ON THE LAGRANGE MULTIPLIERS METHOD IN EXTENDED THERMODYNAMICS OF IRREVERSIBLE PROCESSES

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ABSTRACT

In this paper we consider extended thermodynamic theory based on the postulate that entropy density is a function of the internal energy density and its time derivative. Using fundamental equation and the balance equation for the internal energy density, we can write the entropy balance equation and obtain expressions for the entropy flux and the entropy source. Further we consider tools of the rational thermodynamics, namely Lagrange multiplies method. We start from the entropy balance equation (entropy inequality) and suppose that entropy flux and entropy production are functions of the heat flux and heat flux rate. Definitions of the generalized temperature and new intensive quantity as functions of the Lagrange multipliers lead to the fundamental equation (generalized Gibbs equation) and explicit expressions for the entropy flux and entropy production.

INTRODUCTION

Conventional version of extended irreversible thermodynamics [1-5] is based on the postulate that entropy density s is function of the dissipative fluxes. Let us consider the heat conduction in a rigid isotropic body at rest without source term. For the system under consideration

$$s = s(u, \mathbf{q}), \tag{1}$$

where u is the internal energy density, $\mathbf{q}$ the heat flux. In this paper, we consider extended thermodynamic theory [6-9] based on the postulate that the entropy density s is a function of the internal energy density u and time derivative $\dot{u}$:

$$s = s(u, \dot{u}), \tag{2}$$

where $\dot{u} = \partial u/\partial t$ and t is the time. The total differential of the entropy density has the form

$$ds = \frac{\partial s}{\partial u}\, du + \frac{\partial s}{\partial \dot{u}}\, d\dot{u}. \tag{3}$$

Let us define generalized temperature θ and new intensive quantity Λ in analogy with the classical theory:

$$\theta^{-1} = \frac{\partial s}{\partial u}, \qquad \theta^{-1}\Lambda = \frac{\partial s}{\partial \dot{u}}, \tag{4}$$

where $\theta = \theta(u, \dot{u})$ and $\Lambda = \Lambda(u, \dot{u})$ depend on the additional variable $\dot{u}$. Then, the fundamental equation is given by

$$\theta ds = du + \Lambda d\dot{u},$$

and

$$\frac{\partial s}{\partial t} = \theta^{-1}\frac{\partial u}{\partial t} + \theta^{-1}\Lambda\frac{\partial \dot{u}}{\partial t}. \tag{5}$$

The second differential of the entropy density has the form

$$d^2 s = d\theta^{-1}\, du + d(\theta^{-1}\Lambda)\, d\dot{u}. \tag{6}$$

Further, let us postulate the convexity of s as function of u and $\dot{u}$. Then, we have inequality

$$\frac{\partial \theta^{-1}}{\partial t}\frac{\partial u}{\partial t} + \frac{\partial(\theta^{-1}\Lambda)}{\partial t}\frac{\partial \dot{u}}{\partial t} \leq 0. \tag{7}$$

GENERAL THEORY

The balance equations for the variable u,

$$\rho\dot{u} = -\nabla\cdot\mathbf{q}, \tag{8}$$

(ρ is the mass dencity) relates the extra variables $\dot{u}$ and $\mathbf{q}$. Differentiating equation (8) with respect to time leads to the balance equation for the variable $\dot{u}$:

$$\rho\frac{\partial \dot{u}}{\partial t} = -\nabla\cdot\dot{\mathbf{q}}, \tag{9}$$

where $\dot{\mathbf{q}} = \partial\mathbf{q}/\partial t$. Using balance equations (8), (9), from the fundamental equation (5), we obtain the entropy balance equation:

$$\rho\frac{\partial s}{\partial t} = -\nabla\cdot(\theta^{-1}\mathbf{q}+\theta^{-1}\Lambda\dot{\mathbf{q}})+\mathbf{q}\cdot\nabla\theta^{-1}+\dot{\mathbf{q}}\cdot\nabla(\theta^{-1}\Lambda). \tag{10}$$

We can see that equation (10) is written in the standard form

$$\rho\dot{s} = -\nabla\cdot\mathbf{J}^s + \sigma, \tag{11}$$

where

$$\mathbf{J}^s = \theta^{-1}\mathbf{q} + \theta^{-1}\Lambda\dot{\mathbf{q}} \tag{12}$$

is the entropy flux,

$$\sigma = \mathbf{q}\cdot\nabla\theta^{-1} + \dot{\mathbf{q}}\cdot\nabla(\theta^{-1}\Lambda) \geq 0 \tag{13}$$

is the entropy source. According to the second law of thermodynamics, the entropy production is non-negative. Expression (13) shows that, to the heat flux $\mathbf{q}$, the thermodynamic force $\nabla\theta^{-1}$ corresponds, and to the time derivative $\dot{\mathbf{q}}$, the thermodynamic force $\nabla(\theta^{-1}\Lambda)$ corresponds.

As in classical irreversible thermodynamics we consider total entropy production

$$P = \int \sigma \, dV = \int [\mathbf{q} \cdot \nabla\theta^{-1} + \dot{\mathbf{q}} \cdot \nabla(\theta^{-1}\Lambda)] \, dV, \tag{14}$$

where V is the volume of the system. A part of the time derivative of the entropy production, $d_X P/dt$, has the form

$$\frac{d_X P}{dt} = \int \left[\mathbf{q} \cdot \frac{\partial}{\partial t} \nabla\theta^{-1} + \dot{\mathbf{q}} \cdot \frac{\partial}{\partial t} \nabla(\theta^{-1}\Lambda) \right] dV. \tag{15}$$

Let us transform (15) into

$$\begin{aligned} \frac{d_X P}{dt} = &- \int \left[\frac{\partial\theta^{-1}}{\partial t} \nabla \cdot \mathbf{q} + \frac{\partial(\theta^{-1}\Lambda)}{\partial t} \nabla \cdot \dot{\mathbf{q}} \right] dV + \\ &+ \oint \left[\frac{\partial\theta^{-1}}{\partial t} \mathbf{q} + \frac{\partial(\theta^{-1}\Lambda)}{\partial t} \dot{\mathbf{q}} \right] \cdot \mathbf{n} \, d\Sigma, \end{aligned} \tag{16}$$

where $\mathbf{n}$ is a unit vector directed outside along the normal to the surface, $d\Sigma$ is a surface element. When time-independed boundary conditions take place (θ and Λ are given), the surface integral becones zero. Using equations (8), (9) and inequality (7), we obtain from (16) that

$$\frac{d_X P}{dt} = \int \rho \left[\frac{\partial\theta^{-1}}{\partial t} \frac{\partial u}{\partial t} + \frac{\partial(\theta^{-1}\Lambda)}{\partial t} \frac{\partial \dot{u}}{\partial t} \right] dV \leq 0 \tag{17}$$

Inequality (17) is extended evolution criterion, which is generalization of the Glansdorff-Prigogine criterion.

LINEAR THEORY

To a first approximation, the thermodynamic forces are linearly related to the corresponding fluxes and flux rates. Therefore, from expression (13), we have

$$\nabla\theta^{-1} = R_{11}\mathbf{q} + R_{12}\dot{\mathbf{q}}, \tag{18}$$

$$\nabla(\theta^{-1}\Lambda) = R_{21}\mathbf{q} + R_{22}\dot{\mathbf{q}}. \tag{19}$$

Thus, for a single irreversible process, we have obtained two phenomenological equations. According to the Onsager-Casimir principle, the matrix of the coefficients R_{ij} is antisymmetric, i.e.,

$$R_{12} = -R_{21}. \tag{20}$$

Using phenomenological equations (18) and (19), we replace the thermodynamic forces in expression (13) for the entropy production and obtain expression

$$\sigma = R_{11}\mathbf{q} \cdot \mathbf{q} + R_{22}\dot{\mathbf{q}} \cdot \dot{\mathbf{q}} \geq 0, \tag{21}$$

from which it follows that the diagonal coefficients are positive: $R_{11} > 0$, $R_{22} > 0$.

Let us transform phenomenological equation (18) in the form

$$\frac{R_{12}}{R_{11}} \frac{\partial\mathbf{q}}{\partial t} + \mathbf{q} = -\frac{1}{R_{11}\theta^2} \nabla\theta, \tag{22}$$

and consider Maxwell-Cattaneo law

$$\tau \frac{\partial\mathbf{q}}{\partial t} + \mathbf{q} = -\lambda \nabla T, \tag{23}$$

where T is the local-equilibrium temperature, τ is the relaxation time, λ is the thermal conductivity. Comparing equations (22) and Maxwell-Cattaneo law (23), we find the expression for generalized temperature,

$$\theta = T, \tag{24}$$

and relationship between the coefficients: $R_{11} = 1/\lambda T^2$, $R_{12} = \tau/\lambda T^2$.

Howeve, if heat conduction is governed by the dual-phase-lag equation,

$$\tau \frac{\partial\mathbf{q}}{\partial t} + \mathbf{q} = -\lambda \left(\nabla T + \varepsilon \frac{\partial \nabla T}{\partial t} \right), \tag{25}$$

then the comparison of the equation (22) with equation (25) gives a more complex linear approximation for the generalized temperature:

$$\theta = T + \varepsilon \frac{\partial T}{\partial t}. \tag{26}$$

Thus, in the propozed theory the generalized temperature is defined by the form of the constitutive equation.

LAGRANGE MULTIPLIES METHOD

In the previous sections the methods of classical irreversible thermodynamics was used. Further let us consider tools of the rational thermodynamics, namely Lagrange multiplies method proposed by Liu [10]. We start from the entropy balance equation which we write in the form

$$\rho\dot{s} + \nabla \cdot \mathbf{J} = \sigma \geq 0. \tag{27}$$

Apart from we suppose that entropy flux and entropy production are functions of the heat flux $\mathbf{q}$ and heat flux rate $\dot{\mathbf{q}}$. So that constitutive relations are

$$s = s(u, \dot{u}), \quad \mathbf{J}^s = \mathbf{J}^s(\mathbf{q}, \dot{\mathbf{q}}), \quad \sigma = \sigma(\mathbf{q}, \dot{\mathbf{q}}). \tag{28}$$

Within this theory the constrains are given by the energy balance equation and time derivative of the energy balance equation which can be written in the form

$$\rho\dot{u} + \nabla \cdot \mathbf{q} = 0, \qquad \rho\ddot{u} + \nabla \cdot \dot{\mathbf{q}} = 0. \tag{29}$$

Multiplication of the balance equations by Lagrange multipliers λ_1, λ_2 and insertion this terms to the left-hand side of the entropy inequality (27) give more general expression:

$$\rho\dot{s} + \nabla \cdot \mathbf{J}^s - \lambda_1(\rho\dot{u} + \nabla \cdot \mathbf{q}) - \lambda_2(\rho\ddot{u} + \nabla \cdot \dot{\mathbf{q}}) \geq 0. \tag{30}$$

Let us represent time derivative of u and divergence of $\mathbf{J}^s$ in the form

$$\dot{s} = \frac{\partial s}{\partial u}\dot{u} + \frac{\partial s}{\partial \dot{u}}\ddot{u}, \tag{31}$$

$$\nabla \cdot \mathbf{J}^s = \frac{\partial \mathbf{J}^s}{\partial \mathbf{q}} : \nabla\mathbf{q} + \frac{\partial \mathbf{J}^s}{\partial \dot{\mathbf{q}}} : \nabla\dot{\mathbf{q}}. \tag{32}$$

Using (31) let us make substitution in (30). After rearrangement we obtain inequality

$$\begin{aligned} &\left(\frac{\partial s}{\partial u} - \lambda_1 \right) \rho\dot{u} + \left(\frac{\partial s}{\partial \dot{u}} - \lambda_2 \right) \rho\ddot{u} + \left(\frac{\partial \mathbf{J}^s}{\partial \mathbf{q}} - \lambda_1 \mathbf{U} \right) : \nabla\mathbf{q} + \\ &+ \left(\frac{\partial \mathbf{J}^s}{\partial \dot{\mathbf{q}}} - \lambda_2 \mathbf{U} \right) : \nabla\dot{\mathbf{q}} \geq 0, \end{aligned} \tag{33}$$

where we used equalities

$$\nabla \cdot \mathbf{q} = \mathbf{U} : \nabla \mathbf{q}, \qquad \nabla \cdot \dot{\mathbf{q}} = \mathbf{U} : \nabla \dot{\mathbf{q}}. \tag{34}$$

Since inequality (33) becomes valid for completely arbitrary variation of the values $\dot{u}$, $\ddot{u}$, $\nabla \mathbf{q}$, $\nabla \dot{\mathbf{q}}$ (time derivatives of the independent variables u, $\dot{u}$ and gradients of the flux $\mathbf{q}$ and flux rate $\dot{\mathbf{q}}$), we have

$$\frac{\partial s}{\partial u} - \lambda_1 = 0, \quad \frac{\partial s}{\partial \dot{u}} - \lambda_2 = 0, \tag{35}$$

$$\frac{\partial \mathbf{J}^s}{\partial \mathbf{q}} - \lambda_1 \mathbf{U} = 0, \quad \frac{\partial \mathbf{J}^s}{\partial \dot{\mathbf{q}}} - \lambda_2 \mathbf{U} = 0. \tag{36}$$

Further, let us define generalized temperature θ and new intensive quantity Λ corresponding to variable $\dot{u}$ by the equalities

$$\lambda_1 = \theta^{-1}, \qquad \lambda_2 = \theta^{-1}\Lambda. \tag{37}$$

The first supposition of the classical approach is definitions of the intensive quantities (4). Within proposed theory, based on the Lagrange multipliers methods, definitions of the generalized temperature θ and new intensive quantity Λ (37) are last supposition.

Then, (31), (35) and (37) lead to the expression for $\dot{s}$:

$$\dot{s} = \theta^{-1}\dot{u} + \theta^{-1}\Lambda\ddot{u}. \tag{38}$$

We can see that Lagrange multipliers are functions of u and $\dot{u}$. From (36) we obtain that entropy flux $\mathbf{J}^s$ is linear function of $\mathbf{q}$ and $\dot{\mathbf{q}}$:

$$\mathbf{J}^s = \theta^{-1}\mathbf{q} + \theta^{-1}\Lambda\dot{\mathbf{q}}. \tag{12a}$$

Entropy balance equation (27) and equalities (38), (12a) lead to expression for the entropy production:

$$\sigma = \mathbf{q} \cdot \nabla\theta^{-1} + \dot{\mathbf{q}} \cdot \nabla(\theta^{-1}\Lambda) \geq 0. \tag{13a}$$

Linear theory on the basis of the expression (13a) can be obtained as in the previous section (see formulas (18)-(26)).

Equations (38), (12a) and (13a) are final result of the general theory. Using classical approach, we started from the fundamental equation (5) and obtained the entropy balance equation (11). Lagrange multipliers method permits us to obtain fundamental equation (38) from the entropy balance equation (27).

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