

For 3D, we have

$$E_a = \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2 \\ + \frac{1}{2} c x^2 + \frac{1}{2} c y^2 + \frac{1}{2} c z^2$$

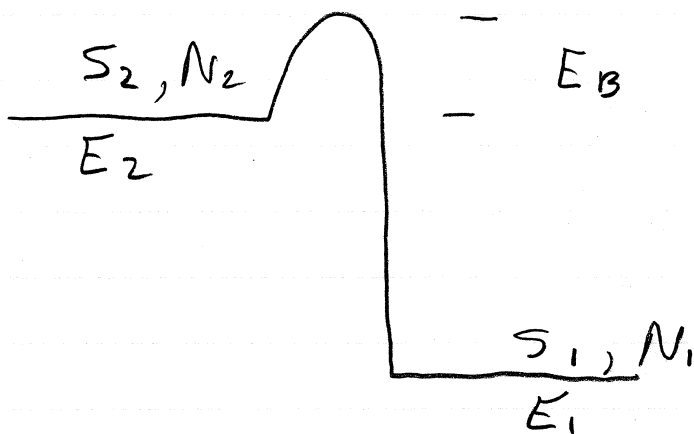
and

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

So

$$\begin{aligned} \langle E_a \rangle &= \int dv_x \frac{1}{2} m v_x^2 P(v_x) \int dv_y P(v_y) \int dv_z P(v_z) \\ &\quad \times \int dx P(x) \int dy P(y) \int dz P(z) \\ &\quad + \dots \\ &\quad + \int dv_x dv_y dv_z P(\vec{v}) \int dx P(x) \int dy P(y) \int dz \frac{1}{2} c z^2 P(z) \\ &= \frac{kT}{2} + \frac{kT}{2} + \frac{kT}{2} + \frac{kT}{2} + \frac{kT}{2} + \frac{kT}{2} \\ &= \frac{6}{2} kT = 3kT. \end{aligned}$$

Each degree of freedom of a gets $\frac{kT}{2}$ from the thermal reservoir B at temperature T.



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

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

Here f is some attempt frequency.

At equilibrium,

$$N_2 k_+ = f N_2 e^{-\frac{E_B - \Delta E}{kT}} = f N_1 e^{-\frac{E_B + \Delta E}{kT}} = N_1 k_-$$

So,

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

Note that N_2/N_1 is independent of E_B

the barrier energy E_B . Note also that

$$N_2 k_+ = N_1 k_- \text{ implies } k_+/k_- = e^{\frac{\Delta E}{kT}}$$

But E_B does affect how long it takes to reach equilibrium.

$$\dot{N}_2 \equiv \frac{dN_2}{dt} = -k_+ N_2 + k_- N_1$$

$$\dot{N}_1 \equiv \frac{dN_1}{dt} = k_+ N_2 - k_- N_1$$

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

$$-\dot{N}_1 = -k_+ (N - N_1) + k_- N_1$$

$$\dot{N}_1 = k_+ (N - N_1) - k_- N_1$$

collapse into

$$\dot{N}_1 = k_+ (N - N_1) - k_- N_1$$

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

$$0 = k_+(N - N_1) - k_-N_1 \quad \text{or}$$

$$(k_+ + k_-)N_1 = Nk_+ \quad \text{or}$$

$$N_1 = \frac{Nk_+}{k_+ + k_-} \equiv N_{1,eq}.$$

The homogeneous equation is

$$\dot{N}_1 = -(k_+ + k_-)N_1$$

$$\frac{dN_1}{N_1} = -(k_+ + k_-)dt$$

$$\ln N_1 = -(k_+ + k_-)t + C$$

$$N_1 = C e^{-(k_+ + k_-)t}$$

$$= N_1(0) e^{-(k_+ + k_-)t}$$

So

$$N_1(t) = C e^{-(k_+ + k_-)t} + \frac{Nk_+}{k_+ + k_-}$$

$$N_1(0) = C + \frac{Nk_+}{k_+ + k_-}$$

So $C = N_1(0) - \frac{Nk_+}{k_+ + k_-}$ and

$$N_1(t) = \left(N_1(0) - \frac{N h_+}{k_+ + h_-} \right) e^{-(k_+ + h_-)t} + \frac{N h_+}{k_+ + h_-}$$

or

$$N_1(t) = N_1(0) e^{-(k_+ + h_-)t}$$

$$+ \frac{N h_+}{k_+ + h_-} \left(1 - e^{-(k_+ + h_-)t} \right)$$

$$= N_1(0) e^{-(k_+ + h_-)t} + N_{1,eq} \left(1 - e^{-(k_+ + h_-)t} \right)$$

In terms of the decay constant

$$\tau = \frac{1}{k_+ + h_-}$$

$$N_1(t) = N_1(0) e^{-t/\tau} + N_{1,eq} \left(1 - e^{-t/\tau} \right)$$

$$\frac{1}{\tau} = k_+ + h_- = f e^{-E_0/hT} + f e^{-(E_0 + \Delta E)/hT}$$

That is,

$$\frac{1}{\tau} = f e^{\frac{-E_B}{kT}} (1 + e^{\frac{-\Delta E}{kT}}).$$

$$\tau = \frac{e^{E_B/kT}}{f (1 + e^{\frac{-\Delta E}{kT}})}$$

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

$$N(t+dt) = (1 - k_+ dt) N(t)$$

and $N(0) = N_0$. This is the differential

equation

$$\frac{N(t+dt) - N(t)}{dt} = \frac{dN}{dt} = -k_+ N(t)$$

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 dt is

$$P_{2 \rightarrow 1}(t) dt = \frac{N(t)}{N(0)} \frac{(-dN)}{N(t)} = \frac{N(t)}{N_0} k_+ dt$$

$$= k_+ e^{-k_+ t} dt \quad (6.31)$$

and it is suitably normalized:

$$\int_0^{\infty} P_{2 \rightarrow 1}(t) dt = \int_0^{\infty} k_+ e^{-k_+ t} dt$$

$$= k_+ \left[\frac{e^{-k_+ t}}{-k_+} \right]_0^{\infty} = 1.$$

Section 6.6.1 showed that if each state of a combined system $a + B$ (a tiny, B big) is equally probable (which maximizes the entropy of the combined system as $S = k \ln \Omega = k \ln \frac{1}{P_0}$), 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

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

in which

$$E_a = \sum E_j P_j$$

and

$$S_a = -k \sum P_j \ln P_j$$

and

$$1 = \sum P_j.$$

The nice way to see this is to use Lagrange's

trick: seek the minimum of

$$\begin{aligned} \mathcal{F}(P_j, \alpha) &= \sum E_j P_j - kT \sum P_j \ln P_j \\ &\quad + \alpha (1 - \sum P_j). \end{aligned}$$

So

$$0 = \frac{\partial \mathcal{F}(P_j, \alpha)}{\partial P_j} = E_j - kT \ln P_j - kT - \alpha$$

$$0 = \frac{\partial \mathcal{F}(P_j, \alpha)}{\partial \alpha} = 1 - \sum P_j.$$

The first equation tells us that

$$-kT \ln P_j = E_j - kT - \alpha$$

or

$$\ln P_j = -\frac{E_j}{kT} + 1 + \frac{\alpha}{kT}$$

or

$$P_j = e^{-E_j/kT + \alpha/kT}$$

The second one tells us that α must be chosen so that the P_j are normalized

$$1 = \sum P_j = \sum e^{-E_j/kT + \alpha/kT}$$

The neat way to do this is to define the partition function Z

$$Z = \sum_j e^{-E_j/kT} \quad (6.33)$$

and then to set

$$P_j = \frac{e^{-E_j/kT}}{Z}$$

for then

$$\sum P_j = \frac{Z}{Z} = 1.$$

What is the minimal value of F_a ?

$$\begin{aligned}
 F_a &= \sum_j E_j P_j + T k \sum_j P_j \ln P_j \\
 &= \sum_j E_j \frac{e^{-E_j/kT}}{Z} + kT \sum_j \frac{e^{-E_j/kT}}{Z} \ln \frac{e^{-E_j/kT}}{Z} \\
 &= \sum_j E_j \frac{e^{-E_j/kT}}{Z} + kT \sum_j \frac{e^{-E_j/kT}}{Z} \left(-\frac{E_j}{kT} \right) - kT \ln Z \\
 &\quad - kT \sum_j \frac{e^{-E_j/kT}}{Z} \ln Z \\
 &= -kT \ln Z \sum_j \frac{e^{-E_j/kT}}{Z} \\
 &= -kT \ln Z.
 \end{aligned}$$

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's closed is

$$P_{II} = \sum P_{IIj} = Z_{II}.$$

We can define

$$F_{aI} = \langle E_a \rangle_I - T S_{aI}$$

and

$$F_{aII} = \langle E_a \rangle_{II} - T S_{aII}.$$

So

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

$$= e^{-(F_{aI} - F_{aII})/kT}$$

$$= e$$

$$= e^{-\Delta F_a/kT}$$

$$= e$$

(6.34)

In the fixed-pressure case,

$$\frac{P_I}{P_{II}} = e^{-\Delta G_a / kT}$$

where

$$G_a = \langle G_a \rangle + p_a V_a - T S_a. \quad (6.16)$$

Since at equilibrium

$$P_I k_{I \rightarrow II} = P_{II} k_{II \rightarrow I}$$

it follows from (6.34) that

$$\frac{k_{I \rightarrow II}}{k_{II \rightarrow I}} = \frac{P_{II}}{P_I} e^{\Delta F_a / kT} \quad (6.35)$$

or that

$$\frac{k_{I \rightarrow II}}{k_{II \rightarrow I}} = e^{\Delta G_a / kT}$$