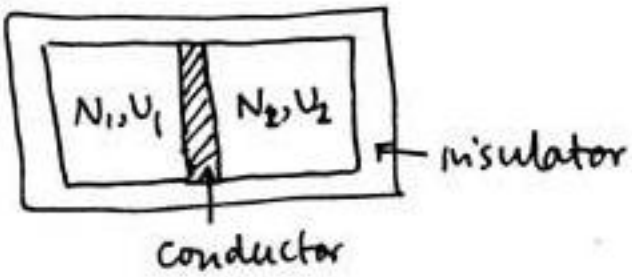
Recap from last time:



Two systems in thermal contact

$N_1, N_2, \quad U = U_1 + U_2$ fixed

For a given value of s_1, multiplicity of whole is product of individual multiplicities :-

$g_1(N_1, s_1) \; g_2(N_2, s - s_1)$

(s_1: fixed; $s - s_1$: varies)

as systems exchange energy by "radiation" - can transfer energy w/o transferring particles

For the whole system we need to $\sum_{s_1}$

$$\Rightarrow \boxed{g(N, s) = \sum_{s_1} g_1(N_1, s_1)\, g_2(N_2, s - s_1)}$$

(Range of summation? $-\frac{1}{2}N_1$ to $+\frac{1}{2}N_1$)

* The most probable configuration will again have a very large degeneracy (as for the sole spin system) and the width of the peak again small

$\Rightarrow$ lets use the continuous approx. again

Let's find the most probable value of s_1, which KK calls $\hat{s}_1$ ("s_1 hat").

We want to maximize

$g_1(N_1, s_1)\, g_2(N_2, s-s_1)$ as a function of s_1 for fixed N_1, N_2, s.

Mathematically this is asking for that function to have a maximum at $\hat{s}_1$:

Let $f \equiv f(N_1, N_2, s, s_1) = g_1(N_1, s_1)\, g_2(N_2, s-s_1)$

Then we need

$$\left.\frac{\partial f}{\partial s_1}\right|_{s_1=\hat{s}_1} = 0$$

and

$$\left.\frac{\partial^2 f}{\partial s_1^2}\right|_{s=\hat{s}_1} < 0$$

↖ so we get a maximum not a minimum or an inflection

Now for a sole system $g_1(N, s) = g(N, 0) \exp\left(-\frac{2s^2}{N}\right)$

so

$$f = g_1(N_1, 0)\, g_2(N_2, 0) \exp\left(-\frac{2s_1^2}{N_1} - \frac{2(s-s_1)^2}{N_2}\right)$$

$$\Rightarrow \frac{\partial f}{\partial s_1} = g_1(N_1, 0)\, g_2(N_2, 0) \exp\left(\frac{-2s_1^2}{N_1} - \frac{2(s-s_1)^2}{N_2}\right) \frac{\partial}{\partial s_1}\left[-\frac{2s_1^2}{N_1} - \frac{2(s-s_1)^2}{N_2}\right]$$

$$\frac{\partial f}{\partial s_1} = f\left[\frac{-4s_1}{N_1} - \frac{4(s-s_1)(-1)}{N_2}\right]$$

So $\frac{1}{f}\frac{\partial f}{\partial s_1} = -4s_1\left(\frac{1}{N_1}+\frac{1}{N_2}\right) + \frac{4s}{N_2}$

Exercise: prove that this IS a maximum

This is zero at $\frac{\hat{s}_1}{N_1} = \frac{(s-\hat{s}_1)}{N_2} = \frac{\hat{s}_2}{N_2}$

or equivalently $\hat{s}_1\left(\frac{N_1+N_2}{N_1N_2}\right) = \frac{s}{N_2}$

i.e. $\frac{\hat{s}_1}{N_1} = \frac{s}{N}$

$$\Rightarrow \boxed{\frac{\hat{s}_1}{N_1} = \frac{\hat{s}_2}{N_2} = \frac{s}{N}} \Rightarrow$$ in thermal equilibrium, both subsystems have the same fractional spin excess!

↖ come back later & relate this to temperature.

KK show (simple algebra) that

if $s_1 = \hat{s}_1 + \delta$

$s_2 = \hat{s}_2 - \delta$ (so that $s = s_1 + s_2 = \hat{s}_1 + \hat{s}_2$ is still the most probable overall s)

then

$$g_1(N_1, \hat{s}_1+\delta)\, g_2(N_2, \hat{s}_2-\delta)$$

$$= \underbrace{g_1(N_1,\hat{s}_1)\, g_2(N_2,\hat{s}_2)}_{\text{max value}} \exp\left(-2\delta^2\left(\frac{1}{N_1}+\frac{1}{N_2}\right)\right)$$

So the function is indeed VERY peaky as a function of s_1 ☺ - substantial deviations (c.f. $\sqrt{N}$) never happen in universe lifetime

General Version

Given 2 subsystems in thermal contact with N_1, N_2, $U = U_1 + U_2$ fixed, degeneracy easily generalizes

$$g(N, U) = \sum_{U_1} g_1(N_1, U_1)\, g_2(N_2, U - U_1)$$

Range of U_1: 0 to U

This is maximized at thermal equilibrium.

Lets apply our continuous approximation ($N \gg 1$)

Then we need to maximise $g(N_1, N_2, U = U_1 + U_2)$

allowing U_1, U_2 to vary

but constraining $U_1 + U_2 = U = \text{constant}$.

N, N_1, N_2 do not vary here

In multivariate calculus we write this as

$$dU = 0 \quad (U = \text{const})$$
$$= dU_1 + dU_2$$

and

$$dg = \left[\left(\frac{\partial g_1}{\partial U_1}\right)_{N_1} dU_1\right] g_2 + g_1 \left[\left(\frac{\partial g_2}{\partial U_2}\right)_{N_2} dU_2\right]$$

by chain rule

$$= 0$$

Using $dU_1 = -dU_2$, find $\frac{1}{g_1}\left(\frac{\partial g_1}{\partial U_1}\right)_{N_1} = \frac{1}{g_2}\left(\frac{\partial g_2}{\partial U_2}\right)_{N_2}$

Entropy (VERY important concept)

$$\boxed{\sigma \equiv \log g}$$ Pure number

$$\sigma(N,U) = \log[g(N,U)]$$

$\Rightarrow$ the thermal equilibrium condition is

$$\boxed{\left(\frac{\partial \sigma_1}{\partial U_1}\right)_{N_1} = \left(\frac{\partial \sigma_2}{\partial U_2}\right)_{N_2}}$$

We call this ↑ ↑ the equality of TEMPERATURES of the two subsystems-

$$\boxed{\frac{1}{\tau} \equiv \left(\frac{\partial \sigma}{\partial U}\right)_N}$$ is the "fundamental temperature"

τ has dimensions of energy.

To convert to absolute temperature (Kelvin scale) we use Boltzmann's constant

$$k_B \cong 1.38 \times 10^{-23}\ J K^{-1}$$

$$\boxed{k_B T = \tau}$$

Boltzmann's headstone says (!!)

$$\boxed{S = k_B \sigma} = k_B \log g$$ "Conventional Entropy"

The more accessible states, the bigger the entropy

(think of it as principle of maximum messiness ☺ c.f. your room)

Then the thermal equilibrium condition is

$$\frac{1}{\tau_1} = \frac{1}{\tau_2}$$

equal temperatures ☺

This is a derivation of the meaning of temperature.

Usually we talk about a temperature T rather than a fundamental temperature τ which has units of energy —

$$\left(\frac{1}{\tau} = \left(\frac{\partial \ln g}{\partial U}\right)_{N_1} \leftarrow \#\right)$$

$$\boxed{\tau \equiv k_B T}$$

$k_B \hat{=} 1.38 \times 10^{-23}$ J/K
Boltzmann's constant

and the conventional entropy S is defined as

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

Boltzmann considered this his finest scientific achievement and had it engraved on his headstone.

Q: When does entropy increase?

Consider 2 systems initially at different temperatures, T_1 & T_2. Let them exchange an amount of heat ΔU.

Total change in entropy?

$$\Delta S = \left(\frac{\partial S_1}{\partial U_1}\right)_{N_1} \Delta U_1 + \left(\frac{\partial S_2}{\partial U_2}\right)_{N_2} \Delta U_2$$

but $\Delta U_1 = -\Delta U_2$

$$\Rightarrow \Delta S = \frac{1}{T_1}(-\Delta U_2) + \frac{1}{T_2}(\Delta U_2)$$

where we used $\frac{1}{T} = \left(\frac{\partial \ln S}{\partial U}\right)_{N,\ldots}$

$$\Rightarrow \Delta S = \left(\frac{1}{T_2} - \frac{1}{T_1}\right)(\Delta U_2)$$

when $T_1 > T_2$, $\Delta S > 0$ if $\Delta U_2 > 0$.

$\Rightarrow$ moving energy from the hotter system to the colder system increases entropy.

Can we show more generally that entropy should always increase if we bring systems into thermal contact?

Consider total degeneracy

$$g(U) = \sum_{U_1} g_1(U_1)\, g_2(U - U_1)$$

All the terms in the sum are positive definite.
One of the terms is the initial degeneracy

$$g_{(0)} = g_1(U_{1(0)})\, g_2(U - U_{1(0)})$$

So the sum will always be bigger than the initial term.

Also, very often, the single biggest term in the expansion can be a LOT bigger than the initial term!

* Evolution to a final state with a bigger degeneracy (and hence bigger entropy) will always happen! This is because the Fundamental Assumption tells us that all accessible states are equally probable.

So $\sigma_{final} = \log (g_1 g_2)_{max}$

$\geq \sigma_{initial} = \log (g_1 g_2)_{01}$.

↑ initial value

LAW ENTROPY INCREASES with time evolution

(The analogy with the messiness of your room may help ...)

- How can we increase entropy? As KK says, we will see that
  - (i) adding particles does it (more states available!)
  - (ii) adding energy (this is slightly more subtle)
  - (iii) increasing the volume (more states!)
  - (iv) breaking up molecules (" ")
  - (v) letting a straightened protein fold up (your hair?)

The Improbable Never Happens at large N:

Unless a system is artificially prepared far from its equilibrium state, you'll never see properties of a macroscopic system deviate from their thermal equilibrium values

(& this will only stay true for the artificially prepared system for a very short time).

- Never, at least, in the lifetime of the universe!

This is why we can safely work assuming that never will all the air molecules of this room spontaneously fluctuate & be in the palm of my hand suffocating us all!

This is true even though the laws of physics are reversible in time ← do not distinguish past from future.

It's just statistics of large numbers that achieves this //.

↑

DEEP!

IMPORTANT!

LAWS OF THERMODYNAMICS (KK pp 48-51)

(0) If $T_1 = T_2$ and $T_1 = T_3$ then $T_2 = T_3$

These statements apply to (and make sense for!) systems in thermal equilibrium.

(1) Heat is a form of energy

(and energy is conserved).

We will get more precise about this one later.

(2) We use the statistical statement

"Entropy always increases
when a constraint internal to a closed system
is removed"

E.g. if U_1, U_2 are allowed to vary (still keeping $U = U_1 + U_2$ fixed so it is a closed system overall) upon thermal contact.

(3) $\sigma \underset{\tau \to 0}{\to}$ constant

For many systems $\sigma \to 0$ as $\tau \to 0$
but this is simply a statement about
equations of state for common systems
and is NOT a fundamental physics requirement!