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On the time variation of entropy

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L58 Letters to the Editor

On the time variation of entropy

Abstract. An earlier result concerning the rate of entropy production for an isolated system near equilibrium is partially extended to the case when the system is well away from equilibrium.

In an earlier paper (Simons 1971) it was pointed out that during the passage to equilibrium for various isolated systems

$$(-)^n S^{(n)} \leqslant 0 \tag{1}$$

where $S^{(n)}$ is the *n*th time derivative of the entropy *S*, or a quantity closely related to this. The discussion given in that paper, however, was restricted to the situation where the properties of the system at all points departed by only a small amount from those relating to a spatially constant equilibrium distribution. It is therefore clearly of interest to examine whether at least some of the results previously obtained can be generalized to the situation when this condition is not imposed and arbitrary variations in physical quantities can occur. In the present communication we consider a very simple irreversible process—conduction in one dimension for an isolated specimen with temperature-independent physical properties—and show that, for arbitrary temperature variations during the passage to equilibrium, the result (1) holds for n = 2; that is

$$\frac{\mathrm{d}^2 S}{\mathrm{d}t^2} \leqslant 0. \tag{2}$$

Consider heat flow in the x direction through an isolated system bounded by the planes x = a and x = b. Then the temperature T(x, t) at any point x in the system satisfies the conduction equation

$$C\left(\frac{\partial T}{\partial t}\right) = K\left(\frac{\partial^2 T}{\partial x^2}\right) \tag{3}$$

with boundary conditions

$$\left(\frac{\partial T}{\partial x}\right)_a = \left(\frac{\partial T}{\partial x}\right)_b = 0 \tag{4}$$

where C and K are respectively the specific heat and thermal conductivity of the medium. The rate of entropy production is given by Landau and Lifshitz (1959) in the form

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \int_{a}^{b} \frac{K}{T^{2}} \left(\frac{\partial T}{\partial x}\right)^{2} \mathrm{d}x \tag{5}$$

and hence

$$\frac{\mathrm{d}^2 S}{\mathrm{d}t^2} = 2K \int_a^b \frac{1}{T} \frac{\partial T}{\partial x} \frac{\partial}{\partial t} \left(\frac{1}{T} \frac{\partial T}{\partial x} \right) \mathrm{d}x. \tag{6}$$

Now it follows from equation (3) that

$$\frac{\partial}{\partial t} \left(\frac{1}{T} \frac{\partial T}{\partial x} \right) = \frac{K}{C} \frac{\partial}{\partial x} \left(\frac{1}{T} \frac{\partial^2 T}{\partial x^2} \right)$$
(7)

and substituting this into equation (6), together with an integration 'by parts', we

derive

$$\frac{\mathrm{d}^2 S}{\mathrm{d}t^2} = -\frac{2K^2}{C} \int_a^b \left\{ \frac{1}{T^2} \left(\frac{\partial^2 T}{\partial x^2} \right)^2 - \frac{1}{T^3} \left(\frac{\partial T}{\partial x} \right)^2 \frac{\partial^2 T}{\partial x^2} \right\} \mathrm{d}x \tag{8}$$

on making use of conditions (4). To prove that the integral in equation (8) is positive we use Schwarz's inequality in the form

$$\int_{a}^{b} \{f(x)\}^{2} dx \int_{a}^{b} \{g(x)\}^{2} dx \ge \left| \int_{a}^{b} f(x) g(x) dx \right|^{2}$$

where $f(x) = T^{-1}(\partial^2 T/\partial x^2)$ and $g(x) = T^{-2}(\partial T/\partial x)^2$. This gives

$$\int_{a}^{b} \frac{1}{T^{2}} \left(\frac{\partial^{2}T}{\partial x^{2}}\right)^{2} \mathrm{d}x \int_{a}^{b} \frac{1}{T^{4}} \left(\frac{\partial T}{\partial x}\right)^{4} \mathrm{d}x \ge \left|\int_{a}^{b} \frac{1}{T^{3}} \left(\frac{\partial T}{\partial x}\right)^{2} \frac{\partial^{2}T}{\partial x^{2}} \mathrm{d}x\right|^{2}.$$
(9)

Now, on integrating 'by parts', and using equations (4), it is readily shown that

$$\int_{a}^{b} \frac{1}{T^{3}} \left(\frac{\partial T}{\partial x}\right)^{2} \frac{\partial^{2} T}{\partial x^{2}} dx = \int_{a}^{b} \frac{1}{T^{4}} \left(\frac{\partial T}{\partial x}\right)^{4} dx$$
(10)

and, since the right hand side of this equality is clearly positive, it follows from inequality (9) that

$$\int_{a}^{b} \frac{1}{T^{2}} \left(\frac{\partial^{2}T}{\partial x^{2}}\right)^{2} \mathrm{d}x \geq \int_{a}^{b} \frac{1}{T^{3}} \left(\frac{\partial T}{\partial x}\right)^{2} \frac{\partial^{2}T}{\partial x^{2}} \mathrm{d}x.$$

Thus, we see from equation (8) that the inequality (2) holds.

The result proved here suggests that further work may well be justified on the possible extension of inequality (1) to apply to isolated systems well away from equilibrium.

Queen Mary College, Mile End Road, London E1, England. S. SIMONS 5th April 1971

LANDAU, L. D., and LIFSHITZ, E. M., 1959, Theory of Elasticity, (London: Pergamon), p. 121. SIMONS, S., 1971, J. Phys. A: Gen. Phys., 4, 11-6.

Isospin structure of an E2 transition matrix element in ²⁷Al and ²⁷Si

Abstract. E2/M1 mixing ratios have been measured for transitions from the second $(3/2^+)$, third $(7/2^+)$ and fourth $(5/2^+)$ excited states of 27 Si. A discrepancy in the magnitudes of the mixing ratios for the $5/2^+ \rightarrow$ ground state transition in 27 Al and 27 Si is confirmed, and is used to estimate the ratio of the isovector to the isoscalar components of the E2 matrix element for the transition.

General considerations (Warburton and Weneser 1969) regarding $\Delta T = 0$ electromagnetic transitions of reasonable strength predict that E2 matrix elements should be largely isoscalar in character, and M1 largely isovector. Comparison of the