On the definition of non-equilibrium entropy

1982 J. Phys. A: Math. Gen. 15 L43

(http://iopscience.iop.org/0305-4470/15/1/009)

J. Phys. A: Math. Gen. 15 (1982) L43–L45. Printed in Great Britain

LETTER TO THE EDITOR

On the definition of non-equilibrium entropy

S Simons

Department of Applied Mathematics, Queen Mary College, Mile End Road, London, E1 4NS, UK

Received 21 September 1981

Abstract. It is pointed out that an argument used in a recent publication for redefining the rate of entropy production in order to ensure that it is non-negative is, in fact, invalid. The error arises from assuming that a first-order correction to the heat conduction equation is valid for all values of the physical parameters.

A recent paper by Casas-Vazquez and Jou (1981) (to be referred to in future as C) considers the modification in the Fourier heat conduction equation

$$\boldsymbol{q} = -\lambda \nabla T \tag{1}$$

(where $\boldsymbol{q}$ and λ are respectively the heat flux and thermal conductivity) suggested by Cattaneo (1958) and others to yield a finite rather than an infinite velocity for thermal disturbances. This modification takes the form

$$\boldsymbol{q} = -\lambda \nabla T - \tau(\partial \boldsymbol{q}/\partial t), \tag{2}$$

where τ is the relaxation time for the thermal flux, and gives rise to a hyperbolic rather than a parabolic differential equation for T. C then consider the rate of entropy production for a volume V

$$\frac{\mathrm{d}s}{\mathrm{d}t} = -\int_V \frac{\boldsymbol{q}\cdot\nabla T}{T^2}\,\mathrm{d}V \tag{3}$$

(Landau and Lifshitz 1970), and comment that this can become negative when equation (2) is used for $\boldsymbol{q}$ if a sufficiently negative value for $(\partial \boldsymbol{q}/\partial t)\cdot\nabla T$ is taken. Since $\mathrm{d}s/\mathrm{d}t$ must be non-negative, C suggest a modification in the definition of entropy to ensure that this non-negative requirement is met.

The main point of the present communication is to suggest that the above argument for the necessity of modifying equation (3) is invalid. The basis for this assertion is that apart from equation (2) there exists a second relation between $\boldsymbol{q}$ and T,

$$C\,\partial T/\partial t = -\mathrm{div}\,\boldsymbol{q} \tag{4}$$

(where C is the specific heat), and we shall now prove that equation (4) implies that for small departures from equilibrium $\mathrm{d}s/\mathrm{d}t$ as given by equation (3) is non-negative.

We consider the situation when the temperature throughout V varies by a small amount from a mean value T_0 so that equation (3) may be put in the form

$$\frac{\mathrm{d}s}{\mathrm{d}t} = -\frac{1}{T_0^2}\int_V (\boldsymbol{q}\cdot\nabla T)\,\mathrm{d}V. \tag{5}$$

We now suppose $T(\boldsymbol{r}, t)$ to represent the deviation of the temperature at position $\boldsymbol{r}$ and time t from the mean value T_0, and express $T(\boldsymbol{r}, 0)$ as a three-dimensional Fourier integral of the form

$$T(\boldsymbol{r}, 0)=\int a(\boldsymbol{p}) \exp(\mathrm{i}\boldsymbol{p} \cdot \boldsymbol{r})\, \mathrm{d}\boldsymbol{p}$$

where the integral is taken over the whole of (real) $\boldsymbol{p}$ space. For $t>0$ we then have

$$T(\boldsymbol{r}, t)=\int a(\boldsymbol{p}) \exp\{\mathrm{i}[\boldsymbol{p} \cdot \boldsymbol{r}+\omega(\boldsymbol{p})t]\}\, \mathrm{d}\boldsymbol{p} \tag{6}$$

where $\omega(\boldsymbol{p})$ is the angular frequency for wavenumber $\boldsymbol{p}$; the form of ω as a function of $\boldsymbol{p}$ has been investigated for various situations by Mikhail and Simons (1975). For T to be real, $a(\boldsymbol{p})$ and $\omega(\boldsymbol{p})$ must satisfy the relations

$$a(-\boldsymbol{p})=a^*(\boldsymbol{p}), \tag{7a}$$

$$\omega(-\boldsymbol{p})=-\omega^*(\boldsymbol{p}). \tag{7b}$$

In the same way $\boldsymbol{q}(\boldsymbol{r}, t)$ can be expressed as

$$\boldsymbol{q}(\boldsymbol{r}, t)=\int \boldsymbol{b}(\boldsymbol{p}) \exp[\mathrm{i}(\boldsymbol{p} \cdot \boldsymbol{r}+\omega t)]\, \mathrm{d}\boldsymbol{p} \tag{8}$$

when equation (4) gives

$$C\omega a(\boldsymbol{p})=-\boldsymbol{p} \cdot \boldsymbol{b}(\boldsymbol{p}),$$

whence

$$\boldsymbol{b}(\boldsymbol{p})=-C\omega \boldsymbol{p} a(\boldsymbol{p})/p^2. \tag{9}$$

We now substitute from equations (6), (8) and (9) into equation (5), leading to

$$\frac{\mathrm{d}s}{\mathrm{d}t}=\frac{\mathrm{i}C}{T_0^2}\int\int\left(p^{-2}(\boldsymbol{p} \cdot \boldsymbol{q})\omega(\boldsymbol{p})a(\boldsymbol{p})a(\boldsymbol{q}) \exp\{\mathrm{i}[\omega(\boldsymbol{p})+\omega(\boldsymbol{q})]t\}\right.$$

$$\left.\times\int_V \exp[\mathrm{i}(\boldsymbol{p}+\boldsymbol{q}) \cdot \boldsymbol{r}]\, \mathrm{d}V\right) \mathrm{d}\boldsymbol{p}\, \mathrm{d}\boldsymbol{q}. \tag{10}$$

Now

$$\int_V \exp[\mathrm{i}(\boldsymbol{p}+\boldsymbol{q}) \cdot \boldsymbol{r}]\, \mathrm{d}V=Z\delta(\boldsymbol{p}+\boldsymbol{q})$$

for some positive Z, and thus we obtain from equation (10)

$$\frac{\mathrm{d}s}{\mathrm{d}t}=-\frac{\mathrm{i}CZ}{T_0^2}\int \omega(\boldsymbol{p})|a(\boldsymbol{p})|^2 \exp\{-2\,\mathrm{Im}[\omega(\boldsymbol{p})]t\}\, \mathrm{d}\boldsymbol{p} \tag{11}$$

using equations (7). Finally, by substituting $-\boldsymbol{p}$ for $\boldsymbol{p}$ in equation (11), together with further use of equation (7b), we obtain the result

$$\frac{\mathrm{d}s}{\mathrm{d}t}=\frac{CZ}{T_0^2}\int \mathrm{Im}[\omega(\boldsymbol{p})]|a(\boldsymbol{p})|^2 \exp\{-2\,\mathrm{Im}[\omega(\boldsymbol{p})]t\}\, \mathrm{d}\boldsymbol{p}. \tag{12}$$

Now it is clear on physical grounds that the amplitude of temperature waves propagating through the medium cannot increase spontaneously with time. Rather, the waves will be positively damped, and this corresponds to

$$\mathrm{Im}[\omega(\boldsymbol{p})] > 0; \tag{13}$$

this result is borne out by the detailed calculations of Mikhail and Simons (1975). It then follows immediately from equation (12) that $\mathrm{d}s/\mathrm{d}t > 0$. The implication of this result is that the modification in $\boldsymbol{q}$ given by equation (2) certainly cannot be true for all values of the various quantities involved, since otherwise the comment of C that $\mathrm{d}s/\mathrm{d}t$ can become negative would be valid. The key to this is simply that the term $-\tau(\partial \boldsymbol{q}/\partial t)$ in equation (2) is only the first-order correction to equation (1), which is valid only when $|\tau(\partial \boldsymbol{q}/\partial t)|$ is not too large. The original arguments for this correction term were of a non-rigorous nature, a rigorous treatment being first given by Simons (1978). This latter approach shows that the required modification of equation (1) when quantities are time dependent depends on the variation with energy of the relaxation time for the particles (e.g. phonons) which conduct the heat. If this variation is too great then the form of the above correction term $-\tau(\partial \boldsymbol{q}/\partial t)$ will always be incorrect. If, however, the variation is sufficiently weak, and in particular if the relaxation time is a constant, then the correction to equation (2) may be expressed as a power series in $\tau(\partial/\partial t)$ of which the first term (apart from a numerical factor) is the above correction term $-\tau(\partial \boldsymbol{q}/\partial t)$. It follows therefore that equation (2) can only hold for sufficiently small values of $|\tau(\partial \boldsymbol{q}/\partial t)|$ and hence the argument of C for modifying equation (3) is invalid.

Finally, we point out that the approach used here may be immediately extended to show that successive derivatives of the entropy alternate in sign; that is

$$(-)^n\, \mathrm{d}^n s/\mathrm{d}t^n \leqslant 0. \tag{14}$$

Some considerable interest has been shown over the past few years in systems which obey inequality (14) (see Simons (1979) for list of references), and it is readily seen from relations (12) and (13) that this inequality will apply to the system considered in this paper.

References

Casas-Vázquez J and Jou D 1981 *J. Phys. A: Math. Gen.* **14** 1225

Cattaneo C 1958 *C.R. Acad. Sci., Paris* **247** 431

Landau L D and Lifshitz E M 1970 *Theory of Elasticity* (London: Pergamon) p 152

Mikhail I F I and Simons S 1975 *J. Phys. C: Solid State Phys.* **8** 3068

Simons S 1978 *Phys. Lett.* **66A** 453

—— 1979 *Phys. Lett.* **73A** 81