Princípios Físicos Aplicados à Fisiologia (PGF5306-1)

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B05

Entropia
Aula 14

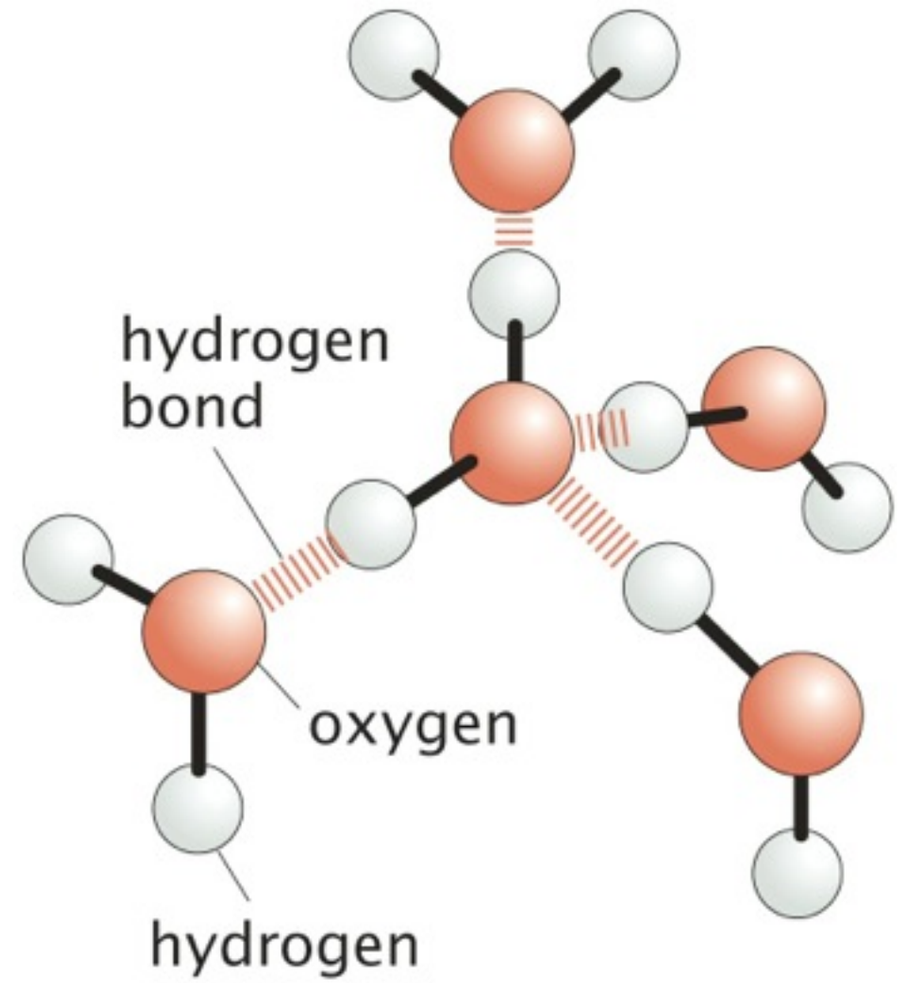

Figure 5.27 Physical Biology of the Cell, 2ed. (© Garland Science 2013)

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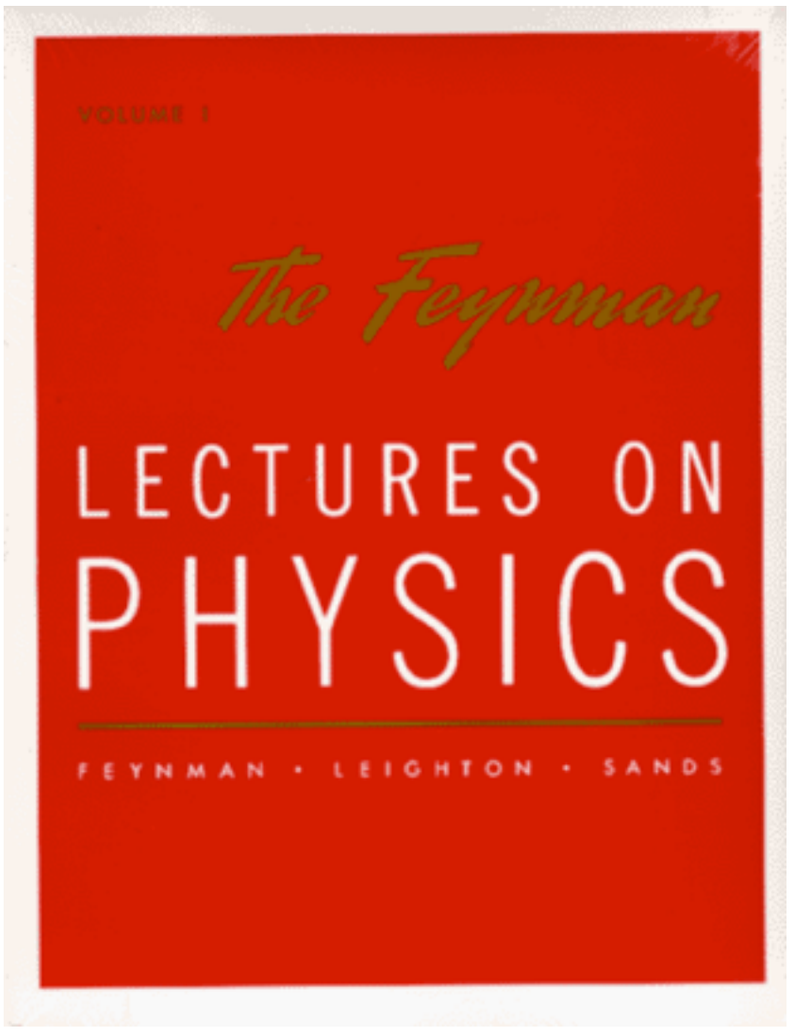
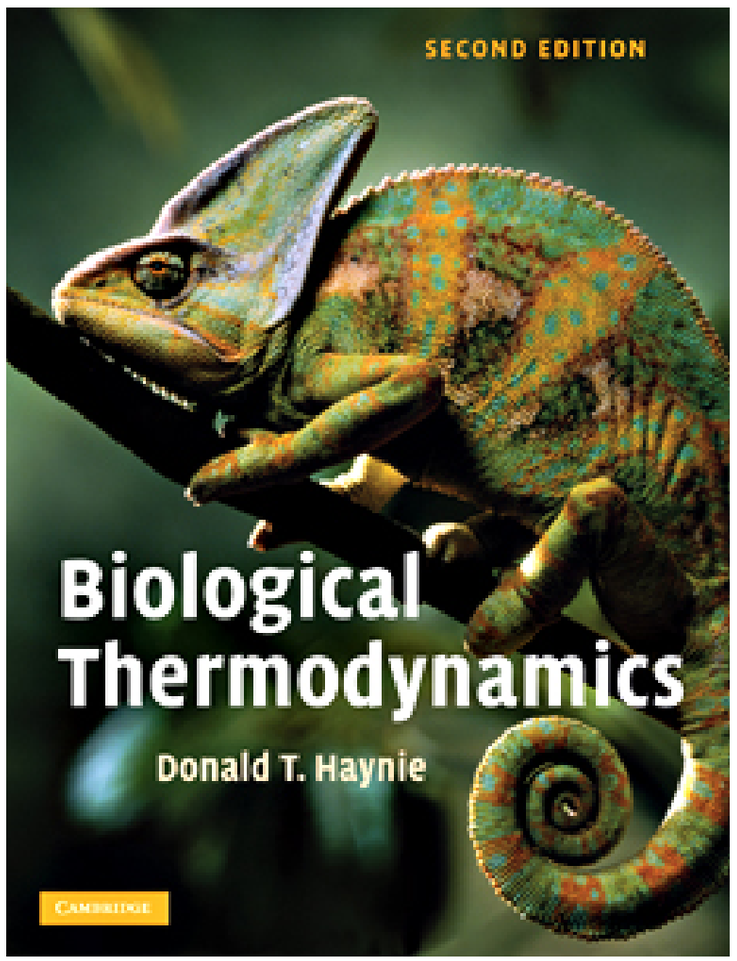
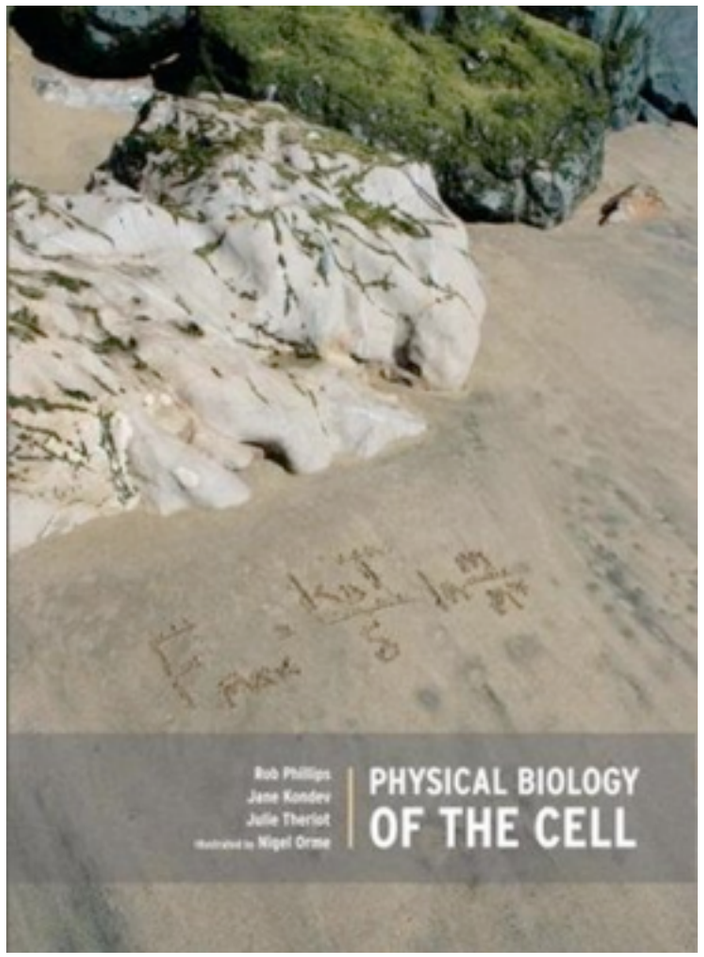
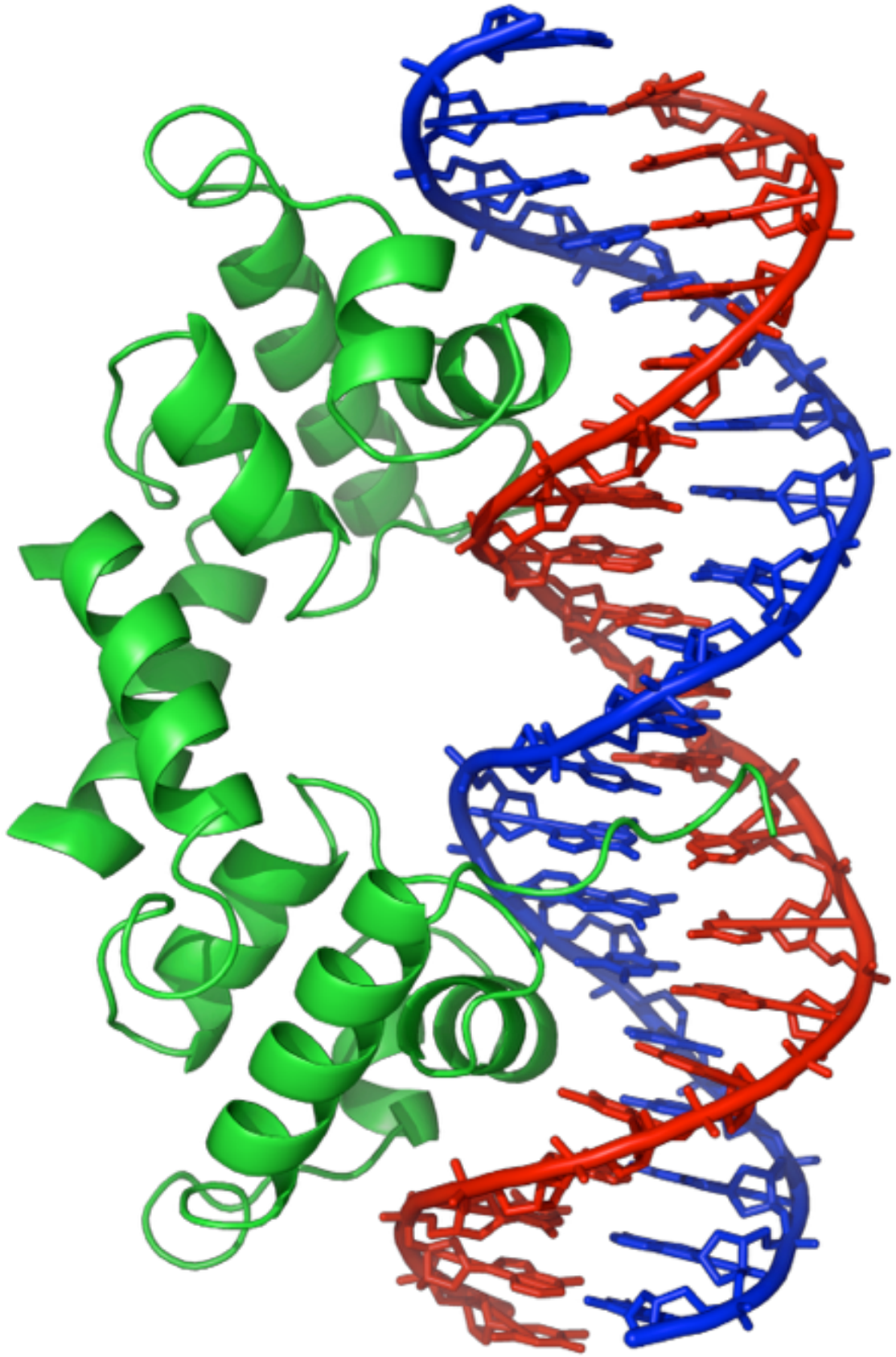






The λ repressor of bacteriophage lambda employs a helix-turn-helix (left; green) to bind DNA (right; blue and red).



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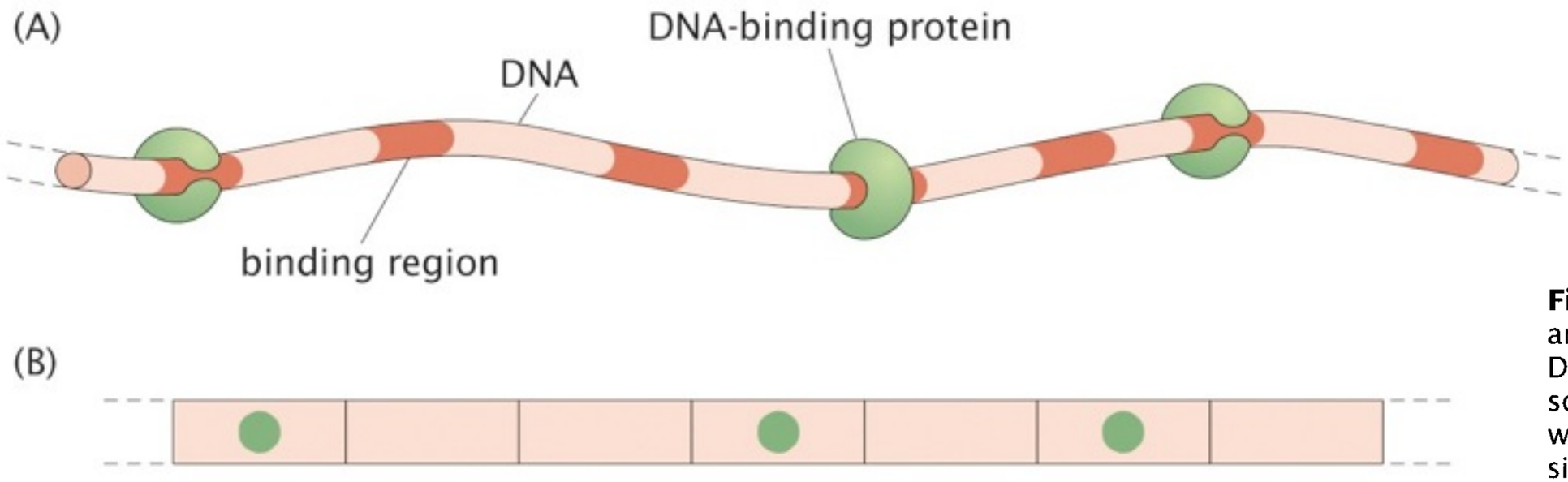

Figure 5.25 Physical Biology of the Cell, 2ed. (© Garland Science 2013)

Figure 5.23 Possible arrangements of proteins on a DNA molecule. (A) The cartoon schematizes a DNA molecule on which there is a series of binding sites which are shaded dark gray. The DNA binding proteins can occupy any of these sites. (B) The lattice model represents a further idealization in which we imagine the DNA molecule as a series of boxes into which we can put the DNA-binding proteins.

$$S = k_{\mathrm{B}} \ln W(N_p; N)$$

$N_p \rightarrow$ Número de proteinas de ligação

$N \rightarrow$ Número de sitios

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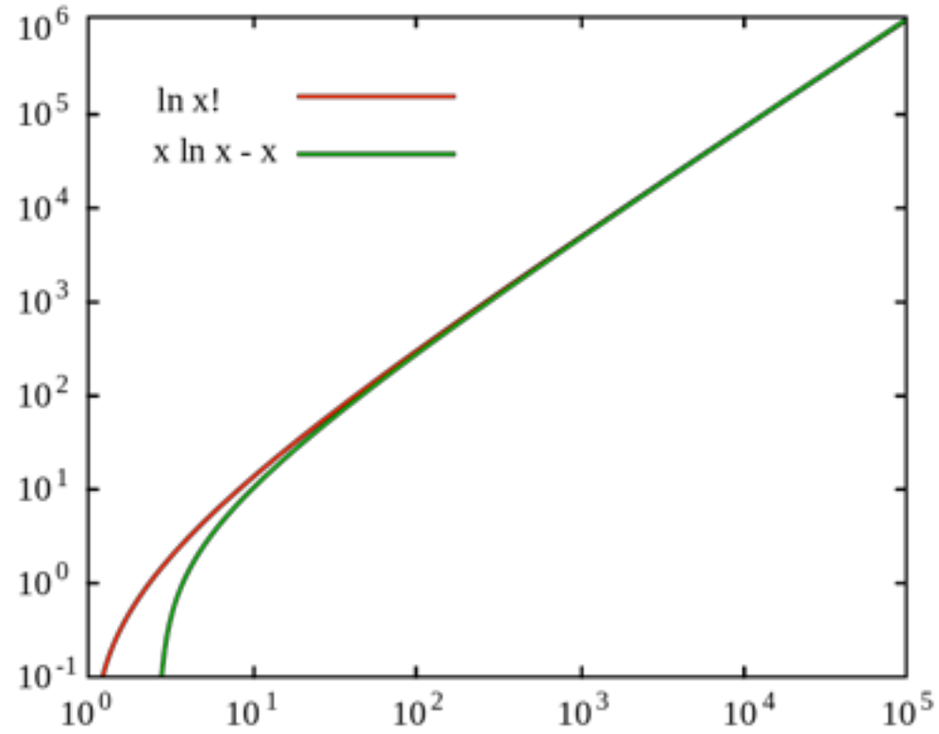
$$W(N_p; N) = \frac{N(N-1)(N-2)\dots(N-N_p+1)}{N_p(N_p-1)\dots 1}$$

$$W(N_p; N) = \frac{N!}{N_p!(N-N_p)!}$$

$$S = k_B \ln \frac{N!}{N_p!(N-N_p)!}$$



Aproximação de Stirling

$$\ln(n!) = n\ln(n) - n + O(\ln(n))$$
$$\approx n\ln(n) - n \text{ (para } n \text{ grande)}$$

$$S = -k_B N[c\ln c + (1-c)\ln(1-c)], \text{ com } c = N_p/N$$

Entropia

$$S = -k_B N[c \ln c + (1-c)\ln(1-c)]\,, \text{ com } c = N_p/N$$

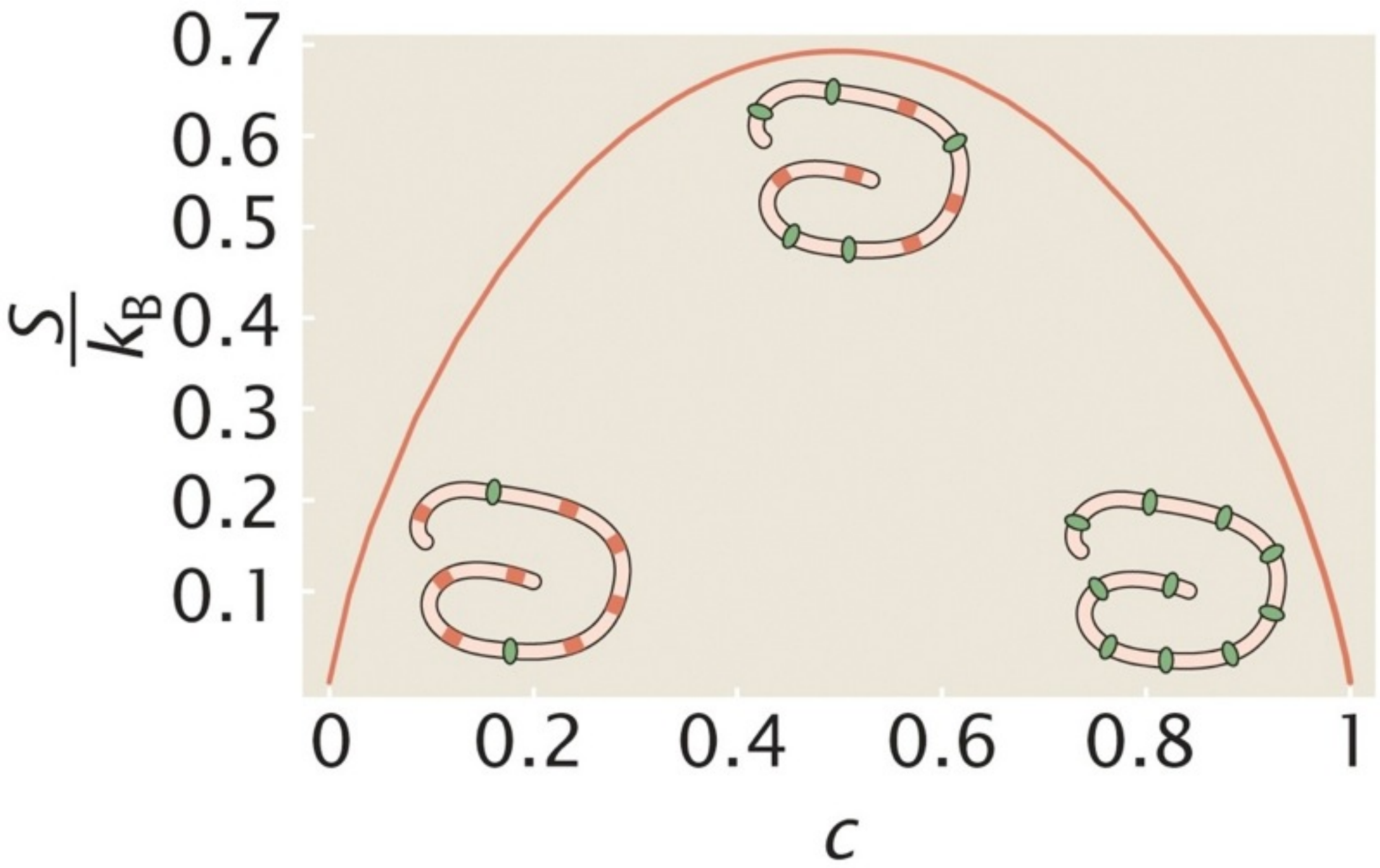


Figure 5.26 Physical Biology of the Cell, 2ed. (© Garland Science 2013)

Íons em água

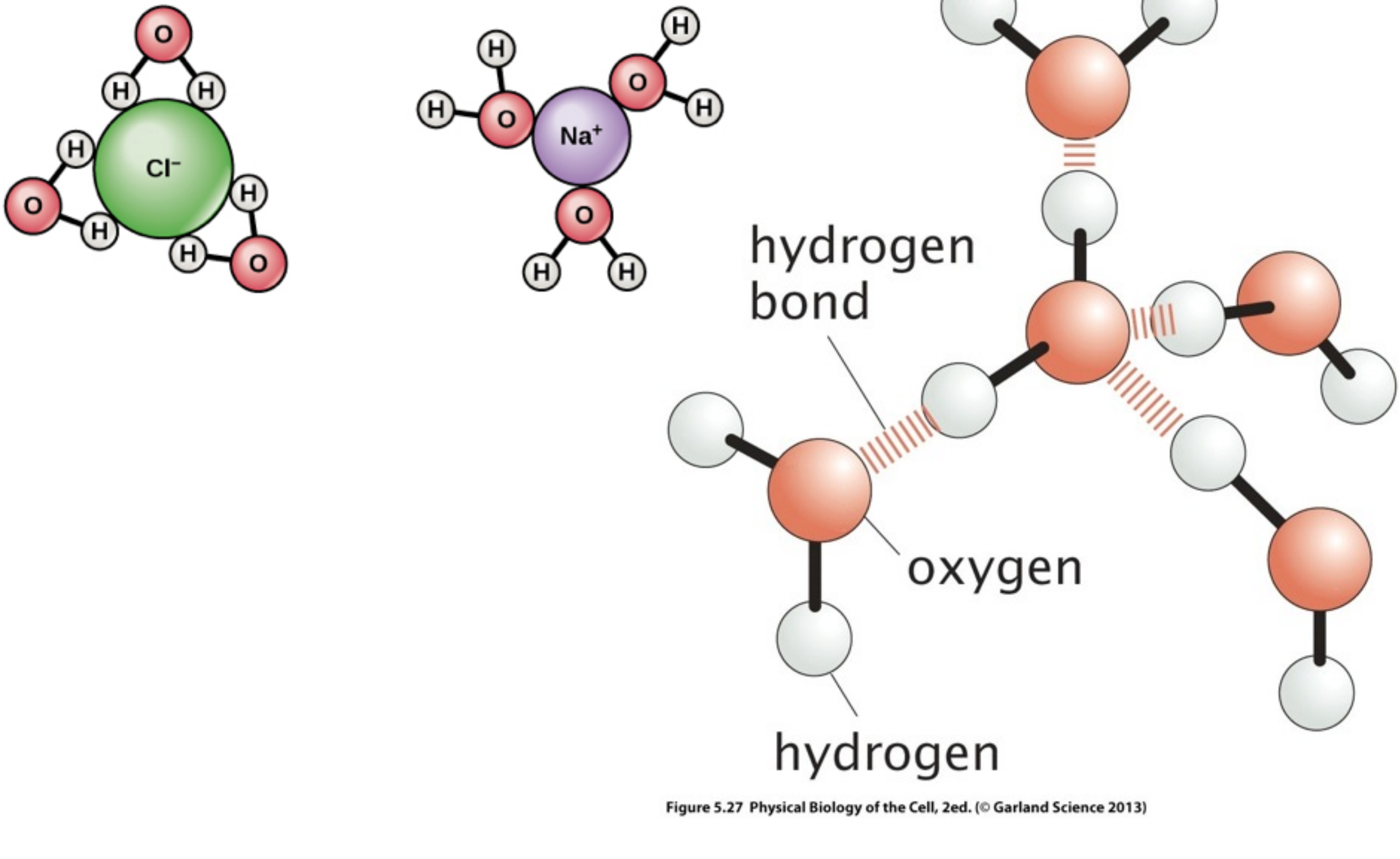


Figure 5.27 Physical Biology of the Cell, 2ed. (© Garland Science 2013)

Entropia (Hidrofobia)

Uma das forças moleculares mais importantes é o efeito hidrofóbico

Quando uma molécula hidrofobica é colocado na água, ela previne as moléculas de água de sua vizinhança de participar de algumas ligações de hidrogênio.

Figure 5.25 The hydrogen bonding network in water. Water molecules participate in hydrogen bonding (illustrated by the striped lines joining adjacent water molecules). A given water molecule can be idealized as having neighbors arranged in a tetrahedral structure.

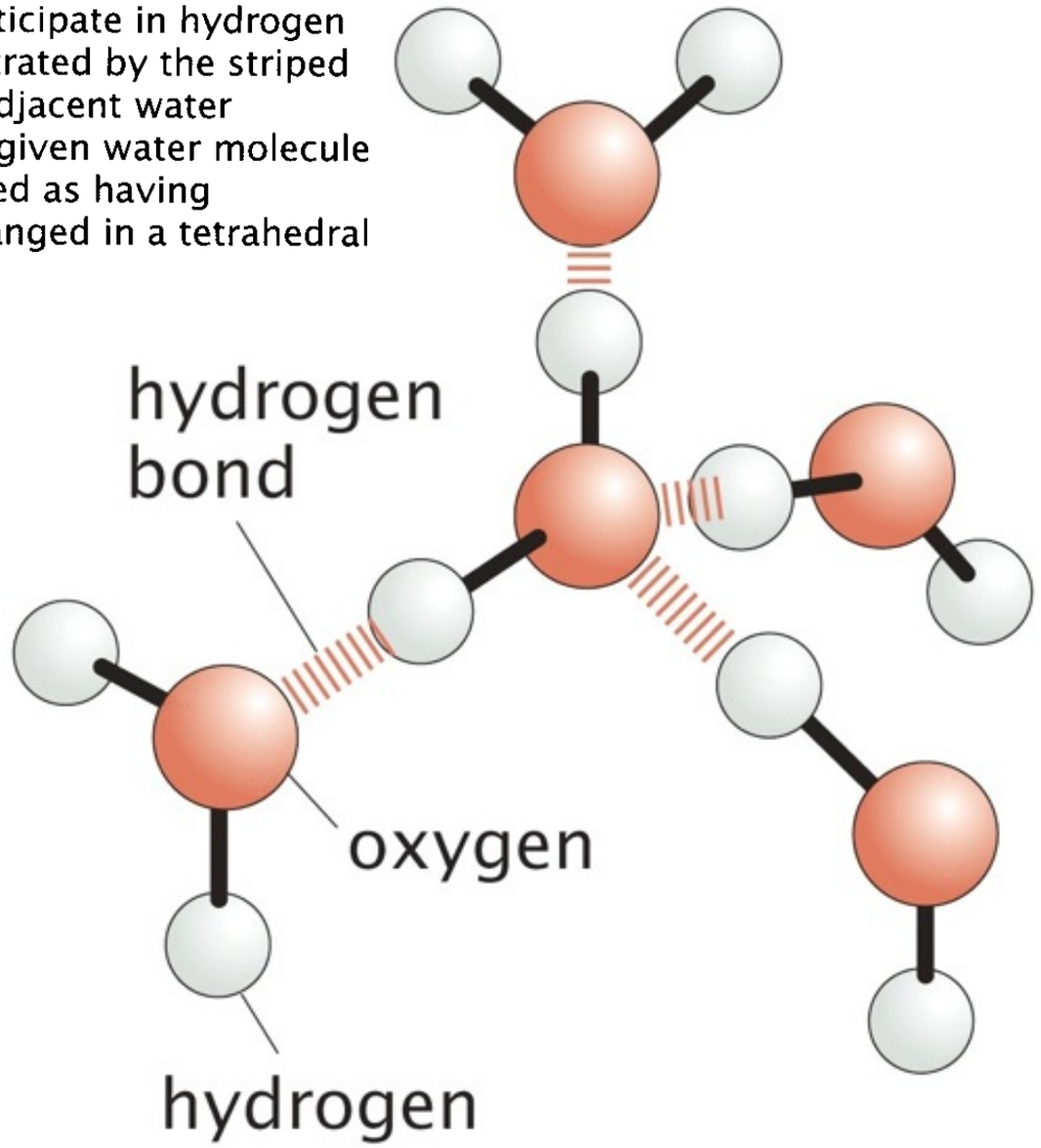


Figure 5.27 Physical Biology of the Cell, 2ed. (© Garland Science 2013)

Entropia (Hidrofobia)

Se retirarmos uma molécula de água e substituirmos por uma hidrofóbica ...

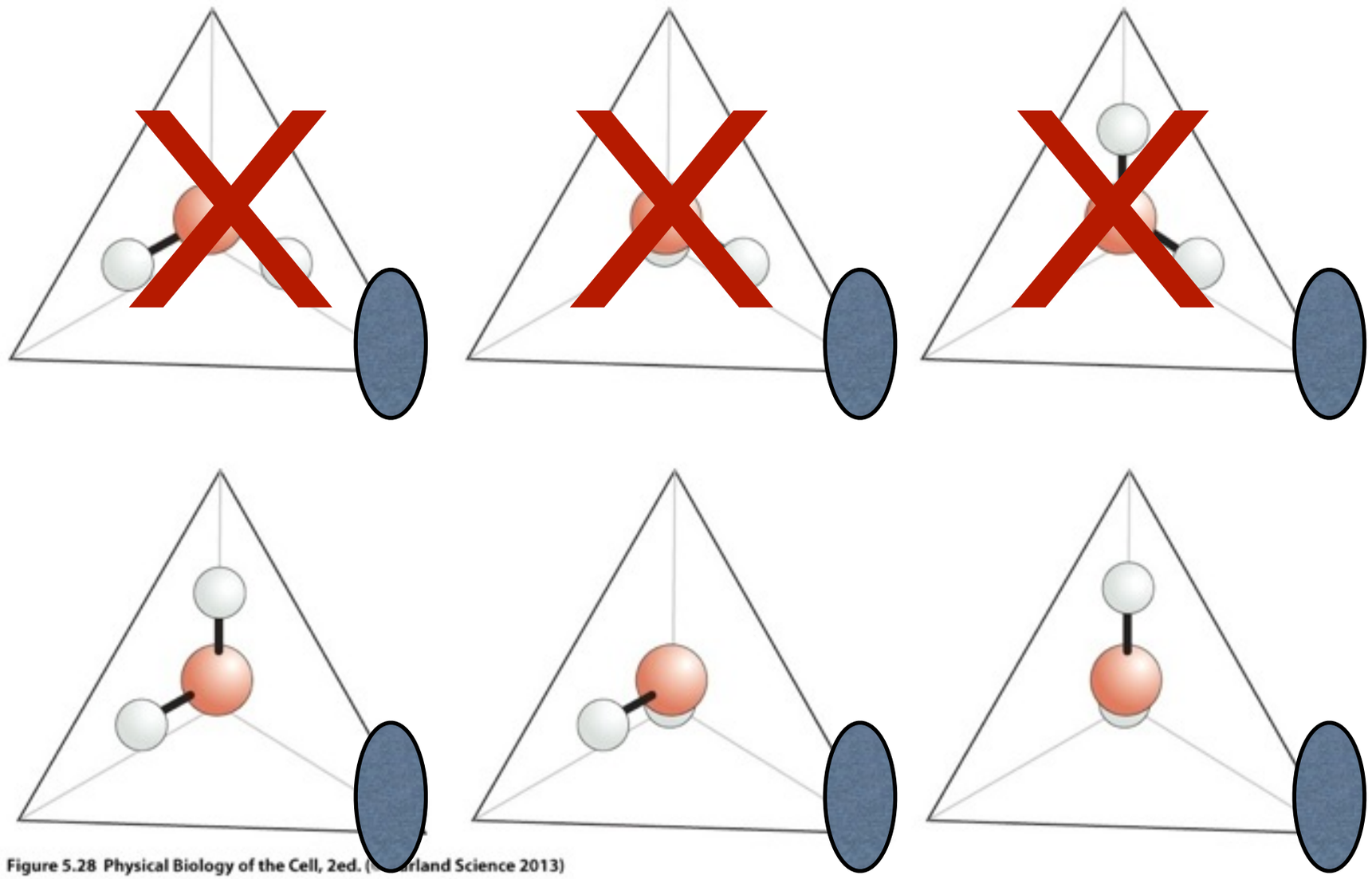


Figure 5.26 Orientations of water molecules in a tetrahedral network. Each image shows a different arrangement of the water molecule that permits the formation of hydrogen bonds with neighboring water molecules. The hydrogen bonds are in the directions of the vertices that are *not* occupied by hydrogens in the figure. (Adapted from K. Dill and S. Bromberg, Molecular Driving Forces, New York, Garland Science, 2003.)

Figure 5.28 Physical Biology of the Cell, 2ed. (arland Science 2013)

Entropia (Hidrofobia)

Na presença de moléculas não polares, para cada molécula de água, apenas metade das orientações são premitidas

$$\Delta S_{\text{Hidrofóbico}} = \underbrace{k_B \ln 3}_{\text{H}_2\text{O restrito}} - \underbrace{k_B \ln 6}_{\text{H}_2\text{O irrestrito}} = -k_B \ln 2$$

Qual o custo entrópico de colocar uma molécula hidrofóbica em água?

$$G = U + pV - TS$$

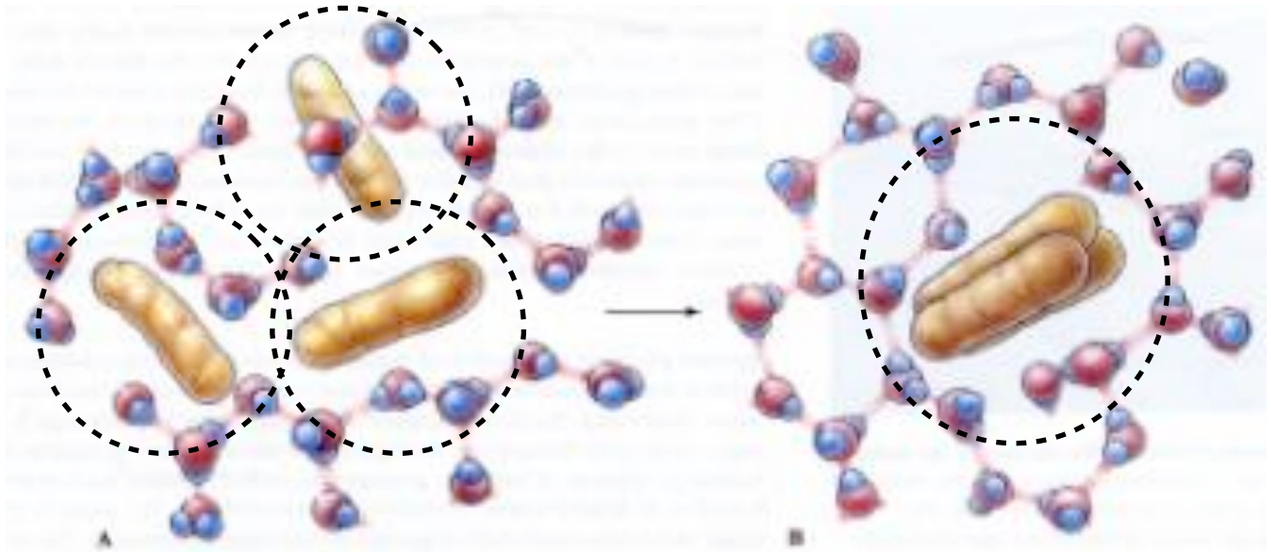
$$\Delta G_{\text{Hidrofóbico}}(n) = n k_B T \ln 2$$

onde n é o número de moléculas de água adjacentes a molécula apolar de interesse

Entropia (Hidrofobia)

$$\Delta G_{\text{Hidrofóbico}}(n) = nk_BT\ln 2$$

Definindo A como sendo a área efetiva da interface entre uma molécula e suas vizinhanças com água



$$1\,\text{nm}^2 \approx [10\,\text{H}_2\text{O}]_{\text{Área Cobertura}}$$

$$\text{Como}\ \ \ln 2 \approx 0.7$$

$$\Delta G \approx \underbrace{(7k_BT/\text{nm}^2)}_{\gamma_{\text{Hidrofóbico}}} \times A$$

Área superficial do O_2 = 0.1~0.2 nm^2

Entropia (Hidrofobia)

Apesar de apolar o custo para dissolver O_2 em água é baixo, quando comparado com grandes moléculas apolares. Os efeitos aparecem em experiencias diárias ...

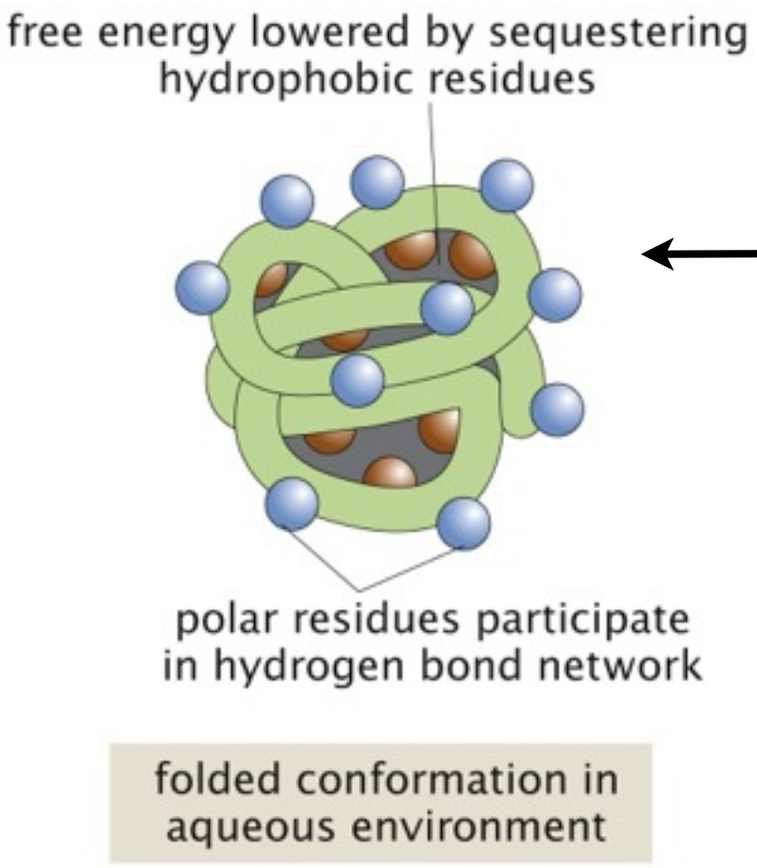
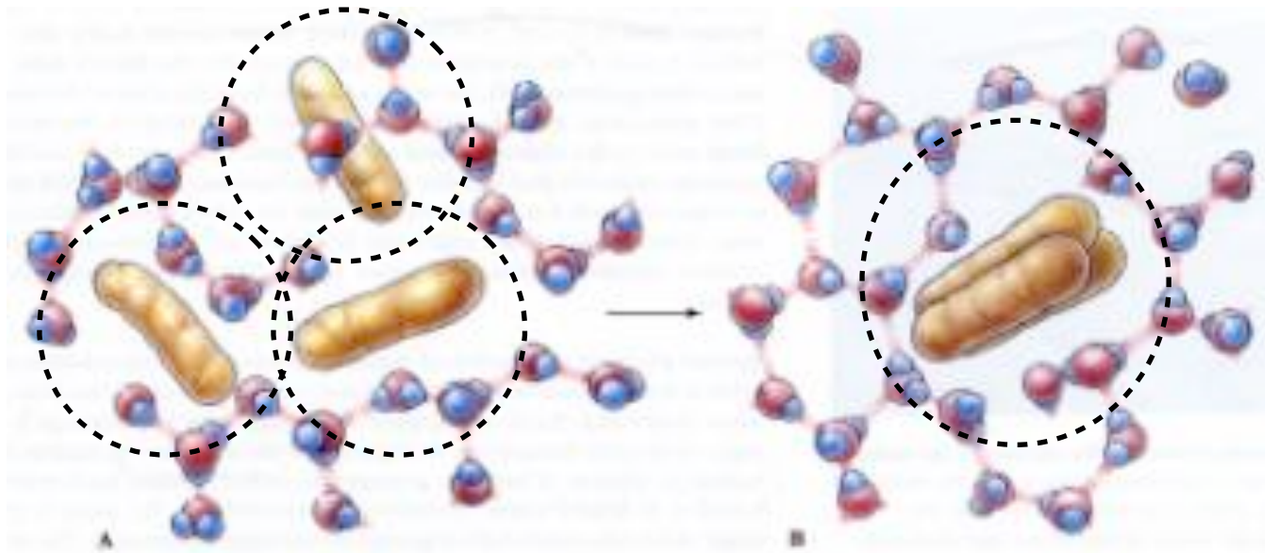


Figure 5.8 (part 2 of 2) Physical Biology of the Cell, 2ed. (© Garland Science 2013)

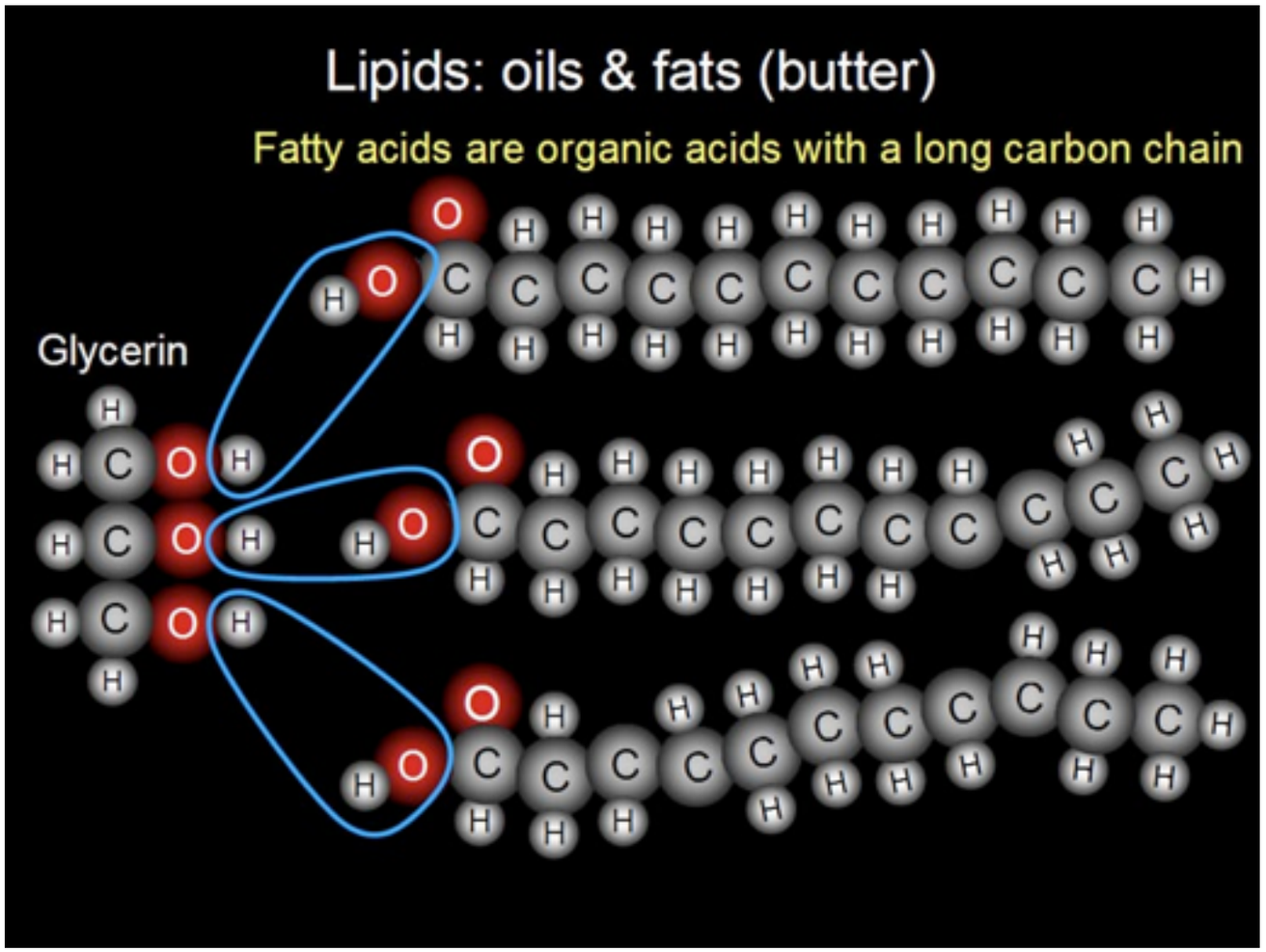
Estrutura Proteica

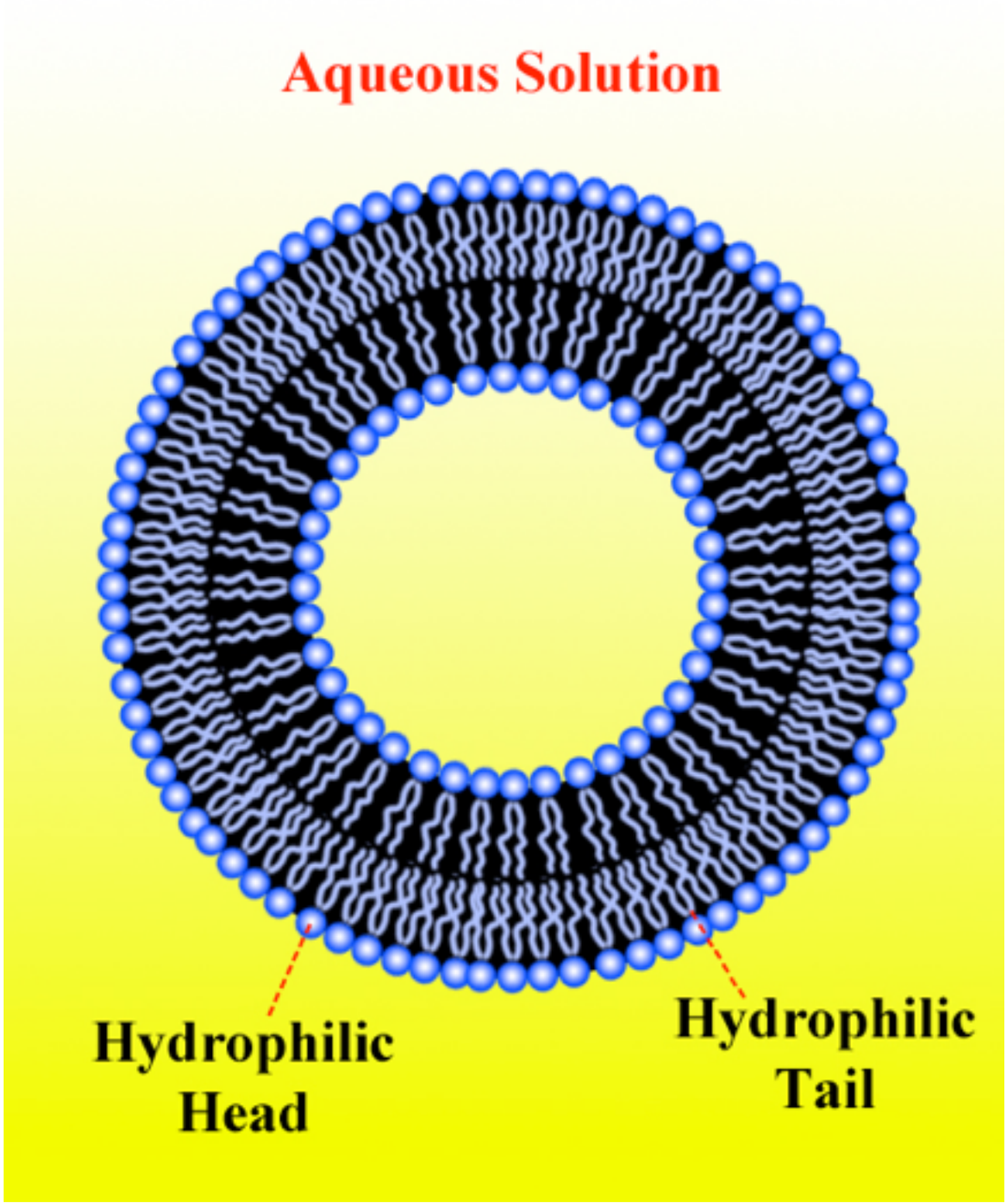
Dificuldade de misturar óleo



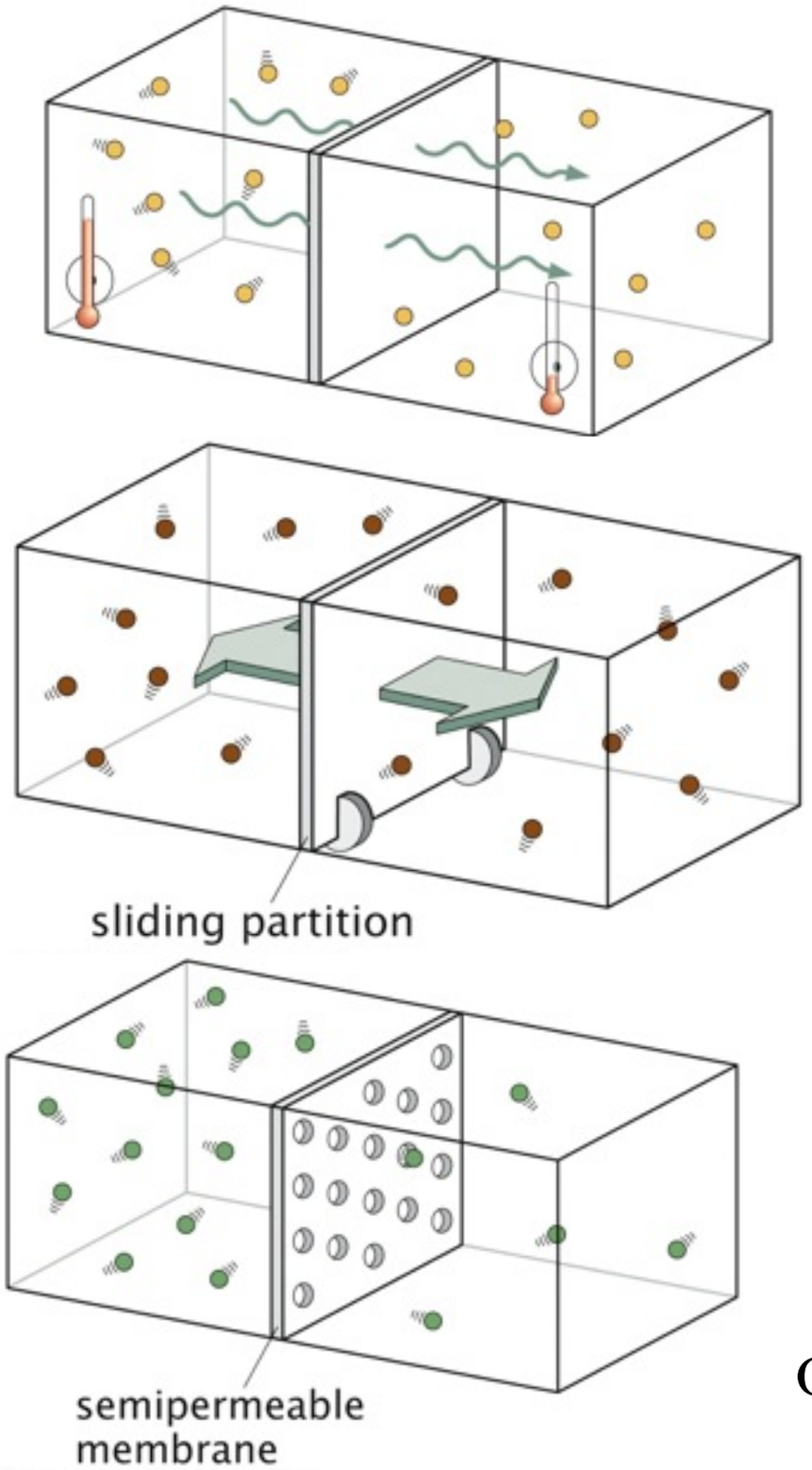
Entropia (Hidrofobia)

Lipídios em água





Maximização da Entropia



O processo de minimização pode:

Ocorrer toca de energia

$$\mathrm{d}S = \left(\frac{\partial S_1}{\partial E_1}\right)\mathrm{d}E_1 + \left(\frac{\partial S_2}{\partial E_2}\right)\mathrm{d}E_2 = 0$$

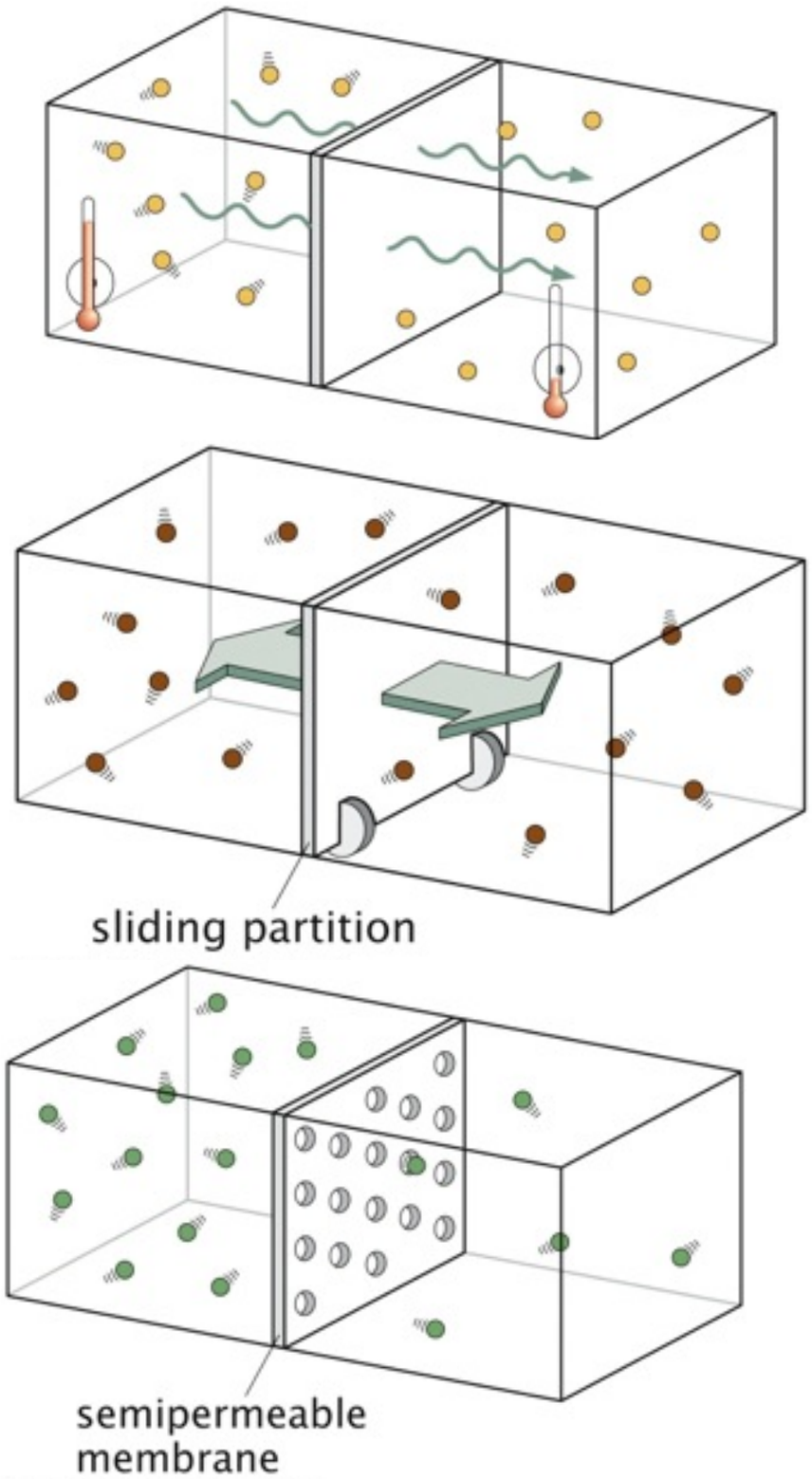
O correr mudança de volume

$$\mathrm{d}S = \left(\frac{\partial S_1}{\partial V_1}\right)\mathrm{d}V_1 + \left(\frac{\partial S_2}{\partial V_2}\right)\mathrm{d}V_2 = 0$$

O correr troca de partículas

$$\mathrm{d}S = \left(\frac{\partial S_1}{\partial N_1}\right)\mathrm{d}N_1 + \left(\frac{\partial S_2}{\partial N_2}\right)\mathrm{d}N_2 = 0$$

Caso os valores de Energia, Volume e Número de partículas permaneçam respectivamente constante:



$$\mathrm{d}E_1 + \mathrm{d}E_2 = 0$$

$$\left(\frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2}\right)\mathrm{d}E_1 = 0$$

$$\mathrm{d}V_1 + \mathrm{d}V_2 = 0$$

$$\left(\frac{\partial S_1}{\partial V_1} - \frac{\partial S_2}{\partial V_2}\right)\mathrm{d}V_1 = 0$$

$$\mathrm{d}N_1 + \mathrm{d}N_2 = 0$$

$$\left(\frac{\partial S_1}{\partial N_1} - \frac{\partial S_2}{\partial N_2}\right)\mathrm{d}N_1 = 0$$

Minimização da Energia Livre

Segunda Lei: $\mathrm{d}S_{\mathrm{Total}} = \mathrm{d}S_{\mathrm{Reservatório}} + \mathrm{d}S_{\mathrm{Sistema}} \geq 0$

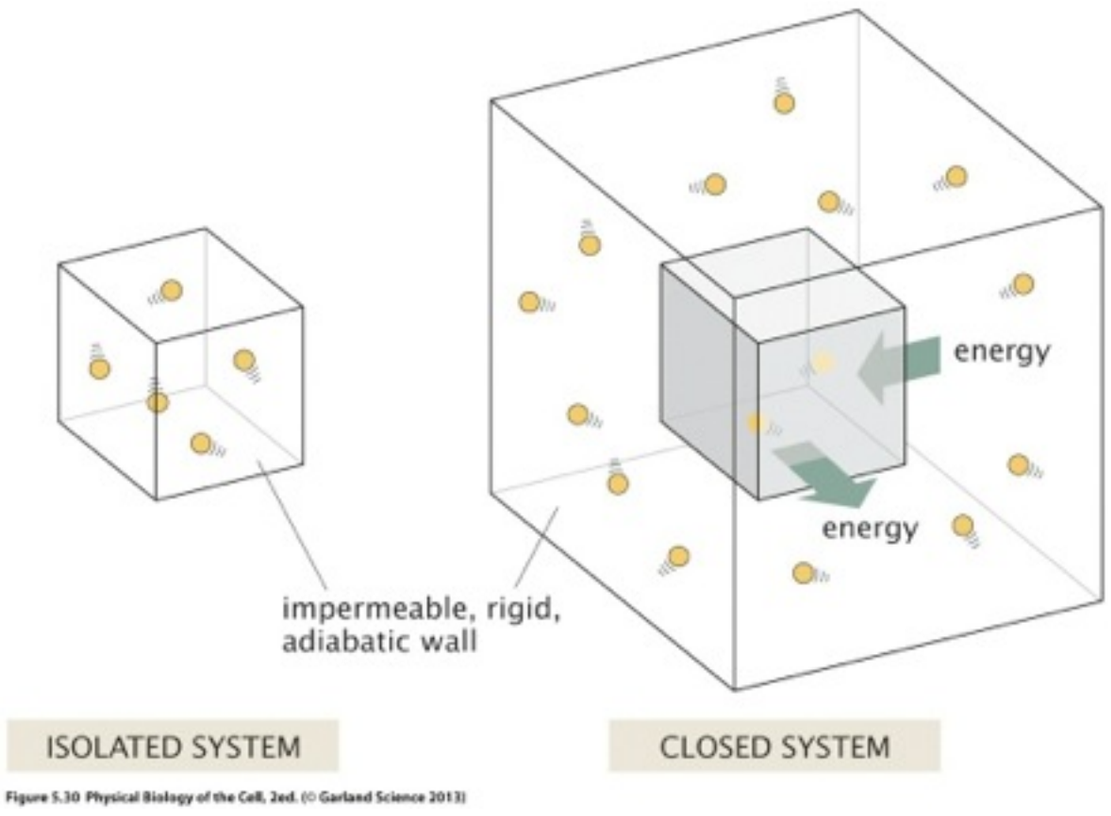


Figure 5.30 Physical Biology of the Cell, 2ed. (© Garland Science 2013)

Primeira Lei:

$$\mathrm{d}E_{\mathrm{R}} = \underbrace{T\mathrm{d}S_{\mathrm{R}}}_{\text{calor adicionado}} - \underbrace{p\mathrm{d}V_{\mathrm{R}}}_{\text{trabalho}}$$

Substituindo uma na outra e assumindo a concervação da Energia e Volume:

$$\mathrm{d}\left(\underbrace{E_{\mathrm{S}} + pV_{\mathrm{S}} - TS_{\mathrm{S}}}_{\text{Energia de Gibs}}\right) \leq 0$$

Exercícios

5.2 The sugar budget revisited
In Chapter 3 we worked out the rate of sugar uptake to provide the construction materials for a dividing bacterium. However, as shown in this chapter, sugar molecules also provide the *energy* needed to perform macromolecular synthesis. Amend the estimate of Chapter 3 to include the fact that sugar supplies construction materials and the energy needed to assemble them. You might find it useful to look at the macromolecular energy costs revealed in Table 5.2. How many sugars are needed to provide the energy and construction materials for making a new cell? Make an estimate for the average rate of sugar uptake for a dividing bacterium in light of this amendment to our earlier estimates.

5.3 A feeling for the numbers: covalent bonds
(a) Based on a typical bond energy of 150 k_BT and a typical bond length of 1.5 Å, use dimensional analysis to estimate the frequency of vibration of covalent bonds.
(b) Assume that the Lennard–Jones potential given by

$$V(r) = \frac{a}{r^{12}} - \frac{b}{r^6}$$

describes a covalent bond (though real covalent bonds are more appropriately described by alternatives such as the Morse potential which are not as convenient analytically). Using the typical bond energy as the depth of the potential and the typical bond length as its equilibrium position find the parameters a and b. Do a Taylor expansion around this equilibrium position to determine the effective spring constant and the resulting typical frequency of vibration.
(c) Based on your results from (a) and (b), estimate the time step required to do a classical mechanical simulation of protein dynamics.

5.5 A feeling for the numbers: comparing multiplicities
Boltzmann's equation for the entropy (eqn 5.29) tells us that the entropy difference between a gas and a liquid is given by

$$S_{gas} - S_{liquid} = k_B \ln \frac{W_{gas}}{W_{liquid}}. \tag{5.61}$$

From the macroscopic definition of entropy as $dS = dQ/T$ we can make an estimate of the ratios of multiplicities by noting that boiling of water takes place at fixed T at 373 K.
(a) Consider a cubic centimeter of water and use the result that the heat needed to boil water (the latent heat of vaporization) is given by $Q_{vaporization} = 40.66$ kJ/mol (at 100 °C) to estimate the ratio of multiplicities of water and water vapor for this number of molecules. Write your result as 10 to some power. If we think of multiplicities in terms of an ideal gas at fixed T, then

$$\frac{W_1}{W_2} = \left(\frac{V_1}{V_2}\right)^N. \tag{5.62}$$

What volume change would one need to account for the liquid/vapor multiplicity ratio? Does this make sense?
(b) In the chapter we discussed the Stirling approximation and the fact that our results are incredibly tolerant of error. Let us pursue that in more detail. We have found that the typical types of multiplicities for a system like a gas are of the order of $W \approx \exp(10^{25})$. Now, let us say we are off by a factor of 10^{1000} in our estimate of the multiplicities, namely, $W = 10^{1000}\exp(10^{25})$. Show that the difference in our evaluation of the entropy is utterly negligible whether we use the first or second of these results for the multiplicity. This is the error tolerance that permits us to use the Stirling approximation so casually!

Table 5.2 Biosynthetic cost in ATP equivalents to synthesize the macromolecules of a single *E. coli* cell.

Class	Biosynthetic cost (aerobic) – ATP equiv.
Protein	4.5×10^9
DNA	3.5×10^8
RNA	1.6×10^9
Phospholipid	3.2×10^9
Lipopolysaccharide	3.8×10^8
Peptidoglycan	1.7×10^8
Glycogen	3.1×10^7