The Boltzmann factor: probability of a molecule or a system being in state i with energy E_i while in equilibrium at temperature T is given by

$$p(E_i) = \frac{1}{Z} e^{-E_i/k_B T}$$

The normalization factor (also called "partition function") is given by

$$Z = \sum_i e^{-E_i/k_B T}$$

This ensures $\sum_i P(E_i) = 1$:

$$\sum_i P(E_i) = \sum_i \frac{1}{Z} e^{-E_i/k_B T} = \frac{1}{Z} \sum_i e^{-E_i/k_B T} = \frac{Z}{Z} = 1$$

The Boltzmann factor: $p(E_i) = \frac{1}{Z} e^{-E_i/k_B T}$

So where does this come from?

It's all from entropy!

For the system to be in equilibrium at temperature T, it must be coupled to a reservoir at temperature T.

Note that

$$E_{\text{tot}} = E_{\text{sys}} + E_{\text{res}}$$

and combined multiplicity is

$$W_{\text{tot}} = \underbrace{W_{\text{sys}}}_{=1} \times W_{\text{res}}$$

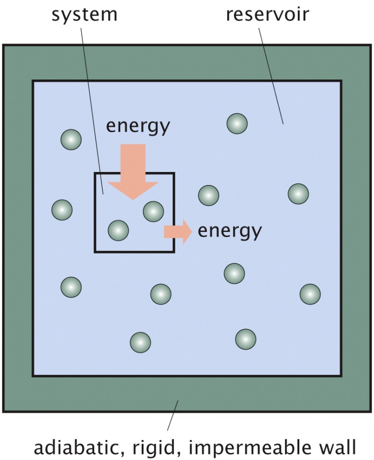

Figure 6.14 Physical Biology of the Cell, 2ed. (© Garland Science 2013)

Remember $W_{\text{tot}} = 1 \times W_{\text{res}}$.

Now take the ratio of the probabilities of the system being in microstate i versus microstate j

$$\frac{p(E_i)}{p(E_j)} = \frac{W_{\text{tot}}(\overbrace{E_i}^{\text{sys}} | \overbrace{E_{\text{tot}} - E_i}^{\text{res}})}{W_{\text{tot}}(E_j | E_{\text{tot}} - E_j)} = \frac{W_{\text{res}}(E_{\text{tot}} - E_i)}{W_{\text{res}}(E_{\text{tot}} - E_j)}$$

Use Boltzmann's entropy, $S = k_B \ln W$, rewrite as $W = e^{S/k_B}$, and plug in:

$$\frac{p(E_i)}{p(E_j)} = \frac{e^{S_{\text{res}}(E_{\text{tot}} - E_i)/k_B}}{e^{S_{\text{res}}(E_{\text{tot}} - E_j)/k_B}}$$

Recall: $\frac{p(E_i)}{p(E_j)} = \frac{e^{S_{\text{res}}(E_{\text{tot}}-E_i)/k_B}}{e^{S_{\text{res}}(E_{\text{tot}}-E_j)/k_B}}$ Taylor expand:

$$S_{\text{res}}(E_{\text{tot}} - E_{\text{sys}}) \simeq S_{\text{res}}(E_{\text{tot}}) - \left(\frac{\partial S_{\text{res}}}{\partial E}\right) E_{\text{sys}} = S_{\text{res}}(E_{\text{tot}}) - \frac{1}{T} E_{\text{sys}}$$

and plug in:

$$\frac{p(E_i)}{p(E_j)} = \frac{e^{[S_{\text{res}}(E_{\text{tot}})-E_i/T]/k_B}}{e^{[S_{\text{res}}(E_{\text{tot}})-E_j/T]/k_B}} = \frac{e^{-E_i/k_BT}}{e^{-E_j/k_BT}}$$

So evidently,

$$p(E_i) = \frac{1}{Z} e^{-E_i/k_BT}$$

What is it good for? A lot! To begin with, computing averages:

For some quantity A that takes on the value A_i in microstate i, we can compute the average

$$\langle A \rangle = \sum_i A_i \, p(i) = \frac{1}{Z} \sum_i A_i e^{-E_i/k_B T}$$

Sometimes the states are continuous and the sum gets replaced by an integral:

$$\langle A \rangle = \int A(q) \, p(q) \, dq = \frac{1}{Z} \int A(q) \, e^{-E(q)/k_B T} \, dq$$

$$= \frac{\int A(q) \, e^{-E(q)/k_B T} \, dq}{\int e^{-E(q)/k_B T} \, dq}$$

Equipartition Theorem: quadratic degrees of freedom have average energy $\frac{1}{2}k_B T$.

So consider an energy $E = c\,q^2$. Here c is some coefficient and q might be a velocity component or position. The average is

$$\langle E \rangle = \frac{\displaystyle\int c\,q^2\,e^{-c\,q^2/k_B T}\,dq}{\displaystyle\int e^{-c\,q^2/k_B T}\,dq}$$

Looks awful! But it's not so bad...

Gaussian integral tricks: starting from

$$I = \int_{-\infty}^{\infty} e^{-\alpha q^2} dq = \sqrt{\frac{\pi}{\alpha}}$$

which is derived in your book.

$$\frac{dI}{d\alpha} = \frac{d}{d\alpha} \int_{-\infty}^{\infty} e^{-\alpha q^2} dq = -\int_{-\infty}^{\infty} q^2 \, e^{-\alpha q^2} dq$$

At the same time, $\dfrac{dI}{d\alpha} = \dfrac{d}{d\alpha}\sqrt{\dfrac{\pi}{\alpha}} = -\dfrac{1}{2\alpha}\sqrt{\dfrac{\pi}{\alpha}}$

So all together then

$$\int_{-\infty}^{\infty} q^2 \, e^{-\alpha q^2} dq = \frac{1}{2\alpha}\sqrt{\frac{\pi}{\alpha}}$$

$$\int_{-\infty}^{\infty} e^{-\alpha q^2} dq = \sqrt{\frac{\pi}{\alpha}} \qquad \int_{-\infty}^{\infty} q^2\, e^{-\alpha q^2} dq = \frac{1}{2\alpha}\sqrt{\frac{\pi}{\alpha}}$$

Back to Equipartition: with $E = c\,q^2$

$$\langle E\rangle = \frac{\displaystyle\int c\,q^2\, e^{-c\,q^2/k_BT}\, dq}{\displaystyle\int e^{-c\,q^2/k_BT}\, dq}$$

where $\alpha = c/k_BT$.

Example: velocity component $\langle \frac{1}{2}mv_x^2\rangle = \frac{1}{2}k_BT$

$$\langle\frac{1}{2}m(v_x^2 + v_y^2 + v_z^2)\rangle = \frac{3}{2}k_BT \quad \Rightarrow \quad \sqrt{\langle v^2\rangle} = \sqrt{\frac{3k_BT}{m}}$$

Stirling's Approximation: $N! = (N/e)^N$ or $\ln N! = N \ln N - N$.
Very useful! To understand this a bit, compare $N!$ to N^N:

$$\begin{aligned} N^N &= N \times \quad N \quad \times \quad N \quad \cdots \times N \\ N! &= N \times (N-1) \times (N-2) \cdots \times 1 \end{aligned}$$

Derivation in HW Problem 5.6. Basic idea is to establish the identity

$$n! = \int_0^\infty x^n e^{-x}\, dx$$

and then to realize this integrand is sharply peaked for large n.

Using Stirling's Approximation

- Ligand-Receptor binding: assume ligands can occupy sites on a lattice. Ω total sites, and L total ligands. Each site is in one of two categories: occupied or unoccupied. Leads to binomial coefficient

$$W = \frac{\Omega!}{(\Omega - L)!L!} = \frac{\Omega^{\Omega}}{(\Omega - L)^{\Omega - L} L^{L}}$$

- Einstein solid: from PHYS 211. N oscillators, q energy units, multiplicity

$$W = \frac{(q + N - 1)!}{q!(N - 1)!} = \frac{(q + N)^{q+N}}{q^{q} N^{N}}$$

for large N and q.

Taking natural log: for Einstein solid

$$W = \frac{(q+N-1)!}{q!(N-1)!} = \frac{(q+N)^{q+N}}{q^q N^N}$$

so

$$S/k_B = \ln W = (q+N)\ln(q+N) - q\ln q - N\ln N$$

What do we get when we take

$$\frac{\partial S/k_B}{\partial q} = \ln(q+N) + (q+N)\frac{1}{q+N} - \ln q + q\frac{1}{q} = \ldots$$

Next time: ligand-receptor binding