$: soma sobre contribuições de primeiros vizinhos



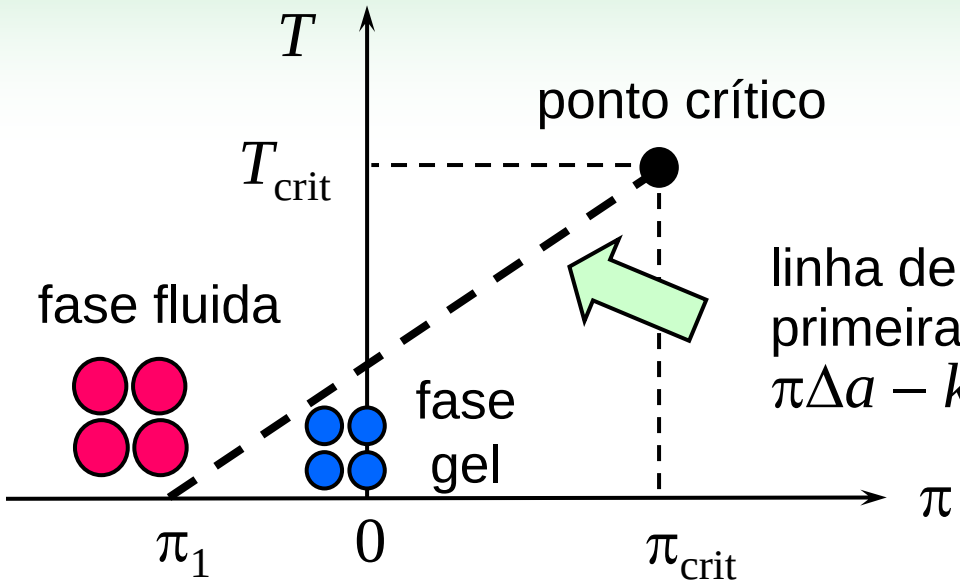
$(\varepsilon_{GG} > \varepsilon_{FF} > \varepsilon_{GF})$

$-\varepsilon_{GG}$ $-\varepsilon_{FF}$ $-\varepsilon_{GF}$

energias de interações atrativas de van der Waals

Mapeamento do problema no modelo de Ising ferromagnético 2-D

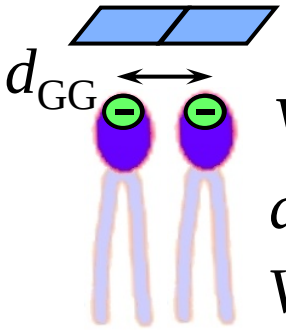
$\Delta\varepsilon = \varepsilon_{GG} - \varepsilon_{FF} > 0$, $\Delta a = a_F - a_G > 0$, z = número de coordenação da rede (= 4, para a rede quadrada), $J = ½\,(\varepsilon_{GG} + \varepsilon_{FF} - 2\varepsilon_{GF}) > 0$



$$\pi_1 = -\frac{z\Delta\varepsilon}{2\Delta a}$$

linha de transições de primeira ordem $H = ½\,(z\Delta\varepsilon/2 + \pi\Delta a - k_B T \ln \Omega) = 0$

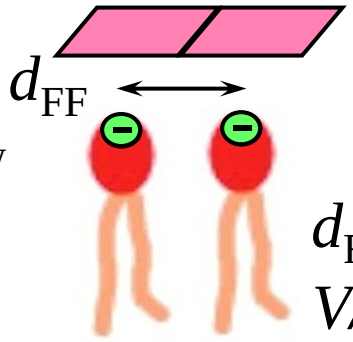
Contribuições adicionais a *U* para lipídios carregados



$V = \Phi q^2/\varepsilon_w$

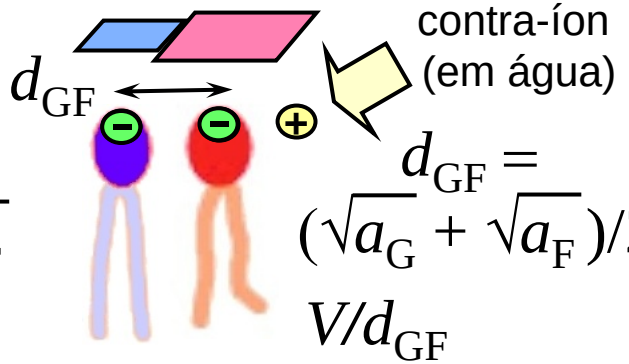
$d_{GG} = \sqrt{a_G}$

V/d_{GG}



$d_{FF} = \sqrt{a_F}$

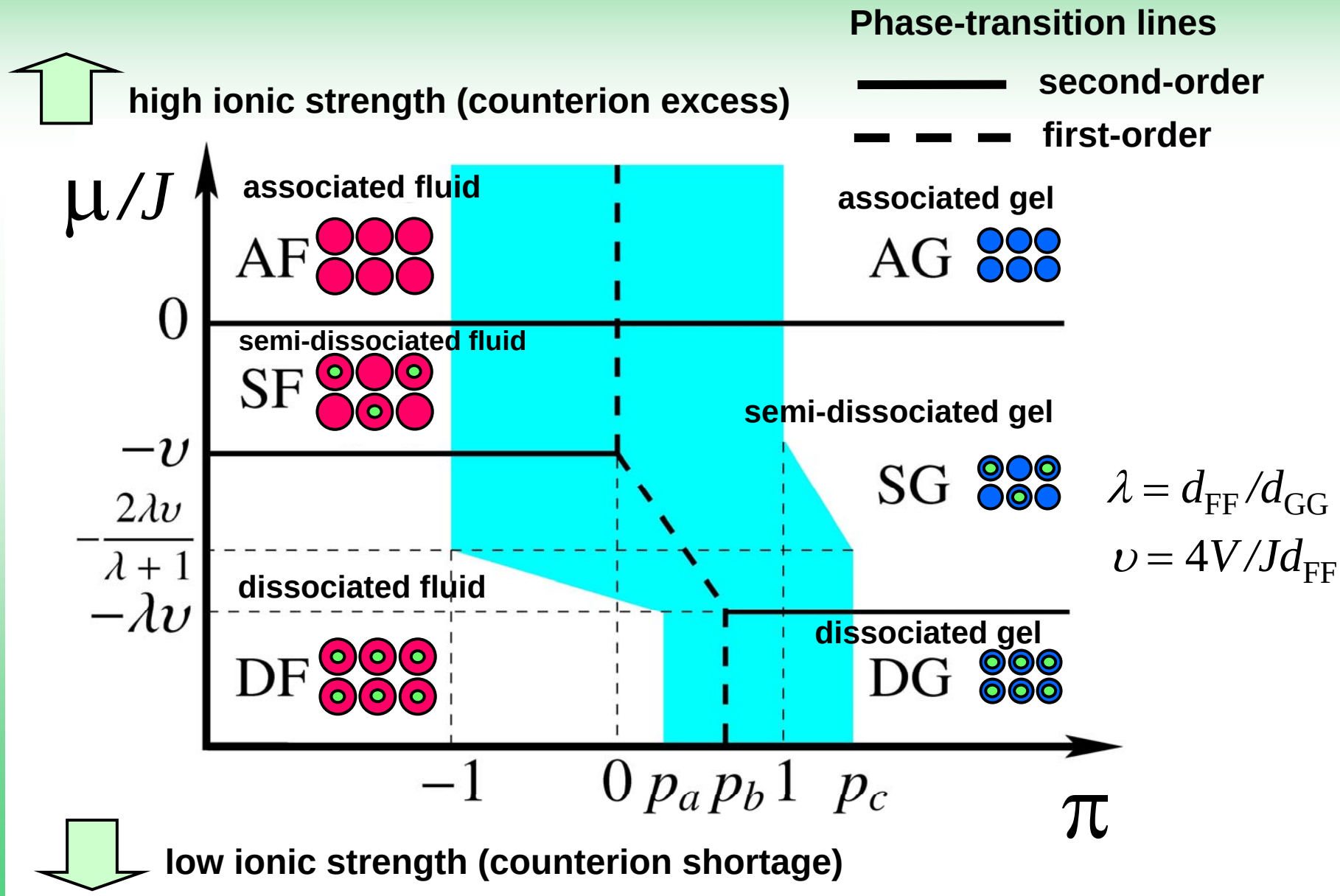
V/d_{FF}



$d_{GF} = (\sqrt{a_G} + \sqrt{a_F})/2$

V/d_{GF}

Results: ground-state ($T = 0$) phase diagram



Theoretical phase diagram and comparison with DSC peaks

first-order transition

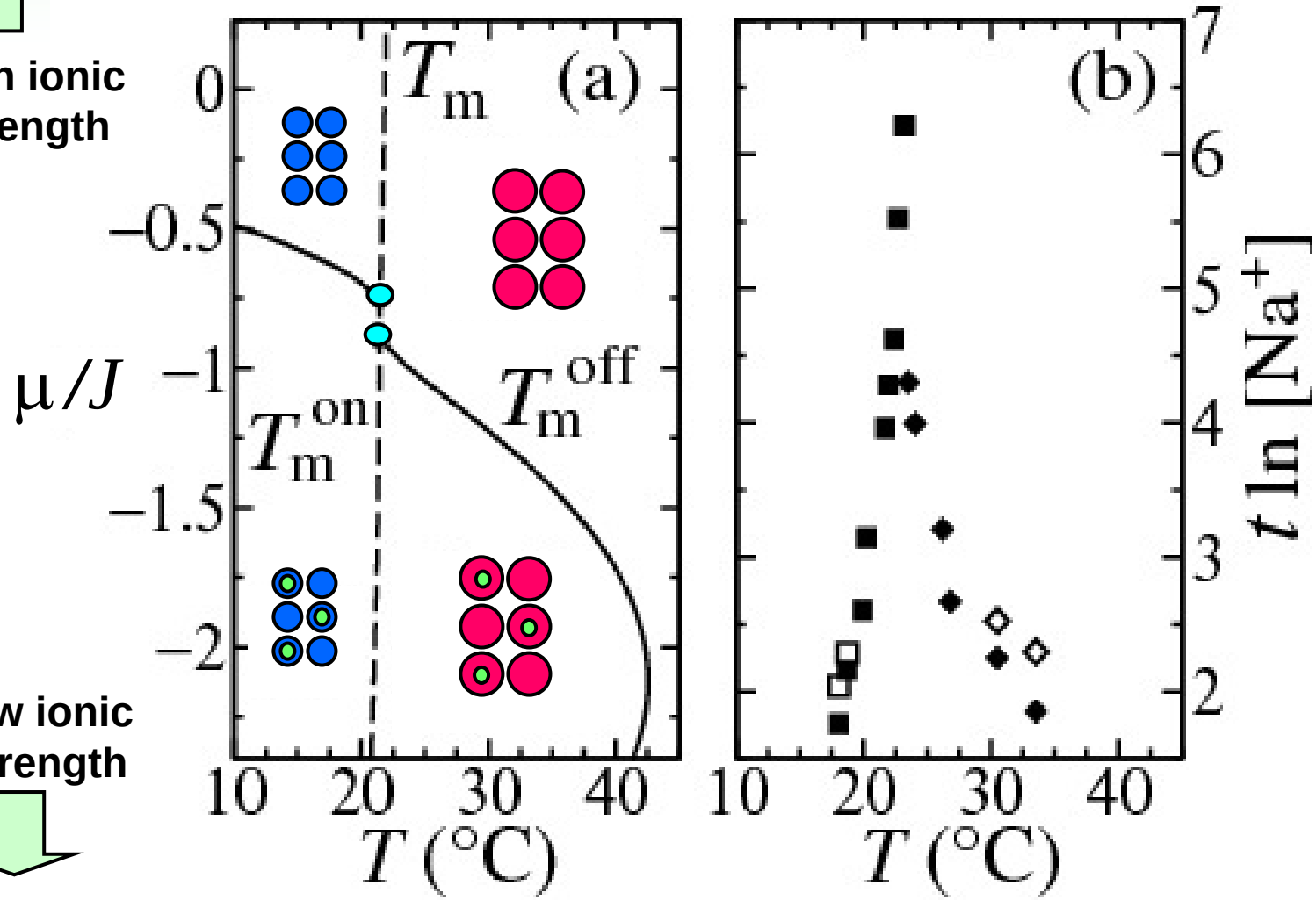
second-order transition

critical-end points

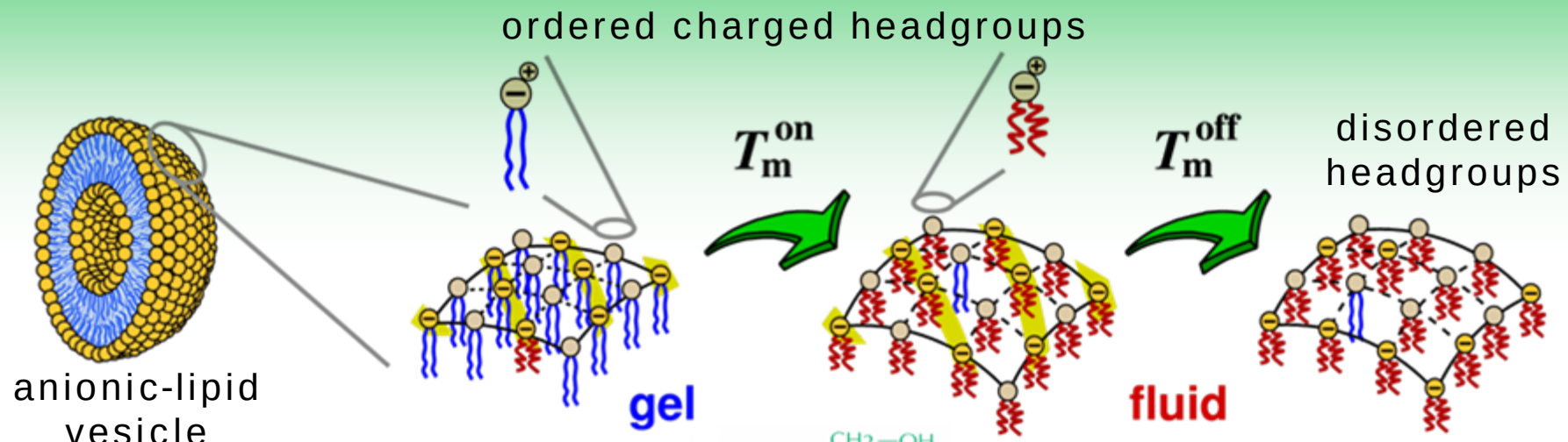
data from R. P. Barroso, Ph.D. thesis (2010)

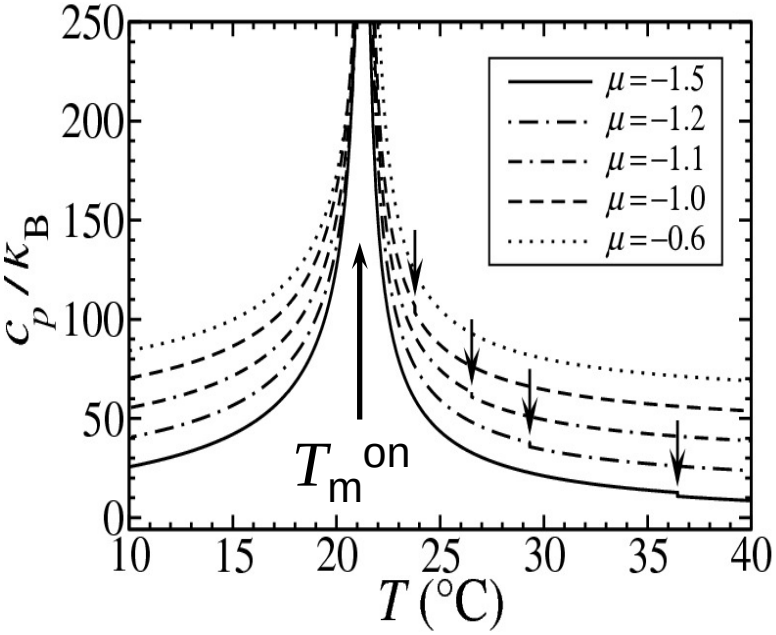
high ionic strength

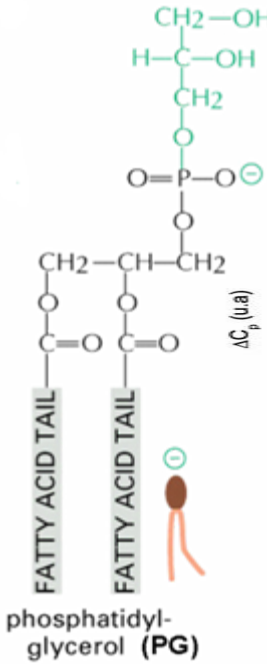
low ionic strength

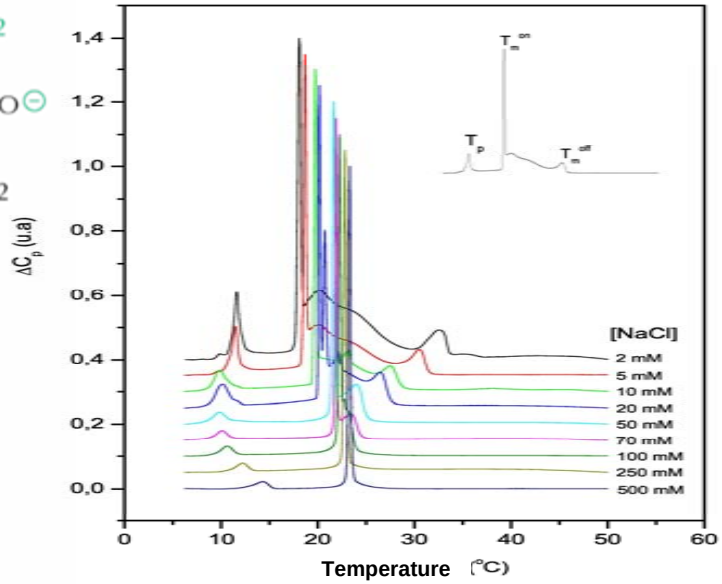


Comparison of theoretical and experimental DSC profiles





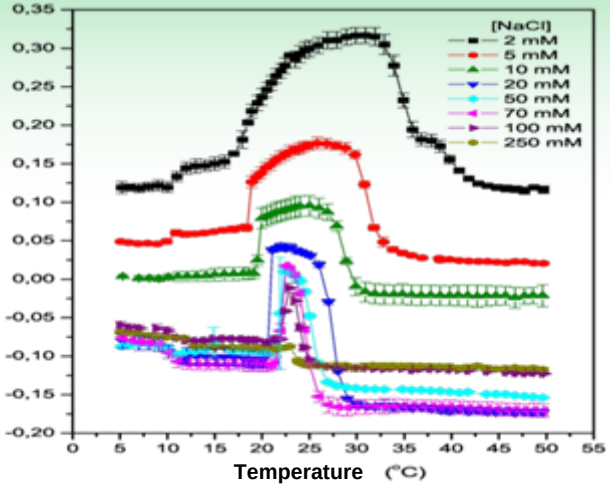




experimental data: R. P. Barroso, Ph.D. thesis, 2010 (Biophysics group IF-USP)

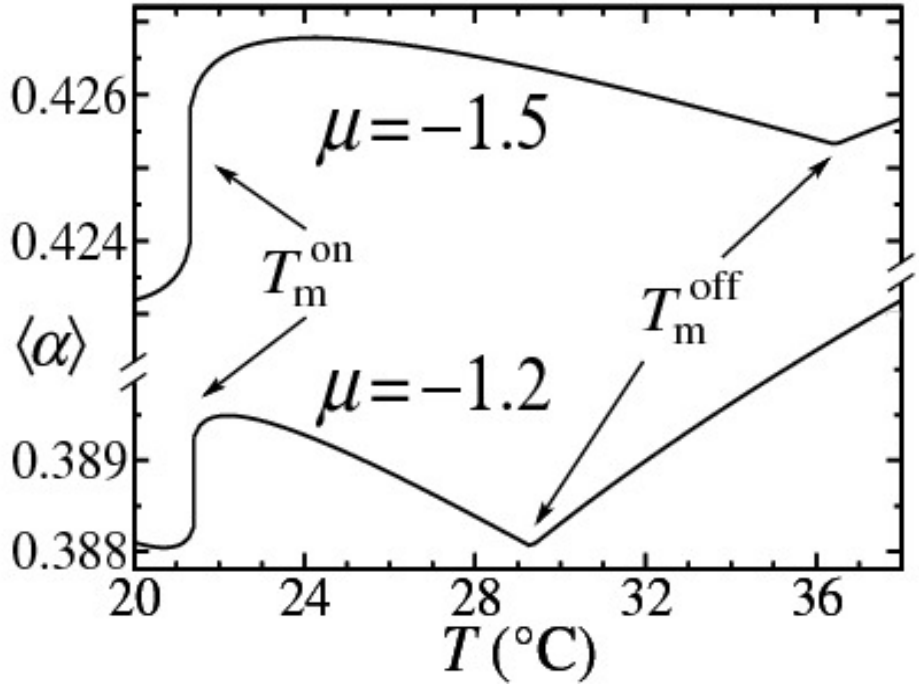
Theoretical degree of ionization α (fraction of charged lipids) and comparison with experiments

σ: conductivity

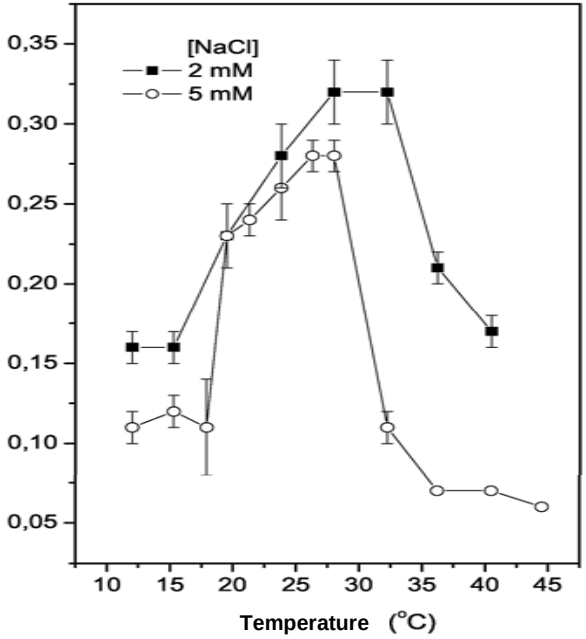


data from R. P. Barroso, Ph.D. thesis, 2010 (Biophysics group IF-USP)

+ electrophoretic mobility data



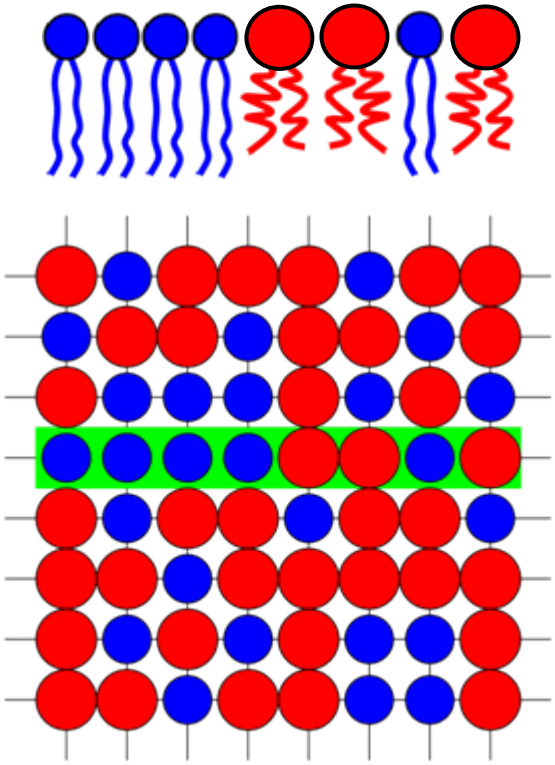
α



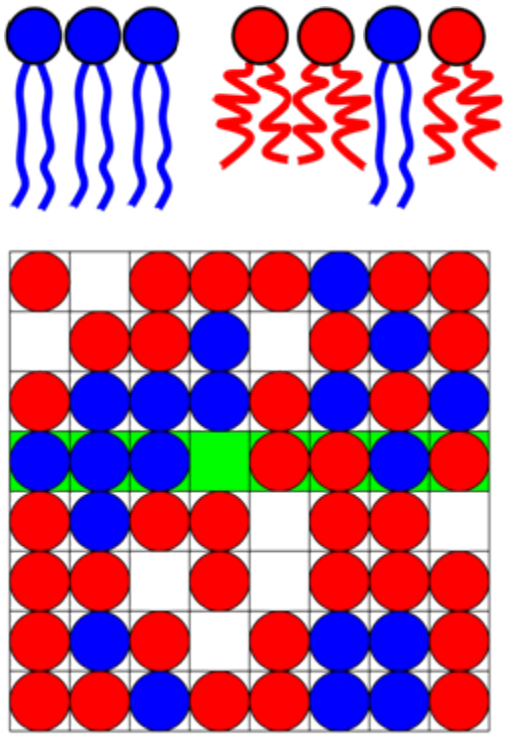
Projetos em andamento/futuros

Variação de área pode ser ***calculada*** num modelo de spin 1.
Inclusão de efeitos eletrostáticos nesta versão aprimorada do modelo.
Inclusão da contribuição dos contra-íons (determinação de μ).

modelo de spin ½
áreas dos estados
distintas e fixas (*ad hoc*)



modelo de spin 1
áreas iguais, mas com
presença de vazios



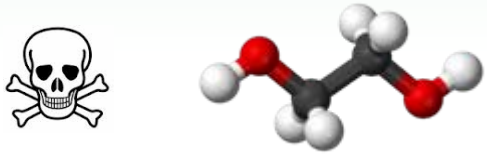
Sistema multicomponente: álcool + água + óleo(s) + polímero(s) + eletrólitos (sais, ácidos ou bases) etc.

mistura bifásica, trifásica ou polifásica

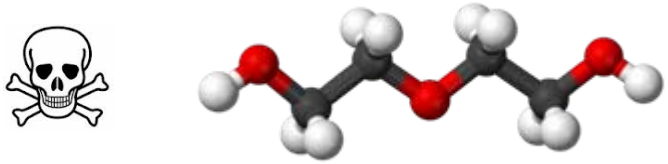
Transições de fase em soluções eletrolíticas de polímeros aquosolúveis

Tese de doutorado de Filipe Leôncio Braga (em andamento)

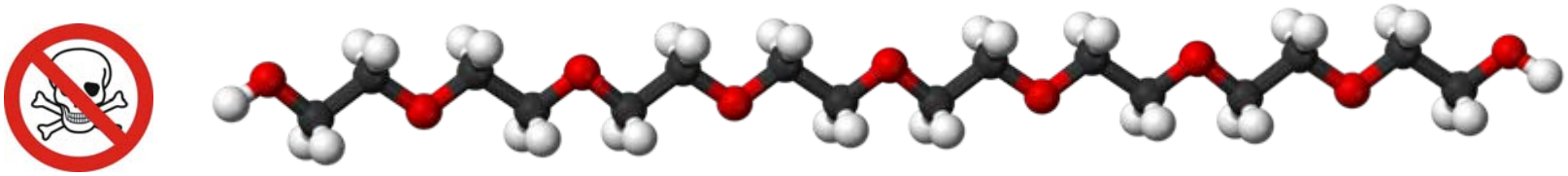
EG: etilenoglicol (monômero)



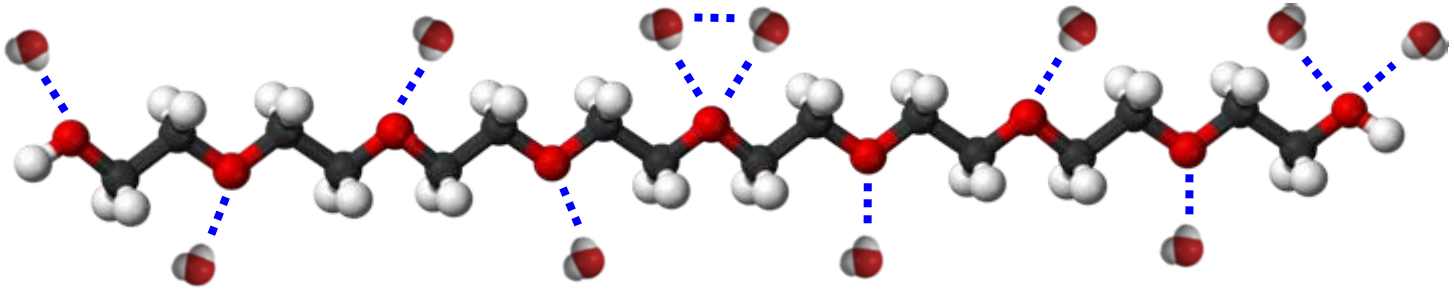
DEG: dietilenoglicol (dímero)



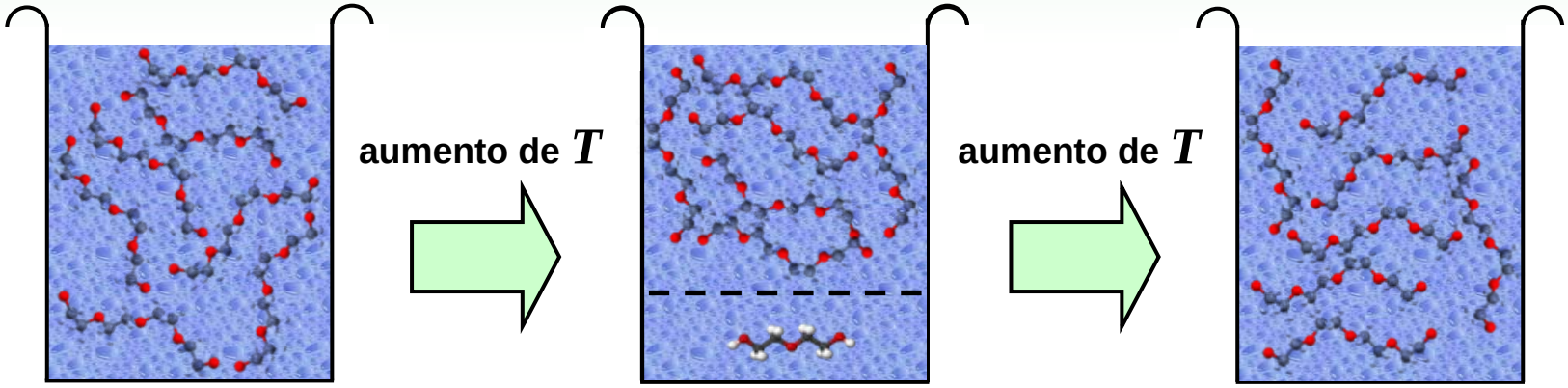
PEG: polietilenoglicol (*N*=8), também chamado PEO (polióxido de etileno)



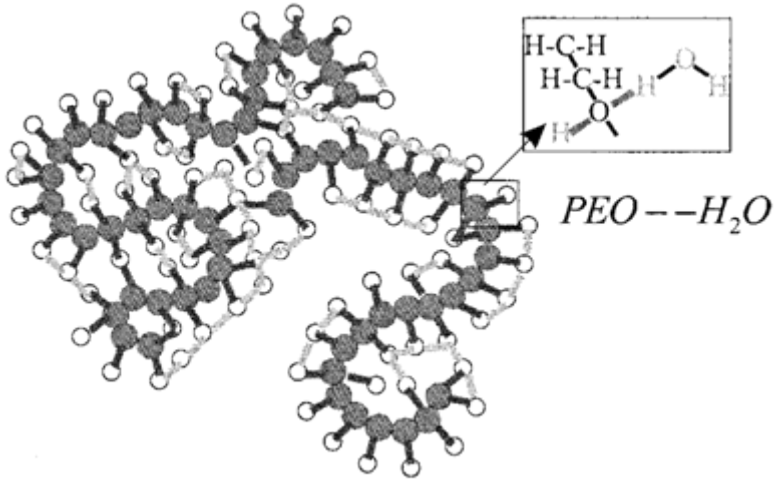
Aquosolubilidade devido à formação de ligações de hidrogênio

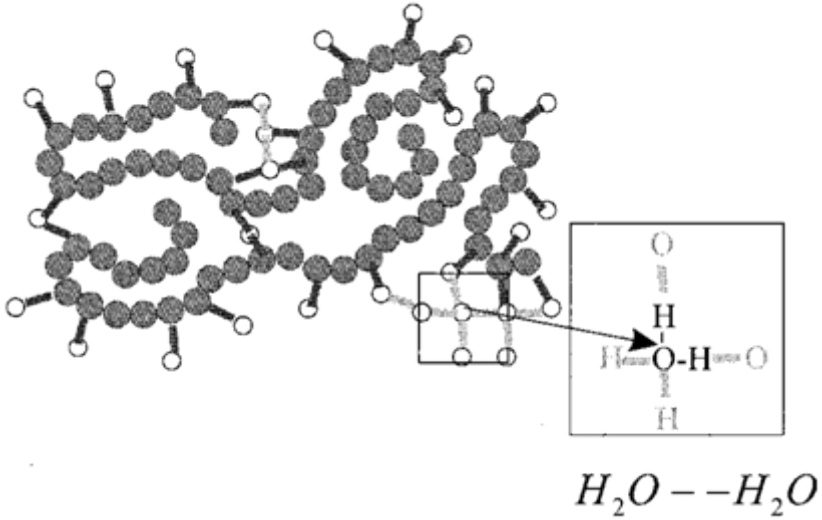


Sistema experimental sem eletrólitos



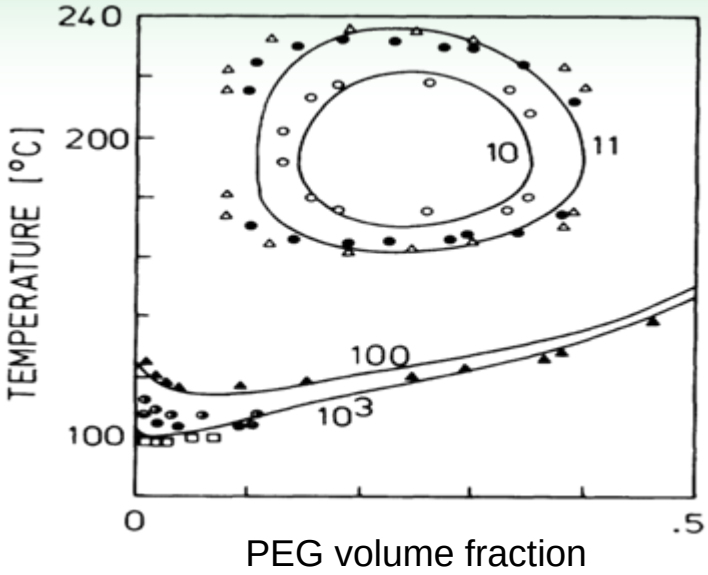
mistura monofásica mistura bifásica mistura monofásica

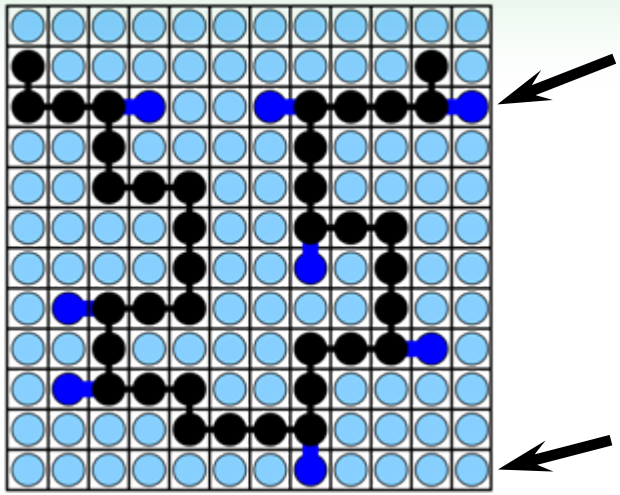




baixas temperaturas temperaturas altas ou intermediárias

Modelo na rede (Flory-Huggins) + formação de ligações de hidrogênio com a água





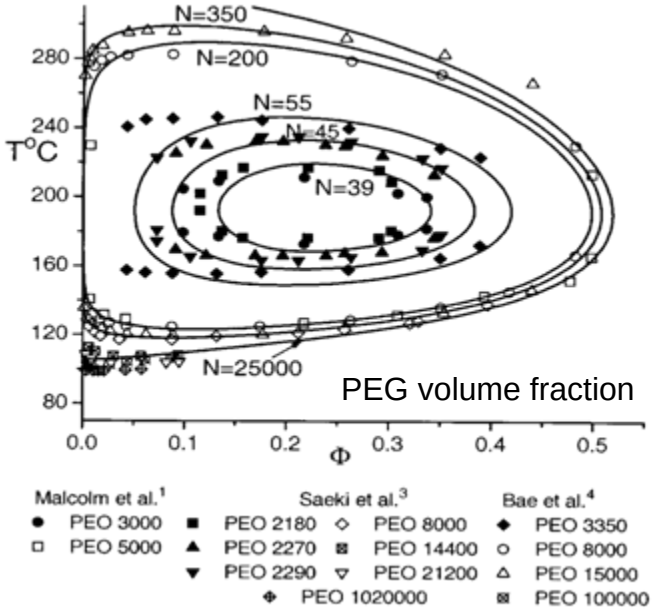
A. Matsuyama, F. Tanaka,

Phys. Rev. Lett. **65**, 341 (1990)

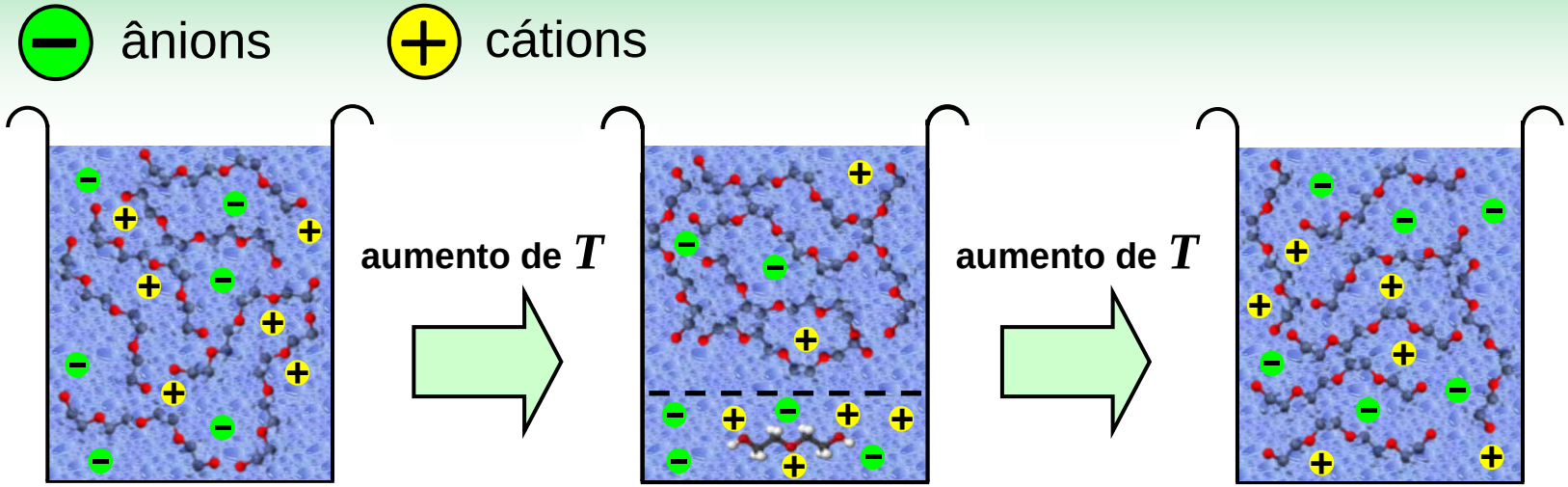
Solução do problema através do equilíbrio químico entre espécies com diferentes números de ligações de hidrogênio.

E. E. Dormidontova,

Macromolecules **35**, 987 (2002)

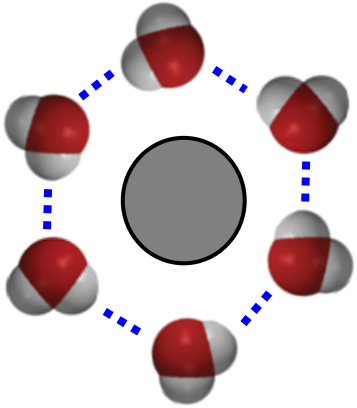


Sistema experimental com eletrólitos

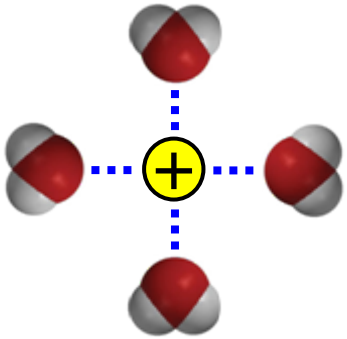


mistura monofásica | mistura bifásica | mistura monofásica

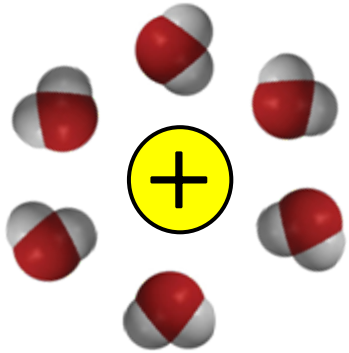
diferentes tipos de hidratação devem ser considerados



soluto apolar
hidratação hidrofóbica



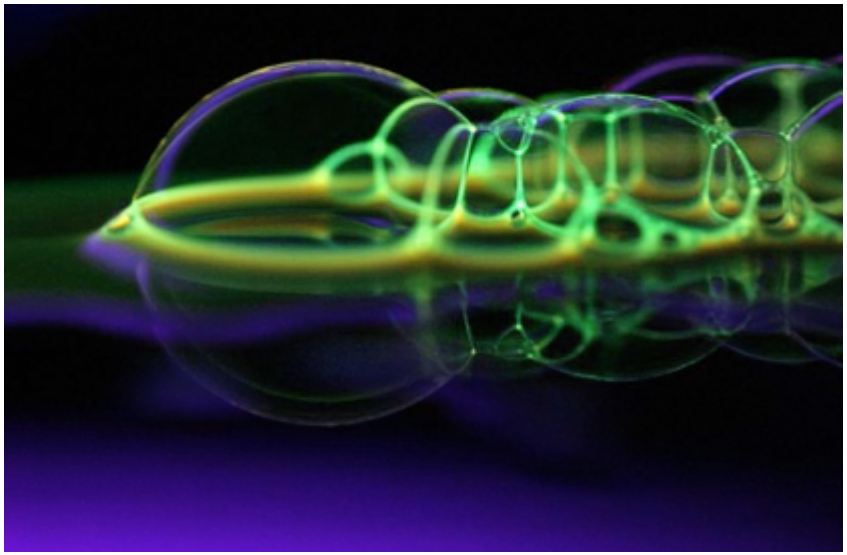
cátion cosmotrópico
forma hidratação



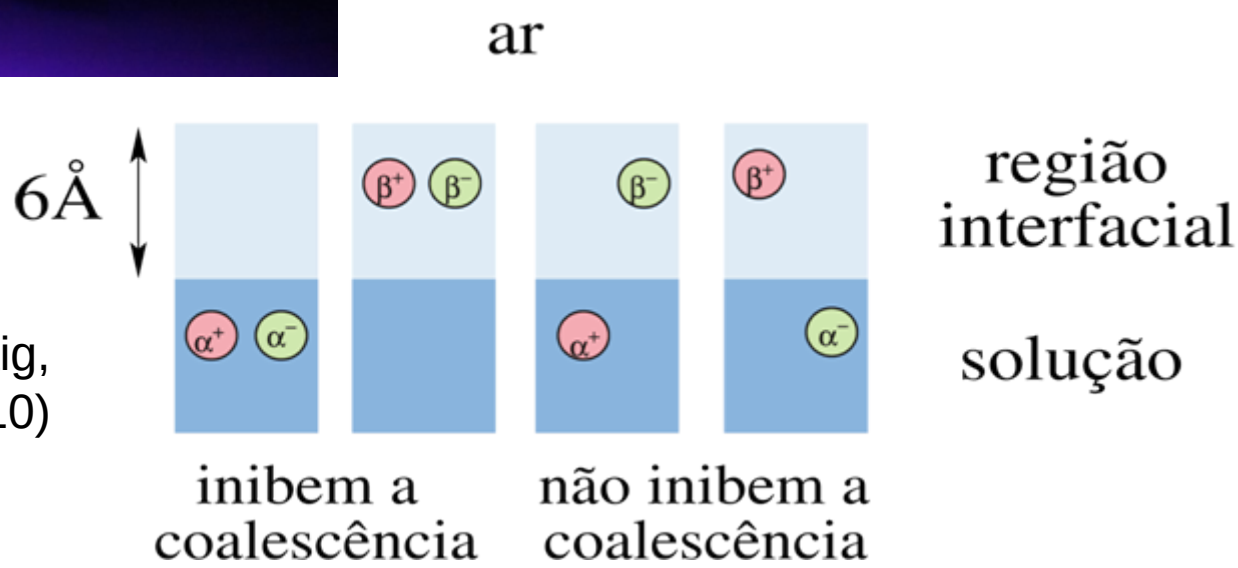
cátion caotrópico
quebra hidratação

Íons em interfaces dielétricas

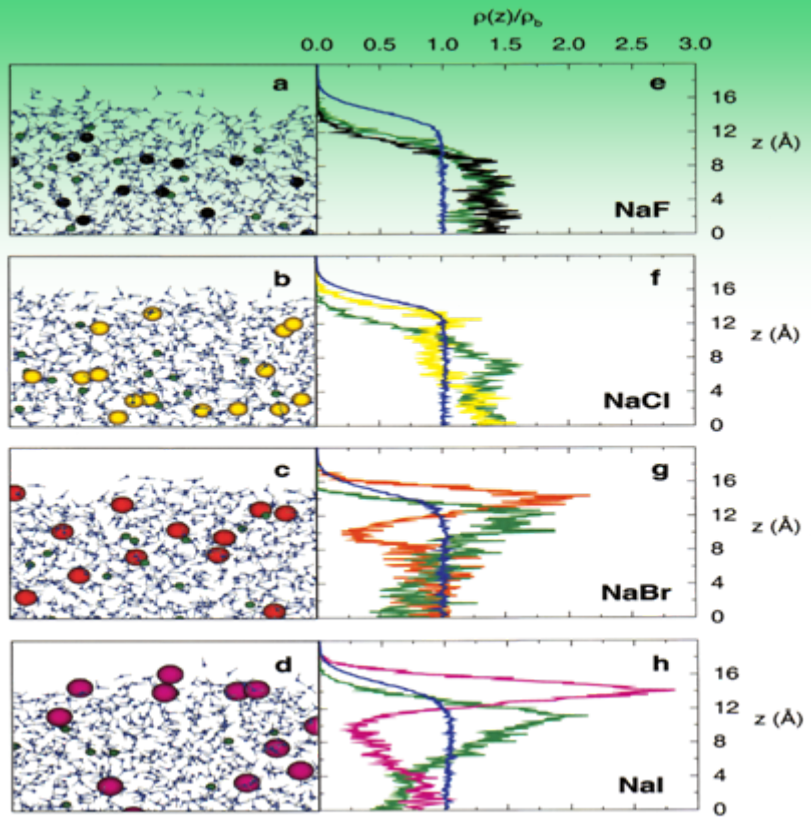
Dissertação de mestrado de Maíra Alves Constantino
M. N. Tamashiro, M. A. Constantino, *J. Phys. Chem. B* **114**, 3583 (2010)



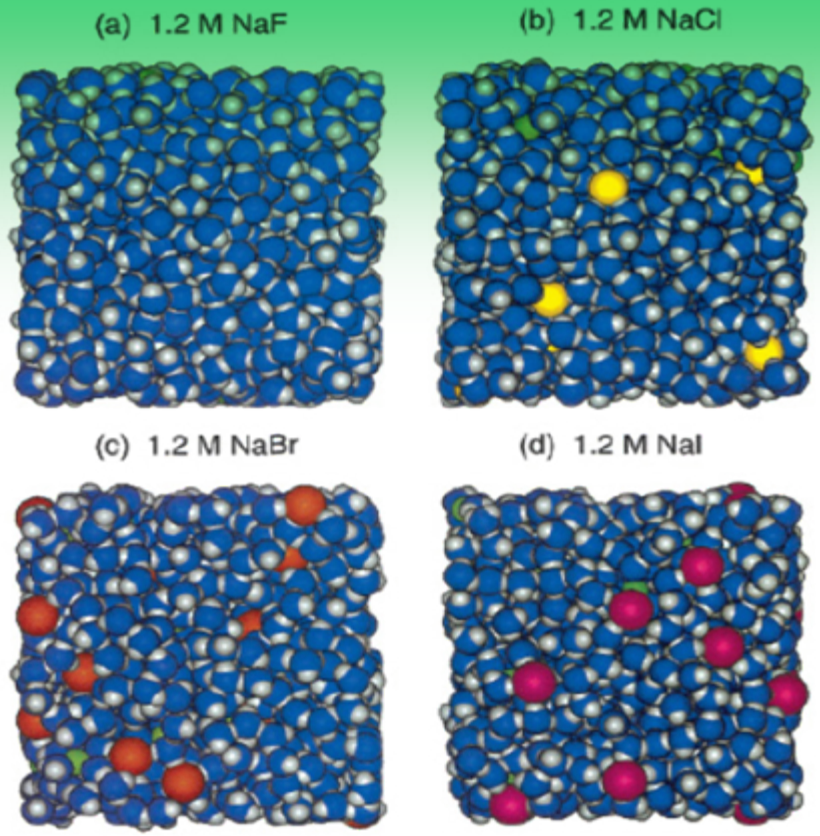
Coalescência de bolhas com eletrólitos (filmes líquidos em ar)



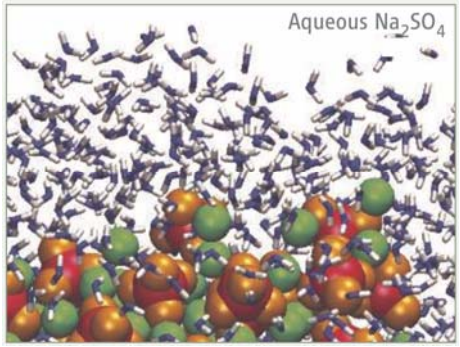
C. L. Henry, V. S. J. Craig, *Langmuir* **26**, 6478 (2010)

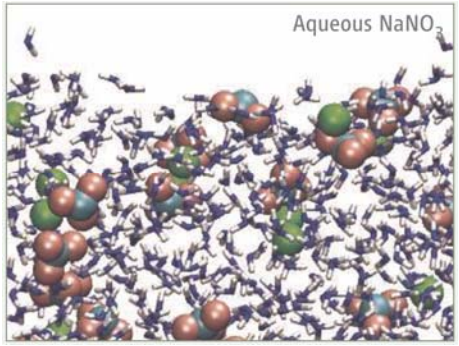


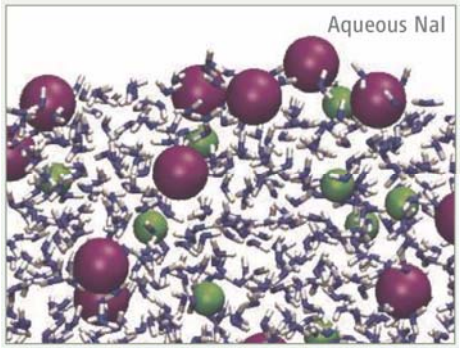
P. Jungwirth, D. J. Tobias,
J. Phys. Chem. B **105**, 10468 (2001)



P. Jungwirth, D. J. Tobias,
J. Phys. Chem. B **106**, 6361 (2002)







D. J. Tobias, J. C. Hemmer, *Science* **319**, 1197 (2008)

Obrigado pela atenção!