Entropy and Temperature

02/01/2021

A few definitions (KK pg. 29, Ch. 2)

Fundamental assumption: A closed system is equally likely to be in any of the quantum states accessible to it.

Closed system: It has constant energy, constant number of particles, constant volume, constant value of all external parameters that might influence the system such as gravitational, electric, magnetic, etc. fields

Accessible quantum state: Its properties are compatible with the physical specifications of the system: energy of the state within range of energy of the system, number of particles of the state within range of number of particles of the system. For large systems we don't know U nor N exactly, but we know

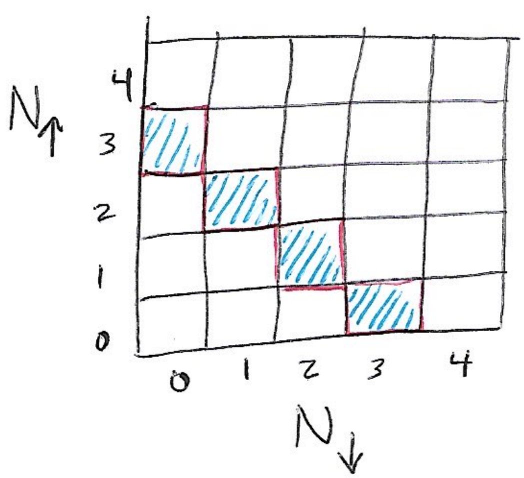
$$\frac{\delta U}{U} \ll 1, \quad \frac{\delta N}{N} \ll 1$$

Just like $s \simeq \delta N \ll N \Rightarrow \frac{\delta N}{N} \ll 1$ for the case of the magnet, the distribution is very narrow and the fluctuations small.

Another aspect of an accessible quantum state is that it can occur in a time scale that is similar or shorter than the experiment.

For example, glass is amorphous SiO_2, and its crystalline form is more energetically favorable, but you can wait your whole life for your window pane to become crystalline, but it won't.

Consider the following:



$$(\uparrow + \downarrow)^3 = \uparrow\uparrow\uparrow + 3\uparrow\uparrow\downarrow + 3\uparrow\downarrow\downarrow + \downarrow\downarrow\downarrow$$

Only the "blue" states are available to the system because it has 3 and only 3 spins.

Now consider only the $3\uparrow\uparrow\downarrow$ state

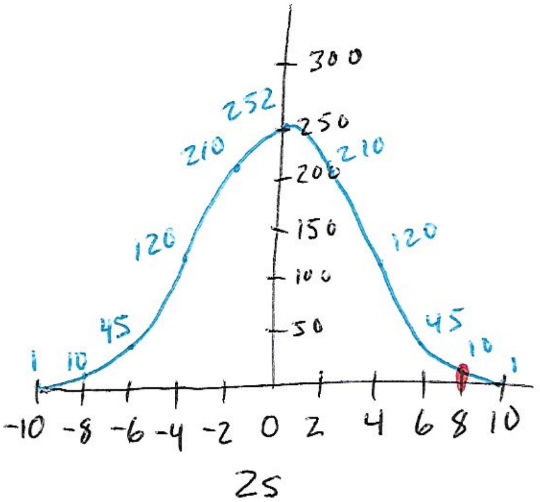
$\uparrow\uparrow\downarrow$, $\uparrow\downarrow\uparrow$, $\downarrow\uparrow\uparrow$ $\qquad g = 3$

The multiplicity g is the number of available states, they are all equally likely.

$P(s) = 1/g$ KK 2.1 $\qquad \langle X \rangle = \sum_s X(s) P(s)$ KK 2.3

$\sum_s P(s) = 1$ KK 2.2 $\qquad \langle X \rangle = \sum_s X(s)(1/g)$ KK 2.4

Now let's consider a larger system, N = 10



KK 1.15

Remember that $g(N,s) = \dfrac{N!}{N_\uparrow ! N_\downarrow !}$

$$g(N,s) = \frac{N!}{(\frac{1}{2}N+s)!\,(\frac{1}{2}N-s)!}$$

For $2s = 8$, $s = 4$: $g(10,4) = \dfrac{10!}{(5+4)!\,(5-4)!}$

$$g(10,4) = \frac{10!}{9!\,1!} = 10$$

a	↓ ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑
b	↑ ↑ ↑ ↑ ↑ ↑ ↓ ↑ ↑ ↑
c	↑ ↑ ↑ ↑ ↑ ↓ ↑ ↑ ↑ ↑
d	↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↓
e	↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↓ ↑
f	↑ ↓ ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑
g	↑ ↑ ↑ ↓ ↑ ↑ ↑ ↑ ↑ ↑
h	↑ ↑ ↓ ↑ ↑ ↑ ↑ ↑ ↑ ↑
i	↑ ↑ ↑ ↑ ↓ ↑ ↑ ↑ ↑ ↑
j	↑ ↑ ↑ ↑ ↑ ↑ ↑ ↓ ↑ ↑

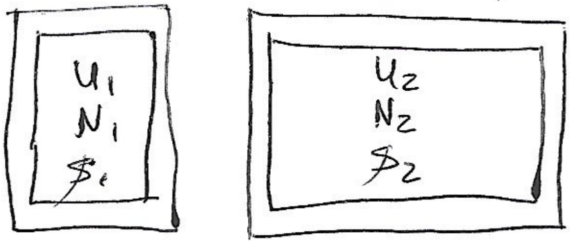
← Fig. 2.2 from KK

An <u>ensemble of systems</u> is composed of many systems, all constructed alike. Each system in the ensemble is a replica of the actual system in one of the quantum states accessible to the system.

KK 2.4

$\langle x \rangle = \sum_s x(s)(1/g)$ is an <u>ensemble average</u>

Consider 2 closed systems $\mathcal{S}_1$ and $\mathcal{S}_2$



$U_1' + U_2' = U_1 + U_2$ since energy is conserved.

that are brought into thermal contact

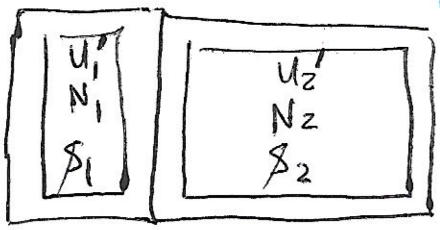


Fig. 2.5 KK

thermal contact means that the two systems can freely exchange energy, but not particles.

Recall that $U = -\vec{m} \cdot \vec{B}$ where m is the magnetic moment and $\vec{B}$ is an external magnetic field, then

Eq KK 2.5

$$U(s) = U_1(s_1) + U_2(s_2) = -2mB(s_1 + s_2) = -2mBs$$

the spin excess is $2s$. Bottom line: U is proportional to s

A configuration is defined as the set of all states with ~~configuration~~ specified values s_1, s_2.

~~The~~ $\mathcal{S}_1$ has $g_1(N_1, s_1)$ accessible states and

$\mathcal{S}_2$ has $g_2(N_2, s_2)$ accessible states.

The total number of states is $g_1(N_1, s_1) g_2(N_2, s_2)$.

When we bring ~~the~~ $\mathcal{S}_1$ and $\mathcal{S}_2$ into thermal contact,

$s = s_1 + s_2 \Rightarrow s_2 = s - s_1$, so the total number of states is

$$g_1(N_1, s_1)\, g_2(N_2, s - s_1) \quad \text{KK Eq. 2.7}$$

~~Exace~~ The multiplicity function $g(N,s)$ is then

$$g(N,s) = \sum_{s_1} g_1(N_1, s_1)\, g_2(N_2, s-s_1)$$ KK Eq. 2.6

we define the <u>most probable configuration</u> as the configuration for which $g(N,s)$ is maximum. This will occur at some value $\hat{s}_1$, so the most probable configuration has multiplicity ~~degener~~ ~~g(N,s)~~ $g_1(N_1, \hat{s}_1)\, g_2(N_2, s-\hat{s}_1)$ KK Eq. 2.8

Let's use energy directly.

Before contact degeneracy is $g_1(N_1, U_1)\, g_2(N_2, U_2)$

After contact $\quad g(N,U) = \sum_{U_1} g_1(N_1, U_1)\, g_2(N_2, U-U_1)$ KK Eq. 2.18

$U = U_1 + U_2$

N_1, N_2

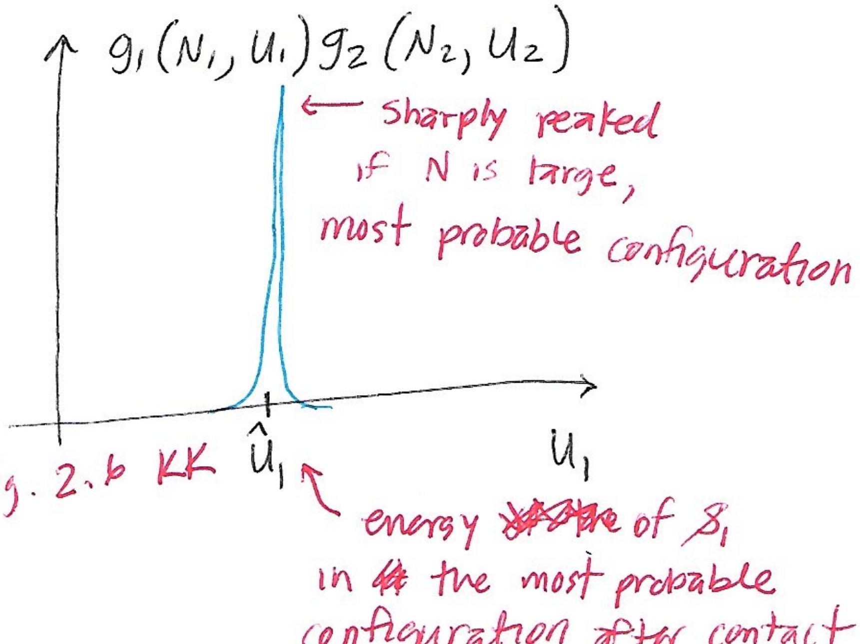


Fig. 2.6 KK

the most probable configuration produces <u>thermal equilibrium values</u>

The peak has a maximum at $dg = 0$

From product rule, ~~dg~~ $dg = d(g_1 \cdot g_2) = g_2 dg_1 + g_1 dg_2$

We can use the total derivative to get dg_1 and dg_2.

$$dg_1(N_1,U_1) = \left(\frac{\partial g_1}{\partial U_1}\right)_{N_1} dU_1 + \left(\frac{\partial g_1}{\partial N_1}\right)_{U_1} \cancel{dN_1}^{\,0}$$

$$dg_2(N_2,U_2) = \left(\frac{\partial g_2}{\partial U_2}\right)_{N_2} dU_2 + \left(\frac{\partial g_2}{\partial N_2}\right)_{U_2} \cancel{dN_2}^{\,0}$$

so

$$dg = \left(\frac{\partial g_1}{\partial U_1}\right)_{N_1} g_2\, dU_1 + g_1\left(\frac{\partial g_2}{\partial U_2}\right)_{N_2} dU_2 = 0$$ KK Eq. 2.19

Also, since energy is conserved $dU = 0 = dU_1 + dU_2$

$$\Rightarrow dU_2 = -dU_1$$

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

$$\frac{\cancel{g_2}}{g_1\cancel{g_2}}\left(\frac{\partial g_1}{\partial U_1}\right)_{N_1} = \frac{\cancel{g_1}}{\cancel{g_1}g_2}\left(\frac{\partial g_2}{\partial U_2}\right)_{N_2}$$ KK Eq. 2.20a

using the logarithmic derivative $\frac{d}{dx}\ln f(x) = \frac{1}{f(x)}\frac{df(x)}{dx}$

$$\left(\frac{\partial \ln g_1}{\partial U_1}\right)_{N_1} = \left(\frac{\partial \ln g_2}{\partial U_2}\right)_{N_2}$$ KK Eq. 2.20b

we define the quantity σ, called the <u>entropy</u>

by $\boxed{\sigma(N,U) = \ln g(N,U)}$ KK. Eq. 2.21

then $\boxed{\left(\frac{\partial \sigma_1}{\partial U_1}\right)_{N_1} = \left(\frac{\partial \sigma_2}{\partial U_2}\right)_{N_2}}$ KK Eq. 2.22

This is the condition for thermal equilibrium for two systems in thermal contact.

Two systems are in thermal equilibrium iff above holds.

★ WHAT IS THE ENTROPY OF THE COMBINED SYSTEM

The number of states available was $g_1 \cdot g_2 = g$

$$\ln g = \ln(g_1 \cdot g_2) = \ln g_1 + \ln g_2 = \sigma_1 + \sigma_2 = \sigma$$

multiplicities are multiplicated, entropies are added.