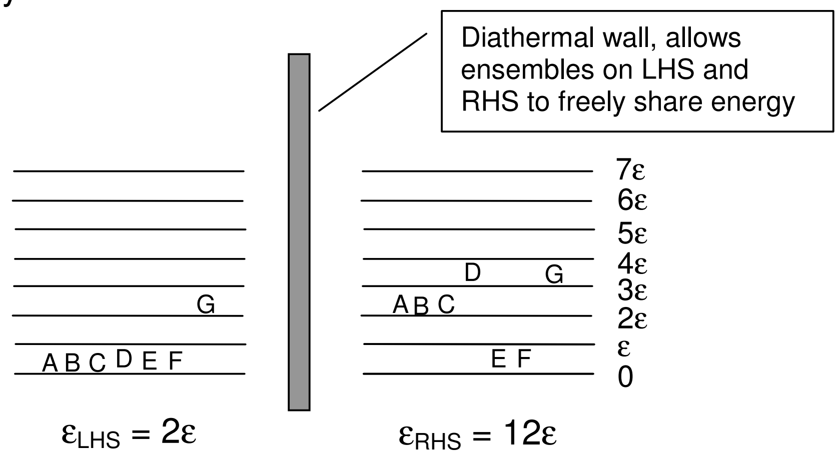
PHY2201 Summary Sheet 11

Microscopic interpretation of entropy:

Two identical "ensembles" each of 7 identical systems are placed in diathermal contact and share a total energy 14ε. Each system can possess energy 0, ε, 2ε, 3ε … What is the most probable distribution of energy ?

One possibility :



Total no. of arrangements on LHS $\Omega_{LHS} = \Omega_{2,7} = 28$,

[$\Omega_{n,k} = \frac{(n+k-1)!}{n!(k-1)!}$]. Likewise $\Omega_{RHS} = \Omega_{12,7} = 18{,}564$. Hence

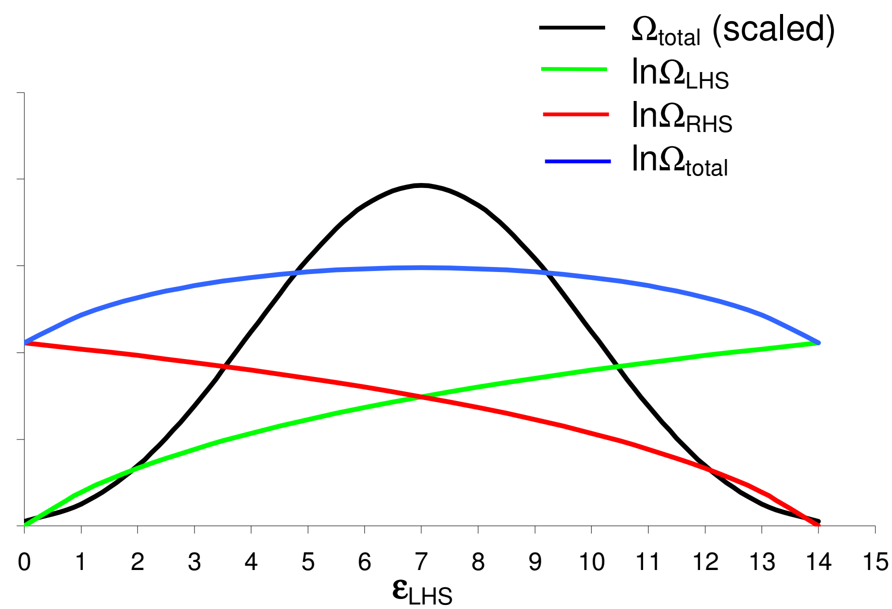
$\Omega_{total} = \Omega_{LHS} \times \Omega_{RHS} = 519{,}792$. Tabulate this for ALL possible sharings :

ε_{LHS}	ε_{RHS}	Ω_{LHS}	Ω_{RHS}	Ω_{total}
0	14	1	38760	38760
1	13	7	27132	189924
2	12	28	18564	519792
3	11	84	12376	1039584
4	10	210	8008	1681680
5	9	462	5005	2312310
6	8	924	3003	2774772
7	7	1716	1716	2944656
8	6	3003	924	2774772
9	5	5005	462	2312310
10	4	8008	210	1681680
11	3	12376	84	1039584
12	2	18564	28	519792
13	1	27132	7	189924
14	0	38760	1	38760
				20058300 (TOTAL)

The "macrostate" of equal energy sharing can be realized in the most number of ways.

Choosing a “microstate” at random, the macrostate of equal energy sharing would occur with 2944656/20058300 = 15% probability. Macrostate of completely uneven sharing [(0,14) or (14,0)] occurs with 2*38760/20058300 = 0.4% probability.

Plot this graphically :-



Over time, the ensembles will spontaneously evolve via random interactions to “visit” all accessible microstates with, *a-priori*, equal probability. If initially in a macrostate of low Ω_{total}, it is thus overwhelmingly likely that at a later time they will be found in a macrostate of high Ω_{total}.

c.f. 2nd law: systems spontaneously evolve from a state of low S to a state of higher S.

$$\boxed{S = k_B \ln \Omega}$$

Boltzmann/Planck hypothesis, 1905. Defines “statistical entropy”

Clausius’s S (“classical” entropy) is an “extensive” variable/function of state i.e. two ensembles a) and b), $S_{total} = S_a + S_b$.

Statistically $\Omega_{total} = \Omega_a \times \Omega_b$, hence

$$
\begin{aligned}
S_{\text{total}} &= k_{\text{B}} \ln \Omega_{\text{total}} \\
&= k_{\text{B}} \ln \Omega_{\text{a}} \Omega_{\text{b}} \\
&= k_{\text{B}} \ln \Omega_{\text{a}} + k_{\text{B}} \ln \Omega_{\text{b}} \\
&= S_{\text{a}} + S_{\text{b}}
\end{aligned}
$$

Hence statistical entropy is also extensive.

Extensive variables – increase with the system size.
Intensive variables – do not increase with the system size.

e.g.

Extensive	Intensive
Mass	Density
Energy	Temperature
Entropy	Pressure
Volume	Specific heat capacity
Heat capacity	