Учреждение образования
«Гомельский государственный университет
имени Франциска Скорины»

Е. Б. ШЕРШНЕВ, А. Н. КУПО, С. А. ЛУКАШЕВИЧ

ОСНОВЫ
МОЛЕКУЛЯРНО-КИНЕТИЧЕСКОЙ ТЕОРИИ

Практическое пособие

для студентов физических специальностей университета

Рецензенты:

кандидат физико-математических наук В. Е. Гайшун,
кандидат физико-математических наук Н. С. Косенок,
кандидат филологических наук Е. В. Сажина

Рекомендовано к изданию научно-методическим советом учреждения образования «Гомельский государственный университет имени Франциска Скорины»

Целью практического пособия является оказание методической помощи иностранным студентам при получении ими знаний в области молекулярной физики, изучении физических понятий, применяемых в молекулярно-кинетической теории.
    Адресовано иностранным студентам физических специальностей.

ОГЛАВЛЕНИЕ

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ВВЕДЕНИЕ

На основе современных научных теорий в изучении молекулярной физики наметились два подхода: макроскопический и молекулярно-кинетический. Первый метод основан на изучении свойств макроскопических тел без учета особенностей их внутреннего строения. Такой метод называется термодинамическим. В этом методе главная роль отводится закону сохранения энергии.

При изучении молекулярно-кинетической теории особое внимание обращается на более глубокое изучение свойств вещества на основе введения представлений об их внутреннем строении. Учитывая то, что вещество состоит из молекул, можно в общих чертах объяснить различие между тремя состояниями вещества – газообразным, жидким и твердым.

Основная цель молекулярно-кинетической теории – рассмотрение макроскопических свойств тел как проявление суммарного действия молекул. В этом случае в теории пользуются статистическим методом, который позволяет определить не поведение отдельных молекул, а только средние величины, характеризующие движение и взаимодействие огромной совокупности частиц.

Именно поэтому молекулярно-кинетическая теория имеет другое название – статистическая физика.

Статистическая физика как научное направление имеет длительную историю развития, но современная ее структура сложилась в начале XX в. благодаря работам Дж. Максвелла, Л. Больцмана и Д. Гиббса.

Оба метода изучения физических явлений – макроскопический и микрофизический – дополняют друг друга.

Настоящее издание включает избранные главы молекулярно-кинетической теории и предназначено для оказания помощи иностранным студентам, обучающимся на факультете физики и ИТ, в овладении знаний в области молекулярной физики, уяснении физических понятий, применяемых в молекулярно-кинетической теории.

Практическое пособие написано на английском языке в соответствии с программой курса общей физики для физических специальностей и может быть использовано для самостоятельной работы.

1 THE ROLE OF RANDOM PROCESSES IN MOLECULAR PHYSICS. BROWNIAN MOTION

1.1 The main provisions of the molecular-kinetic theory

The bodies around us are perceived by us as solid, continuous. Hence the mechanistic representation of such a model of an absolutely solid body, which nevertheless allowed us to understand and use the concepts of coordinate, force, momentum, energy, and others known to us from the course of mechanics. But even to explain such simple properties of substances as the fact that they are in three aggregate states with their features, the model of an absolutely solid body is not suitable. The development of laboratory research methods, engineering and technical means of studying the surrounding objective reality lead to an unambiguous conclusion that all bodies of the real world have a discrete ("discontinuous") structure.

Originated in the V century BC in the works of ancient philosophers, the idea of the discrete structure of matter, which was developed in the VIII–XIX centuries, is now a fully established scientific doctrine, known as the molecular kinetic theory (MKT) of the structure of matter.

When it comes to molecular-kinetic theory, it is always appropriate to quote the outstanding scientist of the XX century, Richard Feynman (1918–1988): "If, in some cataclysm, all of scientific knowledge were to be destroyed, and only one sentence passed on to the next generation of creatures, what statement would contain the most information in the fewest words? I believe it is the atomic hypothesis that all things are made of atoms – little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another. In that one sentence, you will see, there is an enormous amount of information about the world, if just a little imagination and thinking are applied."

Currently, all the variety of laws and conclusions of molecular kinetic theory are based on three immutable rules, known as **the basic provisions of molecular kinetic theory.** We will take them as a starting point in our reasoning.

First provision:

All substances (bodies) – liquid, solid and gaseous – are formed (consist) of the smallest particles-molecules, which themselves consist of atoms ("elementary molecules"). The molecules of a chemical can be simple

or complex, and consist of one or more atoms. Molecules and atoms are electrically neutral particles. Under certain conditions, molecules and atoms can acquire an additional electric charge, and turn into positive or negative ions.

Second provision:

Particles (atoms and/or molecules) are in continuous chaotic motion. In the future, we will use the term "***thermal motion***".

Third provision:

The particles interact with each other with forces that have an electrical nature. The gravitational interaction between the particles is negligible.

We will not dwell in detail on the modern interpretation of each of the presented statements, as well as on the definitions of concepts and terms used in MKT and thermodynamics, but consider what role the case, or rather ***the probability*** of a particular phenomenon, plays in the described processes.

1.2 Statistical and thermodynamic methods in molecular physics

As you know, the random chaotic motion of molecules is called ***thermal motion***. In this case, the average (averaged) kinetic energy of thermal motion (both translational and rotational!) increases with increasing temperature. At relatively low temperatures, the average kinetic energy of the molecules may be less than ***the depth of the potential well*** of the Coulomb interaction field (E0). In this case, the molecules form a condensed state (i. e., a liquid or solid). In this case, the average distance between the molecules will be comparable to a certain characteristic value of $d_0 \cong 10^{-9}$ *м* – we will call it ***the effective diameter of the sphere of molecular action.*** As the temperature increases, the average kinetic energy of the molecule becomes greater than E0, the molecules fly apart, and a gaseous substance is formed.

Even at distances equal to several d_0 (we will later in some of our arguments roughly understand this value as the average diameter of a molecule), the interaction between the particles is negligible, and this allows us to propose a model of an ideal gas, that is, not to take into account the interaction at all. In addition to the absence of Coulomb forces of attraction and repulsion, we will assume that all particles are material points, the interaction between which is reduced only to absolutely elastic collisions.

Such reasonable assumptions, together with the consequences of some theorems from probability theory, allow us to obtain *the basic equation of the molecular kinetic theory (MKT)* of an ideal gas:

$$p = \langle p \rangle = \frac{1}{3}\, nm_0\, \langle v^2 \rangle = \frac{2}{3}\, n\frac{m_0 \langle v^2 \rangle}{2} = \frac{2}{3} n \langle E_k \rangle, \qquad (1)$$

where p – is the pressure of an ideal gas (macroscopic parameter), n – is the concentration of particles(molecules), m_0 – is the mass of a single particle, $\langle v^2 \rangle$ and $\langle E_k \rangle$ – are the average square of the velocity and the average kinetic energy of the translational motion of the particles, respectively.

In this case, the equality:

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3}\langle v^2 \rangle, \qquad (2)$$

where $\langle v_x^2 \rangle$ $\langle v_y^2 \rangle$ $\langle v_z^2 \rangle$ – the mean value of the squares of the projections of the Cartesian coordinate system. It is the expression (2) that is the direct consequence of statistical consideration, namely, from the assumption that all directions of motion in an ideal gas in the absence of external fields are equally probable.

The description of the state of an ideal gas is reduced to the joint use of *dynamic, statistical and thermodynamic methods* for describing systems consisting of a huge number of particles.

In molecular physics, there is a special constant that is closely related to the ideal gas model – the Loschmidt number. This constant is $2{,}6868{\cdot}10^{19}$, and represents the number of minimal structural units (atoms, molecules, ions, electrons, or any other particles) under normal conditions in 1 cm^3 of a substance. This means that, according to the dynamic approach, to record at some point in time the positions and velocities of all the molecules would need to be recorded $6{\cdot}2{,}7{\cdot}10^{19}$ numbers. If some device were to record them at a rate of 1 million/second, it would take $\approx$ 6 million years. It is clear that such a task is technically impossible in principle, and moreover, useless from a practical point of view.

Statistical methods in physics are more widely used than dynamic methods. This is due to the fact that the dynamic method is only effective when applied to systems with a small number of degrees of freedom (for example, to each individual molecule). Most physical systems have a huge *number of degrees of freedom*, and can be studied only by statistical methods.

A system consisting of a huge number of particles can also be considered as "solid", without being interested in its internal structure. In this approach, you need to use the concepts and physical quantities related to the system as a whole (volume, pressure, temperature, and entropy!). The theory constructed in this way is ***phenomenological***. It is not interested in the internal mechanisms of the processes that determine the behavior of the system under study as a whole; this method of studying systems of many particles is called thermodynamic.

Statistical and thermodynamic methods of studying systems consisting of a huge number of identical particles (or groups of identical particles) complement each other. In this case, the dynamic approach is applicable to a single molecule, and leads to such an important concept as the ***number of degrees of freedom.*** At the same time, the number of degrees of freedom ultimately determines the macroscopic (thermodynamic) parameter ***internal energy.***

1.3 Uniform distribution of kinetic energy by degrees of freedom

In the derivation of formula (1), according to the ideal gas model, it is assumed that all particles are the same, all directions of the velocity of a single particle are equally probable in view of their huge number, and there could be only three such directions in Cartesian space. This statement, reflected in the formula (2), unobtrusively suggests the following conclusion: if you divide the kinetic energy into three equal parts, you get the share that falls on each of the Cartesian directions. However, in addition to the translational components of motion, as is known from classical mechanics, there are also rotational components-hence the concept of rotational and translational ***degrees of freedom.***

Consider a lightly moving piston of mass *M* in a cylindrical vessel with an ideal gas (see Figure 1).
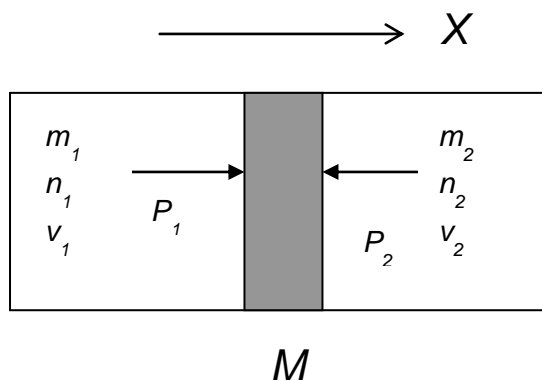

Figure 1 – Balance of the piston with mass *M* in a vessel with an ideal gas

For the mechanical equilibrium of the piston, it is necessary to meet the condition of equal pressure to the left and right of the piston $P1 = P2$ or, according to the basic equation of the MKT:

$$\frac{1}{3} n_1 \, m_1 \left\langle v_{\kappa\theta 1} \right\rangle^2 = \frac{1}{3} n_2 \, m_2 \left\langle v_{\kappa\theta 2} \right\rangle^2.$$

The equality of n concentrations in both parts of the vessel leads to the condition of equality of the average kinetic energies of the molecules on the left and on the right:

$$\left\langle \varepsilon_{k1} \right\rangle = \left\langle \varepsilon_{k1} \right\rangle.$$

In the system under consideration, the piston can move freely only in one direction – along the axis of the cylinder or the axis of the cylinder. In this situation, it is said that the piston has *one degree of freedom*.

For any particle of an ideal gas, taking into account the expressions (1) and (2), we can write:

$$p = \frac{2}{3} n \left\langle \frac{m v^2}{2} \right\rangle = nkT \Rightarrow$$

$$\left\langle E_k \right\rangle = \left\langle \frac{m v^2}{2} \right\rangle = \frac{3}{2} kT = \frac{m}{2} \left\langle v_x^2 + v_y^2 + v_z^2 \right\rangle \Rightarrow$$

$$\left\langle \frac{m v_x^2}{2} \right\rangle = \left\langle \frac{m v_y^2}{2} \right\rangle = \left\langle \frac{m v_z^2}{2} \right\rangle = \frac{1}{2} kT. \tag{3}$$

The obtained relation reflects the content *of the theorem on the uniform distribution of kinetic energy over degrees of freedom.*

The number of degrees of freedom – is the number of independent variables that determine the state of the system, or the number of independent variables ("coordinates") that completely determine the position of the system in space.

In the vast majority of problems, a monatomic gas molecule is considered as a material point, which is attributed to three degrees of freedom of translational motion ($i = 3$). In this case, the energy of the rotational motion can be ignored. However, in the general case – *a polyatomic gas* – it should be taken into account that the molecules can perform both translational and

rotational movements, in this case the number of degrees of freedom changes is taken into account as follows: $i = 3$ − for a monatomic gas, $i = 5$ − for a diatomic gas, and $i = 6$ − for a polyatomic gas (Figure 2).
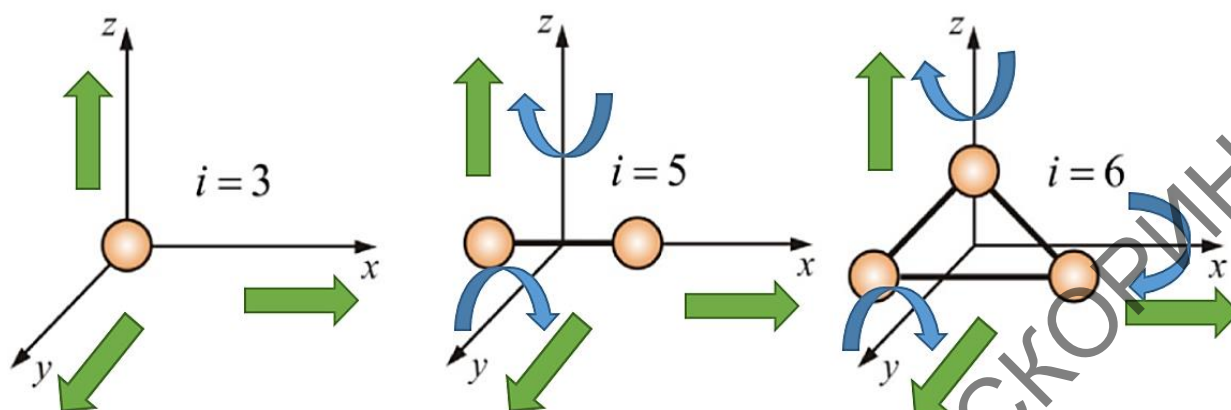

Figure 2 – Number of degrees of freedom of molecules

In classical mechanics, a diatomic gas molecule in the first approximation is considered as a set of two material points rigidly connected by a non-deformable bond. This system, in addition to the three degrees of freedom of translational motion, has two more degrees of freedom of rotational motion. Rotation around the third axis (the axis passing through both atoms) is meaningless. Thus, a diatomic gas has five degrees of freedom ($i = 5$).

A triatomic (generally polyatomic) nonlinear molecule has six degrees of freedom ($i = 6$): three translational and three rotational.

Naturally, there is no rigid bond between the atoms. Therefore, for real molecules, it is also necessary to take into account the degrees of freedom of oscillatory motion.

For a statistical system in a state of thermodynamic equilibrium, each translational and rotational degree of freedom has an average kinetic energy equal to $\dfrac{kT}{2}$, and each vibrational degree of freedom has an average energy equal to kT. The vibrational degree "has" twice as much energy because it accounts not only for kinetic energy (as in the case of translational and rotational movements), but also for potential energy, and the average values of the kinetic and potential energies are the same. Thus, the average energy of a molecule is:

$$\langle \varepsilon \rangle = \frac{i}{2} kT, \tag{4}$$

where $i = i_{\text{translational}} + i_{\text{rotational}} + 2 \cdot i_{\text{oscillatory}}$. We will adhere to the classical consideration, i.e., assume that molecules have a "rigid" bond between atoms; for them, i coincides with the number of degrees of freedom of the molecule.

For further discussion, we will take into account the fact that the piston (see Figure 1) also has a molecular structure. We can calculate the average kinetic energy of the translational motion of its molecules. The velocity of the center of mass can be determined from the expression:

$$u = \frac{1}{M}\sum_i m_i u_{ix}.$$

Then, squaring both parts of the expression and averaging the result over time, we get:

$$\left\langle \frac{Mu^2}{2} \right\rangle = \frac{1}{2M}\sum_i m_i^2 \left\langle u_{ix}^2 \right\rangle.$$

Let all mi be the same, and their number in the entire piston is equal to *N*. Then you can write:

$$\frac{M\left\langle u^2 \right\rangle}{2} = \frac{1}{2M}Nm_i^2\left\langle u_{ix}^2 \right\rangle = \frac{1}{2M}\frac{M}{m_i}m_i^2\left\langle u_{ix}^2 \right\rangle = \frac{m_i\left\langle u_{ix}^2 \right\rangle}{2}.$$

Therefore, using the expression (4), we get:

$$\frac{M\left\langle u^2 \right\rangle}{2} = \frac{m_i\left\langle u_{ix}^2 \right\rangle}{2} = \frac{m_0\left\langle v_x^2 \right\rangle}{2} = \frac{1}{2}kT. \tag{5}$$

The obtained ratio (5) shows that for the piston molecules, 1 degree of freedom also accounts for a fraction of the energy equal to $\frac{kT}{2}$. Therefore, this result is valid not only for rarefied gases, but also for relatively large particles that are in a state of thermodynamic equilibrium with a gas (or liquid in the general case). So, if instead of a piston, a body is placed in the gas so that it interacts with the gas from all sides. Such a body will be able to move freely in any direction and due to the mechanical interaction with the molecules, and its center of mass will make a random movement. Then, for the kinetic energy of such an object, we can write the expression:

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$$\frac{M\langle v^2 \rangle}{2} = \frac{1}{2M}\sum_i m_i^2 \langle v_i^2 \rangle = \frac{1}{M}\sum_i m_i \frac{m_i \langle v_i^2 \rangle}{2} = \frac{1}{M}\sum_i m_i \frac{3}{2}kT = \frac{M}{M}\frac{3}{2}kT = \frac{3}{2}kT. \quad (6)$$

From the obtained expression (6), the following conclusions can be drawn: the translational motion of the center of mass of a macroscopic body accounts for the same energy as the translational motion of a single molecule. At the same time, with an increase in the mass of the particle M, the average square of its velocity will be smaller. In other words, a macroscopic object behaves like a giant molecule. These conclusions allow us to consider the theory of random walk of a Brownian particle, known as the Einstein-Smoluchowski theory.

1.4 Einstein-Smolukhovsky theory

The most striking experimental confirmation of the ideas of the molecular-kinetic theory about the disordered motion of atoms and molecules is the Brownian motion. This is the thermal motion of the smallest microscopic particles suspended in a liquid or gas. It was discovered by the English botanist R. Brown (1827). Brownian particles move under the influence of random impacts of molecules. Due to the chaotic thermal motion of the molecules, these shocks never balance each other. As a result, the velocity of a Brownian particle randomly varies in modulus and direction, and its trajectory is a complex zigzag curve (Figure 3). The theory of Brownian motion was created by A. Einstein (1905). Experimentally, the theory of Einstein was confirmed in the experiments of the French physicist Jean Batist Perrin (1908–1911).
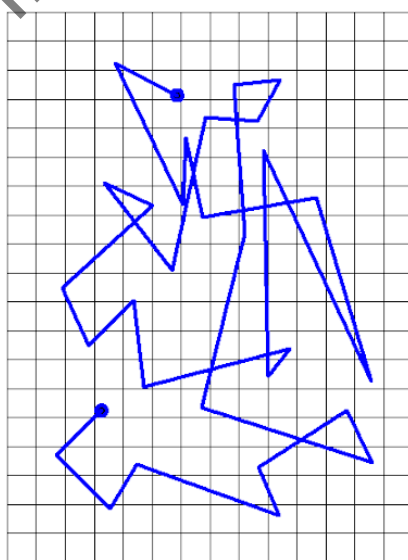
Figure 3 – Model of the trajectory of a Brownian particle

Since the Brownian particle continuously moves chaotically (shakes), it is necessary to choose an adequate parameter that can be calculated (predicted) theoretically. Since the instantaneous motion of a particle along any of the coordinates on the plane (*X* or *Y*) is equally probable, this means that the average displacement both in the projection on the *X*-axis and in the projection on the *Y*-axis for a sufficiently long period of time will be zero – this also applies to the average value of the projection of the particle velocity. Therefore, it is obviously necessary to choose a numerical measure of the trajectory that can be both experimentally observed and theoretically calculated. This value is ***the average square of the displacement*** of the Brownian particle $<x^2>$. In order to obtain the equation of motion of a mechanical particle, we use the basic equation of dynamics, which is a consequence of Newton's second law:

$$m\ddot{\vec{r}} = \vec{F} + \vec{F}_{mp} , \qquad (7)$$

where *r* – is the radius-vector of the Brownian particle, *m* is the mass of the particle, *F* is the resultant of the acting forces, F_{mp} is the force of resistance to motion (the force of viscous friction), which is proportional to the velocity *v* (*b* is the proportionality coefficient):

$$\vec{F}_{mp} = b\vec{v} = b\dot{\vec{r}}. \qquad (8)$$

In the projection on the selected axis, for example *X*, we get:

$$m\ddot{x} = F_x - b\dot{x}. \qquad (9)$$

To get the square of the displacement multiply both parts of the equation by *x*:

$$mx\ddot{x} = xF_x - bx\dot{x}. \qquad (10)$$

Using the differentiation rules, you can get:

$$\frac{d}{dt}x^2 = 2x\dot{x}, \qquad\qquad \frac{d^2}{dt^2}x^2 = 2\dot{x}^2 + 2x\ddot{x}.$$

Therefore:

$$x\dot{x} = \frac{1}{2}\frac{d\left(x^2\right)}{dt}, \qquad\qquad x\ddot{x} = \frac{1}{2}\frac{d^2\left(x^2\right)}{dt^2} - \left(\frac{dx}{dt}\right)^2.$$

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Let's use these relations, and rewrite the expression (10) in the following form:

$$\frac{m}{2}\frac{d^2(x^2)}{dt^2} - m\left(\frac{dx}{dt}\right)^2 = xF_x - \frac{b}{2}\frac{d}{dt}(x^2).$$ (11)

The resulting expression (11) is valid for any particle, and therefore it is also valid for the average values of the quantities included in it, if the averaging is carried out over a large number of particles. Averaging over a large number of particles allows you to write the following expression:

$$\frac{m}{2}\frac{d^2}{dt^2}<x^2> - m<v_x^2> = <xF_x> - \frac{b}{2}\frac{d}{dt}<x^2>$$

in this case, $<xFx> \equiv 0$, since it can be both positive and negative with equal probability. In addition, it follows from formula (3) that:

$$\left\langle \overline{\frac{dx}{dt}}^2 \right\rangle = \left\langle \frac{1}{3}\overline{v^2} \right\rangle$$

hence,

$$m\left\langle \overline{\frac{dx}{dt}}^2 \right\rangle = \frac{2}{3}\frac{m\left\langle \overline{v^2} \right\rangle}{2} = kT.$$

Then in the final form we can write:

$$\frac{m}{2}\frac{d^2\left\langle x^2 \right\rangle}{dt^2} - kT = \frac{b}{2}\frac{d\left\langle x^2 \right\rangle}{dt}.$$ (12)

The basic equation of the MKT considered by us is valid for any particles that do not interact with each other and perform chaotic movements. Whether these are molecules invisible to the eye or significantly larger Brownian particles containing billions of molecules, it does not matter. From the molecular-kinetic point of view, a Brownian particle can be interpreted as a giant molecule. Therefore, the expression for the average kinetic energy of such

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a particle should be the same as for a gas molecule. The velocities of brownian particles, of course, are incomparably smaller, corresponding to their greater mass.

However, in the form obtained (12), the equation is still not convenient for experimental confirmation. This equation can be integrated.

Denoting $\dfrac{d\langle x^2 \rangle}{dt} = Z$ we get:

$$\frac{m}{2}\frac{dZ}{dt} - kT = -\frac{b}{2}Z$$

or

$$\frac{dZ}{dt} = \frac{2}{m}\left(kT - \frac{b}{2}Z\right) = -\frac{b}{m}\left(Z - \frac{2kT}{b}\right)$$

Next, we separate the variables and integrate:

$$\int_0^Z \frac{dZ}{Z - \dfrac{2kT}{b}} = -\int_0^t \frac{b}{m}dt.$$

Applying the Newton-Leibniz formula and return to the replacement of Z.

$$\ln\left|Z - \frac{2kT}{b}\right|_0^Z = -\frac{b}{m}t\Big|_0^t,$$

$$\ln\left|Z - \frac{2kT}{b}\right| = \ln\left|-\frac{2kT}{b}\right| - \frac{b}{m}t,$$

$$Z - \frac{2kT}{b} = \frac{2kT}{b}e^{-\frac{b}{m}t},$$

$$Z = \frac{d}{dt}<x^2> = \frac{2kT}{b}\left(1 - e^{-\frac{b}{m}t}\right).$$

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Under normal experimental conditions, the value of $epx\left(\dfrac{-b \cdot t}{m}\right)$ is significantly less than "1", so in the final form, for finite time intervals, the desired value – the mean square of the displacement – can be represented as:

$$\frac{d}{dt}<x^2> = \frac{2kT}{b},$$

$$\Delta<x^2> = \frac{2kT}{b}\Delta t. \tag{13}$$

The average value of the square of the displacement of a Brownian particle over a time interval Δt along the X-axis, or any other axis, is proportional to this time interval:

$$\Delta<x^2> = 2D\Delta t. \tag{14}$$

The formula (14) allows us to calculate the average value of the square of displacements, and the average is taken for all the particles involved in the phenomenon. But this formula is also valid for the average value of the square of many successive displacements of a single particle over equal time intervals.

From an experimental point of view, it is more convenient to observe the movements of a single particle. Such observations were carried out by J. B. Perrin in 1909. Studying the motion of a Brownian particle, J. Perrin confirmed the independence of the MKT, and also determined the values of the Boltzmann and Avogadro constants.

2 MAXWELL AND BOLTZMANN STATISTICAL DISTRIBUTIONS

2.1 Necessary information from the theory of probability

One of the fundamental concepts of probability theory is the concept of an *event* or chance. An *event* in probability theory refers to any phenomenon in relation to which it makes sense to raise the question whether it can happen or not. An example of an event can be: the loss of the obverse or reverse when throwing a coin, the loss of a certain number of points when "throwing" a dice, the choice of a playing card from the deck, or the hit of a gas molecule in a certain volume of dV space, i.e., the presence of coordinate values lying in the range from x, y, z to $x + dx, y + dy, z + dz$.

An experience in which an event appears or does not appear is called a *test*.

An event is called random if it can either occur or not occur as a result of the test. Two random events are called *equally probable* if, for a sufficiently large number of trials, N, each event appears equally frequently. When a coin is tossed, the appearance of an obverse or reverse is equally likely, since both events occur approximately the same number of times during the trials. For example, the following outcome is possible: the number of tests $N = 100$, the number of appearances of the obverse and reverse, respectively, is 47 and 53 (or vice versa!). Strong deviations are possible, however, the greater the value of N, the less often they are implemented. These are the so-called *fluctuations* (from lat. *fluctuatio* – deviation from the mean).

Events like the coin experience are called *incompatible*, since the appearance of one precludes the appearance of the other.

The sum of two events is an event consisting of the occurrence of one event or the other, or both together. The sum of the two events A and B is symbolically denoted as $A + B$.

The product of two events is an event consisting of the simultaneous occurrence of both events. The product of events A and B is denoted as the product of the symbols of these events (AB).

The probability of a random event is a quantitative measure equal to the frequency of its occurrence in an unlimited number of tests N. For

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example, if an event with the sign A appears N_A times in N tests, the probability of this event is determined by the ratio:

$$P(A) = \lim_{N \to \infty} \frac{N_A}{N}. \tag{15}$$

Two events are called *independent* if the probability of each of these events occurring does not depend on whether the other event occurred. For example, if you draw cards from two different decks.

We give without proof two theorems from the theory of probability, which are necessary for understanding the further material.

Theorem 1. The probability of the sum of two *incompatible* events is equal to the sum of their probabilities:

$$P(A+B) = P(A) + P(B).$$

Theorem 2. The probability of the product of two *independent* events is equal to the product of their probabilities:

$$P(AB) = P(A) \cdot P(B).$$

2.2 Continuous and discrete random variables

If only incompatible events can be realized in the experiment (for example, only discrete numbers from 1 to 6 can fall on the dice, while the number of points "3" excludes all others), then the sum of the probabilities of all N *incompatible events* is equal to one:

$$\sum_{i=1}^{N} P_i = \sum_{i=1}^{N} \frac{N_i}{N} = 1. \tag{16}$$

We will use the relation (16) in the future and will call it ***the condition for normalizing the probabilities*** of p_i.

If the value of a random variable y_i takes a series of N different values, then, as is known, the average value $\langle y \rangle$ is determined by the formula:

$$\langle y \rangle = \frac{1}{N} \sum_{i=1}^{N} y_i. \tag{17}$$

If, in a series of N tests, each possible value of y_i (i = 1, 2, ..., n) is repeated N_i times, then the expression (17), taking into account (15), is converted to the ratio:

$$\langle y \rangle = \frac{1}{N} \sum_{i=1}^{N} y_i = \frac{1}{N} \sum_{i=1}^{N} y_i N_j = \sum_{j=1}^{n} \frac{N_j}{N} \cdot y_j = \sum_{j=1}^{n} p_j y_j. \qquad (18)$$

In statistics, the ratio (18) is called ***the mathematical expectation*** of a random variable y.

The relations (17) and (18) make sense if y is a discrete random variable. Consider the case when the value y is a continuous smooth function of the variable x in the range from a to b, as shown in Figure 4.
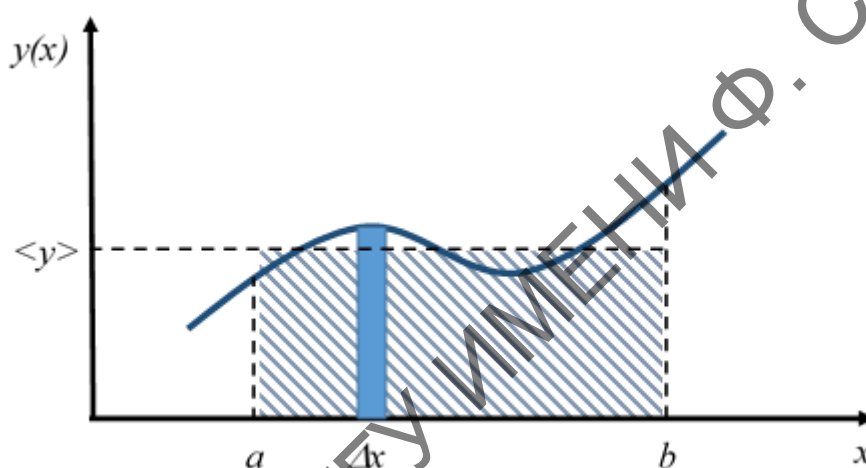

Figure 4 – Calculating the average value of a continuous random variable

If we divide the interval from a to b into N identical sufficiently small intervals Δx, the width of each interval will be equal to:

$$\Delta x = \frac{b-a}{N}.$$

This means that the average value of a continuous random variable y, by analogy with the formula (18), can be calculated using the ratio:

$$\langle y \rangle = \frac{1}{N} \sum_{i=1}^{N} y_i = \frac{1}{b-a} \sum_{i=1}^{N} y_i \cdot \Delta x.$$

Given $\Delta x \to 0$, we arrive at the average y as an integral of y with respect to dx:

$$\langle y \rangle = \frac{1}{b-a} \int\limits_a^b y(x)\,dx. \tag{19}$$

Equation (19) is true, if the variable y is uniformly distributed on the parameter x in the interval *(a; b)*, i. e. $\frac{dp}{dx} = \frac{1}{b-a}$, however, when considering discrete random variable most often the condition $\frac{dp}{dx} = f(x) \rightarrow dp = f(x)\,dx.$

The function $f(x)$ in the expression is called *the probability density* (*distribution function*) of a random variable x. The probability normalization and mathematical expectation will be calculated using certain integrals:

$$\lim_{N \to \infty} \sum_{i=1}^N \Delta P_i = \int\limits_a^b dp = \int\limits_a^b f(x)\,dx = 1, \tag{20}$$

$$\langle y \rangle = \lim_{n \to \infty} \sum_{i=1}^N y_i \Delta p_i = \int\limits_a^b y(x) f(x)\,dx.$$

For example, for $y(x) = x$ and $y(x) = x^2$, using the expressions (20), we find the average value of x and the root-mean-square value of x^2 of the random variable x.

$$\langle x \rangle = \int\limits_a^b x f(x)\,dx, \tag{21}$$

$$\langle x^2 \rangle = \int\limits_a^b x^2 f(x)\,dx.$$

2.3 Barometric formula. Boltzmann distribution

The chaotic motion of the molecules leads to the fact that the gas particles are evenly distributed over the volume of the vessel, so that each unit of volume contains on average the same number of particles. In the equilibrium state, the pressure and temperature of the gas are also the same throughout the entire volume.

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The presence of external forces leads to an "ordered" state of the ideal gas. A classic example: a gas (air) under the influence of gravity. If there were no thermal motion of the molecules, then all of them would "fall" to the earth under the influence of gravity, and all the air would gather in the thinnest layer at the surface of the planet. In the absence of gravity, the molecules would have scattered all over the world. The atmosphere, the air envelope of the Earth, owes its existence in its present form to the presence of both the thermal motion of the molecules and the force of attraction to the Earth.

According to this distribution of molecules, a certain *law of the change in gas pressure with height* is also established.

The air pressure at a certain height x (see Figure 5) is equal to the weight of the vertical column of air acting on a unit area. Therefore, dp is equal to the difference in the weights of the air columns over an area equal to one at heights x and $x + dx$, i. e., it is equal to the weight of the air column with a height of dx with a base area of one unit:

$$dp = -\rho g dx,$$

where p is the density of air (mass per unit volume) and g is the acceleration of gravity.
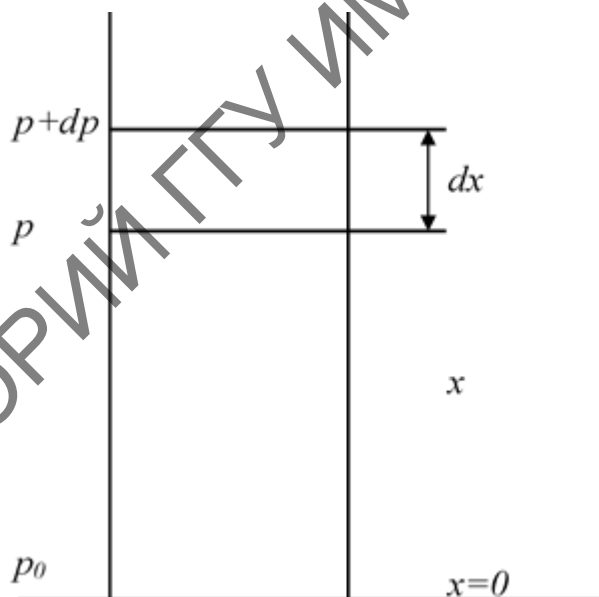

Figure 5 – Height distribution of gas pressure in the gravity field

The density p of a gas is equal to the product of the mass m_0 of the molecule by their concentration n:

$$\rho = m_0 n.$$

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Using the ratio $p = nkT$, we can write:

$$\rho = \frac{m_0 P}{kT} \quad \text{or} \quad dp = -\frac{m_0 g}{kT} p \, dx.$$

The resulting equation can be solved by the method of separation of variables:

$$\frac{dp}{p} = -\frac{m_0 g}{kT} dx,$$

$$\int \frac{dp}{p} = \int -\frac{mg}{kT} dx.$$

If we assume that the temperature at all altitudes is the same (which, generally speaking, is not true), then, integrating this equation, we get:

$$\ln p = -\frac{m_0 g}{kT} + \ln C,$$

where C is the integration constant. From here:

$$\rho(x) = Ce^{-\frac{m_0 g}{kT} x}. \tag{22}$$

The constant C is determined from the condition that at $x = 0$ the pressure $p = p_0$. Substituting these values x and p into equation (22), and replacing x with h (height), we get:

$$p(h) = p_0 e^{-\frac{m_0 g}{kT} h} = p_0 e^{-\frac{Mg}{kR} h}. \tag{23}$$

Equation (23), which establishes the law of decreasing pressure with height, is called the barometric formula. From this equation, it can be seen that the gas pressure decreases with height exponentially.

Since the gas pressure, as we saw earlier, is proportional to the number of molecules n per unit volume ($p = nkT$), the formula (23) also expresses the law of decreasing the concentration of molecules with height:

$$n = n_0 e^{-\frac{m_0 gh}{kT}}. \tag{24}$$

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The resulting barometric formula refers to the case when the gas is under the influence of gravity. The value of *mgh* in the formula (24) is the potential energy of the molecule at height *h*. The "behavior" of a gas will not change if some other potential force acts on it instead of gravity, and the expression for energy has a different form. If a gas is in a force field, so that its particles have some potential energy, then the number of particles with a given energy *U* is determined by the formula:

$$n = n_0 e^{-\frac{U}{kT}}. \tag{25}$$

Or as a relative concentration (probability):

$$\frac{n}{n_0} = e^{-\frac{U}{kT}}. \tag{26}$$

From the formula (26) it can be seen that the fraction $\frac{n}{n_0}$ of particles with a given energy *U*, in addition to the value of this energy itself, depends only on the temperature. This allows us to interpret the temperature itself as a value that determines how the particles are ***distributed*** in terms of energy.

At a constant temperature, the proportion of molecules with a particular energy *U* depends on the value of *U* and decreases rapidly with its growth. This means that the fraction of molecules with very high energy is always very small.

2.4 Maxwell distribution by velocity component

According to the molecular-kinetic theory, no matter how the velocities of molecules change during chaotic collisions, the average square velocity of molecules of mass m_0 in a gas in a state of equilibrium at a constant temperature remains constant and equal to:

$$\langle v_{\kappa \theta} \rangle = \sqrt{\frac{3kT}{m_0}}.$$

This is explained by the fact that in a gas *in a state of equilibrium*, a *certain stationary* (not changing with time) *distribution of molecules in terms of velocities is established*, which obeys a well-defined statistical law.

Maxwell's law is described by a certain function $f(v)$, called *the velocity distribution function* of molecules. If we divide the range of molecular velocities into small intervals equal to vv, then for each velocity interval there will be a certain number of molecules $dN(v)$ having a velocity enclosed in this interval. The function $f(v)$ determines the relative number of molecules $\dfrac{dN(v)}{N}$ whose velocities lie in the range from v to $v + dv$, i. e. $\dfrac{dN(v)}{N} = f(v)\,dv$, from which:

$$f(v) = \frac{dN(v)}{Ndv} = \frac{dn(v)}{ndv}. \tag{27}$$

When considering Maxwell's law of the velocity distribution of molecules, we assume:

– the gas consists of a very large number of identical particles (molecules);

– the molecules are in a state of disordered thermal motion at the same temperature;

– force fields do not affect the gas (there is no preferential direction in the system).

However, you can use the known distribution of molecules in the force field (24)–(26) to"sort" the molecules by velocity.

Consider molecules with velocities in the dv_z range, located in an infinitely thin (thickness dz) gas layer at height z. The volume of this layer coincides with dz (if the cross-sectional area of the gas column in the direction perpendicular to z is $1\,\text{m}^2$), so the number of molecules under consideration is $n(z)f(v_z)\,dv_z dz$, where $n(z)$ is the density (concentration) of the gas at height z. For any constant number of these molecules in two adjacent layers, the equation holds:

$$n(z)f(v_z)dv_z dz = \left(z^*\right)f\left(v_z^*\right)dv^* dz^*. \tag{28}$$

When moving in the gravity field, the horizontal components of the velocity (v_x, v_y) do not change, and the change in v_z is determined by the law of conservation of energy:

$$mgz + \frac{m\nu_z^2}{2} = mgz^* + \frac{m\nu_z^{*2}}{2}. \tag{29}$$

Differentiating equality (29) for the given constant values of z and z^*, we obtain the relation:

$$\nu_z d\nu_z = \nu_z^* d\nu_z^*. \tag{30}$$

connecting the intervals dv_z and dv^*_z, which contain the vertical velocities of the molecules under consideration at altitudes z and z^*. The thicknesses of the layers dz and dz^* from the condition of invariance of the time of motion of the particle are related to each other by the relation:

$$\frac{dz}{\nu_z} = \frac{dz^*}{\nu_z^*}. \tag{31}$$

Multiplying the relations (30) and (31), we get $dv_z\, dz = dv^*_z\, dz^*$, which means that: $n(z)\, f(v_z) = n(z^*)\, f(v^*_z)$. Then, using the Boltzmann distribution in the gravity field (24) for $n(z)$, we obtain:

$$f\left(\nu_z\right) = f\left(\nu_z^*\right) e^{-\frac{m_0 g\left(z - z^*\right)}{kT}}. \tag{32}$$

Given (29) we get:

$$f\left(\nu_z\right) e^{\frac{m_0 \nu_z^2}{kT}} = f\left(\nu_z^*\right) e^{\frac{m_0 \nu^{*2}_z}{kT}}. \tag{33}$$

So the product (33) is a constant independent of v_z, i. e. the desired distribution function has the form:

$$f\left(\nu_z\right) = A e^{-\frac{m_0 \nu_z^2}{2kT}}, \tag{34}$$

$$\frac{dn}{n} = A e^{-\frac{m_0 \nu_z^2}{2kT}} d\nu_z.$$

The constant A can be obtained from the normalization condition (20):

$$\int\limits_{-\infty}^{\infty} \frac{dn}{n} = A \int\limits_{-\infty}^{\infty} e^{-\frac{m_0 v_z^2}{2kT}} \, dv_z = 1.$$

Means:

$$A = \left(\int\limits_{-\infty}^{\infty} e^{-\frac{m_0 v_z^2}{2kT}} \, dv_z \right)^{-1}.$$

When integrating, we use the well-known relation (Poisson integral), $\int\limits_{-\infty}^{\infty} e^{-x^2} \, dx = \sqrt{\pi}$ thus: $A = \left(\dfrac{m_0}{2\pi kT} \right)^{\frac{1}{2}}$. Then the expression for the velocity projection distribution function v_z takes the form :

$$f(v_z) = \frac{dn}{n \cdot dv_z} = \frac{1}{\sqrt{\pi}} \left(\frac{m_0}{2kT} \right)^{\frac{1}{2}} e^{-\frac{m_0 v_z^2}{2kT}}. \tag{35}$$

The general view of the distribution function (35) is shown in Figure 6.
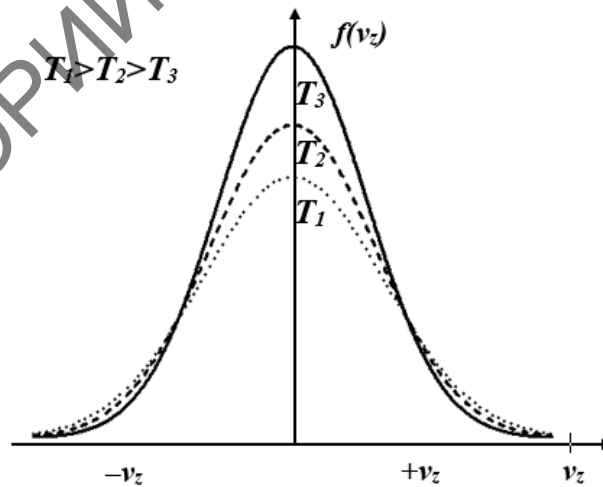

Figure 6 – Maxwell distribution over the velocity component

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The function of the distribution of molecules by the velocity components (35) was obtained by considering a gas in the field of gravity. This does not mean that the type of distribution of molecules in the velocity components is somehow related to the action of gravity, or that it is gravity that creates this distribution. As already mentioned, the barometric formula (24), which we used in the derivation, is itself a consequence of the distribution of molecules in terms of velocities.

2.5 Maxwell's distribution over the velocity modulus and its consequences

The expression (35) obtained for the projection (component) The speed of the z direction is equally valid for the components x and y. Means:

$$\frac{dn}{ndv_z} = Ae^{-\frac{m_0 v_z^2}{2kT}}, \qquad \frac{dn}{ndv_x} = Ae^{-\frac{m_0 v_x^2}{2kT}},$$

$$\frac{dn}{ndv_y} = Ae^{-\frac{m_0 v_y^2}{2kT}}. \tag{36}$$

Now we can also find the probability that the projection of the velocity of the molecule is simultaneously located in three small intervals corresponding to each of the Cartesian directions. In view of chaotic motion, the values of the velocity components for each of the coordinate axes do not depend on the values of the components for the other axes. Therefore, the probability that the velocity of a molecule simultaneously satisfies the three specified conditions is the probability of the product of independent events (Theorem 2).

Let us dn_{xyz} the number of molecules in the unit of the "volume" of the gas velocities whose components on the coordinate axes lie within the limits specified above, then, given that, $v^2 = v_x^2 + v_y^2 + v_z^2$ we can write:

$$\frac{dn_{xyz}}{n} = A^3 e^{-\frac{m_0 v^2}{2kT}} dv_x dv_y dv_z. \tag{37}$$

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The formula (37) can be given a clear graphical interpretation, as shown in Figure 7.
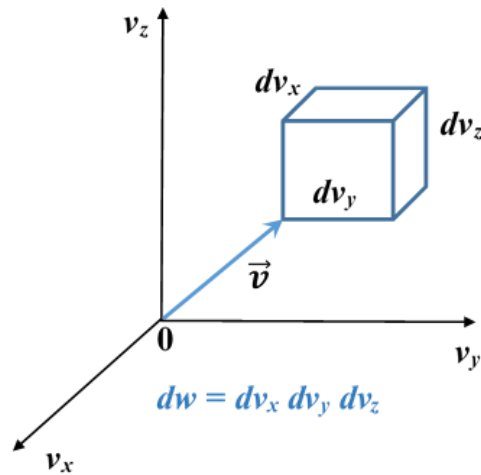

Figure 7 – Is an elementary "volume" in the "space" of velocities

Using the relations (35) and (37), we can obtain the value:

$$\frac{dn_{xyz}}{dw} = n\left(\frac{m_0}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{m_0 v^2}{2kT}} , \qquad (38)$$

which does not depend on the direction of the velocity vector. So if we collect all the molecules of a unit volume of gas whose velocities are enclosed in the range from v to $v + dv$ in all directions, they will be evenly distributed in a spherical layer with a thickness of dv and a radius of v, as shown in Figure 8.
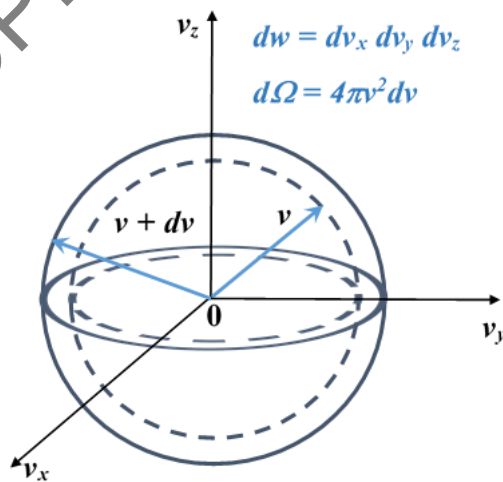

Figure 8 – Ball layer in the "space" of velocities

The number of molecules in the entire layer is the number of molecules per unit volume of the gas, whose velocities lie in the range from v to $v + dv$.

$$dn = n\left(\frac{m_0}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{m_0 v^2}{2kT}} d\Omega.$$

So the desired distribution function:

$$f(v) = \frac{dn}{ndv} = \frac{4}{\sqrt{\pi}}\left(\frac{m_0}{2kT}\right)^{\frac{3}{2}} v^2 e^{-\frac{m_0 v^2}{2kT}} dv. \qquad (39)$$

Formula (39) expresses ***Maxwell's law of the velocity distribution of molecules***. It determines the fraction of molecules of a unit volume of a gas whose velocities are enclosed in a velocity interval equal to dv, which includes this velocity. A general view of the distribution function is shown in Figure 9.
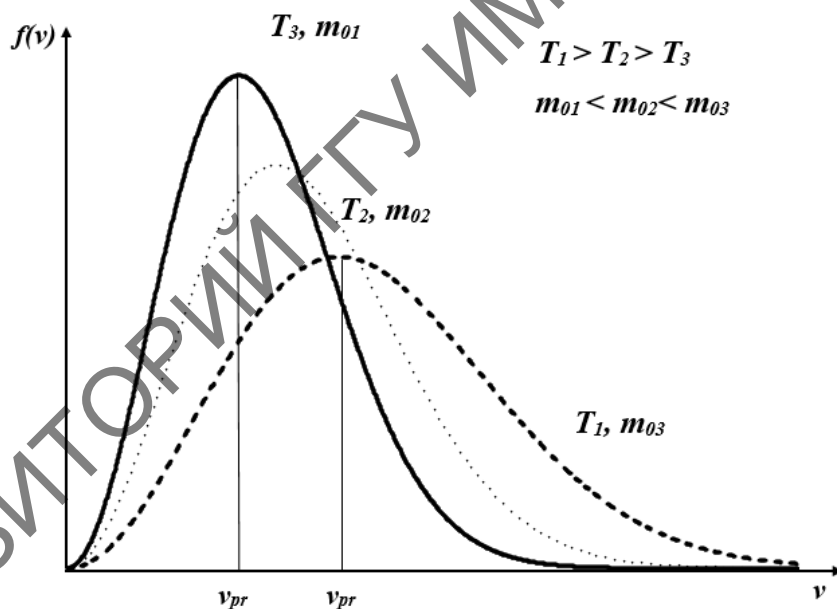

Figure 9 – A general view of the Maxwell distribution function with respect to the velocity modulus

It vanishes at $v = 0$ and at $v \to \infty$: there are no fixed molecules in a gas and no molecules with infinitely high velocities (although the formal limit is the speed of light in a vacuum). As can be seen from Figure 9, the

distribution function has a maximum at a certain value of the velocity v_{pr}. This means that the largest fraction of all gas molecules moves at velocities close to v_{pr}. We can also say that the velocities close to v_{pr}. Ae more common in gas molecules than others, and that the probability that the velocity of the molecule is close to v_{pr} is the greatest. Therefore, the velocity v, which corresponds to the maximum of the Maxwell distribution curve, is called *the most probable velocity*.

As the temperature increases, the velocities of the molecules increase on average, so that the entire curve shifts towards higher velocities. But, the areas bounded by the curves and the velocity axis remain unchanged, as follows from the normalization condition (20). As a result, the maximum of the curve decreases as the temperature increases.

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Производственно-практическое издание

Шершнев Евгений Борисович,
Купо Александр Николаевич,
Лукашевич Светлана Анатольевна

ОСНОВЫ
МОЛЕКУЛЯРНО-КИНЕТИЧЕСКОЙ ТЕОРИИ

Практическое пособие

В авторской редакции