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## On a phenomenological non-equilibrium entropy for a class of rigid heat conductors

J Casas-Vázquez and D Jou

Departament de Termologia, Universitat Autònoma de Barcelona, Bellaterra, Barcelona, Spain

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**Abstract.** From a semi-empirical model for the relaxation time of the heat flux and from a generalised Maxwell relation, we obtain the equations of state of an extended Gibbs equation which describes the dependence of a non-equilibrium entropy on the internal energy and the heat flux. By integration of the Gibbs equation, we obtain an explicit expression for the corresponding non-equilibrium entropy.

### 1. Introduction

While a number of macroscopic quantities have a well defined microscopic equivalent, e.g. the energy and the velocity, some other quantities must be defined on a thermodynamic basis, e.g. the entropy and the absolute temperature. These quantities are well defined at equilibrium, but their significance and definition in non-equilibrium situations is a problematic matter which influences all the subsequent development of thermodynamic theories. Three main approaches have been undertaken in the modern non-equilibrium thermodynamics.

(1) The classical irreversible thermodynamics (de Groot and Mazur 1962, Gyarmati 1970, Glandsdorff and Prigogine 1971) is based on the hypothesis of local equilibrium, which allows us to extend the classical definitions of entropy and of absolute temperature to every elemental volume of the system, even in non-equilibrium.

(2) The rational thermodynamic theories (Truesdell 1969) assume that both the entropy and an empirical temperature are primitive concepts of general validity.

(3) On the assumption that there exists an infinity of functionals that possess the required properties of the entropy, the entropy-free theories (Meixner 1967, Day 1972) try to build a thermodynamics avoiding the definition of a non-equilibrium entropy as a primitive variable; however, they cannot get rid of a primitive non-equilibrium absolute temperature.

Another approach to non-equilibrium thermodynamics has recently been proposed (Müller 1967, Lebon 1978, Jou *et al* 1979, Lebon *et al* 1980, Jou and Casas-Vázquez 1980): the so-called extended irreversible thermodynamics. In this theory, the existence of a non-equilibrium entropy is assumed whose dependence on the dissipative fluxes as well as on the classical thermostatic variables can be expressed through a generalised Gibbs equation. This theory differs from the classical one and from the entropy-free thermodynamics in assuming the existence of a non-equilibrium entropy;

also, it differs from the rational thermodynamics in placing its starting point in a Gibbs equation; finally, it is different from the theories of thermodynamics with internal variables (Biot 1954, Coleman and Gurtin 1967, Kluitenberg 1978, Bataille and Kestin 1979) in that the internal variables are specified *a priori* as the dissipative fluxes.

The aim of this paper is to construct an explicit form of the non-equilibrium entropy for a class of rigid heat conductors. In § 2, we review the generalised Gibbs equation of extended irreversible thermodynamics. In § 3, we discuss a simple, indicative model of the equations of state in metallic rigid conductors and we obtain the non-equilibrium entropy by integration of the Gibbs equation.

## 2. A generalised Gibbs equation for rigid heat conductors

It is well known (Callen 1960) that the complete macroscopic description of thermodynamic systems at equilibrium is contained in the fundamental equation, as for instance the total entropy  $S$  expressed as a function of properly chosen variables. For a rigid heat conductor, the only thermodynamic variable is the total internal energy  $U$ , and the fundamental equation is simply  $S = S(U)$ . The classical description of non-equilibrium states is based on the hypothesis that the fundamental equation remains locally valid, and we then have  $s = s(u)$ , where  $s$  and  $u$  are the entropy and the internal energy per unit mass, respectively.

The evolution of the system can be obtained from the well known energy balance equation

$$\rho \dot{u} = -\nabla \cdot \mathbf{q} \quad (1)$$

where  $\mathbf{q}$  is the heat flux and  $\rho$  the mass density. Since a new variable  $\mathbf{q}$  appears, the description of the system is not closed unless equation (1) is supplemented with an independent relation between  $\mathbf{q}$  and  $u$ . In the classical approach,  $\mathbf{q}$  is related to the spatial distribution of  $u$  by means of the Fourier constitutive equation

$$\mathbf{q} = -\lambda \nabla T \quad (2)$$

where  $\lambda$  is the thermal conductivity. When this equation is introduced into (1) we are led to a parabolic equation for the evolution of  $T$ , and therefore the thermal disturbances propagate at infinite velocity. To avoid this feature, Cattaneo (1958) proposed a generalisation of the Fourier equation with a relaxation term, already motivated by Maxwell (1867), which has the form

$$\mathbf{q} = -\lambda \nabla T - \tau \dot{\mathbf{q}} \quad (3)$$

where  $\tau$  is the relaxation time of the heat flux. While this equation, when introduced into (1), leads to a hyperbolic differential equation and therefore yields a finite velocity for the propagation of thermal disturbances, it however violates the second law of thermodynamics, since it leads for the entropy production to

$$\sigma_s = T^{-2}[\lambda (\nabla T)^2 + \tau \dot{\mathbf{q}} \cdot (\nabla T)]. \quad (4)$$

This expression can be made negative by giving to  $\dot{\mathbf{q}} \cdot (\nabla T)$  a sufficiently negative value. Therefore, the classical formulation is inconsistent with equation (3), which was originally proposed from arguments of the kinetic theory of gases. Equation (3) has been extensively used by many authors (Kranys 1977, Gyarmati 1977, Lebon 1978,

Carrassi 1978, Israel 1976, and references quoted in these papers) and it has been tested from experiments by Rogers (1971).

We now take the point of view of extended irreversible thermodynamics. Instead of expressing  $\mathbf{q}$  in terms of  $\nabla T$ , we consider it as an independent variable. The problem, then, is to find the corresponding evolution equation for  $\mathbf{q}$  in order to construct a thermodynamic theory consistent with equation (3). We assume the existence of a non-equilibrium entropy which depends on  $u$  and  $\mathbf{q}$  and whose differential is given by

$$ds = (\partial s / \partial u) du + (\partial s / \partial \mathbf{q}) \cdot d\mathbf{q}. \quad (5)$$

We assume that  $s$  is sufficiently differentiable in order that the first and the second derivatives can exist. In analogy with the classical definition of absolute temperature, we identify  $(\partial s / \partial u)$  with the inverse of the non-equilibrium absolute temperature

$$T^{-1}(u, \mathbf{q}) = (\partial s / \partial u)_{\mathbf{q}} \quad (6)$$

which can be developed in series of  $\mathbf{q}^2$  giving, up to the first order,

$$T^{-1}(u, \mathbf{q}) = T_{\text{eq}}^{-1}(u) + \beta(u)\mathbf{q}^2 \quad (7)$$

where  $T_{\text{eq}}$  is the local-equilibrium absolute temperature and  $\beta(u)$  is a parameter to be identified. Some authors have defined the absolute temperature as  $T^{-1} = (\partial s / \partial u)_{\mathbf{q}=\mathbf{0}}$ . However, since we aim at obtaining an expression for the non-equilibrium entropy, we need the general expression (7) whether or not we call it temperature.

Also, we have for the second equation of state arising from (5) the following expression, up to second order in the heat flux:

$$(\partial s / \partial \mathbf{q})_{\mathbf{u}} = T_{\text{eq}}^{-1}(u)\alpha(u)\rho^{-1}\mathbf{q} \quad (8)$$

where  $\alpha(u)$  is a parameter that we identify below.

Since (5) is an exact differential, the following generalised Maxwell equation must hold:

$$(\partial T^{-1} / \partial \mathbf{q})_{\mathbf{u}} = [\partial (T_{\text{eq}}^{-1}\rho^{-1}\alpha\mathbf{q}) / \partial u]_{\mathbf{q}} \quad (9)$$

which leads to

$$\beta(u) = \frac{1}{2} d(T_{\text{eq}}^{-1}\rho^{-1}\alpha) / du. \quad (10)$$

In order to identify the function  $\alpha(u)$ , we proceed through the usual development of extended irreversible thermodynamics (Jou *et al* 1979, Lebon *et al* 1980). First of all, we introduce (1) into the time derivative of the entropy,

$$\rho \dot{s} = T^{-1}\rho \dot{u} + T^{-1}\alpha\mathbf{q} \cdot \dot{\mathbf{q}}, \quad (11)$$

and we obtain the following expressions for the entropy flux  $J_s$  and for the entropy production  $\sigma_s$ :

$$\mathbf{J}_s = T^{-1}\mathbf{q}, \quad \sigma_s = \mathbf{q} \cdot (\nabla T^{-1} + T^{-1}\alpha\dot{\mathbf{q}}). \quad (12)$$

Up to second order in the heat flux, the entropy production can be written in the form

$$\sigma_s = \mathbf{q} \cdot (\nabla T_{\text{eq}}^{-1} + T_{\text{eq}}^{-1}\alpha\dot{\mathbf{q}}). \quad (13)$$

As we have said, we look for an equation for  $\dot{\mathbf{q}}$  in terms of  $u$ ,  $\mathbf{q}$  and their spatial gradients. The simplest assumption compatible with the requirements of the second law is, in view of the bilinear character of (13),

$$\nabla T_{\text{eq}}^{-1} + T_{\text{eq}}^{-1}\alpha\dot{\mathbf{q}} = \mu\mathbf{q} \quad (14)$$

with  $\mu \geq 0$ . This leads to the following evolution equation for  $\mathbf{q}$ :

$$\dot{\mathbf{q}} = (T_{\text{eq}}\alpha^{-1}\mu)(\mathbf{q} - \mu^{-1}\nabla T_{\text{eq}}^{-1}). \quad (15)$$

A comparison of this equation with the Maxwell–Cattaneo equation (3) leads to the identification  $\mu = (\lambda T_{\text{eq}}^2)^{-1}$  and  $T_{\text{eq}}\alpha^{-1}\mu = -\tau^{-1}$ , so that we have

$$\alpha = -\tau(\lambda T_{\text{eq}})^{-1}. \quad (16)$$

When this expression of  $\alpha$  in terms of physical quantities is introduced into the generalised Maxwell equation (10), we obtain

$$\beta(u) = -\left(\frac{1}{2}\right) d(\tau\lambda^{-1}T_{\text{eq}}^{-2})/du. \quad (17)$$

In the classical equilibrium thermodynamics, the entropy is not measured directly, but is obtained from the so-called TdS equations (Zemansky 1957), by integration of the specific heat at constant volume and of the coefficient of thermal expansion and of isothermal compressibility, which are indeed well known experimental quantities. Here, however, from a more theoretical point of view, we proceed directly to the integration of the Gibbs equation (5) which, with the interpretations (6) and (16), becomes

$$ds = T^{-1} du - \tau(\rho\lambda T_{\text{eq}}^2)^{-1} \mathbf{q} \cdot d\mathbf{q}. \quad (18)$$

The relaxation time can be measured, at least in principle, from the velocity of propagation of thermal signals, to which it is directly related. Also, the heat conductivity  $\lambda$  is a well known and tabulated quantity. The non-classical part of  $T^{-1}$  can be obtained from the generalised Maxwell relation, and the classical equation of state for  $T_{\text{eq}}$  is known from thermostatics. Therefore, an expression for the non-equilibrium entropy (5) can be obtained by integration of (18).

### 3. A semi-empirical model for the generalised equations of state for a class of rigid conductors

In order to obtain some definite expressions for the equations of state of (18), we have to make some assumptions about the relaxation time  $\tau$ , which is a quantity difficult to measure experimentally. Therefore, we invoke a semi-empirical model in order to obtain an illustrative example of the obtention of a non-equilibrium entropy.

We assume here the example of metallic rigid conductors at room temperature, where the Wiedemann–Franz law (Wannier 1966), relating the thermal and the electric conductivity, is valid. This law allows us to obtain some information about the thermal conductivity, starting from the electrical conductivity, about which much more is known. When the phonon transport of energy is negligible, the Wiedemann–Franz law states that

$$\lambda(\sigma_e T)^{-1} = (\pi^2 k^2 / 3e^2) \quad (19)$$

where  $\sigma_e$ ,  $k$  and  $e$  are respectively the electrical conductivity, the Boltzmann constant and the electric charge of the electron.

The electrical conductivity of the metal is given by (Wannier 1966)

$$\sigma_e = (n_e e^2 / m_e) \tau^* \quad (20)$$

with  $n_e$ ,  $m_e$  and  $\tau^*$  the electron density, electron mass and electron momentum

relaxation time, respectively. Since the heat conduction is a transport phenomenon which, in the situation described here, is directly related to the motion of the electrons, as well as the electrical conduction, we assume, like Wilhelm and Choi (1975), that the heat flux relaxation time  $\tau(T)$  can be identified with  $\tau^*$  and therefore, by combining (19) and (20), we find

$$\tau(T_{\text{eq}}) = b\lambda(T_{\text{eq}})T_{\text{eq}}^{-1} \quad (21)$$

where  $b$  is a constant given by  $b = (3m_e/\pi^2k^2n_e)$ , which is of the order of  $b = 10^{-19} \text{ K}^2 \text{ cm s}^2 \text{ erg}^{-1}$ , which is consistent with a value of  $\tau$  of the order of  $10^{-14} \text{ s}$ . Though this value for  $\tau$  is very small, we have to keep in mind that the lower the temperature of the system, the longer its relaxation time, in general. Of course, the identification of  $\tau$  with  $\tau^*$  is open to discussion, and we remind the reader that we take it only as a simple example for the illustration of the purposes of this paper. With this hypothesis, we obtain the second equation of state of (18). Indeed, from (8) and (16) we have

$$(\partial s/\partial \mathbf{q})_u = -b\rho^{-1}T_{\text{eq}}^{-3}\mathbf{q}. \quad (22)$$

With this information, and through the Maxwell relation (17), we obtain the following equation of state for the non-equilibrium absolute temperature:

$$T^{-1}(u, \mathbf{q}) = T_{\text{eq}}^{-1}(u) + (3b/2\rho)T_{\text{eq}}^{-4}(dT_{\text{eq}}/du)\mathbf{q}^2. \quad (23)$$

We assume that the classical equation of state for the absolute temperature is known from thermostatic measurements, so that all the coefficients in (18) are known. Introducing the subsequent equations of state (22) and (24) into (18) and integrating the corresponding expression, we find for the non-equilibrium entropy

$$s(u, \mathbf{q}) = s_{\text{eq}}(u) - (b/2\rho)(\partial s_{\text{eq}}/\partial u)^3\mathbf{q}^2. \quad (24)$$

Note that this expression applies for heat conduction processes, but that in order to have a more complete description of the system it should be generalised to include electrical conduction. It is seen therefore that the definition of the non-equilibrium entropy depends on which description we use for studying our system (Penrose 1979) and that there is no unique prescription for defining an entropy in non-equilibrium situations.

Some comments can be made also with respect to the non-equilibrium temperature (23). While the numerical value of the non-classical terms in (23) is in fact negligible compared with the value of the classical term, this non-equilibrium temperature deserves some mention from the theoretical point of view. Indeed, the non-equilibrium absolute temperature is a concept common to all non-equilibrium thermodynamic theories. In the local-equilibrium theories, it is simply assumed that it is defined locally by the classical expression, so that there is no fundamental distinction between the classical and the non-equilibrium absolute temperature. In the Coleman–Truesdell–Noll formulation of rational thermodynamics, the non-equilibrium absolute temperature is a primitive quantity which appears from the start in the Clausius–Duhem inequality. On the other hand, in Müller's formulation of rational thermodynamics (Hutter 1977), the absolute temperature is a derived quantity, and instead of absolute temperature there appears the coldness, which is a universal function for some classes of materials (heat conducting fluids, thermoelastic bodies). The coldness  $\Lambda$  generalises the

concept of absolute temperature, and is a function of the primitive empirical temperature  $\theta$  and of its rate of change, i.e.  $\Lambda = \Lambda(\theta, \dot{\theta})$ , in such a way that the local-equilibrium absolute temperature can be identified as the value of  $\Lambda$  when  $\dot{\theta} = 0$ .

Also, even in entropy-free theories, the non-equilibrium absolute temperature cannot be avoided. In this way, Meixner (1967) defines a second temperature, which is different from the local-equilibrium absolute temperature. We note that, as in our formulation, the coldness and the second temperature do not coincide in principle with the local-equilibrium temperature. However, in a rigid heat conductor in a steady non-equilibrium state, both the coldness and the second temperature reduce to the local-equilibrium temperature, while our expression (23) remains different even in this situation. The fundamental problem of the existence and significance of a non-equilibrium entropy and temperature remains an open question (Muschik 1977, Lebon and Lambermont 1977) which is not our concern here.

#### 4. Conclusions

Starting from the assumption of the existence of a non-equilibrium entropy which depends on  $u$  and  $q$ , and assuming it to be sufficiently differentiable, we have identified the coefficients of the corresponding generalised Gibbs equation. Since the experimental results for its equations of state are rather difficult to obtain, and in order to obtain an illustrative expression for the non-equilibrium entropy, we have made a semi-empirical hypothesis on the relaxation time of the heat flux in metallic rigid heat conductors. This has led us to definite and simple expressions for the equations of state.

In particular, we have obtained an expression relating the non-equilibrium absolute temperature to the local-equilibrium absolute temperature. As a definition for the former, we have assumed the validity of the classical expression  $T^{-1} = (\partial s / \partial u)$  with the non-equilibrium entropy. Of course, the validity of this definition is open to criticism, but we can observe that a kinetic definition of temperature also shares an analogous shortcoming, because the latter definition is based on the equipartition theorem, which is only valid at equilibrium. Finally, we have to keep in mind that even in thermostatics, the criterion that allows us to identify  $(\partial s / \partial u)$  as the inverse of the absolute temperature is that the condition of thermal equilibrium between two subsystems in diathermic contact is the equality of these corresponding derivatives in both subsystems. Since our non-equilibrium temperature reduces when  $q = 0$  to the thermostatic temperature, it has this property also and can be called temperature.

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