**Lecture # 4 The Second law, Entropy**

In previous lectures we found that temperature can be related to kinetic energy of molecules in ideal gas. We still do not know how to deal with other substances. We also do not know the answer to very fundamental question. What is temperature, really, and why does heat spontaneously flow from hotter object to a cooler object and never the other way?

This is an example of irreversible process → nature "wants" to distribute energy more "uniformly" and the state that realizes as a result is overwhelmingly more probable! ↔ That is how statistics, which deals with probabilities comes into play. Nature "wants" distributes "uniformly" not only energy but also matter and this is easier example to start with.

Consider tennis ball flying between two players. If we film it and play in reverse, just focusing on a ball, we won't have a clue that time is going backwards (actually we can figure it out).

Consider now following example.



**(1)**
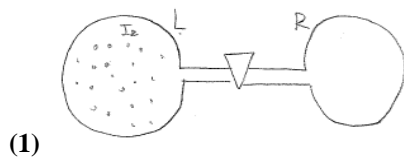
We open valve, and wait for sometime and have gas uniformly distributed in two parts of the system.



**(2)**
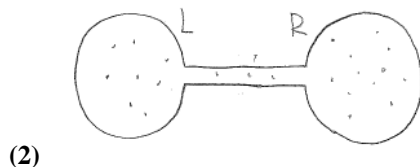
If we film a transition and play it backwards we can certainly say that we are witnessing a miracle. Transition from (2) to (1) never happens in nature, time – reversal symmetry that is present in mechanics is broken in statistically large systems.

In some sense that helps us to define time direction,


(2) Is much much much more probable that (1)
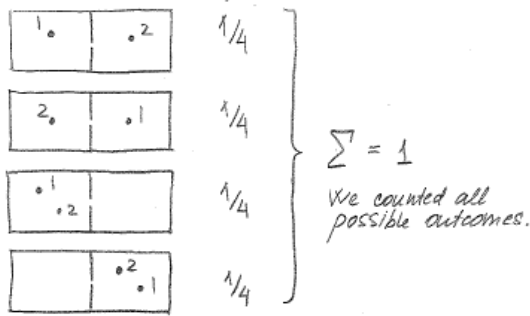
Let's compute how much.
(A1) assumption: each particle has equal probability to be found in left and right part of the system. (Volumes of two compartments are the same).
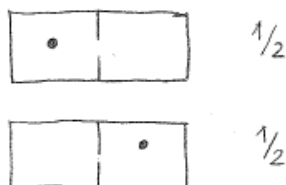


2 Particles
Probabilities of independent events are multiplied.

2 particles.

$\sum = 1$

We counted all possible outcomes.

When we go from 1 molecule to 2-molecule probability of all 'gas' being in left chamber drops twice. Probability of 'gas' being evenly distributed is ¼ + ¼ = ½.

There is an easy formal way to count possible distributions of molecular → symbolic multiplications

→(borrowed from book of Kittel and Krormer).

**(1)** $(L_1 + R_1)(L_2 + R_2) = L_1L_2 + L_1R_2 + R_1L_2 + R_1R_2$

The symbolic term $R_1L_2$ means the first particle is in the right chamber and the second particle is in the left chamber. Total number of possible arrangement is $4 = 2^2$; then the probability to have each combination is ¼. If we do not distinguish particles then we can rewrite (1) as

**(2)** $LL + LR + RL + RR = LL + 2LR + RR$.

The method of symbolic multiplication can be easily extended to large number of molecules.

n = 3

**(3)** $(L_1 + R_1).(L_2 + R_2).(L_3 + R_3) = \underline{(L_1L_2 + L_1R_2 + R_1L_2 + R_1R_2)}(L_3 + R_3)$

We start with all possible Combination for two particles. To each of them the third particle can be added either to the left chamber (multiplication by $L_3$) or to the right chamber (multiplication by $R_3$). Total number of combination is $2^3$. Let's write down the case of indistinguishable molecule.

**(4)** $LLL + 3LLR + 3RRL + RRR$

For N indistinguishable particles,

**(5)** $(L + R)^N = L^N + N L^{N-1} R + \frac{1}{2} N (N - 1) \underline{L^{N-2} R^2} + \quad + R^N$

**(6)** $\sum_{t=0}^{N} \frac{N!}{(N-t)!t!} L^{N-t} R^t$ symbolic binominal expression

**(7)** Usual binominal expression $(x + y)^N = \sum_{t=0}^{N} \frac{N!}{(N-t)!t!} x^{N-t} y^t$

We can extent the method to other interesting but less relevant to physics problems.

   1)  Three chambers problems. Counting configurations – 2 particles.
       $(A_1 + B_1 + C_1)(A_2 + B_2 + C_2)$ total number of state $3^2$

2
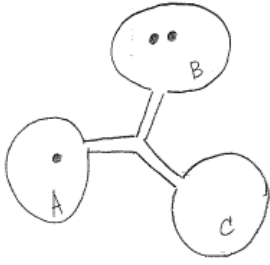
2) Three dicers
   $(1+2+3+4+5+6)$ $(1+2+3+4+5+6)$. $(1+2+3+4+5+6) = 111+112...$total number $6^3$.
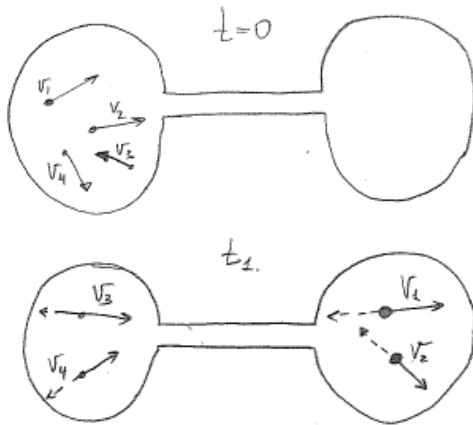   Number of elements in 6x6x6 table

Back to our 2 chamber problem,
If we have $10^{23}$ molecules, probability to find all of them in left chamber is,

$$\textbf{(8)} \quad \frac{1}{2^{10^3}} \approx \frac{1}{10^{69}} - incredibly\ small.$$

$$(2^{10} = 1024 \simeq 10^3)$$

Subtle moment, time reversal.



$T_1$ (time reversal simply means you change sign of all velocities)
Then you are supposed to get back to the configuration when all molecules are in the left chamber?!! Never happens. Another problem: we assume that after long time each particle (molecule) can be found in left or right chamber with equal probability. In perfect world this is not necessary true. Say our left chamber is a perfect cube.
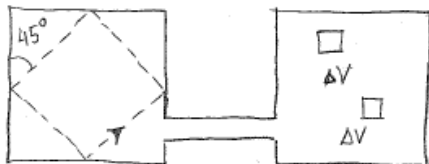


The molecule will follow the same trajectory and will never get into the right chamber. There are mechanisms that break 'perfect ness' and in fact in reality a molecule 'explores' whole system and can be found in any sub-volume $\Delta V$ with equal probability. We may argue about exact mechanisms of exactly how this happens, but huge number of observation led us to believe in it.

(FP) **Fundamental Postulate** (assumption) **of thermal physics**
Closed system is equally likely to be in any of the quantum states accessible to it. All accessible quantum state are assumed to be equally probable – there are no reasons to prefer one state to accessible states.

Entropy is a logarithm of the number of accessible state times the Boltzmann constant.

## What is Quantum state?
Ideal gas is not a good example to start with because first we need to learn how to count quantum state.

**(9)** Entropy of ideal gas $S = Nk \left[ \ln \left( \frac{V}{N} \left( \frac{4\pi mV}{3Nh^2} \right)^{\frac{3}{2}} \right) + \frac{5}{2} \right]$ is not so simple to compute.

## Quantum two level systems – collection of non-interacting spins in magnetic field
(This is also real life problem of paramagnetic) It will also help us to understand energy flow.

Say we have 10 magnets spins each having magnetic moment $\pm$ m. Each magnetic moment can be oriented in two ways, up or down. Two state orientation is purely quantum property projection of spin on $z$ axis may only take discrete value $+ \frac{1}{2}$ $- \frac{1}{2}$ .
One of the possible spin arrangements,



It is the same as our problem with molecules in a container with two compartments. So if we want to count number of possible arrangements we use symbolic multiplication. Specific arrangement SA 1 is an example of quantum state of the system. Spin–up, Spin-down are quantum state for a single spin. (Note that- particle in the left chamber is not q. state of particle)
Quantum state – specific arrangements of spins
**(10)** Spin excess $\quad 2S = N_\uparrow - N_\downarrow \qquad N_\uparrow + N_\downarrow = N$

We want to introduce spin excess because it is macroscopic, experimentally detectable parameters.

**(11)** $\qquad\qquad N_\uparrow = \frac{1}{2}N + S \qquad N_\uparrow = \frac{1}{2}N - S$

How many specific arrangements (quantum states) correspond to a given number $N$ and $S$? Use symbol multiple, to get it

**(12)** $\underline{(\uparrow + \downarrow) \times (\uparrow + \downarrow) \times (\uparrow + \downarrow) \times (\uparrow + \downarrow)\ldots\ldots\ldots}$ Total number is $2^N$. This symbolic product allows two write down all possible configuration of the system.

If we care only about configurations that have specific number of spins up and spins down (and not their exact positions) we may write the above expression in more compact way using binominal expression

**(13)** $(\uparrow + \downarrow)^N = \sum_{t=0}^{N} \frac{N!}{(N-t)!t!} \uparrow^{N-t} \downarrow^t$

Where term $\frac{N!}{(N-t)!t!}$ tells us how many configurations of a type $\uparrow^{N-t} \downarrow^t$ we have.

Another way to write this expression is

**(14)** $$(\uparrow + \downarrow)^N = \sum_{S=-\frac{1}{2}N}^{s=\frac{1}{2}N} \frac{N!}{\left(\frac{1}{2}N+S\right)!\left(\frac{1}{2}N-S\right)!} \uparrow^{\frac{1}{2}N+S} \downarrow^{\frac{1}{2}N+S}$$

The coefficient of in front of the term $\uparrow^{\frac{1}{2}N+S} \downarrow^{\frac{1}{2}N-S}$ is the number of states having $N_\uparrow = \frac{1}{2}N + S$

magnets up and $N_\uparrow = \frac{1}{2}N - S$ magnets down.

$$g(N,S) = \frac{N!}{\left(\frac{1}{2}N+S\right)!\left(\frac{1}{2}N-S\right)!} = \frac{N!}{N_\downarrow!N_\uparrow!} \quad \text{multiplicity function.}$$

---- the number of states having the same value of *S*. (the reason for the definition emerges when we apply magnetic field. In magnetic field states with different *S* have different energy, so the g (N, S) is equal the multiplicity (degeneracy) of an *energy* level in magnetic field.

We found that multiplicity (number of accessible configuration) for *N* spins can be written as

**(15)** $$g\left(N_\uparrow, N\right) = \frac{N!}{\left(N-N_\uparrow\right)!\left(N_\uparrow!\right)}$$

**Very important statement: probability to find a configuration with given number of spins up is equal to the multiplicity that corresponds to this number of spins divided by total number of configurations of the system (*if energy of all configurations is the same*).**

**(16)** $$P(N_\uparrow, N) = \frac{g\left(N_\uparrow, N\right)}{\sum_{t=0}^{N} \frac{N!}{(N-t)!t!}} = \frac{\frac{N!}{\left(N-N_\uparrow\right)!\left(N_\uparrow!\right)}}{2^N}$$

Expression (1) can be re-written with other variable: $S$ – spin excess $2S = N_\uparrow$ - N, where $N_\uparrow + N_\downarrow = N$

**(17)** $$g(N,S) = \frac{N!}{\left(\frac{1}{2}N+S\right)!\left(\frac{1}{2}N-S\right)!}$$

We want to find more simple expression for (16) and (17) when *N* is very large,

ln g (N, S) = ln (N!) – ln (N↑!) – ln (N↓!)

We use Sterling approximation to evaluate N!

**(18)** $$N! \simeq (2\pi N)^{\frac{1}{2}} N^N \exp\left[-N + \frac{1}{12N} + .......\right] \quad \text{(Look at math appendix in textbook)}$$

For large *N*, $\frac{1}{12N}$ can be neglected in comparison with *N*. Then after taken logarithm of both sides of equation (3) we find,

5

**(19)** $\ln(N!) = \frac{1}{2}\ln(2\pi) + \left(N + \frac{1}{2}\right)\ln N - N$

Similarly we get

**(20)** $\ln(N_\uparrow!) = \frac{1}{2}\ln(2\pi) + \left(N_\uparrow + \frac{1}{2}\right)\ln N_\uparrow - N_\uparrow$

**(21)** $\ln(N_\downarrow!) = \frac{1}{2}\ln(2\pi) + \left(N_\downarrow + \frac{1}{2}\right)\ln N_\downarrow - N_\downarrow$

**(22)** Equation (19) can be further re-written as

$$\ln(N!) = \frac{1}{2}\ln(2\pi) + \left(N + \frac{1}{2}\right)\ln N - N = \frac{1}{2}\ln(2\pi) + \frac{1}{2}\ln N - \frac{1}{2}\ln N + \left(N + \frac{1}{2}\right)\ln N - N =$$

$$= \frac{1}{2}\ln\left(\frac{2\pi}{N}\right) + \left(N_\uparrow + N_\downarrow + \frac{1}{2} + \frac{1}{2}\right)\ln N - \left(N_\uparrow + N_\downarrow\right)$$

Subtracting (21) and (20) from (19) we have

**(23)**

$$\ln N! - \ln N_\uparrow! - \ln N_\downarrow! = \ln\frac{N!}{N_\uparrow!N_\downarrow!} = \ln g(N,S) \cong \frac{1}{2}\ln\left[\frac{2\pi}{N2\pi 2\pi}\right] - \left(N_\uparrow + \frac{1}{2}\right)\ln\frac{N_\uparrow}{N} - \left(N_\downarrow + \frac{1}{2}\right)\ln\frac{N_\downarrow}{N}$$

**(24)** $\ln\left(\frac{N_\uparrow}{N}\right) = \ln\left[\frac{1}{N}\cdot\left(\frac{1}{2}N + S\right)\right] = \ln\left(\frac{1}{2} + \frac{S}{N}\right) = \ln\left[\frac{1}{2}\cdot\left(1 + \frac{2S}{N}\right)\right] = \ln\frac{1}{2} + \ln\left(1 + \frac{2S}{N}\right) = -\ln 2 + \frac{2S}{N} - \frac{2S^2}{N^2}$

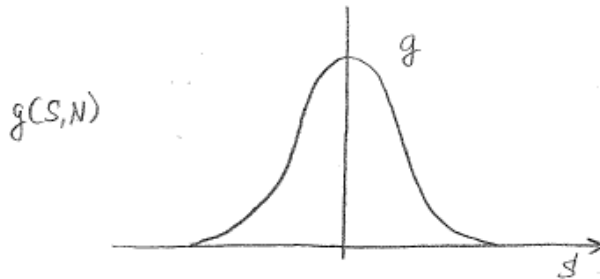We have used the Taylor expansion $\ln(1 + x) = x - \frac{1}{2}x^2$

**(25)** $\ln\left(\frac{N_\downarrow}{N}\right) = \ln\left[\frac{1}{N}\left(\frac{1}{2}N - S\right)\right] = \ln\left[\frac{1}{2}\cdot\left(1 - \frac{2S}{N}\right)\right] = -\ln 2 - \frac{2S}{N} - \frac{2S^2}{N^2}$

Now substitute (25) and (24) into (23) we have

$$\ln g \cong \frac{1}{2}\ln\left(\frac{1}{2\pi N}\right) - \left(\frac{1}{2}N + S + \frac{1}{2}\right)\left(-\ln 2 + \frac{2S}{N} - \frac{2S^2}{N^2}\right) - \left(\frac{1}{2}N - S + \frac{1}{2}\right)\left(-\ln 2 - \frac{2S}{N} - \frac{2S^2}{N^2}\right) =$$

$$= \frac{1}{2}\ln\left(\frac{1}{2\pi N}\right) + N\ln 2 + N\frac{2S^2}{N^2} - \frac{4S^2}{N} + \ln 2 + \frac{2S^2}{N^2}$$

**(26)** $\ln g \cong \frac{1}{2}\ln\frac{2}{\pi N} + N\ln 2 - \frac{2S^2}{N}$

We take exponent of both sides of (11)

**(27)** $g = \sqrt{\frac{2}{\pi N}}\cdot 2^N \exp\left(-\frac{2S^2}{N}\right)$    It is the Gaussian distribution.



$S$ – is integer, 0, 1, 2, 3.……… however we formally consider $S$ as continuous variable then integral

**(28)** $\int\limits_{-\infty}^{+\infty} g\,(S,N)ds = 2^N$   - correct number of all possible combinations.

Let's consider an example, system of ten spins and compare expression (27) which is strictly speaking is valid only at N >> 1 and the exact expression for multiplicity. Same statistics applies for 10 molecules in chamber with two compartments left and right.

$N = 10,\ N_\uparrow = \dfrac{1}{2}N + S,\ 2S = N_\uparrow - N_\downarrow,$

| $N_\uparrow$ | S | g (S) Gaussian | $g\,(S) = \dfrac{N!}{N_\uparrow!N_\downarrow!}$ | Probability P(S) |
|---|---|---|---|---|
| 0 | | 1.74 | | |
| 1 | | 10.53 | | |
| 2 | | 42.7 | | |
| 3 | | 116.09 | | |
| 4 | | 211.534 | | |
| 5 | | 258.369 | 252 | |
| 6 | | | | |
| 7 | | | | |
| 8 | | | | |
| 9 | | | | |
| 10 | | | | |

**The width of the Gaussian distribution**.

$\exp\left(-\dfrac{2S^2}{N}\right) = 1$,   S=0 – maximum of the Gaussian distribution

$\exp\left(-\dfrac{2S^2}{N}\right) = \dfrac{1}{2}$,  $S^2 = \left(\dfrac{\ln 2}{2}N\right)$  corresponds the half of the maximum of the distribution.  $S \approx \sqrt{\dfrac{N}{2}}$ determines the width of the Gaussian distribution.

**Average Values**
Remember our example for time-averaged force

**(30)** $\left\langle F\ \right\rangle = \dfrac{1}{T} \int\limits_{t_1}^{t_2} F\ (t)\ dt$

The average value, or mean value of a function $f$ (S) taken over a probability distribution function $P(S)$ is defined as

**(31)** $\left\langle F \right\rangle = \sum\limits_{S} f\,(S).P(S)$,  Provided that the distribution function is normalized to unity.

$\sum\limits_{S} P(S) = 1$

$P(S) = \dfrac{1}{2^N}.g\,(S,N)$  normalized probability for Binominal distribution

Example 1. Find the average value of the spin for a system of 10 spins having binominal probability distribution

$$f_1 = S \qquad \langle S \rangle = \sum_{S=-5}^{S=5} S\,P(S) = ?$$

$$f_2 = S^2 \qquad \text{remember we used this arrangement to compute } V_{rms} = \sqrt{\overline{v^2}}$$

$$\langle S^2 \rangle = \sum_S S^2\,P(S) = \sum_S S^2\,\frac{1}{2^N}\,g(S,N)$$

## Energy of Magnetic Spin System

The thermal properties of the model system become physically relevant when the elementary magnets are placed in a magnetic field. If the energy of the system is specified, then only the states having this energy may occur.

**(32)** $U = -\vec{m}.\vec{B}$ - The energy of interaction of a single magnetic moment $\vec{m}$ with magnetic field $\vec{B}$.
B is measures in Tesla (T).

What is the dimension of $\vec{m}$ ?

What direction, parallel or antiparallel to $\vec{B}$, does magnetic moments "want" to take?

For a model system of $N$ elementary magnets each with two allowed orientation in a uniform magnetic field, the total potential energy $U$ is

**(33)** $U = \sum_{i=1}^{N} U_i = -\vec{B} \sum_{i=1}^{N} \vec{m_i} = -mB\,(N_\uparrow - N_\downarrow) = -2SmB = -MB$, $S$ is the spin excess. Notice we have dropped vectors.

$M = 2Sm$ – total magnetic moment

Let's sketch the energy levels of our model magnetic system of 10 spins assuming that magnetic field takes up direction.

| $N_\uparrow$ | $S$ | $U(s)/mB$ | $g(s)$ |
|---|---|---|---|
| 0 | -5 | +10 | 1 |
| 1 | -4 | 8 | 10 |
| 2 | -3 | 6 | 45 |
| 3 | -2 | 4 | 120 |
| 4 | -1 | 2 | 210 |
| 5 | 0 | 0 | 252 |
| 6 | 1 | -2 | 210 |
| 7 | 2 | -4 | 120 |
| 8 | 3 | -6 | 45 |
| 9 | 4 | -8 | 10 |
| 10 | 5 | -10 | 1 |

In this example the spectrum of values of the energy $U$ is discrete. Constant spacing a special feature of the particular model, but that will not affect the generality of arguments. The value of the energy for the moments that interact only with the external magnetic field is completely determined the value S.

**(34)** $\Delta U = U(S) - U(S+1) = 2mB$ – energy spacing.

In our next few steps we consider energy exchange between two spin systems in magnetic field. This will lead us to the definition of entropy and temperature.

**Let's repeat what is fundamental assumption (FA)**
A closed system is equally likely to be in any of the *quantum state accessible* to it.
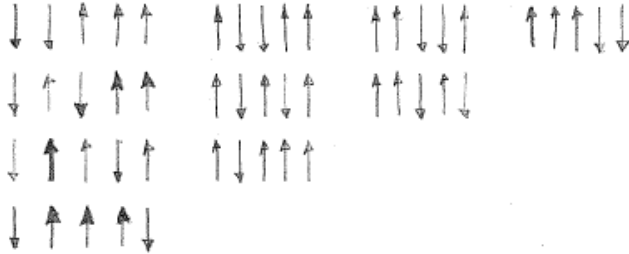A closed system will have constant energy, a constant number of particles, constant volume, and constant values of external parameters that may influence the system, including gravitational, electric and magnetic fields.

A quantum state is *accessible* if its properties are comparable with the physical specification of the system: the energy of the state must be equal to specified number

**Example:**
System 5 spins in magnetic field. 3 spines are up.   2 spins are down.
Accessible states   all this states are equally probable

$$\downarrow\downarrow\uparrow\uparrow\uparrow \quad \uparrow\downarrow\downarrow\uparrow\uparrow \quad \uparrow\uparrow\downarrow\downarrow\uparrow \quad \uparrow\uparrow\uparrow\downarrow\downarrow$$

$$\downarrow\uparrow\downarrow\uparrow\uparrow \quad \uparrow\downarrow\uparrow\downarrow\uparrow \quad \uparrow\uparrow\downarrow\uparrow\downarrow$$

$$\downarrow\uparrow\uparrow\downarrow\uparrow \quad \uparrow\downarrow\uparrow\uparrow\uparrow$$

$$\downarrow\uparrow\uparrow\uparrow\downarrow$$

Spin excess $2S = N_\uparrow - N_\downarrow$, $S = -\dfrac{1}{2}$, Multiplicity $g\left(5, -\dfrac{1}{2}\right) = \dfrac{5!}{3!2!} = 10$

Is this state $\uparrow\uparrow\uparrow\downarrow\downarrow$ accessible? Why? What energy does this state have?

Unusual properties of a system may sometimes make it impossible for certain states to be accessible during the time the system is under observation. Examples are glass, amorphous Si. Such exclusions can be recognized by common sense. We treat all quantum states of the system as accessible unless they are excluded by the specification of the system and the time of measurements.

## Most probably configuration of two systems
Let two systems $S_1$ and $S_2$ be brought into contact so that the energy can be transferred freely from one to the other. This is called thermal contact.
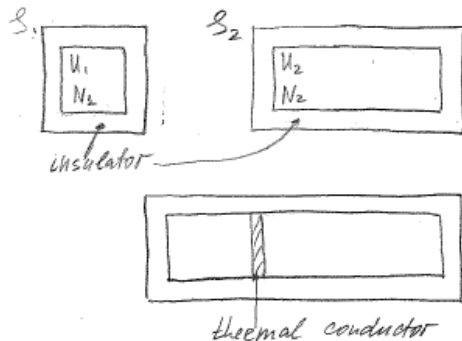


Composed system has constant energy $U = U_1 + U_2$. But energy exchange between two subsystems will occur. The direction of the energy flow is not simply a matter of whether the energy of one system is greater than the energy of the other. A constant total energy can be shared in many ways between two systems.
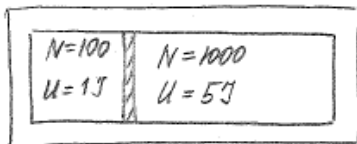


In which direction will energy flow?

**The most probable division of the total energy is that for which the combined system has the maximum number of accessible states.** (this is essentially the fundamental assumption or the second law of thermodynamics expressed in different words)

Example, two spin systems in magnetic field.
$$N_1 = 10 \quad N_{1\uparrow} = 5 \quad N_2 = 5 \quad N_{2\uparrow} = 1$$

Multiplicity
$$g_1 = \frac{10!}{5!5!} = 252 \qquad g_2 = \frac{5!}{4!1!} = 5$$

$U_1 = 0, \quad U_2 = +3mB.$
Total number of states accessible for composed system with the above energy separation is given by
$$g_T = g_1 g_2 = 252 \times 5 = 1260 \text{ (Why?)}$$

Let's now flip one spin down in system $S_1$, and flip one spin up in system $S_2$. This corresponds to the energy transfer from the system 2 to the system 1.

$$N_1 = 10 \quad N_{1\uparrow} = 4 \quad N_2 = 5 \quad N_{2\uparrow} = 2$$
$$U_1 = -mB(N_{1\uparrow} - N_{1\downarrow}) = 2mB \qquad U_2 = -mB(N_{2\uparrow} - N_{2\downarrow}) = mB$$
$$g_1 = \frac{10!}{6!4!} = 210 \qquad g_2 = \frac{5!}{3!2!} = 10$$

Total number of different quantum states accessible for composed system with
$N_1 = 10, N_{1\uparrow} = 4, N_2 = 5, N_{2\uparrow} = 2$ is
$$g_T = g_1 g_2 = 210 \times 10 = 2100$$

Let's now, starting from $N_{1\uparrow} = 5$, $N_{2\uparrow} = 1$, flip one spin up in system $S_1$ and flip one spin down in system $S_2$.
$$N_1 = 10, \quad N_{1\uparrow} = 6; \quad N_2 = 5, \quad N_{2\uparrow} = 0$$
$$U_1 = -mB(N_{1\uparrow} - N_{1\downarrow}) = -2mB, \qquad U_2 = -mB(N_{2\uparrow} - N_{2\downarrow}) = 5mB$$
$$g_1 = \frac{10!}{6!4!} = 210 \qquad g_2 = \frac{5!}{5!1!} = 1$$
$$g_T = g_1 g_2 = 210 \times 1 = 210$$

Question, in what direction does energy likely flow?

**Second law, Entropy, Temperature**
The multiplicity function (number of all possible arrangements) of the combined system is related to the product of the individual systems 1 and 2 by the relation.
$$\textbf{(34)} \quad G(N, S) = \sum_{S_1} g_1(N_1, S_1) g_2(N_2, S - S_1)$$

Where $S$ is the total spin excess for combined system. $S_1$ is the total spin excess of the first system. If $N_2 \gg N_1$ the summation of $S_1$ is from $-\frac{1}{2}N_1$ to $\frac{1}{2}N_1$

A configuration is a set of all states that have specific values $S_1$ and $S_2$. The combined system is closed $\Rightarrow$ $S_1 + S_2 = S = const$ in magnetic field because energy is conserved. The first system has $g_1(N_1, S_1)$ accessible states that can be combined with any of $g_2(N_2, S_2)$ accessible states of the second system:

$$\textbf{(35)} \quad g(N_1, N_2, S, S_1) = g_1(N_1, S_1) g_2(N_2, S - S_1) = g_1(N_1, S_1) g_2(N_2, S_2)$$

eq. (35) has maximum for some value of $S_1$, say $\hat{S}_1$ ("S, hat"). **The configuration for which $g_1 g_2$ is a maximum is caller the most probable configuration.**

The equation (34) for the number of accessible state of two model spin systems in thermal contact may be generalized to any two systems in thermal contact with constant total energy $U_1 + U_2 = U = const$

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

Sum is over all values of $U_1 \le U$.

$g_1(N_1, U_1)$ is a number of accessible states of system 1 at energy $U_1$. The configuration of combined system is specified by the value $U_1$, together with constants $U$, $N_1$, $N_2$.
Notice that systems 1 and 2 do not need to be the same. For example system 1 may be spin system and system 2 – an ideal gas.

**Let' again repeat the fundamental assumption**
**The most probable division of the total energy is that for which the combined system has the maximum number of accessible states.**

Mathematically this corresponds to the condition that the multiplicity of the combined system
**(36)** $g(N_1, N_2, U, U_1) = g_1(N_1, U_1) g_2(N_2, U - U_1) = g_1(N_1, U_1) g_2(N_2, U_2)$ takes maximum as a function of $U_1$. This means that

**(36)** $dg = \left( \dfrac{\partial g_1}{\partial U_1} \right)_{N_1} g_2 \, dU_1 + \left( \dfrac{\partial g_2}{\partial U_2} \right)_{N_2} g_1 \, dU_2 = 0$

**(37)** $dU_1 = - dU_2$ because $U_1 + U_2 = U = const$

We got (36) by taking differential of one configuration $g_1(N_1, U_1) g_2(N_2, U_2)$ . If this configuration is most probable $dg = 0$.

Combining (36) and (37) we have

**(38 )** $\dfrac{1}{g_1} \left( \dfrac{\partial g_1}{\partial U_1} \right)_{N_1} = \dfrac{1}{g} \left( \dfrac{\partial g_2}{\partial U_2} \right)_{N_2} \Rightarrow \left( \dfrac{\partial \ln g_1}{\partial U_1} \right)_{N_1} = \left( \dfrac{\partial \ln g_2}{\partial U_2} \right)_{N_2}$

Let us now introduce a concept of entropy. Definition of entropy

(39) $S = k_B \ln g$

Then the equation (38) can be re-written as

**(40 )** $\left( \dfrac{\partial S_1}{\partial U_1} \right)_{N_1} = \left( \dfrac{\partial S_2}{\partial U_2} \right)_{N_2}$

Here symbols $N_1$ and $N_2$ may symbolize not only the number of particles but all constrains on the systems like volume, pressure and external fields.
The equilibrium (37) immediately leads us to the concept of temperature. We know that if we bring two systems in contact and wait for the thermal equilibrium to be established the most probable situation that we will see experimentally is $T_1 = T_2$. It therefore has to be equivalent to equation (39). We *define* temperature as

Encyclopedia Britannica, 11$^{th}$ ed. (1905): " The utility of the conception of entropy… is limited by the fact that it does not correspond directly to any directly measurable physical property, but is merely a mathematical function of the definition of absolute temperature."

We see that the situation is opposite; we need the concept of entropy to define temperature.
Example: we remove some amount of energy from system $S_1$ and add it to system $S_2$; $T_1 > T_2$.
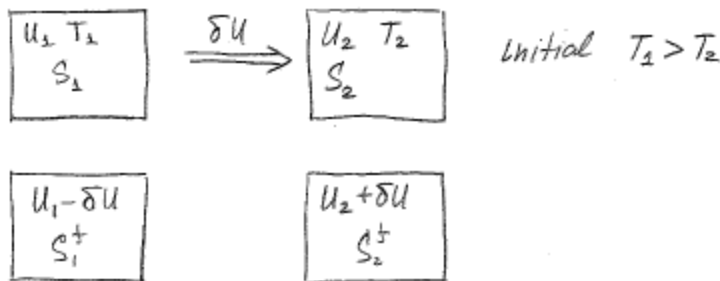


Entropy of combined system
$S_T = S_1(N_1, U_1) + S_2(U_2, N_2)$  (Why do we have sum here?)

$$\delta S_t = \left(\frac{\partial S_1}{\partial U_1}\right)_{N_1} \delta U_1 + \left(\frac{\partial S_2}{\partial U_2}\right)\delta U_2 = \left(\frac{-1}{T_1}+\frac{1}{T_2}\right)\delta U$$

$\delta U_1$ is negative because we remove energy from the system 1.

$\delta S_t > 0$, the entropy of combined system increased as a result of energy transfer.

# Numerical example
 (A) Sample copper 10 g $T_A = 350$ k.
 (B) Sample copper 10 g $T_B = 290$k
 (A) Sample and (B) sample are brought in thermal contact. What are the energy terms for? Specific heat of copper $C_V = 0.389$ J/gk.
 $$\Delta U = C_V (T_A - T_F) =$$

# What is the change of entropy of two samples when a transfer of 0.1 J has taken place almost immediately after initial contact.

# what is the change of entropy after the system has reached thermal equilibrium.

## **Law of thermodynamics**
Zheroth law:
If two systems are in thermal equilibrium with a third system they must be in thermal equilibrium with each other.
$(T_1 = T_3$ and $T_2 = T_3) \Rightarrow T_1 = T_2$

First law – Heat is a form of energy. Energy is conserved.

Second law – Entropy of a closed system takes maximum possible value consistent with the constrains imposed on the system. Entropy of a closed system increases if constrains interval to the system are removed.

Kelvin – Plank "It is impossible for any cyclic process to occur whose sole effect is the extraction of heat from a reservoir and the performance of the equivalent amount of work."

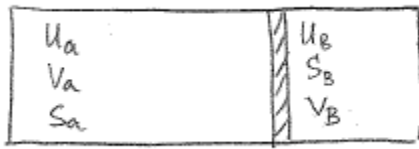Third law – The entropy of a system approaches a constant value as the temperature approaches zero.

$$\Delta S = \frac{\Delta U}{T}$$

Exception: glasses frozen in disorder

This also means $C_V \to 0$

$$dS = \frac{dU}{T} = \frac{C_V dT}{T} \qquad S = \int_0^T \frac{C_V dT}{T}$$ Integral diverges unless $C_V \to 0$, $T \to 0$.

## Mechanical Equilibrium and pressure



Two subsystems can exchange energy and volume with each other. The total energy and total volume are fixed. According to the second law of the thermodynamics in equilibrium the system has to have maximum entropy. Therefore the derivatives of total $S$ must be zero with respect both of a closed system increases if constrains interval to the system are removed $V_A$ and $V_B$ variations.

$$0 = dS = \left(\frac{\partial S_a}{\partial U_a}\right)_{V_a} dU_a + \left(\frac{\partial S_b}{\partial U_B}\right)_{V_B} dU_B + \left(\frac{\partial S_a}{\partial V_a}\right)_{U_a} dV_a + \left(\frac{\partial S_B}{\partial V_B}\right)_{U_B} dV_B$$

$$T_a = \left(\frac{\partial S_a}{\partial U_a}\right)_V \qquad T_B = \left(\frac{\partial S_b}{\partial U_B}\right)_V$$

$T_A = T_B$   condition of thermal equilibrium.

$$dV_a = -dV_B$$

$$dS = \left(\frac{\partial S_a}{\partial V_a}\right)_U dV_a + \left(\frac{\partial S_B}{\partial V_B}\right)_U dV_B = 0$$   -   condition of mechanical equilibrium. Or in the other way

$$\left(\frac{\partial S_a}{\partial V_a}\right)_U = \left(\frac{\partial S_b}{\partial V_B}\right)_U$$   . But we know that condition of mechanical equilibrium corresponds to $P_a = P_B$

We can therefore write a definition of pressure (using appropriate modification to get dimensions right

$$P = T\left(\frac{\partial S}{\partial V}\right)_{U,N}$$