

Reference: An Intro to Stat, Thermo. by T.C. Hill Dover

Sec. 1.2

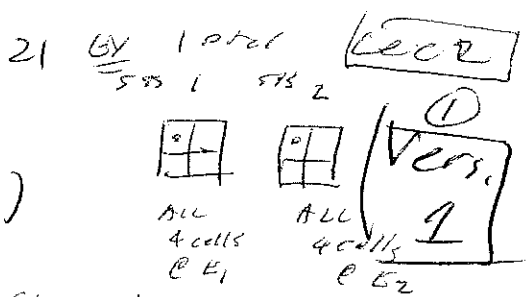
$$N_1, N_2, U_1, U_2, V, \text{ fixed}$$

$$E^{(0)} = U_1 + U_2 = \text{fixed}$$

1) $\Omega = \Omega(E^{(0)}) = \Omega_1(E_1) \Omega_2(E_2)$

$\therefore \Omega = \Omega(E^{(0)})$ (1.1)

$$= \Omega_1(E_1) \Omega_2(E^{(0)} - E_1)$$



3) when the 2 systems come into thermal contact, ~~then~~ sys. 1 evolves to an equilibrium energy of $\bar{E}_1$ and

sys. 2 $\rightarrow \bar{E}_2$. Question: What is $\bar{E}_1$ and $\bar{E}_2$?

for each prob posn (system energy) = system microstates in sys 1, + those of system energies = 11 microstates in system 2

$\therefore \Omega = \Omega_1 \cdot \Omega_2 = (4) \cdot (4)$

Also Argument Important Postulate 1

The probabilities of any given (Macro)system passing ~~into~~ ~~out of~~ any microstate compatible w/ ~~any~~ given system volume, V , ~~and~~ system particle number, N , AND given system energy, E , are equal.

5) Important *
Postulate 2 *

~~and~~ The number of microstates,
 $\Omega_1 = \Omega(E, V, N)$
 Available to any given
macro system reaches a
MAXIMUM when the Macro system
 reaches thermal equilibrium.

6) Based on Post. 2, we
 can ~~be~~ mathematically
 determine the equilibrium (Macro)
 States for sys. 1 & sys 2

By taking the derivative of
 (and then by using the max/min rule).
 (1.1) :

$$(2.1) \quad \left. \frac{\partial \Omega(E_1)}{\partial E_1} \right|_{E_1} = \left. \frac{\partial \Omega_1}{\partial E_1} \right|_{E_1} \Omega_2(E_2) + \frac{\partial \Omega_2}{\partial E_2} \left(\frac{\partial E_2}{\partial E_1} \right) \Omega_1(E_1)$$

$$= 0 \quad (\text{MAX/MIN rule})$$

~~Q 6 cont'd~~

7) From (1.1) $E^{(0)} = E_1 + E_2$

$$E_2 = E^{(0)} - E_1$$

$$\Rightarrow \frac{\partial E_2}{\partial E_1} = \frac{dE_2}{dE_1} = -1$$

$\therefore (2.1) \Rightarrow$

$$\left| \frac{1}{\Omega_1} \frac{\partial \Omega_1}{\partial E_1} \right|_{\bar{E}_1} = \left| \frac{1}{\Omega_2} \frac{\partial \Omega_2}{\partial E_2} \right|_{\bar{E}_2}$$

or

$$\boxed{\left| \frac{\partial \ln(\Omega_1)}{\partial E_1} \right|_{\bar{E}_1} = \left| \frac{\partial (\ln \Omega_2)}{\partial E_2} \right|_{\bar{E}_2}} \quad (3.1)$$

⊕ So, when the macrosystem is in (thermal) equilibrium,
 (3.1) applies/holds,

8) Define β as

$$\boxed{\beta \equiv \left. \frac{\partial \ln \Omega(E, V, N)}{\partial E} \right|_{E=\bar{E}, N, V}}$$

$\therefore$ (3.1) ^{ALSO} CAN BE EXPRESSED AS

$$\boxed{\beta_1 = \beta_2} \quad (3.2)$$

(continue to)

a) we can follow Boltzmann and next connect the microscale parameter, $\Omega \equiv \Omega(E, V, N)$, to macroscale equilibrium thermodynamics.

a) express/recognize that Ω is a fn of V, N, E :

$$\Omega = \Omega(E, V, N) \text{ or equiv. } \ln \Omega = \ln \Omega(E, V, N)$$

b) ^{mathematically} after V, N fixed:

$$d\Omega = \frac{\partial \Omega}{\partial E} dE$$

$$d(\ln \Omega) = \frac{\partial (\ln \Omega)}{\partial E} \bigg|_{V, N} dE$$

$$+ \frac{\partial (\ln \Omega)}{\partial V} \bigg|_{E, N} dV \xrightarrow{V \text{ fixed}} 0$$

$$+ \frac{\partial (\ln \Omega)}{\partial N} \bigg|_{E, V} dN \xrightarrow{N \text{ fixed}} 0$$

$$\therefore \boxed{d(\ln \Omega) = \frac{\partial (\ln \Omega)}{\partial E} \bigg|_{V, N} dE} \quad (4.1)$$

SP9, 13 L2 (5)

c) choose S as a
thermodynamic generating
function [a fn from
 which all other thermo
 vbls / fns = (u, h, p, T) ~~or~~
 can be derived] which,
 crucially, is the macroscopic
measure / equivalent of Ω ,
 ~~Φ~~ (or equivalently, $\ln \Omega$).

ONCE ~~Φ~~ IS SO ~~chosen~~, chosen,
 then express S as
 a fn of U, N, E :

$$\boxed{S = S(E, U, N)} \quad (5.1)$$

d) FROM (5.1) & the (exact) differential of S
 is:

$$(5.2) \quad \boxed{dS = \left. \frac{\partial S}{\partial E} \right|_{U, N} dE + \left. \frac{\partial S}{\partial U} \right|_{E, N} dU + \left. \frac{\partial S}{\partial N} \right|_{E, U} dN}$$

SP4 13 L2 (6)

e) for the example ~~above~~
under consideration, where
 V_N and N are fixed,

$$\boxed{ds = \left. \frac{\partial S}{\partial E} \right|_{V, N} dE} \quad (6.1)$$

f) TAKE THE ratio of (4.1)
and (6.1):

$$\boxed{\frac{d(\ln \Omega)}{ds} = \frac{\left(\left. \frac{\partial (\ln \Omega)}{\partial E} \right) \right|_{N, V}}{\left(\left. \frac{\partial S}{\partial E} \right) \right|_{N, V}}} \quad (6.2)$$

⊕ ~~⊕~~ $d(\ln \Omega)$ and ds represent
resp., the Δ^B in $\ln \Omega$
and S produced by
a change in system energy,
 dE .

& will show/prove that

$$\boxed{\left. \frac{\partial S}{\partial E} \right|_{N, V} = \frac{1}{T}} \quad (6.3)$$

SP9 13 L2
(*)

g) so, using (6.3) in (6.2) we get

$$\boxed{\frac{d(\ln \Omega)}{ds} = \beta T} \quad (7.1)$$

h) Argue^{guess} that @ equilibrium,
for a system (say system L in
our example) of given E
and N , changes in
(due to variations in system energy, E , dE)
 s , ds , are proportional
to associated changes
in $\ln \Omega$, $d \ln \Omega$:

$$\therefore * \boxed{ds = K d(\ln \Omega)} \quad (7.2)$$

⊕ $K = \text{constant of proportionality}$

⊕ Boltzmann argued that
 K is a universal constant

or more specifically,
 that (7.2), (or its integrated
 equivalent, ^{below} is a universal
 law that holds, regardless
 of the atomic/molecular
 constituents making up the
SPB macro-system.

i) we can integrate (7.2)
 By: a) defining the entropy
 of a system in its
 lowest energy state = ground
 state as 0, i.e. $\boxed{S=0}$ ~~at~~
 when the system is in its
lowest possible energy
state, and,

b) recognizing/assuming that
 the number of microstates,

SP4. B Lec 2
(8)

Ω , available to the macro-system, in its ground state, is either 1,

or some small number,

Ω_{min} , where the latter

applies when there

are more than 1 ~~macro~~

~~macro~~ ground states, i.e.,

a degenerate ground state.

④ In the latter case, ~~we~~

~~we assume that~~ Ω_{min} ~~may or~~
may not be ~~calculated~~ small ~~so that~~

~~that~~ $\ln \Omega = \ln(\Omega_{min})$ is small.

④ Assuming that ~~our system has~~

a single ground state,

$$\text{then } \boxed{\Omega_{min} = 1 \Rightarrow \ln \Omega = 0}$$

SP4. 13 Lec 2
(10)

In this case, ~~we can~~
if we integrate (7.2), we get:

$$S(V, N, E) - S_{\min} = k \left[\ln \Omega(V, E, N) - \ln \Omega_{\min} \right]$$

$\downarrow$ $\Omega_{\min}$ $\downarrow$ state
 $\equiv 0$

$$\therefore S(V, E, N) = k \ln \Omega(V, E, N) \quad (10.1)$$

⊕ Boltzmann's Epic
Relationship tying
microscale physics
to macroscale
equilibrium thermo.