Molecular Physics. Statistics

Lecture 08
Probability theory.
Probability Distributions
Statistical Entropy

Thermodynamic Approach

- defines correlations between the observed physical quantities (macroscopic),

- relies mostly on the experimentally established dependencies

- allows generally to consider the physical essence of the problem -

- does not require precise information about the microscopic structure of matter.

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Statistical approach strongly complements thermodynamics. BUT! To implement it effectively we need proper mathematical tools – first of all – the probability theory.

This will be the focus of today's lecture!…

Probability = the quantitative measure of possibility for certain event to occur.
EXAMPLE 1. Eagle and Tails Game:
Test = throw of a coin;
Results of a test (events); eagle...   tail

If the game is honest – possibilities to obtain each result must be equal.
Quantitative measure of possibility = probability: P_e=0,5 – eagle; P_t=0,5 - tail.
P = 1 is the probability of a "valid" event, which will occur for sure.
P_e + P_t=1 – either eagle or tail will fall out for sure (if rib is excluded ☺).

The rule of adding probabilities P (1 OR 2) = P(1) + P(2)
The normalization rule: the sum of probabilities for all possible results of a test is evidently valid and thus is equal to 1.
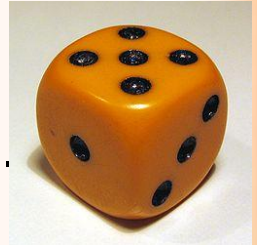
Probability = he quantitative measure of possibility for certain event to occur.
EXAMPLE 2. Dice game. Test = throw of a dice;
Results of a test (events); 1, 2, 3, 4, 5, 6
If the game is "honest": $P(1) = P(2) = P(3) = P(4) = P(5) = P(6) = 1/6$.

Example 2.1: Probability to obtain the odd number as the result of a test:
$P(1) + P(3) + P(5) = 1/6 + 1/6 + 1/6 = 1/2$

Example 2.2: Probability to obtain "double 6": from the first throw $P(6) = 1/6$, and then – out of this probability only 1/6 of chances that 6 will occur again.
Finally $P(6 \text{ AND } 6) = P(6)P(6) = 1/6*1/6 = 1/36$

The rule of multiplying probabilities $P (1 \text{ AND } 2) = P(1)P(2)$

EXAMPLE 3. Rotating of a top toy.
If initially the red mark was exactly to the right from the top toy's axis (in direction X), after rotation stops - it may stop at any angle .

The question: what is the probability that the toy wil

stop EXACTLY turned by the angle φ from the initial

orientation? The answer: P(φ) = 0 (!) – as ***absolutely***

precise experiments are impossible in principle. There
always will be some error, or deviation, or uncertainty.

The CORRECT question: what is the probability for the top toy to stop within

certain range of angles: between φ and (φ + dφ)?
Evidently, this probability MAY depend on φ and MUST be proportional to dφ:
dP(φ to φ + dφ) = f(φ)dφ
Here f(φ) is the *probability distribution function*.

SO: the PROBABILITY for the top toy to stop between φ and $(\varphi + d\varphi)$ equals: $dP(\varphi$ to $\varphi + d\varphi) = f(\varphi)d\varphi$
$f(\varphi)$ is the *probability distribution function*.

The Normalization Rule: the integration of the probability distribution function over the range of all possible results MUST give 1
In our example: $\int_0^{2\pi} f(\varphi)d\varphi = 1$

The Even Distribution: if all possible results are equally probable – the distribution function equals constant.
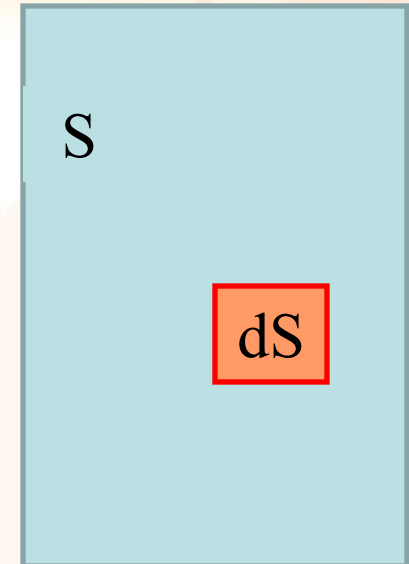In our example: $f(\varphi) = Const = 1/2\pi$

EXAMPLE 4: a point is dropped (randomly) on the table with the area S. What is the probability that it will fall within the little square within dS?

f(x,y) = C: the *even probability distribution function*.

The Normalization Rule: $\int_S$ Cdxdy = CS = 1 => C = 1/S

The result: dP(dS) = f(x,y)dS = dS/S

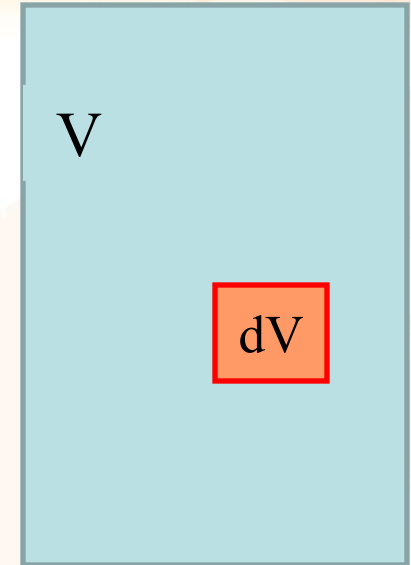EXAMPLE 5: Molecules in gas – at the state of thermal equilibrium, when the concentration of molecules is the same all throw the volume are evenly distributed over all the coordinates:

$$f(x,y,z) = Const = 1/V =$$

$$dP(x,y,z) = f(x,y,z)dV = dxdydz/V$$

V

dV

Knowing the distribution of a random x we may calculate its average value <x>:

$$\langle x \rangle = \int x \, dP_x = \int x f(x) \, dx,$$

Moreover, we may calculate the average for any function $\psi(x)$:

$$\langle \psi(x) \rangle = \int \psi(x) \, dP_x = \int \psi(x) f(x) \, dx$$

THE PROPERTIES OF AVERAGES.

• Average of the sum of two values equals to the sum of their averages

$$<x + y> = <x> + <y>$$

• Average of the product of two values equals to the product of their averages ONLY in case if those two values DO NOT depend on each other

$$<xy> = <x><y> \; only \; \textit{if x and y are independent variables}$$

Examples: in case of even distribution of molecules
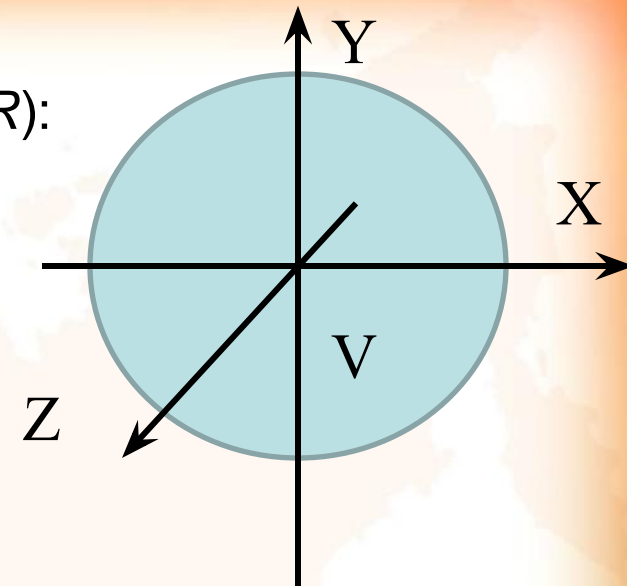over certain spherical volume V (balloon with radius R):

$$\langle x \rangle = \int x dP_x = \int x f(x) dx, = 0$$

$<x + y> = 0; \quad <x\,y> = 0$

$<x^2> = \ R^2/5 > 0$

$<r^2> = < x^2 + y^2 + z^2 > = 3R^2/5 > <r>^2$

$<r> = <(x^2 + y^2 + z^2)^{1/2}> = 3R/4$

Calculation – 'live''…

$<r> = <(x^2 +y^2 +z^2)^{1/2}> = 3R/4$ - average

$(<r^2>)^{1/2} = 0{,}6^{1/2}R > <r>$ - squared average

$<x> = 0; \quad <x^2>^{1/2} = R/5^{1/2} > 0$
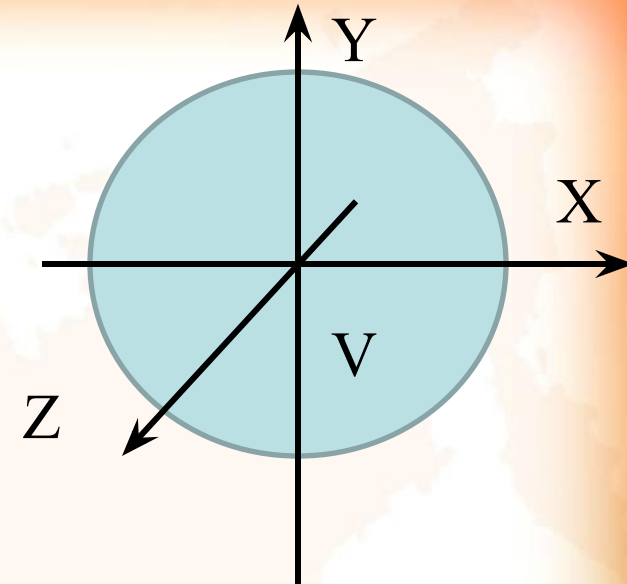
Median average r_{med} ; the quantity of molecules with $r<r_{med}$ equals to the quantity of molecules with $r>r_{med}$

$r_{med}=R/2^{1/3}=0{,}7937R >$

$(<r^2>)^{1/2} =0{,}7756R >$

$<r> =0{,}75R$

This all is about even distribution of molecules over space in spherical balloon.
What about the distribution of molecules over velocities and energies?
It can be spherically symmetric, but it can not be *even* as formally there is no upper limit of velocity…

Eagle and Tails game

EXAMPLE 1: One throw of a coin = one Test ($N = 1$)

Test Results: type 1 – "Tail";   type 0 – "Eagle"

If we do very many tests (throws)

$$P_i = \lim_{N \to \infty} \frac{N_i}{N_\text{T}} = 0{,}5 \quad \text{both for types 1 and 0.}$$

N_T – number of tests (throws),

N_i – number of tests with the result of the type i

P_i – probability to obtain the result of the type i

$$P_i = \lim_{N \to \infty} \frac{N_i}{N}$$

EXAMPLE 2: 1 Test (or one series of tests) = 2 throws of a coin ($N = 2$)
Test results (types):

0 –2 Eagles

1 –1 Eagle and 1 Tail   or

2 –2 Tails

$$P_i = \lim_{N \to \infty} \frac{N_i}{N_{\text{T}}}$$ = 0,25 probability of types 0 and 2
= 0,5 – probability of type 1

N – the length of a test series (in this case $N = 2$) ,

N_T – total number of tests

N_i – number of tests with result of the type i

P_i – probability to obtain the result of the type i

The product of probabilities:

The first test – the probability of result "1" - P_1

The second test – the probability of result "2" = P_2.

The probability to obtain the result '1' at first attempt and then to obtain result '2' at second attempt equals to the product of probabilities

$$P(1 \text{ AND } 2) = P(1 \cap 2) = P_1 P_2$$

EXAMPLE: Eagle AND Tail = ½ * ½ = ¼

The SUM of probabilities:

One test – the probability of result "1" - P_1; the probability of result "2" = P_2.

The probability to obtain the result '1' OR '2' equals to the SUM of probabilities: $P(1^T \text{OR } 2) = P(1 \cup 2) = P_1 + P_2$

EXAMPLE: Eagle OR Tail = ½ + ½ = 1

EXAMPLE 2: (Eagle AND Tail) OR (Tail AND Eagle) = ¼ + ¼ = ½

General Case: The test length = N (N throws = 1 test)

All the types of test results can be numbered i from 0 to N by the number of the tailspins in each test. Each type of results will have the probability, proportional to the number of variants, that produce that result

Type   Number of variants producing this type of result

i = 0   1 (all the throws = eaglespins)

i = 1 N (only one there was a tailspin (either at first throw, or at the 2nd, or at the 3rd, … or at the last)

i = 2 $N(N-1)/2$

i = 3 $N(N-1)(N-2)/6$

…..

i = k $N(N-1)(N-2)….(N-k+1)/k! = N!/k!(N-k)!$

….

i = N-1 N

i = N 1 (all the throws = tailspins)

The test series has the length N (*N* throws = attempts)
Number of variants to obtain the result of the type k (with k tailspins):

$$\Omega_k = N!/k!(N-k)! \qquad \Sigma\Omega_k = 2^N$$

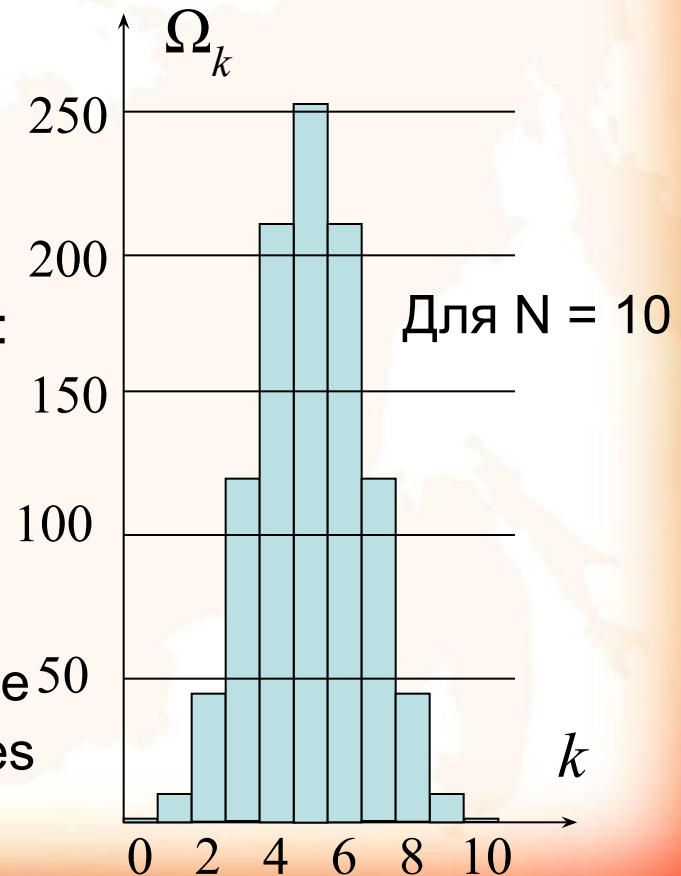Probability to obtain the result of the type k:

$$P_k = N!/k!(N-k)!2^N$$

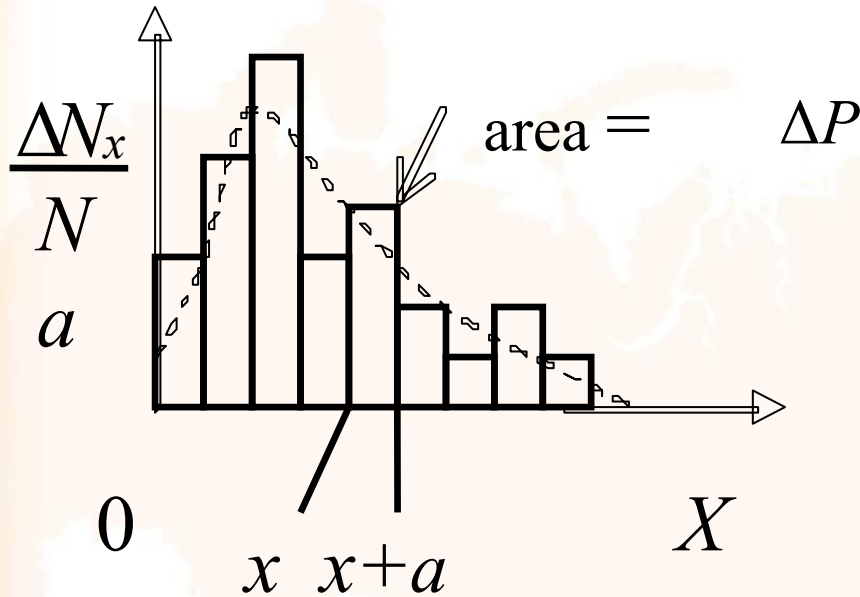If $N >> 1$ we may apply the Sterling's approximation:

$$ln(n!) \sim= n\ ln(n/e)$$

$$P_k = (2/\pi N)^{1/2} exp(-2(k-N/2)^2/N)$$

here $n = (k - N/2)$ – is the deviation of the obtained result from the average *N/2*. Probabilities are noticeable when $n < \sim N^{1/2} << N$
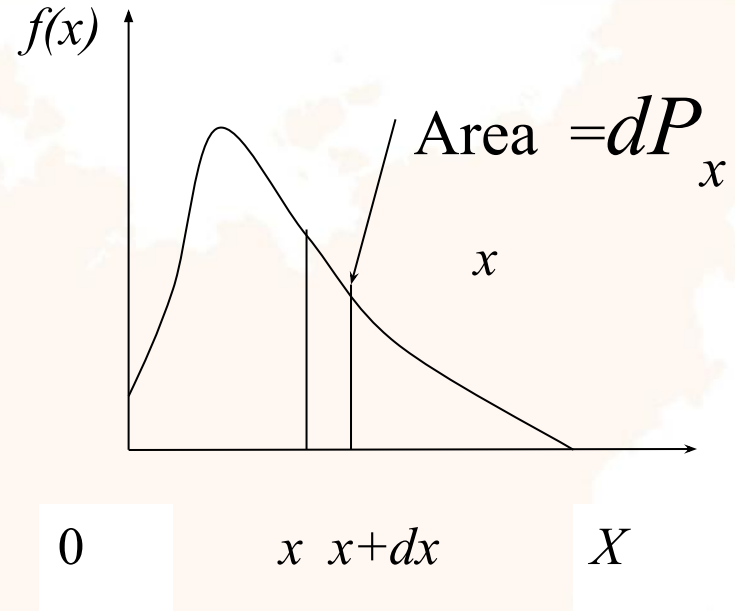
Для N = 10

BAR CHART

Smooth CHART – distribution function

$$\frac{\Delta N_x}{N}$$

a

area = ΔP

0

x $x+a$

X

$f(x)$

Area $=dP_x$

x

0   x $x+dx$ X

$$dP_x = f(x)dx$$

$$f(x) = \lim_{N\to\infty}\frac{dN_x}{Ndx} = \lim_{x\to\infty}\frac{\Delta P_x}{\Delta x} = \frac{dP_x}{dx}$$

$$\sum_i P_i = \frac{\sum N_i}{N} = 1,$$

$$\int dP_x = \int f(x)dx = 1$$

$N -$ number pf tests,

$N_i -$ number of results of the type i

$P_i -$ probability of the result of the type i

$$P_i = \lim_{N \to \infty} \frac{N_i}{N}$$

For continuously distributed quantities X:
differential probability to find the random value X within the range from X to X + dx

$$dP(x) = f(x)dx$$

$f(x)$ – is the probability distribution function

Probability to find the random value X within the range from x_1 to x_2 :

$$P(x_1 \le x \le x_2) = \int_{x_1}^{x_2} f(x)dx$$

For continuously distributed quantities the probability to have exactly some value x_0, is equal to zero $P(x = x_0) = 0$.

$$P_k = (2/\pi N)^{1/2} exp(-2(k-N/2)^2/N) \Rightarrow \qquad f(x) = \frac{1}{\sqrt{2\pi}\sigma} \; e^{-\frac{(x-\mu)^2}{2\sigma^2}}$$
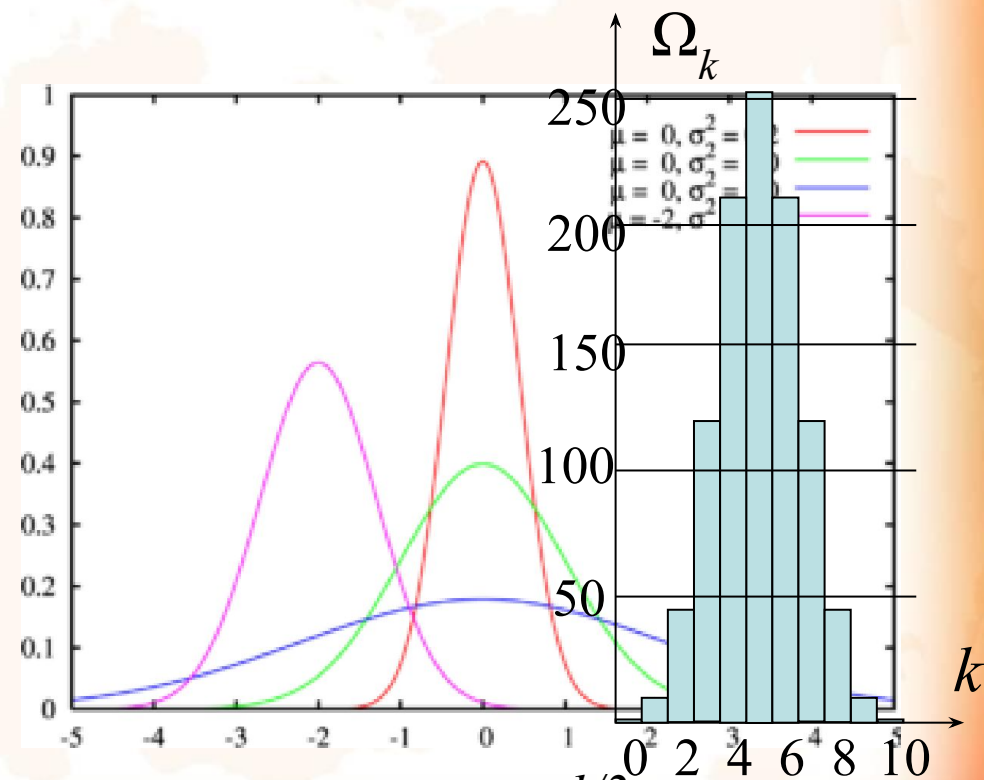
The normal (or Gauss) distribution – is the smooth approximation of the Newton's binomial formula

Parameters of Gauss distribution:

x − some random value

μ — the most probable (or expected) value of the random (the maximum of the distribution function)

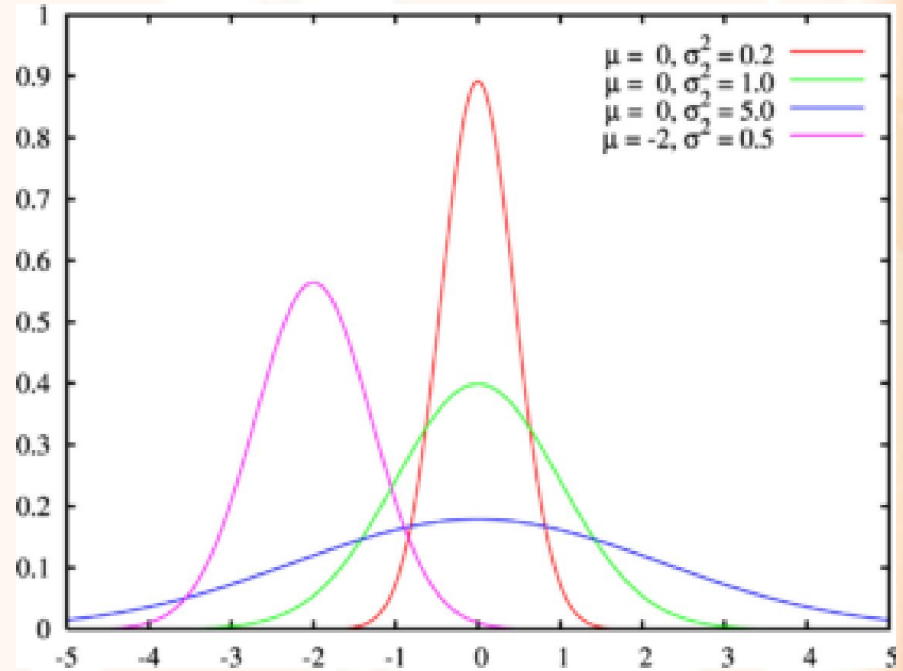σ — dispersion of the random value.

In case of the Eagles and Tails game: $\mu = N/2, \sigma = (N/2)^{1/2} << N$

Gauss Distribution

The normal distribution is very often found in nature.

Examples:

• Eagle and Tails game

• Target striking

• the deviations of experimental results from the average (the dispersion of results = the experimental error)

Normal (Gauss) Distribution and Entropy

Number of variants leasing to the result k (if N =10):

$$\Omega_k = N!/k!(N-k)! \qquad \Sigma\Omega_k = 2^N$$

Type   Realizations (variants)

k = 0   0000000000

k = 1   1000000000   0100000000
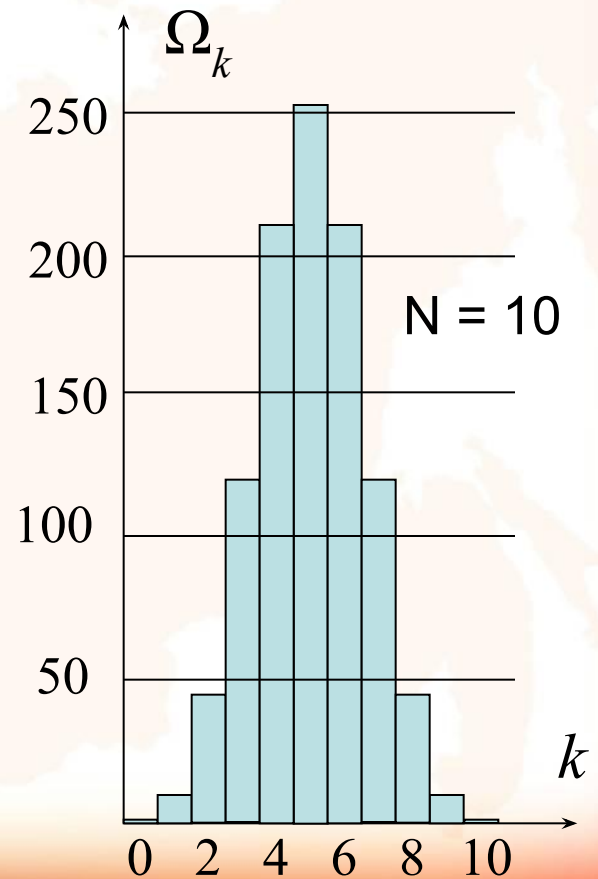   0010000000 … 0000000001

…

k = 5   0100110011   1101000101 … -
       - total 252 variants.

If N>>>1 – figures may be exponentially high

1. The more realizations are possible – the higher is the probability of the result.

2. The more realizations are possible – the less looks the "degree of order" in this result

Ω_k

250

200

150

100

50

N = 10

k

0 2 4 6 8 10

The more realizations are possible – the more is the probability of it and the less is the "degree of order" in this result. For long series of tests (N>>>1) numbers of variants of realizations may be exponentially high and it may be reasonable to apply logarithmic functions)

The definition of the entropy of probability: $S(k) = ln(\Omega_k)$ -

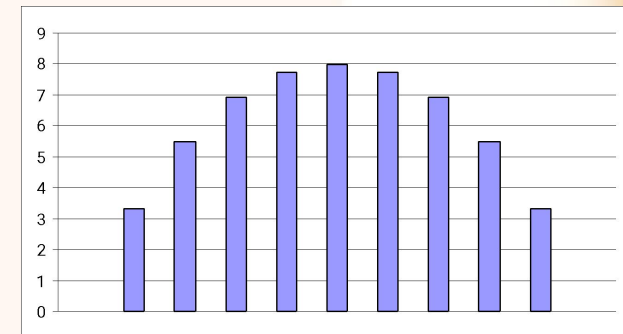If N = 10
S(0) = S(10) = ln(1) = 0
S(5) = ln(252) = ~5,6

N = 10

$$S(k) = Aln(P_k) = Aln(\Omega_k) - ANln2$$

The higher is the "order" – the lower is entropy

The higher is probability – the higher is entropy

$$P(k \, и \, i) = P_k P_i => S(k \, и \, i) = S(k)+S(i)$$

Entropy is the additive function!

Type of result   Realizations

k = 0   0000000000

k = 1   1000000000   0100000000 ...

k = 5   0100110011   1101000101 …

Any information or communication can be coded as a string of zeroes and units: 011001010111001001010111110001010111…. (binary code)

To any binary code with length N (consisting of N digits, k of which are units and (N-k) – are zeroes) we may assign a value of entropy:

S(N,k) = ln($\Omega_{N,k}$), where $\Omega_{N,k}$ – is the number of variants how we may compose a string out of k units and (N-k) zeroes

• Communications, looking like 00000000..   111111111… S = 0

• Communications with equal number of units and zeroes have maximal entropy .

• Entropy of 2 communications equals to the sum of their entropies.

Any information or communication can be coded as a string of zeroes and units: 0110010101110010010101111110001010111…. (binary code)

The entropy of information or communication, containing k units and (N-k) zeroes is defined like: $S(N,k) = \ln(\Omega_{N,k})$, where $\Omega_{N,k}$ – is the number of variants how we may compose a string out of k units and (N-k) zeroes

• Communications, looking like 00000000..   111111111… S = 0 … the informational value of such 'communication' is also close to zero

• Communications with equal number of units and zeroes have maximal entropy . Most probably they are the sets of randomly distributed symbols, thus also having practically no informational value

• Entropy of 2 communications equals to the sum of their entropies.
Real informative communications as a rule

• do include fragments with noticeable predominance of either zeroes or units, and

• Have the entropy noticeably different from both maximum and minimum

The deffinition of entropy as the measure of disorder (or the measure of informational value) in informatics was first introduced by Claude Shannon in his article «A Mathematical Theory of Communication», published in Bell System Technical Journal in 1948

Those ideas still serve as the base for the theory of connunications, tmethods on encoding and decoding, are used in linguistics etc…
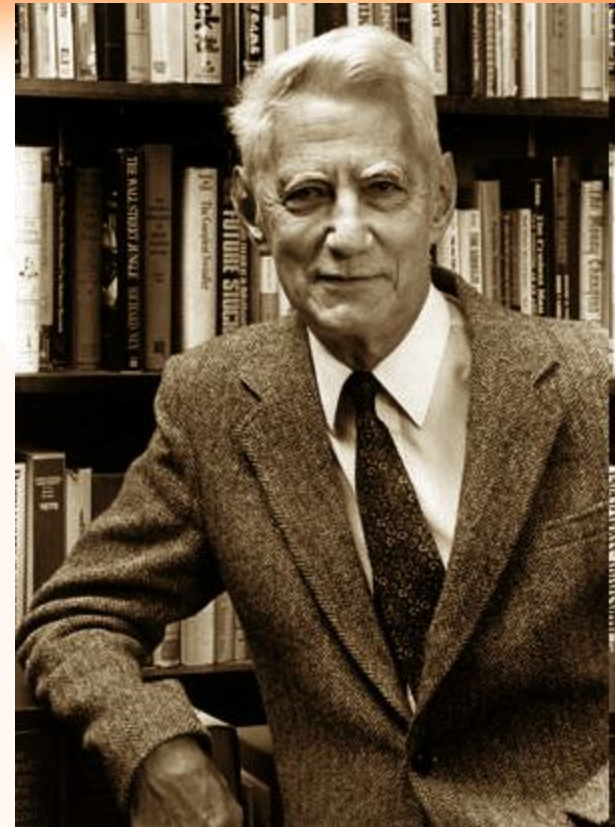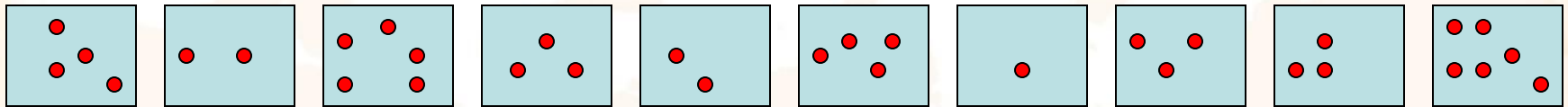

Claude Elwood Shannon
1916 - 2001

Statistical Entropy in Physics

Imagine that we have K possible "states" and we have N "molecules" that can be somehow distributed over those "states"

The row of numbers $(n_1, n_2, \ldots n_K) = n(i)$ forms what is called the «macro-state» of the system. Each macro-state can be realized by the tremendously great number of variants $\Omega(n(i))$. The number of variants of realization is called the "statistic weight" of the macro-state.

The more is the "statistic weight" – the greater is the probability to realize this state.

Even distribution of molecules over space has the biggest statistical weight and thus id usually associated with thermo-dynamical equilibrium.

Statistical Entropy in Molecular Physics: the logarithm of the number of possible micro-realizations of a state with certain macro-parameters, multiplied by the Boltzmann constant.
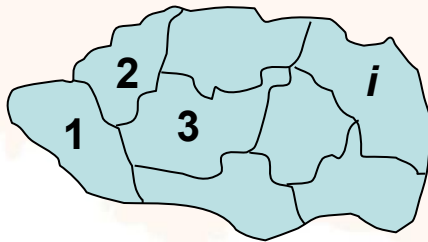
$$S = k \ln \Omega \qquad \text{J/K}$$

1. In the state of thermodynamic equilibrium, the entropy of a closed system has the maximum possible value (for a given energy).
2. If the system (with the help of external influence)) is derived from the equilibrium state - its entropy can become smaller. BUT…
3. If a nonequilibrium system is left to itself - it relaxes into an equilibrium state and its entropy increases
4. **The entropy of an isolated system for any processes does not decrease, i.e. ΔS > 0 ,** as the spontaneous transitions from more probable (less ordered) to less probable (more ordered) states in molecular systems have negligibly low probability

5. The entropy is the measure of disorder in molecular systems.

For the state of the molecular system with certain macroscopic parameters we may introduce the definition of Statistical Entropy as the logarithm of the number of possible micro-realizations (the statistical weight of a state Ώ) - of a this state, multiplied by the Boltzmann constant.

$$S = k \ln \Omega \quad \text{J/K}$$

Entropy is the additive quantity.

$$p = p_1 p_2 ... p_N \qquad p_i \; \square \; \Omega_i \qquad \Omega = \Omega_1 \Omega_2 ... \Omega_N$$

$$S = k \ln \Omega = k \left(\ln \Omega_1 + \ln \Omega_2 + ... + \ln \Omega_N \right) \quad \Rightarrow \quad S = \sum_{i=1}^{N} S_i$$

Not a strict proof, but plausible considerations.

- the number of variants of realization of a state (the statistical weight of a state) shall be higher, if the so called phase volume, available for each molecule (atom), is higher: Phase volume $\Omega_1 \sim Vp^3 \sim VE^{3/2} \sim VT^{3/2}$

- the phase volume for N molecules shall be raised to the power N: $\Omega \sim V^N T^{3N/2}$.

For multy-atomic molecules, taking into account the possibilities of rotations and oscillations, we shall substitute 3 by i : $\Omega \sim V^N T^{iN/2}$

- As molecules are completely identical, their permutations do not change neither the macro-state, nor the micro-states of the system. Thus we have to reduce the statistical weight of the state by the factor $\sim N!$ (the number of permutations for N molecules)

$$\Omega \sim V^N T^{iN/2} / N!; \quad S = k\ ln\ \Omega = kNln(VT^{i/2}/NC) =$$
$$= v(Rln(V/v) + c_V lnT + s_0)$$

$$\Omega \sim V^N T^{iN/2} /N!; \quad S=k \ln \Omega =kNln(VT^{i/2}/NC)=$$
$$= v(Rln(V/v) + c_V lnT +s_0)$$

The statistical entropy proves to be *the same physical quantity*, as was earlier defined in thermodynamics without even referring to the molecular structure of matter and heat!

~

"The increase of disorder, or the increase of the Entropy, of the Universe over time -

is one of the possibilities to define the so-called "Time arrow", that is the direction of time, or the ability to distinguish the past from the future,

Stephen Hawking

(1942-2018)
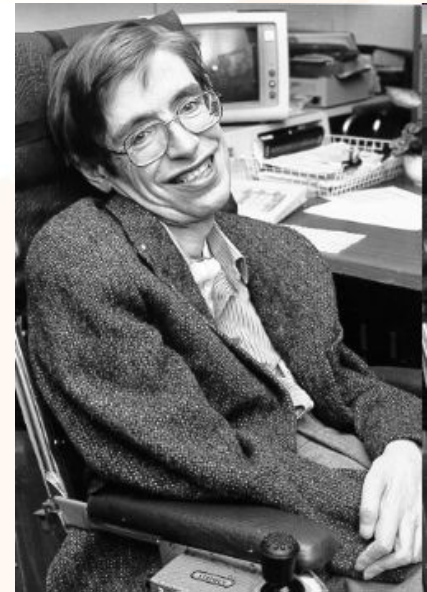
The Distributions of Molecules over Velocities and Energies Maxwell and Boltzmann Distributions

That will be the Focus of the next lecture!

Thank You for Attention!