

HEAT, TEMPERATURE, ENTROPY

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Abstract. The history of such notions as heat, temperature, and entropy is considered. The notions were created and evolved both with technique's requirements and during the advancement of heat science. Some examples from different fields of mathematics which had a great impact on the notion evolution are given. The deduction of Maxwell and Boltzmann distributions is fully considered. The tragedy of pioneers, who worked in this field, is also discussed.

1. Notions and theories

According to present views [1], all the sciences are based on definite notions. A notion is a concept which obtained its name, for example, space, time, energy, mass, wave, particle etc. Certain of notions give a more precise definition to objects or phenomena which one observes, but most notions are beyond the reach of look-outs. Sometimes the notions are well-defined but, as a rule, the fundamental notions of science give only a vague idea of something. This is a circumstance worthy of being noted.

In the Middle Ages the science has the name scholasticism. Scholastics attached great importance to general notions (in Latin – *universalis*) [2]. Some of them, realists (from *realis* – real), reasoned that the reality of notions depends on a degree of generalization. The higher is the degree, the greater is their objective reality and the less they depend on intelligence. Therefore the general notions exist independently of partial objects and they were even at that time when the objects did not exist. Their opponents, nominalists (from *nomen* – name), gave their view on the problem in the following manner. The general notions do not exist in reality but they are only the names of similar things, so the general is only a consequence of unit things. According to moderate nominalism – known also under the name conceptualism (from *conceptus* – thought, idea) – the general notions exist, but they exist in consciousness.

Not going further to the heart of the matter, we may say that the notions, whatever origin they have, are very important for science. Nobel Prize winner in physics (1937) George Pudget Thomson (1892–1975) claimed that the notions are more fundamental than theories, because the theories are formulated in the terms of notions. Usually a physical theory is an assertion, as a rule in a mathematical form, on the relation between notions [1]. With the passage of time, the sense of notions is changing, especially it is noticeably in a language, but a notion name is more conservative and in most cases remains. At the same time, the notions enlarge their sphere of application; the notions of one science penetrate into other sciences where they also can change their sense.

Among the fundamental notions are heat, temperature and entropy. The first two are more accurate definitions of common notions; the third one is a very complex notion. The simplest and best understood definitions, one can find, as a rule, in handbooks and dictionaries. At that,

it is necessary to pay attention to the origin of a notion, especially to what the notion means in the language from which it was incorporated into science. It helps to understand better the sense of a notion. However, even textbooks are unable once too often to give a person clear and unambiguous comprehension of a notion. This is especially true in regards to temperature and entropy in physics. Here students, and not only students, have difficulties trying to understand their meaning.

In this paper we consider the evolution of these notions, which sense is constantly varying as physics develops.

2. Temperature and heat

Definitions. In the Russian Dictionary of Foreign Words [2] one can find such definition. Temperature [*< lat. *temperatura* – state*] – the degree of heating a body (or its thermal state) measured with the help of a special instrument, *thermometer*. In the Longman Dictionary of English Language and Culture [3], there is the same definition. Temperature – the degree of heat and coldness of a place, object, etc. In the Russian Physical Handbook [4], there are two definitions: the physical quantity characterizing the degree of heating a body is named a temperature; the absolute temperature is the measure of an average kinetic energy of ideal gas molecules in forward movement. The Russian Encyclopedic Dictionary [5] gives such definition: temperature [from lat. *temperatura* – appropriate mixture], it is the physical quantity characterizing the state of thermodynamic equilibrium of a system.

In the Russian Physical Encyclopedic Dictionary [6] we read: “Temperature [from lat. *temperatura* – appropriate mixture, normal state] – the physical quantity characterizing the state of thermodynamic equilibrium of a macroscopic system. Then the Dictionary gives examples what properties of physical systems are defined by a temperature. At the end, there is the following definition: “Temperature is defined as the derivative of body energy as a whole with respect to entropy.” Apparently this definition is taken from the well-known Course of Theoretical Physics by Landau and Lifshits [7] where the authors said the following: “The quantity inverse to the derivative of body entropy with respect to energy is named the absolute temperature.”

In many books on statistical physics and statistical mechanics, there are no definition of temperature and heat at all. The rare exceptions are, e.g. [7–9]. In [7, 8] macroscopic quantities are divided into two classes: mechanical and thermal (thermodynamic). The latter appear as a result of statistical regularities and have no sense if to apply them to non-macroscopic systems. At that, the temperature is said as the notion that characterizes not so much behavior of a molecule or a small group of molecules as the state of a macroscopic system as a whole. In [9] the temperature is introduced as the measure of thermal motion intensity in bodies surrounding a system considered.

We see the following:

- Common consent is observed when the temperature is thought as the commonplace degree of heat and coldness of a place, object, etc.
- As for the word origin of temperature and its initial meaning, there is no consent.
- The effort to give the physical sense to the notion ‘temperature,’ on the basis of macro or micro approach considered, results in the situation when it is necessary to introduce many new notions. So the incomprehensible term is explained through more unintelligible words.

Origin of notions. First of all we will try to examine the origin of word ‘temperature’. A temperature can’t be measured directly. Temperature change can be judged by changing physical properties of bodies. These are volume, pressure, electrical resistance, radiation intensity, etc. The first instruments to measure a temperature, thermometers [from gr. *θερμη* – heat + *μετροω* – measure], were done at the end of the XVI – at the beginning of the XVII century. The term itself appeared in Fahrenheit (1686–1736), Réaumur (1683–1757), Celsius (1701–

1744) *scala* – staircase] and the different temperature units: Fahrenheit degree, Réaumur degree, degree centigrade. It is worth to note that English word ‘grade’ descends from Latin word ‘*gradus*’ which means a step.

Thanks to thermometers, quantitative thermal measurements start at the beginning of the XVIII century [10]. At that time, the member of the St. Petersburg Academy Georg Wolfgang Krafft (1701–1754) in the paper “Various experiments with heat and cold” suggested to solve the following problem: to define the temperature of two portions of a liquid taken at different temperatures. From that time on, the temperature has begun to be treated as the phenomenon of appropriate mixture leading to a normal state. However, at that time scientists did not feel the difference between heat and temperature so that they used different terms: degree of heat, quantity of heat, grade of heat. Quite often, these terms meant one and the same. Experiments on heating and melting of solids came to conclusion that it was necessary to distinguish these terms, as well as to introduce new notions.

In 1754–55 Joseph Black (1728–1799) revealed that during the ice melting a thermometer showed one and the same temperature as long as all ice melted [10, 11]. Black was the first who distinguished temperature and quantity of heat. He introduced new terms: thermal capacity as the amount of heat required to raise the temperature of a body one degree, and hidden melting heat. However, the unit of heat quantity, i.e. the amount of heat required to raise the temperature of 1 gramme of water 1 degree centigrade, was introduced only almost a hundred years later in 1852. The unit of heat quantity was received the name calorie [from lat. *calor* – hot, burning].

At present, the set of methods that deals with measuring thermal effects accompanying various physical, chemical and biological processes is given the name calorimetry [from lat. *calor* – hot, burning + *μετρεω* – measure]. By thermometry is meant a part of physics that deals with methods and facilities of measuring temperature.

Nature of heat. In parallel with the experimental studies there also have been efforts to comprehend the nature of heat. Sir Francis Bacon (1561–1626), Lord Chancellor in time of King Jacob I, had an intention of creating the voluminous writing “*Magna Reconstructio*”, but he had time to write only one part under the name “*Novum organum*” (1620). In this work Bacon formulated the rule that is referred to by his name [11]. According the rule, to write speak, reflect, and act without the facts that should govern a thought, means to sail without a pilot, and means to plunge into immeasurable ocean without a compass and the helm. Bacon divided the scientists of his time into two classes: empiricists and dogmatists. The empiricists [from gr. *εμπειρια* – experience, handicraft], like ants, carry facts of every sort and kind into their ant hill. The dogmatists [from gr. *δογμα* – doctrine, opinion, decree], like spiders, weave web from themselves. But in Science it is necessary to work like bees, to extract material from environment and to convert it rationally. On the basis of his rule, Bacon came to conclusion that “Heat itself, or quid ipsum of Heat, is Motion and nothing else.”

René Descartes (1596–1650) [in lat. Renati Cartesius] wrote in his main work *Principia philosophiae* (1644) the following. “Flame body consists of smallest particles, quickly and violently moving separately from each other. This motion is named sometimes heat, sometimes light. All variety of heat, color and light originates from different types of motion. The particles that rotate most quickly arouse feeling of red light, those that rotate not so quickly do us the feel of yellow light, and the slowest rotation gives green or blue; the order of lights corresponding to the arrangement of the rainbow colors. The small particles are being not only in flame but they continue their motion in all bodies. However here their action is not so strong, and because they are very little, one can’t observe them.”

Why did Descartes take rotational motion as a basis for heat, contrary to Bacon who preferred displacement-type motion? Maybe the reason, why he did it, consists in the following. Although displacement is a more habitual type of motion, Descartes has developed the model

of rotational motion of Universe. With the help of this model, he explained to his contemporaries the phenomenon that startled them. The nearer are the planets to the Sun, the shorter is their period of rotation. For this reason Descartes thought that the rotational motion is more fundamental. Nevertheless, we can say that Bacon was a forerunner of thermal conductivity and Descartes that of kinetic theory of heat and pyrometry. Pyrometry [from gr. $\pi\rho$, $\pi\rho\rho$ – fire, flame + $\mu\epsilon\tau\rho\epsilon\omega$ – measure] is a set of optical methods for noncontact measuring of a temperature.

Along with the achievements of physics in the study of heat, chemistry made a great progress at the beginning of the XVIII century. Oxygen [from gr. $\sigma\zeta\nu$ – $\gamma\epsilon\gamma\omicron\varsigma$ – sour, vinegar + origin, birth] was discovered by Karl Wilhelm Scheele (1742–1786) only in 1771, so early explanation of burning and oxidation was based on phlogiston. It was believed that phlogiston [from gr. $\phi\lambda\omicron\gamma\epsilon\omicron\varsigma$ – blazing, flaming] is a volatile, invisible, imponderable substance escaping from bodies during burning. By analogy with phlogiston, it was presumed that there was a special fluid, elastic and imponderable, that transfers heat from more heated parts of a body to less heated. The fluid was named thermogène (calorigenic substance).

On the basis of this concept Jean Baptiste Joseph Fourier (1768–1830) suggested the theory of heat propagation in solids. Starting from the equation of diffusion

$$\frac{1}{D} \frac{\partial T}{\partial t} = \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2},$$

where T is the temperature, t is the time, $D=k/(c\rho)$ is the coefficient of thermal diffusion, k is thermal conductivity, c is specific heat, ρ is the density, Fourier developed the method of separations of time and space variables. In 1807 he presented a long paper to l'Académie des Sciences de Paris on heat diffusion in special continuous bodies. Of the examiners, Laplace, Monge, and Lacroix were in favor of accepting his work, but Lagrange was strongly opposed to it. The basis of Fourier method was the function representation by trigonometric series. It contradicted Lagrange's own slashing criticism of trigonometric series in his treatment of the vibrating string problem in the 1750's. The paper was never published.

A prize problem on heat diffusion was proposed in 1810, and Fourier sent in the revised version of his 1807 paper, together with a new analysis of heat diffusion in infinite bodies. Fourier's paper won the competition, but the jury, probably again at the insistence of Lagrange, made criticisms on the grounds of "rigor and generality." The referees' criticisms of the 1811 prize essay, concerning its defects of rigor and lack of generality, were political in many respects. Poisson and Biot, outclassed revivals in the theory of heat diffusion, tried for years to denigrate Fourier's achievements. Fourier considered criticism as an unjustified reproach. He expanded the mathematical part of the paper into his book '*Théorie analytique de la chaleur*', which was published only in 1822. In virtue of the generality, the powerful mathematical tools that Fourier invented for the solution of the linear partial differential equations at given boundary conditions, became the basis for all the methods of mathematical physics concerning the integration of such equations. Fourier planned to write an extended treatment of the physical aspects of heat diffusion in a separate book, '*Théorie physique de la chaleur*', but it was never achieved [12].

3. Steam engine and Carnot cycle

English bourgeois revolution (1640–1660) and the following agrarian reforms at the second half of the XVIII century created conditions for the industrial revolution [13]. In England many machines were invented, first of all, spinning frame and loom. However, the growth of machinery industry was hindered by absence of a universal engine that can be used in any place, not only where was water. Such engine was created by James Watt (1736–1819). After some years of painstaking work, Watt made the steam engine of double action with a torsion

shaft and a thickener. The double action means that contrary to the previous engines, Watt's engine works during piston motion in a cylinder both in forward stroke and reverse. The thickener (condenser) saved three quarters of fuel in comparison of Newcomen's engine. Watt's engine did not demand rest and replaced the work of hundred horses. From that time aggregate capacity is measured in horse-powers and then in watts (1 horse-power equals 736 watts)

Watt's steam engine became the main motive power of industry. "Without Watt's inventions British nation was not able to satisfy vast expenses on the last wars against France" said the President of the Board of Trade of that time [11]. However, the theory of a steam engine was absent for a long time. Watt obtained his first patent in 1769, but only in 1824 there appeared the book by Nicolas Leonard Sadi Carnot (1796–1832) "Reflections on the driving force of fire and on machines that are able to realize this force". Carnot considered not only steam engines but a thermal engine in general [10]. "To think over the principle of obtaining motion from heat comprehensively, it is necessary to study it irrespective of any mechanism, any definite motive; it requires careful consideration that can be applied not only to steam engines, but to all conceivable thermal machines whatever substance is operating." According to Carnot, the origin of driving force is indebted not to a waist of thermogène (calorigenic substance), but to transition of this substance from a hot body to a cold one. To describe the process, Carnot introduced the concept of cycles into the doctrine of heat.

Carnot cycle (1824) is usually represented as a diagram (Fig. 1) suggested by Benois Paul Émile Clapeyron (1799–1864). Clapeyron expressed Carnot's idea in a mathematical form. At that he used such notion as ideal gas. The word 'gas' originates to Greek word $\chi\alpha\omicron\varsigma$ (chaos). In the antiquity, chaos meant the primary, formless state, infinite space that existed before the world creation [14]. The term 'gas' was introduced into science by van Gelmont (1577–1644). He discovered carbon-dioxide gas.

The ideal gas is the model in which there is no interaction of particles. For the ideal gas the following laws are valid.

$$pV \Big|_{T=const} = const, \quad \text{R. Boyle (1662), E. Mariotte (1676);}$$

$$\frac{p}{T} \Big|_{V=const} = const, \quad \text{J.A.C. Charles (1787);}$$

$$\frac{V}{T} \Big|_{p=const} = const, \quad \text{J.L. Gay-Lussac (1802).}$$

If to consider these laws being independent, then the state of ideal gas will be defined by three physical magnitudes: pressure p , volume V , and temperature T . Clapeyron (1834) has found the equation of state for the ideal gas that combined all the laws. Later D.I. Mendeleev (1874) has shown that the constant in Clapeyron's equation had the sense of universal gas constant R ; and the equation took the form

$$pV = RT.$$

This relationship is often referred to as Clapeyron – Mendeleev equation.

Therefore the state of ideal gas is defined by two magnitude from three ones, e.g. p and V , i.e. by a point on the plane p – V . If the state changes, the defining point is describing a curve on the plane p – V . The curve is named the diagram of a process considered. If the ideal gas returns into an initial state, then the process is circular and forms a cycle. In this case the diagram will be closed.

Consider Carnot cycle for the ideal gas that will be a model of working medium (Fig. 1). The working medium (vapor under a piston) receives the heat quantity Q_1 from a heater at the temperature T_1 . At that, the vapor expands and does work (isotherm ab). Then expanding again, the vapor cools to the temperature T_2 (adiabat bc). During this process the vapor does

not absorb and does not give up heat. It is worth noting that the word ‘adiabat’ originates from the Greek word $\alpha\text{-}\delta\text{i}\alpha\beta\alpha\tau\omicron\varsigma$ (intransitive). At the temperature T_2 the vapor contacts with a cooler and gives to it the heat quantity Q_2 (isotherm cd). After that, compressing again, the vapor returns into the initial state (adiabat da).

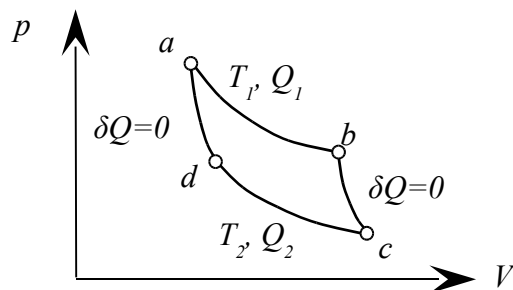


Fig. 1. Carnot cycle.

We see that Carnot cycle is the reversible circular process which turns heat into work. If the temperature difference $T_1 - T_2$ between a heater and a cooler is constant, the working medium produces the work

$$A = Q_1 - Q_2 = \frac{T_1 - T_2}{T_1} Q_1$$

in one Carnot cycle. The work is equal to the square of the quadrangle $abcd$. The coefficient of efficiency is equal to

$$\eta = \frac{A}{Q_1} = \frac{T_1 - T_2}{T_1}.$$

This means that any heat can produce work only if there is a temperature drop.

“Apparently that an analogy has a share in all discoveries, but in some ones it has the lion's share” said Hungarian mathematician György Polya (1887-1985). Carnot graduated from École Polytechnique. As an engineer, he built water engines. At that time in France steam engines were coming into use. Carnot was young and new engines attracted his attention. He knew that in order a water mill could work, water must fall from a higher level to a lower one. Carnot supposed that heat could be likening to water. To produce work, heat, similar to water, must fall from a higher level to a lower one. A height difference for water is just the same as a temperature drop for heat. Using this analogy, Carnot formulated the principle that later was referred to by his name: to produce work, it is necessary to have two sources of heat with different temperatures. It should be emphasized that Carnot thought out the ideal cycle for the ideal thermal engine which cannot be exceeded with any real engine.

4. Curvilinear integral and entropy

For Carnot cycle we have two processes: the transition of heat into work and transition of the heat with a higher temperature to the heat with a lower temperature. In reality both processes are proceeding simultaneously. For example, in Watt's steam engine, a piston divides a cylinder into two parts. When the vapor over the piston executes work isothermally, the vapor under the piston, being in contact with a thickener, behaves itself adiabatically [11]. To compare different processes, Rudolf Clausius (1822–1888) has formulated the equivalence principle for transformations [10]. According to the principle, arising the heat quantity Q with temperature T from work is characterized by the equivalent Q/T . Clausius suggested also considering an arbitrary cyclic process as a sum of large quantity of elementary Carnot cycles [6].

Let us find the heat quantity Q that is necessary to produce work. For this purpose divide the process into infinitesimal elementary processes corresponding to infinitesimal changes of the quantities p , V , T [15]. If only one quantity changes, the heat quantity is proportional to the increment of respective variable. If all three variables change simultaneously, then according to the superposition principle for small actions [16] the total increment ΔQ is equal to the sum of partial increments, i.e.

$$\Delta Q \cong A \Delta p + B \Delta V + C \Delta T .$$

During the isothermal process ab the increment $\Delta T=0$ whereas for the adiabatic process bc the magnitude $C=0$. Hence

$$Q_1 = \sum \Delta Q = \int_{abc} A d p + B d V .$$

Analogously

$$Q_2 = \sum \Delta Q = \int_{adc} A d p + B d V$$

By virtue of the equation of state $pV/T=Q/T=R$, the equivalents of the two transformations abc and adc are equal, i.e.

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} ,$$

or

$$\int_{abc} \frac{1}{T_1} (A d p + B d V) = \int_{adc} \frac{1}{T_2} (A d p + B d V) .$$

This equality means that the curvilinear integral does not depend on a path of integration; therefore the equality is valid for any temperature T . Under the change of integration direction the integral changes only the sign [15]. Hence replacing the integration path adc in the second integral with cda and combining two integrals into one, we obtain Clausius equality [6]

$$\oint \frac{1}{T} (A d p + B d V) = \oint \frac{\delta Q}{T} = 0 .$$

Path-independent integral signifies that its integrand is a total differential of some function, i.e.

$$\frac{\delta Q}{T} = d S .$$

The function S was introduced by Clausius in 1865 and received the name entropy [10]. Usually [2–6] this name is explained as it be the combination of two Greek words: $\epsilon\nu$ [in] and the noun $\tau\rho\omicron\pi\eta$ [turn, turning, change] throwing away the preposition. In that case the name has sense ‘transformation’. However it is interesting to note that in Greek language there is also the word $\epsilon\nu\tau\rho\omicron\pi\alpha$ which completely coincides with the German word Entropie and means trick, ruse.

The function δQ is not a total differential, so to emphasize its distinction, one uses the symbol of variation δ . Differential d [from lat. *differentia* – difference] is the main linear part of a function increment. The term variation was introduced by Joseph Louis Lagrange in 1762 in order to designate a small deflection of a magnitude from its base value. The expression $\delta Q/T$ is named reduced heat quantity, the inverse temperature $1/T$ being an integrating multiplier.

5. Motion, molecules, and probability

It is known [14] that the field of science in which the sum of cumulative knowledge is the largest is the first rank science. This field forms ideas and terminology of small fields of sci-

ence. In the XVIII – XIX centuries, mechanics was the first rank science. Within the framework of mechanics, analytical methods were developed for solving different problems. The methods were based on using differential and integral calculus. In comparison with mechanics the science of heat did only first steps and so used notions and terminology of mechanics.

Thermodynamics, as the science on the most general properties of macroscopic systems that are in the state of thermal equilibrium and on the transitions between these states, was developed by analogy with mechanics. As a basis, the principles generalizing numerous experimental observations were taken. These principles are fulfilled independently of the concrete nature of bodies forming a system; therefore one can develop macroscopic theories of heat even on the concept of thermogène.

Nevertheless scientists tried to gain a more penetrating insight into heat nature. They developed the views of Bacon and Descartes who connected heat with motion. However these efforts were done in the manner of Aristotle on the basis of reasoning. “One should not to attribute heat to thickening some fine specially assigned matter. Heat is an internal rotational motion of constrained matter” (M.V. Lomonosov, 1711–1765). “Heat is vibrational motion of body particles; for gases and liquids it can be rotational motion” (Humphrey Davy, 1778–1829). “Heat is vibrational motion of body particles” (Thomas Young, 1773–1829). “Heat is the motion that changed its form; this is the motion of body particles” (Carnot, 1796–1832). “Heat is not a substance; this is a dynamical form of mechanical effect” (William Thomson (lord Kelvin), 1824–1851).

Rudolf Clausius (1822–1888) “has also tried to gain an understanding of the internal state of a heated body and has some idea about it”. He considered gas pressure as a shock effect of molecules on a wall. “Motion of molecule constituents and a wall leads to interaction of these internal motions. Depending on phases that have the motions at the instant of the shock, these motions can influence on the motion of a whole molecule in a different manner. But for large number of molecules, the average situation is such as though the molecules were reflected by the wall according to laws similar to the reflection laws for elastic spheres off a fixed wall. To define pressure, it makes no difference if instead of a mean equality to accept that equality exists at each shock”. Using Newton laws, Clausius has calculated mean-square velocity of molecules, their average free path, average number of collisions, and connected all these values with gas pressure [10].

Clausius introduced also two hypotheses (1857). “Gas molecules are so small that it is possible not to take their volume into consideration. They interact only when they are in immediate vicinity. They are moving in all possible directions so any direction is as much probable as all the others.” This new theory Clausius named kinetic one. Clausius’s hypotheses now are known under the name ‘hypothesis of an ideal gas’ and ‘hypothesis of molecular chaos’.

Clausius’s ideas have gained recognition. James Clerk Maxwell (1831–1879) in the work, elucidating the dynamical theory of gases (1859), emphasized that from the molecular hypothesis one can derive many properties of matter. Maxwell derived the distribution function for molecule velocities. Now it is written in the form [17]

$$f(\mathbf{v}) = N \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \exp \left(-\frac{mv^2}{2kT} \right)$$

Here N is the number of molecules, $mv^2/2$ is the kinetic energy of a molecule, kT is the heat energy, and k is the constant, equal to the ratio of gas constant R to Avogadro constant. Planck has named the constant k in honor of Boltzmann by his name. The function $f(\mathbf{v})$ can be obtained by different ways [18].

Give the modern treatment of initial mathematical proof given by Maxwell. Let we have a gas of N identical molecules. Denote the number of molecules having velocities in the range

from \mathbf{v} to $\mathbf{v}+d\mathbf{v}$ by $f(\mathbf{v}) d\mathbf{v}$. Let the gas be homogenous and isotropic, and external forces are absent. The gas homogeneity means that the velocity of any molecule does not depend on its coordinates. In virtue of space isotropy, the function $f(\mathbf{v})$ does not depend on the direction of vector \mathbf{v} and therefore is the function of its absolute value only. Hence

$$f(\mathbf{v}) = f(v^2),$$

or in the Cartesian coordinates

$$f(v^2) = f(v_x^2 + v_y^2 + v_z^2).$$

Denote the number of molecules having the velocities in the range

$$(v_x^2, v_x^2 + dv_x^2)$$

by

$$g(v_x^2) dv_x^2.$$

In virtue of space isotropy

$$g(v_x^2) = g(v_y^2) = g(v_z^2).$$

The functions f and g are proportional to the probability that random numbers take on values v^2 and v_x^2, v_y^2, v_z^2 , respectively. For independent random values we have

$$f(v_x^2 + v_y^2 + v_z^2) = g(v_x^2) g(v_y^2) g(v_z^2).$$

Write down the total differential of this function

$$\begin{aligned} df &= \frac{\partial f}{\partial v_x^2} dv_x^2 + \frac{\partial f}{\partial v_y^2} dv_y^2 + \frac{\partial f}{\partial v_z^2} dv_z^2 \\ &= g(v_y^2) g(v_z^2) \frac{dg(v_x^2)}{dv_x^2} dv_x^2 + g(v_x^2) g(v_z^2) \frac{dg(v_y^2)}{dv_y^2} dv_y^2 + g(v_x^2) g(v_y^2) \frac{dg(v_z^2)}{dv_z^2} dv_z^2. \end{aligned}$$

From this it follows that

$$\frac{\partial f}{\partial v_i^2} = g(v_j^2) g(v_k^2) \frac{dg(v_i^2)}{dv_i^2}, \quad i, j, k = x, y, z.$$

Multiply the both parts of this equality by $g(v_i^2)$ and divide by $f(v^2)$. Then we have

$$\frac{1}{f} \frac{\partial f}{\partial v_i^2} = \frac{1}{g(v_i^2)} \frac{dg(v_i^2)}{dv_i^2}, \quad i = x, y, z.$$

The left part of this equality depends on v_x, v_y, v_z , but the right part can depend on either v_x , or v_y , or v_z only. Since these conditions can not be satisfied simultaneously, this means that both parts are equal to one and the same constant. We denote it by β . From this it follows that we have three equations

$$\frac{1}{g(v_i^2)} \frac{dg(v_i^2)}{dv_i^2} = \beta, \quad i = x, y, z.$$

Integrating we obtain

$$g(v_i^2) = A_i \exp(\beta v_i^2), \quad i = x, y, z,$$

where A_i is a constant. Therefore

$$f(v^2) = A \exp(\beta v^2).$$

The integrating constant can be found from the normalizing condition

$$\int_{-\infty}^{\infty} f(v^2) d\mathbf{v} = N,$$

where N is the number of molecules,

$$d\mathbf{v} = v^2 \sin\theta d\theta d\varphi dv.$$

Hence

$$\int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\varphi \int_{-\infty}^{\infty} v^2 f(v^2) dv = 4\pi A \int_0^{\infty} v^2 \exp(\beta v^2) dv = N.$$

The integral has physical sense if $\beta < 0$, so

$$I = \int_0^{\infty} v^2 \exp(-\beta v^2) dv.$$

Take the integral. Denote $v^2 = t$. Then

$$v = \sqrt{t}, \quad dv = 1/2 \sqrt{t}$$

and the integral takes the form

$$I = \frac{1}{2} \int_0^{\infty} t^{1/2} \exp(-\beta t) dt = \frac{\Gamma(3/2)}{2 \beta^{3/2}}.$$

Because

$$\Gamma(3/2) = (1/2) \Gamma(1/2), \quad \Gamma(1/2) = \sqrt{\pi},$$

we have

$$A = (\beta/\pi)^{3/2} N.$$

Consequently

$$f(v^2) = (\beta/\pi)^{3/2} N \exp(\beta v^2).$$

To find the constant β , we need additional information. This can be an equation describing some property of a gas, or a physical model explaining the properties at the molecular level. Take, for example, the equation of state for the ideal gas

$$pV = NkT.$$

Here p is the gas pressure, V is the volume of the gas, k is Boltzmann constant, and T is the absolute temperature. The gas pressure is the force acting on a unit square of a vessel that contains the gas. In its turn, the force is the change of a linear momentum of gas molecules per unit time as a result of collision with a wall.

Suppose that all the gas molecules, having the velocities in the range from \mathbf{v} to $\mathbf{v}+d\mathbf{v}$, collide with the wall that is normal to the z -axis. Since the wall mass is much larger than the molecule mass, in this case a center-of-gravity system coincides with a laboratory one. For a molecule, collision with the wall leads to only the change of its linear momentum which is equal in magnitude but opposite in sign. In other words, the molecule recoils without energy loss. The linear momentum change per one collision is equal to $2mv_z$, where m is the molecule mass. The number of molecules colliding with the wall per unit time equals $(v_z/V) f(\mathbf{v}) dv$. Consequently

$$p = \frac{2m}{V} \int_{-\infty}^{\infty} v_z^2 f(\mathbf{v}) d\mathbf{v}.$$

For the isotropic system $v_x^2 = v_y^2 = v_z^2 = v^2/3$ and besides, the number of molecules moving along a positive axis of coordinates is equal to the number of molecules moving in the opposite direction. Therefore

$$p = \frac{m}{3V} \int_{-\infty}^{\infty} v^2 f(\mathbf{v}) d\mathbf{v} = \frac{m}{3V} 4\pi A \int_0^{\infty} v^4 \exp(-\beta v^2) dv.$$

The integral

$$I = \int_0^{\infty} v^4 \exp(-\beta v^2) dv$$

after the change of variable $v^2=t$ reduces to the gamma function

$$I = \frac{1}{2} \int_0^{\infty} t^{3/2} \exp(-\beta t) dt = \frac{\Gamma(5/2)}{2\beta^{5/2}} = \frac{3\sqrt{\pi}}{2^3\beta^{5/2}}.$$

As a consequence, the equation of state for the ideal gas takes the form

$$pV = N \frac{m}{2\beta}.$$

Therefore the constant β is defined by the expression

$$\beta = \frac{m}{2kT}.$$

Now we can write down the distribution function for molecule velocities in the form

$$f(\mathbf{v}) = N \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \exp\left(-\frac{mv^2}{2kT}\right).$$

Here the exponent index is the dimensionless ratio of the kinetic energy of a molecule $mv^2/2$ to the heat energy kT . The function obtained is named Maxwell's distribution function (1859).

For the model of ideal gas discussed we can write down this function as the product of three identical distribution functions

$$g(v_i^2) = \sqrt[3]{N} \left(\frac{m}{2\pi kT} \right)^{\frac{1}{2}} \exp\left(-\frac{mv_i^2}{2kT}\right), \quad i = x, y, z,$$

each of them being a normal distribution or Gauss's distribution (Carl Friedrich Gauss, 1777–1855) [19, 20]. Comparing the function $f(v_i)$ with the canonic form of Gauss's distribution, we find the variance and mean deviation

$$\sigma_i^2 = kT/m, \quad \eta = \sigma\sqrt{2/\pi} = \sqrt{2kT/\pi m}.$$

These values give us the mean-root square velocity and mean velocity for molecule motion along the axes of coordinates

$$\overline{v_i^2} = \frac{kT}{m}, \quad \overline{v_i} = \sqrt{\frac{2kT}{\pi m}}.$$

Denote

$$mv_i^2/2kT = u_i.$$

Then the distribution function takes the form

$$g(u_i) = A_i \exp(-u_i), \quad i = x, y, z.$$

This is the gamma distribution [20, 21] with the parameter $\alpha_i=1$. Convolving all the three distributions we obtain again the gamma distribution with the parameter $\alpha=3$. At this, the dispersion increases three times, i.e.

$$\sigma^2 = \overline{v^2} = \frac{3kT}{m}.$$

Therefore in addition to the formal mathematical definition of temperature as an integrating divisor, it is possible to give a clear physical definition. We can say now that *a temperature is a quantity that is proportional to the variance of the distribution function for velocities of ideal gas molecules.*

6. Molecules, discreteness, and entropy

We emphasized already that the thermodynamic approach is not connected with any concrete ideas of thermal motion. In his time Josiah Willard Gibbs (1839–1903) has transformed thermodynamics from mechanical theory of heat into a general theoretical scheme that can be applied to all physical and chemical processes. Universality of thermodynamics had both positive as well as dramatic consequence for science where two tendencies were formed: phenomenological approach and atomistic one. The phenomenologists reasoned that the aim of science consists in description of nature phenomena on the basis the principles determined experimentally. In particular, the energetics considered energy as one of the main notions of science; other notions such as matter, force being derivative and even superfluous. For example, Ernst Mach (1838–1916) and his followers regarded atoms and molecules as pure fantasy.

Ludwig Eduard Boltzmann (1844–1906) was an adherent of atomistic approach [10, 17]. He noted that Maxwell's distribution gave the probability of the fact that velocity of a molecule was in the range from \mathbf{v} to $\mathbf{v}+d\mathbf{v}$ at arbitrary coordinate distribution. Boltzmann set himself an inverse problem: to find a function that should be able to give the distribution of particles in a space at any velocity distribution. For ideal gas in external field Boltzmann obtained the expression that gave the density of particles at point \mathbf{r}

$$n(\mathbf{r}) = n_0 \exp\left(-\frac{U(\mathbf{r})}{kT}\right).$$

Here n_0 is the density of particles in the absence of field, $U(\mathbf{r})$ is the potential energy of a particle in a field. The formula gives the coordinate distribution for particles of ideal gas and is labeled as Boltzmann distribution (1868). If to combine Maxwell distribution with Boltzmann one, we obtain the joint distribution that referred to as Maxwell-Boltzmann distribution for classic ideal gas.

However the main achievement of Boltzmann consists in the following. In 1877 Boltzmann introduced the hypothesis according to which a gas molecule could lose and get only discrete portion of energy multiple to some least value ε [10]. "Before collision each of both colliding molecules has vis viva (living force) θ , or ε , or 2ε , and so on. In consequence of some reason, it will occur that after collision none of colliding molecules takes a living force which is not in this series". Unfortunately for Boltzmann, he considered it only as a fiction that did easier a mathematical treatment of problem. Nevertheless Boltzmann set the problem to find the distribution law that should be able to define how many molecules from the total number N had energies θ , ε , 2ε , At this, he supposed that the molecules, being in one and the same energy state, were indistinguishable. However, there appears a new complex when a molecule of some energy state change place with a molecule of other energetic state. The number of complexes n_i , by which it is possible to realize a given energy state i , defines the probability of this state. In virtue of the assumptions done, the number of distribution ways in energy state for N molecules equals to

$$W = \frac{N!}{n_0! n_1! n_2! \dots}.$$

Suppose that at thermal equilibrium different microscopically distinguishable distributions of particles in states with one and the same total energy have equal probability. Macroscopic state can be realized by several microscopically different states, but the most probable state is such to which corresponds the largest number W of microscopically different states. It should be emphasized that in mechanics the equilibrium state of a system is stable if the potential energy of the system is minimum. Consequently both in mechanics and in science of heat, the condition of stability is the extremum of some characteristic for a system.

Take for such characteristic not the value of W , but the value of its logarithm $\ln W$ that is equal to

$$\ln W = \ln N! - \sum_i n_i!$$

For large number n , the following formula takes place (James Stirling, 1692–1770)

$$\ln n! = n \ln n - n.$$

Applying the formula, we obtain

$$\ln W = N \ln N - N - \sum_i (n_i \ln n_i - n_i).$$

To find the extremum of some function $f(x_1, x_2, \dots, x_n)$, one can use the method of Lagrange multipliers (Joseph Louis Lagrange, 1797). For this purpose [19], one needs to construct a new function L (Lagrange function), by adding binding equations $g_k(x_1, x_2, \dots, x_n) = 0$ multiplied by undetermined multipliers α_k (Lagrange multipliers) to the old function; here $k=1, 2, \dots, m$. Thereafter one needs to find the extremum of the new function, without any additional conditions, considering variables x_i, α_k as independent. Thereby Lagrange function

$$L(x_1, x_2, \dots, x_n, \alpha_1, \alpha_2, \dots, \alpha_m) = f(x_1, x_2, \dots, x_n) + \sum_{k=1}^m \alpha_k g_k(x_1, x_2, \dots, x_n)$$

has a variable value that depends on several functions, i.e. it is a functional for which the extremum condition is given by $\delta L = 0$.

In our case $f = \ln W$, its variation is

$$\delta f = - \sum_i (\delta n_i) \ln n_i.$$

Besides, we have the binding equations

$$\sum_i n_i = N, \quad \sum_i n_i \varepsilon_i = E, \quad (E \text{ is the total energy}),$$

variations of which are equal to zero, i.e.

$$\delta g_1 = \sum_i \delta n_i = 0, \quad \delta g_2 = \sum_i (\delta n_i) \varepsilon_i = 0.$$

Thereby the extremum condition takes the form

$$\delta L = \sum_i \delta n_i (\ln n_i - \alpha - \beta \varepsilon_i) = 0,$$

where α, β are Lagrange multipliers. The variations δn_i are arbitrary; therefore the terms in parentheses must be equal to zero

$$\ln n_i - \alpha - \beta \varepsilon_i = 0.$$

Consequently

$$n_i = \exp(\alpha) \exp(\beta \varepsilon_i).$$

From the normalizing condition we have

$$\sum_i n_i = \exp(\alpha) \sum_i \exp(\beta \varepsilon_i) = N,$$

so we can exclude the redundant multiplier α with the help of the expression

$$\exp(\alpha) = N / \sum_i \exp(\beta \varepsilon_i) = N / Z.$$

Here

$$Z = \sum_i \exp(\beta \varepsilon_i)$$

is the sum of all multipliers $\exp(\beta \varepsilon_i)$ throughout all states ε_i .

Suppose that ε_i is the kinetic energy of a gas molecule. In this case n_i represents Maxwell's distribution function for which $\beta = 1/kT < 0$. Consequently

$$n_i = \frac{N}{Z} \exp\left(-\frac{\varepsilon_i}{kT}\right),$$

where the constant Z is named statistical sum or sum of states (from ger. *Zustandssumme*). The function obtained is named Boltzmann's distribution function (1877).

Later on Boltzmann refused the initial quantum hypothesis which he considered only as a useful mathematical tool. He replaced the sum by an integral, n_i by the continuous function f , and introduced the function

$$H = \int f \ln f \, d\mathbf{v},$$

where \mathbf{v} is the velocity of a molecule. The last expression is the average value of $\ln f$.

Earlier (1872) Boltzmann considered collisions in inhomogeneous gas and has derived the integro-differential equation [17]

$$\frac{\partial f}{\partial t} + \mathbf{v} \nabla f = \int (f' f'_1 - f f_1) \sigma \, d\mathbf{v}_1.$$

The functions f, f_1 of the integrand denote the functions $f(\mathbf{v}), f(\mathbf{v}_1)$, where \mathbf{v}, \mathbf{v}_1 are the velocities of two molecules before a collision respectively; the same functions marked by primes after the collision, σ is the scattering cross section. On the basis of this equation, Boltzmann proved his famous H -theorem [17] according to which

$$\frac{dH}{dt} \leq 0 \dots$$

This means that the function H either decreases or remains constant with time. Later on Planck has shown that $S = -kH$. Thus with the help of discrete (quantum) approach and kinetic equation Boltzmann gave the first microscopic proof of the law of increasing entropy. This formula is cut out on the Boltzmann's tombstone as an epitaph.

7. Fate and metamora

It should be emphasized that the fate of many investigators who have tried to gain a more penetrating insight into nature of heat and use heat in practice was far from being unclouded. Solomon de Cos, who lived in times of Francis Bacon, suggested using the force of vapor to drive a carriage or a ship. He has written the book "The reason of driving forces" and asserted that his discovery will enrich the country that will be ready to accept it. He was announced being insane because he wanted to do something from boiling water and was put into asylum [11].

The opponents of James Watt have drawn him into a suit affirming that he invented only ideas. Although Watt has won the seven year law, he wrote with a touch of bitterness: “World over, I am afraid above all of predators in science and arts. They pursued me cruelly. If I had had no excellent memory, their brazen impudence would have compelled me to think that I have done nothing for improving a steam engine. The scoundrels, to whom I was of avail, even claimed that my improvements not only deserved no attention, but even were harmful for national wealth” [11].

Julius Robert Mayer (1814–1878) was one of the first who determined the mechanical equivalent of heat and discovered the law of conservation of energy for non-mechanical phenomena. In 1841 he had written the paper in which he wrote “Motion, heat, and, how we intend to show in future, electricity is the phenomenon that can be reduced to one force. They are measured by each other and transfer into each other according to certain laws”. The paper was sent to the journal “Annalen der Physik” but was not published. It was lying in the table of the editor during 36 years and was found after his death. Moreover, Mayer was ruthlessly persecuted in press accounts; he was accused of megalomania and was subjected to compulsory medical treatment in a mental hospital. In 1850 he tried to commit suicide having thrown himself out a window, and became lame [10].

Boltzmann had written the book “Lectures on Gas Theory” (1896–1898). In the preface he wrote [17]: “Before Hertz’s experiments even the formula of Maxwell’s theory of magnetism were considered as useless because of their complexity. I hope that the theory of gases will not meet such attitude. It would be the greatest tragedy for science if the theory of gases be buried in oblivion through hostile attitude accidentally formed. I feel myself a lone weak person who is unable to withstand a routine of time. However, I have still forces to give such form of the theory of gases in order that it would be unnecessary for its future rebirth to discover too much again.” In 1906 Boltzmann had committed suicide.

Six years later the situation has changed [10]. In 1912 Hendrik Anton Lorenz (1853–1928) noted: “Now it is impossible to have some doubt in the existence of molecules. Their reality has become the fact that is almost observable directly. Molecules exist for us just as many other objects that are invisible directly. Austrian physicist Boltzmann won an honor for doing the first successive approach to this problem and establishing connection between probability and thermodynamic functions, in particular between entropy”.

8. Conclusions

Making the summary we can say the following. Maxwell’s approach leads to conclusion: a temperature is a value that is proportional to the variance of the distribution function for velocities of ideal gas molecules. Boltzmann’s approach establishes connection between entropy and the distribution function. Entropy is an average value of the logarithm of the distribution function for energies of ideal gas molecules. As for connection between heat and other forms of motion, this question in Boltzmann’s time remained at the level of hypotheses. It should be emphasized that in the twentieth century the notions of heat, temperature, and entropy were modified. This problem will be considered in the next lecture.

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