Thermodynamic and gas-dynamic entropy. Entropy as a functional and a state function

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ABSTRACT - *In present paper the entropy, which is a state functional of thermodynamic and gas-dynamic systems, is studied. In this case the state of thermodynamic system describes the entropy, which depends of the thermodynamic variables, and the state of gas-dynamic describes the entropy, which depends on the space-time variables.*

Keywords - Entropy, the state functionals, skew-symmetric forms, principles of thermodynamics, phase transitions, the state of gas-dynamic system

1. INTRODUCTION

Material systems (material media) such as the thermodynamic, gas-dynamic, cosmic systems and others are specified by such physical quantities like energy, velocity, pressure, and density. One more quantity that specifies the change of the material system state is necessary.

The material system state depends on the interaction of physical quantities between which a certain connection has to exist since they refer to a single material system. A quantity that must describe the change of material system state has to be a functional (in contrast to physical quantities, which are functions) since it describe the interaction of physical quantities, namely, the interactions of functions. For various material systems the action functional, entropy, Pointing's vector, Einstein's tensor, wave function and others are examples of such functionals.

The specific feature of such functionals is the fact that, under additional conditions (conditioned by some degrees of freedom) the state functions are realized from such functionals. This describes a transition of material system from non-equilibrium state into a locally-equilibrium state. The state and the change of the material system states depend on the interaction between conservation laws which appear to be noncommutative.

The analysis of the consistence of the conservation law equations enables to disclose the mechanism of interaction of the conservation laws and to understand a physical meaning of functionals (the state functionals) describing the material system states.

Such results have been obtained by using skew-symmetric forms [1]. In addition to exterior forms, the skew-symmetric forms, which are obtained from differential equations and, in distinction to exterior forms, are evolutionary, were used.

In present paper, the entropy, which is a functional of the state of thermodynamic and gas-dynamic systems, is studied.

2. THERMODYNAMIC ENTROPY

The thermodynamics is based on the first and second principles of thermodynamics that were introduced as postulates [2].

The first principle of thermodynamics can be written as [2]: $dE + \delta w = \delta Q$, where dE is the change of energy of the thermodynamic system, δw is the work done by the thermodynamic system (this means that δw is expressed in terms of the system parameters), δQ is an amount of the heat influx into the system (i.e. the external action onto the system). Since the term δw can be expressed in terms of the system parameters and specifies an actual (rather than virtual) change, it can be designated by dw, and hence, the first principle of thermodynamics takes the form

$$dE \,+\, dw \,=\, \delta Q \tag{1}$$

[Here, it should be called attention to the fact that relation (1) includes the term dE, which describes the energy variation, and the term dw describing the work. This points out to the fact that the first principle of thermodynamics is not a conservation law for energy since it includes the work dw. The first principle of thermodynamics follows from two conservation laws, namely, the conservation law for energy and the conservation law for linear momentum, and it describes the interaction of these two laws, which appear to be noncommutative and, as it will be demonstrated below, its interaction defines the change of the system thermodynamic state.]

It is known that the change of the thermodynamic system state is described by entropy. In this case, if the entropy change is a differential, this means that there exists a state function, and this points out to the fact that the thermodynamic system state is a equilibrium one.

The change of the thermodynamic system parameters on which the thermodynamic system state depends is described by the left-hand side of relation (1), i.e. by the expession $dE \,+\, dw$. Because of this, to understand what is the entropy change, one has to investigate the expression $dE \,+\, dw$.

The expression $dE \,+\, dw$ is a differential skew-symmetric form. This form may be a differential if it is a closed exterior form. In this case the differential of this form must be equal to zero. (It is known that the differential of a differential, namely, the differential of a closed form, is equal to zero.)

From relation (1) it follows that

$$d(dE \,+\, dw) = d\,\delta Q \,\neq 0 \tag{2}$$

That is, the form $(dE \,+\, dw)$ is not a differential.

From this it follows the the entropy change is not a differential.

If the entropy differential were exist, this would mean that the entropy is a state function. And this would point out to the fact that the thermodynamic system state is a equilibrium one. The absence of the entropy differential (in this case the entropy is a functional) means that the thermodynamic system is in a non-equilibrium state.

In this case it is evident that the reason of the non-equilibrium state is an internal force which magnitude is defined by following relation

$$d\,\delta Q \neq 0 \qquad\qquad (3)$$

(If would be $d\,\delta Q = 0$, then the entropy differential would exist, and this will point out to a equilibrium, without internal force, state of thermodynamic system.) A quantity that acts as an internal force can grow. It is a reason of the instability development in the thermodynamic system.

The nonequilibrium is caused by the fact that the heat influx into the system, which are not potential ones, cannot be directly converted into the physical quantities of thermodynamic system and made up a nonmeasurable quantity that just acts as an internal force.

Thus one can see that from the first principle of thermodynamics it follows that the thermodynamic system exposed to heat actions turns out to be in a non-equilibrium state. However, as it will be shown below, from the first principle of thermodynamics it follows that the thermodynamic system can change to the locally equilibrium state.

The non-equilibrium state of thermodynamic system can change under the action of internal force. To this case it corresponds a self-variation of relation (1). Under this changing the relation (1), it can be realized the conditions of degenerate transformation (a transformation with nonconservation differential) when from the nonvanishing differential $d(dE + dw) = d\,\delta Q \neq 0$ (see, formula (2)), one obtains a differential that is exterior, being true only at given conditions, the example of which is an integrating factor. This describes the transition of thermodynamic system from the non-equilibrium state to locally-equilibrium one.

Let us consider the case when the work performed by the system is carried out through the compression. Then $dw = p\,dV$ (here p is the pressure and V is the volume) and $dE + dw = dE + p\,dV$. As it is known, the form $dE + p\,dV$ can become a differential if there is the integrating factor θ (a quantity which depends only on the system parameters), where $1/\theta = pV/R$ is called the temperature T [2]. (That is, the temperature $T = pV/R$ is realized).

In this case it is realized the differential form $(dE + p\,dV)/T$ that turns out to be a differential. Really, if to substitute the value of temperature into the second term, one obtains the expression $(dE + p\,dV)/T = dE/T + RdV/V$, which can be integrated since the energy depends only on the temperature. And this means that the differential form $(dE + p\,dV)/T$ turns out to be a differential.

The realization of differential form $(dE + p\,dV)/T$ means that the entropy differential is realized. But this differential is interior one that is valid only at availability of integrating factor $1/T$.

Thus, if the integrating factor $\theta = 1/T$ has been realized, then from relation (1), which corresponds to the first principle of thermodynamics, it follows that it is realized the entropy differential:

$$dS_T = (dE + p\,dV)/T = \delta Q/T \qquad (4)$$

This means that it is obtained the relation which corresponds to the second principle of thermodynamics:

$$dS_T = \delta Q/T \qquad (5)$$

The realization of the differential of entropy S_T points to the fact that entropy S_T becomes a state function and the thermodynamic system transforms to a locally-equilibrium state. (It should be emphasized that the total state of thermodynamic system remains to be nonequilibrium, and this fact follows from the first principle of thermodynamics).

The transition to a locally-equilibrium state (under realization of integrating factor or other integrating conditions caused by any degrees of freedom) relates to the transition of nonmeasurable quantity (see (3)), which acts as an internal force, to the characteristics of the thermodynamics system itself. The phase transitions, origination of any formations such as fluctuations are examples of this phenomenon.

(Relation (5), which corresponds to the second principle of thermodynamics, takes place when the heat influx is the only action onto the system. In the case when the system experiences a certain mechanical action, in the right-hand side of relation (5) it may appear the term related to the mechanical action. In this case the condition of degenerate transformation, in particular, the integrating factor may not be realized. In this case the entropy proves to be a functional rather than a state function.)

Thus, the first principle of thermodynamics follows from the conservation laws for energy and linear momentum, and the second principle of thermodynamics follows from the first one under the fulfillment of the condition of integrability, i.e. a realization of the integrating factor (the inverse temperature).

Here it should be emphasized that *the second principle of thermodynamics, unlike the first principle of thermodynamics, fulfills only discretely, namely, only under realization of integrating factor.*

In the case examined above a differential of entropy (rather than entropy itself) becomes a closed form. In this case entropy manifests itself as a thermodynamic potential, namely, a function of state.

For entropy to be a closed form itself, i.e. a conservative quantity (the differential of closed form is equal to zero), one more condition has to be realized. Such a condition could be a realization of the integrating direction, an example of that is the speed of sound: $a^2 = \partial p/\partial \rho = \gamma\,p/\rho$. In this case it is valid the equality $ds = d(p/\rho^\lambda) = 0$ from which it follows that entropy $s = p/\rho^\lambda = $ const is a closed form (of zero degree). [However this does not mean that a state

of the gaseous system is identically isoentropic. Entropy is a constant only along the integrating direction (for example, on the adiabatic curve or on the front of the sound wave), whereas in the direction normal to the integrating direction the normal derivative of entropy has a break].

Under realization of the integrating direction the transition from the variables E, V to the variables p, ρ is a degenerate transformation.

It worth underline that both temperature and the speed of sound are not continuous thermodynamic variables. They are variables that are realized in the thermodynamic processes if the thermodynamic system has any degrees of freedom. One can see the analogy between the inverse temperature and the speed of sound: the inverse temperature is the integrating factor and the speed of sound is the integrating direction.

A closed static system, if left to its own devices, can tend to a state of total thermodynamic equilibrium. This corresponds to tending the system functional to its asymptotic maximum. In the dynamical system the tending of the system to a state of total thermodynamic equilibrium can be violated by dynamical processes and transitions to a state of local equilibrium.

3. GAS-DYNAMIC ENTROPY

Above we analyzed the peculiarities of entropy as a functional and a state function of thermodynamic system. Such entropy depends on the thermodynamic variables. Entropy is also a functional and a state function of gas-dynamic system. However, in this case it depends on the space-time variables. In the gas-dynamic system the thermodynamic entropy characterizes only *the state of a gas* rather then the state of gas-dynamic system itself. Below we will consider the simplest case, namely, a flow of ideal (inviscous, heat nonconductive) gas.

Assume that the gas is a thermodynamic system in the state of local equilibrium (whenever the gas dynamic system itself may be in non-equilibrium state), that is, the following relation is fulfilled [2]:

$$Tds \,=\, de \,+\, pdV \qquad (6)$$

where T, p and V are the temperature, the pressure and the gas volume, s and e are entropy and internal energy per unit volume. The entropy s in relation (6) is a thermodynamic state function and depends on the thermodynamic variables. For the gas dynamical system the thermodynamic state function describes only the state of the gas-dynamic element (a gas particle).

Further we introduce two frames of reference: the first is an inertial one and the second is an accompanying one that is connected with the manifold made up by the trajectories of elements of a gas-dynamic system. (The Euler and Lagrangian coordinate systems can be regarded as examples of such frames of reference.)

In the inertial frame of reference the equation of conservation law for energy of ideal gas can be written as [3]

$$\frac{Dh}{Dt} - \frac{1}{\rho}\frac{Dp}{Dt} \,=\, 0 \qquad (7)$$

where D/Dt is the total derivative with respect to time. Here $\rho = 1/V$ and h are respectively the density and enthalpy of the gas.

By expressing the enthalpy in terms of internal energy e with the help of formula $h = e + p/\rho$ and using relation (6), the equation (7) can be reduced to the form

$$\frac{Ds}{Dt} = 0 \tag{8}$$

Since the total derivative with respect to time is that along the trajectory, in the accompanying frame of reference (that is connected with the manifold made up by the trajectories of the system elements) equations (8) take the form:

$$\frac{\partial s}{\partial \xi^1} = A_1 \tag{9}$$

where ξ^1 is the coordinate along the trajectory. For ideal gas $A_1 = 0$ (see equation (8)). [In the case of viscous heat-conducting gas described the Navier-Stokes equations the expression A_1 can be written as (see [3])

$$A_1 = \frac{1}{\rho}\frac{\partial}{\partial x_i}\left(-\frac{q_i}{T}\right) - \frac{q_i}{\rho T}\frac{\partial T}{\partial x_i} + \frac{\tau_{ki}}{\rho}\frac{\partial u_i}{\partial x_k}$$

Here q_i is the heat flux and τ_{ki} is the viscous stress tensor.]

In the accompanying frame of reference the equation of conservation law for linear momentum can be presented as [3]

$$\frac{\partial s}{\partial \xi^\nu} = A_\nu \tag{10}$$

where ξ^ν is the coordinate in the direction normal to the trajectory. [In the case of two-dimensional flow of ideal gas one can obtain the following expression for the coefficient A_ν [3]:

$$A_\nu = \frac{\partial h_0}{\partial \nu} + (u_1{}^2 + u_2{}^2)^{1/2}\zeta - F_\nu + \frac{\partial U_\nu}{\partial t}$$

where $\zeta = \partial u_2/\partial x - \partial u_1/\partial y$.]

Equations (9) and (10) can be convoluted into the relation

$$ds = \omega \tag{11}$$

where $\omega = A_\mu d\xi^\mu$ is the first degree skew-symmetric differential form and $\mu = 1, \nu$. (A summing over repeated indices is carried out.)

Since the conservation law equations are evolutionary ones, the relation obtained is also an evolutionary relation. In this case the skew-symmetric form ω is evolutionary one as well.

When describing actual processes, relation (11) turns out to be not identical since the evolutionary form ω is not closed and is not a differential, its commutator is nonzero.

The differential of evolutionary form ω is expressed as $d\omega = \sum K_{1\nu} d\xi^1 d\xi^\nu$, where $K_{1\nu}$ are components of the form commutator. Without accounting for terms that are connected with the deformation of the manifold made up by

the trajectories, the differential of evolutionary form ω will be expressed as $d\omega = \sum K_{1\nu} d\xi^1 d\xi^\nu$, where

$$K_{1\nu} = \partial A_\nu / \partial \xi^1 - \partial A_1 / \partial \xi^\nu \qquad (12)$$

are the components of the form commutator. The coefficients A_μ of the form ω have been obtained either from the equation of the conservation law for energy or from that for linear momentum. This means that in the first case the coefficients depend on the energetic action and in the second case they depend on the force action. In actual processes energetic and force actions have different nature and appear to be inconsistent. The commutator of the form ω constructed of the derivatives of such coefficients is nonzero. Since the commutator of the form ω is nonzero, this means that the differential of the form ω is nonzero as well. Thus, the form ω proves to be unclosed and is not a differential. In the left-hand side of relation (11) it stands a differential, whereas in the right-hand side it stands an unclosed form that is not a differential. Such a relation cannot be an identical one.

The nonidentity of this relation points to the fact that the entropy is a functional since the differential of entropy does not exist.

If from relation (11) the differential of entropy could be obtained, this would point to the fact that entropy is a state function. And this would mean that the state of a gas-dynamic system is a equilibrium one.

But, since relation (7) is a nonidentical relation, from that one cannot obtain the differential of entropy and find the state function. This means that the gas-dynamic system is in a non-equilibrium state.

The nonequilibrium means that in a gas-dynamic system an internal force acts. It is evident that the internal force is described by the commutator of skew-symmetric form ω. (If the evolutionary form commutator be zero, the evolutionary relation would be identical, and this would point to the equilibrium state, i.e. the absence of internal forces.) Everything that gives a contribution into the commutator of the evolutionary form ω leads to emergence of internal force that causes the non-equilibrium state of a gas-dynamic system. (Here, it should be called attention to the fact that the entropy, which enters into the evolutionary relation for a gas-dynamic system, depends on space-time variables rather then on thermodynamical variables like the entropy entered into the thermodynamical relation. The state of gas-dynamic system is characterized by the entropy, which depends on space-time variables. And the entropy that depends on thermodynamical variables characterizes a state of thermodynamic system. In the gas-dynamic system, as it was already noted, the entropy depended on thermodynamical variables characterizes only the state of a gas rather then the state of gas-dynamic system itself.)

The nonidentical evolutionary relation is selfvarying one. This point to the fact that the gas system state changes, but keeps to be nonequilibrium.

It turns out that from nonidentical evolutionary relation it can be obtained identical relation from which one can obtain the entropy differential (this will

point out to the transition of a gas-dynamic system into a locally-equilibrium state). This is possible in the case if from the evolutionary skew-symmetric form ω in the right-hand side of nonidentical evolutionary relation it is realized a closed skew-symmetric form, which is a differential.

But from the evolutionary unclosed skew-symmetric form, which differential is nonzero, one can obtain a closed exterior form with a differential being equal to zero only under degenerate transformation, namely, under a transformation that does not conserve a differential. Degenerate transformations can take place under additional conditions, which are related with degrees of freedom. The conditions of degenerate transformation can be realized under selfvarying of nonidentical evolutionary relation.

Realization of the conditions of degenerate transformation leads to realization of pseudostructure π (the closed dual form) and formatting the closed inexact form ω_π. On the pseudostructure π from evolutionary relation (11) it is obtained the identical relation

$$ds_\pi = \omega_\pi \qquad (13)$$

from which the differential ds_π can be obtained. This means that we have a realization of entropy as a state function of gas-dynamic system, whose availability points to the locally-equilibrium state of the gas-dynamic system.

The realization of gas-dynamic state function (entropy as a function of space-time variables) points out to the transition from the nonequilibrium state to the locally equilibrium one. This process is accompanied by emergence of the gas-dynamic observable formations such as waves, vortices and so on. In this case the quantity, which is described by the commutator of unclosed form ω and acts as an internal force (producing the nonequilibrium system state), defines the intensity of these formations.

One can see that in gas-dynamic system, even in the case of ideal gas, it is possible the origination of formations that lead to emergence of vorticity. (In the case of viscous gas, the evolutionary form commutator will contain the terms related to viscosity and heat conduction. These terms are responsible for emergence of turbulent pulsations.)

4. CONCLUSION

It was shown that the entropy is a functional which describes the state of both thermodynamic and gas-dynamic systems. The state of thermodynamic system is described by entropy that depends on thermodynamic variables, whereas the state of gas-dynamic system is described by entropy that depends on space-time variables. In the gas-dynamic system the thermodynamic entropy characterizes only the state of a gas (element of a gas-dynamic system) rather then the state of gas-dynamic system itself.

The role of entropy in the description of evolutionary processes relates to the fact that the entropy possesses a duality. It can at once be both functionals and state functions. As a functionals it describes the non-equilibrium

state of a medium, and as a function it describes the locally-equilibrium state. The transition from functionals to state functions (under degenerate transformation) decribes the mechanism of phase transitions and origination of various formations such as fluctuations, waves, vortices and others.

[Studying the instability of the thermodynamic and gas-dynamic systems on the basis of the analysis of entropy behavior was carried out in publications by Prigogine and co-authors [4,5].

As it has been shown by Prigogine, the development of instability in thermodynamic systems and the entropy increase in irreversible processes are due to production of so called "excess entropy". (In present paper such "excess entropy" is a quantity which acts as internal force: the quantity $d\,\delta Q \neq 0$ (see (3)) for thermodynamic system and the commutator for gas-dynamic system). However, Prigogine did not showed that the "excess entropy" can convert into measurable parameters of the system itself at phase transitions and, as a result, can lead to emergence of various structures and formations.

Studying the instability gas-dynamic systems on the basis of the analysis of entropy behavior was carried out in publications by Prigogine and co-authors [5]. In their papers the entropy was considered as a thermodynamic function of state (though its behavior along the trajectory was analyzed). By means of such state function one can trace the development (in gas fluxes) of the thermodynamic instability only. To investigate the gas-dynamic instability it is necessary to consider the entropy as a gas-dynamic state function, i.e. as a function of space-time variables.]

5. REFERENCES

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