Physics/Mathematical physics, theoretical physics

On the definitions of entropy and temperature in the extended thermodynamics of irreversible processes

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Abstract

New definitions of entropy and temperature for uniform systems that fast exchange heat with the environment are considered. Instead of the known local equilibrium hypothesis, a local uniformity hypothesis is proposed. Within the proposed formalism of extended thermodynamics of irreversible processes, dual-phase-lag transfer equations are obtained. ***To cite this article: S.I. Serdyukov, C. R. Physique 8 (2007).***
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Résumé

Sur les définitions de l'entropie et de la température dans une généralisation de la thermodynamique aux processus irréversibles. On considère de nouvelles définitions de l'entropie et de la température pour des systèmes uniformes dont l'échange de chaleur avec l'environnement est rapide. Pour remplacer l'habituelle hypothèse d'équilbre local, on propose une hypothèse d'uniformité locale. Dans le cadre de la généralisation de la thermodynamique aux processus irréversibles proposée ici, on obtient des équations de transfert retardées. ***Pour citer cet article : S.I. Serdyukov, C. R. Physique 8 (2007).***
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1. Introduction

The concepts of entropy and temperature are among the most important both in classical and non-equilibrium thermodynamics. The theoretical definition of temperature is still a matter of discussion [1–5], and this problem is most complex for unsteady states of non-equilibrium systems.

The definitions of entropy and temperature are closely related to the development of the formalism of irreversible thermodynamics and are a significant challenge of extended thermodynamics. Classical irreversible thermodynam-

ics [6] is based on the local equilibrium hypothesis, according to which a nonuniform (and, hence, non-equilibrium) system can be considered as a locally equilibrium system. Therefore, the state of a nonuniform system can be specified by the same set of variables as that for an equilibrium system. For example, if the entropy S of the equilibrium system is a function of the internal energy U and volume V, i.e., $S = S(U, V)$, then the state of the nonuniform system can be specified by the internal energy density u and the specific volume v, which depend on spatial coordinates, and

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

where s is the entropy density.

The conventional version of extended irreversible thermodynamics (EIT) [7–9] is based on the assumption that the entropy density is a function of both conventional thermodynamic variables and the corresponding dissipative fluxes:

$$s = s\big(u, v; \mathbf{J}, \mathring{\mathbf{P}}^v, p^v\big) \tag{2}$$

where $\mathbf{J}$ is the heat flux, $\mathring{\mathbf{P}}^v$ is the viscous pressure tensor, and p^v is the bulk pressure. Within the framework of the conventional version of EIT, the generalized entropy density s and the generalized temperature θ, to a first approximation, are quadratic functions of the dissipative fluxes $\mathbf{J}$, $\mathring{\mathbf{P}}^v$, and p^v. For example, if we consider only the heat conduction in a solid, which is described by the Maxwell–Cattaneo equation, then

$$s = s_e - \frac{\tau_1 v}{2\lambda T^2} \mathbf{J} \cdot \mathbf{J}, \qquad \theta^{-1} = T^{-1} + \alpha^* \mathbf{J} \cdot \mathbf{J} \tag{3}$$

where $s_e = s_e(u, v)$ is the local-equilibrium entropy density, T is the local-equilibrium temperature, τ_1 is the relaxation time, λ is the thermal conductivity of the medium, and α^* is a coefficient.

Meanwhile, it is easy to show that extended thermodynamics based on postulate (2) is an incomplete theory. It is sufficient to consider a uniform (gradientless) system that undergoes fast heating or cooling, remaining uniform. Since the state of this system changes in finite time, it cannot be considered an equilibrium system. Because of the fast change in the state, relaxation phenomena may occur (e.g., fast heating of electrons in metal in comparison with heating of lattice). However, because of the absence of fluxes in the uniform system, postulate (2) reduces to classical postulate (1) and the extended theory turns out to be inapplicable.

In this Note, we will consider another version of extended thermodynamics, which proceeds from the postulate that additional variables are generally the material time derivatives of the conventional variables [10,11]:

$$s = s(u, v; \dot{u}, \dot{v}) \tag{4}$$

This approach allows one to obtain dual-phase-lag heat-conduction and diffusion equations [11,12] and formulate an extended evolution criterion [13], which is a generalization of the known Glansdorff–Prigogine criterion.

In this Note, we will give new definitions of generalized temperature and entropy, which would be applicable to unsteady states, and will extend the local equilibrium hypothesis. On the basis of postulate (4), we will consider the formalism of extended thermodynamics, which leads to the dual-phase-lag transfer equations:

$$\mathbf{J} + \tau_1 \frac{\partial \mathbf{J}}{\partial t} = -\lambda \nabla T - \varepsilon \frac{\partial \nabla T}{\partial t} \tag{5}$$

$$\mathring{\mathbf{P}}^v + \tau_2 \frac{\partial \mathring{\mathbf{P}}^v}{\partial t} = -2\eta \left(\mathring{\mathbf{V}} + \lambda_2 \frac{\partial \mathring{\mathbf{V}}}{\partial t} \right) \tag{6}$$

$$p^v + \tau_0 \frac{\partial p^v}{\partial t} = -\zeta \left(\nabla \cdot \mathbf{v} + \lambda_0 \frac{\partial \nabla \cdot \mathbf{v}}{\partial t} \right) \tag{7}$$

where τ_2, τ_0, ε/λ, λ_2, and λ_0 are the relaxation (retardation) times, η is the steady-state shear viscosity, ζ is the bulk viscosity, $\mathring{\mathbf{V}}$ is traceless deformation rate tensor ($\mathbf{V} = \frac{1}{2}[\nabla \mathbf{v} + (\nabla \mathbf{v})^+]$ is the symmetric part of the velocity gradient $\nabla \mathbf{v}$), t is the time. Eqs. (5)–(7) are more realistic than hyperbolic telegraph type equations. For example, Eq. (5) more accurately describes the heat propagation on the metal surface exposed to short-pulse laser irradiation [14,15]. Dual-phase-lag equations can not be obtained within thermodynamic theory on the basis of the postulate (2).[1]

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[1] To obtain the dual-phase-lag transfer equations from EIT, it should be assumed that fluxes of the dissipative fluxes are further additional variables [16,17].

2. Generalised entropy and temperature and hypothesis of local uniformity

Initially, let us consider again a uniform closed one-component system that does work and fast exchanges heat with the environment, remaining uniform. According to the first law of thermodynamics, there is a state function called the internal energy U, which is related to the heat dQ[2] supplied to the system and the work $p\,dV$ done by the system by the expression

$$dQ = dU + p\,dV \tag{8}$$

where V is the volume of the system and p is pressure. Considering the variation of the quantities U and V with time, we can rewrite the latter expression as

$$\dot{Q} = \dot{U} + p\dot{V} \tag{9}$$

For an adiabatically isolated system, we have $dQ = 0$, and, hence, the pressure can be expressed through the thermo-dynamic quantities U and V:

$$p = p(U, V) = -\frac{\partial U}{\partial V} \tag{10}$$

In classical thermodynamics, the entropy S introduced by Clausius is related to the heat change and the absolute temperature T by the integral relation $S_B - S_A = \int_A^B T^{-1}\,dQ$, where S_A is the entropy of the system in initial state A and S_B is the entropy of the system in final state B. The integral relation allows one to proceed to the differential form $T\,dS = dQ$.

In this Note, we will generalize these equalities by postulating that a central role in the extended theory is played by the heat-exchange rate $\dot{Q}$. Let us suppose that the generalized temperature θ and the generalized entropy S depend on the quantity $\dot{Q}$, i.e., $\theta = \theta(U, V; \dot{Q})$ and $S = S(U, V; \dot{Q})$. Further, let us assume that the change in the generalized entropy in the transition from state A into state B is related not only to the heat change dQ but also to the change $d\dot{Q}$ in the heat supply rate:

$$S_B - S_A = \int_A^B \theta^{-1}\big(dQ + \Lambda\,d\dot{Q}\big) \tag{11}$$

where $\Lambda = \Lambda(U, V; \dot{Q})$ is a new intensive quantity. Considering the transition from one state into the other, we can proceed from the integral relation (11) to the differential relation

$$\theta\,dS = dQ + \Lambda\,d\dot{Q} \tag{12}$$

Using equalities (8) and (9), from (12), we obtain

$$\theta\,dS = dU + p\,dV + \Lambda\big(\dot{U} + p\dot{V}\big) \tag{13}$$

According to expression (13), we can write

$$S = S\big(U, V; \dot{U} + p\dot{V}\big) \tag{14}$$

Thus, the entropy can be regarded as a function of U, V, and a single additional variable $\dot{U} + p\dot{V}$. The temperature θ and the intensive quantity Λ are also extended thermodynamic quantities:

$$\theta = \theta\big(U, V; \dot{U} + p\dot{V}\big) = \left(\frac{\partial S}{\partial U}\right)^{-1}_{V, \dot{U}+p\dot{V}}, \qquad \Lambda = \Lambda\big(U, V; \dot{U} + p\dot{V}\big) = \theta\left[\frac{\partial S}{\partial(\dot{U} + p\dot{V})}\right]_{U,V}$$

However, the pressure $p = p(U, V)$ is introduced within the framework of the first law of thermodynamics (10) and is not an extended quantity.

Thus, we considered the uniform system that is generally a non-equilibrium system because of the fast heat ex-change with the environment. To construct a formalism of extended thermodynamics of irreversible processes, instead

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[2] Here, we will not use other notations for a small amount of heat (e.g., δQ), implying that dQ is not the exact differential of the state variables U and V.

of the local equilibrium hypothesis, we propose a *local uniformity hypothesis*: the system that is nonuniform as a whole will be regarded as uniform at each point. This means that the non-equilibrium system should be described in terms of the same variables u, v, and $\dot{u} + p\dot{v}$. Then, instead of the fundamental relation (13), we obtain a similar relation in the form

$$\theta \, ds = du + p \, dv + \Lambda \, d(\dot{u} + p\dot{v}) \tag{15}$$

Relation (15) shows that the entropy density is a function of the same variables:

$$s = s(u, v; \dot{u} + p\dot{v}) \tag{16}$$

Obviously, the local uniformity hypothesis is less rigorous than the local equilibrium hypothesis.

The heat supply rate $\dot{u} + p\dot{v}$, as u and v, is an extensive variable. Therefore, as in classical thermodynamics, we can proceed from differential form (15) to the equality

$$\theta s = u + pv + \Lambda(\dot{u} + p\dot{v}) \tag{17}$$

Further, we consider an approximate dependence of the entropy on the variable $\dot{u} + p\dot{v}$. Let us assume that all the intensive quantities in equality (17) are independent of $\dot{u} + p\dot{v}$ and are functions of only u and v, i.e., $\theta(u, v; \dot{u} + p\dot{v})$ and $\Lambda(u, v; \dot{u} + p\dot{v})$ reduce to $T(u, v)$ and $\Lambda(u, v)$, respectively (pressure is independent of the additional variable by definition). Then, from equality (17), we obtain

$$s = s_e + T^{-1}\Lambda(u, v)(\dot{u} + p\dot{v}) \tag{18}$$

where $s_e = T^{-1}u + T^{-1}pv$ is the local equilibrium entropy density. The latter equality enables one to find an approximate expression for the generalized temperature:

$$\theta^{-1} = \left(\frac{\partial s}{\partial u}\right)_{v, \dot{u}+p\dot{v}} = T^{-1} + \alpha\rho(\dot{u} + p\dot{v}) \tag{19}$$

where

$$\alpha = v\left[\frac{\partial(T^{-1}\Lambda)}{\partial u}\right]_{v, \dot{u}+p\dot{v}} \tag{20}$$

is a coefficient. Thus, we revealed a linear approximate dependence of the generalized s and θ^{-1} on the additional variable, which differs fundamentally from result (3) of the conventional version of extended irreversible thermodynamics.

3. Balance equations

Further, the continuity equation and the internal energy balance equation are considered in the form

$$\rho\frac{dv}{dt} = -\nabla \cdot \mathbf{v}, \qquad \rho\frac{du}{dt} = -\nabla \cdot \mathbf{J} - \mathbf{P} : \nabla\mathbf{v} \tag{21}$$

where $\mathbf{P}$ is the pressure tensor ($\mathbf{P} = p\mathbf{U} + \mathbf{P}^v$, where $\mathbf{U}$ is unit matrix). Eqs. (21) can be transformed into one equation

$$\rho\left(\frac{du}{dt} + p\frac{dv}{dt}\right) = -\nabla \cdot \mathbf{J} - \mathbf{P}^v : \nabla\mathbf{v} \tag{22}$$

Along with Eq. (22), let us also consider the balance equation for the quantity $\dot{u} + p\dot{v}$. For this purpose, Eq. (22) should be rewritten in the form

$$\dot{u} + p\dot{v} = -v\nabla \cdot \mathbf{J} - v\mathbf{P}^v : \nabla\mathbf{v} \tag{23}$$

and its left and right-hand sides should be considered. Further, in the well-known equality [6]

$$\rho\frac{da}{dt} = \frac{\partial(\rho a)}{\partial t} + \nabla \cdot (\rho a\mathbf{v})$$

where a is a field quantity, let us make the change of variables $a = \dot{u} + p\dot{v}$ in the left-hand side and the change of variables $a = -v\nabla \cdot \mathbf{J} - v\mathbf{P}^v : \nabla \mathbf{v}$ in the right-hand side. This yields the balance equation for the variable $\dot{u} + p\dot{v}$ in the form

$$\rho \frac{\mathrm{d}(\dot{u} + p\dot{v})}{\mathrm{d}t} = -\nabla \cdot (\partial_t \mathbf{J} + \mathbf{v}\nabla \cdot \mathbf{J} + \mathbf{v}\mathbf{P}^v : \nabla \mathbf{v}) - \partial_t(\mathbf{P}^v : \nabla \mathbf{v}) \tag{24}$$

where $\partial_t \equiv \partial/\partial t$ is the partial time derivative. Apparently, in the balance equation (24), $\partial_t \mathbf{J} + \mathbf{v}\nabla \cdot \mathbf{J} + \mathbf{v}\mathbf{P}^v : \nabla \mathbf{v}$ is the flux of $\dot{u} + p\dot{v}$ and $-\partial_t(\mathbf{P}^v : \nabla \mathbf{v})$ is the source of $\dot{u} + p\dot{v}$.

Let us now consider the entropy balance equation. Using the generalized equation (15) and balance equations (22) and (24), the time derivative of the entropy density can be transformed to the form

$$\rho \frac{\mathrm{d}s}{\mathrm{d}t} = -\nabla \cdot \left[\theta^{-1}\mathbf{J} + \theta^{-1}\Lambda(\partial_t \mathbf{J} + \mathbf{v}\nabla \cdot \mathbf{J} + \mathbf{v}\mathbf{P}^v : \nabla \mathbf{v})\right] + \mathbf{J} \cdot \nabla\theta^{-1} - \theta^{-1}\mathbf{P}^v : \nabla \mathbf{v}$$
$$+ (\partial_t \mathbf{J} + \mathbf{v}\nabla \cdot \mathbf{J} + \mathbf{v}\mathbf{P}^v : \nabla \mathbf{v}) \cdot \nabla(\theta^{-1}\Lambda) - \theta^{-1}\Lambda\partial_t(\mathbf{P}^v : \nabla \mathbf{v}) \tag{25}$$

Comparing this equality with the entropy balance equation $\rho\, \mathrm{d}s/\mathrm{d}t = -\nabla \cdot \mathbf{J}_s + \sigma$, one can obtain the following expressions for the entropy flux $\mathbf{J}_s$ and the entropy production σ:

$$\mathbf{J}_s = \theta^{-1}\mathbf{J} + \theta^{-1}\Lambda(\partial_t \mathbf{J} + \mathbf{v}\nabla \cdot \mathbf{J} + \mathbf{v}\mathbf{P}^v : \nabla \mathbf{v}) \tag{26}$$

$$\sigma = \mathbf{J} \cdot \nabla\theta^{-1} - \theta^{-1}\mathbf{P}^v : \nabla \mathbf{v} + (\partial_t \mathbf{J} + \mathbf{v}\nabla \cdot \mathbf{J} + \mathbf{v}\mathbf{P}^v : \nabla \mathbf{v}) \cdot \nabla(\theta^{-1}\Lambda) - \theta^{-1}\Lambda\partial_t(\mathbf{P}^v : \nabla \mathbf{v}) \geqslant 0 \tag{27}$$

From expression (26), it is seen that the entropy flux depends on the heat flux and the flux of the quantity $\dot{u} + p\dot{v}$. The sign of inequality (27) is determined by the second law of thermodynamics.

Using the decompositions $\mathbf{P}^v = p^v\mathbf{U} + \overset{\circ}{\mathbf{P}}{}^v$ and $\mathbf{P}^v : \nabla \mathbf{v} = \overset{\circ}{\mathbf{P}}{}^v : \overset{\circ}{\mathbf{V}} + p^v\nabla \cdot \mathbf{v}$, the expression for the entropy production can be transformed to the form

$$\sigma = \mathbf{J} \cdot \nabla\theta^{-1} + (\partial_t \mathbf{J} + \mathbf{v}\nabla \cdot \mathbf{J} + \mathbf{v}\mathbf{P}^v : \nabla \mathbf{v}) \cdot \nabla(\theta^{-1}\Lambda) - \theta^{-1}\overset{\circ}{\mathbf{P}}{}^v : (\overset{\circ}{\mathbf{V}} + \Lambda\partial_t\overset{\circ}{\mathbf{V}}) - \theta^{-1}\Lambda(\partial_t\overset{\circ}{\mathbf{P}}{}^v) : \overset{\circ}{\mathbf{V}}$$
$$- \theta^{-1}p^v(\nabla \cdot \mathbf{v} + \Lambda\partial_t\nabla \cdot \mathbf{v}) - \theta^{-1}\Lambda(\partial_t p^v)\nabla \cdot \mathbf{v} \geqslant 0 \tag{28}$$

Here, $\nabla(\theta^{-1}\Lambda)$ in expression (28) is interpreted as a thermodynamic force and $\partial_t \mathbf{J} + \mathbf{v}\nabla \cdot \mathbf{J} + \mathbf{v}\mathbf{P}^v : \nabla \mathbf{v}$ is interpreted as the corresponding flux. The quantities $\overset{\circ}{\mathbf{P}}{}^v$ and $\partial_t\overset{\circ}{\mathbf{P}}{}^v$ are a flux and its time derivative; they correspond to the thermodynamic forces $-\theta^{-1}(\overset{\circ}{\mathbf{V}} + \Lambda\partial_t\overset{\circ}{\mathbf{V}})$ and $-\theta^{-1}\Lambda\overset{\circ}{\mathbf{V}}$, respectively. Similarly, the flux p^v and its rate $\partial_t p^v$ correspond to the thermodynamic forces $-\theta^{-1}(\nabla \cdot \mathbf{v} + \Lambda\partial_t\nabla \cdot \mathbf{v})$ and $-\theta^{-1}\Lambda\nabla \cdot \mathbf{v}$. Entropy production is also a bilinear form. In the particular case where $\Lambda = 0$, the expressions for the entropy flux and the entropy source reduce to the classical expressions.

To a first approximation, the thermodynamic forces are linearly related to the corresponding fluxes and flux rates. Therefore, taking into account different tensor dimensions of $\mathbf{J}$, $\overset{\circ}{\mathbf{P}}{}^v$ and p^v, we have

$$\nabla\theta^{-1} = R'_{11}\mathbf{J} + R'_{12}(\partial_t \mathbf{J} + \mathbf{v}\nabla \cdot \mathbf{J} + \mathbf{v}\mathbf{P}^v : \nabla \mathbf{v}) \tag{29}$$

$$\nabla(\theta^{-1}\Lambda) = R'_{21}\mathbf{J} + R'_{22}(\partial_t \mathbf{J} + \mathbf{v}\nabla \cdot \mathbf{J} + \mathbf{v}\mathbf{P}^v : \nabla \mathbf{v}) \tag{30}$$

$$-\theta^{-1}(\overset{\circ}{\mathbf{V}} + \Lambda\partial_t\overset{\circ}{\mathbf{V}}) = R_{11}\overset{\circ}{\mathbf{P}}{}^v + R_{12}\partial_t\overset{\circ}{\mathbf{P}}{}^v \tag{31}$$

$$-\theta^{-1}\Lambda\overset{\circ}{\mathbf{V}} = R_{21}\overset{\circ}{\mathbf{P}}{}^v + R_{22}\partial_t\overset{\circ}{\mathbf{P}}{}^v \tag{32}$$

$$-\theta^{-1}(\nabla \cdot \mathbf{v} + \Lambda\partial_t\nabla \cdot \mathbf{v}) = \tilde{R}_{11}p^v + \tilde{R}_{12}\partial_t p^v \tag{33}$$

$$-\theta^{-1}\Lambda\nabla \cdot \mathbf{v} = \tilde{R}_{21}p^v + \tilde{R}_{22}\partial_t p^v \tag{34}$$

where R'_{ij}, R_{ij}, and $\tilde{R}_{ij}$ $(i, j = 1, 2)$ are phenomenological coefficients. According to the Onsager–Casimir principle, the matrices formed by the coefficients R'_{ij}, R_{ij}, and $\tilde{R}_{ij}$ in expressions (29)–(34) are antisymmetric, i.e. $R'_{12} = -R'_{21}$, $R_{12} = -R_{21}$, and $\tilde{R}_{12} = -\tilde{R}_{21}$.

Eqs. (29), (31), and (33) will be considered in the next section, where it is shown that these equations lead to new constitutive equations. Phenomenological equations (30), (32), and (34) allow one to reveal the relationship of the quantities $\nabla(\theta^{-1}\Lambda)$ and $\theta^{-1}\Lambda$ and dissipative fluxes. The significance of these equations is not considered in this work, since this requires special investigation.

4. Constitutive equations

Neglecting the quantity $\mathbf{v}(\nabla \cdot \mathbf{J} + \mathbf{P}^v : \nabla \mathbf{v})$ on the right-hand side of Eq. (29), we write Eqs. (29), (31), and (33) in the form

$$R'_{11}\mathbf{J} + R'_{12}\partial_t \mathbf{J} = \nabla \theta^{-1} \tag{35}$$

$$R_{11}\mathring{\mathbf{P}}^v + R_{12}\partial_t \mathring{\mathbf{P}}^v = -\theta^{-1}\big(\mathring{\mathbf{V}} + \varLambda\partial_t \mathring{\mathbf{V}}\big) \tag{36}$$

$$\tilde{R}_{11} p^v + \tilde{R}_{12}\partial_t p^v = -\theta^{-1}(\nabla \cdot \mathbf{v} + \varLambda\partial_t \nabla \cdot \mathbf{v}) \tag{37}$$

Using the balance equation (22), let us represent the generalized temperature (18) as a linear function of $\nabla \cdot \mathbf{J} + \mathbf{P}^v : \nabla \mathbf{v}$:

$$\theta^{-1} = T^{-1} - \alpha(\nabla \cdot \mathbf{J} + \mathbf{P}^v : \nabla \mathbf{v}) \tag{38}$$

Let us take the gradient of the left- and right-hand sides of the last equality. Neglecting the term $(\nabla \alpha)(\nabla \cdot \mathbf{J} + \mathbf{P}^v : \nabla \mathbf{v})$, we have

$$\nabla \theta^{-1} = \nabla T^{-1} - \alpha\nabla(\nabla \cdot \mathbf{J} + \mathbf{P}^v : \nabla \mathbf{v}) \tag{39}$$

Using equalities (38) and (39), we replace the temperature and the temperature gradient on the right-hand sides of Eqs. (35)–(37). Neglecting higher-order terms $(\mathbf{P}^v : \nabla \mathbf{v})(\mathring{\mathbf{V}} + \varLambda\partial_t \mathring{\mathbf{V}})$ and $(\mathbf{P}^v : \nabla \mathbf{v})(\nabla \cdot \mathbf{v} + \varLambda\partial_t \nabla \cdot \mathbf{v})$, we obtain the phenomenological equations

$$R'_{11}\mathbf{J} + R'_{12}\partial_t \mathbf{J} = \nabla T^{-1} - \alpha\nabla(\nabla \cdot \mathbf{J} + \mathbf{P}^v : \nabla \mathbf{v}) \tag{40}$$

$$R_{11}\mathring{\mathbf{P}}^v + R_{12}\partial_t \mathring{\mathbf{P}}^v = -\big(T^{-1} - \alpha\nabla \cdot \mathbf{J}\big)\big(\mathring{\mathbf{V}} + \varLambda\partial_t \mathring{\mathbf{V}}\big) \tag{41}$$

$$\tilde{R}_{11} p^v + \tilde{R}_{12}\partial_t p^v = -\big(T^{-1} - \alpha\nabla \cdot \mathbf{J}\big)(\nabla \cdot \mathbf{v} + \varLambda\partial_t \nabla \cdot \mathbf{v}) \tag{42}$$

It is seen that, in the equations obtained, fluxes of different dimensions interact.

Let us further consider three limiting cases and find a relationship between the coefficients of the obtained phenomenological equations with the coefficients of constitutive equations (5)–(7).

Limiting case 1: Let us initially consider the case where there is no convective transfer ($\mathbf{v} = 0$). Then, (40)–(42) reduce to a single equation

$$R'_{11}\mathbf{J} + R'_{12}\partial_t \mathbf{J} = \nabla T^{-1} - \alpha\nabla(\nabla \cdot \mathbf{J}) \tag{43}$$

Let us replace the term $\nabla(\nabla \cdot \mathbf{J})$ in this equation using the equality

$$\rho C_v \partial_t \nabla T = -\nabla(\nabla \cdot \mathbf{J}) \tag{44}$$

which is obtained from the balance equation $\rho C_v \partial_t T = -\nabla \cdot \mathbf{J}$ at constant ρC_v. As a result, from Eq. (43), we obtain the dual-phase-lag heat-conduction equation

$$\mathbf{J} + \frac{R'_{12}}{R'_{11}}\frac{\partial \mathbf{J}}{\partial t} = -\frac{1}{R'_{11}T^2}\nabla T + \frac{\alpha\rho C_v}{R'_{11}}\frac{\partial \nabla T}{\partial t} \tag{45}$$

Comparing (45) with (5), we find a relationship between the coefficients:

$$R'_{11} = \frac{1}{\lambda T^2}, \qquad R'_{12} = \frac{\tau_1}{\lambda T^2}, \qquad \alpha = -\frac{\varepsilon}{\rho C_v \lambda T^2} \tag{46}$$

It is seen from (46) that the coefficient α is negative or zero. The expression for α allows one to find a relationship of $\varLambda$ with the coefficients ε and λ. From the definition of the coefficient α (20) and equality (46), we obtain the equation

$$T\frac{\mathrm{d}\varLambda}{\mathrm{d}T} - \varLambda + \frac{\varepsilon}{\lambda} = 0, \qquad v = \mathrm{const}, \qquad \dot{u} + p\dot{v} = \mathrm{const}, \qquad C_v = \mathrm{const} \tag{47}$$

whose solution gives a relationship of $\varLambda$ with T and ε/λ. In the general case, the relaxation time ε/λ is a function of temperature. In a particular case where $\varepsilon/\lambda = \mathrm{const}$, it is easy to see after substitution that the quantity $\varLambda$ is also temperature-independent and

$$\varLambda = \frac{\varepsilon}{\lambda} = \mathrm{const} \tag{48}$$

Thus, the quantity Λ reduces to the relaxation time ε/λ when the relaxation time is constant.

Limiting case 2: Let us consider the case where $\alpha = 0$ and $T = $ const (θ reduces to T and the convective transfer occurs at constant temperature). Let us also assume that the liquid is incompressible ($\nabla \cdot \mathbf{v} = 0$) and there are only shear strains. Then, Eqs. (40) and (42) degenerate and, from Eq. (41), we obtain

$$\overset{\circ}{\mathbf{P}}{}^v + \frac{R_{12}}{R_{11}}\partial_t\overset{\circ}{\mathbf{P}}{}^v = -\frac{1}{R_{11}T}\left(\overset{\circ}{\mathbf{V}} + \Lambda\partial_t\overset{\circ}{\mathbf{V}}\right) \tag{49}$$

Comparing Eq. (49) with (6), we find expressions for the phenomenological coefficients and Λ:

$$R_{11} = \frac{1}{2\eta T}, \qquad R_{12} = \frac{\tau_2}{2\eta T}, \qquad \Lambda = \lambda_2 \tag{50}$$

Limiting case 3: Let us consider again the case where $\alpha = 0$ and $T = $ const. Let us now assume that there are only volumetric strains and there are no shear strains ($\overset{\circ}{\mathbf{V}} = 0$). Then, Eqs. (40) and (41) degenerate and, from Eq. (42), we obtain

$$p^v + \frac{\tilde{R}_{12}}{\tilde{R}_{11}}\partial_t p^v = -\frac{1}{\tilde{R}_{11}T}(\nabla \cdot \mathbf{v} + \Lambda\partial_t\nabla \cdot \mathbf{v}) \tag{51}$$

Comparing Eq. (51) with Eq. (7), we find again expressions for the phenomenological coefficients and Λ:

$$\tilde{R}_{11} = \frac{1}{\zeta T}, \qquad \tilde{R}_{12} = \frac{\tau_0}{\zeta T}, \qquad \Lambda = \lambda_0 \tag{52}$$

It is seen that, in the three limiting cases, the intensive quantity Λ reduces to the relaxation coefficients ε/λ (48), λ_2 (50), and λ_0 (52). Previously [18], the λ_2 values were experimentally determined for a number of well-known liquids and polymer solutions.

In this section, we have identified all the coefficients of Eqs. (40)–(42). Using the expressions for the coefficients (46), (50), and (52), we represent Eqs. (40)–(42) in the form

$$\mathbf{J} + \tau_1\frac{\partial\mathbf{J}}{\partial t} = -\lambda\nabla T + \frac{\varepsilon}{\rho C_v}\left[\nabla(\nabla \cdot \mathbf{J}) + \nabla\left(\overset{\circ}{\mathbf{P}}{}^v : \overset{\circ}{\mathbf{V}}\right) + \nabla(p^v\nabla \cdot \mathbf{v})\right] \tag{53}$$

$$\overset{\circ}{\mathbf{P}}{}^v + \tau_2\frac{\partial\overset{\circ}{\mathbf{P}}{}^v}{\partial t} = -2\eta\left(1 + \frac{\varepsilon}{\rho C_v\lambda T}\nabla \cdot \mathbf{J}\right)\left(\overset{\circ}{\mathbf{V}} + \lambda_2\frac{\partial\overset{\circ}{\mathbf{V}}}{\partial t}\right) \tag{54}$$

$$p^v + \tau_0\frac{\partial p^v}{\partial t} = -\zeta\left(1 + \frac{\varepsilon}{\rho C_v\lambda T}\nabla \cdot \mathbf{J}\right)\left(\nabla \cdot \mathbf{v} + \lambda_0\frac{\partial\nabla \cdot \mathbf{v}}{\partial t}\right) \tag{55}$$

Thus, we obtained the constitutive equations, which, in particular cases, reduce to dual-phase-lag equations (5), (6), and (7), respectively. In Eqs. (53)–(55), dissipative fluxes of different dimensions interact, but these equations differ significantly from the corresponding equations of the conventional version of EIT.

5. Conclusions

In this Note, we gave new definitions of generalized entropy and temperature for uniform systems that fast exchange heat with the environment. We introduced a local uniformity hypothesis and proceeded to description of nonuniform systems. The approach proposed enabled us to develop a formalism of extended thermodynamics of irreversible processes within which only one additional variable, $\dot{u} + p\dot{v}$, and only one corresponding intensive quantity, Λ, are introduced. Within the framework of this version, constitutive equations (53)–(55) were obtained, which, in particular cases, reduce to dual-phase-lag heat-conduction and convective-transfer equations. Further development of the formalism of extended thermodynamics that uses phenomenological equations (30), (32), and (34) will reveal new advantages of the proposed approach in comparison with the conventional version of extended irreversible thermodynamics.

Acknowledgements

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