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Justification of Provisions of Thermodynamics by Methods of Differential Geometry of Multidimensional Spaces

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Abstract: The researches in axiomatization of thermodynamics are especially urgent because the thermodynamics is a basis of many physical sciences. This science possesses the universal theory with high capacity for development and opportunities for application of her method in other scientific areas. Development of axiomatic approaches in thermodynamics is an important problem when studying difficult systems. In this study the ways of the axiomatic theory creation in classical thermodynamics are considered using the mathematical methods of differential geometry. Advantages of geometry is obvious: presentation, clearness and explanation of many concepts and provisions. Researches in this direction allow to formulate new approach for creation of the deductive theory and to open the geometrical content in the basic thermodynamics concepts: entropy, energy, enthalpy, thermodynamic potentials, etc. Some results of the executed researches are given.

Key words: Axiomatics, thermodynamics, entropy, energy, geometrical justification of provisions of thermodynamics, opportunities

INTRODUCTION

The axiomatic method is one of the ways of deductive creation of scientific theories. In thermodynamics process of science axiomatization has been lasted for more than 100 years and intended to determine the basic concepts, establish the regularities and fundamental laws.

The analysis of the references devoted to a problem of axiomatization of thermodynamics has shown that the amount of works based on geometrical representations of multidimensional thermodynamic spaces isn't enough. This direction of researches is presented by Falk and Jung (1959) articles most of all and partially by Caratheodory (1964) and Mlodzeevsky (1956)'s research. However, today it is not clear how to represent thermodynamic processes and objects by spatial geometrical structures and relations. Methods of differential geometry allow to formulate axiomatic approaches to fundamentals of thermodynamics using the geometrical description of space of conditions of thermodynamic systems and to receive new data on content of thermodynamic values.

The purpose of this article is to enquire the opportunity of applying the methods and instruments of differential geometry for the creation of nonconventional system for representation of thermodynamic provisions based on geometrical models of conditions, processes and ratios.

SOME EXISTING SYSTEMS OF EXPOSITION OF THERMODYNAMIC FUNDAMENTALS

There are two main systems of exposition of thermodynamic fundamentals. Traditional Klauzius's approach is usually criticized for too close connection with processes of thermal machine operations, inconsistency of some provisions and short expression of a mathematical formalism (Falk and Jung, 1959; Caratheodory, 1964; Gukhman, 1986; Afanasyeva-Erenfest, 1928; Frankfurt, 1964; Born, 1964). Disadvantages of other system offered by Caratheodory (1964) are abstractness and formally mathematical approach to setting of thermodynamic concepts. It doesn't correspond to style of thermodynamic researches and breaks physical clarity and simplicity of basic provisions.

The problem of axiomatization of entropy doctrine is considered one of the most important directions in improvement of thermodynamic theory. It is showed that according to axiomatic Caratheodory's approach the energy conservation law for many parameters can be represented by differential Pfaff equation in the form:

$$dQ = P_1(z_1, z_2, \ldots, z_n)dz_1+\ldots+P_n(z_1, z_2, \ldots, z_n)dz_n$$

Where:
Q = Quantity of heat
z_k = System parameters and values
$P_k(z_1, \ldots, z_n)$ = Functions of these parameters

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This statement proceeds from logical and mathematical structure of the energy conservation law. Caratheodory postulated the principle of adiabatic unattainability in the form of universal property of all physical systems and has proved justice of the theorem. There are points in the vicinity of any point in the n-dimensional space which are not achievable without disturbance of the adiabatic equation dQ = 0. Then, this equation is holonomic and the integrating divider for it exists (Caratheodory, 1964). Further, Caratheodory shows that an equation divider for elementary quantity of heat is absolute temperature in the form of universal function of empirical temperature. He defined the general integral of the Pfaff equation for quantity of heat in a differential form as entropy of the system, ds = dQ/T. In this axiomatic version of exposition of thermodynamic fundamentals the problem of justification of entropy's existence is solved (Gukhman, 1986).

At formulation of axiomatic theory on the basis of linear differential forms Falk and Jung (1959) proceeded from judgment that classical creation of thermodynamics is not really strict and doesn't conform to the requirements of an axiomatic method. They paid attention to the fact that the equation of the energy conservation law in the form dQ = du+dA belongs to processes but not to conditions. It is about functions on variety of curves which arguments are curves of spaces of conditions. According to this statement, authors come to an important conclusion that the formulation of the first law of thermodynamics is closely connected with a concept of continuous space of conditions of thermodynamic systems. Falk and Jung followed on the way of new creation of the theory which is based on using the regularities of linear differential forms in multidimensional continual spaces. However, their axioms are also not apparent and don't obviously follow from experience. Nevertheless, they have offered geometrical approach to axiomatization of thermodynamics based on the theory of linear differential forms for the first time.

GEOMETRICAL REPRESENTATION OF THERMODYNAMIC PROBLEMS

One of the approaches in a solving of thermodynamic axiomatization problem is based on a geometrical formalism. It assumes representation the space of conditions of thermodynamic systems in the form of continuous multidimentional space (continuum). Apart from that the possibility of setting the quantity of heat Q(M) in each point of the space is postulated in the form of the continuous scalar field of an empirical measure depending on state parameters (Shevtsova *et al*., 2016; Averin, 2014; Averin *et al*., 2016; Zviagintseva, 2016). In addition, in the vicinity of any point M the axiom which allows to present communication between the quantity of heat and analytic function of temperature $T = T(z_1, z_2, \ldots, z_n)$ in any process 1 is accepted. This function of temperature can be determined as absolute temperature in the form $dQ = c_l \cdot dT$. For reasonable setting a type of function of temperature $T = T(z_1, z_2, \ldots, z_n)$ the connection between this value and empirical temperature t = t(M) is established. Each thermodynamic state is unambiguously characterized by this connection. Geometrical representation of judging problem in differential geometry of multidimensional spaces can be described in the following way.

Let's create geometrical n-dimensional space of variables for parameters of properties of a thermodynamic system Ω^n where $z = (z_1, z_2, \ldots, z_n)$, z_k in Ω^n. Points of this space correspond to n-dimensional sets of values of all variables $z_1, z_2, \ldots, z_n$. Thus, the condition of any object in n-dimensional space at each moment will be displayed by a multidimensional point $M = M(z_1, z_2, \ldots, z_n)$. Process of changing of an object condition in time is a multidimensional curve which is described by this point M in space Ω^n. The set of conditions of any substance can be presented by some multidimensional domain in this space. The processes of changing of conditions of this substance are the curves lying in the field. Domains of conditions correspond to a set of substances and series of curves to the same processes.

The basic principles using at geometrical axiomatization of classical thermodynamics are included in the following researches by Averin (2014), Averin *et al*. (2016) and Zviagintseva (2016).

The continual principle of representation of numerical information in space Ω^n is put in the basis of using methods. According to this principle environment in the form of multidimensional space of parameters of properties is considered continuous, unstructured. And each element of space is connected with all next elements taking into account the regularities common to the studied subject domain. It allows to consider thermodynamic dependences and available experimental data described by them as any selection of the continuous environment of an infinite set of thermodynamic conditions.

The second principle is based on a hypothesis that thermodynamic data, dependences and equations of conditions create some geometrical images in continual space a condition point, a process curve, a surface of a set of conditions or the scalar field of thermodynamic value. These images can be presented in the form of multidimensional geometrical models. For this purpose, we consider that some empirical measure W set to correspondence with each state (each point M). W is the value which characterize the object state in a complex. This value in general unambiguously characterizes a thermodynamic condition and depends on parameters of attributive properties z_1, z_2, ..., z_n.

The third principle is concerned with a possibility of statistical modeling and description of conditions, the equations of conditions and processes in geometrical space of variables on the basis of available thermodynamic dependences received in experience.

The fourth principle defines a possibility of the phenomenological description of an empirical measure field in geometrical space Ω^n using the modeling functions. In relation to continual space Ω^n it is possible to formulate some axioms which allow to construct models of continual space of conditions based upon the available experimental data.

We associate with each point M in the space of conditions of system Ω^n a real number W which we will call an empirical measure of an observed condition. The value W(M) is point function and forms the scalar field which is continuous in the field Ω^n.

Let's assume that in the field Ω^n. it is possible to set an analytic continuous function $T = T(z_1, z_2, ..., z_n)$. We will create the mathematical model on the basis of this function. If we know the type of function $T = T(z_1, z_2, ..., z_n)$ and values of variables $z_1, z_2, ..., z_n$ in the field Ω^n it is possible to construct one more scalar field which we will call the simulation environment. For creation the phenomenological model in general we will formulate the following axiom.

Let's suppose that in space of system conditions Ω^n. scalar fields of values W and T are unambiguously related to one another. If in the vicinity of any point M some process of l is carried out, then for the line of process the relation $dW = c_l \cdot dT$ is valid where c_l are empirical values which are functions of process and defined in experience. Similar approach allows to receive Pfaff equation for the description of any process l in geometrical continual space in the following form:

$$dW = c_1 \cdot \left(\frac{\partial T}{\partial z_1}\right) dz_1 + c_2 \cdot \left(\frac{\partial T}{\partial z_2}\right) + ... + c_n \cdot \left(\frac{\partial T}{\partial z_n}\right) dz_n,\ c_k = \left(\frac{\partial W}{\partial T}\right)_{z_1, z_{k-1}, z_k, ..., z_n} \quad (1)$$

Values c_k generally can depend on parameters of properties. Equation 1 represents a Pfaff differential form which in mathematical expression can be holonomic or nonholonomic.

In turn value T in the field Ω^n can be represented concerning parameters of properties in the form of various functional dependences in the classes of uniform or multiplicative functions. It is established by researchers by Averin (2014), Averin *et al*. (2016) and Zviagintseva (2016) that under these requirements in space Ω^n for creation the geometrical models of data description it is possible to use the quasilinear multidimensional equations in private derivatives of the first order which are closely connected with Pfaff equations of a form (1). Such approach allows to apply the methods of solution the multidimensional equations in private derivatives of the first order based on the theory of characteristic functions and to prove the following theorem. Entropy in thermodynamic representation is an arc length of the characteristic for the directional field. And this field is generated by the scalar field of empirical measure of condition W.

All it enables to analyze the thermodynamic fundamentals in another way because it gives the chance to formulate the principles of entropy's and energy's existence as state functions. It also permits to receive the energy conservation law and the law of increasing entropy as investigations for multidimensional thermodynamic systems in the form taken for today (Averin, 2014, 2015).

GEOMETRICAL MODELS OF PERFECT GAS IN THERMODYNAMICS

The main equations of perfect gas are represented by simple and evident dependences as reliant on two variables pressure p and specific volume υ. Let's analyze the multidimensional thermodynamic system in general case and receive dependences for perfect gas. In work (Averin, 2014), it is shown that in the vicinity of any point M in a space of conditions Ω^n the integrating divider for Eq. 1 is existed in the form of function of absolute temperature. It is represented as a product of functions depending on parameters $T = \phi_1(z_1)\cdot, ..., \cdot \varphi_n(z_n)$ and turns this equation into total differential. At the same time the general integral of Eq. 1 is state function of entropy in a form:

$$ds = \frac{dW}{T} = c_1 \cdot \frac{\phi_1'(z_1)}{\phi_1(z_1)} dz_1 + c_2 \cdot \frac{\phi_2'(z_2)}{\phi_2(z_2)} dz_2 + ... + c_n \cdot \frac{\phi_n'(z_n)}{\phi_n(z_n)} dz_n \quad (2)$$

Let's receive the differential equation for the description of the scalar field of an empirical measure. From the relation $T = \varphi_1(z_1)\cdot, ..., \cdot\varphi_n(z_n)$ in the vicinity of point M we have following dependences:

$$\frac{\partial T}{\partial z_k} = \frac{\phi_k'(z_k)}{\phi_k(z_k)} \cdot T \text{ and } \frac{1}{c_k}\left(\frac{\partial W}{\partial z_k}\right) = \frac{\phi_k'(z_k)}{\phi_k(z_k)} \cdot T \text{ because } \frac{\partial W}{\partial z_k} = c_k \cdot \left(\frac{\partial T}{\partial z_k}\right) \quad (3)$$

By summing relations (Eq. 3) we will receive the linear non-uniform differential equation in private derivatives of the first order:

$$\frac{\phi_1(z_1)}{c_1 \cdot \phi_1'(z_1)}\left(\frac{\partial W}{\partial z_1}\right)+\frac{\phi_2(z_2)}{c_2 \cdot \phi_2'(z_2)}\left(\frac{\partial W}{\partial z_2}\right)+\ldots+\frac{\phi_n(z_n)}{c_n \cdot \phi_n'(z_n)}\left(\frac{\partial W}{\partial z_n}\right)=n \cdot T \quad (4)$$

Generally, the solution to Eq. 4 is carried out by method of characteristics (Elsgolts, 1969) which are defined by system of the ordinary differential equations:

$$ds = n \cdot c_1 \cdot \phi_1'(z_1)\frac{dz_1}{\phi_1(z_1)} = n \cdot c_2 \cdot \phi_2'(z_2)\frac{dz_2}{\phi_2(z_2)} = \ldots = n \cdot c_n \cdot \phi_n'(z_n)\frac{dz_n}{\phi_n(z_n)} = \frac{dW}{T} \quad (5)$$

where, s is the parameter which is entropy in representation (Eq. 2). If we add all summands by Eq. 5 except the last, then we will receive exactly the Eq. 2.

It is known that for Eq. 4 characteristics are defined by system (Eq. 5). The set of surfaces which are orthogonal to these characteristics can be obtained from a scalar product of vector:

$$\vec{F} = \frac{\phi_1(z_1)}{c_1 \cdot \phi_1'(z_1)}e_1 + \frac{\phi_2(z_2)}{c_2 \cdot \phi_2'(z_2)}e_2 + \ldots + \frac{\phi_n(z_n)}{c_n \cdot \phi_n'(z_n)}e_n$$

and unit vector:

$$e = e_1 \cdot dz_1 + e_2 \cdot dz_2 + \ldots + e_n \cdot dz_n = 0$$

exactly $(\vec{F} \cdot e)=0$. The last relation can be presented in expanded form of multidimensional Pfaff equation:

$$\frac{\phi_1(z_1)}{c_1 \cdot \phi_1'(z_1)}dz_1 + \frac{\phi_2(z_2)}{c_2 \cdot \phi_2'(z_2)}dz_2 + \ldots + \frac{\phi_n(z_n)}{c_n \cdot \phi_n'(z_n)}dz_n = 0 \quad (6)$$

At original hypotheses this equation will be total differential. Therefore, there is a potential $P(z_1, z_2, \ldots, z_n) = C$ of space of conditions Ω_n which can be represented as a set of surfaces which are orthogonal to lines of entropy. For some types of functions of an absolute index it is possible to receive simple functions of potential. For example, for perfect gas we present an absolute temperature for two parameters of properties in the form $T = \phi_1(z_1) \cdot \phi_2(z_2) = z_1 \cdot z_2 / R_i$ and accept $z_1 = \upsilon$; $z_2 = p$ and $c_1 = c_p$; $c_2 = c_\upsilon$. Then entropy and potential will be, respectively equal:

$$s - s_0 = c_p \cdot \ln\left(\frac{\upsilon}{\upsilon_0}\right) + c_\upsilon \cdot \ln\left(\frac{p}{p_0}\right); \; P - P_0 = \frac{1}{2}\left(\frac{\upsilon^2 - \upsilon_0^2}{c_p} + \frac{p^2 - p_0^2}{c_\upsilon}\right) \quad (7)$$

Let's consider the value $du = c_\upsilon \cdot dT$ which we will determine as change of energy of perfect gas. Energy du is total differential because value dt is total differential by definition. Let's accept the quantity of heat Q as an empirical measure and represent this value dQ = T·ds using the energy conservation law:

$$dQ = du^* + P \cdot d\upsilon, \; du^* = \frac{c_p - R_i}{R_i} \cdot p \cdot d\upsilon + \frac{c_\upsilon}{R_i} \cdot \upsilon \cdot dp \quad (8)$$

where, u^* is any value. Let's assume that du is total differential, then by applying Euler criterion, it is possible to show that du_* is a total differential under requirement: $c_p - c_\upsilon = R_i$. The last relation presents the known Maier equation for perfect gas at which justice value du^* identically equals du:

$$du^* = du = \frac{c_\upsilon}{R_i} d(p \cdot \upsilon) = c_\upsilon \cdot dT \quad (9)$$

Thus, Eq. 8 is represented by energy of perfect gas in the form:

$$dQ = du + p \cdot d\upsilon \quad (10)$$

If we do not impose severe constraints on interrelation of values cp, cu and r then value du^* won't be a total differential. It is quite natural that on the basis of experimental data it is necessary to show justice of the following provision: for all definitional range of conditions of real gases with low pressure Maier equation is always carried out. However, thermodynamic experimental data indicates that for real gases this relation can be used only as the approximate equation. In the theory of ideal gas usually the requirement $c_p - c_\upsilon = R_i$ strictly holds. So, some abstract model of ideal gas is put into practice. Only conditions of simple gases with low pressure correspond to this model.

INTERRELATION OF ENTROPIES AT THE DESCRIPTION OF IDEAL GAS CONDITIONS

Thus, depending on the type of empirical measure, it is possible to prove the principle of entropy's existence and to offer different types of entropy of thermodynamic system's condition. Entropy is characteristic function of space of system's condition and the general integral of the corresponding Pfaff (Eq. 1). It is possible to look for

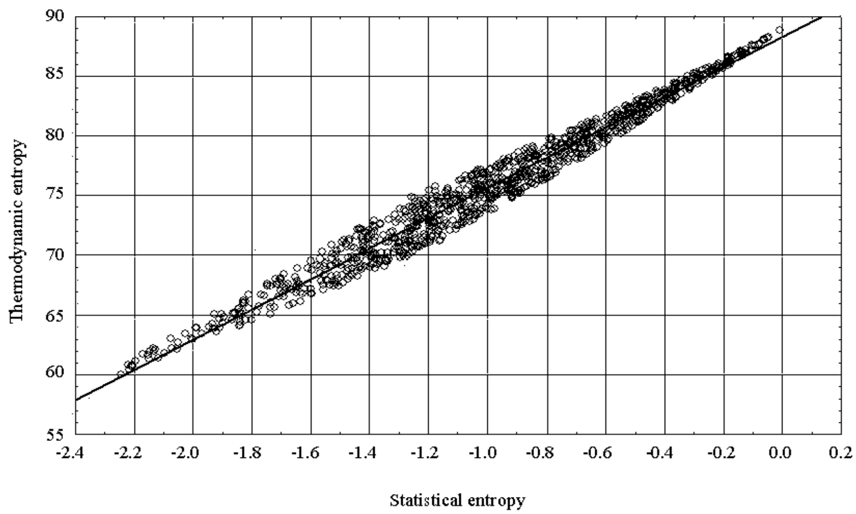

Fig. 1: Interrelation of thermodynamic entropy s_t and statistical entropy $s_w = \ln(w)$ for hydrogen's conditions

interrelations in the form of regression dependences between various integrals of Pfaff equation. This gives the chance to find statistical entropy, proceeding from an assessment of probability of joint events connected to observation of indicators of ideal gas condition pressure and specific volume.

Therefore, if two various empirical measures are set to correspondence with the same thermodynamic system's condition it is possible to define different types of entropy, for example, thermodynamic and statistical entropy. And according to skilled data we can establish connection between them. At determining statistical entropy as the complex characteristic of thermodynamic system's condition we will consider a joint event of synchronous observation of specific volume's indicators and pressure's indicators of ideal gas. We will assume geometrical probability of this joint event's observation w as an empirical measure W. It is known that the corresponding geometrical probabilities w are defined by the ratio of rectangle's area which is formed by an observed point (a condition with predetermined specific volume and pressure of ideal gas) to whole geometrical rectangular area. In this area the chosen gas submits to laws of ideal gas.

Also, if we know hydrogen's parameters given to perfect condition it is possible to define thermodynamic entropy of gas condition. Let's use the tables of thermodynamic properties of gases for this purpose (Rivkin, 1987). At formation of these tables it was supposed that gas submits to the equation of ideal gas:

$$p \cdot \upsilon = R_i \cdot T$$

where, R_i an individual gas constant. Value of gas entropy is defined by expression:

$$s_t = \int_0^T \frac{c_p dT}{T} - R \cdot \ln p = s^0 - R \cdot \ln p \qquad (11)$$

Precision of tables of gase's thermodynamic properties in the temperature range from -50 to 1500°C is 0.5%. For hydrogen this range approximately corresponds to ranges of pressure's changing from p_{min} = 80 kPa to p_{max} = 280 kPa and specific volume's changing from υ_{min} = 9 to υ_{max} = 9 m^3/kg. At modeling by thermodynamic parameters of hydrogen it is possible to determine statistical entropy in the form of $S_w = k \cdot \ln(w)$, where k is any coefficient.

On the basis of skilled data, using methods of the regression analysis, let's receive the relation equation between thermodynamic and a statistical entropies of hydrogen's conditions in a form:

$$s_t = 88.268 + 12.659 \cdot s_w \qquad (12)$$

Here, entropy is defined by Eq. 11 and data of tables (Eq. 14) and $s_w = \ln(w)$. In turn the corresponding relation equation between entropies of nitrogen's conditions will be a form:

$$s_t = 8.708 + 1.001 \cdot s_w \qquad (13)$$

Correlation coefficients of Eq. 12 and 13 equal to 0.99, results of the regression analysis are given on Fig. 1. The executed analysis shows that for any ideal gas dependence between thermodynamic and a statistical entropies has a form $s_t = \alpha + b \cdot s_w$ where coefficients a and b have the special values for each ideal gas.

Upshots: While constructing the axiomatics of thermodynamics using of geometrical ideas of space of conditions of thermodynamic systems in the form of the continuous multidimensional environment is also extremely important. If we consider parameters of a system's condition as the Cartesian coordinates, the similar geometrical environment can be presented in the form of continual space of n-measurements. This space will have certain regularities which are characterized by Pfaff equations for certain physical value.

CONCLUSION

Thus, entropy is characteristic function of a system's condition and geometrically represents as an arc length of the vector line of a gradient of the scalar field of an empirical measure. Potential is a level surface which is orthogonal to vector lines. In case of justice of the hypotheses accepted above, for any thermodynamic system the law can be formulated which is a multidimensional analog of the energy conservation law in essence. At the same time the amount of energy is the mathematical function connected to absolute temperature and presenting an empirical measure in the form of the additive sum. Also, according to empirical measure different types of entropy of thermodynamic system's condition can be offered. For example, it is shown that for various conditions of ideal gas close relations between thermodynamic and a statistical entropies are existed. Such connections point out at certain similarity of these values.

At the same time K. Caratheodory's principle of "adiabatic unattainability" can be considered as a result of existence of some value in multidimensional space of conditions of the scalar field. Proceeding from it, the idea of geometrical axiomatization of thermodynamics appears. And so representation the thermodynamic models objects, structures and relations by differential geometry are possible.

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