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About the Molecular and Photon Theory of Gases

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Editorial

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Editorial

Imperfection of the modern molecular and kinetic theory of heat is shown. More complete theory of warmth has to include, except kinetic energy of molecules, also potential energy of interaction of molecules. Besides, it is necessary to consider radiations of molecules of the thermal photons rendering both direct mechanical impact, and the weakening action on intermolecular communications.

The accounting of all listed factors is carried out in the molecular and photon theory developed by authors. The modern molecular theory of substance is obviously imperfect. Tell a set of the facts about it, we will sort some of them. But, to understand shortcomings of the modern theory, in particular theories of gases, we will begin with history of creation of the molecular and kinetic theory of heat.

The official history of the scientific theory of the kinetic theory of heat begins with fundamental work of Daniil Bernoulli "Hydrodynamics, or notes about forces and the movements of liquids" written in 1738. In the tenth part "About properties and the movements of elastic liquids, in particular air" [1]. D. Bernoulli laid the foundation of the kinetic theory of gases and liquids. It "... gives a conclusion of gas laws from model of billiard balls in the work, outputs Boyle-Mariotta's law and uses conservation law of mechanical energy to show that at change of temperature pressure changes in proportion to a square of speed of particles. This work for the first time gives right, statistical justification of the kinetic theory. Much the processed edition of this work appeared then in 1738. Work was forgotten till 1859" [2].

Since D. Bernoulli's work was forgotten, in 1816 George Gerapat, having rethought the available facts, wrote the article "About Physical Properties of Gases" [3]. In this article Gerapat irrespective of Bernoulli proves kinetic model of gases. And, if Bernoulli, according to a level of development of science of the time, assumed that air (only known gas of that time) is a uniform substance, at the time of writing of article by Gerapat it was already known that air is a mix of gases [4]. Therefore Gerapat mentions nitrogen, hydrogen and oxygen [3]. Thus he draws conclusions those physical properties of gases various (chemically) submit to uniform laws. Thereby Gerapat, though it is implicit, but accurately distinguishes physical and chemical properties of gases. Recognizing distinctions of chemical properties of gases, he specifies that physical properties of gases are similar and can be explained within uniform model.

As wreath of development of kinetic model of gases (MKT) it is possible to consider fundamental work of Rudolf Klauzius [5]. In this work Klauzius enters the concepts "length of free run" and "ideal gas". And all work of Klauzius is devoted to exclusively kinetic model of gases. After this fundamental work the concept "ideal gas-such gas which at the same time submits to Boyle's law-Marriott and Gay-Lussac" was brought [5]. In 1834 Clapeyron published the equation on the basis of a combination of laws of Boyle-Mariotta and Gay-Lussac, thus it is possible to tell that the mentioned laws are special cases of the law of Clapeyron. From here equivalent definition follows: "ideal gas – gas which submits to Clapeyron's equation". D. I. Mendeleyev during 1872-1874 made numerous experiments on check and specification of the law of Clapeyron, theoretical improvement of the mentioned equation was also carried out. As a result in 1874 D. I. Mendeleyev offered the formulation of the equation of ideal gas which is used so far. Therefore the equation is called as Clapeyron-Mendeleyev's equation.

As a result it is possible to tell that according to modern views ideal gas is the gas submitting to Clapeyron-Mendeleyev's equation. Klazius doesn't mention in the fundamental work why he called gas which submits to separate laws, "ideal". Only, why it could do it, it because these laws (Boyle-Mariotta and Gay-Lussac) "ideally" lay down in an outline only of kinetic model of gas known at that time. Any other arguments at Klauzius it wasn't obvious. Nevertheless, since then in scientific and educational literature the imperative was formed that "ideal gas is a gas which submits to laws of ideal gas", and "laws of ideal gas are laws to which ideal gas submits". It would be possible not to pay attention if not it is a curious collision to it. Any gases submit to "laws of ideal gas" in very narrow ranges of external conditions (pressure and temperature), in other cases gases don't submit to these laws. I.e. the same gas, with one pressure (and temperatures) is ideal gas, and under all other conditions (pressure and temperature) – is nonideal (real) gas.

About the similar I wrote still Lomonosov in 1849 [6]. It is known that further experiences with gases completely confirmed correctness of Lomonosov: "Using the theory, Lomonosov gave an exact mathematical conclusion of the law of Boyle-Mariotta. This one already was a great achievement: authors of the law Englishman Boyle and Frenchman Marriott didn't manage to make it. But, Lomonosov made something much bigger. It predicted inevitability of deviations from Boyle-Mariotta's law at very big compression of gas. And this prediction of Lomonosov completely came true" [7]. In 1873 Van der Vaals almost completely repeated reasoning's of Lomonosov and removed the well-known equation [8].

In modern literature any equations different from Clapeyron's equation - Mendeleyeva, call the equations of real gases [3]. Actual "reality" in the equations of real gases only that they don't coincide with Clapeyron-Mendeleyev's equation which, purely administratively, is recognized to call "the equation of ideal gas". Additions which entered Van der Vaals at a conclusion of the equation in 1873 into Clapeyron's equation consisted in addition in the equation of "ideal gas" of two *parameters an and b*. Which are called as Van der Vaals's constants. And "*the constant b* defines that part of volume which is inaccessible to motion of the molecules owing to their final sizes.

The amendment *of a/V2* gives the internal pressure *of pi* caused by a mutual attraction of molecules to each other" [9]. In other words, Van der Vaals's theory adds two properties to modern axioms of "ideal gas": it, final sizes of molecules of gas and force of a mutual attraction. But such properties all possess without exception gases, so existence of these properties don't depend on concrete chemical properties of these or those gases, so, can be freely brought in axioms of "the generalized ideal gas". If to refuse a paradigm that ideal gas only gas at which completely are absent interaction of molecules, and consisting of the molecules which don't have the sizes can be called.

Actually, though Van der Vaals also improved the equation of a condition of gas in comparison with Clapeyron's equation, but thus didn't bring anything heat, new in the theory. All warmly containing in substance including warmth of gases, admits only a type of kinetic energy of molecules of substance. As deification of the mechanical theory of heat it is possible to consider nuclear and oscillatory model of melting of crystals of Lindemann [10]. Lindemann's criterion is based on the concept that melting happens when the relation of a root of average and square fluctuation (RMSF) in provisions of atoms in provisions of an equilibrium lattice and the distance to the next neighbor reaches critical value. In other words, when kinetic energy of atoms in a crystal reaches critical value, the crystal collapses and the substance passes into a liquid state. Lindemann's criterion is the most popular in theories of melting in view of its simplicity and logical validity, but only within the kinetic theory of heat. But, since exclusively kinetic theory of heat admits modern scientific literature, respectively, it is possible to tell that Lindemann's criterion is the only thing evidence-based model of melting. Lindemann's criterion has a set of shortcomings and is exposed to criticism from the different parties, we will note only some, in line with our research program.

The first that we will note, it that the fact of existence of criterion of melting. The matter is that crystals pass from crystal to a liquid state, not gradually as it would be necessary to expect proceeding from statistical sense of criterion of Lindemann, and jump, at a certain temperature. Many scientific works are devoted to this fact, nevertheless, the fact still has no full disclosure.

The second, the American professor G. E. Ulenbek in the lectures was distressed: "The question consists in, whether it is possible to show that a size U minimum on coordinates of particles g1, g2..., rN corresponds to their arrangement in knots of any correct lattice that as we know, is carried out actually [11]. This question sounds quite modestly, but so far we have no mathematical

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methods which would allow to solve it. I speak about it only to explain, what area of new difficulties we enter here. If we don't even know why there are solid bodies, how we will be able to understand why there is a melting?" [11]. But, dear professor was mistaken a little, the issue of existence of solid bodies at any temperature can be resolved, but by other methods, not statistical. The fact of existence of a liquid phase in certain limits of temperatures is more unclear. This fact is well-known, nevertheless is, as a rule, ignored. The matter is that any substance can be in a firm and gaseous state at any temperature, and here any substance can be in a liquid state only at a temperature above a threefold point below than the critical. Below a threefold point the substance doesn't melt, and is sublimated, i.e. evaporates. Above a critical point, also doesn't melt, and passes into a condition of a fluid, a special phase state at which the substance has liquid density, but thus properties of gas [10]. In particular, the substance in a condition of a fluid has no interface of phases, and occupies all volume as it is inherent in gases. And only in the range of temperatures between a threefold point and critical there is a transition from a firm state to liquid states, and transition from liquid to a gaseous phase. This fact also can't be explained by Lindemann's criterion in any way. T.E, a problem not in that, "why crystals melt?", and in that "why crystals melt only in the limited range of temperatures, and at other temperatures at once pass into gas, passing a liquid phase?"

The third fact contradicting Lindemann's criterion is an existence of abnormal substances, for example waters, tin, etc. Anomaly consists that density of a liquid phase at a temperature of melting is higher, than density firm a phase. I.e., distances between neighbors decreases, and interaction falls. And the last that we will note that water and some other substances in some area have a negative inclination of the line of melting, i.e. at increase in pressure temperature of melting doesn't increase as at the majority of substances, and decreases. So for water, with a normal pressure of $tpl = 0^{o}$ with, and with a pressure of 209 MPas, $tpl = -22^{o}$ C [12]. I.e., again, at reduction of distance between the next atoms of force of atomic communications decrease.

All listed disagreements of the modern molecular theory easily are removed, within the molecular and photon hypothesis stated by authors [13]. Really, it is known that all atoms at a temperature above absolyutnony zero radiate thermal waves, or thermal photons. In too time from works of classics it is known that electromagnetic radiation puts mechanical pressure and except pressure put randomly facing gas molecules according to MKT, it is necessary to consider also pressure upon molecules of gas of randomly radiated thermal photons [14]. Besides, it is necessary to consider that thermal photons, actually represent the electromagnetic field extending in space. In turn intermolecular communications have the electromagnetic nature. Thermal photons not only make mechanical impact on molecules, but also influence in touch molecules among themselves, at sufficient intensity, reducing molecular communications.

For effective participation of thermal photons in behavior of heated bodies and gases, two conditions are necessary: first, vigor of thermal photons which depends on heating temperature, and secondly, the increased density of molecules of the thermal photons perceiving influence. Thus intensity of an electromagnetic field directly depends on energy of photons, i.e. the energy of photons is higher, the intensity of an electromagnetic field reducing potential forces of interaction of molecules is stronger. At temperature increase energy of photons increases, so, increases, not only mechanical pushing apart between molecules, at the expense of pressure of electromagnetic radiation, but also force of intermolecular communications goes down.

On the other hand, the increase in pressure leads to temperature increase that obviously says that except kinetic energy which the modern molecular theory recognizes as the only basis of warmth, it is necessary to recognize also potential energy of molecules as a component of thermal energy. Increase of pressure leads to increase in density of molecules, and increase in density in turn, leads to compression of a molecular lattice which interferes with the radiation of thermal photons outside, thermal photons are locked within a molecular lattice. From temperature increase and pressure unusual properties of a fluid are explained by this double effect. When at temperatures above critical density of gas becomes higher, than the liquid density, but gas isn't condensed in liquid, and continues to keep properties of the gas having almost untied molecules. Gas passes into a condition of molecular and photon gas.

The phenomenon of a liquid state is explained by that only in limited limits molecular and photon substance can exist in a coherent state. At a temperature below a threefold point photons are too weak, poorly electromagnetic field weakening molecular communications is more exact. And at high temperature, above critical, the weakening action of an electromagnetic field of thermal photons so strongly that completely suppresses all molecular communications and molecules

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are absolutely free, even at the density of the liquid exceeding density.

The additional researches conducted by authors allow to judge that entering into the molecular theory of gases not only potential energy of interaction of molecules as it is made in Van der Waals's theory, but also molecular and photon interactions, behavior prediction accuracy in critical area in comparison with Van der Waals's theory of such substances as water and hydrocarbons allows to raise.

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