Last time we introduced the concept of entropy to describe processes that are reversible or not. For an ideal gas:

$$\Delta S = \int_I^F \frac{dQ}{T} = N k_B \ln\left(\frac{T_F}{T_I}\right) + N k_B \ln\left(\frac{V_F}{V_I}\right)$$

In particular, we needed a way to describe what happens when a gas is allowed to freely expand into a volume.

$$\Delta Q = 0$$
$$\Delta E_{int} = 0$$
$$W = 0$$

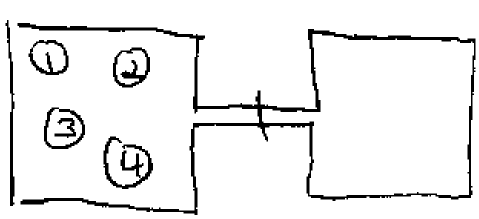
We sort of lost the opportunity for the gas to do something useful

$$\Delta S = N k_B \ln\left(\frac{V_F}{V_I}\right)$$ & for equal volumes A = B

$$\Delta S = N k_B \ln(2)$$

Lets consider approaching this problem in another way. Lets look at 4 distinct gas molecules.

Before we open the value, all 4 gas molecules are in box A



After we open the value, we have several possibilities

| Box A | Box B | # ways | |
|---|---|---|---|
| 1 2 3 4 | | 1 | $\frac{4!}{(4-0)!(4-4)!}$ |
| 1 2 3 | 4 | 4 | $\frac{4!}{(4-1)!(4-3)!}$ |
| 1 2 4 | 3 | | |
| 1 3 4 | 2 | | |
| 2 3 4 | 1 | | |
| 1 2 | 3 4 | 6 ways | $\frac{4!}{(4-2)!(4-2)!}$ |
| 1 3 | 2 4 | | |
| 1 4 | 2 3 | | |
| 2 3 | 1 4 | | |
| 2 4 | 1 3 | | |
| 3 4 | 1 2 | | |
| 1 | 2 3 4 | 4 | $\frac{4!}{(4-3)!(4-1)!}$ |
| 2 | 1 3 4 | | |
| 3 | 1 2 4 | | |
| 4 | 1 2 3 | | |
| | 1 2 3 4 | 1 way | $\frac{4!}{(4-4)!4!}$ |

for N particles

$$\frac{N!}{N_A!\,N_B!}$$

For us, we have a maximum when $N_A = N_B$

if we generalize: $\boxed{\frac{N!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!} = g}$ actually not too bad

as N gets bigger & bigger, the state with the highest multiplicity dominates. (A big number)

now, consider $\ln(N!) \sim N\ln N - N$

$$\ln g = (N\ln N - N) - \left(\frac{N}{2}\ln\frac{N}{2} - \frac{N}{2}\right) - \left(\frac{N}{2}\ln\frac{N}{2} - \frac{N}{2}\right)$$
$$= N\ln(2)$$

We immediately want to say

S is related to $k_B \ln(g)$

since we started out in our example

with $g = \frac{N!}{N!\,0} = 1$

and ended with $\frac{N!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!} = g$

or $\Delta S = S_f - S_i = N k_B \ln(2) - N k_B \ln(1)$

$= N k_B \ln(2)$ as we got before

⇒ Fundamental Assumption: All states are equally likely

Sometimes figuring out the multiplicity is a counting game. Lets take the example in your book. We have 5 particles and 6 units of energy to distribate amongst the particles. One way to calculate the number of states is to consider loading a bag with 6 white marbles and 4 black marbles, drawing them one at a time. We may get a distribation that looks like

● ○○ ●● ○○○ ● ○

0 units

1 unit

One particle got 0 units

one particle got 2

3 units

There are 10 ways to draw the 1st marble
9 — 2nd
8 — 3rd
⋮ — ⋮

(Fundamental Principle of Counting)

or 10! ways to draw these 10

Now, we don't really care "which" black marble goes where, so, since there are 4! ways to arrange the black marbles for each choice we actually have $\frac{10!}{4!}$ ways to arrange these. & since we don't care where "which" energy marble went where, and there are 6! ways to arrange the white marbles there are really only $\frac{10!}{6!\,4!}$ ways to arrange these 6 units of energy among 5 particles or 210 ways. Or in general

"# of particles" or states

"# of quanta"

$$\frac{(N + U/\varepsilon - 1)!}{(N-1)!\,(U/\varepsilon)!}$$

total energy

example $\frac{dQ}{T} = \Delta S$ or $dS$

expect $\frac{dS}{dQ} = \frac{1}{T}$ ?

consider a solid that has N atoms & hence 3N ways to osillate

(our old way we might expect

$$\langle E_{INT}\rangle = \langle U\rangle = \left(\tfrac{1}{2}m\langle v_x^2\rangle + k\langle x^2\rangle\right) + \tfrac{1}{2}m\langle v_y^2\rangle + \tfrac{1}{2}k\langle y^2\rangle + \tfrac{1}{2}m\langle v_z^2\rangle + \tfrac{1}{2}k\langle z^2\rangle\Big)$$

or 6 degrees of freedom

and hence

$$\Delta E_{INT} = 3Nk_B\Delta T = \Delta Q$$

$$E_{int} = 3Nk_BT$$

if $S = k_B \ln g$

$$g = \frac{(3N + {U_{tot}}/{\varepsilon} - 1)!}{(3N-1)!\,(U/\varepsilon)!}$$

where we get $\varepsilon$ from

$$E = \hbar\omega(n_x + \tfrac{1}{2}) + \hbar\omega(n_y + \tfrac{1}{2}) + \hbar\omega(n_z + \tfrac{1}{2})$$

and $E$ behaves as $\hbar\omega(n)$

where $n = U/\hbar\omega$ hence $\varepsilon = \hbar\omega$

$\uparrow$ # units of energy

& we're forgetting the $\frac{1}{2}$'s for now

for large $N$ & $n \gg N$

$$g = \frac{(3N + U/\varepsilon)!}{(3N)!\,(U/\varepsilon)!}$$

$\left(\ln(N!) \sim N\ln(N) - N\right)$

$\ln(1+x) \sim x$ small $x$

$$\frac{S}{K_B} = \ln(g) = \left(3N + \frac{U}{\varepsilon}\right)\ln\left(3N + \frac{U}{\varepsilon}\right) - \left(3N + \frac{U}{\varepsilon}\right)$$
$$- 3N\ln 3N + 3N - \frac{U}{\varepsilon}\ln\frac{U}{\varepsilon} + \frac{U}{\varepsilon}$$

now, lets assume $\varepsilon$ is small & $U$ is large so that the available states are well populated ($\frac{U}{\varepsilon} \gg N$) more energy quanta than oscillators

$$\frac{S}{K_B} = \left(3N + \frac{U}{\varepsilon}\right)\ln\left[\left(\frac{U}{\varepsilon}\right)\left(1 + \frac{3N}{U/\varepsilon}\right)\right] - 3N\ln 3N - \frac{U}{\varepsilon}\ln\frac{U}{\varepsilon}$$
$$= \left(3N + \frac{U}{\varepsilon}\right)\ln\frac{U}{\varepsilon} + \left(3N + \frac{U}{\varepsilon}\right)\ln\left(1 + \frac{3N}{U/\varepsilon}\right) - 3N\ln 3N - \frac{U}{\varepsilon}\ln\frac{U}{\varepsilon}$$
$$= 3N\ln\left(\frac{U}{\varepsilon}\right) + \left(3N + \frac{U}{\varepsilon}\right)\left(\frac{3N}{U/\varepsilon}\right) - 3N\ln 3N$$
$$= 3N\ln\left(\frac{U}{\varepsilon}\right) + 3N\left(1 + \frac{3N}{U/\varepsilon}\right) - 3N\ln 3N \sim 3N\ln U - 3N\ln\varepsilon + 3N - 3N\ln N$$

(note: $g \sim e^{3N}\left(\frac{U}{3N\varepsilon}\right)^{3N}$) $\quad \frac{1}{K_B}\frac{dS}{dU} = \frac{3N}{U}, \quad \frac{dS}{dU} = \frac{3Nk_B}{U} = \frac{1}{T}$

so $U = 3Nk_BT$ again, cool so far

Now lets examine another property of this solid. Remember last time we said that a few arrangements of possible states would win out. Recall for our 2 volumes

$$g_o = \frac{N!}{\frac{N}{2}!\,\frac{N}{2}!}$$

lets vary each $\frac{N}{2}$ by $\sqrt{\frac{N}{2}}$ pretending these are gaussian

$$g_{new} = g_o \frac{\frac{N}{2}!\ \frac{N}{2}!}{\left(\frac{N}{2}-\sqrt{\frac{N}{2}}\right)!\ \left(\frac{N}{2}+\sqrt{\frac{N}{2}}\right)!}$$

$$\ln(g_{new}) = \ln(g_{old}) + 2\left(\frac{N}{2}\ln\left(\frac{N}{2}\right) - \cancel{\frac{N}{2}}\right) - \left(\frac{N}{2}-\sqrt{\frac{N}{2}}\right)\ln\left(\frac{N}{2}-\sqrt{\frac{N}{2}}\right)$$
$$\cancel{-\left(\frac{N}{2}-\sqrt{\frac{N}{2}}\right)} - \left(\frac{N}{2}+\sqrt{\frac{N}{2}}\right)\ln\left(\frac{N}{2}+\sqrt{\frac{N}{2}}\right) - \cancel{\left(\frac{N}{2}+\sqrt{\frac{N}{2}}\right)}$$

$$= \ln g_{old} + N\ln\frac{N}{2} - \left(\frac{N}{2}-\sqrt{\frac{N}{2}}\right)\ln\left(\frac{N}{2}\right)\left(1-\sqrt{\frac{2}{N}}\right)$$
$$- \left(\frac{N}{2}+\sqrt{\frac{N}{2}}\right)\ln\left(\frac{N}{2}\right)\left(1+\sqrt{\frac{2}{N}}\right)$$

$$= \ln g_{old} - \left(\frac{N}{2}-\sqrt{\frac{N}{2}}\right)\underbrace{\ln\left(1-\sqrt{\frac{2}{N}}\right)}_{-\sqrt{\frac{2}{N}}} - \left(\frac{N}{2}+\sqrt{\frac{N}{2}}\right)\underbrace{\ln\left(1+\sqrt{\frac{2}{N}}\right)}_{\sqrt{\frac{2}{N}}}$$

$$= \ln g_{old} - 2 \Rightarrow g_{new} \sim g_{old}/e^2$$

consider, for a mole of atoms, this is a part in $10^{-12}$ change! ($N$ on order $10^{24}$)

Con sider the arrangement that wins in our solid. One particular macro state (arrangement of the energy) $W$, has a multiplicity:

$$W = \frac{N!}{N_0!\,N_1!\,N_2!\,N_3!\,N_4!\cdots\cdots N_n!}$$

if $N$ is large & $n$ is large so that many states are populated, we'll have a most popular $W$. And well say that $W$ is so sharp that $W \sim g$ so that $S = k_B \ln W$. What happens if we change the energy of the system by a quanta. Entropy should increase

$$W' = \frac{N!}{\cdots\,(N_4-1)!\,(N_5+1)!\cdots}$$

so that the change in entropy

$$\frac{\Delta S}{K_B} = \ln W' - \ln W = \frac{\varepsilon_5 - \varepsilon_4}{k_B T} \leftarrow \text{one quanta}$$

notice, all terms will cancel out except for those with $N_4$ & $N_5$

cancel

$$\frac{\Delta S}{K_B} = -\left[(N_4-1)\ln(N_4-1) - \cancel{(N_4-1)}\right] - \left[(N_5+1)\ln(N_5+1) - \cancel{(N_5+1)}\right]$$

$$+ N_4 \ln N_4 - \cancel{N_4} + N_5 \ln N_5 - \cancel{N_5}$$

$$= -\left[(N_4-1)\ln(N_4)\left(1-\tfrac{1}{N_4}\right)\right] - \left[(N_5+1)\ln(N_5)\left(1+\tfrac{1}{N_5}\right)\right] + N_4 \ln N_4 + N_5 \ln N_5$$

$$= -(N_4-1)\ln N_4 - (N_4-1)\underbrace{\ln\left(1-\tfrac{1}{N_4}\right)}_{-1/N_4} - (N_5+1)\ln N_5 - (N_5+1)\underbrace{\ln\left(1+\tfrac{1}{N_5}\right)}_{1/N_5} + N_4 \ln N_4 + N_5 \ln N_5$$

$$= \ln N_4 + 1 - \tfrac{1}{N_4} - \ln N_5 - 1 - \tfrac{1}{N_5} \sim \ln N_4 - \ln N_5 = \ln\left(\frac{N_4}{N_5}\right)$$

or $N_4 = N_5 e^{\Delta E/k_B T}$ or $N_5 = N_4 e^{-\Delta E/k_B T}$