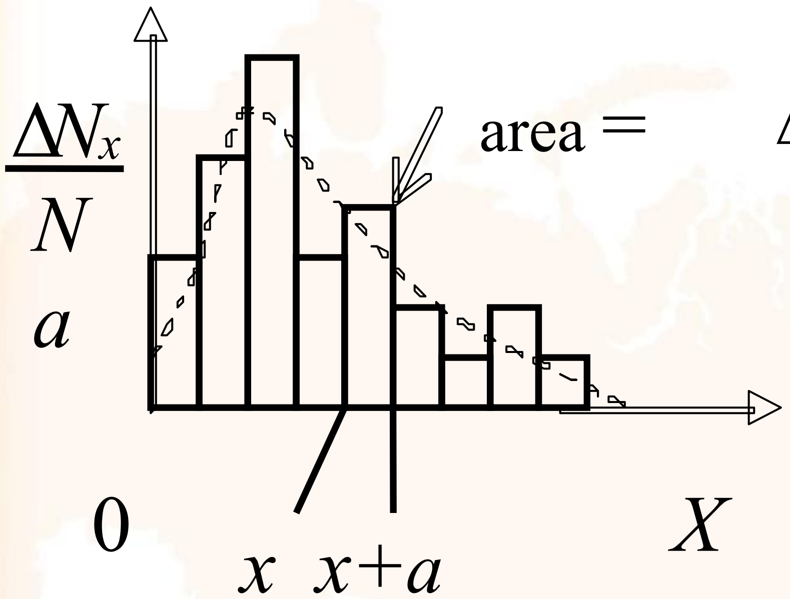
Lecture 09

The Distribution of Molecules over Velocities

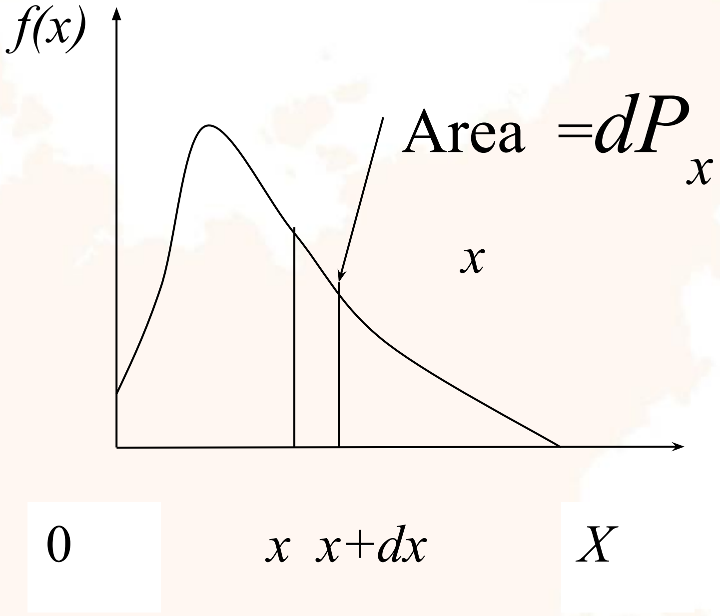
Maxwell Distribution

SOME MATHEMATICS: the probability distribution

BAR CHART



Smooth CHART – distribution function



$$dP_x = f(x)dx$$

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

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

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

Normal distribution

$$P_k=(2/\pi N)^{1/2}\exp(-2(k-N/2)^2/N) \Rightarrow \quad f(x) = \frac{1}{\sqrt{2\pi}\sigma}\, e^{-\frac{(x-\mu)^2}{2\sigma^2}};$$

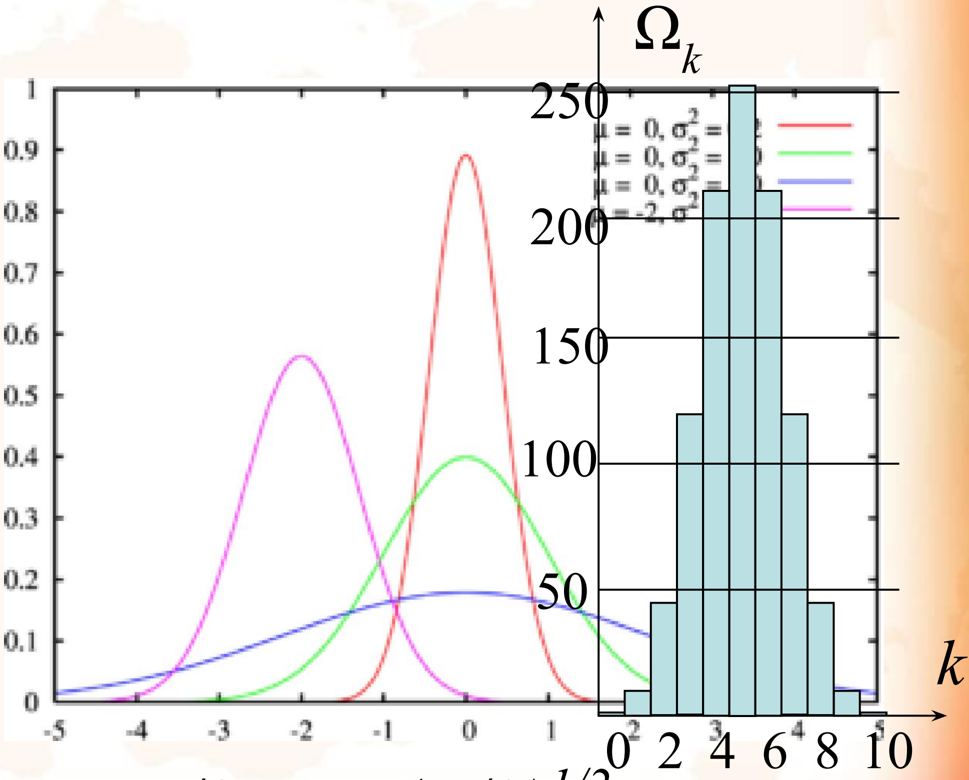
The normal (or Gauss) distribution – is the smooth approximation of the Newton’s binomial formula

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: $\mu = N/2, \sigma = (N/2)^{1/2} << N$

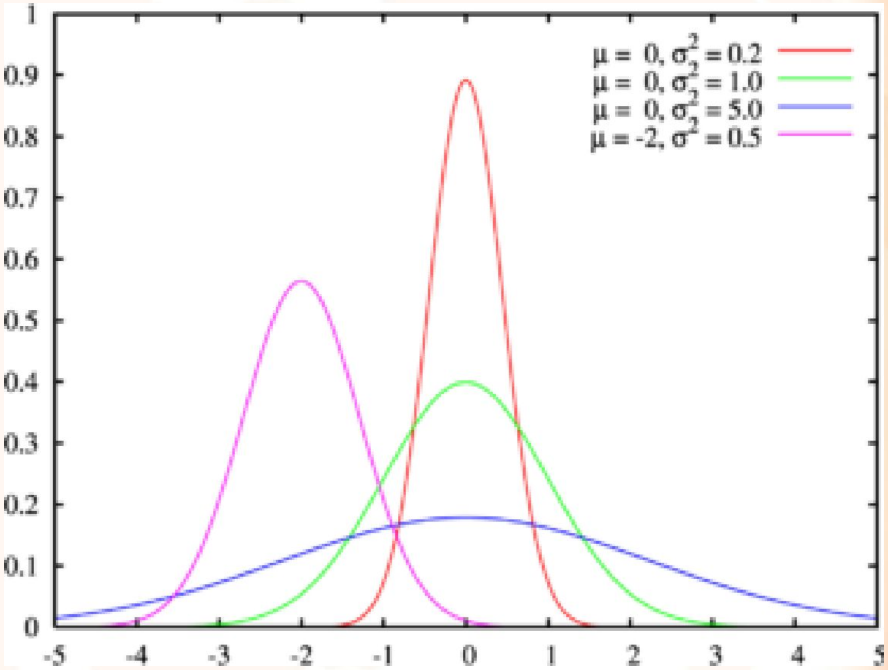
Gauss Distribution

$$f(x) = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{(x-\mu)^2}{2\sigma^2}}$$

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)



Statistical Entropy in Physics.

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. $\Delta S \geq 0$** , as the spontaneous transitions from more probable (less ordered) to less probable (more ordered) states in molecular systems have negligibly low probability

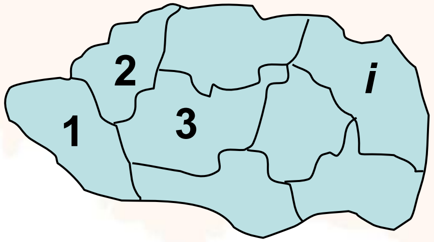
5. The entropy is the measure of disorder in molecular systems.

Statistical Entropy in Physics.

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 Ω) - of a this state, multiplied by the Boltzmann constant.

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

Entropy is the additive quantity.



$$p = p_1 p_2 \dots p_N \qquad p_i \propto \Omega_i \qquad \Omega = \Omega_1 \Omega_2 \dots \Omega_N$$

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

Statistical Entropy and the Entropy of Ideal Gas

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 rotational and oscillational motion, 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 macrostate, nor the microstates of the system. Thus we have to reduce the statistical weight of the state by the factor ~ $N!$ (the number of permulations for N molecules)

$$\Omega \sim V^N T^{iN/2} / N!; \quad S = k \ln \Omega = kN \ln(VT^{i/2}/NC) =$$

$$= \nu(R \ln(V/\nu) + c_V \ln T + s_0)$$

Statistical Entropy and the Entropy of Ideal Gas

$$\Omega \sim V^N T^{iN/2}/N!; \quad S = k\ln\Omega = kN\ln(VT^{i/2}/NC) =$$

$$= v(R\ln(V/v) + c_V\ln T + s_0)$$

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!

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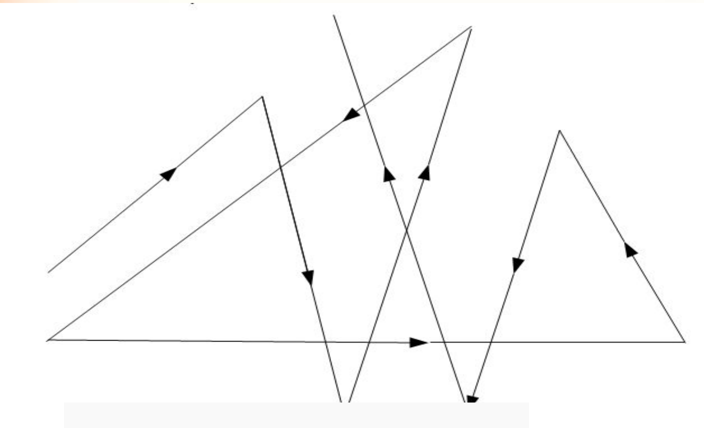
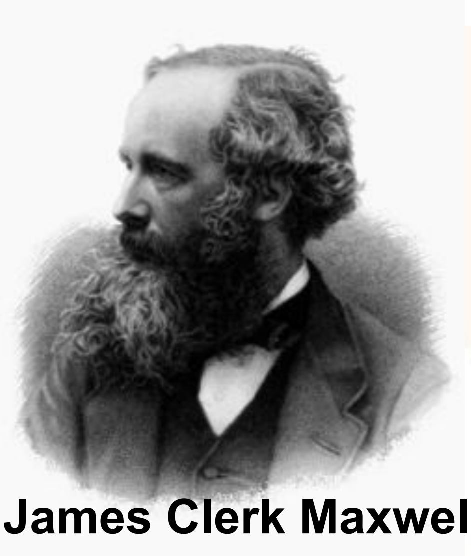
The Distributions of Molecules over Velocities and Energies Maxwell and Boltzmann Distributions

That will be the Focus of the next lecture!

Distribution of molecules over velocities





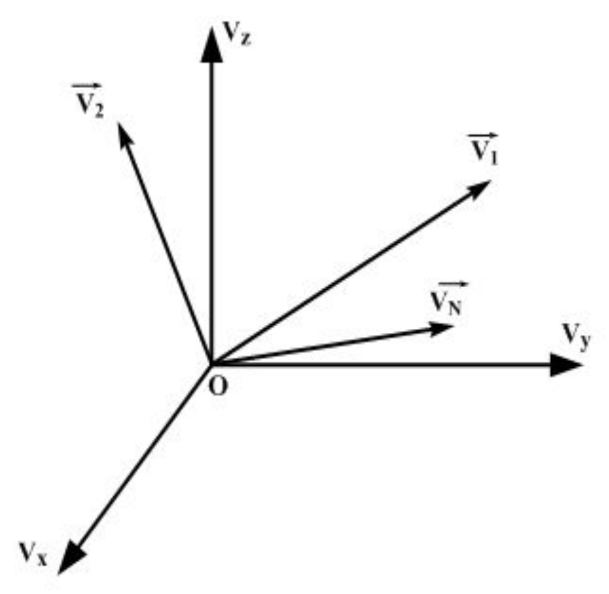
James Clerk Maxwell
1831-1879

If gas is in thermodynamic equilibrium state –the macroscopic parameters (temperature, pressure) are kept stable and the distribution of molecules over velocities and energies remains also stable in time and space.
This distribution was first derived in 1859 by J.C.Maxwell.

Distribution of molecules over velocities

Each velocity vector can be presented as a point in the *velocity space*,

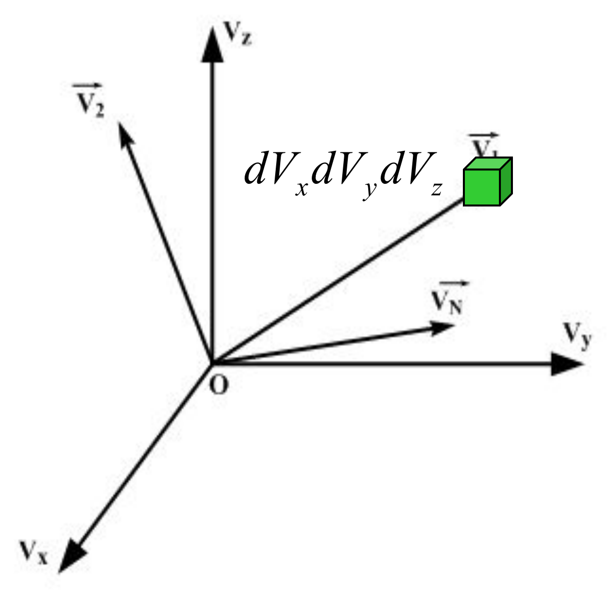
As all the directions are equal – the distribution function can not depend on the direction, but only on the modulus of velocity $f(V)$



Distribution of molecules over velocities

The probability to have the x-component of the velocity within the range between V_x and $V_x + dV_x$

$$dP\left(V_x, V_x + dV_x\right) = \varphi\left(V_x\right) dV_x$$



The probability that the end of the 3-dimensional velocity vector V, will fir into the small cube $dV_x dV_y dV_z$ nearby the velocity $\boldsymbol{V}$ can be calculated by multiplying probabilities:

$$dP(V) = \varphi\left(V_x\right)\varphi\left(V_y\right)\varphi\left(V_z\right) dV_x dV_y dV_z$$

From the other hand, as all the directions are equal, this probability may depend only on the modulus of velocity

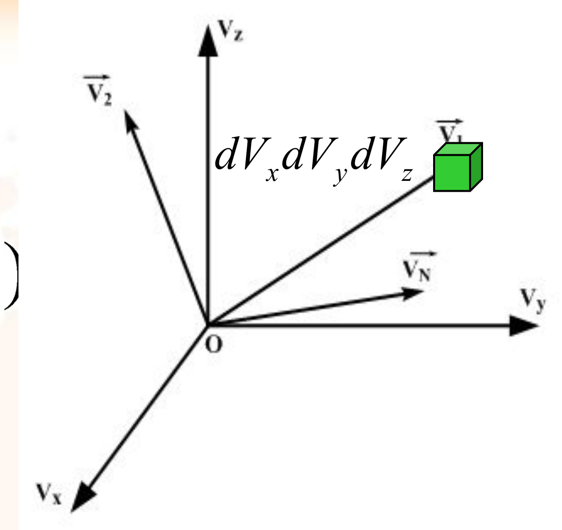
$$f\left(V\right) = \varphi\left(V_x\right)\varphi\left(V_y\right)\varphi\left(V_z\right)$$

Distribution of molecules over velocities

Noe some mathematics:

$$f(V)=\varphi(V_x)\varphi(V_y)\varphi(V_z)$$

$$\ln(f(V))=\ln(\varphi(V_x))+\ln(\varphi(V_y))+\ln(\varphi(V_z))$$

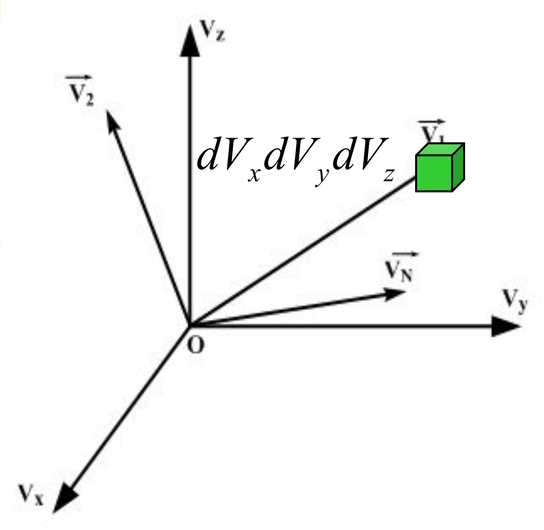


We will calculate the derivative by dV_x

$$\frac{f'(V)}{f(V)}\frac{\partial V}{\partial V_x}=\frac{\varphi'(V_x)}{\varphi(V_x)} \Rightarrow \frac{f'(V)}{f(V)}\frac{1}{V}=\frac{\varphi'(V_x)}{\varphi(V_x)}\frac{1}{V_x}=\alpha$$

as $$\frac{\partial V}{\partial V_x}=\frac{V_x}{\sqrt{V_x{}^2+V_y{}^2+V_z{}^2}}=\frac{V_x}{V}$$

Distribution of molecules over velocities



The only function which satisfies the equation:

$$\frac{f'(V)}{f(V)}\frac{1}{V} = \frac{\varphi'(V_x)}{\varphi(V_x)}\frac{1}{V_x} = \alpha$$

as well as the initial condition

$$f(V) = \varphi(V_x)\varphi(V_y)\varphi(V_z)$$

is:

$$\varphi(V_x) = A\exp\left(\frac{\alpha V_x^2}{2}\right)$$

here α must be negative! $\alpha < 0$

Distribution of molecules over velocities

$$\varphi(V_x) = A\exp(\frac{\alpha V_x^{2}}{2}) \qquad \alpha = -|\alpha|$$

From normalization condition $\int_{-\infty}^{+\infty}\varphi(V_x)dV_x = 1$ we obtain:

$$A\int_{-\infty}^{+\infty}\exp(-\frac{|\alpha|V_x^{2}}{2})dV_x = 1 \Longrightarrow A = \sqrt{\frac{|\alpha|}{2\pi}}$$

The Poisson integral:

$$\int_{-\infty}^{+\infty}\exp(-X^2)dX = \sqrt{\pi}$$

Probability Distribution and Average Values

Knowing the distribution of a random value 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 *ψ(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

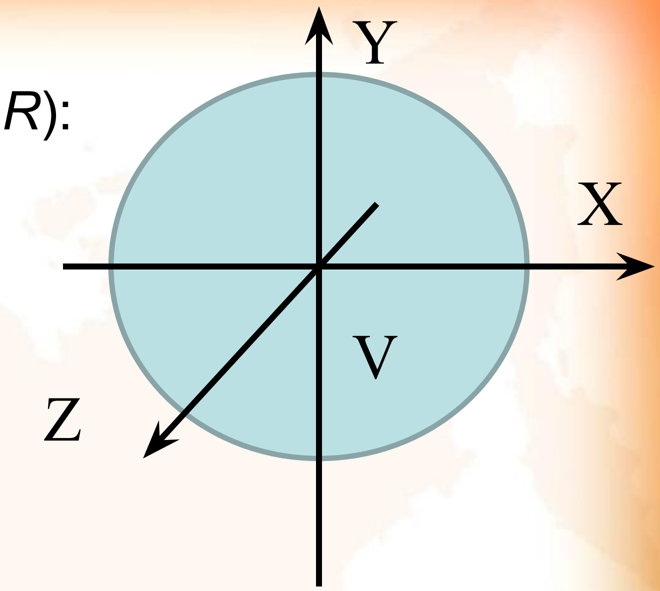
$$<x + y> = <x> + <y>$$

- 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 if x and y are independent variables*

Probability Distribution and Average Values

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



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

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

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

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

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

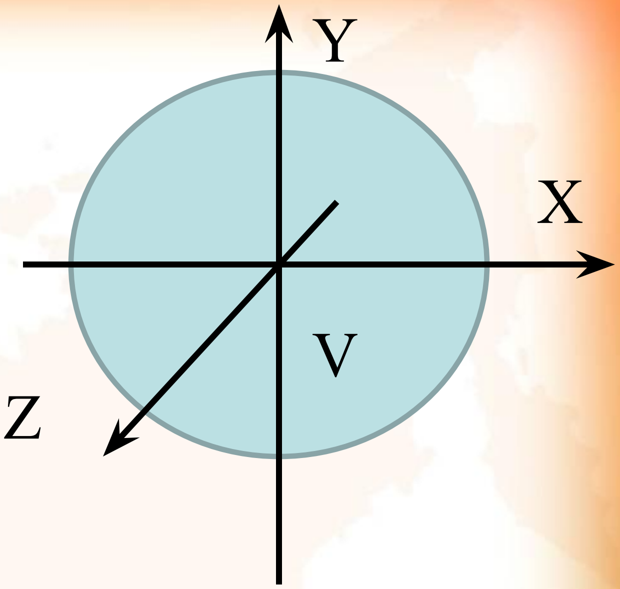
Calculation – on the blackboard…

Different Kinds of Averages

$\langle r\rangle = \langle (x^2+y^2+z^2)^{1/2}\rangle = 3R/4$ - *average*

$(\langle r^2\rangle)^{1/2} = 0,6^{1/2}R > \langle r\rangle$ - *squared average*

$\langle x\rangle = 0; \quad \langle x^2\rangle^{1/2} = R/5^{1/2} > 0$



Median average r_{med} *; the quantity of molecules with* $r<r_{med}$ *equals to the quantity of molecules with* $r>r_{med}$

$r_{med} = R/2^{1/3} = 0,7937R > (\langle r^2\rangle)^{1/2} = 0,7756R > \langle r\rangle = 0,75R$

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…

Distribution of molecules over velocities

$$\varphi(V_x) = A\exp(\frac{\alpha V_x{}^2}{2}) \qquad \alpha = -|\alpha| \qquad A = \sqrt{\frac{|\alpha|}{2\pi}}$$

The average of the squared velocity equals to:

$$\left\langle V_x{}^2 \right\rangle = \int\limits_{-\infty}^{+\infty} V_x{}^2 \varphi(V_x) dV_x = \sqrt{\frac{|\alpha|}{2\pi}} \int\limits_{-\infty}^{+\infty} V_x{}^2 \exp(-\frac{|\alpha| V_x{}^2}{2}) dV$$

This integral once again can be reduced to the Poisson integral:

$$\left\langle V_x{}^2 \right\rangle = \frac{1}{|\alpha|} ; \Rightarrow \varphi(V_x) = \sqrt{|1/2\pi < V_x^2 >} \exp(-V_x^2 / 2 < V_x^2 >)$$

Distribution of molecules over velocities

$$\varphi(V_x) = \sqrt{|1/2\pi < V_x^2 >}\exp(-V_x^2/2 < V_x^2 >)$$

The basic assumption of thermodynamics (every degree of freedom accumulates the same energy):

$$\left\langle \frac{mV_x{}^2}{2} \right\rangle = \frac{m}{2}\left\langle V_x{}^2 \right\rangle = \frac{1}{2}kT \quad \Rightarrow \quad \left\langle V_x{}^2 \right\rangle = kT/m$$

$$\varphi(V_x) = \sqrt{\frac{m}{2\pi kT}}\exp\left(-\frac{mV_x{}^2}{2kT}\right)$$

Distribution of molecules over velocities

$$\varphi(V_x) = \sqrt{\frac{m}{2\pi kT}}\exp(-\frac{mV_x^{\;2}}{2kT})$$

The distribution over absolute values of velocities:

$$f(V) = \varphi(V_x)\varphi(V_y)\varphi(V_z)$$

,

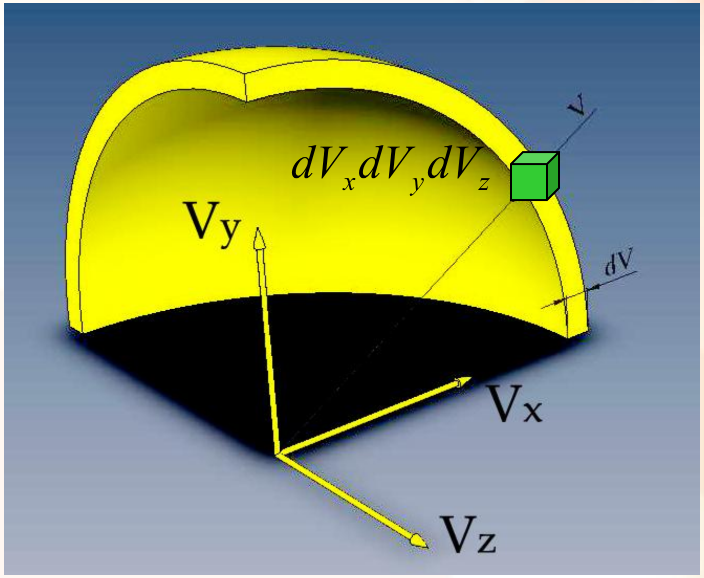
$$\varphi(V_y) = \sqrt{\frac{m}{2\pi kT}}\exp(-\frac{mV_y^{\;2}}{2kT}) \qquad \varphi(V_z) = \sqrt{\frac{m}{2\pi kT}}\exp(-\frac{mV_z^{\;2}}{2kT})$$

$$f(V) = \left(\frac{m}{2\pi kT}\right)^{3/2}\exp(-\frac{mV^2}{2kT})$$

Distribution of molecules over velocities

Function

$$f(V)=\left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left(-\frac{mV^2}{2kT}\right)$$



defines the probability that velocity is within the “cubic” range:

$$dV_x dV_y dV_z$$

$$dP = f(V)\,dV_x dV_y dV_z$$

Probability to find the absolute value of the velocity between V and $V+dV$

$$dP = f(V)4\pi V^2 dV = F(V)dV$$

$$F(V) = 4\pi V^2 f(V)$$ - Maxwell’s function

Maxwell’s Function

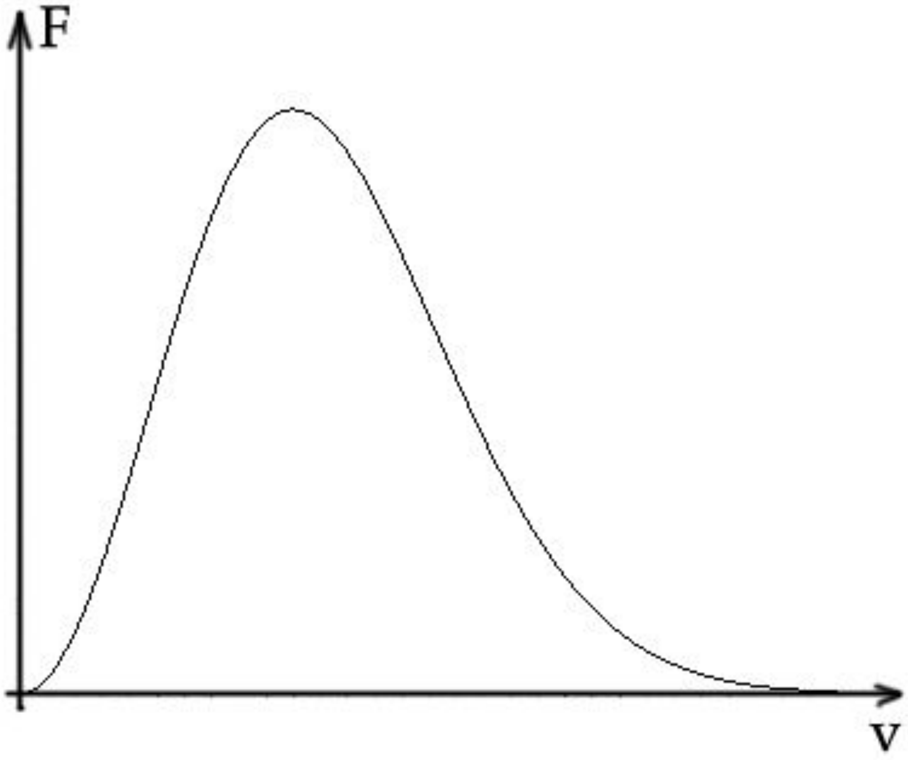
$$F(V) = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mV^2}{2kT}\right) 4\pi V^2$$

$$V << V_{вер}$$

$$F(V) \propto V^2$$

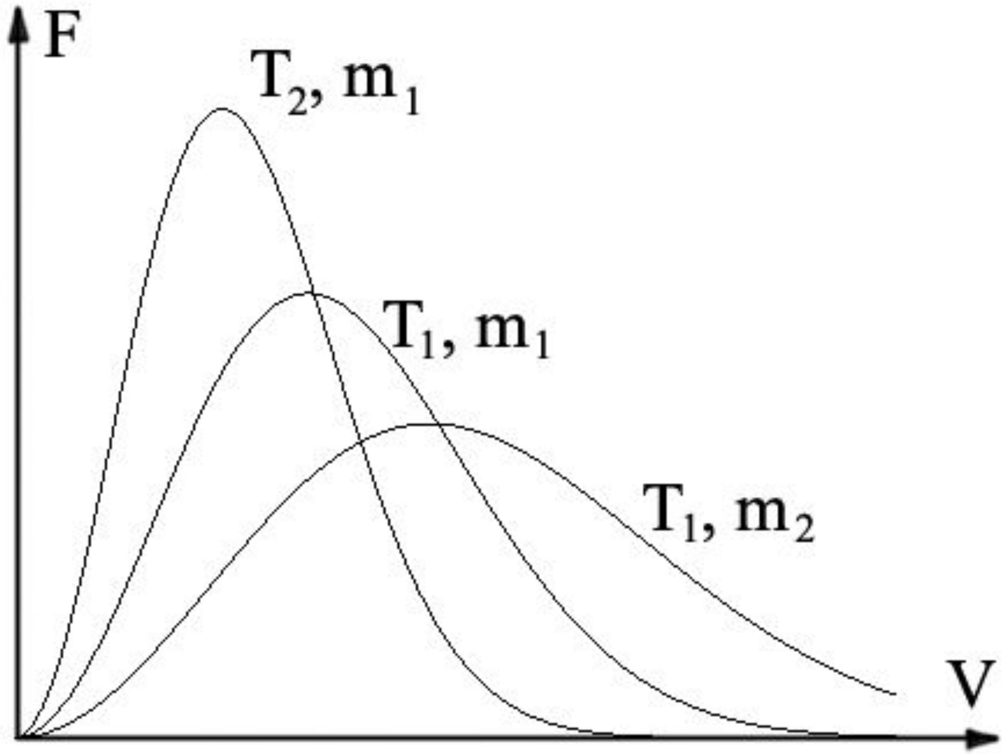
$$V >> V_{вер}$$

$$F(V) \propto \exp\left(-\frac{mV^2}{2kT}\right)$$



$$T_2 = T_1/2$$

$$m_2 = m_1/2$$



Area under the curve is always equal to 1

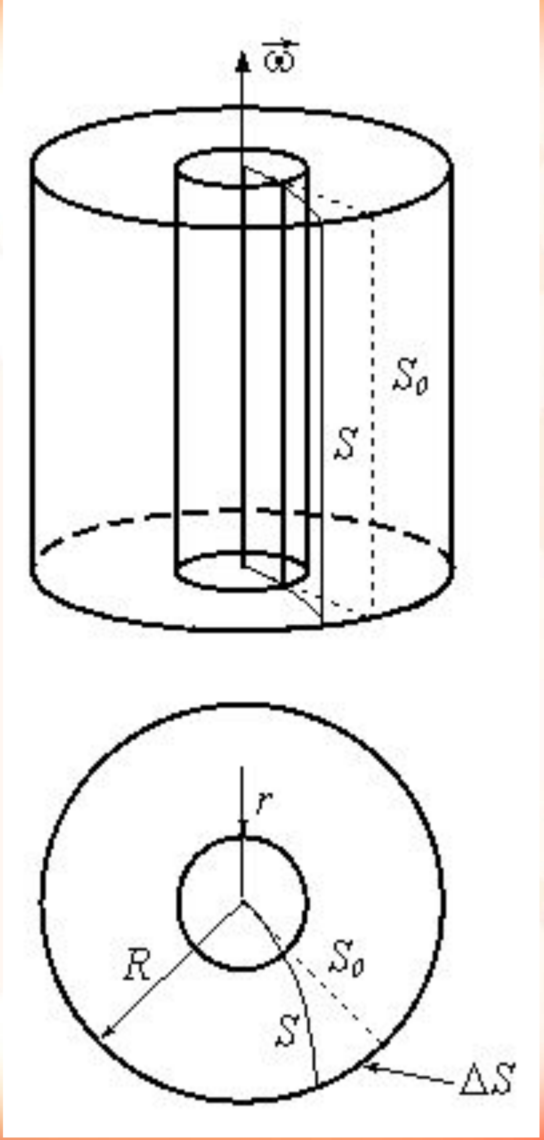
Stern’s experiment (1920)

- The outer cylinder is rotating

$$\Delta S = R\omega\Delta t$$

$$\Delta t = \frac{R}{V}$$

$$V = \frac{\omega R^2}{\Delta S}$$



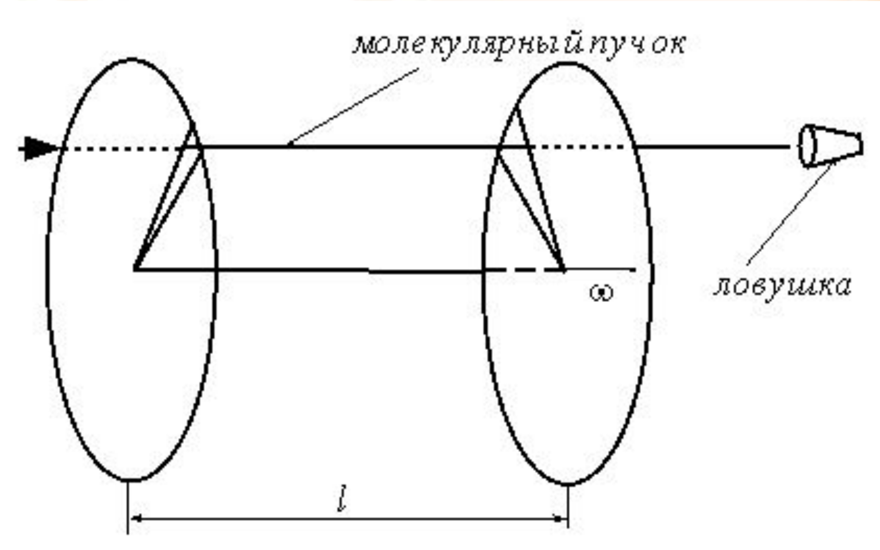
Lammert's Experiment (1929)

- Two rotating discs with radial slots. One is rotating ahead of the other. The angle distance is φ

$$t_1 = {}^{l}\!/_{V}$$

$$t_2 = {}^{\omega l}\!/_{\varphi}$$

$$V = {}^{\omega l}\!/_{\varphi}$$



Most probable velocity.

Most probable velocity corresponds to the maximum of the Maxwell's function)

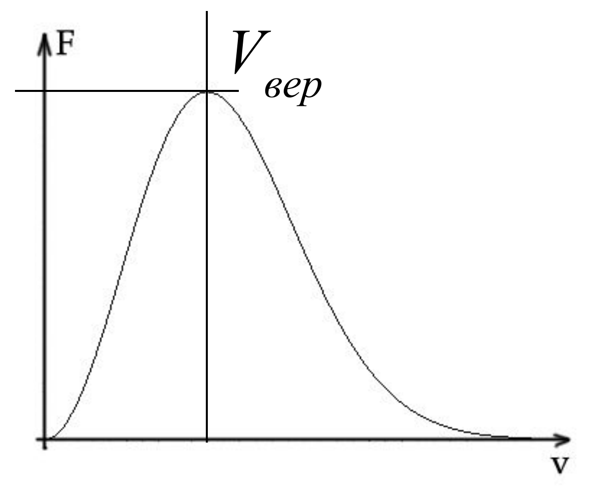
$$\frac{dF(v)}{dv} = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} V\exp\left(-\frac{mV^2}{2kT}\right)\left(2-\frac{mV^2}{kT}\right) = 0$$

Most probable velocity

$$V_{вер} = \sqrt{\frac{2kT}{m}}$$

The value of the Maxwell's function maximum:

$$F\left(v_{вер}\right) = \frac{4}{\sqrt{\pi e}}\sqrt{\frac{m}{2kT}} = \frac{4}{\sqrt{\pi e}}\frac{1}{v_{вер}}$$



Average velocity.

Average velocity by deffinition

$$\langle V\rangle = \int V dP = \int_0^\infty V F(V) dV$$

For Maxwell's function:

$$\langle V\rangle = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_0^\infty V^3\exp\left(-\frac{mV^2}{2kT}\right)dV$$

$$\langle V\rangle = \sqrt{\frac{8kT}{\pi m}}$$

Average squared velocity.

Average squared velocity by definition

$$V_{ср.кв.} = \sqrt{\left\langle V^2 \right\rangle}$$

$$\left\langle V^2 \right\rangle = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \int_0^\infty V^4 \exp\left(-\frac{mV^2}{2kT} \right) dV$$

$$V_{ср.кв.} = \sqrt{\frac{3kT}{m}}$$

Three kinds of average velocities

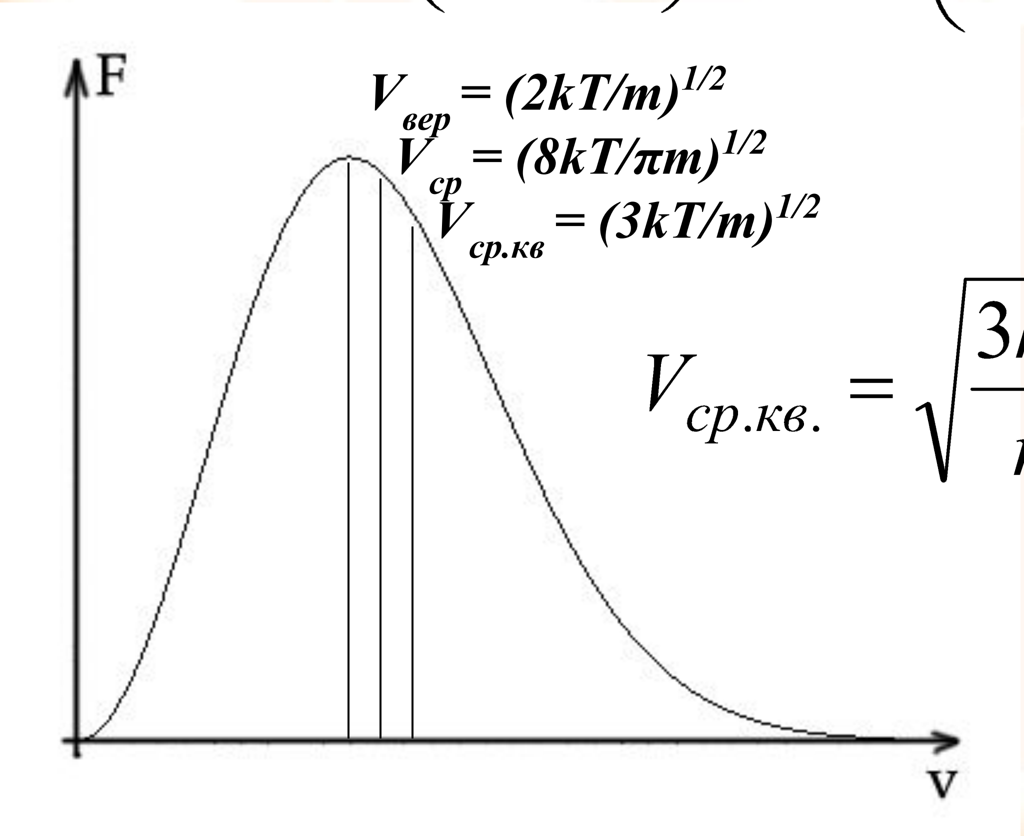
Most probable: $$V_{вер} = \sqrt{\frac{2kT}{m}}$$

Averge: $$\langle V \rangle = \sqrt{\frac{8kT}{\pi m}}$$

Average squared: $$V_{ср.кв.} = \sqrt{\frac{3kT}{m}}$$

Maxwell's Function

$$F(V)=\left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left(-\frac{mV^2}{2kT}\right)4\pi V^2$$



$V_{\text{вер}} = (2kT/m)^{1/2}$

$V_{\text{ср}} = (8kT/\pi m)^{1/2}$

$V_{\text{ср.кв}} = (3kT/m)^{1/2}$

$$V_{\text{ср.кв.}}=\sqrt{\frac{3kT}{m}}>\langle V\rangle=\sqrt{\frac{8kT}{\pi m}}>$$

$$>\ V_{\text{вер}}=\sqrt{\frac{2kT}{m}}$$

Example: The mixture of oxygen and nitrogen (air) has the temperature *T* = *300 K*. What are the average velocities of two types of molecules:

$$\langle V_{O_2} \rangle = \sqrt{\frac{8kT}{\pi m_{O_2}}} \qquad \langle V_{N_2} \rangle = \sqrt{\frac{8kT}{\pi m_{N_2}}}$$

$$\langle V_{O_2} \rangle = \sqrt{\frac{8 \cdot 8{,}31 \cdot 300}{3{,}14 \cdot 32 \cdot 10^{-3}}} = 0{,}45 \cdot 10^3 \, {}^{м}\!/_{c} = 450 \, {}^{м}\!/_{c}$$

$$\langle V_{N_2} \rangle = \sqrt{\frac{8 \cdot 8{,}31 \cdot 300}{3{,}14 \cdot 28 \cdot 10^{-3}}} = 0{,}48 \cdot 10^3 \, {}^{м}\!/_{c} = 480 \, {}^{м}\!/_{c}$$

Energy distribution function

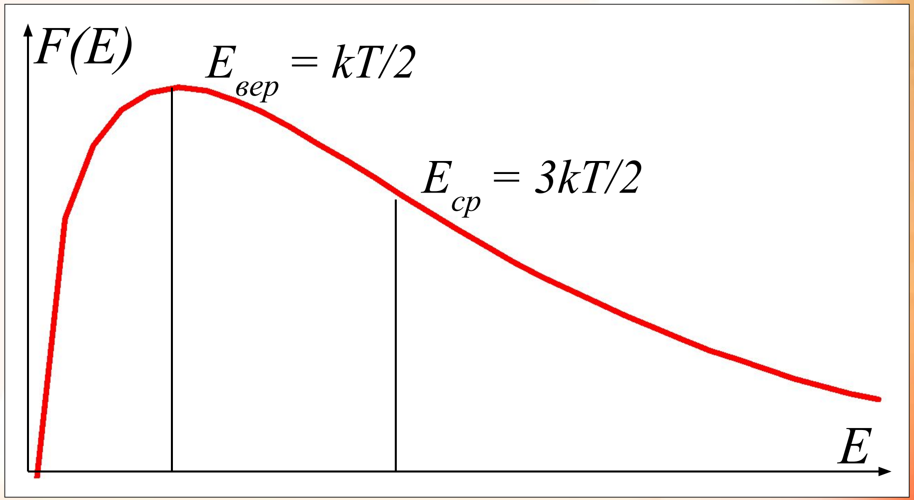
$$F(V)=\left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left(-\frac{mV^2}{2kT}\right)4\pi V^2$$

$$F(V)dV = F(E)dE;$$
$$E = mV^2/2;$$
$$dV = dE/(2mE)^{1/2}$$

$$F(E)dE=\frac{2}{\sqrt{\pi}}\sqrt{\frac{E}{kT}}\exp\left(-\frac{E}{kT}\right)\frac{dE}{kT}$$

$$\int F(E)dE = 1$$

$$<\mathbf{E}> = \int E\,F(E)dE = \mathbf{3kT/2}$$



Energy distribution function

$$F(V)=\left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left(-\frac{mV^2}{2kT}\right)4\pi V^2$$

$F(V)dV = F(E)dE;$

$E = mV^2/2;$

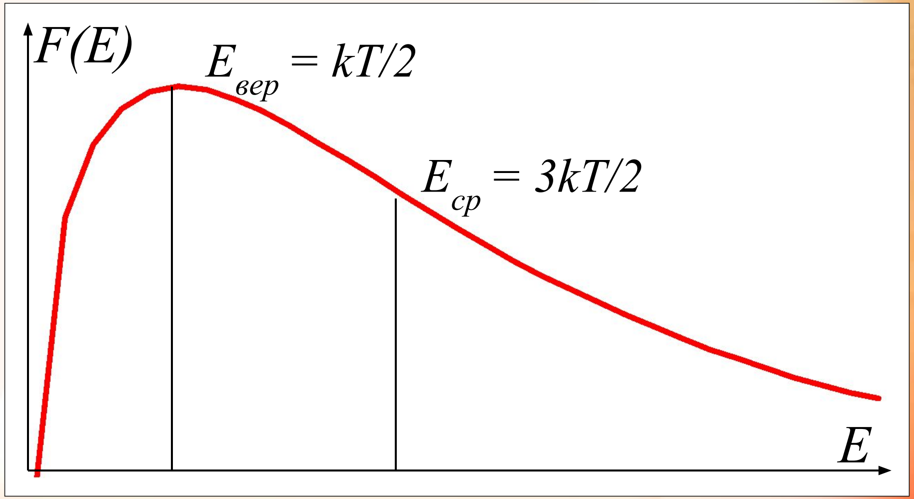
$dV = dE/(2mE)^{1/2}$

$$F(E)dE=\frac{2}{\sqrt{\pi}}\sqrt{\frac{E}{kT}}\exp\left(-\frac{E}{kT}\right)\frac{dE}{kT}$$

$$\langle E\rangle = 3kT/2$$

This is the distribution of molecules over kinetic energies. he question is: how the distribution will look like, if to take into account also the potential energy (gravity)?

That will be the topic of the next lecture..



Thank You for Attention!