

Lecture 4: Mechanical and Chemical Equilibrium In the Living Cell (Contd.)

Lecturer:
Brigita Urbanc
Office: 12-909
(E-mail: *brigita@drexel.edu*)

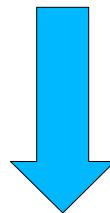
Course website:

www.physics.drexel.edu/~brigita/COURSES/BIOPHYS_2011-2012/

How do we find the equilibrium state or configuration?

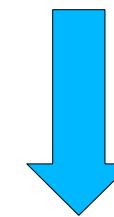
Are thermal fluctuations important?

NO



minimize potential energy

YES



minimize free energy

Finding displacement/charge density that minimizes the total potential energy

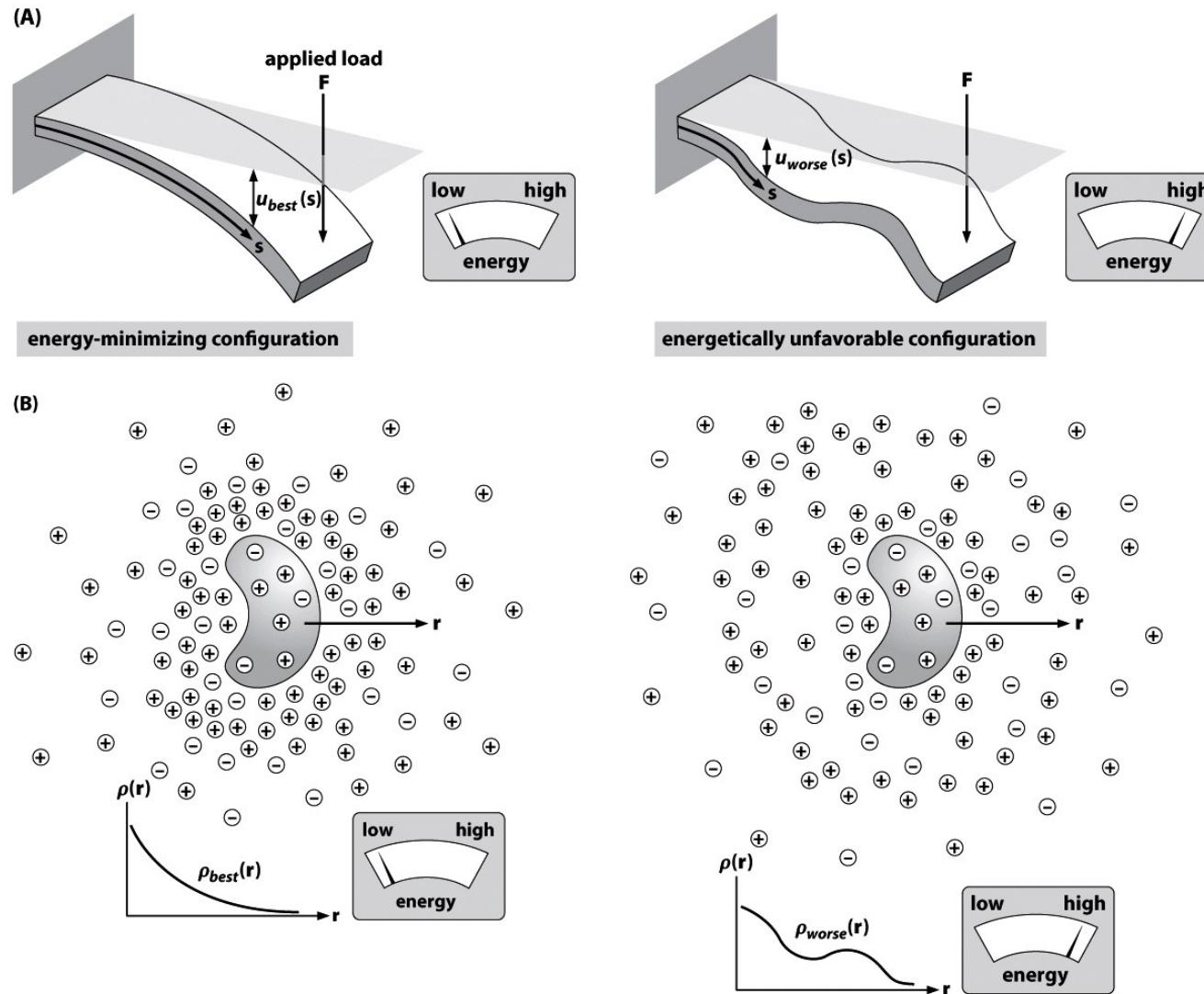


Figure 5.16 Physical Biology of the Cell (© Garland Science 2009)

Potential energy function: $f(u_1, u_2)$

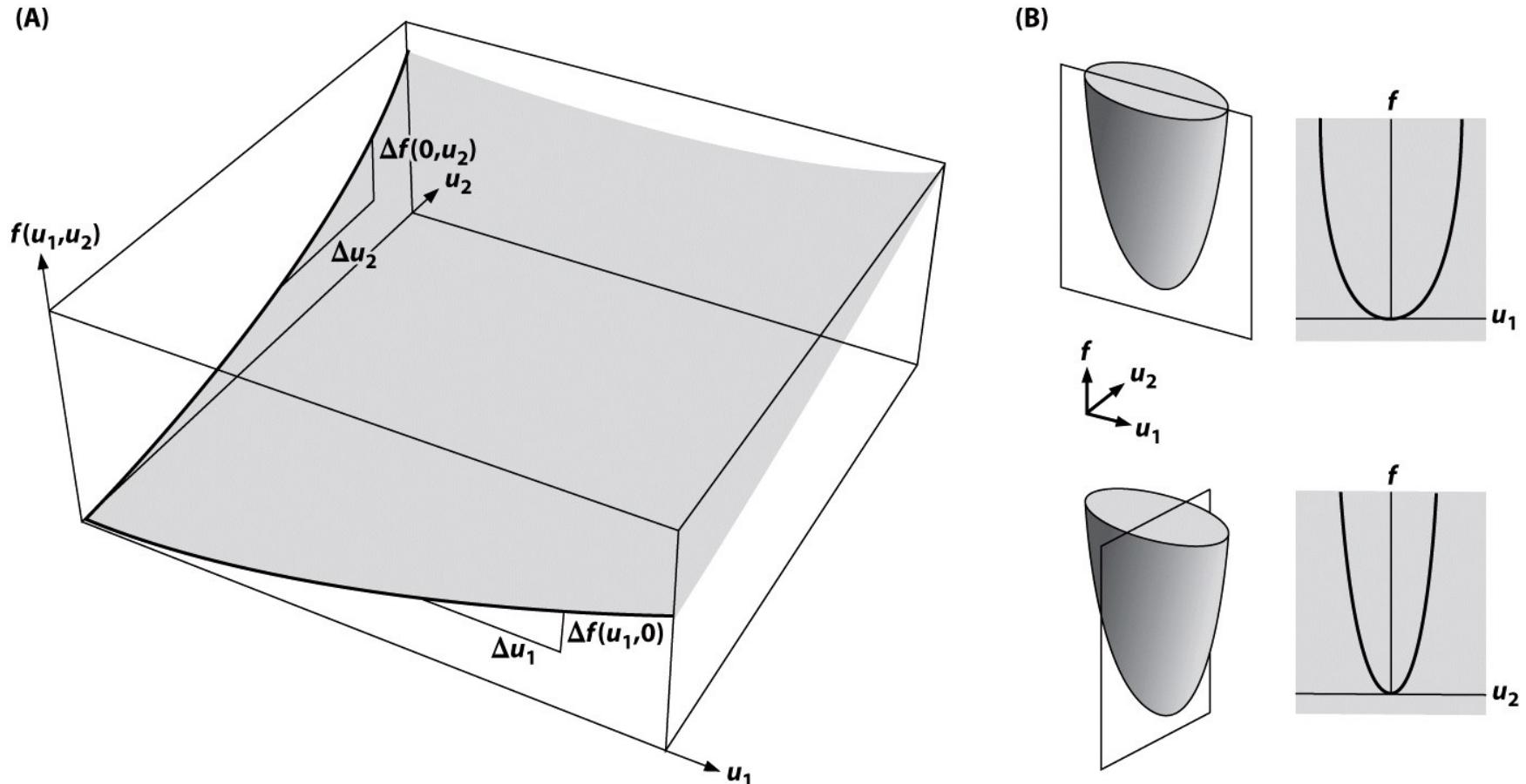


Figure 5.17 Physical Biology of the Cell (© Garland Science 2009)

Find a minimum:

$$\partial f(u_1, u_2) / \partial u_1 = 0$$

$$\partial f(u_1, u_2) / \partial u_2 = 0$$

For example:

$$f(u_1, u_2) = \frac{1}{2} (A_{11} u_1^2 + A_{22} u_2^2 + 2A_{12} u_1 u_2)$$

results in:

$$A_{11} u_1 + A_{12} u_2 = 0$$

$$A_{21} u_1 + A_{22} u_2 = 0$$

Expansion in a Taylor series around local/global minima

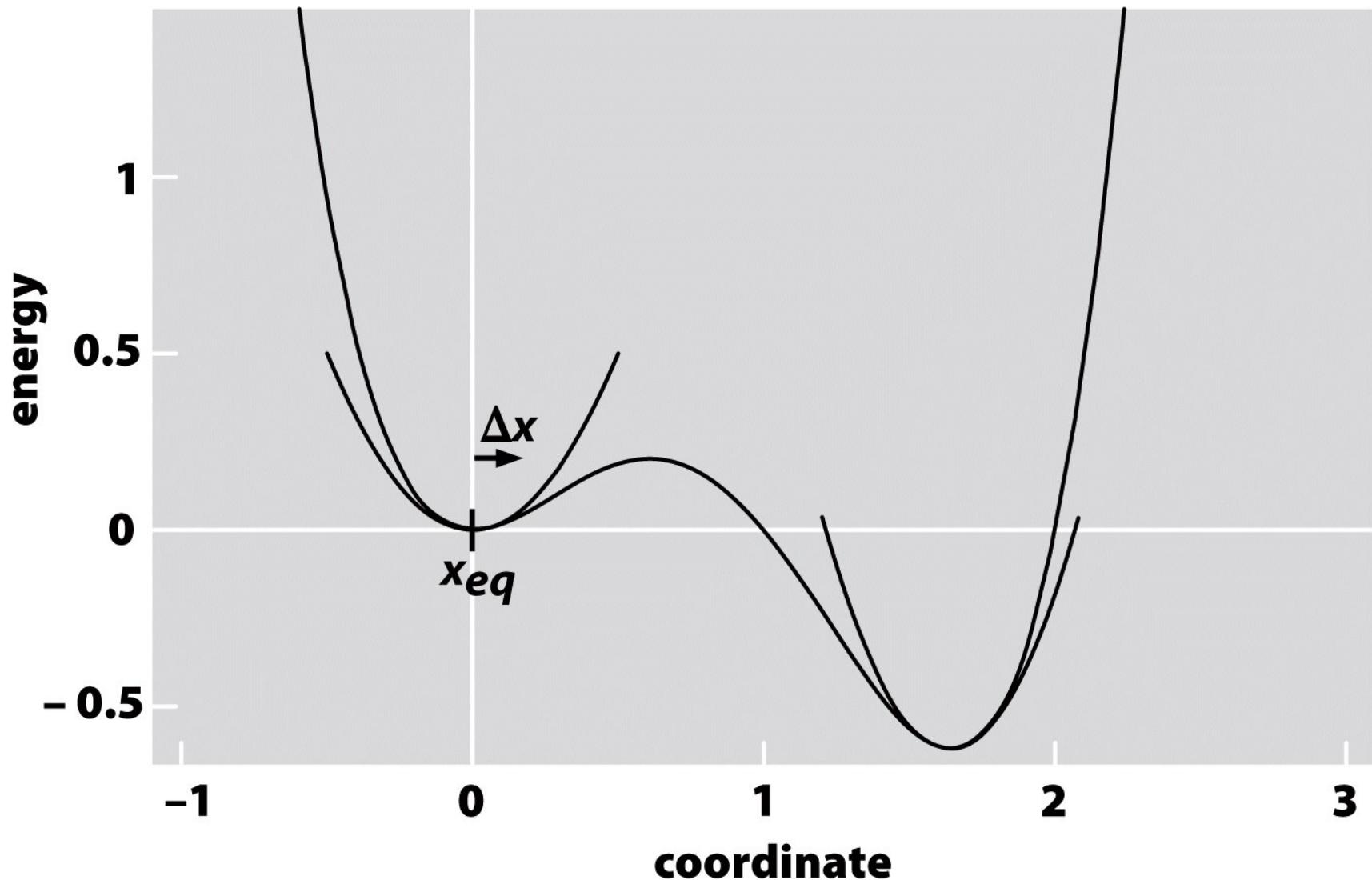


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Taylor expansion for $\cos(x)$ as a function of order n

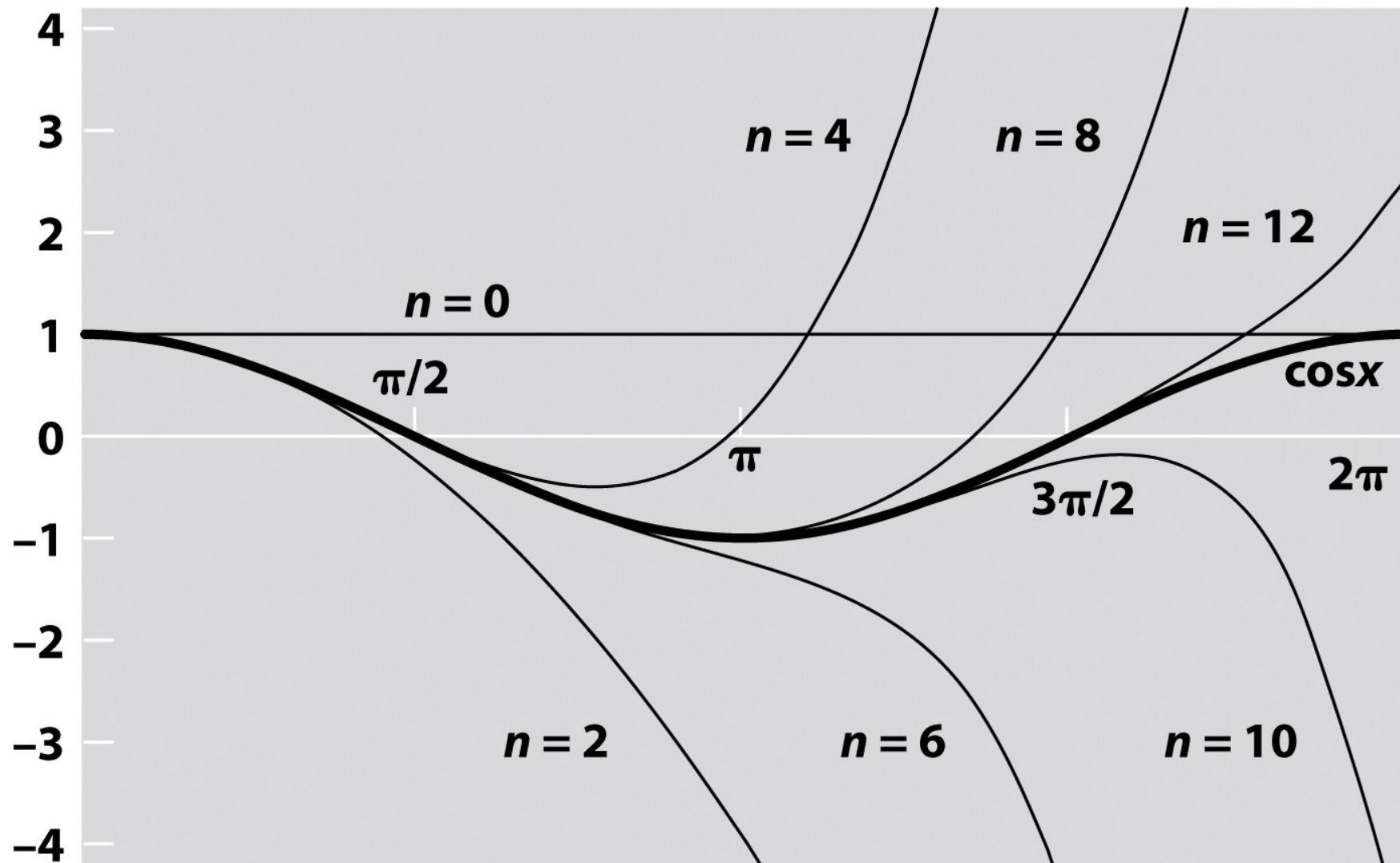


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Elastic stretching model: Young modulus E

- define *strain*: $\epsilon = \Delta L/L$; note that in general, $\epsilon = \epsilon(x,y,z)$
- $F = -k \Delta a$ or $F/A = E \Delta L/L$ (A ... cross section area)
- E measures the stiffness of the beam; F/A ... stress
- $n_A = A/a_0^2$, $n = L/a_0$; $F = n_A k \Delta a = A E \Delta L/L = AE \Delta a/a_0$
$$E = k/a_0$$

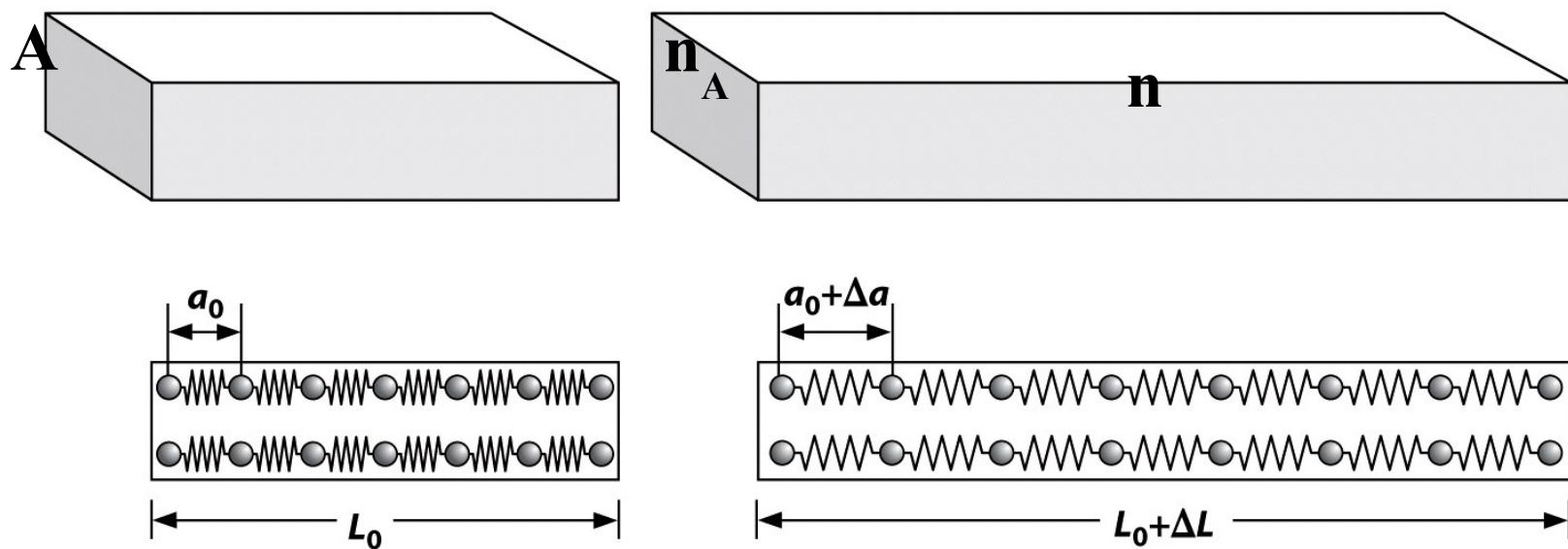
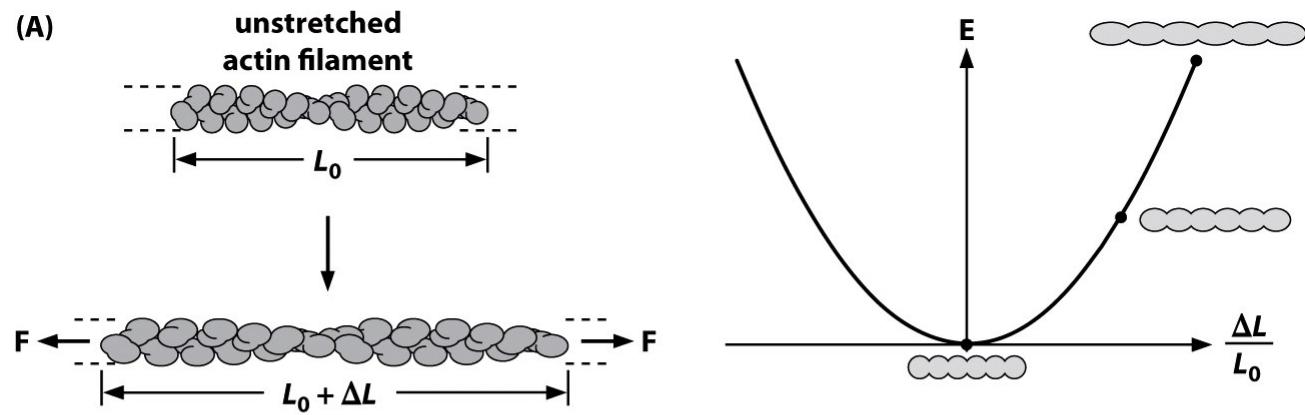


Figure 5.21 Physical Biology of the Cell (© Garland Science 2009)

Elastic deformation energy: a quadratic function of the strain

$$E_{\text{strain}} = \frac{1}{2} EA \int (\Delta L/L)^2 dx E_{\text{strain}} = \frac{1}{2} EA \int [du(x)/dx]^2 dx$$

F-actin filament



lipid bilayer

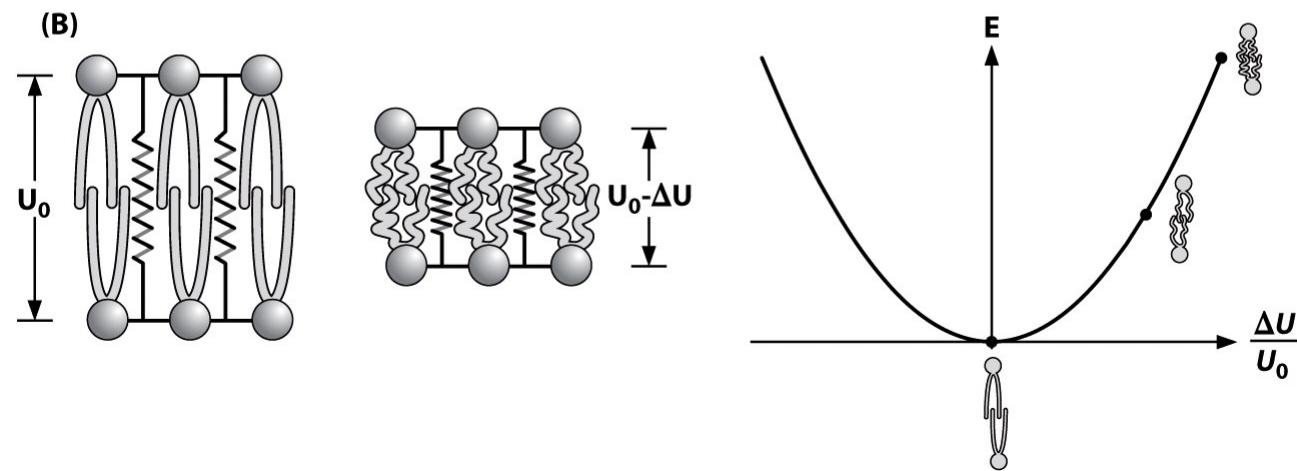
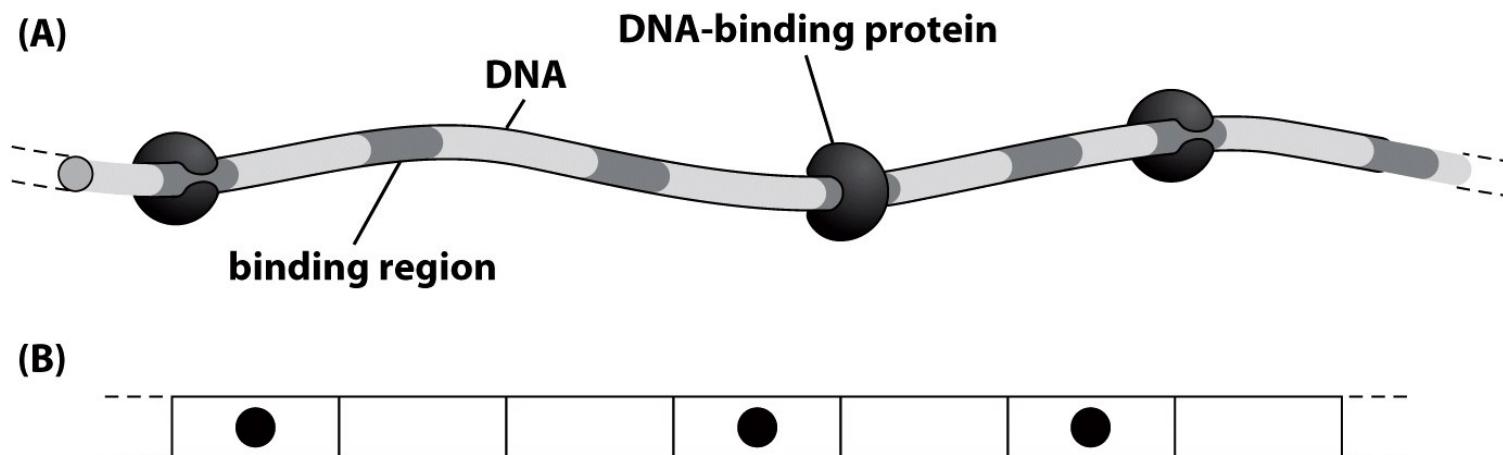


Figure 5.22 Physical Biology of the Cell (© Garland Science 2009)

Finding the macromolecule configuration that minimizes the total Gibbs free energy

$$F = E - TS; S = k_B \ln W; W \dots \# \text{ of microstates or } \textit{multiplicity}$$

Example: possible arrangements of N_p proteins on a DNA with N binding sites



lattice model of DNA/protein complexes

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$$S = k_B \ln W(N_p; N)$$

$$W(N_p; N) = N! / [N_p! (N - N_p)!]$$

For example: 10 copies of Lac repressor protein for 5×10^6 DNA binding sites within *E. coli* genome

$$N = 5 \times 10^6; N_p = 10 \quad W \sim 3 \times 10^{40}$$

$$S = k_B \ln\{N! / [N_p! (N - N_p)!]\}$$

Using Stirling's approximation, we get:

$$S/k_B \approx N \ln(N) - N - [N_p \ln(N_p) - N_p] - [(N - N_p) \ln(N - N_p) - (N - N_p)]$$

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

Entropy is maximal at $c = \frac{1}{2}$

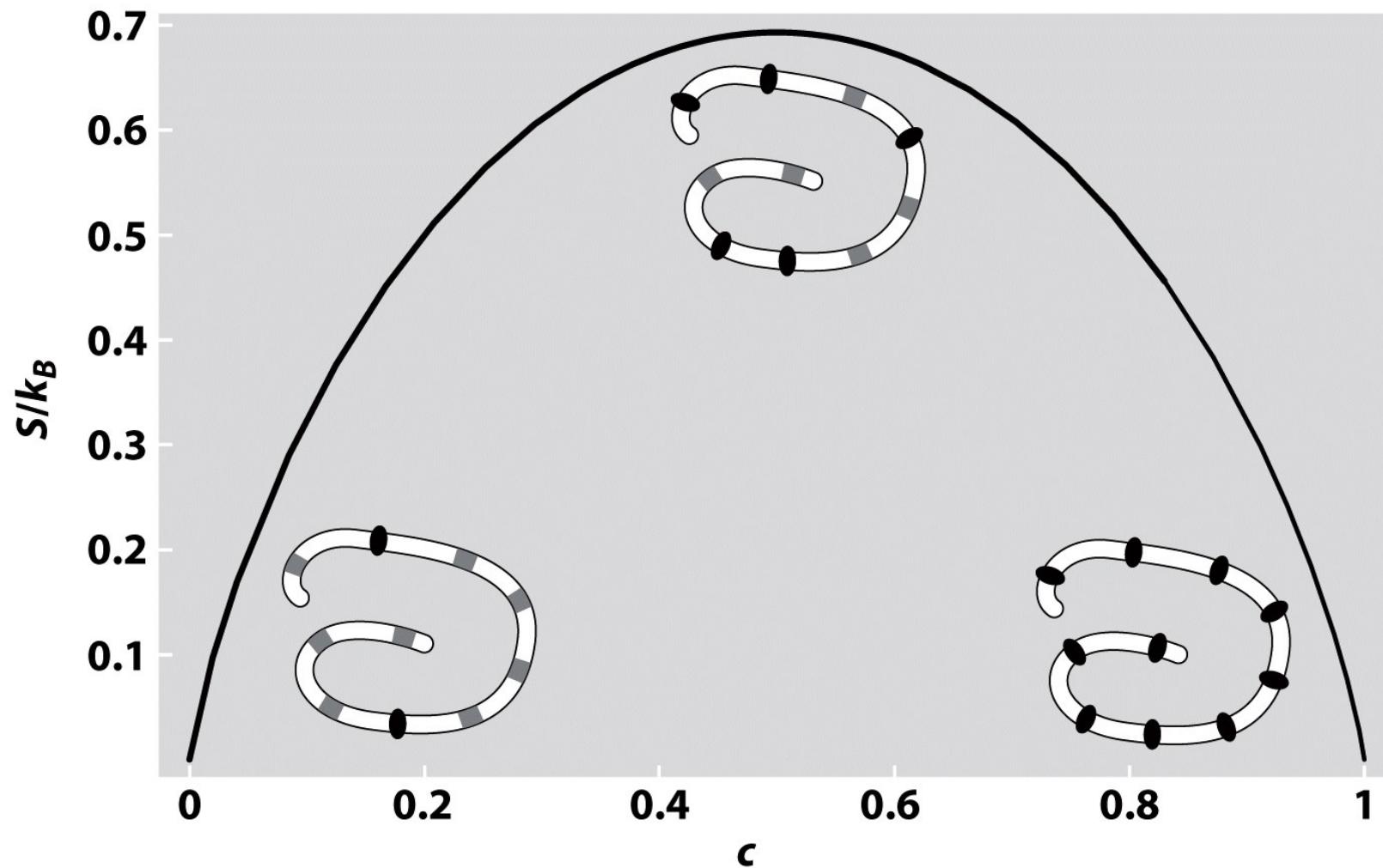


Figure 5.24 Physical Biology of the Cell (© Garland Science 2009)

Hydrophobic Effect is Related to Entropy of Water Molecules

Nonpolar (hydrophobic) molecules in solution deprive water molecules of the capacity to form hydrogen bonds and consequently take away part of their orientational entropy.

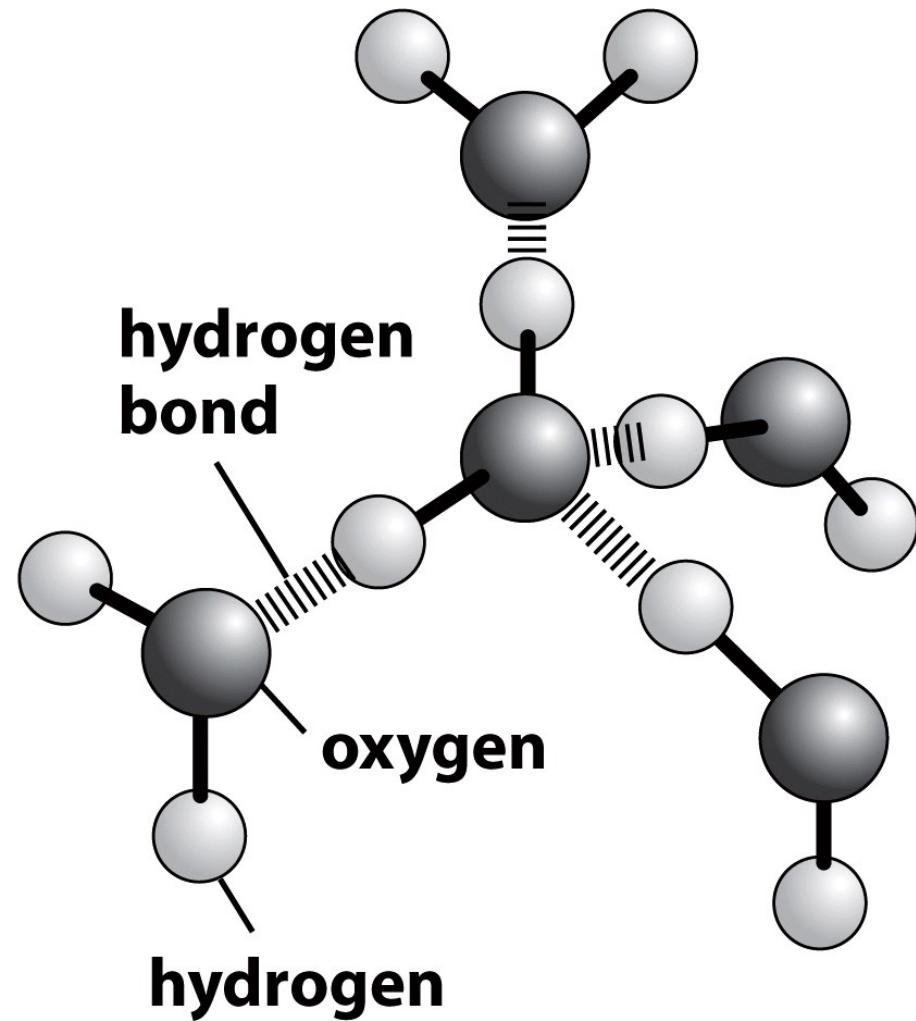


Figure 5.25 Physical Biology of the Cell (© Garland Science 2009)

Local tetrahedral arrangement of water molecules: 6 possible orientations of central H₂O molecule

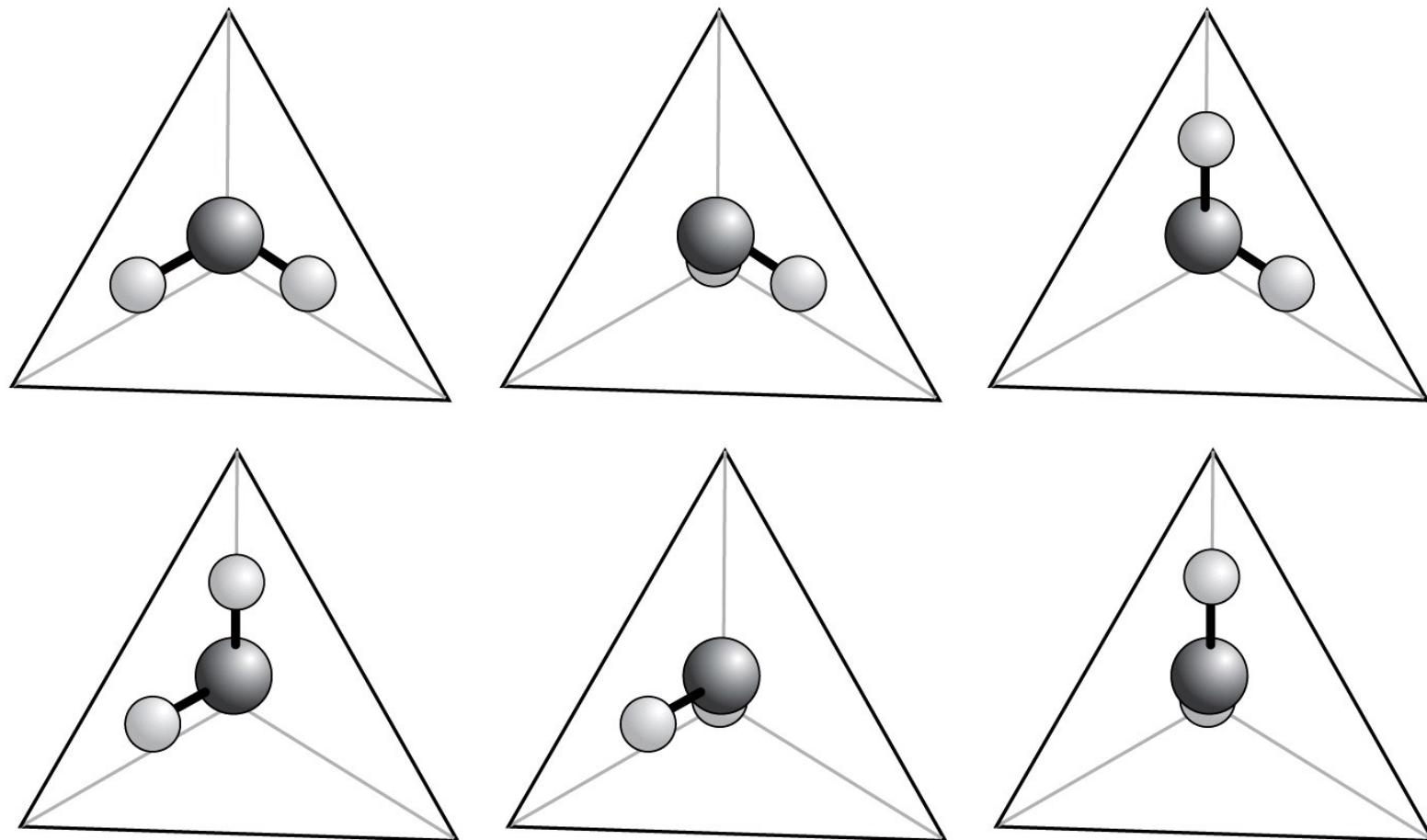


Figure 5.26 Physical Biology of the Cell (© Garland Science 2009)

When one of the four H₂O neighbors is populated by a nonpolar (hydrophobic) molecule: 3 of 6 configurations are forbidden, thus:

$$\Delta S_{\text{hydrophobic}} = k_B \ln 3 - k_B \ln 6 = -k_B \ln 2$$

$$\Delta G_{\text{hydrophobic}} = n k_B T \ln 2$$

n ... # of water molecules adjacent to the nonpolar molecule

$$\Delta G_{\text{hydrophobic}} = \gamma_{\text{hydrophobic}} A_{\text{hydrophobic}}$$

Examples: **-oxygen molecule O₂ in water: ~k_BT**

-octane in water: ~ 15 k_BT

Isolated system:

- can do no work on the environment and *vice versa*
- no heat can flow from it or *vice versa*
- no external fields
- no particle flow

Macroscopic equilibrium of an isolated system \equiv a system with a maximal entropy, that is, the largest number of microscopic realizations.

Consider three different *isolated* two-compartment systems such
That the barrier separating the two compartments (1,2) permits:

(A) energy flow: $E_1 + E_2 = E_{\text{tot}} = \text{const.}$

(B) volume change: $V_1 + V_2 = V_{\text{tot}} = \text{const.}$

(C) particle flow: $N_1 + N_2 = N_{\text{tot}} = \text{const.}$

Examine the total entropy: $S_{\text{tot}} = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2)$

(A) Energy flow:

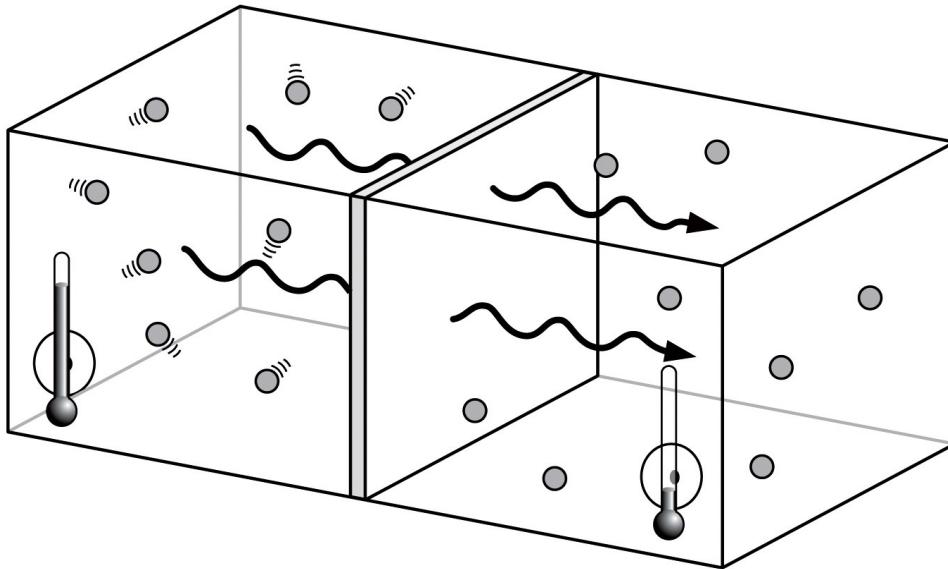


Figure 5.27a Physical Biology of the Cell (© Garland Science 2009)

Maximal entropy principle:

$$dS = (\partial S / \partial E_1) dE_1 + (\partial S / \partial E_2) dE_2 = [(\partial S / \partial E_1) - (\partial S / \partial E_2)] dE_1 = 0$$

where we considered: $dE_2 = -dE_1$

$(\partial S / \partial E_{12}) = 1/T_{12}$... thermodynamic definition of temperature

$$\mathbf{T_1 = T_2}$$

(B) Volume change:

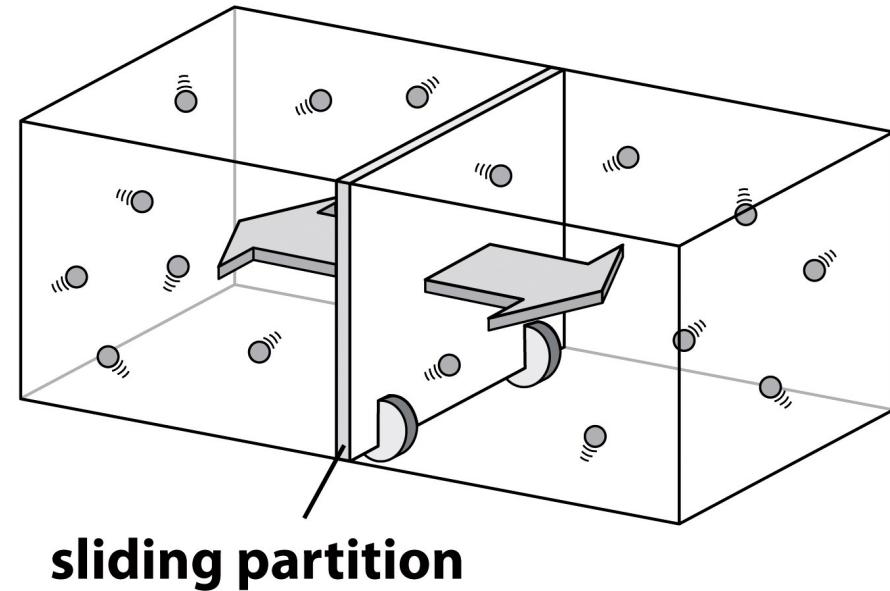


Figure 5.27b Physical Biology of the Cell (© Garland Science 2009)

Maximal entropy principle:

$$dS = (\partial S / \partial V_1) dV_1 + (\partial S / \partial V_2) dV_2 = [(\partial S / \partial V_1) - (\partial S / \partial V_2)] dV_1 = 0$$

where we considered: $dV_2 = -dV_1$

$$(\partial S / \partial V_{12})_{EN} = p_{12} / T \dots \text{TD identity}$$

$$\mathbf{p}_1 = \mathbf{p}_2$$

(C) Particle flow:

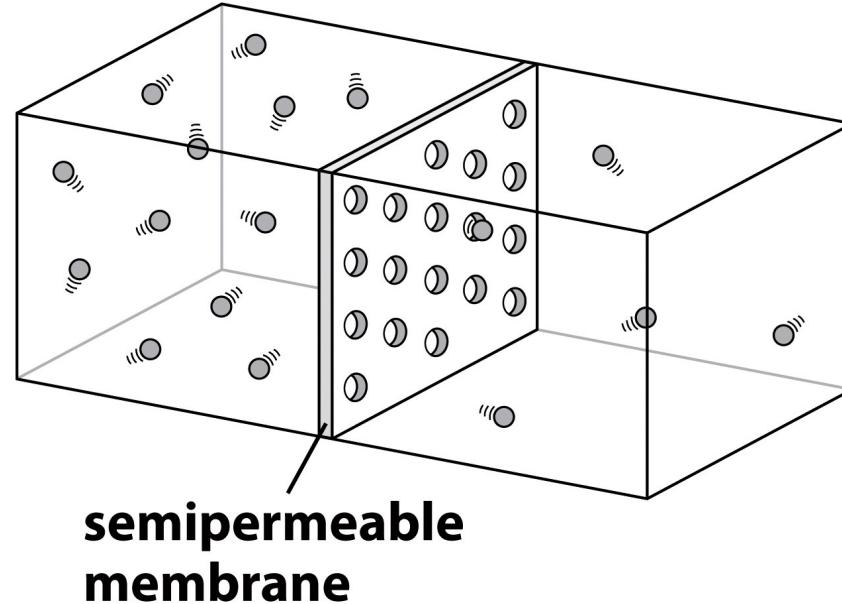


Figure 5.27c Physical Biology of the Cell (© Garland Science 2009)

Maximal entropy principle:

$$dS = (\partial S / \partial N_1) dN_1 + (\partial S / \partial N_2) dN_2 = [(\partial S / \partial N_1) - (\partial S / \partial N_2)] dN_1 = 0$$

where we considered: $dN_2 = - dN_1$

$- (\partial S / \partial N_{12})_{EV} = \mu_{12} / T$... TD definition of a chemical potential μ :

$$\mu_1 = \mu_2$$

Isolated versus closed system: Maximizing entropy versus Minimizing free energy

Closed system exchanges energy and work (volume changes) with environment.

closed system +
environment
=
isolated system

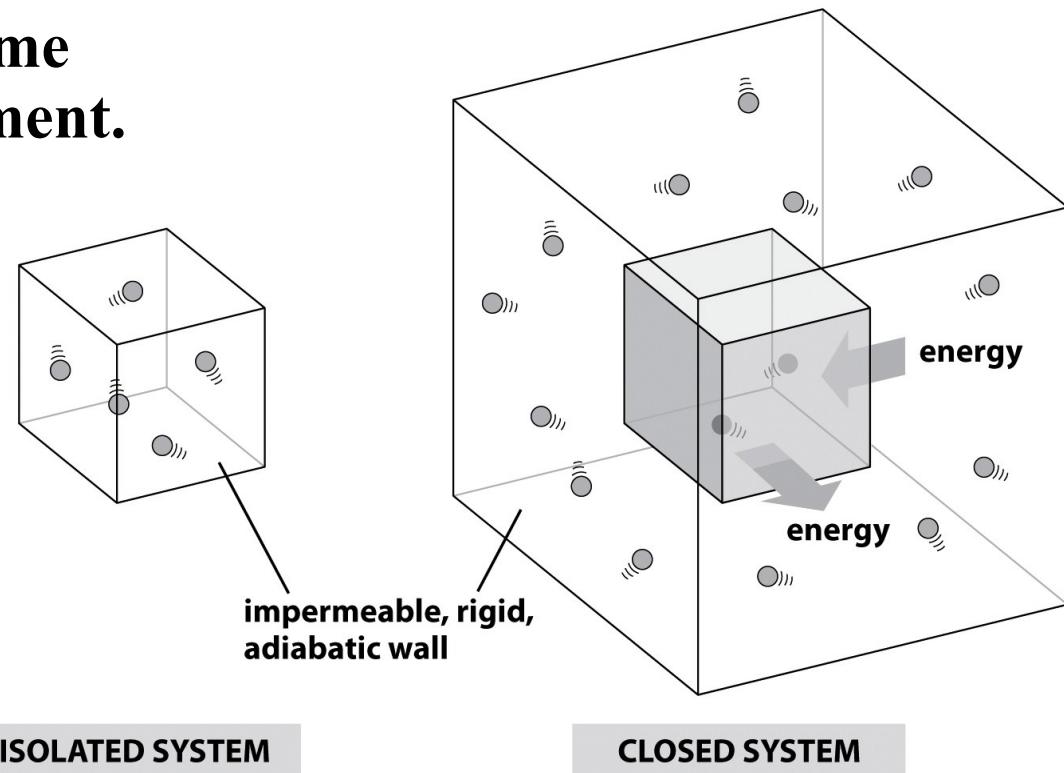


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Open system exchanges energy, work (volume changes), and matter with environment.

maximizing the entropy of a closed system and environment

\leftrightarrow

minimizing the free energy of a closed system only:

$$dS_{\text{TOT}} = dS_r + dS_s \geq 0$$

$$dE_r = T dS_r - p dV_r \text{ (first law of TD)}$$

(heat added – work done) by reservoir

$$dS_r = (dE_r + p dV_r)/T$$

$$dS_{\text{TOT}} = dS_s + dE_r/T + p dV_r/T \geq 0$$

$$dE_r = - dE_s \quad \& \quad dV_r = - dV_s$$

$$dS_s - dE_s/T - p dV_s/T \geq 0$$

$$\Leftrightarrow dG = d(E_s + p V_s - TS_s) \leq 0$$

At fixed T,p; the free energy G of a closed system is minimized!