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Review of Extended Irreversible Thermodynamics

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Abstract: *In non-equilibrium thermodynamics, Extended irreversible thermodynamics (EIT), together with classical irreversible thermodynamics (CIT) and rational thermodynamics (RT) has been among the mainstream ofresearch. Critical analysis of EIT has been discussed in this paper.*

Keywords: Non-Equilibrium Thermodynamics, Extended Irreversible Thermodynamics

I. INTRODUCTION

Extended Irreversible Thermodynamics applied independent variables the dissipative fluxes in addition to the classical variables such as internal energy, density, mass concentrations, deformation tensor for the description non-equilibrium phenomena. In the first versions of EIT[9-15], the extra variables were selected to be the usual thermo-hydrodynamic fluxes as the heat flux, the viscous pressure tensor, the electric flux, and the diffusion flux. Later, higher-order fluxes, such as the flux of the heat flux, were included.

Other keystones in the construction of EIT are the formulation of evolution equations for the fluxes and the establishment of a generalized Gibbs equation expressing the dependence of the non-equilibrium entropy with respect to the basic variables. These lines of thought define a general framework, in which coexist several different methods of approach, with either physical or mathematical emphasis and have fostered efforts towards a unified view.

II. GENERALIZED ENTROPY IN A ONE-COMPONENT FLUID

As in CIT, EIT attributes a chief role to entropy. It is assumed that the entropy of a one-component fluid depends locally not only the classical conserved variables, such as internal energy u, specific volume v. But also on the fluxes, namely q (heat flux), p^v (bulk viscous pressure) and $\overset{0}{p^v}$ (deviatoric part of the viscous pressure tensor).

let us consider the basic laws of mass. Momentum and energy for a one-component fluid:

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \boldsymbol{v}) \tag{1}$$

$$\frac{\partial (\rho \boldsymbol{v})}{\partial t} = -\nabla \cdot (p + \rho \boldsymbol{v}\boldsymbol{v}) + \rho \boldsymbol{F} \tag{2}$$

$$\frac{\partial (\rho u)}{\partial t} = -\nabla \cdot (\boldsymbol{q} + \rho u \boldsymbol{v}) - \mathbf{P}^{\mathrm{T}} : \nabla \boldsymbol{v} \tag{3}$$

where $\boldsymbol{v}$ is the barycentric velocity, $\boldsymbol{F}$ the external body force such as gravity or the Lorentz force due to electromagnetic fields, and an upper index T denotes transposition. The total pressure tensor P is related to the viscous pressure P^{v} by $\mathbf{P} = p^{U} + \mathbf{P}^{v}$. where p is the equilibrium pressure and $\boldsymbol{U}$ the identity tensor; as usual, P^{v} is split into parts: a bulk pressure $\mathbf{P}^{\mathrm{v}}(= \frac{1}{3}$ trace $\mathbf{P}^{\mathrm{v}})$ and a deviatoric part $\overset{0}{p^v}$ so that $\mathbf{P}^{v} = p^{vU} + \overset{0}{p^v}$

The generalized entropy S(u, v, q, p^{v} , $\mathrm{p}^{0\mathrm{v}}$) is supposed to possess the following properties:(i) it is an additive quantity, (ii) it is a convex function of the whole set of variables, and (iii) its rate of production is locally positive. In differential form, the entropy can be written as

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$$ds = \frac{1}{\theta}du + \frac{1}{\theta}\pi v dv - \frac{1}{\theta}\boldsymbol{v}\alpha_0 dp^v - \frac{1}{\theta}\boldsymbol{v}\alpha_1 . dq - \frac{1}{\theta}\boldsymbol{v}\overset{0}{\alpha_2} : d\,\overset{0}{\mathbf{P}^v} \tag{4}$$

where all the extensive quantities s, u, $v$are measured per unit mass. In analogy with the classical theory, an absolute temperature $\theta$and a generalized pressure π as partial derivatives of the entropy with respect to the internal energy and the volume, respectively were defined in formalism of EIT[9-15], read as

$$\frac{\partial s}{\partial u} = \frac{1}{\theta}\left(u, v, q, p^v, \overset{0}{\mathbf{P}^v} \right) \tag{5}$$

$$\frac{\partial s}{\partial v} = \frac{1}{\theta}\left(u, v, q, p^v, \overset{0}{\mathbf{P}^v} \right) \tag{6}$$

$$\frac{\partial s}{\partial q} = -\frac{1}{\theta}\boldsymbol{v}\alpha_1\left(u, v, q, p^v, \overset{0}{\mathbf{P}^v} \right) \tag{7}$$

$$\frac{\partial s}{\partial p^v} = -\frac{1}{\theta}\boldsymbol{v}\alpha_2\left(u, v, q, p^v, \overset{0}{\mathbf{P}^v} \right) \tag{8}$$

where α_1 ,α_0 and $\alpha_2$are vector, scalar, and tensor fields, respectively. For simplicity we assume that the above equations of state do not contain nonlinear terms in the fluxes. It follows that $\alpha_1 = \alpha_{10} q . \alpha_0 = \alpha_{00} p^v , \overset{0}{\alpha_2} = \alpha_{21} \overset{0}{P^v}$, $\theta^{-1} = \theta^{-1}$ $(u, v) = T^1 (u, v)$ and $\pi = \pi(u, v) = p(u, v)$ where α_{10}, α_{00} and α_{21} are scalar functions of u, and v. From eq.(41) and the balance equations of energy and mass, one obtains for ds/dt , the material time derivative of s ,

$$\rho\frac{ds}{dt} = -\frac{1}{T}\nabla \cdot q - \frac{1}{T}p^v \nabla \cdot \boldsymbol{v} - \frac{1}{T}\overset{0}{\mathbf{P}^v} : \overset{0}{\mathbf{V}} - \frac{1}{T}\alpha_{10}\boldsymbol{q} \cdot \boldsymbol{q} - \frac{1}{T}\alpha_{21}\overset{0}{\mathbf{P}^v} : \left(\overset{0}{\mathbf{P}^v} \right) \tag{9}$$

in which $\overset{0}{\mathbf{V}}$ is the deviatoric traceless part of the symmetric velocity gradient tensor and $\overset{0}{\mathbf{P}^v}$ denotes the material time derivative. This equation can be cast in the general form of a balance equation

$$\rho\frac{ds}{dt} - \nabla \cdot \boldsymbol{J}^s = \sigma^s \tag{10}$$

on the condition that we identify the expressions for the entropy flux $\boldsymbol{J}^s$ and the entropy production σ^s . A general expression of the entropy flux $\boldsymbol{J}^s$ for isotropic systems is, up to second order in the fluxes,

$$\boldsymbol{J}^s = \theta^{-1}\boldsymbol{q} + \beta' p^v \boldsymbol{q} + \beta'' \overset{0}{P^v} \cdot \boldsymbol{q} \tag{11}$$

where the coefficients β and β are functions of u and v. In the linear approximation in the fluxes, the second and third terms in the right-hand side are negligible and θcan be identified with the local-equilibrium temperature, so the eq.(11) reduces to the expression of the classical theory of irreversible processes, namely $\boldsymbol{J}^s = T^{-1}\boldsymbol{q}$.

III. PHYSICAL INTERPRETATION OF NON-EQUILIBRIUM ENTROPY

Consider a volume element of a homogeneous fluid which is sufficiently small so that within it the spatial variations of pressure and temperature are negligible; if the fluid element is subject to a heat flux $\boldsymbol{q}$ and a viscous pressure $\overset{0}{P^v}$ (viscous bulk effects are ignored), it is then asked which entropy may be ascribed to it. To answer this question, the volume is suddenly isolated, i.e. bounded by adiabatic and rigid walls, and allowed to decay to equilibrium. The decay

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of $\boldsymbol{q}$ and $\overset{0}{P}{}^{v}$ to their final vanishing equilibrium values is accompanied by a production of entropy, so that the final equilibrium entropy value is given by

$$\rho^{s}_{eq\cdot f} = \rho s_i + \int_0^\infty \sigma^s dt. \tag{12}$$

Indices i and f refer to the initial non-equilibrium state and the final equilibrium state respectively, s is the entropy per unit mass and σ is the rate of entropy production per unit volume. The second term in the right-hand side of eq.(12) corresponds to the non-compensated heat introduced by Clausius and will be commented on below. Its explicit form in the case of the Maxwill-Cattano equation[9-15] may be obtained as follows

. Let $t = 0$ be the instant at which the volume element is isolated. On identifications $\mu_1 = \left(\lambda T^2\right)^{-1}$ and $\mu_2 = \left(2\eta T\right)^{-1}$ with

$$\sigma^s = \left(\lambda T^2\right)^{-1} \boldsymbol{q}\cdot\boldsymbol{q} + \left(2\eta T\right)^{-1} \overset{0}{\mathbf{P}}{}^{v} : \overset{0}{\mathbf{P}}{}^{v} \tag{13}$$

If the decay of $\boldsymbol{q}$ and $\overset{0}{\mathbf{P}}{}^{v}$ is governed by the Maxwell-Cattaneo equation, we have

$$\boldsymbol{q}(t) = \boldsymbol{q}(0)\exp\left(-t/\tau_1\right),\ \overset{0}{\mathbf{P}}{}^{v}(t) = \overset{0}{\mathbf{P}}{}^{v}(0)\exp\left(-t/\tau_2\right). \tag{14}$$

Inserting these expressions into (13)and integrating with respect to the time, one obtains for the non-equilibrium entropy in the steady state

$$\rho s = \rho s_{eq} - \left(\tau_1/2\lambda T^2\right)\boldsymbol{q}(0)\cdot\boldsymbol{q}(0) - \left(\tau_2/4\eta T\right)\overset{0}{\mathbf{P}}{}^{v}(0) : \overset{0}{\mathbf{P}}{}^{v}(0) \tag{15}$$

which is the integrated form of the entropy in the absence of bulk viscous pressure. The above derivation is indicative as it assigns a meaning to the non-classical terms in the equation for the entropy, by relating them to a physical operational definition.

IV. CRITICAL ANALYSIS OF EIT

- EIT clearly emphasizes the strong correlation between the transport equations and thermodynamics. One cannot formulate transport equations independently of their thermodynamic background. It follows with the introduction of relaxation terms in the transport equations results in a modification of the expression of entropy whereas the presence of non-local terms leads to a generalization of the expression of the entropy flux.
- EIT has given meaning to temperature and entropy in non-equilibrium states, and the relation between the *H*-theorem and the formulation of the second law in non-equilibrium processes.
- Another important problem is the formulation of non-equilibrium equations of state whereas; in classical irreversible thermodynamics such fundamental questions do not arise as they are avoided by appealing to the local equilibrium postulate.
- The use of the equilibrium slow variables complemented by fast variables taking the form of fluxes of mass, momentum and energy is generally sufficient to solve a great variety of problems. The time-evolution equations of these variables generalize the classical transport equations of Fourier, Fick, and Newton. An increasing number of variables are necessary to describe high-frequency responses of systems. The density correlation function has been derived by including higher-order fluxes.
- Another difference between EIT and the classical theories is the formulation of non-equilibrium equations of state. A generalized equation of state is a consequence of the existence of a non-equilibrium temperature different from the classical local-equilibrium temperature introduced is most formalism. Kinetic theory developments indicate that the non-equilibrium temperature is directly related to the translational kinetic

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energy of the particles in the plane normal to the heat flux. Similar conclusions hold for the non-equilibrium pressure and non-equilibrium chemical potential which are also allowed to be flux dependent.

- Radiation hydrodynamics is another example of non-classical heat transport. A particularly interesting result arising from EIT is that it imposes that a signal such as the heat flux, cannot reach an unbounded valve but is 'saturated' by a limiting value equal to the energy density times a maximum speed. This saturation effect cannot be described by the classical Fourier law.
- The domain of application of EIT is that of polymer solutions, as they exhibit rather long relaxation times for the viscous pressure tensor. EIT has proved to be of use in obtaining the relevant constitutive equations. In contrast to the formalisms based on internal variables, EIT identifies from the start the viscous pressure as an additional variable. This allows one to unify the description of very large classes of material systems, passing from ideal gases to viscoelastic materials.

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