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Variational setting for reversible and irreversible fluids with heat flow

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Abstract

This paper derives and discusses variational formulations for heat flows subject to physical constraints that involve the (generally) non-conserved balance of internal energy and the entropy representation kinetics in the form of the Cattaneo equation of heat. Another approach is also outlined which uses the (generally) non-conserved balance of the entropy and the energy-representation counterpart of the Cattaneo equation called Kaliski's equation. Results of nonequilibrium statistical mechanics (Grad's theory) lead to nonequilibrium corrections to entropy and energy of the fluid in terms of the nonequilibrium density distribution function, *f*. These results also yield coefficients of the wave model of heat such as: relaxation time, propagation speed and thermal inertia. With these data a quadratic Lagrangian and a variational principle of Hamilton's type follows for a fluid with heat flux in the field representation of fluid motion. For an irreversible heat transfer we show that despite of generally non-canonical form of the matter tensor the coefficients in source terms of the variational conservation laws can be suitably adjusted, so that physical (source-less and canonical) conservation laws are obtained for the energy and momentum. We discuss canonical and generalized conservation laws and show the satisfaction of the second law under the constraint of canonical conservation laws.

Keywords: Irreversible flows; Conservation laws; Grad solution; Variational principles; Wave equations

1. Introduction

In this paper we use the framework of extended thermodynamics of fluids to discuss variational principles for irreversible energy transfer and help that can be obtained from statistical theories when describing nonequilibrium thermodynamic systems and evaluating kinetic or flux-dependent terms in energies and macroscopic Lagrangians. Especially, we treat statistical aspects of thermodynamic and transport properties of nonequilibrium fluids with heat flow by applying an analysis that uses Grad's results [1] to determine nonequilibrium corrections Δs or Δe to the energy e or entropy s in terms of the nonequilibrium density distribution function f. To find corrections to the energy e or kinetic potential L we use corrections Δs and a relationship that links energy and entropy representations of thermodynamics. We also evaluate coefficients of wave model of heat, such as: relaxation time, propagation speed and thermal inertia factors, g and θ. With these data we formulate a variational principle of Hamilton's or least action-type for fluids with heat flux in the field or Eulerian representation of fluid motion. Analyzing the variational extremum we display an approach that adjoints a given set of constraints to a kinetic potential L and transfers the original variational formulation to the space of associated Lagrange multipliers. By considering limiting reversible process we evaluate canonical components of energy-momentum tensor along with associated conservation laws. We show that despite of the generally non-canonical form of conservation laws produced by Noether's theorem the approach that adjoints constraints to given kinetic potential works efficiently. In fact, the approach leads to exact imbedding of constraints in the potential space of Lagrange multipliers, implying that the appropriateness of the constraining set should be verified by physical rather than mathematical criteria. Our

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analysis shows that the approach is particularly useful in the field (Eulerian) description of transport phenomena, where equations of thermal field follow from variational principles containing state adjoints rather than original physical variables. Exemplifying process is hyperbolic heat transfer, but the approach can also be applied to coupled parabolic transfer of heat, mass and electric charge. With various gradient or non-gradient representations of physical fields in terms of state adjoints (quantities similar to those used by Clebsch in his representation of hydrodynamic velocity) useful action-type criteria emerge. Symmetry principles are effective, and components of the formal energy-momentum tensor can be found. The limiting reversible process, with ignored random effects, provides a suitable reference frame. Focusing on heat flow, our work represents, in fact, an approach that shows the methodological advantage of approaches borrowed from the optimal control theory in variational descriptions of irreversible transport phenomena.

2. Statistical data, constraints and composite performance criteria

Statistical theories are useful [1] to evaluate nonequilibrium corrections to energy and other thermodynamic potentials in situations when a continuum is inhomogeneous and this inhomogeneity is associated with presence of irreversible fluxes. To illustrate benefits resulting from suitable findings in the field of nonequilibrium statistical thermodynamics, heat transfer in locally nonequilibrium fluids is analyzed [2].

Quite essential in these analyses is the connection between various representations of thermodynamics of nonequilibrium fluids and a relationship (resembling the Gouy–Stodola law) that links energy and entropy pictures. Thanks to this relationship nonequilibrium corrections to the energy can be found from those known for the entropy of the Grad's theory. These energy corrections will next be used to construct suitable kinetic potentials L and formulate variational principles.

In this setting we work in the energy and Lagrangian representations of thermodynamics and focus on formulation of a linear variational description for heat transfer in incompressible continua.

While the linearity of the theory is certainly an approximation, it is simple and lucid enough to illustrate a (relatively unknown) variational approach based on adjoining known process equations as "constrains" to a "kinetic potential L" (the integrand L of an action functional).

The present approach is optimization-type; it differs from more conventional variational ones in that the action functional is systematically constructed rather than assumed from the beginning. Once a variational theory is developed for an assumed L it may easily be modified for improved kinetic potentials which take more subtle effects into consideration. Equations of constraints (reversible or irreversible) follow in the form of their "representations" in the space of Lagrange multipliers; they are extremum conditions for the action containing a composite (constraint involving) Lagrangian Λ or its gauge counterparts. As long as representations describing physical variables of state in terms of Lagrange multipliers are known in their explicit form, the whole variational formalism can be transferred to the adjoint space of these multipliers, i.e. a variational principle can be formulated in this (adjoint) space. The Lagrangian can also be used to obtain the matter tensor for the continuum with heat flow and associated conservation laws.

In the final part of the paper we show that the acceptance of canonical conservation laws, constructed for a limiting reversible process, along with variational extremum conditions assures the satisfaction of the second law of thermodynamics, the property that renders the variational theory considered a candidate to be the physical one.

Moreover, formal conservation laws, evaluated from Noether's theorem, are the process integrals that provide additional insight on the transformation of energy in the irreversible system.

3. Energy and entropy representations in thermodynamics of heat flow

Now our task is to recall some basic knowledge on the thermodynamics of heat flow without local equilibrium. A process description will be developed that will next be used to construct suitable lagrangians, variational principles and conservation laws. We work in the framework of extended thermodynamics of fluids [3]. We restrict ourselves to incompressible, one-component continuum with heat flow.

Consider a continuum with the heat flow at a nonequilibrium state, say A, off but near the Gibbs surface, when the local equilibrium assumption is inapplicable, Fig. 1. The energy at the state A is the nonequilibrium internal energy. This internal energy depends not only on the usual state variables (wherever they have meaning), but also on nonequilibrium variables such as heat flux or diffusive entropy flux. Here we select the heat flux, $\mathbf{q}$, as the nonequilibrium variable of choice. It is treated as an unconstrained internal variable which relaxes to equilibrium. Nonequilibrium energy density of a continum, ρ_e, or its specific energy e, is a function of density ρ, specific entropy s and diffusive entropy flux $\mathbf{j}_s$ or heat flux $\mathbf{q}$. For a continuum as a stable macroscopic system, its equilibrium internal energy density ρ_e^{eq} is the minimum of ρ_e with respect to unconstrained $\mathbf{j}_s$ or $\mathbf{q}$, at constant ρ and s. As $\rho = v^{-1}$, the reciprocal of specific volume, the minimum of ρ_e (or e itself) with respect to $\mathbf{j}_s$ or $\mathbf{q}$ occurs at constant entropy s and volume v which are proper variables at which the energy attains minimum at equilibrium. This is in agreement with basic thermodynamics [4]. Since $\mathbf{j}_s$ or $\mathbf{q}$ are *diffusive* fluxes, the minimum occurs for $\mathbf{j}_s = 0$ or $\mathbf{q} = 0$.

For a given nonequilibrium state at a point A, Fig. 1, two equilibrium reference states, at points B and C, say,

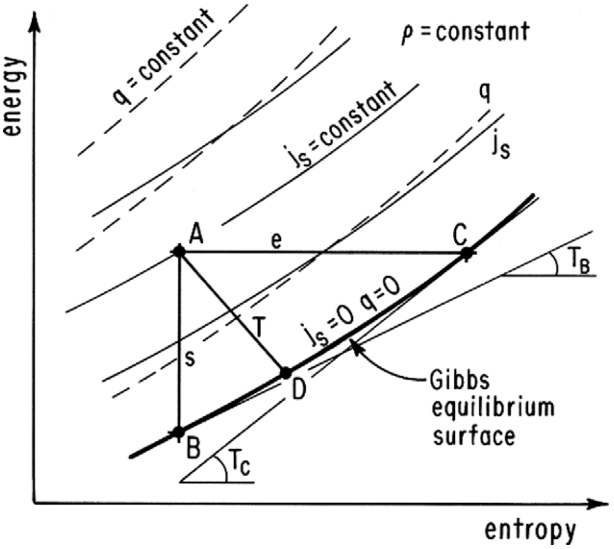

Fig. 1. Diverse reference equilibria (B, D, C, etc.) for a given disequilibrium state A. The line of constant nonequilibrium temperature linking states A and D corresponds with a numerical value of T between T_B and T_C.

correspond, respectively, to the energy and entropy representation. Likewise the point D refers to the free energy representation. A researcher knowing entropy s (e.g., from distribution function f corresponding to A) formulates his description of state A in terms of equilibrium parameters at B, for a set of variables, here the components of the entropy flux $\mathbf{j}_s$. Yet, one who knows energy e can base his view on the heat flux $\mathbf{q}$ and equilibrium at C. When point A moves the equilibrium states (B, C and D) vary.

The conventional picture of motion in terms of Hamilton's principle corresponds to following the behavior of B and the kinetic energy of entropy flux, whereas the kinetic theory view corresponds to tracking of C and the deviation of entropy from equilibrium. The transition from one view to the other is possible [2].

It is important to realize that for a single nonequilibrium state the use of the entropy representation and energy representation establish two different equilibrium states located on the Gibbs surface. This of course, is because of the difference in what is held constant. The distance between two reference equilibrium states (B and C) increases with the distance of the state A from the Gibbs surface. This distance can also be measured in terms of the modulus of the flux $\mathbf{j}_s$ or in terms of the differences $\Delta e = AB$ or $\Delta s = AC$.

When the curvature of the Gibb's surface can be neglected, corresponding to the near-equilibrium situation, the two disequilibrium excesses are linked by an equality resembling the Gouy–Stodola law

$$(e - e_{\mathrm{eq}})_{s,\rho} = -T(s - s_{\mathrm{eq}})_{e,\rho} \tag{1}$$

This states that the energy released during the isoentropic relaxation equals the product of the absolute temperature and the entropy deficiency in the system caused by the presence of the heat flux $\mathbf{q}$ or the entropy flux, $\mathbf{j}_s$.

4. Nonequilibrium corrections to energy or entropy in terms of distribution function

It is essential that the entropy representation is assumed in the Grad's formalism of the kinetic theory [1]. Hence the specific energy of an ideal gas or fluid with heat at the point A is equal to the specific energy at equilibrium C in Fig. 1. The reference temperatures and pressures that appear in the expressions of kinetic theory are T(C) and P(C). From the formalism one finds disequilibrium corrections Δs or Δe in terms of the nonequilibrium density distribution function f. Here we recapitulate the results of several different works [3–6] all using Grad's [1] solution of the Boltzmann equation in macroscopic predictions for dilute gas of rigid spheres.

The molecular velocity distribution function, f, out of equilibrium but close to it is given as

$$f(\mathbf{C}) = f^{\mathrm{eq}}(\mathbf{C})(1 + \varphi_1) \tag{2}$$

where f^{eq} is local equilibrium (Maxwell–Boltzmann) distribution pertaining to the entropy representation equilibrium (point C, Fig. 1). f and f^{eq} are scalars, but functions of the peculiar velocity $\mathbf{C} = \mathbf{c} - \mathbf{u}$, and φ_1 is a function of the deviation from equilibrium. This deviation is expressed in terms of the gradT in the Chapman–Enskog method and in terms of the heat flux $\mathbf{q}$ in the Grad's method. Using Eq. (2) in the entropy definition, one integrates the expression $f \ln f$ over all of the space of the molecular velocity $\mathbf{c}$,

$$\rho_s = -k_{\mathrm{B}} \int f \ln f \,\mathrm{d}\mathbf{c} \tag{3}$$

Proceeding with development of ρ_s up to second order in φ_1, one expands $\rho_s = \rho_s^{\mathrm{eq}} + \rho_s^{(1)} + \rho_s^{(2)}$, with local equilibrium entropy

$$\rho_s^{\mathrm{eq}} = -k_{\mathrm{B}} \int f^{\mathrm{eq}} \ln f^{\mathrm{eq}} \,\mathrm{d}\mathbf{c} \tag{4}$$

and nonequilibrium correction

$$\rho_s^{(1)} = -k_{\mathrm{B}} \int f^{\mathrm{eq}} \varphi_1 \ln f^{\mathrm{eq}} \,\mathrm{d}\mathbf{c} = 0 \tag{5}$$

Again, this proves that one deals with the entropy representation where the entropy is maximum at equilibrium. A counterpart of the above equation in the energy representation

$$\rho_e^{(1)} = -\int f^{\mathrm{eq}} \varphi_1 m \mathbf{c}^2 \,\mathrm{d}\mathbf{c} = 0 \tag{6}$$

would correspond to the minimum energy. The second order correction to the entropy density (in entropy representation) is

$$\rho_s^{(2)} = \rho \Delta s = -\frac{1}{2} k_{\mathrm{B}} \int f^{\mathrm{eq}} \varphi_1^2 \,\mathrm{d}\mathbf{c} \tag{7}$$

Hence, in view of the relation between Δe and Δs implied by Fig. 1 or Eq. (1)

$$\Delta e = -\frac{1}{2} k_{\mathrm{B}} T \rho^{-1} \int f^{\mathrm{eq}} \varphi_1^2 \,\mathrm{d}\mathbf{c} \tag{8}$$

Since the state A is close to the equilibrium surface, the multiplicative factors containing conventional thermodynamic variables can always be evaluated at arbitrary equilibrium points (B or C in Fig. 1). However, in Eqs. (1), (9) and (10), they were evaluated (in the kinetic theory) for the case of the isoenergetic equilibrium (point C, Fig. 1). The function φ_1, obtained in Grad's method when the system's disequilibrium is maintained by a heat flux $\mathbf{q}$ is

$$\varphi_1 = \frac{2}{5}(m/Pk_B^2T^2)\left(\frac{1}{2}m\mathbf{C}^2 - \frac{5}{2}k_BT\right)\mathbf{C}\cdot\mathbf{q} \tag{9}$$

where m is the mass of a molecule ([1,3]). From Eqs. (7)–(9) one obtains for the entropy deviation

$$\Delta s = -\frac{1}{5}(m/\rho Pk_BT^2)\mathbf{q}^2 \tag{10}$$

and for the energy deviation, Eq. (1), with entropy flux $\mathbf{j}_s = \mathrm{q}T^{-1}$

$$\Delta e = \frac{1}{5}(m^2/k_B\rho^2)\mathbf{j}_s^2 = \frac{1}{2}\rho^{-2}g\mathbf{j}_s^2 \tag{11}$$

Eqs. (10) and (11) hold to the accuracy of the 13th moment of the velocity [1]. When passing from Eq. (10) to (11) state equation $P = \rho k_BTm^{-1}$ is used and a constant g is defined as

$$g \equiv \frac{2mT\rho}{5Pk_B} = \frac{2m^2}{5k_B^2} \tag{12}$$

Here we abandoned the entropy representation. Pressure in Eqs. (9) and (12) is that of an ideal gas, given by the definition used in the kinetic theory ([1]). Eq. (11) with constant g defined by Eq. (12) is the characteristic feature of the ideal monoatomic gas (dilute Boltzmann gas composed of hard spheres). For arbitrary fluids (polyatomic gases, dense monoatomic gases and liquids) one can retain the form of the last expression in Eq. (11) by using a general definition of g obtained by noting that

$$g(\rho,s) \equiv \rho_{\mathrm{eq}}^2(\partial^2e/\partial\mathbf{j}_s^2)_{\mathrm{eq}} \tag{13}$$

In the ideal gas case the derivative $\partial_2e/\partial\mathbf{j}_s^2 = (2/5)(m^2/k_B^2\rho^2)$ from Eq. (11) and the definition (12) is recovered form definition (13). Eq. (13) is consistent with a hypothesis about the equality of the kinetic and static nonequilibrium energy corrections in a thermal shock-wave front [5]. The hypothesis can be used to compute $(\partial^2e/\partial\mathbf{j}_s^2)^{\mathrm{eq}}$ for arbitrary fluids as $T/(\rho c_pG)$ and hence g as $T\rho/(c_pG)$, where G is the shear modulus. Equilibrium values of thermodynamic parameters can be applied in such expressions. For an ideal gas the shear modulus is just the pressure P (the result of Maxwell) and $c_p = 5k_B/(2m)$. These results allow one to recover definition (12) from the expression $g = T\rho/(c_pG)$; they support the hypothesis mentioned above. Yet, for the purpose of general considerations the use of the implicit dependence of g on the basic variables (ρ, s) is often enough, i.e., the function $g(\rho, s)$ will be used when passing to arbitrary fluids. Use of some entropy flux adjoints, $\mathbf{a}_s$ and $\mathbf{i}_s$, is suitable. They are defined, respectively, by equations

$$\mathbf{a}_s(s,\rho,\mathbf{j}_s) = \partial\Delta e(s,\rho,\mathbf{j}_s)_{\rho,s}/\partial\mathbf{j}_s = g\rho^{-2}\mathbf{j}_s \tag{14}$$

and

$$\mathbf{i}_s(s,\rho,\mathbf{j}_s) = g\rho^{-1}\mathbf{j}_s = gs\mathbf{v}_s = gs(\mathbf{u}_s - \mathbf{u}) \tag{15}$$

The entropy diffusion velocity $\mathbf{v}_s = \mathbf{u}_s - \mathbf{u} = \mathbf{j}_s/\rho s = \mathbf{j}_s/\rho_s$ appears in Eq. (15). One may also introduce therein the product k_Bgs which has the dimension of mass. For the ideal gas this product is $m_s = 2/5(m^2sk_B^{-1})$ which is a measure of heat inertia.

In the model of a constant g, nonequilibrium temperature $T_{(B)}$ is equal to the equilibrium temperature $T(\rho, s)$ which is both the measure of mean kinetic energy of an equilibrium and the derivative of energy with respect to the entropy. This equality emerges because, above, we have chosen the entropy flux $\mathbf{j}_s$, not the heat flux $\mathbf{q}$, as the nonequilibrium variable in energy function e. If one differentiates the nonequilibrium entropy s with respect to the energy holding $\mathbf{q}$ constant, then a quantity $T_{(C)}$ of Jou et al. [3] follows, which differs from the reciprocal of the corresponding equilibrium temperature T^{eq} by a term quadratic in $\mathbf{q}$. In general, the "nonequilibrium temperatures" (understood as the fifth moment of the nonequilibrium density functions) are not the measures of mean kinetic energy.

The knowledge of inertial coefficients, such as g, from statistical mechanics considerations helps to calculate two basic quantities in the model of heat transfer with finite wave speed. They are: thermal relaxation time τ and the propagation speed, c_0. Of several formulae available that link quantities τ and g, probably the following expression

$$\tau = \mathbf{k}g(\rho T)^{-1} \tag{16}$$

is most useful ([6, p. 199]). It links thermal relaxation time τ with thermal conductivity $\mathbf{k}$, inertia g and state parameters of the system. As, by definition, the propagation speed of the thermal wave $c_0 = (a/\tau)^{1/2}$, where $a = k/(\rho c_p)$ is thermal diffusivity, the quantity c_0 may be determined from the formula

$$c_0 = \left(\frac{a}{\tau}\right)^{1/2} = \left(\frac{T}{c_pg}\right)^{1/2} \tag{17}$$

Substituting to this expression the ideal gas data, i.e. g of Eq. (12) and $c_p = 5k_B/(2m)$, yields propagation speed in the ideal gas

$$c_0 = \left(\frac{T}{c_pg}\right)^{1/2} = \left(\frac{k_BT}{m}\right)^{1/2} \tag{18}$$

(thermal speed). Thus the results of nonequilibrium statistical mechanics help to estimate numerical values of damped-wave model of heat transfer. The coefficients τ and c_0 are used below in a variational principle for wave heat transfer. One more coefficient that is quite useful in the wave theory of heat is that describing a thermal mass per unit of entropy

$$\theta = Tc_0^{-2} \tag{19}$$

[6]. For the ideal gas, Eq. (18) yields the coefficient θ as

$$\theta = mk_{\mathrm{B}}^{-1} \tag{20}$$

We can now set a variational description for linear wave heat flow satisfying Cattaneo model.

5. An approach adjoining a given set of constraints to a kinetic potential

For the heat conduction process described in the entropy representation by the Cattaneo equation of heat and the conservation law for internal energy, the set of constraints is

$$\frac{\partial \mathbf{q}}{c_0^2 \partial t} + \frac{\mathbf{q}}{c_0^2 \tau} + \nabla \rho_e = 0 \tag{21}$$

and

$$\frac{\partial \rho_e}{\partial t} + \nabla \cdot \mathbf{q} = 0 \tag{22}$$

where the density of the thermal energy ρ_e satisfies $\mathrm{d}\rho_e = \rho c_{\mathrm{v}} \mathrm{d}T$, c_0 is propagation speed for the thermal wave, τ is thermal relaxation time, and $D = c_0^2 \tau$ is the thermal diffusivity. Eq. (22) assumes the conservation of the thermal energy (rigid medium in which viscous dissipation is ignored). In irreversible processes the paths of entropy or energy differ from those of the matter. For simplicity we assume constant values of involved fields at the boundary. We ignore the vorticity properties of the heat flux.

The energy-representation counterpart of the Cattaneo equation,

$$\frac{\partial \mathbf{j}_s}{c_s^2 \partial t} + \frac{\mathbf{j}_s}{c_s^2 \tau} + \nabla T = 0 \tag{23}$$

uses diffusive entropy flux $\mathbf{j}_s$ instead of heat flux $\mathbf{q}$. The coefficient c_s is defined as

$$c_s \equiv (\rho c_{\mathrm{v}} \theta^{-1})^{1/2}, \tag{24}$$

where $\theta = Tc_0^{-2}$, and thermal diffusivity $\mathbf{k} \equiv \rho c_{\mathrm{v}} c_0^2 \tau$. Eq. (23) is Kaliski's equation [6,11]. For an incompressible medium one may apply this equation in the form

$$\frac{\partial \mathbf{j}_s}{c_0^2 \partial t} + \frac{\mathbf{j}_s}{c_0^2 \tau} + \nabla \rho_s = 0 \tag{25}$$

which uses the entropy density ρ_s as a field variable.

Yet, in this paper we focus on action and extremum conditions in entropy representation (Eqs. (21) and (22) in variables $\mathbf{q}$ and ρ_e). For Eqs. (23)–(25) a comprehensive action approach will be developed in another paper. Action approaches should be distinguished from entropy-production approaches [6,7]. Here an action is assumed that absorbs constraints (21) and (22) by Lagrange multipliers, the vector $\boldsymbol{\psi}$ and the scalar ϕ

$$A = \int_{t_1,V}^{t_2} \varepsilon^{-1} \left\{ \frac{1}{2} \frac{\mathbf{q}^2}{c_0^2} - \frac{1}{2} \rho_e^2 - \frac{1}{2} \varepsilon^2 + \boldsymbol{\psi} . \left(\frac{\partial \mathbf{q}}{c_0^2 \partial t} + \frac{\mathbf{q}}{c_0^2 \tau} + \nabla \rho_e \right) + \varphi \left(\frac{\partial \rho_e}{\partial t} + \nabla \cdot \mathbf{q} \right) \right\} \mathrm{d}V \mathrm{d}t. \tag{26}$$

As kinetic potentials can be very diverse, the conservation laws for energy and momentum substantiate the form (26). In Eq. (26), ε is the energy density at an equilibrium reference state, the constant which ensures the action dimension for A, but otherwise is unimportant. Yet we assume that the actual energy density ρ_e is close to ε, so that the variable ρ_e can be identified with the constant ε in suitable approximations.

We call the multiplier-free term of the integrand of Eq. (26)

$$L \equiv \frac{1}{2} \varepsilon^{-1} \left\{ \frac{\mathbf{q}^2}{c_0^2} - \rho_e^2 - \varepsilon^2 \right\} \tag{27}$$

the kinetic potential of Hamilton type for heat transfer. It is based on the quadratic form of an indefinite sign, and it has usual units of the energy density. Not far from equilibrium, where ρ_e is close to ε, two static terms of L yield altogether the density of thermal energy, ρ_e. Indeed, in view of admissibility of the *a posteriori* approximation $\rho_e = \varepsilon$ in Eq. (27), the kinetic potential (27) represents – in the framework of the linear heat theory – the Hamiltonian structure of a difference between "kinetic energy of heat", and the nonequilibrium internal energy, ρ_e. To secure correct conservation laws, no better form of L associated with a nonlinear model was found in the entropy representation. The theory obtained in the present case is a linear one.

Vanishing variations of action A with respect to multipliers $\boldsymbol{\psi}$ and ϕ recover constraints, whereas those with respect to state variables $\mathbf{q}$ and ρ_e yield representations of state variables in terms of $\boldsymbol{\psi}$ and ϕ. For the accepted Hamilton-like structure of L,

$$\mathbf{q} = \frac{\partial \boldsymbol{\psi}}{\partial t} - \frac{\boldsymbol{\psi}}{\tau} + c_0^2 \nabla \varphi \tag{28}$$

and

$$\rho_e = -\nabla \boldsymbol{\psi} - \frac{\partial \phi}{\partial t}. \tag{29}$$

These equations enable one to transfer variational formulation to the space of Lagrange multipliers.

For the accepted structure of L, the action A, Eq. (26), in terms of the adjoints $\boldsymbol{\psi}$ and ϕ is

$$A = \int_{t_1,V}^{t_2} \varepsilon^{-1} \left\{ \frac{1}{2c_0^2} \left(\frac{\partial \boldsymbol{\psi}}{\partial t} - \frac{\boldsymbol{\psi}}{\tau} + c_0^2 \nabla \phi \right)^2 - \frac{1}{2} \left(\nabla \cdot \boldsymbol{\psi} + \frac{\partial \phi}{\partial t} \right)^2 - \frac{1}{2} \varepsilon^2 \right\} \mathrm{d}V \mathrm{d}t. \tag{30}$$

Its Euler–Lagrange equations with respect to $\boldsymbol{\psi}$ and φ are

$$\frac{\partial}{\partial t}\left\{\frac{1}{c_0^2}\left(\frac{\partial\boldsymbol{\psi}}{\partial t}-\frac{\boldsymbol{\psi}}{\tau}+c_0^2\nabla\phi\right)\right\}+\frac{1}{\tau c_0^2}\left(\frac{\partial\boldsymbol{\psi}}{\partial t}-\frac{\boldsymbol{\psi}}{\tau}+c_0^2\nabla\phi\right)-\nabla\left(\nabla\cdot\boldsymbol{\psi}+\frac{\partial\phi}{\partial t}\right)=0 \tag{31}$$

and

$$-\frac{\partial}{\partial t}\left(\nabla\cdot\boldsymbol{\psi}+\frac{\partial\phi}{\partial t}\right)+\nabla\cdot\left(\frac{\partial\boldsymbol{\psi}}{\partial t}-\frac{\boldsymbol{\psi}}{\tau}+c_0^2\nabla\varphi\right)=0. \tag{32}$$

It is easy to see that (31) and (32) are the original equations of the thermal field, Eqs. (21) and (22), in terms of the potentials $\boldsymbol{\psi}$ and ϕ. Their equivalent form below shows damped-wave nature of the transfer process. In fact, Lagrange multipliers $\boldsymbol{\psi}$ and ϕ of this (source-less) problem satisfy certain inhomogeneous wave equations. In terms of the modified quantities $\boldsymbol{\Psi}$ and $\boldsymbol{\Phi}$ satisfying $\boldsymbol{\Psi}=\psi\tau c_0^2$ and $\boldsymbol{\Phi}=-\phi\tau c_0^2$ these equations are

$$\nabla^2\boldsymbol{\psi}-\frac{\partial^2\boldsymbol{\psi}}{c_0^2\partial t^2}+\frac{\partial\boldsymbol{\psi}}{\tau c_0^2\partial t}=\mathbf{q} \tag{33}$$

and

$$\nabla^2\Phi-\frac{\partial^2\Phi}{c_0^2\partial t^2}+\frac{\partial\Phi}{\tau c_0^2\partial t}=\rho_e. \tag{34}$$

As both original state variables ($\mathbf{q}$, ρ_e) and adjoints ($\boldsymbol{\psi}$, ϕ) appear in these equations, they represent, in fact, mixed formulations of the theory. Still they are interesting as they show that for given densities $\mathbf{q}$ and ρ_e thermal energy transfer can be broken down to potentials. The situation is similar to that in electromagnetic theory or in gravitation theory, where the specification of sources (electric four-current or matter tensor, respectively) defines the behavior of the field potentials. An important case is the reversible "ballistic" process with $\tau\to\infty$. In this process undamped thermal waves propagate with the speed c_0 and satisfy d' Alembert's equation for potentials, energy density and temperature T.

6. Source term in internal energy equation

However, the construction of a suitable action A in the space of potentials by the direct substitution of the representation equations to the accepted kinetic potential L is generally incorrect. In fact, the method of direct substitution of representations into L is valid only for linear constraints that do not contain sources. This may be exemplified when the internal energy balance contains a source term $a'\mathbf{q}^2$, where a' is a positive constant. The augmented action integral (26) should now contain the negative term $-a'\mathbf{q}^2$ in its ϕ term. The energy density representation remains unchanged, whereas the heat flux representation follows in a generalized form

$$\mathbf{q}=(1-2a'\phi c_0^2)^{-1}\left(\frac{\partial\boldsymbol{\psi}}{\partial t}-\frac{\boldsymbol{\psi}}{\tau}+c_0^2\nabla\phi\right) \tag{35}$$

Substituting Eqs. (29) and (35) into action A of Eq. (26) (L of Eq. (27)) shows that the action based on the accepted kinetic potential L in terms of the potentials acquires the form

$$A=\int_{t_{1,V}}^{t_2}\varepsilon^{-1}\left\{\frac{1}{2c_0^2}(1-2a'\phi c_0^2)^{-2}\left(\frac{\partial\boldsymbol{\psi}}{\partial t}-\frac{\boldsymbol{\psi}}{\tau}+c_0^2\nabla\phi\right)^2\right\}\mathrm{d}V\mathrm{d}t-\int_{t_{1,V}}^{t_2}\varepsilon^{-1}\left\{\frac{1}{2}\left(\nabla\cdot\boldsymbol{\psi}+\frac{\partial\phi}{\partial t}\right)^2+\frac{1}{2}\varepsilon^2\right\}\mathrm{d}V\mathrm{d}t. \tag{36}$$

However the Euler–Lagrange equations for this action are not process constraints in terms of potentials, i.e. L itself fails to provide a correct variational formulation for constraints with sources. It is the vanishing term with constraints that contributes to the properties of the functional extremum in the augmented action A, Eq. (26). The way to improve the situation is to substitute the obtained representations to a transformed augmented action in which the only terms rejected are those that constitute total time or space derivatives. The latter can be selected via partial differentiation within the integrand of the original action A. (As we know from the theory of the functional extrema the addition of subtraction of terms with total derivatives and divergences do not change extremum properties of a functional.) When this procedure is applied to the considered problem and total derivatives are rejected, a correct action follows in the form

$$A=\int_{t_{1,V}}^{t_2}\varepsilon^{-1}\left\{\frac{1}{2c_0^2}(1-2a'\phi c_0^2)^{-1}\left(\frac{\partial\boldsymbol{\psi}}{\partial t}-\frac{\boldsymbol{\psi}}{\tau}+c_0^2\nabla\phi\right)^2\right\}\mathrm{d}V\mathrm{d}t-\int_{t_{1,V}}^{t_2}\varepsilon^{-1}\left\{\frac{1}{2}\left(\nabla\cdot\boldsymbol{\psi}+\frac{\partial\phi}{\partial t}\right)^2+\frac{1}{2}\varepsilon^2\right\}\mathrm{d}V\mathrm{d}t \tag{37}$$

This form differs from that of Eq. (36) only by the power of the term containing the constant a', related to the source. With the representation Eqs. (29) and (35), action (37) yields the proper Cattaneo constraint (21) and the generalized balance of internal energy which extends Eq. (22) by the positive source term $a'\mathbf{q}^2$. Eq. (37) proves that the four-dimensional potential space ($\boldsymbol{\psi}$, ϕ) is sufficient to accommodate the exact variational formulation for the problem with a source. Yet, due to the presence of this source, the variational formulation does not exist in the original four-dimensional original space ($\mathbf{q}$, ρ_e), and, if somebody insists to exploit this space plus possibly a necessary part of the potential space, the following action is obtained from Eqs. (21), (29), (35) and (37)

$$A=\int_{t_{1,V}}^{t_2}\varepsilon^{-1}\left\{(1-2a'\phi c_0^2)\frac{\mathbf{q}^2}{2c_0^2}-\frac{1}{2}\rho_e^2+\frac{1}{2}\varepsilon^2\right\}\mathrm{d}V\mathrm{d}t \tag{38}$$

This form of Λ shows that, when original state space is involved, the state space required to accommodate the variational principle must be enlarged by inclusion of the Lagrange multiplier ϕ as an extra variable. In fact, Eq. (38) proves that original state space ("physical space") is lacking sufficient symmetry (Vainberg's theorem [6]). Yet, as Eq. (38) shows, the adjoint space of potentials ($\boldsymbol{\psi}$, ϕ), while also four-dimensional as space ($\mathbf{q}$, ρ_e), *can* accommodate the variational formulation. Why is this so? Because the representation equations do adjust themselves to the extremum requirement of Λ at given constraints, whereas the given constraints without controls cannot exhibit any flexibility.

7. Canonical tensor and conservation laws

The validity of the constraint-adjoining variational approach rests crucially on inclusion of all physically relevant relationships treated as "constraints". As they are "physical" they must satisfy or constitute physical laws by assumption. For example, the Cattaneo model includes the conservation law for thermal energy; this law is an implicit ingredient of the variational formulation. For an applied Λ formal conservation laws may, however, be determined from Noether's theorem; some of them may constitute relationships of the physical interest.

In general, Λ used to describe irreversible processes are not suitably gauged to assure physical (canonical) components of the formal energy–momentum tensor. Addition to Lagrangians Λ gauge terms does not change their stationarity conditions, but does change the components of the energy–momentum tensor. Because the gauging does not change the stationarity conditions of the original Lagrangian Λ, physical (canonical) conservation laws are secured for gauged Λ (some are recovered from the variational model as "constraints").

As the formal components of the energy–momentum tensor (obtained via Noether's theorem for an irreversible Λ's) may have no physical meaning and hence may be of little interest, its physical components and correct conservation laws can be derived at the reversible limit of $\tau \to \infty$ (undamped wave process). A basic postulate for this procedure is that nontruncated physical components of the matter tensor and conservation laws are the same for reversible and irreversible processes (the postulate which is, in fact, applied in the Onsager's theory [6]).

Here we determine conservation laws for the energy and momentum for Noether's theorem for our model at its reversible limit. The energy-momentum tensor also called the matter tensor is defined as

$$G^{jk} \equiv \sum_l \frac{\partial v_l}{\partial \chi^j}\left[\frac{\partial \Lambda}{\partial(\partial v_l/\partial \chi^k)}\right] - \delta^{jk}\Lambda \tag{39}$$

where δ^{jk} is the Kronecker delta and $\boldsymbol{\chi} = (\mathbf{x}, t)$ comprises the spatial coordinates and time. The conservation laws are valid in absence of external fields; they describe then the vanishing four-divergences (∇, $\partial/\partial\tau$) of G^{jk}. Our approach here follows those in [8,9], accordingly components of G^{jk} are calculated for a reversible Λ whose gauge form is obtained from the reversible limit of Eq. (26) at $\boldsymbol{\psi} = 0$ and $\tau \to \infty$ by use of the divergence theorem along with differentiation by parts. In our problem

$$\Lambda = \varepsilon^{-1}\left\{\frac{1}{2}\left(\frac{\partial \phi}{\partial t}\right)^2 - \frac{1}{2}(c_0\nabla\phi)^2 - \frac{1}{2}\varepsilon^2\right\} \tag{40}$$

In terms of the physical variables

$$\Lambda = \varepsilon^{-1}\left\{\frac{1}{2}\rho_e^2 - \frac{1}{2}\frac{q^2}{c_0^2} - \frac{1}{2}\varepsilon^2\right\} \tag{41}$$

The matter tensor $G = G^{jk}$ has the following structure

$$\mathbf{G} = \begin{bmatrix} \mathbf{T} & -\boldsymbol{\Gamma} \\ \mathbf{Q} & E \end{bmatrix}, \tag{42}$$

where $\mathbf{T}$ is the stress tensor, $\boldsymbol{\Gamma}$ is the momentum density, $\mathbf{Q}$ is the energy flux density, and E is the total energy density.

When external fields are present, the kinetic potential L contains explicitly some of coordinates χ^j. Then the balance equations are satisfied rather than conservation laws

$$\sum_k \left(\frac{\partial G^{jk}}{\partial \chi^k}\right) + \frac{\partial \Lambda}{\partial \chi^j} = 0 \tag{43}$$

for j, $k = 1,2,\ldots,4$. Eq. (43) is the formulation of balance equations for momentum ($j = 1,2,3$) and energy ($j = 4$).

We recall the assumption of small deviation from equilibrium at which that model is physically consistent. With this assumption and for the gauged reversible limit of Eq. (26) at $\boldsymbol{\psi} = 0$ and $\tau \to \infty$, gauge action assures that components of the energy-momentum (matter) tensor are multiplier-independent. These components are given below. They describe: momentum density Γ^α, stress tensor $T^{\alpha\beta}$, total energy density E, and density of the total energy flux, Q^β, which approximately equals q^β.

The momentum density for the mass flow of the medium at rest is, of course, $\mathbf{J} = 0$, where $\mathbf{J}$ is the mass flux density. The momentum component of heat flow can be determined from Lagrangian (40) and Eq. (39) for $j = 4$

$$\Gamma^\alpha = -G^{\alpha 4} = -\frac{\partial \varphi}{\partial x^\alpha}\frac{\partial \Lambda}{\partial(\partial\varphi/\partial t)} = -\varepsilon^{-1}\frac{\partial \varphi}{\partial t}(\nabla\varphi)^a \tag{44}$$

Using "reversible" representations $\mathbf{q} = c_0^2\nabla\varphi$ and $\rho_e = -\partial\phi/\partial t$ leads to the momentum density of heat in physical variables

$$\Gamma^\alpha = -G^{\alpha 4} = c_0^{-2}\frac{\rho_e}{\varepsilon}q^\alpha \cong c_0^{-2}q^\alpha \tag{45}$$

In a vector form, $\boldsymbol{\Gamma} = \mathbf{q}c_0^{-2}$. Clearly, the momentum of heat vanishes in the Fourier's case ($c_0 \to \infty$).

The stress tensor T^{ab} has the form

$$T^{ab} = -\varepsilon^{-1}c_0^2(\nabla\varphi)^a(\nabla\varphi)^b - \delta^{ab}\Lambda \tag{46}$$

or in physical variables

$$T^{\alpha\beta} = -\varepsilon^{-1}c_0^{-2}q^\alpha q^\beta - \delta^{\alpha\beta}\Lambda \tag{47}$$

After substituting stationary Lagrangian into T^{ab} we obtain

$$T^{\alpha\beta} = -\varepsilon^{-1}c_0^{-2}q^\alpha q^\beta - \delta^{\alpha\beta}\varepsilon^{-1}\left\{\frac{1}{2}\rho_e^2 - \frac{1}{2}\mathbf{q}^2 c_0^{-2} - \frac{1}{2}\varepsilon^2\right\} \tag{48}$$

This quantity represents stresses caused by the pure heat flow; it vanishes at equilibrium.

Canonical energy density follows as the Legendre transform of the Lagrangian Λ with respect to rate change of ϕ in time

$$E = \varepsilon^{-1}\left\{\frac{1}{2}\left(\frac{\partial\phi}{\partial t}\right)^2 + \frac{1}{2}(c_0\nabla\phi)^2 + \frac{1}{2}\varepsilon^2\right\} \tag{49}$$

or in terms of the physical variables

$$E = G^{44} = \varepsilon^{-1}\left\{\frac{1}{2}\frac{q^2}{c_0^2} + \frac{1}{2}\rho_e^2 + \frac{1}{2}\varepsilon^2\right\} \cong \frac{1}{2}\frac{q^2}{\varepsilon c_0^2} + \rho_e \tag{50}$$

The energy of resting medium with heat flux is the sum of the kinetic energy of heat and equilibrium thermal energy.

Finally, we find density of energy flux in both frames

$$G^{4\beta} \equiv \frac{\partial\phi}{\partial t}\frac{\partial\Lambda}{\partial(\partial\phi/\partial x^\beta)} = \rho_e\varepsilon^{-1}c_0^2(\nabla\phi)^\beta \tag{51}$$

$$G^{4\beta} = Q^\beta = \varepsilon^{-1}\rho_e q^\beta \cong q^\beta. \tag{52}$$

In the quasi-equilibrium situation ρ_e is very close to ε, then the formal density of the energy flux G^{4b} coincides with the heat flux density, $\mathbf{q}$. As the heat flux, $\mathbf{q}$, is both the process variable and the entity resulting from the variational procedure, the fact that it is recovered here may be regarded as a positive test for the self-consistency of the procedure.

The associated conservation laws for the energy and momentum have the form

$$\partial\left(\frac{1}{2}\varepsilon^{-1}c_0^{-2}\mathbf{q}^2 + \rho_e\right)\Big/\partial t = -\nabla\cdot(\varepsilon^{-1}\rho_e\mathbf{q}) \tag{53}$$

$$\frac{\partial(c_0^{-2}\varepsilon^{-1}\rho_e q^\alpha)}{\partial t} = \nabla \cdot\left\{\varepsilon^{-1}\left(-c_0^{-2}q^\alpha q^\beta + \delta^{\alpha\beta}\left(\frac{1}{2}\mathbf{q}^2c_0^{-2} - \frac{1}{2}\rho_e^2 + \frac{1}{2}\varepsilon^2\right)\right)\right\} \tag{54}$$

As they were derived for reversible paths we call them canonical conservation laws. The energy conservation law (53), which stems from Eqs. (50) and (52), refers to non-equilibrium total energy E that differs from the nonequilibrium internal energy ρ_e by the presence of the "kinetic energy of heat", explicit in L of Eq. (27) or in Eq. (50). The necessity of distinction between E and ρ_e is caused by the finite thermal momentum (45) in the frame of stationary skeleton of rigid solid. The results stemming from the quadratic kinetic potential (27) seem acceptable when the system is close to equilibrium.

We shall now show how the above canonical conservation laws follow directly from the reversible equations of motion. In the reversible "ballistic" case Cattaneo equation (21) assumes a truncated form

$$\frac{\partial\mathbf{q}}{c_0^2\partial t} + \nabla\rho_e = 0 \tag{55}$$

Its scalar multiplication by $\mathbf{q}$ yields

$$\frac{\partial\mathbf{q}^2}{2c_0^2\partial t} + \mathbf{q}\cdot\nabla\rho_e = 0 \tag{56}$$

or, after performing the differentiation by parts

$$\frac{\partial\mathbf{q}^2}{2c_0^2\partial t} + \nabla\cdot(\mathbf{q}\rho_e) - \rho_e\nabla\cdot\mathbf{q} = 0 \tag{57}$$

Using the energy conservation (22), Eq. (57), yields

$$\frac{\partial\mathbf{q}^2}{2c_0^2\partial t} + \nabla\cdot(\mathbf{q}\rho_e) + \rho_e\frac{\partial\rho_e}{\partial t} = 0 \tag{58}$$

Dividing this equation by the equilibrium energy ε we can put the above result into the form

$$\frac{\partial\mathbf{q}^2}{2\varepsilon c_0^2\partial t} + \frac{\rho_e}{\varepsilon}\frac{\partial\rho_e}{\partial t} + \nabla\cdot(\varepsilon^{-1}\mathbf{q}\rho_e) = 0 \tag{59}$$

Closely to the equilibrium, i.e. when ρ_e is close to ε, we find the vanishing four-divergence

$$\frac{\partial}{\partial t}\left(\frac{\mathbf{q}^2}{2\varepsilon c_0^2} + \rho_e\right) + \nabla\cdot(\varepsilon^{-1}\mathbf{q}\rho_e) = 0 \tag{60}$$

which is equivalent with the energy balance (53).

8. Irreversible motions satisfying Cattaneo and Kaliski's equation

In the irreversible case we multiply by $\mathbf{q}$ the non-truncated Cattaneo formula, Eq. (21),

$$\frac{\partial\mathbf{q}}{c_0^2\partial t} + \frac{\mathbf{q}}{c_0^2\tau} + \nabla\rho_e = 0 \tag{21}$$

and obtain a generalization of formula (59)

$$\frac{\partial\mathbf{q}^2}{2\varepsilon c_0^2\partial t} - \frac{\rho_e}{\varepsilon}\nabla\cdot\mathbf{q} + \nabla\cdot(\varepsilon^{-1}\mathbf{q}\rho_e) = -\frac{\mathbf{q}^2}{\varepsilon c_0^2\tau} \tag{61}$$

Yet, the combination of this equation with energy balance (22)

$$\frac{\partial\mathbf{q}^2}{2\varepsilon c_0^2\partial t} + \frac{\rho_e}{\varepsilon}\frac{\partial\rho_e}{\partial t} + \nabla\cdot(\varepsilon^{-1}\mathbf{q}\rho_e) = -\frac{\mathbf{q}^2}{\varepsilon c_0^2\tau} \tag{62}$$

yields not a conservation law but another balance equation, a differential result with an energy source

$$\frac{\partial}{\partial t}\left(\frac{\mathbf{q}^2}{2\varepsilon c_0^2} + \rho_e\right) + \nabla\cdot(\varepsilon^{-1}\mathbf{q}\rho_e) = -\frac{\mathbf{q}^2}{\varepsilon c_0^2\tau} \tag{63}$$

This shows the violation of the energy conservation for the Cattaneo equation (21), and leads to the strange conclusion that (21) constitutes a physically admissible model only in the reversible case of an infinite τ. This is certainly not a property that is commonly attributed to the Cattaneo model, thus a further analysis is required.

Admitting an energy source in balance (22), i.e.

$$-\nabla \cdot \mathbf{q} = \frac{\partial \rho_e}{\partial t} - a'\mathbf{q}^2 \tag{64}$$

and using such extended balance in Eq. (61) we find

$$\frac{\partial \mathbf{q}^2}{2\varepsilon c_0^2 \partial t} + \frac{\rho_e}{\varepsilon}\frac{\partial \rho_e}{\partial t} - \frac{\rho_e}{\varepsilon} a'\mathbf{q}^2 + \nabla \cdot (\varepsilon^{-1}\mathbf{q}\rho_e) = -\frac{\mathbf{q}^2}{\varepsilon c_0^2 \tau} \tag{65}$$

From this formula we observe that for a' satisfying

$$a' = \frac{1}{\rho_e c_0^2 \tau} \tag{66}$$

the conservation of total energy is assured in the form of Eqs. (59) and (60). The positive value of a' in Eq. (66) means the generation of the internal energy in the dissipative system, as described by Eq. (64).

Likewise, after multiplying by $\mathbf{j}_s$ the nontruncated Kaliski's equation (23)

$$\frac{\partial \mathbf{j}_s}{c_s^2 \partial t} + \frac{\mathbf{j}_s}{c_s^2 \tau} + \nabla T = 0 \tag{23}$$

we find

$$\frac{\partial \mathbf{j}_s^2}{2c_s^2 \partial t} + \nabla \cdot (T\mathbf{j}_s) - T\nabla \cdot \mathbf{j}_s = -\frac{\mathbf{j}_s^2}{c_s^2 \tau} \tag{67}$$

Under the assumption of the entropy conservation Eq. (67) would yield an equation

$$\frac{\partial \mathbf{j}_s^2}{2c_s^2 \partial t} + \nabla \cdot (T\mathbf{j}_s) + T\frac{\partial \rho_s}{\partial t} = -\frac{\mathbf{j}_s^2}{c_s^2 \tau} \tag{68}$$

thus leading to the following energy balance

$$\frac{\partial}{\partial t}\left(\frac{\mathbf{j}_s^2}{2c_s^2} + \rho_e\right) + \nabla \cdot (T\mathbf{j}_s) = -\frac{\mathbf{j}_s^2}{c_s^2 \tau} \tag{69}$$

This result means that the assumption of the conserved entropy would result in the violation of the energy conservation law.

Yet, for a 'physical' entropy satisfying the non-conserved balance

$$-\nabla \cdot \mathbf{j}_s = \frac{\partial \rho_s}{\partial t} - a\mathbf{j}_s^2 \tag{70}$$

the total energy balance follows from Eqs. (67) and (70) in the form

$$\frac{\partial}{\partial t}\left(\frac{\mathbf{j}_s^2}{2c_s^2} + \rho_e\right) + \nabla \cdot (T\mathbf{j}_s) - Ta\mathbf{j}_s^2 = -\frac{\mathbf{j}_s^2}{c_s^2 \tau} \tag{71}$$

This form shows the satisfaction of the energy conservation for

$$a = \frac{1}{Tc_s^2 \tau} \tag{72}$$

Importantly, even when the conservation laws are satisfied in irreversible processes in their canonical form the related extremum action and potential representations of physical variables do explicitly contain potentials not only their derivatives.

We may thus claim that whenever a irreversible process occurs with the coefficient a satisfying Eq. (72), canonical conservation laws can be obtained from the Noether's theorem. In other cases, perhaps non-physical, this theorem yields generalized non-canonical conservation laws. These laws may be seen as extensions of the canonical conservation laws of Section 7, these extensions including variational adjoints and their derivatives besides of the original state variables. In fact, non-canonical conservation laws can be evaluated for any irreversible action, gauged or not. Yet, one must expect the following:

1. Components of the energy-momentum tensor may depend on both state variables and adjoints (Lagrange multipliers). In particular, this may also apply to Lagrangian Λ in any form, i.e. no gauging will exist which would lead to Λ dependent only on the state variables.
2. Extended energy and momentum balances may contain both state variables and adjoints (Lagrange multipliers). For many processes no gauging will exist leading to Λ that would depend on state variables only.
3. Lagrange multipliers cannot generally be eliminated from equations of irreversible motion (irreducible problem). An analogous situation is known in the Pontryagin's principle, where the adjoint variables cannot generally be eliminated except of some special cases, such as in the Horn's method of eliminating adjoints, where the dimensionality of state and control vectors is the same [10].

Canonical conservation laws, obtained for reversible paths, involve only state variables and are believed to be physical relationships satisfied by any natural process, reversible or not. As shown below the physical consequence of satisfaction of canonical conservation laws in the realm of irreversible processes is the second law of thermodynamics.

9. Satisfaction of second law of thermodynamics

In the variational theory of heat the satisfaction of the second law is not explicit, thus we shall derive it by considering entropy properties. The entry of **G** we need to apply now is $G^{44} = E$ as it is the total energy which is both global and exact conservative property. The density of the conserved energy, E, is a basic variable in the Gibbs relation that links the entropy density ρ_s with E and the current $\mathbf{q}$. The equality

$$\frac{1}{2}\varepsilon^{-1}c_0^{-2}\mathbf{q}^2 + \rho_e(\rho_s) = E \tag{73}$$

shows that entropy density ρ_s is a function $S_{\rm v}$ of E and $\mathbf{q}$ of the following structure

$$\rho_s(\rho_e) = S_{\rm v}\left(E - \frac{1}{2}\varepsilon^{-1}c_0^{-2}\mathbf{q}^2\right) \tag{74}$$

Thus at the constant mass density the differential of $S_{\rm v}$ satisfies an extended Gibbs equation

$$\begin{aligned} \mathrm{d}S_{\rm v} &= (\partial\rho_s/\partial\rho_e)\mathrm{d}\left(E - \frac{1}{2}\varepsilon^{-1}c_0^{-2}\mathbf{q}^2\right) \\ &= T^{-1}\mathrm{d}E - T^{-1}\varepsilon^{-1}c_0^{-2}\mathbf{q}\cdot\mathrm{d}\mathbf{q} \end{aligned} \tag{75}$$

Taking into account that $c_0 = (a/\tau)^{1/2} = (\mathbf{k}/\rho c_{\rm v}\tau))^{1/2}$, where $\mathbf{k}$ is the thermal conductivity, one finds $c_0^{-2} = \rho c_{\rm v}\tau/k = \varepsilon T^{-1}\tau\mathbf{k}^{-1}$, and the above differential expressed in terms of $\mathbf{k}$ is

$$\mathrm{d}S_{\rm v} = T^{-1}\mathrm{d}E - T^{-2}\tau\mathbf{k}^{-1}\mathbf{q}\cdot\mathrm{d}\mathbf{q} \tag{76}$$

Calculating the four-divergence of the entropy flow (∇, $\partial/\partial t$) and using the global conservation law for the energy E, in fact, the canonical energy of Eqs. (53) and (60), we obtain in terms of expressions containing $\mathbf{k}$ or c_0

$$\begin{aligned} \frac{\partial S_v}{\partial t} + \nabla\cdot\left(\frac{\mathbf{q}}{T}\right) &= \mathbf{q}\cdot\left(\nabla T^{-1} - \frac{1}{\varepsilon T c_0^2}\frac{\partial\mathbf{q}}{\partial t}\right) \\ &= \frac{\mathbf{q}}{kT^2}\cdot\left(-k\nabla T - \tau\frac{\partial\mathbf{q}}{\partial t}\right) \end{aligned} \tag{77}$$

But, since Eq. (21) is a simple transformation of the original Cattaneo equation

$$\tau\frac{\partial\mathbf{q}}{\partial t} + \mathbf{q} = -\varepsilon\tau c_0^2 T^{-1}\nabla T = -k\nabla T \tag{78}$$

we arrive at the expression

$$\frac{\partial S_v}{\partial t} + \nabla\cdot\left(\frac{\mathbf{q}}{T}\right) = \frac{\mathbf{q}^2}{\varepsilon\tau c_0^2 T} \equiv \frac{\mathbf{q}^2}{kT^2} = a\mathbf{j}_s^2 \tag{79}$$

where $a = \mathbf{k}^{-1}$ is the thermal resistivity. This equation describes the second law of thermodynamics in the identically satisfied form; it holds in both classical irreversible thermodynamics (CIT) and extended irreversible thermodynamics (EIT; [3]). Keeping in mind that Eq. (78) is, as Eq. (21), the result of the variational approach, we have obtained confirmation that the approach yields the results in agreement with the second law of thermodynamics. This seems to prove that the accepted kinetic potential (27) has properties of admissible physical entity to describe the heat flow not far from equilibrium. Yet, far from equilibrium an appropriate L may not exist in the present approach that is consistent with the Cattaneo theory. A complementary approach involving the Kaliski equations [11] can be more fruitful.

Possessing a kinetic potential that produces only suitable variational equations is by no means sufficient to ascertain that a field theory is sufficient as a whole from the physical viewpoint. This is, in fact, the main reason to test Noether integrals, conservation laws and entropy production stemming from the kinetic potential (27). The positive result of these tests proves that total energy density, thermal momentum and all remaining values of the energy-momentum tensor, G^{jk}, are physically admissible in the range of admissibility of linear Cattaneo model (21) and (22). Thus, we can accept kinetic potential (27) as the entity leading to physical results. In fact, from an infinite variety of kinetic potentials possible in the heat flux framework we accept the sole kinetic potential (27) to restitute both the Cattaneo equations and associated extended thermodynamic theory (Eqs. (45)–(54) and (75)–(79), in agreement with EIT [3]).

10. Conclusions

We have shown the reality of expectation that equations of nonequilibrium heat transfer may be described by variational principles of least action-type in which equations of conservation and kinetics are adjoined to a given kinetic potential, as in optimization approaches. Variational formulations based on action-type functionals used here differ substantially from formulations encountered in thermodynamics of Onsager and Prigogine. The method of variational potentials (applicable to various L) may provide a relation between these two types of variational settings. Consistency of applied constraints, formal and physical, is always an important issue.

The theory of a limiting reversible process serves as a basis and indicator when evaluating canonical conservation laws that involve only state variables and are believed to be physical relationships constraining any natural process, reversible or not. The physical consequence of satisfaction of these canonical conservation laws in the realm of variational irreversible processes is the second law of thermodynamics.

The changes caused by the irreversibility imply the necessity to adjoint to the kinetic potential both sort of equations: those describing kinetics and those representing conservation laws. Unnecessity of adjoining kinetic expressions seems to be valid only in limiting reversible process, where the physical information does not decrease. Yet, in irreversible situations, more constraints seems necessary in the action functional. In fact, the thermodynamic irreversibility complicates potential representations of physical fields in comparison with the representations describing the reversible evolution.

The problem of thermal energy transfer can be broken down to the problem of potentials, as in the case of electromagnetic and gravitational fields. We have displayed inhomogeneous equations describing heat transfer in terms of thermal potentials and sources of the field. These equations contain the sources of the thermal field: heat flux $\mathbf{q}$ and energy density ρ_e.

In the heat transfer theory, these results describe a situation similar to that in the electromagnetic and gravitational field theories, where the specification of sources (electric four-current or the matter tensor, respectively) defines the behavior of the potentials.

In view of the approximations contained in the linear structure of the Cattaneo kinetics, Lagrangian (27) and energy conservation (60) it is worth stressing that the theory based on the variational formulation of Kaliski's kinetics, Eq. (23) or Eqs. (25) and (70), may require less approximations because the related kinetic potential L can be formulated without the restrictive notion of equilibrium reference energy ε. The variational formulation of Kaliski's equations will, therefore, be the subject of a further effort.

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References

[1] H. Grad, Principles of the theory of gases, in: S. Flugge (Ed.), Handbook der Physik, vol. 12, Springer, Berlin, 1958.

[2] S. Sieniutycz, R.S. Berry, Conservation laws from Hamilton's principle for nonlocal thermodynamic equilibrium fluids with heat flow, Phys. Rev. A 40 (1989) 348–361.

[3] D. Jou, J. Casas-Vazquez, G. Lebon, Extended Irreversible Thermodynamics, Springer, Heidelberg, 1993.

[4] H. Callen, Thermodynamics and an Introduction to Thermostatistics, Wiley, New York, 1998.

[5] S. Sieniutycz, Thermodynamics of coupled heat, mass and momentum transport with finite wave speed. I. Basic ideas of theory; II. Examples of transformations of fluxes and forces, Int. J. Heat Mass Transfer 24 (1981) 1723–1732, and 24 (1981) 1759–1769.

[6] S. Sieniutycz, Conservation Laws in Variational Thermo-Hydrodynamics, Kluwer Academic Publishers, Dordrecht, 1994.

[7] S. Sieniutycz, Variational thermomechanical processes and chemical reactions in Distributed Systems, Int. J. Heat Mass Transfer 40 (1997) 3467–3485.

[8] J.J. Stephens, Alternate forms of the Herrivel-Lin variational principle, Phys. Fluids 10 (1967) 76–77.

[9] R.L. Seliger, G.B. Whitham, Variational principles in continuum mechanics, Proc. Roy. Soc.A 302 (1968) 1–25.

[10] S. Sieniutycz, Optimization in Process Engineering, Wydawnictwa Naukowo-Techniczne, Warszawa, 1978.

[11] S. Kaliski, Wave equation of heat conduction, Bull. Acad. Pol. Sci. Ser. Sci. Tech. 13 (1965) 211–219.