We recall the trick (3.13-3.14)
\[
\int_{-\infty}^{\infty} dy \, y^2 e^{-by^2} = -\frac{d}{db} \int_{-\infty}^{\infty} dy \, e^{-by^2} = \frac{1}{2} \sqrt{\frac{\pi}{b^3}}.
\]

So,
\[
\int_{-\infty}^{\infty} dv \, \frac{1}{2} m v^2 P(v) = \int_{-\infty}^{\infty} dv \, \frac{1}{2} m v^2 \sqrt{\frac{m}{2\pi \hbar T}} e^{-\frac{m v^2}{2\hbar T}}
\]
\[
= \frac{1}{2} m \sqrt{\frac{m}{2\pi \hbar T}} \int_{-\infty}^{\infty} dv \, v^2 e^{-\frac{m v^2}{2\hbar T}}
\]
\[
= \frac{1}{2} m \sqrt{\frac{m}{2\pi \hbar T}} \frac{1}{2} \sqrt{\pi \left(\frac{2\hbar T}{m}\right)^3}
\]
\[
= \frac{m}{4} \sqrt{\left(\frac{2\hbar T}{m}\right)^2} = \frac{m}{4} \frac{2\hbar T}{m} = \frac{\hbar T}{2}.
\]

Similarly,
\[
\int_{-\infty}^{\infty} dx \, \frac{1}{2} m x^2 P(x) = \frac{\hbar T}{2}.
\]

So,
\[
E_a = \frac{1}{2} \hbar T + \frac{1}{2} \hbar T = \hbar T
\]

as required by the equipartition of energy.
For 3D, we have

\[ E_a = \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2 \]

\[ + \frac{1}{2} c x^2 + \frac{1}{2} c y^2 + \frac{1}{2} c z^2 \]

and

\[ P(\vec{v}, \vec{z}) = P(v_x) P(v_y) P(v_z) P(x) P(y) P(z). \]

So

\[ \langle E_a \rangle = \int d\vec{v} \frac{1}{2} m v_x^2 P(v_x) \int d\vec{v} P(v_y) \int d\vec{v} P(v_z) \]

\[ \times \int dx P(x) \int dy P(y) \int dz P(z) \]

\[ + \ldots \]

\[ + \int d\vec{v} d\vec{v} P(\vec{v}^2) \int dx P(x) \int dy P(y) \int dz \frac{1}{2} c^2 \]

\[ \frac{1}{2} \int dx \int dy \int dz \frac{1}{2} c^2 P(z) \]

\[ = \frac{\hbar T}{2} + \frac{\hbar T}{2} + \frac{\hbar T}{2} + \frac{\hbar T}{2} + \frac{\hbar T}{2} + \frac{\hbar T}{2} \]

\[ = \frac{3}{2} \hbar T = 3 \hbar T. \]

Each degree of freedom of a gets \(\frac{\hbar T}{2}\) from the thermal reservoir \(B\) at temperature \(T\).
\[ \frac{S_2, N_2}{E_2} \quad - \quad \frac{S_1, N_1}{E_1} \quad - \quad E_B \quad - \quad \frac{-E_B}{kT} \quad - \quad \frac{-(E_B + \Delta E)/kT}{-} \]

\text{rate } N_2 \rightarrow N_1 \text{ is } N_2 k_+ = f N_2 e^{- \left(\frac{E_B + \Delta E}{kT}\right)}

\text{rate } N_1 \rightarrow N_2 \text{ is } N_1 k_- = f N_1 e^{- \left(\frac{-E_B}{kT}\right)}

Here \( f \) is some attempt frequency.

At equilibrium,

\[ N_2 k_+ = f N_2 e^{- \left(\frac{E_B + \Delta E}{kT}\right)} = f N_1 e^{- \left(\frac{-E_B}{kT}\right)} = N_1 k_- \]

\[ \frac{N_2}{N_1} = e^{- \frac{\Delta E}{kT}} \quad \text{at equilibrium (6.27)} \]

Note that \( N_2/N_1 \) is independent of the barrier energy \( E_B \). Note also that \( N_2 h_+ = N_1 h_- \) implies \( k_+/k_- = e^{\frac{\Delta E}{kT}} \).
But $E_B$ does affect how long it takes to reach equilibrium.

\[ \dot{N}_2 = \frac{dN_2}{dt} = -h + N_2 + h - N_1 \]

\[ \dot{N}_1 = \frac{dN_1}{dt} = k + N_2 - k - N_1 \]

Now $N_1 + N_2 = N$ the total number of molecules (or systems). So the two equations collapse into

\[ -\dot{N}_1 = -k + (N - N_1) + h - N, \]

\[ \dot{N}_1 = k + (N - N_1) - h - N. \]

This is a first-order inhomogeneous equation. One solution of the inhomogeneous equation is $\dot{N}_1 = 0$. 

\[ 0 = k_+ (N - N_1) - k_- N_1 \quad \text{or} \quad (k_+ + k_-)N_1 = N k_+ \quad \text{or} \quad N_1 = \frac{N k_+}{k_+ + k_-} \equiv N_{eq} \]

The homogeneous equation is:

\[ \frac{dN_1}{N_1} = -(k_+ + k_-) \, dt \]

\[ \ln N_1 = - (k_+ + k_-) t + c \]

\[ N_1 = e^{- (k_+ + k_-) t} \]

So

\[ N_1(t) = C e^{- (k_+ + k_-) t} + \frac{N k_+}{k_+ + k_-} \]

\[ N_1(0) = C + \frac{N k_+}{k_+ + k_-} \]

So \[ C = N_1(0) - \frac{N k_+}{k_+ + k_-} \] and
\[ N_1(t) = \left( N_1(0) - \frac{N k_+}{k_+ + k_-} \right) e^{-(k_+ + k_-)t} + \frac{N k_+}{k_+ + k_-} (1 - e^{-(k_+ + k_-)t}) \]

or

\[ N_1(t) = N_1(0) e^{-(k_+ + k_-)t} + N_{1,0} (1 - e^{-(k_+ + k_-)t}) \]

In terms of the decay constant

\[ \tau = \frac{1}{k_+ + k_-} \]

\[ N_1(t) = N_1(0) e^{-t/\tau} + N_{1,0} (1 - e^{-t/\tau}) \]

\[ \frac{1}{\tau} = h_+ + h_- = \frac{-E_0 \hbar T}{\hbar} + \frac{-(E_0 + \Delta E) \hbar T}{\hbar} \]
That is,
\[ \frac{1}{T} = \frac{-E_B}{kT} \left( 1 + e^{-\frac{-\Delta E}{kT}} \right). \]

So the time to reach equilibrium rises exponentially with the barrier energy \( E_B \).

Suppose a single kind of molecule can exist in and jump between states \( S_1 \) and \( S_2 \). Say \( N_0 \) start out in \( S_2 \). If \( N(t) \) is the number in \( S_2 \) at time \( t \), then
\[ N(t + dt) = (1 - k_{-1} dt) N(t) \]
and \( N(0) = N_0 \). This is the differential
\[
\frac{N(t+\Delta t) - N(t)}{\Delta t} = \frac{dN}{dt} = -k_+ N(t)
\]

whose solution is

\[
N(t) = N(0) e^{-k_+ t} = N_0 e^{-k_+ t}.
\]

The probability of a molecule staying in \( S_2 \) till time \( t \) and then hopping to \( S_1 \) in \( \Delta t \) is

\[
P_{2-\rightarrow 1}(t) \Delta t = \frac{N(t)}{N(0)} \frac{-dN}{N(t)} = \frac{N(t)}{N_0} k_+ \Delta t
\]

\[
- k_+ t = k_+ e^{-k_+ t} \Delta t \quad (6.31)
\]

and it is suitably normalized:

\[
\int_0^\infty P_{2-\rightarrow 1}(t) \Delta t = \int_0^\infty k_+ e^{-k_+ t} \Delta t
\]

\[
= k_+ \left[ \frac{e^{-k_+ t}}{-k_+} \right]_0^\infty = 1.
\]
Section 6.6.1 showed that if each state of a combined system $a + B$ (a thing, $B$ big) is equally probable (which maximizes the entropy of the combined system as $S = k \ln S = k \ln \frac{1}{p_0}$), then the distribution of states of $a$ is

$$P_j \propto e^{-E_j/kT}$$

which is the Boltzmann distribution.

The Boltzmann distribution also minimizes the free energy

$$F_a = E_a - TS_a \quad (6.32)$$

in which

$$E_a = \sum E_j P_j$$

and

$$S_a = -k \sum P_j \ln P_j$$
\[ 1 = \sum P_j. \]

The nice way to see this is to use Lagrange's trick: seek the minimum of

\[ F(p_j, \alpha) = \sum E_j p_j - T \ln \sum p_j + \alpha (1 - \sum p_j). \]

So,

\[ 0 = \frac{\partial F(p_j, \alpha)}{\partial p_j} = E_j - kT \ln p_j - kT - \alpha \]

\[ 0 = \frac{\partial F(p_j, \alpha)}{\partial \alpha} = 1 - \sum p_j. \]

The first equation tells us that

\[-kT \ln p_j = E_j - kT - \alpha\]

or

\[ \ln p_j = -\frac{E_j}{kT} + 1 + \frac{\alpha}{kT}. \]
ou

\[ P_j = e^{-\frac{E_j}{kT} + 1 + \alpha/kT} \]

The second one tells us that \( \alpha \) must be chosen so that the \( P_j \) are normalized

\[ 1 = \sum P_j = \sum e^{-\frac{E_j}{kT} + 1 + \alpha/kT} \]

The next way to do this is to define the partition function

\[ Z = \sum_{j} e^{-\frac{E_j}{kT}} \tag{6.33} \]

and then to set

\[ P_j = \frac{e^{-\frac{E_j}{kT}}}{Z} \]

for then

\[ \sum P_j = \frac{Z}{Z} = 1. \]
What is the minimal value of $F_a$?

$$F_a = \sum_j E_j P_j + T k \sum P_j \ln P_j$$

$$= \sum_j \frac{E_j}{k} \frac{e^{rac{-E_j}{kT}}}{Z} + kT \sum \frac{e^{rac{-E_j}{kT}}}{Z} \ln \frac{e^{rac{-E_j}{kT}}}{Z}$$

$$= \sum \frac{E_j}{k} \frac{e^{rac{-E_j}{kT}}}{Z} + kT \sum \frac{e^{rac{-E_j}{kT}}}{Z} \left( -\frac{E_j}{kT} \right)$$

$$= -kT \sum \frac{e^{rac{-E_j}{kT}}}{Z} \ln Z$$

$$= -kT \ln Z$$.

So the minimal free energy is

$$F_a = -kT \ln Z_a$$.

Suppose a macromolecule can exist in $N_1$ "open" states and in $N_2$ "closed" ones. The probability that the molecule is
open then is

\[ P_I = \sum P_{ij} = Z_I \]

and the probability that it is closed is

\[ P_{II} = \sum P_{iij} = Z_{II} \].

We can define

\[ F_{aI} = \langle Ea \rangle_I - TSa_I \]

and

\[ F_{aII} = \langle Ea \rangle_{II} - TS_{aII} \].

So,

\[ \frac{P_I}{P_{II}} = \frac{Z_I}{Z_{II}} = e^{\ln Z_I} = e^{- F_{aI}/kT} \]

\[ - (F_{aI} - F_{aII})/kT \]

\[ = e \]

\[ - \Delta F_{a}/kT \]

\[ = e \] \hspace{1cm} (6.34)
In the fixed-pressure case,

\[ \frac{p_I}{p_{II}} = e^{-\frac{\Delta G_a}{kT}} \]

where

\[ G_a = \langle E_a \rangle + p_a V_a - TS_a \]  \hspace{1cm} (6.16)

Since at equilibrium

\[ p_I k_{I-II} = p_{II} k_{II-I} \]

it follows from (6.34) that

\[ \frac{k_{I-II}}{k_{II-I}} = \frac{p_{II}}{p_I} = e^{\frac{\Delta F}{kT}} \]

or that

\[ \frac{k_{I-II}}{k_{II-I}} \Delta G_a / kT = e \]  \hspace{1cm} (6.35)