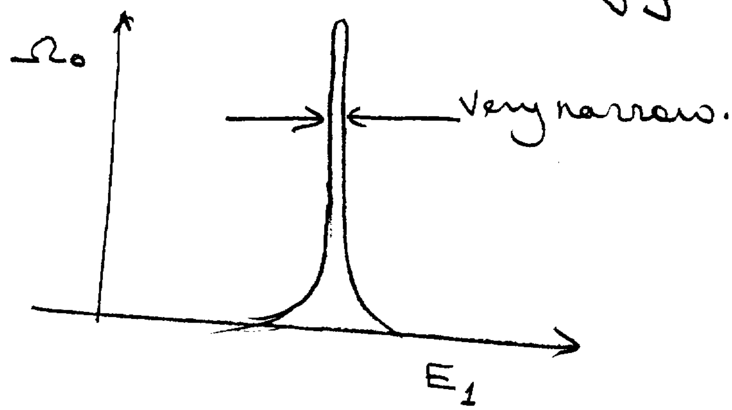
Chapter 8 Entropy and the Second Law

We saw ~~that~~ $\Omega_0 \propto E^{\eta/2}$

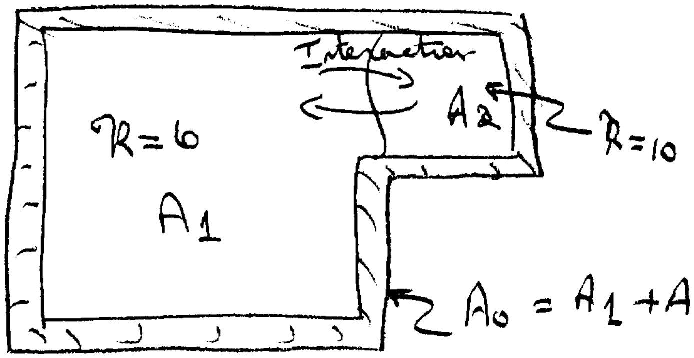
so ~~that~~ $\Omega_0 \uparrow$ rapidly as $E \uparrow$.

So you would expect ~~that~~ when 2 systems interact, the # of accessable states in the combined system is very sensitive to the dist^{n} of available energy.



We'll investigate and show this by some examples.

A. Microscopic Examples



$$E_0 = E_1 + E_2 = \text{constant}$$

$$\Omega_0 = \Omega_1 \, \Omega_2$$

$$\Omega \propto E^{R/2} \Rightarrow \Omega_1 \propto E_1^{\,3} \quad \Rightarrow \Omega_1 = E_1^{\,3}$$

$$\Omega_2 \propto E_2^{\,5} \qquad \Omega_2 = E_2^{\,5}$$

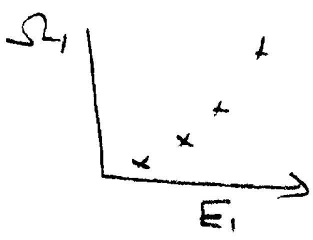
(assume const = 1)

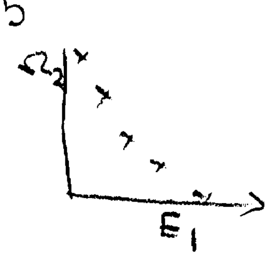
Further, assume energy quantum = 1

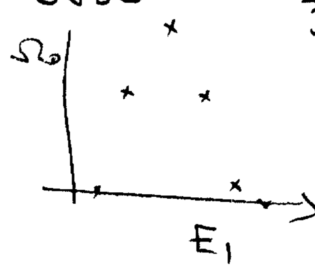
+ $E_0 = E_1 + E_2 = 5$

Here is how we can distribute the energy:

	E_1	E_2	Ω_1 (E_1^3)	Ω_2 (E_2^5)	$\Omega_0 = \Omega_1 \Omega_2$	
6 ways	0	5	0	3125	0	
	1	4	1	1024	1024	
	2	3	8	243	1944	⟸ Most prob. configuration (½ the time)
	3	2	27	32	864	
	4	1	64	1	64	
	5	0	125 (5^3)	0	0	
					3896	$\frac{1944}{3896} = 0.50$







Now let's double $\mathcal{R}$

$\mathcal{R}_1 = 12 \qquad \Omega_1 = E_1^{\,6}$

$\mathcal{R}_2 = 20 \quad \Rightarrow \quad \Omega_2 = E_2^{\,10}$

$E_0 = E_1 + E_2 = 5$ as before.

Now we get

	E_1	E_2	Ω_1	Ω_2	$\Omega_0 = \Omega_1 \Omega_2$	
6 possibilities	0	5	0	9.77×10^6	0	
	1	4	1	1.05×10^6	1.05×10^6	
	2	3	64	5.90×10^4	3.78×10^6	⟸ most prob. (68% of the time)
	3	2	729 ← 3^6	1.02×10^3	0.744×10^6	
	4	1	4.10×10^3	1	0.004×10^6	$\frac{3.78}{5.57} = 0.68$
	5	0	1.56×10^4	0	0	
					5.57×10^6	

Distn is similar to prev. case but peakier.

Now let's increase $\mathcal{R}$ by 10 times

$$\mathcal{R}_1 = 120 \quad \Rightarrow \quad \Omega_1 \propto E_1^{60}$$
$$\mathcal{R}_2 = 200 \qquad \Omega_2 \propto E_2^{100}$$

← still not a very big system

We get

E_1	E_2	Ω_1	Ω_2	Ω_0
0	5	0	7.9×10^{69}	0
1	4	1	1.6×10^{60}	1.6×10^{60}
2	3	1.2×10^{18}	5.2×10^{47}	6.2×10^{65} ⇐ most prob. (99.9997% of the time)
3	2	4.2×10^{28}	1.3×10^{30}	5.5×10^{58}
4	1	1.3×10^{36}	1	1.3×10^{36}
5	0	8.7×10^{41}	0	0
				6.2×10^{65}

So we can say that it is almost certain that the combined system will be in the "$E_1=2$, $E_2=3$" state. There is a small chance it will be otherwise.

Now imagine $\mathcal{R}_1 + \mathcal{R}_2 \sim$ Avagadro's number (6.023×10^{23})

You'll almost never find the system in any state but the most probable state, the one that maximizes the number of accessible states

B. Macroscopic Examples

Let's go for it: $E_0 = E_1 + E_2 = 5$ as before

but $N_1 = 6\times10^{24}$

$N_2 = 10\times10^{24}$ } This is now of macro size.

E_1	E_2	Ω_1	Ω_2	Ω_0
0	5	0	$10^{6.99\times10^{24}}$	0
1	4	1	$10^{6.02\times10^{24}}$	$10^{6.02\times10^{24}}$
2	3	$10^{1.81\times10^{24}}$	$10^{4.77\times10^{24}}$	$10^{6.58\times10^{24}}$ ⟸
3	2	$10^{2.86\times10^{24}}$	$10^{3.01\times10^{24}}$	$10^{5.87\times10^{24}}$
4	1	$10^{3.61\times10^{24}}$	1	$10^{3.61\times10^{24}}$
5	0	$10^{4.19\times10^{24}}$	0	0
				$10^{6.58\times10^{24}}$

most prob. is $10^{0.56\times10^{24}}$ more probable than all the others combined.

Compare this to the age of the universe: 10^{18} sec.

Odds are, you'd never find the system in any other state than the most probable, which is the one that has the most accessible states.

C. The Second Law

So far we have:

When 2 interacting systems are in equilibrium, the various system variables will be such that the number of states available to the combined system is a maximum.

This implies, as 2 interacting systems approach equilibrium, the number of states available increases

ie $\Delta\Omega_0 > 0$

This is the second law

Note. This "law" is based on probabilities but the chance of this "law" being broken is so small that we ignore it safely.

D. Entropy

Ω is a large number, so to work with more reasonable numbers we define:

$$\text{Entropy}, \quad S \equiv k \ln \Omega \qquad [\text{units} = J/K]$$

k: Boltzmann's const

(we'll fix it later to be $1.381 \times 10^{-23}\ J/K$
$= 0.864 \times 10^{-4}\ eV/K$

Thus, since $\Omega_0 = \Omega_1 \Omega_2$

$$S_0 = k \ln \Omega_0 = k \ln(\Omega_1 \Omega_2) = k \ln \Omega_1 + k \ln \Omega_2$$
$$= S_1 + S_2$$

So it behaves like $E_0 = E_1 + E_2$

$$V_0 = V_1 + V_2$$
$$N_0 = N_1 + N_2$$
$$\vdots$$

Entropy is simply a convenient measure of the number of accessible states.

- finite, manageable size
- additive.

At equilibrium $\Delta S_0^{\equiv m} = 0$

$\therefore$ $\boxed{\text{Second law:} \quad \Delta S_0 \geq 0}$

Example

3 interacting systems

$\Omega_1 = 10^{10^{24}}$

$\Omega_2 = 2 \times 10^{10^{24}}$

$\Omega_3 = 3 \times 10^{2 \times 10^{24}}$

What is Ω_0, S_1, S_2, S_3 & S_0?

$$\Omega_0 = 1 \times 2 \times 3 \times 10^{(1+1+2)\times 10^{24}} = 6 \times 10^{4 \times 10^{24}}$$

$$S_1 = k \ln\left(10^{10^{24}}\right) = k \ln\left[\left(e^{2.3}\right)^{10^{24}}\right] = 10^{24} \cdot k \times 2.3$$

$$S_2 = k \ln\left(2 \times 10^{24}\right) = \underbrace{k \ln 2}_{\text{small cf}} + k \ln\left[\left(e^{2.3}\right)^{10^{24}}\right] = 2.3 \times 10^{24} k$$

$$S_3 = k \ln\left(3 \times 10^{2 \times 10^{24}}\right) = k \ln 3 + k \ln\left[\left(e^{2.3}\right)^{2 \times 10^{24}}\right] = 4.6 \times 10^{24} k$$

$$S_0 = S_1 + S_2 + S_3 = 9.2 \times 10^{24} k$$