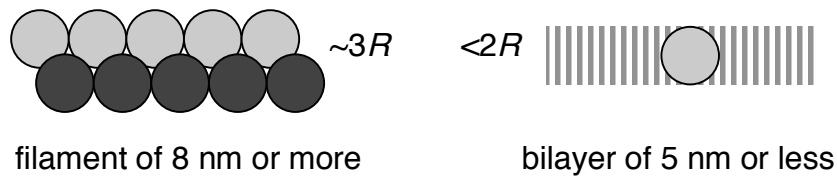


4xx Intro 4 - Soft materials and the Boltzmann factor

Protein size

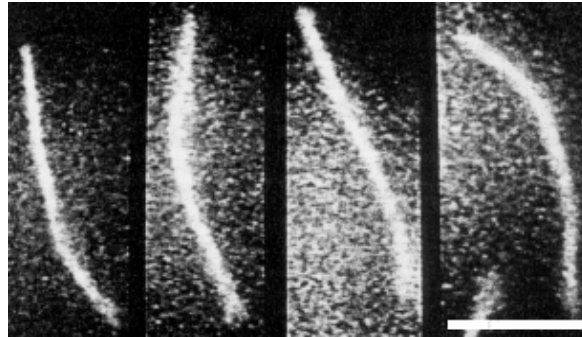
- 1000 base pairs of DNA \leftrightarrow 330 amino acids @ 3 bp/AA
- 115 D per amino acid, averaged over a large protein
- for actin, $375 \times 115 = 43,000$ D (actual is 42,000 D)
- mass = $4.3 \times 10^4 \times 1.67 \times 10^{-27} = 7.0 \times 10^{-23}$ kg
- if density = 10^3 kg/m³, globule occupies a volume of $7.0 \times 10^{-23} / 10^3 = 7.0 \times 10^{-26}$ m³
- radius of equivalent sphere is $R = (3 \times 7.0 \times 10^{-26} / 4\pi)^{1/3} = 2.6$ nm

Size of structural elements

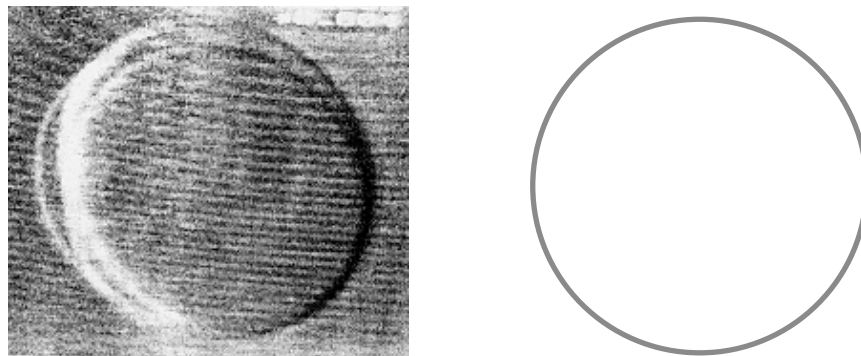


Structural elements are soft

rhodamine-labelled actin (bar = 5 μ m) (from Isambert *et al.*)



bilayers (from Yeung and Evans)



Energy scales

Binding of atoms within a molecule tends to be much stronger than the binding between molecules. Covalent bonds within a molecule have energies that are at least a hundred times the thermal energy scale $k_B T$:

<i>Bond</i>	<i>Energy</i>		
	(kJ/mol)	(eV/bond)	($k_B T$ /bond)
C - C	350	3.6	140
C - O	310	3.2	124
C - H	415	4.3	166
O - H	463	4.8	186
C = C	610	6.3	244
C = O	740	7.7	299
C ≡ C	836	8.7	338

$$[1 \text{ kJ/mol} = 1.04 \times 10^{-2} \text{ eV/bond} = 0.40 k_B T/\text{bond}]$$

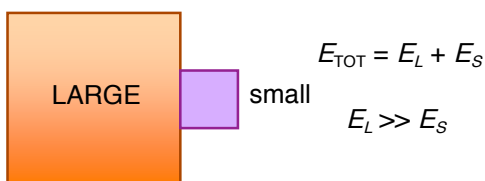
Hydrogen bonds within and between segments of molecules, such as between base pairs in DNA are much weaker, but still larger than $k_B T$ (H-bonds are indicated by \cdots)

<i>Hydrogen bond</i>	<i>Energy</i>		
	(kJ/mol)	(eV/bond)	($k_B T$ /bond)
C - H \cdots N	12 - 20	0.13 - 0.21	5 - 8
C - H \cdots O	24	0.25	10
N - H \cdots O	16 - 24	0.17 - 0.25	6 - 10
O - H \cdots O	20 - 28	0.21 - 0.29	8 - 11
F - H \cdots O	44	0.46	18

The deformations of soft materials, which do not involve bond-breaking, involve smaller energy scales again.

Temperature and entropy

Any configuration available to a system can be characterized by its energy (more than one configuration may have the same energy). At $T > 0$, the system samples many configurations as it exchanges energy with its environment. To see how the energy fluctuations, let's examine two systems, L and S , in thermal contact.



System S is the subject of our observations, while L is the reservoir; L has far more energy than S . We specify that L and S exchange energy only with each other, so that their total energy, E_{TOT} , is a constant:

$$E_{\text{TOT}} = E_L + E_S. \quad (1)$$

We now specify E_{TOT} to be a particular value E_o , say $E_{\text{TOT}} = E_o = 10^6$ Joules. We are interested in a particular state r of the small system with energy E_r , such that

$$E_S = E_r \quad \text{and} \quad E_L = E_o - E_r. \quad (2)$$

Just to make sure that the notation is clear: E_S , E_L and E_{TOT} are general parameters, while E_r and E_o represent a specific choice of energies.

We define the number of states of the large system having energy E_L to be

$$\Omega_L(E_L) = [\textit{number of states of large system with } E_L]. \quad (3)$$

The number of states of the large system $\Omega_L(E_L)$ varies, perhaps even rapidly, with E_L , but its logarithm varies more slowly, and can be expanded in a series around the specific value $E_L = E_o$:

$$\ln \Omega_L(E_o - E_r) = \ln \Omega_L(E_o) - [\partial \ln \Omega_L / \partial E_L]_o E_r + \dots \quad (4)$$

where the derivative of $\ln \Omega_L$ with respect to E_L is evaluated at $E_L = E_o$. The minus sign in front of the derivative arises because the energy E_L of the large system decreases by E_r when the energy of the small system increases by E_r . Higher order terms can be neglected since $E_r \ll E_o$. The derivative $[\partial \ln \Omega_L / \partial E_L]_o$ characterizes the large system around $E_L = E_o$, and does not depend on E_r ; hence, it is notationally convenient to replace this derivative with a single symbol

$$[\partial \ln \Omega_L / \partial E_L]_o \equiv \beta. \quad (5)$$

It can be shown that β^{-1} , bearing units of energy, has the properties of a temperature; the physical temperature scale is set through $T = 1 / k_B \beta$, where k_B is Boltzmann's constant ($k_B = 1.38 \times 10^{-23}$ J/K).

Returning now to Eq. (4), the derivative on the right-hand side can be replaced by β

$$\begin{aligned} \ln \Omega_L(E_o - E_r) &= \ln \Omega_L(E_o) - \beta E_r + \dots, \\ \Rightarrow \Omega_L(E_o - E_r) &= \Omega_L(E_o) \exp(-\beta E_r). \end{aligned} \quad (6)$$

The number of configurations available to a system affects its behavior at finite temperature. For instance, the molecules of a gas are more likely to be found scattered throughout the volume of a container than collected together in one of its corners, all other things being equal. Mathematically, we say that a system at fixed volume minimizes its free energy $E - TS$, rather than just minimizes its energy E , where S denotes entropy; an even more general expression for the free energy is needed if the volume or the number of particles is not fixed. Entropy increases logarithmically with the number of states Ω accessible to the system,

$$S = k_B \ln \Omega(\langle E \rangle), \quad (7)$$

where Ω is a function of the mean energy $\langle E \rangle$ of the system (see Sec. 6.6 of Reif, 1965). Because TS enters the free energy with a minus sign, the free energy of a system falls as its entropy rises, a process that can occur spontaneously.

Boltzmann factor

We have selected a particular state r of the small system with energy E_r . The probability \mathcal{P}_r of the small system being in this state is proportional to the number of states of the *large* system having the appropriate value of E_L ; that is, $\mathcal{P}_r \propto \Omega_L(E_o - E_r)$ or

$$\mathcal{P}_r \equiv A \Omega_L(E_o - E_r), \quad (8)$$

where the proportionality constant A is a characteristic of the *large* system. The value of A can be determined through the condition that the small system must always occupy an available state, although it may occupy different states as time passes:

$$\sum_r \mathcal{P}_r = 1, \quad (9)$$

where the sum is over all of the states r available to the small system. We replace $\Omega_L(E_o - E_r)$ in Eq. (8) by its functional dependence on E_r in Eq. (6) to obtain

$$\mathcal{P}_r = A \Omega_L(E_o - E_r) = [A \Omega_L(E_o)] \exp(-\beta E_r). \quad (10)$$

This is the Boltzmann factor, and it shows that the probability of the small system being in a specific state r with energy E_r is a function of the energy of the state r and of the temperature of the large system with which it is in thermal contact. The two factors in the square braces of Eq. (10) are both constants, and can be rolled into one as

$$\mathcal{P}_r = Z^{-1} \exp(-\beta E_r). \quad (11)$$

To be properly normalized,

$$Z = \sum_r \exp(-\beta E_r). \quad (12)$$

Example: harmonic oscillator

As an application of the Boltzmann factor, we consider the one-dimensional motion of a particle in the quadratic potential $V(x)$ characteristic of Hooke's law for springs,

$$V(x) = k_{sp} x^2 / 2, \quad (13)$$

where k_{sp} is the spring constant and x is the displacement from equilibrium. For a given value of x , Eq. (13) is the corresponding potential energy, and the Boltzmann factor $\exp(-\beta k_{sp} x^2 / 2)$ provides the likelihood that the particle can be found with that energy.

Now, x is a continuous variable, so one talks of the probability $\mathcal{P}(x)dx$ of the particle having a displacement between x and $x + dx$. The continuous version of Eq. (12) is

$$\mathcal{P}(x)dx = dx \cdot \exp(-\alpha x^2) / \int \exp(-\alpha x^2) dx, \quad (14)$$

where the combination $\beta k_{sp}/2$ has been replaced with a single constant α

$$\alpha \equiv \beta k_{sp}/2. \quad (15)$$

Eq. (14) can be used to evaluate the fluctuations in x about $x = 0$:

$$\begin{aligned} \langle x^2 \rangle &= \int x^2 \mathcal{P}(x) dx \\ &= \alpha^{-1} \int z^2 \exp(-z^2) dz / \int \exp(-z^2) dz \\ &= \alpha^{-1} (\sqrt{\pi} / 2) / \sqrt{\pi} = 1 / 2\alpha. \end{aligned} \quad (16)$$

where the integrals over x run from $-\infty$ to $+\infty$. Hence

$$\langle x^2 \rangle = 1 / \beta k_{sp} = k_B T / k_{sp}. \quad (17)$$