

## Realization of Equilibrium Distributions of Molecules in Gases

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**Abstract:** It is shown that all possible distributions of molecules of an ideal gas with zero dimensions of monatomic molecules that collide elastically with each other are in equilibrium, and with nonzero dimensions an equilibrium universal distribution of the gas molecules along the velocities and angular momentum must arise. In a real gas in an isolated system, due to dissipation, evolution goes simultaneously toward the universal distribution and toward the occurrence of an equal-velocity distribution, and also towards the degradation of the gas due to the decrease of the molecular velocities to zero values. In a non-isolated system, the real gas has a distribution close to the Maxwell distribution.

**Keywords:** Maxwell Distribution, Equal-Velocity Distribution, Universal Distribution, Ideal Gas, Ultimate Gas, Real Gas.

### 1. Introduction

In the nineteenth century, most physicists believed that molecules of a gas in equilibrium move at the same speed, but in arbitrary directions. The mistake was that, in their opinion, the surrounding gas was equilibrium. In 1859, Maxwell first showed in [1] that gas molecules in thermal equilibrium are not uniformly distributed over their velocities, but according to the law of Gauss errors [2], which, as applied to statistical mechanics, is called the "Maxwell distribution". The derivation of the distribution is based on the formulation and solution of the corresponding functional equation [1-5]. In 1872 Ludwig Boltzmann proposed an equation for describing the evolution of a one-particle distribution function of an ideal gas [6, 7], whose solution also gave a similar distribution [8-10]. For this reason, this distribution is also called the Maxwell-Boltzmann distribution.

After the publication of the above-mentioned works of Maxwell and Boltzmann [1, 6] in the scientific papers of different authors, it was directly asserted that this distribution is the only stable distribution, and therefore it is unique and equilibrium. The existence of a unique distribution, to which all other distributions tend over time, has not been proven for a long time and has been the subject of discussion for a long time [2]. To prove the truth of the Maxwell distribution as early as 1920 by Stern and Gerlach, in 1929, Lambert and later by other researchers was conducted experimental verification of the law of Maxwell distribution. The obtained experimental dependences of the distribution coincide with the theoretical ones [4, 5], which should confirm the equilibrium nature of the Maxwell distribution. However, no theoretical justification of the equilibrium of this distribution has been made. At the same time, the above mentioned experimental data, equally to confirm not only the equilibrium, but the Maxwell distribution stationarity. This difference is crucial, because it is from the equilibrium qualification depends not only many of the technologies and statistical physics theory but also cosmology, philosophy and other sciences. Modern studies in the field of equilibrium and nonequilibrium states determined by stationary and non-stationary solutions of the Bogolyubov equations for a sequence of distribution functions are carried out on the basis of the thermodynamic limit procedure for nonequilibrium states [11]. At the same time, the limit itself, based on the concept of entropy, seems doubtful, since entropy, according to the arguments of [12], is not a measure of disorder. In other works, the problems of the distribution of the mean free paths of molecules [13, 14], statistical structures, the interaction of distribution functions with electrodynamics and geometries [15], the confrontation of the rules of behavior prescribed by a thermostat for each microstate separately, and the properties of the system itself are determined its response to the requirements of the thermostat [16]. Essential for determining the distribution functions is that they are based on the "possibility" of such a distribution, and not what it really is. Reality must be deduced from the

limitation of such initial possibilities. These limitations should be prompted by experience. As a rule, all definitions for distribution functions do not impose any restrictions on the number of particles in the system under consideration. Distribution functions assume some conditions that ensure the fact of their existence. The number of particles in the system can be completely arbitrary, in particular, it can be equal to unity [15]. The distribution, as applied to one molecule, is understood as the distribution of the possible states of this molecule over time [9]. In this connection, the meaning of the concept of "temperature of a molecule" appeared, as an extrapolation of the concept of "temperature" with a decrease in the number of molecules to one molecule [17, 18]. As a result of this approach, the meaning of the distribution of gas molecules over their temperatures has appeared [19, 20].

### The purpose of this work was:

1. Using the analysis of the mechanism of collisions of molecules in ideal and real gases, find out the equilibrium or stationarity of the possible distributions of molecules in such gases.
2. Show that the functional equations of Maxwell and Boltzmann have not one but two solutions: one solution corresponds to the Maxwell distribution, and the other to the distribution of equal molecular velocities.
3. To justify the need to introduce the meaning and concept of "extremely ideal gas", all possible distributions of the molecules of such a gas are equilibrium, and therefore the entropy of such a gas does not increase with time.
4. Show that in an ideal gas, the molecules of which have nonzero sizes, it is assumed that a universal distribution of molecules will be observed, both in velocity and in angular momentum, which will also be equilibrium.
5. Show that in a real gas, due to dissipation associated with a change in the angular momentum of molecules during collisions, evolution goes towards a universal distribution, and due to dissipation due to overcoming the resistance of the medium, it leads to gas degradation.

The scope of the results of this work, in addition to their purely theoretical significance for the general theory of gases, is the use of real distributions, not necessarily equilibrium, in the chemistry of gas-solid-phase processes, when the kinetics and chemical composition of the products of such reactions depend on the distribution of molecules of the surrounding gas environment [20, 21].

## 2. Search for equilibrium distributions

In all the conclusions of Maxwell's distribution described in the literature, both methods similar to the Maxwell method and the Boltzmann equation ignored the second solution of the corresponding functional equations. Consider the version of Maxwell's method described in the monograph [5]. It is based on the fact that the establishment of molecular equilibrium is due to the existence of an interaction between molecules. In collisions between molecules, their directions of motion change continuously, and a chaotic motion is established in the gas with a uniform velocity distribution along the directions in space. But along with the change in the direction of the flight, there is also a change in the velocities of the molecules in absolute magnitude. In the opinion of [5], if at the initial instant of time all molecules had identical velocities, then disorderly collisions between them would lead to the fact that some of the molecules would accidentally receive excess kinetic energy at the expense of other molecules, correspondingly losing some of the energy. Because of this, the equality of the velocities of the gas molecules breaks down and a certain part of the molecules appears in the gas, having larger and smaller velocities corresponding to the Maxwell distribution. After simple reasoning, the functional equation [5] is obtained for a stationary state (which will subsequently be considered as an equilibrium state):

$$n(v_1^2)n(v_2^2) = n(v_3^2)n(v_4^2), \quad (1)$$

where  $n(v_1)$ ,  $n(v_2)$ ,  $n(v_3)$ ,  $n(v_4)$  — number of molecules in which the molecular velocities per unit of time vary from  $v_1$ ,  $v_2$  values to  $v_3$ ,  $v_4$  values. This number is equal to the number of molecules in

which the velocities vary from  $v_3, v_4$  to  $v_1, v_2$ , respectively. Since in the process of collision the energy of the molecules is conserved, for the direct and inverse processes one can write down the energy conservation law (the factor  $m/2$  is omitted):

$$v_1^2 + v_2^2 = v_3^2 + v_4^2 \quad (2)$$

Expressing  $v_4$  by means  $v_1, v_2, v_3$  of (2), we rewrite (1) in the form

$$n(v_1^2)n(v_2^2) = n(v_3^2)n(v_1^2 + v_2^2 - v_3^2) \quad (3)$$

After logarithmizing (3) and differentiating the resulting equality with respect to the arguments  $v_1^2$  и  $v_2^2$  (taking into account their independence), we have

$$\frac{dn(v_1^2)}{n(v_1^2)dv_1^2} = \frac{dn(v_1^2 + v_2^2 - v_3^2)}{n(v_1^2 + v_2^2 - v_3^2)d(v_1^2 + v_2^2 - v_3^2)} \quad (4)$$

$$\frac{dn(v_2^2)}{n(v_2^2)dv_2^2} = \frac{dn(v_1^2 + v_2^2 - v_3^2)}{n(v_1^2 + v_2^2 - v_3^2)d(v_1^2 + v_2^2 - v_3^2)} \quad (5)$$

Comparing equations (4) and (5), we obtain

$$\frac{dn(v_1^2)}{n(v_1^2)dv_1^2} = \frac{dn(v_2^2)}{n(v_2^2)dv_2^2}, \quad (6)$$

Taking into account the independence of the velocities, the solution of the functional equation (6) is possible under the condition that the left and right sides of equation (6) are equal to some constant value  $\alpha$ , the value of which is found from the normalization conditions. Further arguments lead to the Maxwell distribution formula. But from the form of equation (6) it is easy to see that when the velocities are equal

$$v_1 = v_2 = v_i, \quad (7)$$

where  $v_i$  — the velocity of any other gas molecule, the functional equation is also satisfied. It follows from this that the solution (7), corresponding to the equal-velocity distribution of the molecules, is the second solution of the initial equation (1), which determines the stationarity (or equilibrium) of the state of the system.

The situation is similar in the derivation of the Maxwell distribution from the Boltzmann kinetic equation [8]. Assuming that the equilibrium distribution of particles in space is homogeneous for time-independent distributions, the Boltzmann equation has the form [10]:

$$0 = \left( \frac{\partial f_a}{\partial t} \right)_{st} = \sum_b I_{ab} [f_a, f_b] = \sum_b \int d\mathbf{p}_b v_{ab} d\sigma_{ab} \{f'_a f'_b - f_a f_b\}, \quad (8)$$

where the functional that determines the change in the number of particles of type  $a$  due  $a$  to collisions with particles of sort  $b$  (including due to collisions of particles of one kind) is the collision integral; the indices  $a$  and  $b$  characterize two colliding particles;  $\mathbf{p}_b$  — momentum of particle  $b$  before collision;  $v_{ab} d\sigma_{ab}$  — the number of scattered particles divided by the number of dissipated particles in a unit volume of gas;

$f'_a, f'_b, f_a, f_b$  — of the distribution of particles of type  $a$  and  $b$  before and after the collision. This equation will be satisfied if

$$f'_a f'_b = f_a f_b \quad (9)$$

The solution of this functional equation for  $f_a \neq f'_a; f_b \neq f'_b$ , respectively, leads to the Maxwell distribution [10]. The trivial solution for  $f_a = f_b = f'_a = f'_b$  is not considered and is not discussed. Namely, this solution corresponds to an equal-rate distribution. Thus, there are at least two formally equilibrium distributions of gas molecules.

The Boltzmann  $H(t)$  function, taken with the opposite sign, represents the entropy  $S$  of a unit volume of the nonequilibrium state of the gas [8, 10]:

$$S = -H(t) = -\sum_a \int d\mathbf{p}_a f_a(\mathbf{p}_a, t) \ln f_a(\mathbf{p}_a, t) \quad (10)$$

From the Boltzmann  $H$ -theorem it follows that

$$\frac{dH}{dt} \leq 0; \quad \frac{dS}{dt} \geq 0 \quad (11)$$

Thus, the Boltzmann kinetic equation allowed us to conclude that in the nonequilibrium state the entropy of the gas increases with increasing time. Since the entropy is maximal in the state of thermodynamic equilibrium, the relations (11) mean that as the time increases, the nonequilibrium state of the gas relaxes, approaching the equilibrium state. But the question arises: to what equilibrium state: to Maxwell's distribution or to an equal-speed state?

### 3. Ideal gas

The derivation of formulas (10, 11) was based on [3, 8, 10] on the tacit assumption that spontaneous fluctuations are possible in the gas, and it is they that release the gas for a short time from the equilibrium state to the nonequilibrium state, after which the corresponding relaxation occurs. Also, by default, it is assumed that the mechanism of occurrence of these fluctuations consists in collisions of gas molecules with each other [5]. However, for an ideal gas in which particles represented as solid balls (or balls with a hard core) absolutely colliding with each other and with the walls of the vessel, as it turned out, such assumptions are not satisfied.

According to [23], modern physics offers an ideal gas model in which the volumes are zero and claims that this does not affect anything, and calculations will be much easier. Indeed, since in the derivation of the basic laws of an ideal gas the dimensions of the molecules are not taken into account in any way, and in the case of even real gases the total volume of molecules calculated from their effective dimensions is much less than the volume of the vessel in which this gas is located, then the molecules of an ideal gas just material points [24]. The upper limit of the dimensions of the molecules of an ideal gas, according to [7], corresponds in order of magnitude to nitrogen at normal pressure and room temperature [25].

From the point of view of statistical mechanics, if molecules move chaotically in space, the probability of collision is proportional to their dimensions and decreases with decreasing radius, becoming zero for zero particle sizes. But from the point of view of classical mechanics this is not so if one considers not the general chaotic motion of molecules, but the motion of a particular pair of colliding molecules. Then, for example, if two molecules move towards each other in a strictly straight line, if nothing external to these molecules interferes with this movement, then a head-on collision is inevitable, and the probability of it is unity, regardless of the size of these molecules. And, therefore, the probability of a head-on collision is equal to

unity for particles of zero radius. The same can be said if the molecular trajectories intersect at any other angle different from  $180^{\circ}$ . And since the limit of "arbitrarily small dimensions" of molecules is zero size, a gas consisting of molecules of zero size is also ideal. You can even give it a separate name, "Ultimate Ideal Gas" (UIG).

In work [25], calculations of pair and many-particle elastic collisions for a one-atom limit-ideal gas were carried out. The results showed that in an isolated system, any evolution of the distribution of gas molecules at their velocities of such a gas is impossible: the process of elastic collisions is cyclical. After a series of collisions, the distribution of gas molecules, after passing through a series of intermediate states, returns to the initial distribution, regardless of what it was. The entropy of such a gas does not change with time. In a non-isolated system, it is possible to get into the system of extraneous molecules of the same UIG (or escape from it). In this case a new distribution of molecules arises and for some time until new molecules have entered the system (or left it), this new distribution will exist, but it will not evolve. From what has been said, an important conclusion follows: all possible distributions of the molecules of the ultimate ideal gas are in equilibrium.

The question of the equilibrium of the distribution of an ideal gas, whose molecules are monatomic, spherical and have nonzero dimensions, remains open. In the case of elastic collisions of such molecules in the case when the center of one molecule enters the periphery of the other, their rotation may occur. By virtue of the law of conservation of momentum and the elasticity of molecules, a series of collisions can also lead to a cyclic return through a certain number of collisions to the initial state. But the appearance or change in the speed of rotation of the colliding molecules will occur, obviously, due to a change in their kinetic energy, and, consequently, the speed of their movement. In this case, even a collision of molecules with identical velocities will lead to the fact that the velocities of the molecules after the collision will become different. As a result, an equilibrium state should arise in which the distribution of gas molecules will be observed, simultaneously, both in terms of velocities and in the moments of the pulse. We call this distribution a "universal distribution". If we single out only the velocity distribution from it, then, perhaps, it will be the Maxwell distribution. But such calculations have not yet been carried out by anybody, therefore, an important priority in this field is the derivation of the formula for the universal distribution of gas molecules by their velocities and angular momentum.

#### 4. Real gas

In a real gas, energy dissipation always occurs during each collision of molecules. For binary collisions, the dissipation is determined by the Newton's recovery coefficient [26, 27]:

$$k = \frac{|w_1 - w_2|}{|v_1 - v_2|} = -\frac{w_1 - w_2}{v_1 - v_2} \quad (12)$$

This result follows from the fact that before the impact must be  $v_1 > v_2$  (otherwise the impact will not occur), and after impact the velocities of the molecules will be due  $w_2 \geq w_1$  to the impermeability of the bodies. After an absolutely inelastic impact ( $k = 0$ ), and for an elastic collision ( $k = 1$ ), the colliding molecules move with the same velocity. In an isolated system, dissipation can occur for two fundamentally different reasons. The first reason (dissipation of the first kind) is associated with the act of collision of molecules, when the colliding molecules acquire momentum moments due to the kinetic energy of these molecules. Evolution of the state of a real gas due to only dissipation of the first kind will obviously be the same as for an ideal gas, i.e. a universal distribution of molecules along the velocities and moments of their momenta should arise. However, in a real gas there is also a dissipation of the second kind, which is not connected with the act of collision of molecules. It is determined by overcoming the resistance of electromagnetic and other fields, the viscosity of the medium (water, air, vacuum, etc.), in which the collision occurs.

If only the dissipation of the second kind acted, then in real gas at the molecular velocity, with time, as can be seen from equation (12), they will equalize on one side, and on the other hand decrease to zero values. Therefore, the action of dissipation of the second kind leads to a degradation of the gas. The simultaneous action of both dissipations in an isolated system will naturally lead to a universal distribution, which eventually degrades to an Absolute distribution in which all velocities and moments of the molecular momenta (if quantum effects are not taken into account) will have zero values.

In a non-isolated system, in addition to the processes taking place in an isolated system, external factors (weather change, man-made emissions, natural disasters, etc.) cause fluctuations in the gaseous medium that cancel out the degenerative phenomena occurring in it. To some extent, external factors should also be attributed to virtual processes occurring in a vacuum and leading to possible real effects on molecules. As a result, there is a stationary state in which a distribution close to the Maxwell distribution is observed for the molecular velocities, but exactly unequal to it, since the influence of external factors depends on many random causes, depending on time and location.

## 5. Conclusions

1. The analysis of the mechanism of collisions of molecules in ideal and real gases. The equilibrium or stationarity of the possible distributions of molecules in such gases is clarified.
2. It is shown that Maxwell's and Boltzmann's functional equations have two solutions: one solution corresponds to Maxwell's distribution, and the other to the distribution of equal velocities of molecules.
3. It was found that all possible distributions of the molecules of an extremely ideal gas (gas with zero molecular sizes, elastically colliding with each other) are equilibrium. The entropy of such a gas does not increase over time.
4. An assumption has been made that in an ideal gas, the molecules of which have nonzero dimensions, a universal distribution of molecules will be observed, both in velocity and in angular momentum, which will also be equilibrium. If we single out only the velocity distribution from it, then perhaps it will be the Maxwell distribution.
5. It is shown that in a real gas in an isolated system, due to the first kind of dissipation, associated with a change in the angular momentum of the molecules during the collision, evolution goes towards the universal distribution, and due to the second kind of dissipation (overcoming the resistance of the medium), the velocities of the gas molecules are equalized and reducing these speeds to zero values, i.e. to gas degradation.
6. In a non-isolated system, the real gas has a distribution close to the Maxwell distribution.
7. The problem is to find a formula for the universal equilibrium distribution of gas molecules according to their velocities and angular momentum.

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