Is $\ddot{S} \leq 0$?

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Abstract. It is shown for three distinct physical systems that the second time derivative of the entropy remains negative throughout the return to equilibrium, for arbitrary initial displacements from this state.

1. Introduction

Conventional thermodynamic reasoning shows that for an isolated system proceeding to equilibrium, the entropy S satisfies

$$\dot{S} \geq 0 \tag{1}$$

(where the dot notation signifies differentiation with respect to time). Interest has been aroused recently in examining whether higher time derivatives of S may also possess a definite sign; in particular, whether

$$\ddot{S} \leq 0 \tag{2}$$

or even

$$(-1)^n \, d^n S/dt^n \leq 0 \tag{3}$$

for $1 \leq n \leq \infty$ (Harris 1967, 1968a, b, Maass 1970, McElwain and Pritchard 1969, Pritchard et al 1974, Pritchard 1975, Shear 1968, Simons 1969, 1970, 1971a, b, 1972, Yao 1971). The above result (3) has generally only been shown to hold for certain systems close to equilibrium, but the 'convexity' property (2) has been proved for various systems arbitrarily displaced from equilibrium. These include certain chemical reactions, heat conduction and (subject to certain simple models) gas molecule interactions.

The purpose of the present paper is to investigate further the range of application of equation (2) for systems well away from equilibrium. In §§ 2 and 3 we consider two macroscopic systems; the discharge of a capacitor through a resistor and the motion of a sphere through a gas, showing that in both cases the result (2) holds. In § 4 we deal with a system described at an atomic level—the scatter of particles (molecules, electrons, neutrons, phonons, etc) by fixed scattering centres and show that for isotropic scatter the property (2) is true.

2. Discharge of a capacitor

Consider a capacitor C with charge q discharging through a resistor R. The rate of heat production is $R\dot{q}^2$ and assuming this to be instantaneously distributed throughout the

resistor at uniform temperature $T(t)$, we have

$$\dot{S} = (R/T)\dot{q}^2 \tag{4}$$

assuming no heat lost from the resistor. Now, the discharge is governed by the equation

$$-R\dot{q} = q/C \tag{5}$$

and hence we obtain from equation (4),

$$\dot{S} = q^2/(C^2RT). \tag{6}$$

Differentiating this with respect to time gives

$$\ddot{S} = \frac{1}{C^2}\left(\frac{2q\dot{q}}{RT} - \frac{q^2\dot{T}}{R^2T^2}\frac{\mathrm{d}(RT)}{\mathrm{d}T}\right). \tag{7}$$

Now, $\dot{q} < 0$, $\dot{T} > 0$ and $\mathrm{d}(RT)/\mathrm{d}T > 0$ since electrical resistance increases with temperature more rapidly than T^{-1}. Thus all the terms in equation (7) are negative and result (2) follows.

3. Motion of a sphere in a gas

We consider here the case of a sphere given an initial velocity and subsequently slowed down due to the resistance of the gas through which it moves. We are interested in the situation where the sphere is moving with arbitrary velocity, possibly greater than the gas molecular velocity, and therefore require an expression for the gas resistance valid under these circumstances. This has only been obtained in detail for the case where the gas molecular mean free path is substantially greater than the sphere dimensions, and we shall therefore confine our attention to this situation. The problem here has been considered by Baines *et al* (1965) and Williams (1973) who show that, as far as the temperature and sphere velocity v are concerned, the resistive force F always takes the form

$$F = mTg(v^2/T) \tag{8}$$

where m is the mass of the sphere, and the precise form of the function g depends on the gas density and the area and surface properties of the sphere. It follows immediately from equation (8) that the motion of the sphere is described by the equation

$$\dot{v} = -Tg(v^2/T). \tag{9}$$

The rate of heat production is given by $-(\mathrm{d}/\mathrm{d}t)(\frac{1}{2}mv^2)$, and if we assume this to be instantaneously distributed between the sphere and gas at uniform temperature $T(t)$, we have

$$\dot{S} = -mv\dot{v}/T = mvg(v^2/T) \tag{10}$$

from equation (9). Thus

$$\ddot{S} = m\left[\dot{v}g\left(\frac{v^2}{T}\right) + vg'\left(\frac{v^2}{T}\right)\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{v^2}{T}\right)\right]. \tag{11}$$

Now since v is continually decreasing and T is correspondingly increasing, it follows that $\dot{v} \leq 0$ and $(\mathrm{d}/\mathrm{d}t)(v^2/T) \leq 0$. Making use of the explicit form of g as given by Baines

et al (1965) and Williams (1973), it is readily shown that $g' > 0$, which corresponds to the gas resistance increasing as v increases. It is therefore seen from equation (11) that the inequality (2) holds.

4. Particle scatter

In this section, we consider entropy production during the approach to equilibrium for a system of particles each with the same energy, being scattered by fixed centres. The precise nature of the particles (whether molecules, electrons, phonons, neutrons etc) only enters the calculation as regards the type of statistics which the particles obey. For simplicity we shall suppose the particles to obey Boltzmann statistics, although the calculation may be readily extended to cover Bose–Einstein and Fermi–Dirac statistics.

Let f_p be the number of particles in the state labelled p. Then the entropy S of the system is given by

$$S = -k \sum_p f_p \ln f_p \tag{12}$$

and

$$\dot{S} = -k \sum_p \dot{f}_p \ln f_p \tag{13}$$

since $\sum_p f_p$ is constant. It is readily shown by an approach similar to that used in proving the standard H theorem (e.g. Chapman and Cowling 1960) that $\dot{S} \geq 0$, the equality sign applying only in equilibrium when all f_p are equal. On differentiating equation (13) again, we find

$$\ddot{S} = \ddot{S}_1 + \ddot{S}_2 \tag{14}$$

where

$$\ddot{S}_1 = -k \sum_p f_p^{-1} \dot{f}_p^2 \quad\text{and}\quad \ddot{S}_2 = -k \sum_p \ddot{f}_p \ln f_p. \tag{15}$$

It is clear that $\ddot{S}_1 \leq 0$.

To deal with $\ddot{S}_2$, we consider the basic equation giving the development in time of f_p. This is

$$\dot{f}_p = \sum_q T_{pq}(f_q - f_p) \tag{16}$$

where T_{pq} is the relevant matrix scattering operator. Hence

$$\ddot{f}_p = \sum_q T_{pq}(\dot{f}_q - \dot{f}_p)$$

and substituting this into equation (15) gives

$$\ddot{S}_2 = k \sum_{pq} T_{pq}(\dot{f}_p - \dot{f}_q) \ln f_p = k \sum_{pq} T_{pq} \dot{f}_p \ln(f_p/f_q) \tag{17}$$

on exchanging p and q in the term involving $\dot{f}_q$, and using microscopic reversibility in the form of the symmetry relation

$$T_{pq} = T_{qp}. \tag{18}$$

Finally we substitute from equation (16) for $\dot{f}_p$, and obtain

$$\ddot{S}_2 = -k \sum_{pqr} T_{pq} T_{pr} (f_p - f_r)(\ln f_p - \ln f_q). \tag{19}$$

The only general property of the matrix T_{pq}, apart from the above symmetry relation (18), is that $T_{pq} \geq 0$ corresponding to a non-negative transition probability. One would now like to be able to prove on the basis of these two general properties alone that $\ddot{S} \leq 0$. This, we have not been able to do. However, we have been able to prove that if the particle scattering is isotropic, then $\ddot{S} \leq 0$. Such scattering is characterized by T_{pq} being independent of q for given p, and we can readily see that it must then also be independent of p, since

$$T_{pq} = T_{pr} = T_{rp} = T_{rs}$$

for all p, q, r, s, making use of the symmetry relation (18). Thus for isotropic scatter equation (19) becomes

$$\ddot{S}_2 = -kT^2 \sum_{pqr} (f_p - f_r)(\ln f_p - \ln f_q). \tag{20}$$

We exchange p and q in this summation and adding the resulting expression to that in (20), we find

$$\ddot{S}_2 = (-kT^2/2) \sum_{pqr} (f_p - f_q)(\ln f_p - \ln f_q).$$

Since the sign of $\ln f_p - \ln f_q$ is the same as that of $f_p - f_q$, it follows that $\ddot{S}_2 \leq 0$, and hence that $\ddot{S} \leq 0$.

It would clearly be of interest to be able to prove this result without the isotropy assumption, and if this were done successfully, to attempt to generalize it to the more complex types of interactions that can occur between gas molecules and between phonons and electrons, and which require a more complicated expression than (16) (non-linear in the f's) for their description.

References

Baines M J, Williams I P and Asebiomo A S 1965 *Mon. Not. R. Astron. Soc.* **130** 63–74
Chapman S and Cowling T G 1960 *The Mathematical Theory of Non Uniform Gases* (Cambridge: University Press) chap 4
Harris S 1967 *J. Math. Phys.* **8** 2407–10
—— 1968a *J. Chem. Phys.* **48** 3723–5
—— 1968b *J. Chem. Phys.* **48** 4012–3
Maass W 1970 *J. Phys. A: Gen. Phys.* **3** 331–4
McElwain D L S and Pritchard H O 1969 *J. Am. Chem. Soc.* **91** 7693–702
Pritchard H O 1975 *Can. J. Chem.* **53** 1756–60
Pritchard H O, Labib N I and McElwain D L S 1974 *Can. J. Chem.* **52** 2618–21
Shear D B 1968 *J. Chem. Phys.* **48** 4144–7
Simons S 1969 *J. Phys. A: Gen. Phys.* **2** 12–3
—— 1970 *Phys. Lett.* **33A** 154–5
—— 1971a *J. Phys. A: Gen. Phys.* **4** 11–6
—— 1971b *J. Phys. A: Gen. Phys.* **4** L58–9
—— 1972 *J. Phys. A: Gen. Phys.* **5** 1537–44
Williams M M R 1973 *J. Phys. D: Appl. Phys.* **6** 744–58
Yao S J 1971 *J. Chem. Phys.* **54** 1237–8