

# Coloides e Superfícies

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Bloco 3 térreo, sala 307

**Coloides**, colar em grego “κολιέ”

Thomas Graham (1805-1869)

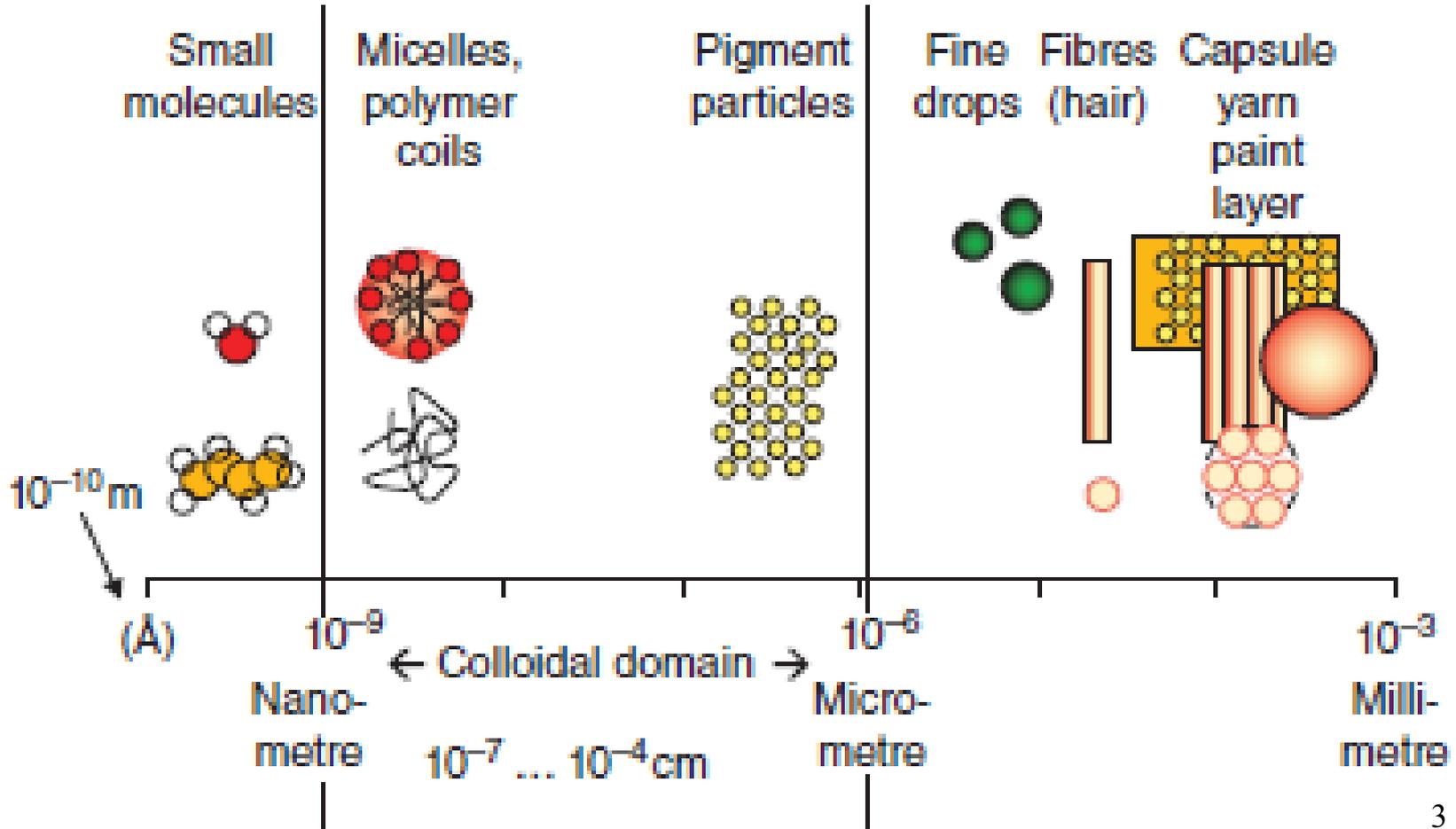


**Superfícies**, latim “superficiem”

- extensão de terra ou ao limite de um corpo
- aspecto exterior de alguma coisa
- magnitude/grandeza que indica a extensão de um corpo em duas dimensões (comprimento e largura)

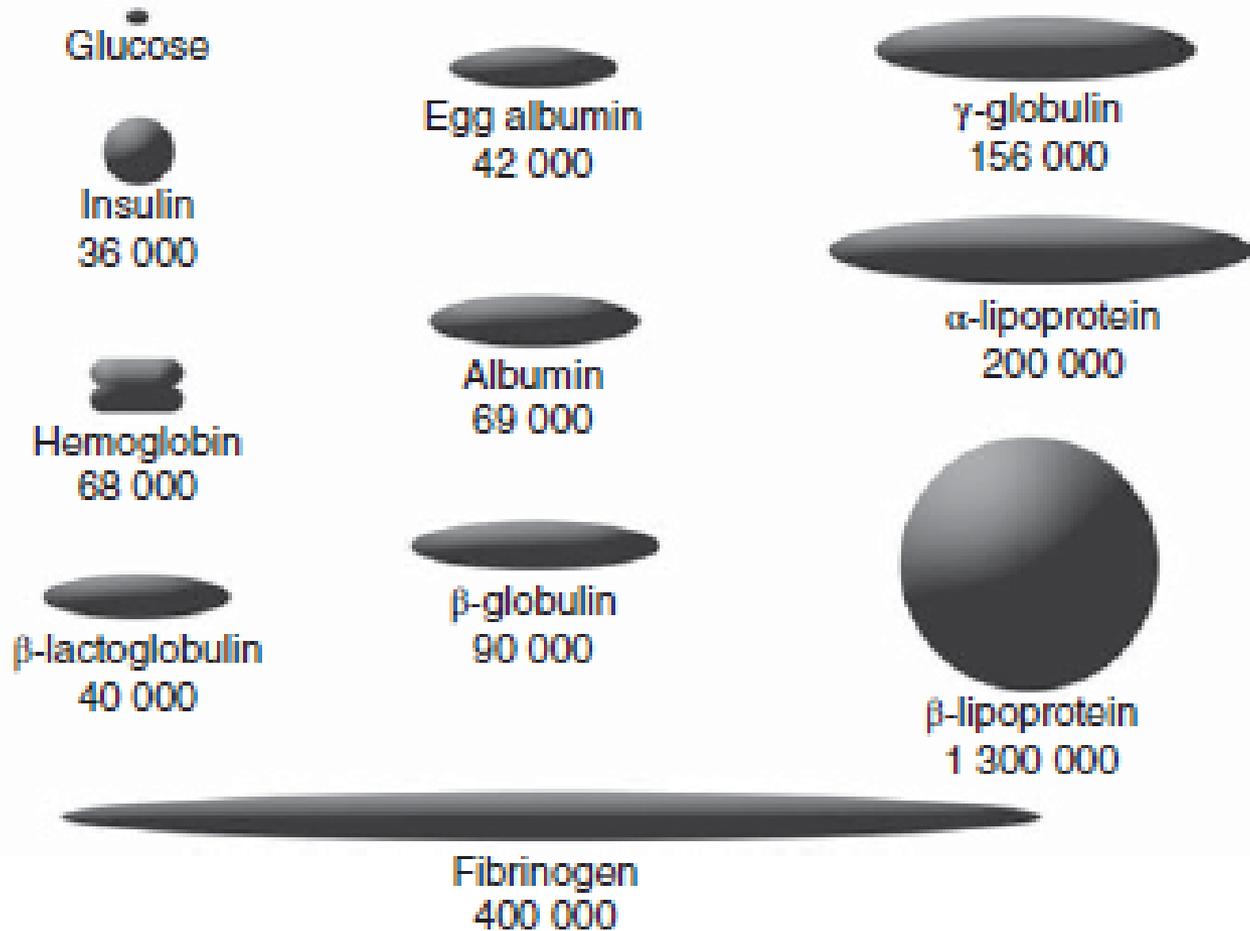
# Colóides: estruturas esféricas com dimensões típicas na faixa de 1nm a 1 μm.

Tamanho



# Forma

Scale  
100 Å



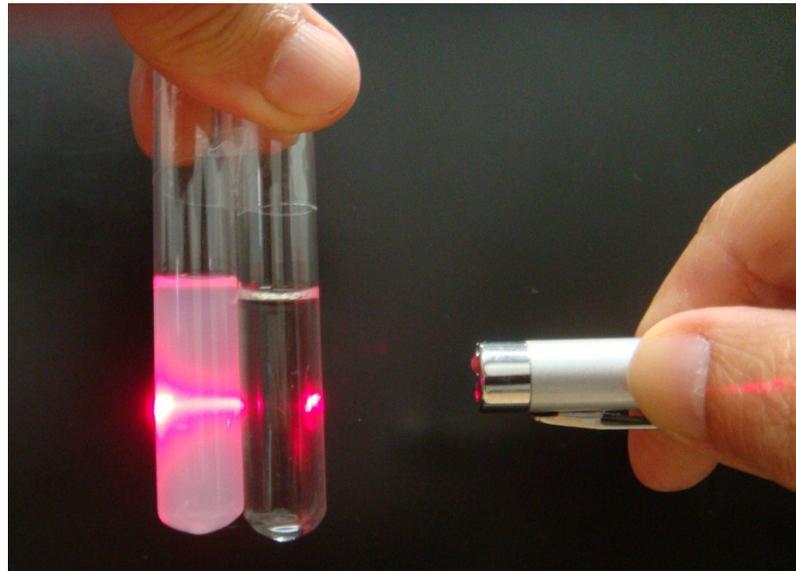
**Dispersões coloidais são compostas por uma fase dispersa (coloides) e uma fase contínua.**

		Continuous phase		
		Gas	Liquid	Solid
Dispersed phase	Gas	None	Foam (shaving cream)	Solid foam (polystyrene cup)
	Liquid	Liquid aerosol (fog, mist)	Emulsion (mayonnaise, milk)	Gel (gelatin)
	Solid	Solid aerosol (dust, smoke)	Sol (paint, mud)	Solid sol (Stained glass)

## Como diferenciar dispersões coloidais de soluções verdadeiras?

coloides dispersam fortemente a luz, pois as partículas dispersas têm tamanhos semelhantes ao comprimento de onda da luz visível → **efeito de Tyndall**

Macromoléculas dissolvidas em um solvente assumem dimensões coloidais ( $< \sim 20$  nm) e causam espalhamento de luz difícil de ser observado a olho nu



# FORÇAS INTERMOLECULARES

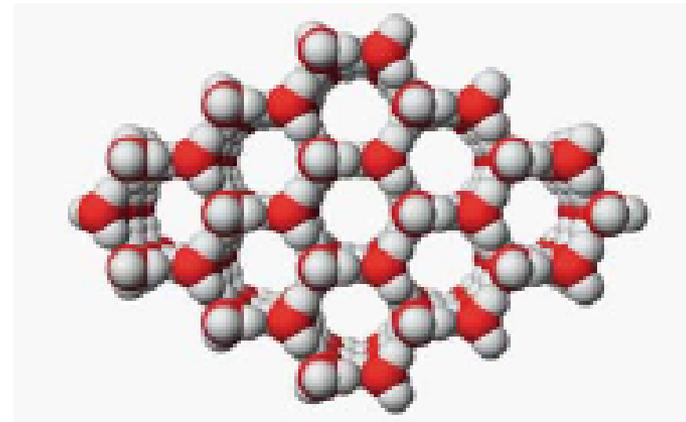
- Atuam na formação e no comportamento dos coloides e superfícies
- Dependem da:
  - Natura química das moléculas
  - Posição das moléculas (energia potencial)
  - Temperatura do meio (energia cinética)

Have studied **INTRA**molecular forces—the forces holding atoms together to form molecules.

Now turn to forces between molecules — **INTER**molecular forces.

Forces between molecules, between ions, or between molecules and ions.

## Inter-molecular Forces



$\epsilon_0$  = const. dielétrica  
vácuo =  
 $8.854 \times 10^{-12} \text{ C}^2 \text{J}^{-1} \text{m}^{-1}$

<b>Tipo de interação</b>	<b>Potencial x Distância</b>	<b>Energia típica (kJ/mol)</b>
Íon – íon	$\frac{(ze)_1(ze)_2}{(4\pi\epsilon_0\epsilon)r}$	100 a 600
Íon-dipolo permanente	$\frac{(ze)_1\mu_2\cos\theta}{(4\pi\epsilon_0\epsilon)r^2}$	15-60
<b>Dipolo perman. - dipolo permanente (Keesom)</b>	$\frac{2(ze)_1\mu_2\cos\theta}{3(4\pi\epsilon_0\epsilon)^2k_B r^6}$	2
<b>Dipolo perman. - dipolo induzido (Debye)</b>	$\frac{\alpha_1\mu_2^2 + \alpha_2\mu_1^2}{(4\pi\epsilon_0\epsilon)^2 r^6}$	2
<b>Dipolo induzido -dipolo induzido (London)</b>	$\frac{3h}{2} \frac{\omega_1\omega_2}{(\omega_1+\omega_2)} \frac{\alpha_1\alpha_2}{(4\pi\epsilon_0\epsilon)^2 r^6}$	1 a 2

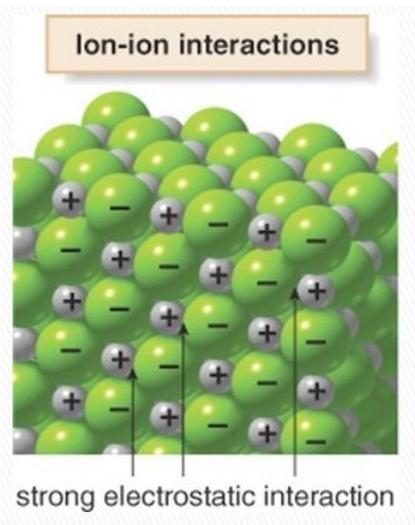
Forças de van der Waals

Ligações de H:  
~ 10 a 40 kJ/mol

## Tipo de interação

Íon – íon

$$V_{12} = \frac{(ze)_1(ze)_2}{(4\pi\epsilon_0\epsilon)r}$$



## NaCl

p.f. = 801 °C

p.e. = 1413 °C

Solubilidade

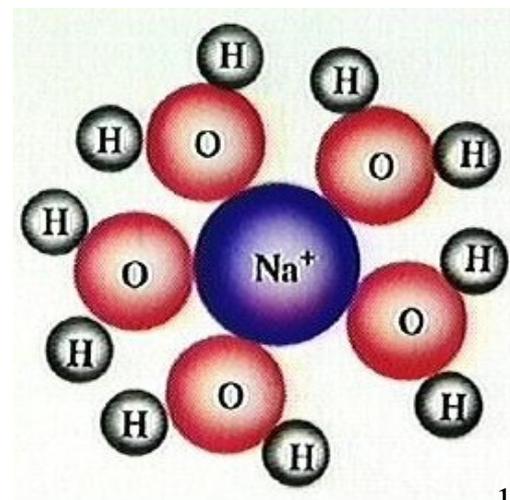
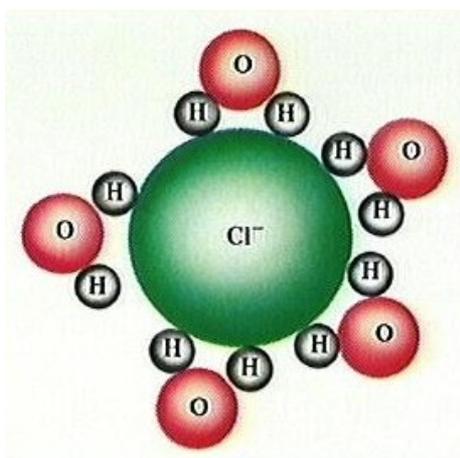
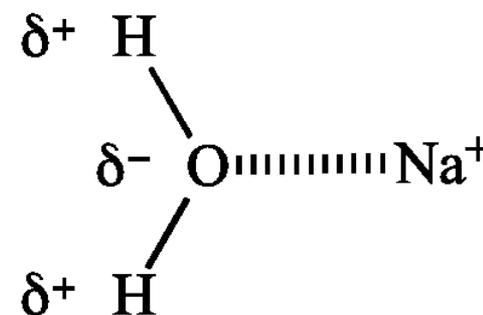
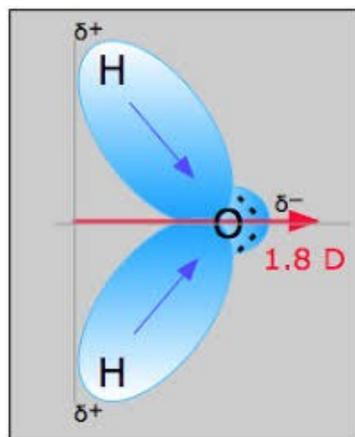
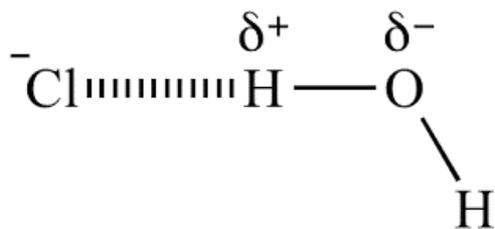
359 g/L (H<sub>2</sub>O),  $\epsilon = 80$

14,9 g/L (CH<sub>3</sub>OH),  $\epsilon = 32,7$

# Tipo de interação

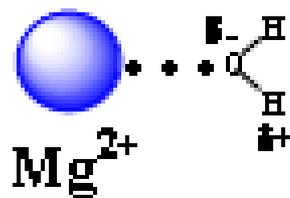
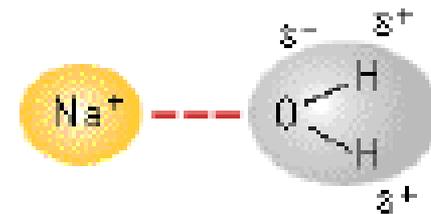
Íon – dipolo permanente

$$V_{12} = \frac{(ze)_1 \mu_2 \cos\theta}{(4\pi\epsilon_0\epsilon)r^2}$$

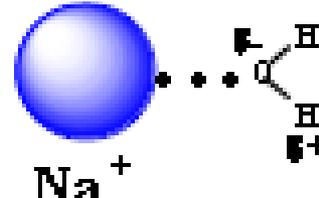


$$1D = 3.336 \times 10^{-30} \text{ C m}$$

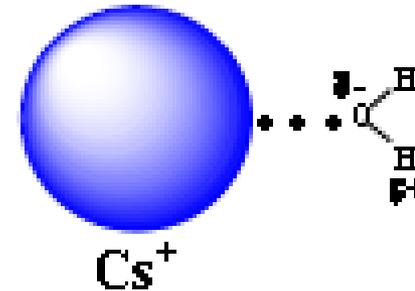
# Attraction Between Ions and Permanent Dipoles



$\text{Mg}^{2+}$



$\text{Na}^+$



$\text{Cs}^+$

-1922 kJ/mol

-405 kJ/mol

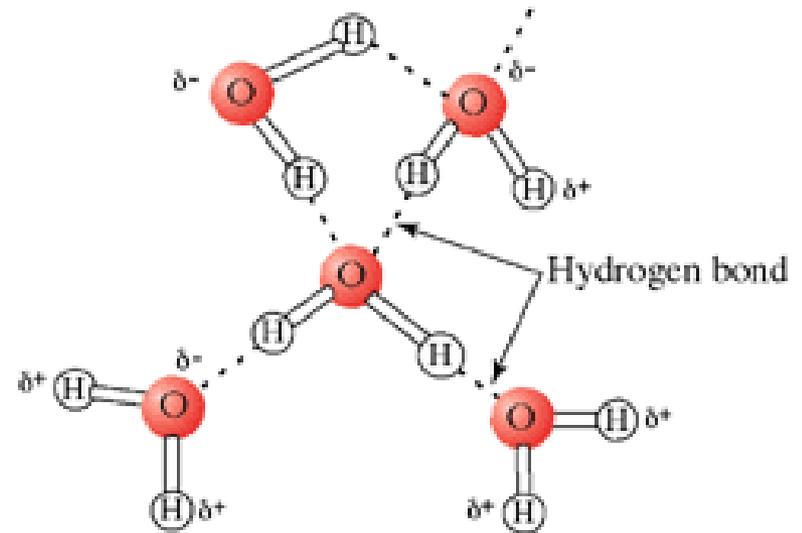
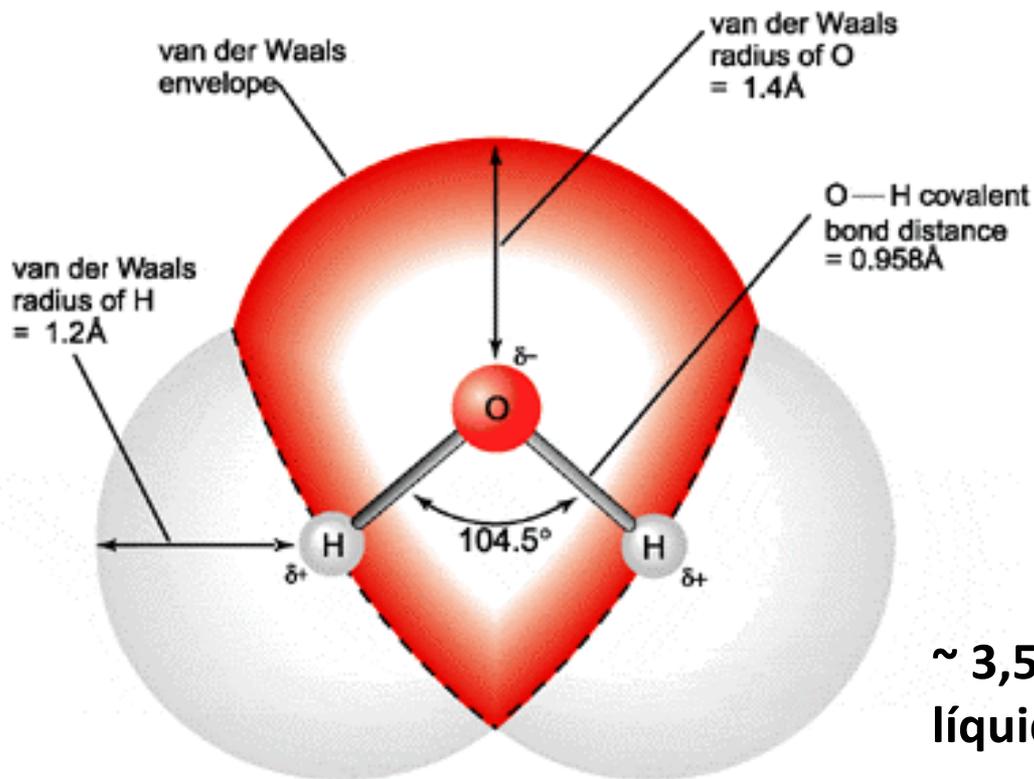
-263 kJ/mol

Attraction between ions and dipole depends on **ion charge** and **ion-dipole distance**.

Measured by  $\Delta H$  for  $\text{M}^{n+} + \text{H}_2\text{O} \rightarrow [\text{M}(\text{H}_2\text{O})_x]^{n+}$

# Tipo de interação

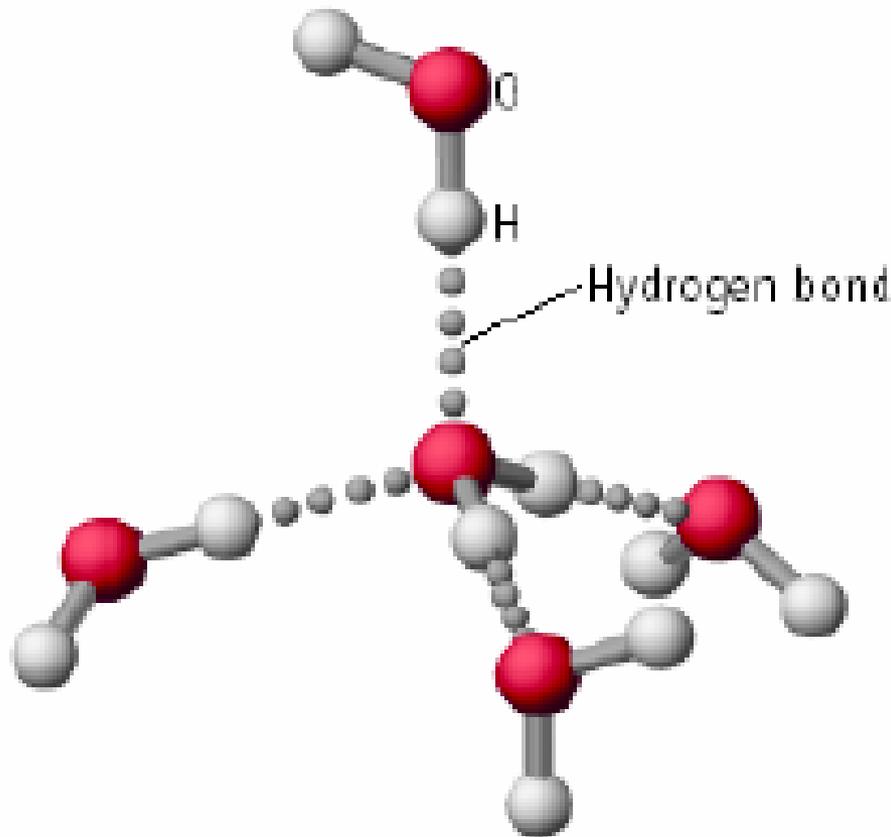
## Ligações de H (F, N, O)



~ 3,5 ligações de H/molécula na água líquida, alta  $E_{cin} \sim 10^{-12}$  s

# Hydrogen Bonding in H<sub>2</sub>O

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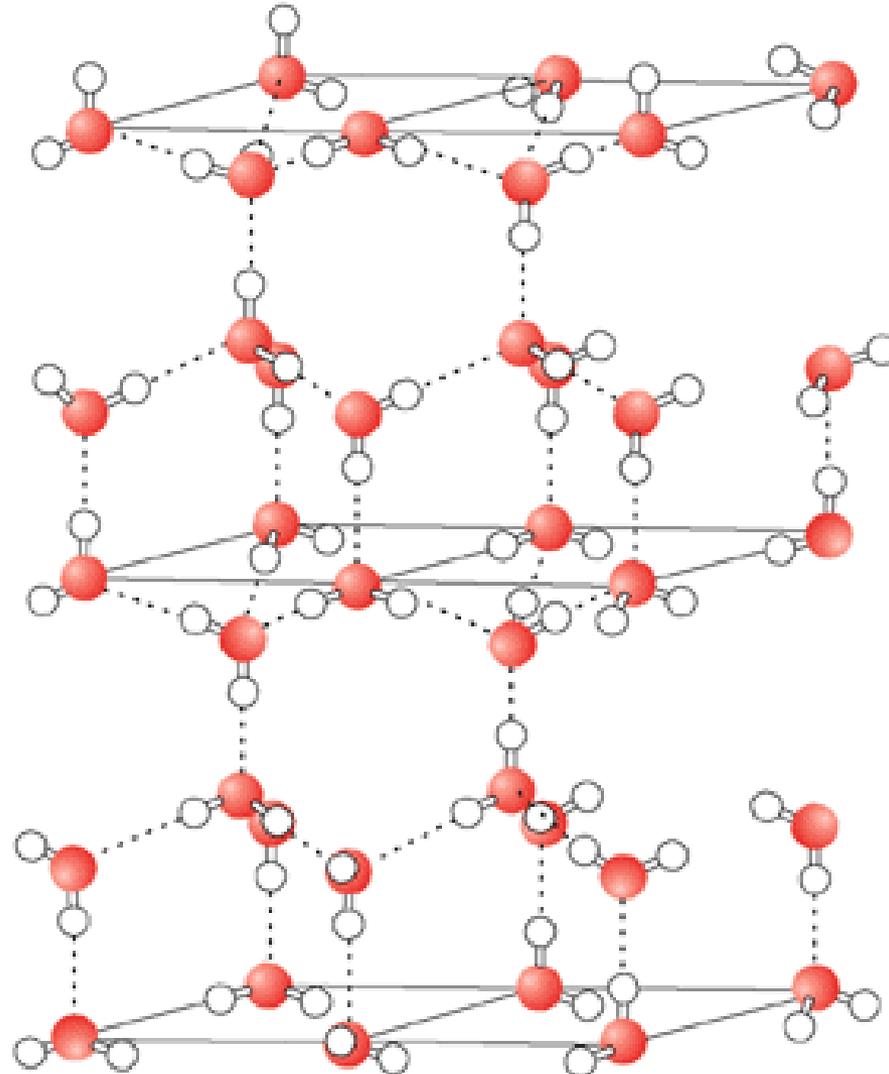


H-bonding is especially strong in water because

- the O—H bond is very polar
- there are 2 lone pairs on the O atom

Accounts for many of water's unique properties.

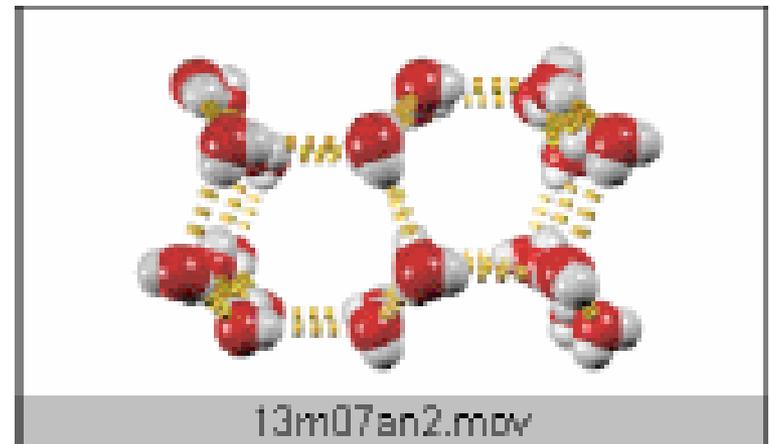
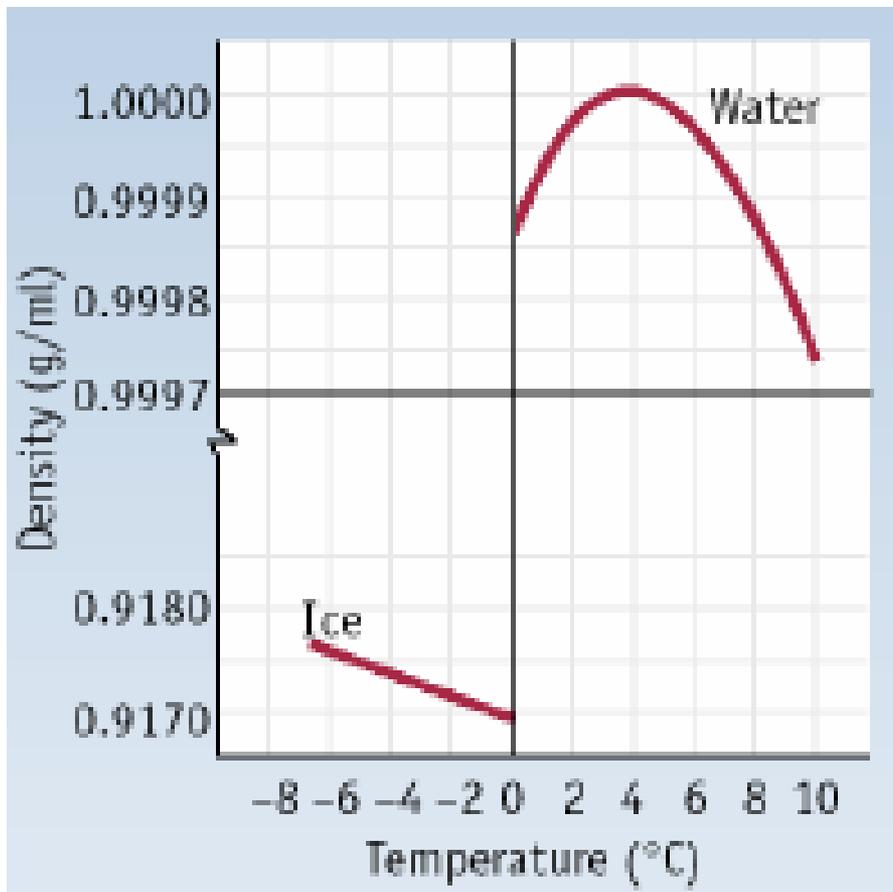
**Gelo (baixa  $E_{cin}$ ): 4 ligações de H → as moléculas estão mais afastadas que no líquido, formando estrutura hexagonal e cavidades → menor densidade que líquido**



# Hydrogen Bonding in H<sub>2</sub>O

**Ice has open lattice-like structure.**

**Ice density is < liquid and so solid floats on water.**

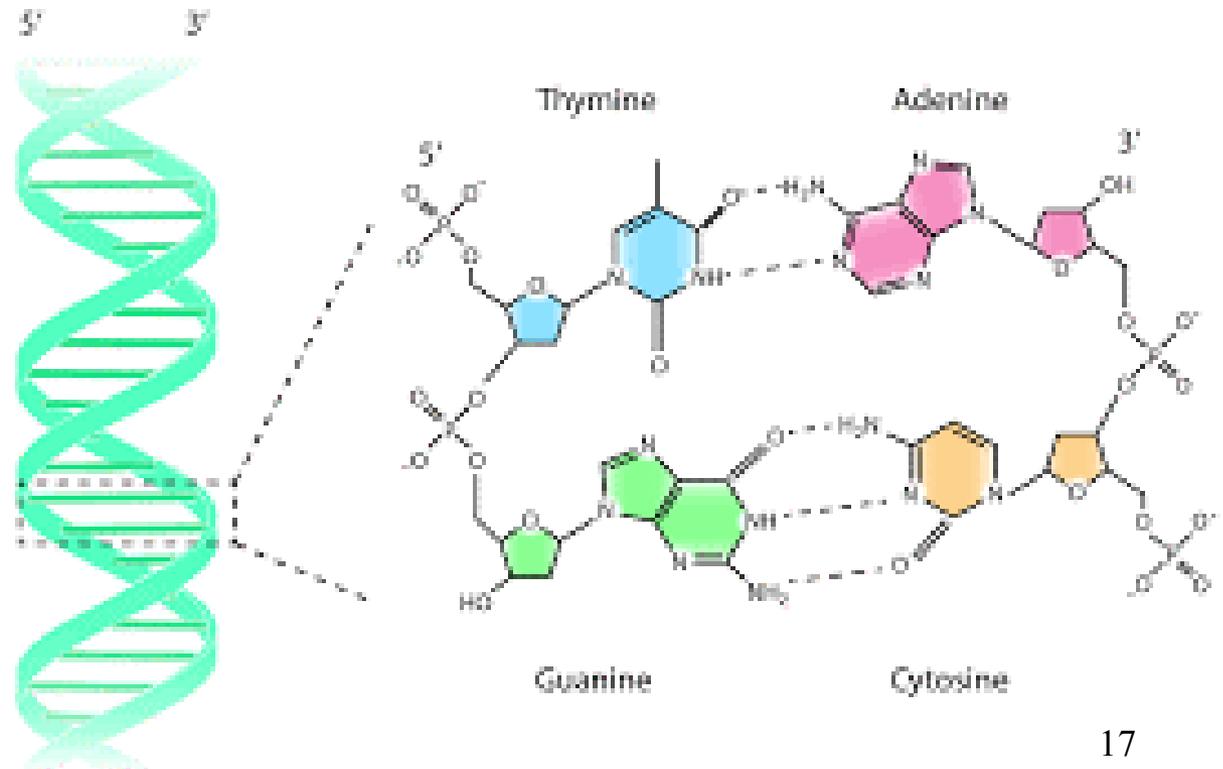


p.e.  $\text{CH}_3\text{CH}_2\text{OH} = 79\text{ }^\circ\text{C}$ , momento dipolar = 1,7 D

p.e.  $\text{CH}_3\text{OCH}_3 = -25\text{ }^\circ\text{C}$ , momento dipolar = 1,3 D

p.e.  $\text{H}_2\text{O} = 100\text{ }^\circ\text{C}$

p.e.  $\text{H}_2\text{S} = -60\text{ }^\circ\text{C}$



# FORÇAS DE VAN DER WAALS

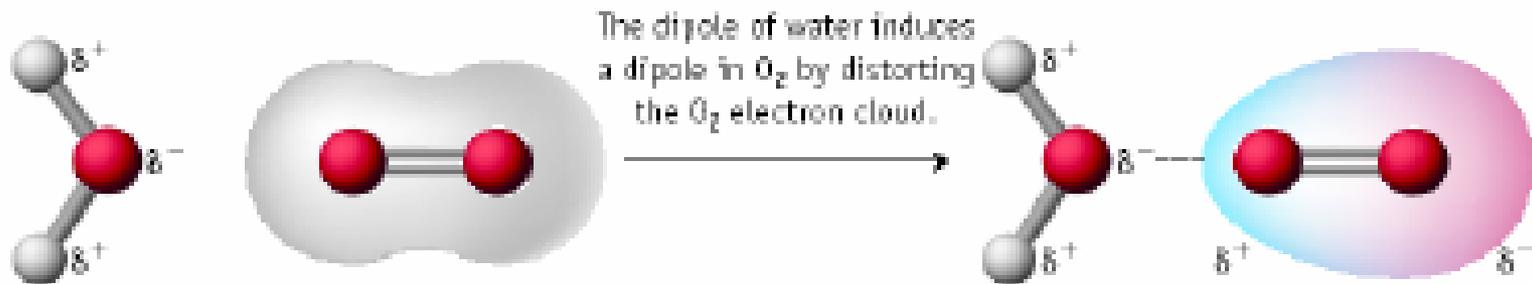
- SÃO INTERAÇÕES ENTRE DIPOLO-DIPOLO OU DIPOLO-DIPOLO INDUZIDO QUE GOVERNAM PROPRIEDADES MACROSCÓPICAS DA MATÉRIA (KEESOM + DEBYE + LONDON);
- SÃO SEMPRE INTERAÇÕES ATRATIVAS;
- SÃO DE CURTO ALCANCE ( $E_{\text{potencial}}$ );
- ESPECIALMENTE IMPORTANTES PARA MOLÉCULAS ORGÂNICAS.

## **Implicações macroscópicas:**

- Calor de vaporização de líquidos
- Viscosidade
- Coesão ou adesão
- Auto-associação
- Estabilidade coloidal

# FORCES INVOLVING INDUCED DIPOLES

How can non-polar molecules such as  $O_2$  and  $I_2$  dissolve in water?



The water dipole **INDUCES** a dipole in the  $O_2$  electric cloud.

13m05an2.mov

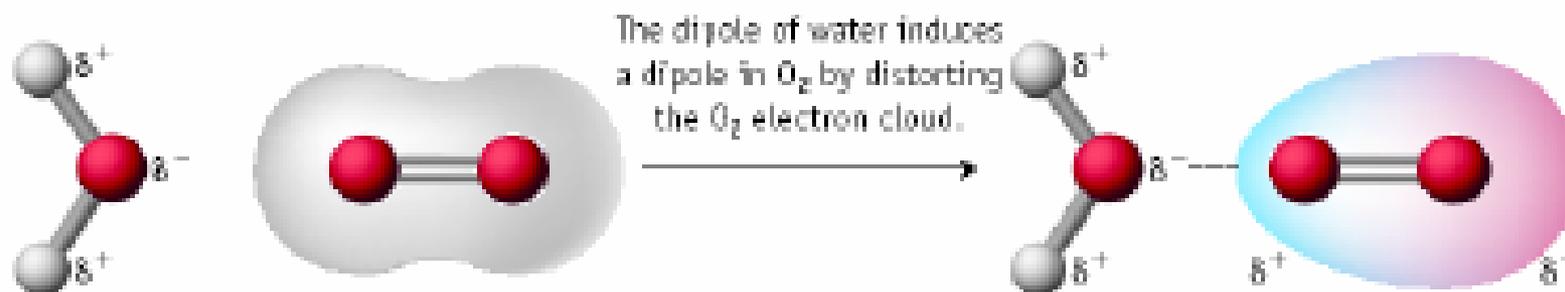
Dipole-induced dipole

# FORCES INVOLVING INDUCED DIPOLES

Solubility increases with mass the gas

**Table 13.2 • The Solubility of Some Gases in Water\***

Gas	Molar Mass (g/mol)	Solubility at 20 °C (g gas/100 g water)†
H <sub>2</sub>	2.01	0.000160
N <sub>2</sub>	28.0	0.000190
O <sub>2</sub>	32.0	0.000434



## FORCES INVOLVING INDUCED DIPOLES

The magnitude of the induced dipole depends on the tendency to be distorted.

Higher molec. weight  $\rightarrow$  larger induced dipoles.

<u>Molecule</u>	<u>Boiling Point (°C)</u>
CH <sub>4</sub> (methane)	- 161.5
C <sub>2</sub> H <sub>6</sub> (ethane)	- 88.6
C <sub>3</sub> H <sub>8</sub> (propane)	- 42.1
C <sub>4</sub> H <sub>10</sub> (butane)	- 0.5

$\epsilon_0$  = const. dielétrica  
vácuo =  
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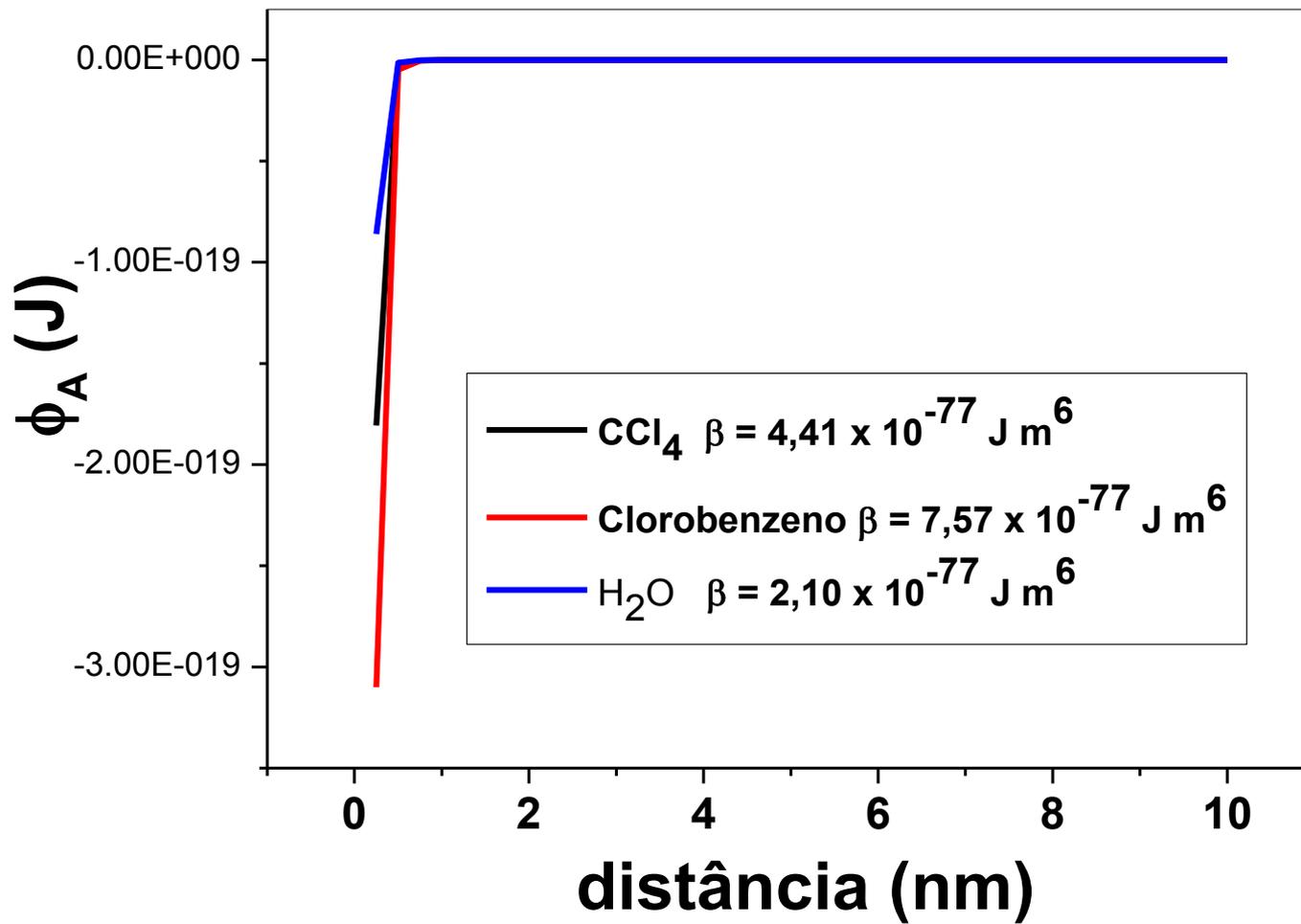
Forças de van der Waals

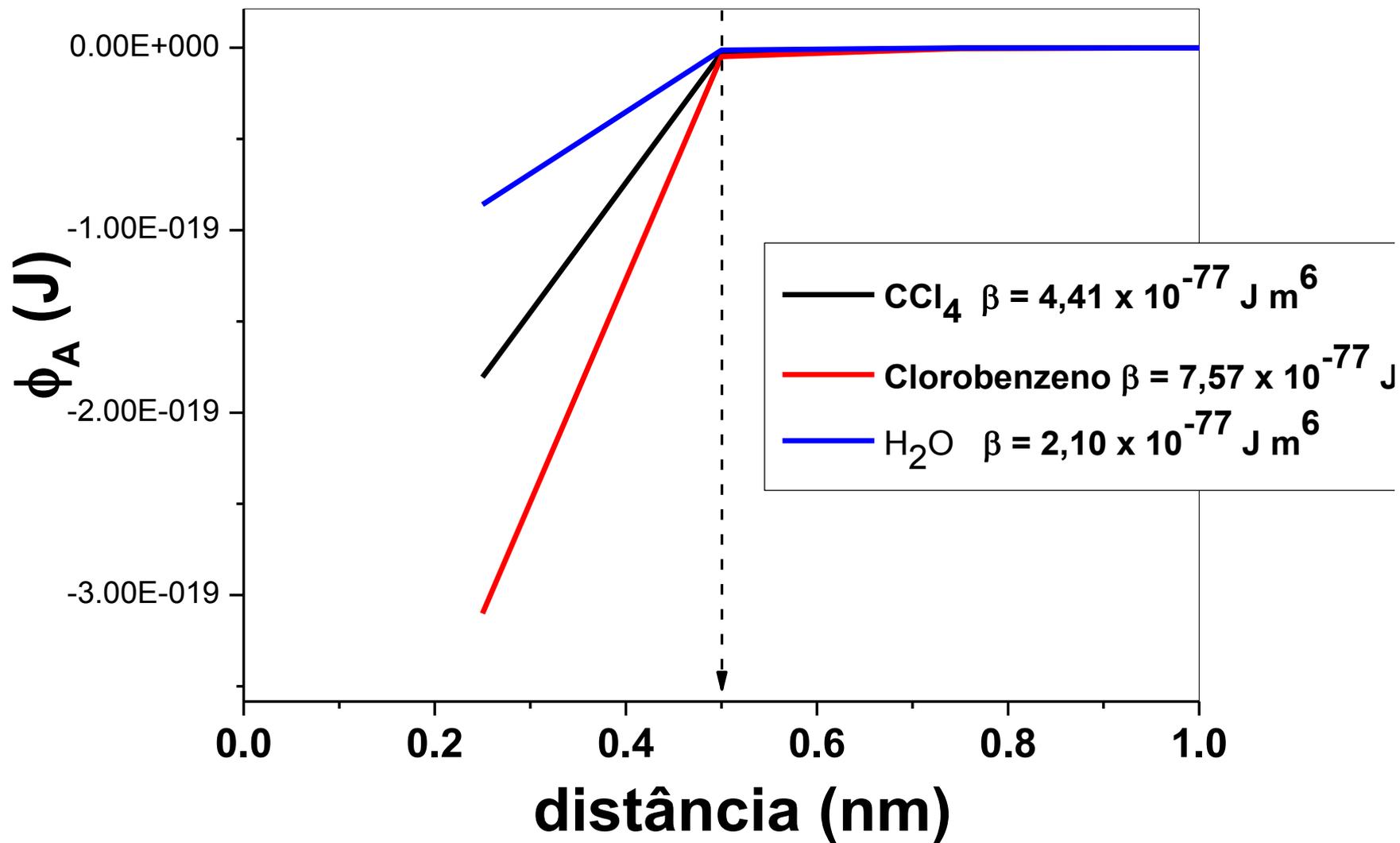
Ligações de H:  
~ 10 a 40 kJ/mol

Para calcular como varia o potencial de atração de van der Waals ( $\Phi_A$ ) com a distância entre 2 moléculas iguais em função da distância ( $x$ ):

$$\Phi_A = -\frac{1}{(4\pi\epsilon_0)^2} \left( 2\alpha_{0,1}\mu_1^2 + \frac{2\mu_1^4}{3k_B T} + \frac{3}{4}h\nu_1\alpha_{0,1}^2 \right) x^{-6} = -\beta_{11}x^{-6}$$

$\beta_{11}$

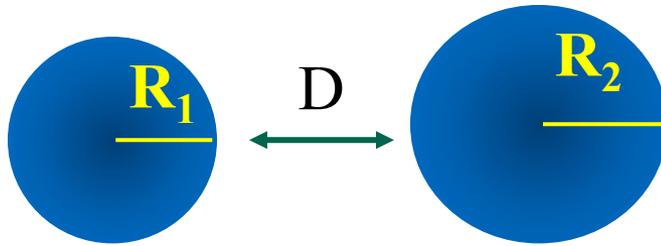




Vídeo: tensão superficial da água

$$\sigma_1 = \sigma_1^d + \sigma_1^p$$

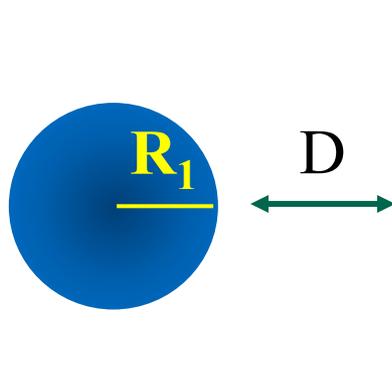
Liquid Name	Surface Tension	Disperse Part	Polar Part
N,N-dimethyl-Formamid	37.1	29.0	8.1
n-Decane	23.9	23.9	0.0
n-Heptane	20.4	20.4	0.0
n-Hexane	18.4	18.4	0.0
n-Octane	21.8	21.8	0.0
n-Tetradecane	25.6	25.6	0.0
nitro-Ethane (Schultz)	31.9	27.5	4.4
nitro-Methane (Schultz)	36.8	29.8	7.0
Phthalic-acid-diethylester 22°	37.0	30.0	7.0
sym-tetrabromo-Ethane (Ström)	49.7	49.7	0.0
sym-tetrachloro-Ethane (Ström)	36.3	36.3	0.0
tetrachloro-Methane (Schultz)	27.0	26.7	0.3
Toluene (Schultz)	28.4	26.1	2.3
Tricresyl-phosphate (Fowkes)	40.9	39.2	1.7
<b>Water</b>	<b>72.8</b>	<b>26.0</b>	<b>46.8</b>
Water (Busscher)	72.1	19.9	52.2
Water (Rabel) 22°	72.3	18.7	53.6
Water (Ström) 20°	72.8	21.8	51.0
α-bromo-Naphthalene (Busscher)	44.4	44.4	0.0
α-brom-Naphthalene (Ström)20°	44.6	44.6	0.0



Entre duas esferas  
Se  $D \ll R_1, R_2$

$$\phi_A = -\frac{A_H R_1 R_2}{6D R_1 + R_2}$$

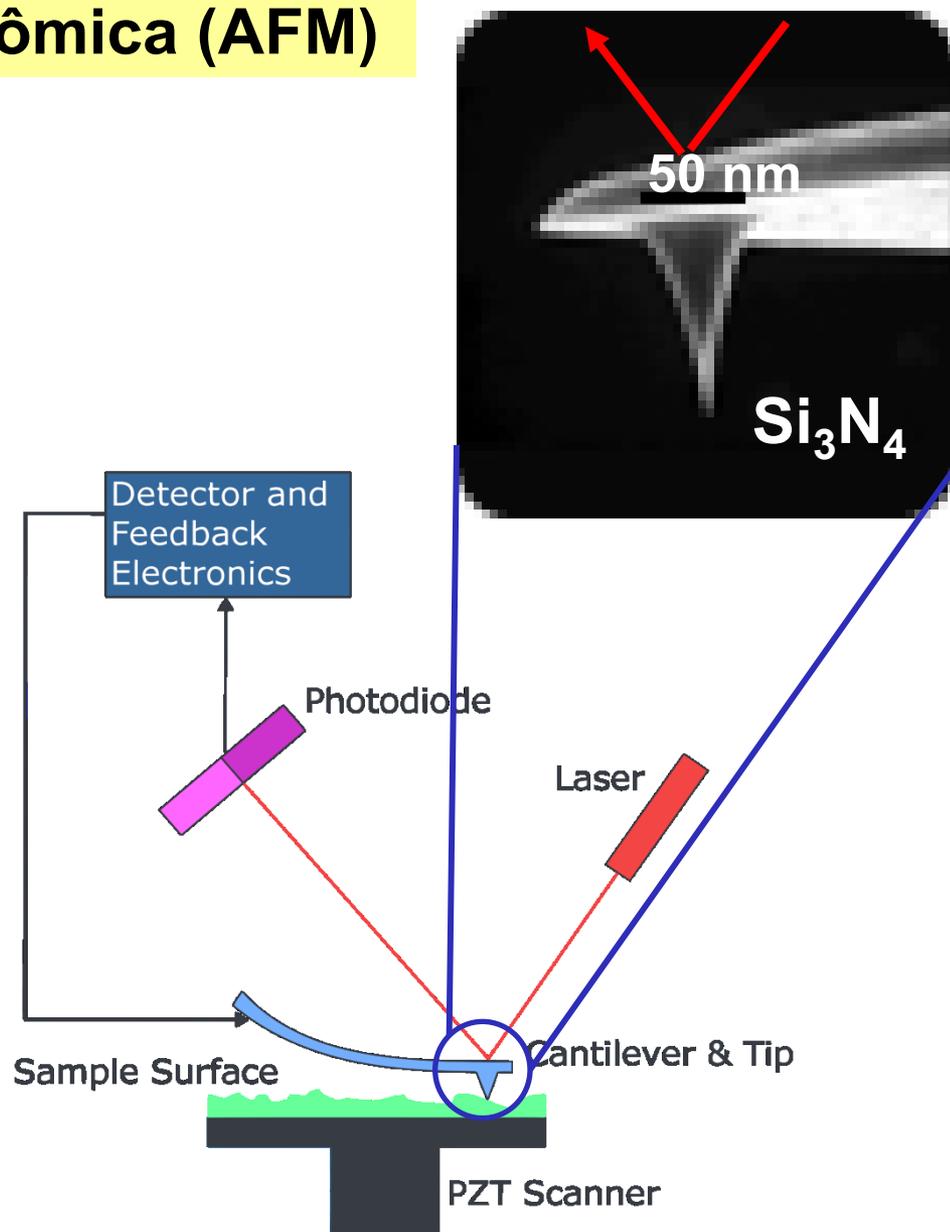
$A_H$  = constante de Hamaker  
(para dois materiais idêntico no ar/vácuo  $\sim \beta_{11}$ )



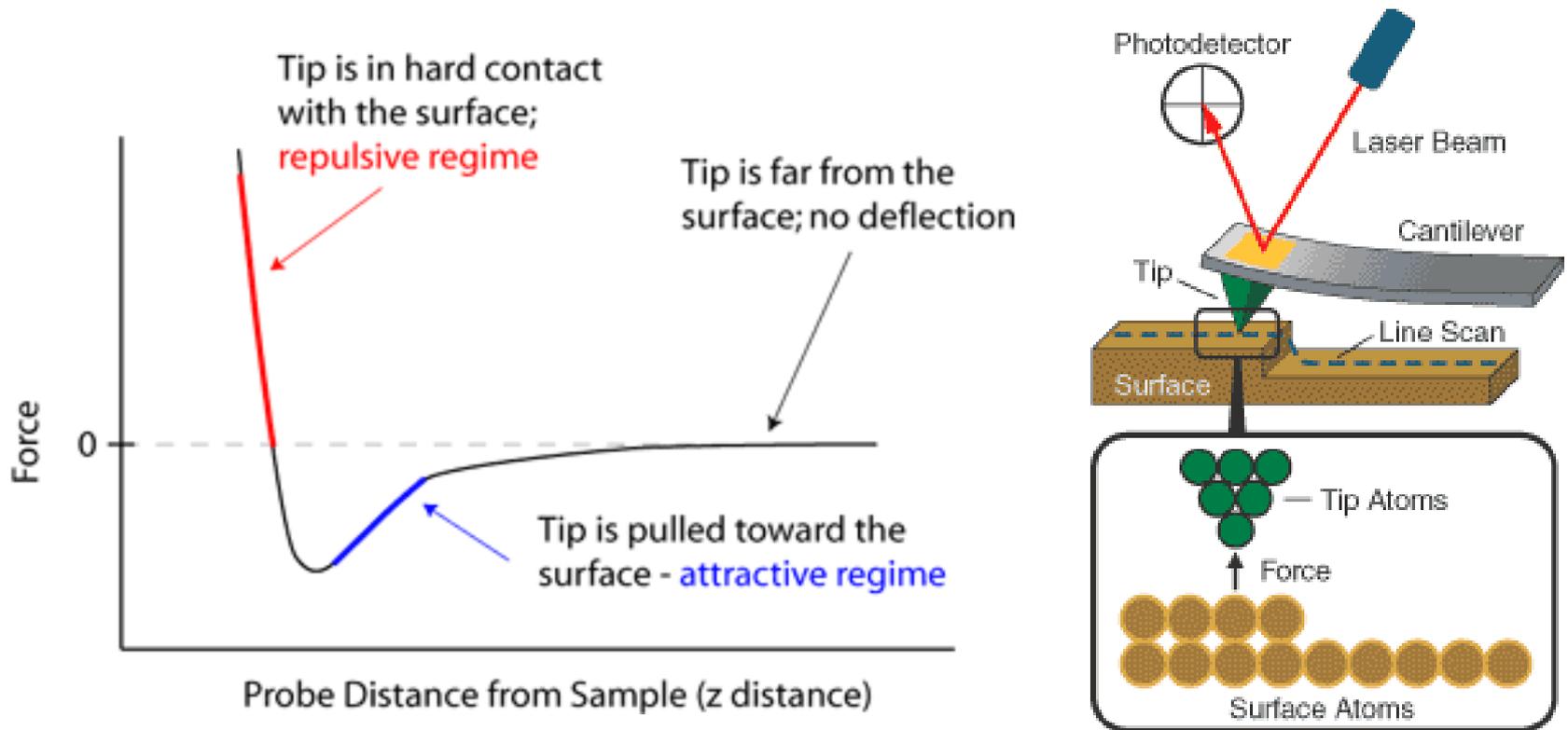
Entre uma esfera e um plano ( $R_2 \rightarrow \infty$ )

$$\phi_A = -\frac{A_H R_1}{6D}$$

# Microscopia de força atômica (AFM)



# Microscopia de força atômica (AFM)



<https://www.youtube.com/watch?v=s6KqJS1GZNE>

<https://www.youtube.com/watch?v=8gCf1sEn0UU>

AFM



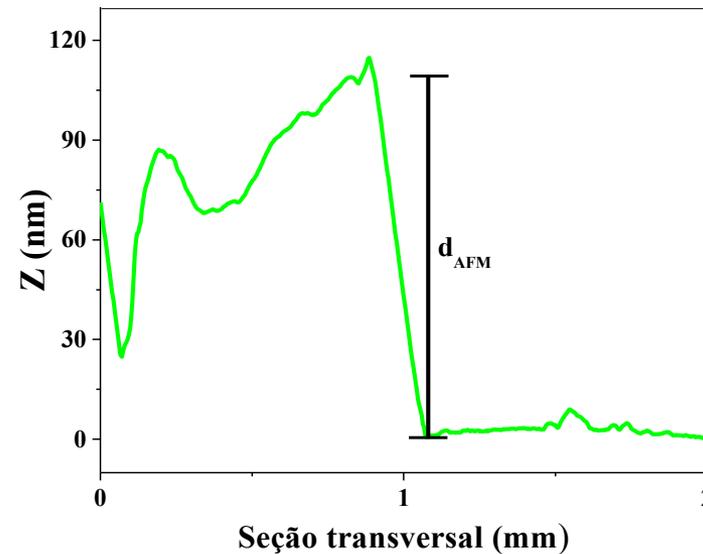
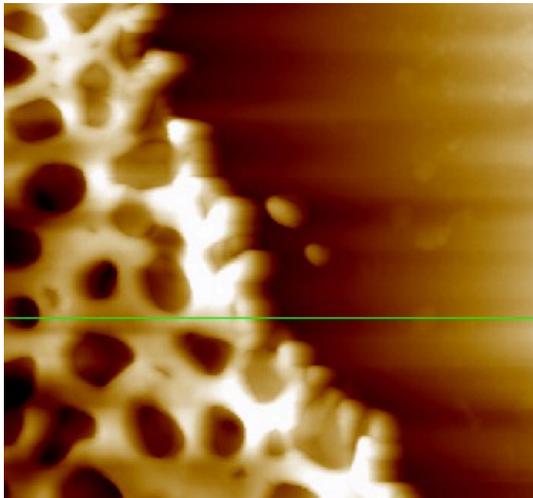
Topografia

Espessura

Rigidez

Forças de adesão

Condutividade elétrica ou magnética



**Figura 4.** Ilustração da determinação da espessura dos filmes por AFM através da medição da distância pico-vale em uma micrografia ( $2 \times 2$ )  $\mu\text{m}^2$  obtida de um filme de éster de celulose

*Tese de Doutorado de Leandro S. Blachechen, IQUSP, 2014*

## Bibliografia

- Principles of Colloid and Surface Chemistry, 3rd ed. P. C. Hiemenz and R. Rajagopalan, Marcel Dekker, 1997, cap. 10.
- Introdução da química dos colóides e de superfícies, D. J. Shaw, Ed. Edgard Blücher Ltda, 1975.
- Livros de química geral.