GENERAL EXPRESSION OF ENTROPY PRODUCTION BASED ON THERMOMASS THEORY

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ABSTRACT

The entropy production in the classical irreversible thermodynamics (CIT) is expressed as a bilinear form of generalized (driving) forces and conjugated (driven) fluxes, which suffers from the arbitrariness of decomposition of the forces and the fluxes, and the possible negative entropy production in non-Fourier heat conduction problems (heat waves). In this paper, we present a general form of entropy production for heat conduction based on the thermomass model at first, which is the product of the friction force and the drift velocity of thermomass divided by temperature, and holds true for both Fourier and non-Fourier heat conduction. Then the similar generalization of the expression of entropy production for other kinds of linear and non-linear transport processes is proved to be applicable. Such general expression for entropy production is consistent with that in extended irreversible thermodynamics, where the entropy of a system depends not only on the classical variables, but also on the dissipative fluxes, for example, the heat flux in heat conduction problems.

Key words: entropy production, thermomass model, classical irreversible thermodynamics, extended irreversible thermodynamics, non-linear transport processes

1. Introduction

The establishment of classical irreversible thermodynamics (CIT) can be traced back to 1931, when Onsager postulated the reciprocal relations in two of his papers [1]. He wrote the “dissipation-function” with a bilinear form of “forces” and “velocities”. The theory was further developed by Prigogine [2, 3], de Groot *et al.* [4-9] and the “dissipation-function” was clarified to be entropy production, σ^s. The entropy production in CIT is a bilinear product of the thermodynamic (generalized) forces, or driving forces $\boldsymbol{X}$ and conjugated fluxes, or driven fluxes $\boldsymbol{J}$ [4, 7]

$$\sigma^s = \sum_{\alpha} \boldsymbol{J}_\alpha \boldsymbol{X}_\alpha \ . \tag{1}$$

The CIT assumes a linear relation between the thermodynamic forces and fluxes, so it is also regarded as linear irreversible thermodynamics. The CIT has been applied well in many fields. For instance, the reciprocal relations facilitate the analyses on cross effects of various irreversible processes, such as thermoelectric and thermophoresis effects; the least dissipation of energy [1] and minimum entropy production principle for stationary states [2, 3] based on variational principles can derive the transport equations and be used for thermodynamic optimization of irreversible processes [10-12].

However, the CIT is still imperfect. For instance, the decomposition of the forces and fluxes in the expression of entropy production is to some extent arbitrary [4, 13,14]. For instance, the thermodynamics force in heat conduction processes can be defined as $-\nabla T$, $-\nabla \ln T$ or ∇T^{-1} in Fourier’s picture, energy picture or entropy picture, respectively [15]. It was realized soon after the establishment of reciprocal relations that the ambiguity of selection of these forces and fluxes is harmful for the reciprocity theorem [16]. The physical identification of thermodynamic forces and fluxes is highly required and regarded as one of the most fundamental questions about CIT [14, 16]. On the other hand, the linear relations between forces and fluxes do not stand in some cases. The chemical reactions and rheological flows are generally characterized by nonlinear constitutive equations [4, 13, 14]. The linear heat conduction law is applicable only in normal practical conditions. When combined with the energy conservation relation, the linear Fourier's law of heat conduction will lead to a parabolic evolution function for state variables, which predicts the non-physical infinite propagation speed of thermal perturbation. Great efforts have been made to establish more general laws for irreversible processes in extreme conditions. The Cattaneo-Vernotte (CV) model [17-19] (c.f. Eq. (7))for heat conduction containing the relaxation term of heat flux can give a hyperbolic evolution function and remove the paradox of infinite propagation speed, and is also applicable to modify the Fick's law [20] and Newton's viscosity law (i.e. the Maxwell model for viscoelasticity) [21-23]. Since the heat flux is not proportional to the temperature gradient or the thermodynamic force, the entropy production is no longer positive semi-definite, which seems to violate the second law of thermodynamics [13, 24]. The deviation from linearity undermines the CIT theories. This motivates the development of extended irreversible thermodynamics (EIT) [13, 24-39], which introduces fluxes as independent variables and redefines some concepts, such as temperature and entropy. The entropy production is defined as a new form in the framework of EIT and keeps positive semi-definite in extreme conditions, such as heat transport at high frequencies and short wavelengths. However, the physical meaning of modified generalized forces has not been clarified till now.

The thermomass (TM) model [40-47] has been developed in recent years to establish a general relation for heat conduction on the basis of the first principle. Based on the Einstein's mass-energy equivalence relation, the TM model gives a governing equation for heat conduction covering nonlocal and nonlinear effects, which can be ascribed to the inertia of thermomass. This model is also useful to study the unusual transport phenomena in nano-scale systems [47]. Comparisons of the TM model with EIT and phonon hydrodynamics have been carried out. It was found that the constitutive equation for heat transport by different theories is consistent [35, 44, 45]. The entropy production for hyperbolic heat conduction based on the TM model was also derived and found to be analogous with the results in EIT [46]. In the present paper, the physical essences of forces and fluxes are further examined in assistance of the TM theory to develop a general expression for entropy production in irreversible transport processes, which is applicable in both ordinary and fast transient conditions.

2. Generalized Entropy Production in EIT

We start from the entropy production for transport processes in CIT

$$\sigma^s = \boldsymbol{q}\cdot\nabla\left(\frac{1}{T}\right) - \frac{1}{T}\mathbf{P}^v : \nabla\boldsymbol{u}_\mathrm{f} - \sum_{k=1}^{N}\boldsymbol{J}_k\cdot\nabla\left(\frac{\mu_k}{T}\right) + \frac{1}{T}\boldsymbol{i}\cdot\nabla\varphi_\mathrm{e}\,, \tag{2}$$

where $\boldsymbol{q}$ is the heat flux vector, T is the temperature, $\mathbf{P}^v$ is the stress tensor, $\boldsymbol{u}_\mathrm{f}$ is the velocity of fluid, $\boldsymbol{J}_k$ is the diffusion flux, μ_k is the chemical potential, $\boldsymbol{i}$ is the current density, and φ_e is the electric potential. Equation (2) characterizes the irreversibility induced by transport of heat, momentum, mass fraction and charge and consists of a sum of products of flow quantities (thermodynamic fluxes) and gradients of intensive state variables (thermodynamic forces). This expression keeps semi-positive definite as long as the linear transport relations hold

$$\boldsymbol{q} = -\kappa\nabla T\,, \text{ (Fourier's law for heat conduction)} \tag{3a}$$

$$\boldsymbol{J}_k = -\sum_{j=1}^{N}\rho D_{kj}\nabla c_j\,, \text{ (Fick's law for mass diffusion)} \tag{3b}$$

$$\boldsymbol{i} = -\frac{1}{r_\mathrm{e}}\nabla\varphi_\mathrm{e}\,. \text{ (Ohm's law for electrical conduction)} \tag{3c}$$

$$\mathbf{P}^v = -2\eta\nabla\boldsymbol{u}_\mathrm{f}\,, \text{ (Newton's law for viscous flow)} \tag{3d}$$

where κ is the thermal conductivity, η is the viscosity, D is the diffusivity, ρ is the density, c_k is the mass ratio defined by ρ_k/ρ, and r_e is the electric resistance. When co-existing, these processes present cross effects, such as thermoelectric and thermal diffusion. In these cases the linear transport relations become

$$\boldsymbol{q} = L_{qq}\nabla\left(1/T\right) - \sum_{k=1}^{N} L_{qk}\nabla\left(\mu_k/T\right) + L_{qe}\nabla\left(\varphi_e/T\right), \tag{4a}$$

$$\boldsymbol{J}_k = L_{kq}\nabla\left(1/T\right) - \sum_{j=1}^{N} L_{kj}\nabla\left(\mu_j/T\right) + L_{ke}\nabla\left(\varphi_e/T\right), \tag{4b}$$

$$\boldsymbol{i} = L_{eq}\nabla\left(1/T\right) - -\sum_{k=1}^{N} L_{ek}\nabla\left(\mu_k/T\right) + L_{ee}\nabla\left(\varphi_e/T\right). \tag{4c}$$

where $\boldsymbol{L}$ are phenomenological coefficients and required to be symmetric according to Onsager's reciprocal relation.

However, the above linear laws have some inherent theoretical defects. For example, in rigid bodies or fluids at rest, when combined with the energy conservation relation

$$\rho\frac{\partial u}{\partial t} = -\nabla\cdot\boldsymbol{q}\,, \tag{5}$$

the Fourier's law of heat conduction leads to a parabolic equation for temperature evolution

$$\rho C_V\frac{\partial T}{\partial t} = \nabla\cdot\left(\kappa\nabla T\right). \tag{6}$$

where u is the internal energy density and C_V is the specific heat. Though this equation is enough to most engineer applications, it predicts an infinite propagation speed of thermal perturbation and profiles temperature evolution incorrectly for fast transient heating problems. To remove this defect, the Cattaneo-Vernotte (CV) model [17-19] was proposed as

$$\tau_{\text{CV}}\frac{\partial\boldsymbol{q}}{\partial t} + \boldsymbol{q} = -\kappa\nabla T\,. \tag{7}$$

where τ_{CV} is the relaxation time in CV model. The relaxation time is generally very small (~10^{-12} s) for condensed matters. Nevertheless, this modification causes new problems, as the deviation from the linear law breaks the semi-positive definitiveness of the classical entropy production,

$$\sigma^s = \frac{\kappa\nabla T\cdot\nabla T}{T^2} + \frac{\tau_{\text{CV}}}{T^2}\frac{\partial\boldsymbol{q}}{\partial t}\cdot\nabla T\,. \tag{8}$$

Equation (7) can be negative because of its second term on the right-hand side, which has been verified by numerical calculations [13, 24] and seems to violate the second law of thermodynamics. The EIT theory assumes the heat flux $\boldsymbol{q}$ to be a new state variable, and changes the definition of entropy

$$s = s_{\text{eq}} - \frac{1}{2}\frac{\tau_{\text{CV}}}{\rho\kappa T^2}\boldsymbol{q}\cdot\boldsymbol{q}\,. \tag{9}$$

So, the EIT generalizes the entropy production for heat conduction [13, 25]

$$\sigma^{\text{s}}_{\text{EIT}} = \frac{1}{\kappa T^2}\boldsymbol{q}\cdot\boldsymbol{q}\,. \tag{10}$$

It is always semi-positive definite for the heat waves (as shown in Fig. 1). The modified entropy production is exactly the same as the classical expression of Eq. (2) if the Fourier's law holds. For heat conduction in fluids, Müller *et al.* [26-28] choose heat flux and stress tensor as independent variables, and the transport process agrees with the kinetic theory of gases from a derivation based on Grad's 13 moment distribution. In this case the entropy production is positive definite with a quadratic form of heat flux and stress tensor. The same analyses can be made for other transport processes and the generalized entropy production in EIT to the lowest order of flux becomes

$$\sigma^s = \frac{1}{\kappa T^2}\boldsymbol{q}\cdot\boldsymbol{q} + \frac{1}{2\eta T}\mathbf{P}^v:\mathbf{P}^v + \frac{1}{T}\sum_{k=1}^{N}\boldsymbol{J}_k\cdot\frac{R}{M_k\rho_k}\mathbf{D}^{-1}\boldsymbol{J}_k + \frac{1}{T}r_e\boldsymbol{i}\cdot\boldsymbol{i}, \tag{11}$$

where D is the diffusion matrix of Fick's law in Eq. (3c), R is the gas constant, and M_k is the molecular mass of species k. This expression keeps semi-positive in short wave length or high frequency phenomena since it has a quadratic structure. Taking the similar decomposition as in CIT, it is noticed that the thermodynamic forces are no longer the gradient of intensive state variables but proportional to the flow quantities. Therefore, the thermodynamic forces in EIT cannot be regarded as driving forces. This difference has been discussed by Llebot *et al.* [13, 25] for thermoelectric effect, and the definitions in EIT were revealed to be closer to Onsager's original proof of reciprocal relations. However, the decomposition and physical meaning of thermodynamic forces and fluxes in the generalized entropy production are not clarified.

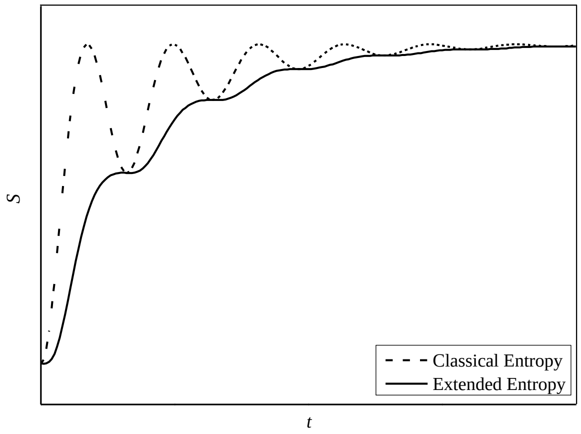

Fig 1: The evolutions of the classical equilibrium entropy SCIT and the extended entropy SEIT in an adiabatic system

3. TM Model Based General Entropy Production for Heat Transport

3.1 Thermomass model

According to the Einstein's mass-energy equivalence relation, the thermal energy divided by the square of light speed in vacuum, is part of the "proper mass" of a system. That means "a piece of iron weighs more when red-hot than when cool" [48,49]. From this point of view, the mass increase of a condensed matter, m_{h}, due to thermal vibrations is

$$m_{\mathrm{h}} = \frac{mC_V T}{c^2}, \tag{12}$$

where m is the mass of a body, C_V represents the specific heat capacity at constant volume, and c is the speed of light in vacuum. Thus the density of the thermomass ρ_{h} with a unit of kg·m^{-3} is

$$\rho_{\mathrm{h}} = \frac{\rho C_V T}{c^2}. \tag{13}$$

The drift velocity of the thermomass, $\boldsymbol{u}_{\mathrm{h}}$, can be extracted from the heat flux

$$\boldsymbol{u}_{\mathrm{h}} = \frac{\boldsymbol{q}}{\rho C_V T}. \tag{14}$$

The governing equations of heat conduction have been obtained in analogy with porous hydrodynamics

$$\frac{\partial \rho_{\mathrm{h}}}{\partial t} + \nabla \cdot \left(\rho_{\mathrm{h}} \boldsymbol{u}_{\mathrm{h}} \right) = 0\,, \tag{15}$$

$$\rho_{\mathrm{h}} \frac{\partial \boldsymbol{u}_{\mathrm{h}}}{\partial t} + \left(\rho_{\mathrm{h}} \boldsymbol{u}_{\mathrm{h}} \cdot \nabla \right) \boldsymbol{u}_{\mathrm{h}} + \nabla p_{\mathrm{h}} = \boldsymbol{f}_{\mathrm{h}}\,, \tag{16}$$

where the first and second terms in Eq. (16) represent the inertia effect, $\boldsymbol{f}_{\mathrm{h}}$ is the friction force, and p_{h} is the pressure of thermomass. The thermal pressure can be derived from the Debye state equation for dielectric solids

$$p_{\mathrm{h}} = \gamma \rho_{\mathrm{h}} C_V T = \frac{\gamma \rho \left(C_V T \right)^2}{c^2}\,, \tag{17}$$

where γ is the Grüneisen parameter. Equation (15) gives the thermomass (energy) conservation relation when Eqs. (13) and (14) are substituted into it. Equation (16) represents the governing equation for heat transport. For bulk materials, the heat conduction process is analogous with the fluid flow in porous media wherein the friction force is proportional to the flow rate

$$\boldsymbol{f}_{\mathrm{h}} = -\beta \rho_{\mathrm{h}} \boldsymbol{u}_{\mathrm{h}}\,. \tag{18}$$

The momentum equation (16) will reduce to the Fourier's conduction law in conditions with negligible inertia of thermomass, which means a balance between the driving and friction forces

$$\nabla p_{\mathrm{h}} = \boldsymbol{f}_{\mathrm{h}}\,, \tag{19}$$

Inserting Eq. (17) into Eq. (19) and comparing with the Fourier's law, the friction coefficient β can be determined as

$$\beta = \frac{2\gamma \rho C_V^2 T}{\kappa}\,. \tag{20}$$

where κ is the thermal conductivity. Thus, the general heat conduction equation can be written as

$$\tau_{\mathrm{TM}} \frac{\partial \boldsymbol{q}}{\partial t} + 2\boldsymbol{l} \cdot \frac{\partial \boldsymbol{q}}{\partial x} - b\kappa \nabla T + \kappa \nabla T + \boldsymbol{q} = 0\,, \tag{21}$$

with

$$\tau_{\mathrm{TM}} = \frac{\kappa}{2\gamma \rho C_V^2 T}\,, \tag{22a}$$

$$\boldsymbol{l} = \frac{\boldsymbol{q}\kappa}{2\gamma C_V \left(\rho C_V T \right)^2} = \boldsymbol{u}_{\mathrm{h}} \tau_{\mathrm{TM}}\,, \tag{22b}$$

$$b = \frac{q^2}{2\gamma \rho^2 C_V^3 T^3} = Ma_{\mathrm{h}}^2\,, \tag{22c}$$

where τ_{TM} is the lagging time between the temperature gradient and the heat flux; $\boldsymbol{l}$ is the characteristic length of heat conduction [47], which is a measure of the spatial inertia effects, i.e. the steady state non-Fourier heat conduction occurs and the boundary slip should be considered at the scale; Ma_{h} is the thermal Mach number defined as the ratio of the drift velocity, u_{h}, to the thermal wave speed in the phonon gas, u_{hs}. The first three terms on the left-hand side of Eq. (21) come from the inertia effects. The fourth term represents the effect of the pressure gradient (driving force), and the last term is proportional to the resistance force. Equation (21) reduces to the CV model when the second and third inertia terms are neglected, which profiles the heat waves for fast transient perturbation. The third inertia term implies that the effective thermal conductivity will reduce when the heat flux is high enough, which agrees with the experimental results for nanotubes and nanowires when considering slip boundary conditions [47]. Cimmelli *et al.* [35] obtained a similar equation to Eq. (21) based on the concept of dynamical non-equilibrium temperature, and the non-local effect could be obtained by a nonlinear solution of the phonon Boltzmann equation, which is consistent with the theory of phonon hydrodynamics [45]. The above mentioned thermomass theory is limited to the conduction in rest rigid bodies. When dealing with heat conduction in fluids or moving media, more terms are supposed to contribute to the time derivative of heat flux. Christov and Jordan [50] proposed a material derivative to remove the paradox in second sound propagation in moving rigid media in an inertia frame. More generally, Müller and Ruggeri [26] established constitutive equations for heat and momentum transfer in fluids in a non-inertia frame by extended thermodynamics and kinetic theory. The time derivative of heat flux consists of two additional terms, $\delta q_i / \delta t = \dot{q}_i + q_k \left(\partial v_i / \partial x_k\right) - 2q_k W_{ik}$, where v is the fluid velocity and W is the angular velocity matrix. The first additional term $q_k \left(\partial v_i / \partial x_k\right)$ is from the requirement of objectivity, the so-called Jaumann derivatives. The second additional term $-2q_k W_{ik}$ can be rewritten as $-2c^2(\rho_h u_h)_k W_{ik}$ with Eqs. (13)-(14) and regarded as a Coriolis inertia term due to the effects in a non-inertia frame.

3.2. General Expression of Entropy Production in Heat Transport

The expression of entropy production in the heat transport process can be established based on the TM model. Since it aims to evaluate the dissipation in the system, the TM model expresses entropy production as a product of friction force and velocity just as the viscous dissipation in hydrodynamics [46]

$$\sigma_{\mathrm{TM}}^{\mathrm{s}} = -\frac{1}{T}\boldsymbol{F}_{\mathrm{h}} \cdot \boldsymbol{u}_{\mathrm{h}} = \frac{1}{\kappa T^2}\boldsymbol{q} \cdot \boldsymbol{q}\,, \tag{23}$$

with

$$\boldsymbol{F}_{\mathrm{h}} = -\frac{\rho C_V \boldsymbol{q}}{\kappa} = \boldsymbol{f}_{\mathrm{h}} \Big/ \left(\frac{2\gamma C_V T}{c^2}\right) = \boldsymbol{f}_{\mathrm{h}} / \xi\,. \tag{24}$$

The dimensionless coefficient ξ relating $\boldsymbol{F}_{\mathrm{h}}$ to $\boldsymbol{f}_{\mathrm{h}}$ comes from the ratio of the mechanical energy of thermomass E_{h} to internal energy u

$$\xi = \frac{\mathrm{d}E_{\mathrm{h}}}{\mathrm{d}u} = \frac{\mathrm{d}p_{\mathrm{h}} + \rho_{\mathrm{h}} u_{\mathrm{h}} \mathrm{d}u_{\mathrm{h}}}{\mathrm{d}u}\,. \tag{25}$$

E_{h} consists of a potential part and a kinetic part. In ordinary cases, the potential part corresponding to the internal energy is dominant. The kinetic part should be considered in extreme conditions such as high frequency or heating with huge power rate, when the temperature profile is not enough to characterize the transport process. Equation (24) indicates that $\boldsymbol{F}_{\mathrm{h}}$, with units of $\mathrm{N \cdot m^{-3}}$, is the dissipative force per unit volume, i.e. the friction force per unit volume. Equation (23) gives a semi-positive definite expression and agrees with the solid curve in Fig. 1.

In EIT, the generalized force in the expression of the generalized entropy production is [13]

$$\boldsymbol{X} = \nabla \theta^{-1} - \frac{\tau}{\kappa \theta^2}\frac{\partial \boldsymbol{q}}{\partial t}\,. \tag{26}$$

where θ is the non-equilibrium temperature, which reduces to T when high order terms are negligible. If the relaxation time τ is selected as Eq. (22a), the generalized force appears as

$$-\boldsymbol{X} = \frac{\nabla T}{T^2} + \frac{1}{2\gamma \rho C^2 T^3}\frac{\partial q}{\partial t} = \frac{c^2}{2\gamma \rho C^2 T^3}\left[\nabla p_{\mathrm{h}} + \frac{\partial\left(\rho_{\mathrm{h}} \boldsymbol{u}_{\mathrm{h}}\right)}{\partial t}\right] = \frac{1}{\rho C_V T^2 \xi}\boldsymbol{f}_h\,. \tag{27}$$

Hence the generalized force in EIT is actually the friction force in the thermomass model. The first term on the right-hand side of Eq. (26)

represents the driving force, and the second term means the inertia effect. If the partial differential operator in Eq. (26) is substituted by the material time derivative [35], equation (22) reduces to Eq. (16) exactly.

In CIT, the thermodynamic force in Eq. (2) is called “driving force”, which is the cause of flux [5, 8]. From the viewpoint of the thermomass theory, this force is a friction (dissipative) force, with the same units to the body force in continuum mechanics. Hence, the reason for the invalidity of traditional expression of Eq. (2) in extreme conditions is because it is the friction force rather than the driving force that determines the dissipation or irreversibility of the transport processes.

5. Conclusion

(a) The momentum balance equation (Eq. (16)) of heat conduction based on the thermomass model is the balance of the driving force, inertia force and resistance force. The driving force balanced with the resistance just corresponds to the Fourier’s law of heat conduction. Since entropy production represents the irreversibility of transport processes, the expression of entropy production should be the product of the friction force, rather than the driving force, and the velocity divided by temperature. This general definition of entropy production is applicable not only to the Fourier heat conduction but also to non-Fourier phenomena, such as heat waves and nanoscale heat conduction with superhigh heat flux.

(b) The analyses based on the themomass theory can be extended to other transport processes, such as mass diffusion, electrical conduction and momentum transport processes. The physical essence of the linear transport relations is the balance between the driving forces and friction forces with the inertia force ignored. The general expression of entropy production for irreversible processes is the product of the friction forces and drift velocities, divided by the temperature. The decomposition of forces and fluxes is no longer arbitrary with this physical identification. The general expression is especially necessary for nonlinear transport processes (e.g. heat waves, anomalous diffusion) induced by the inertia effects, while the classical expression cannot keep semi-positive definite in these cases.

(c) The general expression of entropy production based on the thermomass theory agrees with that based on EIT, though from different frameworks of thermophysics. The EIT characterizes the irreversible systems with additional flux variables, i.e. the drift velocities multiplied by the density of extensive properties. It is reasonable since the velocities are actually independent variables in dynamical systems. For the thermomass model, however, the inertia force is taken into account in the conservation equation. The consistency of both theories will deepen the understanding of irreversible thermodynamics.

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