

On the definition of non-equilibrium entropy

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1982 J. Phys. A: Math. Gen. 15 L565

(<http://iopscience.iop.org/0305-4470/15/10/008>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 30/05/2010 at 14:55

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

On the definition of non-equilibrium entropy

G Lebon[†], J Casas-Vazquez[‡] and D Jou[‡]

[†] Department of Mechanics, University of Liège, B6, Sart Tilman, 4000 Liège, Belgium

[‡] Departamento de Termologia, Universidad Autonoma de Barcelona, Bellaterra, Spain

Received 14 May 1982, in final form 9 July 1982

Abstract. In a recent letter to the editor, criticisms were raised against an argument that we used in previous publications to justify a modification in the definition of the non-equilibrium entropy. These criticisms call for some comments that are developed in the present note.

In previous publications (Lambermont and Lebon 1973, Lebon 1978, Jou *et al* 1979, Lebon *et al* 1980, Casas-Vazquez and Jou 1981, Lebon and Jou 1982), we proposed a new definition for entropy in non-equilibrium which was justified by both macroscopic and microscopic arguments. One of these arguments was that the usual expression for the entropy production in a rigid heat conductor (Prigogine 1961, De Groot and Mazur 1962)

$$\frac{dS}{dt} = - \int_V \mathbf{q} \cdot \frac{\nabla T}{T^2} dV \quad (1)$$

can become negative when the classical Fourier law is replaced by the Maxwell-Cattaneo relation (Maxwell 1867, Cattaneo 1958)

$$\tau \dot{\mathbf{q}} + \mathbf{q} = -\lambda \nabla T. \quad (2)$$

The notations are those of Casas-Vazquez and Jou (1981) and Simons (1982).

The above argument is contested by Simons (1982). Simons argues that if a phenomenological law like (2) fails to give $dS/dt > 0$, then the most logical attitude is to replace (2) by another more general expression, without modifying the definition of entropy. Our point of view is the opposite. To maintain $dS/dt > 0$, we keep the Maxwell-Cattaneo relation but we introduce a generalised entropy, depending not only on T but also on \mathbf{q} , treated as an independent variable.

We agree with Simons that it is not consistent to handle the Maxwell-Cattaneo relation jointly with the classical definition of entropy. It is indeed not coherent to couple a state equation like $s(T)$ that is of order zero in the relaxation time τ with a Maxwell-Cattaneo relation that is of order one in τ .

Our attitude diverges on how to generalise: Simons suggests to extend the Maxwell-Cattaneo relation by including higher-order derivatives $\tau^n \partial^n / \partial t^n$ ($n = 2, 3, \dots$). As for us, we propose a new definition of entropy in the framework of extended irreversible thermodynamics.

Simons' (1982) demonstration runs as follows. He shows that $dS/dt > 0$, independently of any particular phenomenological equation. He concludes that if a phenomenological equation does not give $dS/dt > 0$, then such an equation is inadequate.

Although correct, Simons' treatment lacks generality. It is strictly linear since it is based on a Fourier analysis. Moreover, the energy balance is used in the form

$$c\dot{T} = -\nabla \cdot \mathbf{q} \quad (c = \text{constant}) \quad (3)$$

which implies that the state equation for the internal energy u is of the form

$$u = cT. \quad (4)$$

Finally, Simons assumes that T remains close to its equilibrium uniform value T_0 . All these restrictions limit notably the range of Simons' demonstration.

Instead of considering, like Simons, the class of rigid conductors obeying (4), let us handle the systems obeying the Maxwell–Cattaneo relation but not the state equation (4). Instead of Simons' equation (11), we obtain now

$$\frac{dS}{dt} = \frac{Z}{T_0^2} \lambda \int \frac{|a|^2 |\mathbf{p}|^2}{1 + \tau^2 |\omega|^2} (1 - \tau \text{Im } \omega) \exp \{-2 \text{Im} [\omega(\mathbf{p})]t\} d\mathbf{p}. \quad (5)$$

Clearly, dS/dt can become negative if $\tau \text{Im } \omega > 1$, which is in particular achieved for large values of τ . Simons would deduce from such a result that the Maxwell–Cattaneo relation is inappropriate. For our part, we say that dS/dt as given by (1) can no longer represent the positive entropy production. We then express the internal energy (or the entropy) as a function of T and the heat flux in such a way that the generalised entropy production is positive, whatever the values \mathbf{q} and ∇T may take, provided (2) is satisfied. As shown in Casas-Vazquez and Jou (1981), the generalised entropy may be written as

$$\rho s(T, \mathbf{q}) = \rho s_0(T) - \frac{1}{2} \tau (\lambda T^2)^{-1} \mathbf{q} \cdot \mathbf{q} \quad (6)$$

where s_0 is the usual equilibrium entropy per unit mass.

The difference between Simons' and our approach may still be viewed under the following perspective. Since the Maxwell–Cattaneo relation is a first-order differential equation in \mathbf{q} , it demands an initial condition for \mathbf{q} . This opens the way to two possibilities.

(i) One may consider that the freedom in the choice of the initial \mathbf{q} is limited by the constraint that (1) must be positive. In this case, it is not necessary to modify the classical entropy and Simons' view is correct.

(ii) One may consider that \mathbf{q} behaves as a new independent variable of the theory. In this case, it is obvious that (1) may become negative with a convenient choice of the initial value of \mathbf{q} .

One of the criteria allowing us to decide between the possibilities (i) or (ii) is to compare with the kinetic theory. This has been achieved for a viscous heat conducting gas and a phonon gas and has indicated that the second choice is the most fruitful, both from the macroscopic (Lebon 1978, Lebon *et al* 1980) and the microscopic (Grad 1958, Akacsu and Daniels 1970) points of view.

It must finally be pointed out that the argument contested by Simons is of minor importance in the elaboration of our theory. The decisive argument was instead to note that a state equation like $s(T)$ coupled with Fourier's law leads to thermal disturbances propagating with an infinite velocity, which is physically inadmissible. This difficulty is circumvented by selecting $s = s(T, \mathbf{q})$ together with the Maxwell–Cattaneo relation.

The authors wish to thank Dr Peckover, Warrington, for his relevant comments.

References

- Akacsu A and Daniels E 1970 *Phys. Rev. A* **2** 962
Casas-Vazquez J and Jou D 1981 *J. Phys. A: Math. Gen.* **14** 1225
Cattaneo C 1958 *C.R. Acad. Sci., Paris* **247** 431
De Groot S R and Mazur P 1962 *Non-Equilibrium Thermodynamics* (Amsterdam: North-Holland)
Grad H 1958 *Principles of the kinetic theory of gases* in *Encyclopedia of Physics* vol XII (Berlin: Springer)
Jou D, Casas-Vazquez J and Lebon G 1979 *J. Non-Equil. Thermodyn.* **4** 239
Lambermont J and Lebon G 1973 *Phys. Lett.* **42** A 499
Lebon G 1978 *Bull. Cl. Sci. Acad. Roy. Belg.* **64** 456
Lebon G and Jou D 1982 *J. Chem. Phys.* **15** (July) in press
Lebon G, Jou D and Casas-Vazquez J 1980 *J. Phys. A: Math. Gen.* **13** 275
Maxwell J C 1867 *Phil. Trans. R. Soc.* **157** 49
Prigogine I 1961 *Introduction to Irreversible Processes* (New York: Interscience)
Simons S 1982 *J. Phys. A: Math. Gen.* **15** 143