The sign of d^2S/dt^2 for a non-linear problem

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LETTER TO THE EDITOR

The sign of $\ddot{S}$ for a non-linear problem

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Abstract. Using an exact, recently obtained solution of the non-linear Boltzmann equation for a particular type of molecular interaction, we show that the corresponding second time derivative of the entropy remains negative during the passage to equilibrium. The signs of higher derivatives are considered.

It has been shown that for various isolated systems the second time derivative of the entropy S satisfies the inequality

$$\ddot{S} \leqslant 0 \tag{1}$$

during the passage to equilibrium (Harris 1967, 1968a, b, 1971, Maass 1970, McElwain and Pritchard 1969, Pritchard *et al* 1974, Pritchard 1975, Shear 1968, Simons 1969, 1970, 1971a, b, 1972, 1976, Yao 1971), while for a subset of these systems

$$(-1)^n \mathrm{d}^n S/\mathrm{d}t^n \leqslant 0 \tag{2}$$

for $1 \leqslant n \leqslant \infty$. The systems satisfying (1) include assemblies of gas molecules, but for realistic situations the result (1) has then only been proved in the case of linear interactions corresponding to small deviations from equilibrium. Now, an exact analytic solution of the full *non-linear* Boltzmann equation has recently been obtained by Krook and Wu (1976) for the case where the intermolecular differential cross section is inversely proportional to the molecular relative velocity, and it was therefore felt worthwhile investigating the sign of $\ddot{S}$ for this situation.

In their treatment, Krook and Wu introduce a dimensionless time variable, τ $(= t/t_0$ for some constant time $t_0)$, and show that the distribution function $f(\boldsymbol{v}, \tau)$ corresponding to a solution of the time-dependent non-linear Boltzmann equation, can be expressed in the form

$$f(\boldsymbol{v}, \tau) = \frac{\exp(-v^2/2K\beta^2)}{2(2\pi K\beta^2)^{3/2}} \left(\frac{5K-3}{K} + \frac{1-K}{K^2}\frac{v^2}{\beta^2}\right) \tag{3}$$

where $\beta^2 = kT/m$ and

$$K = 1 - \exp(-\tau/6). \tag{4}$$

The solution (3) is valid for $\frac{3}{5} \leqslant K \leqslant 1$, and the first of these inequalities restricts the solution to $\tau \geqslant \tau_0 \sim 5\cdot 5$.

The entropy S of the system is given by

$$S=-k\int f\ln f\,\mathrm{d}\boldsymbol{v},$$

and so

$$\ddot{S}=-k\int[\ddot{f}\ln f+(\dot{f}^2/f)]\,\mathrm{d}\boldsymbol{v}.$$

Substituting into here from equations (3) and (4) gives

$$\ddot{S}=\frac{-k(1-K)^2}{18\pi^{1/2}K^3t_0^2}\left\{\int_0^\infty \mathrm{e}^{-x^2}\left(2(1-K)x^8+(-21+17K)x^6\right.\right.$$
$$\left.+\frac{5}{2}(21-13K)x^4+\frac{15}{4}(-7+3K)x^2\right)\left[-x^2+\ln\left(\frac{5K-3}{K}+\frac{2(1-K)x^2}{K}\right)\right]\mathrm{d}x$$
$$\left.+\frac{(1-K)^2}{4}\int_0^\infty x^2\,\mathrm{e}^{-x^2}\left(\frac{(4x^4-20x^2+15)^2}{(5K-3)+2(1-K)x^2}\right)\mathrm{d}x\right\}, \qquad (5)$$

using the substitution $v=\beta(2K)^{1/2}x$. As the integrals in equation (5) could not in general be performed analytically, they were computed numerically, using the technique of Gauss–Hermite quadrature, for various values of K lying in the range $0{\cdot}6<K\leqslant 1$. The only difficulty arising here was the case of $K=0{\cdot}6$, when the first integrand diverges at $x=0$, due to the logarithmic term. This case ($K=0{\cdot}6$) could,

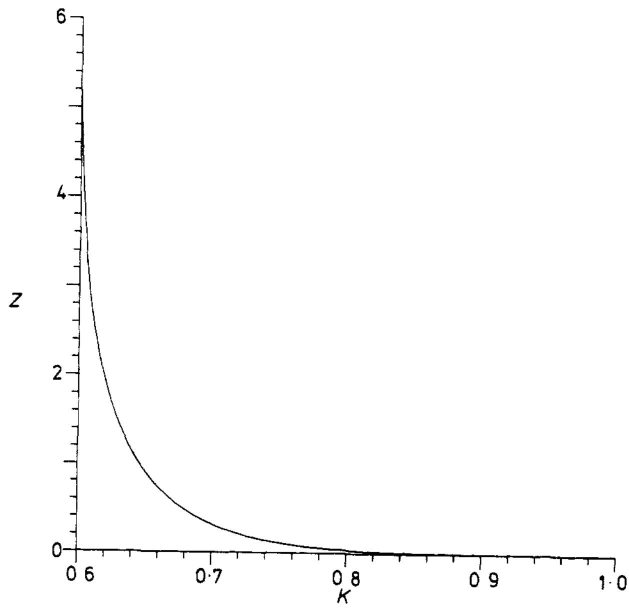

Figure 1. A graph of $Z\,[=(-18\pi^{1/2}t_0^2/k)\ddot{S}]$ against K.

however, be dealt with analytically using the standard result for

$$\int_0^\infty t^n \, \mathrm{e}^{-pt} \ln t \, \mathrm{d}t$$

quoted in Erdélyi *et al* (1954).

The results are shown in figure 1 where we have plotted a graph of $Z = (-18\pi^{1/2} t_0^2/k)\ddot{S}$ against K for $0{\cdot}6 \leqslant K \leqslant 1$. It is seen that Z remains positive throughout the range, showing that the result (1) holds for the present situation. It is also clear from this graph that

$$\mathrm{d}^3S/\mathrm{d}t^3 \geqslant 0 \qquad \text{and} \qquad \mathrm{d}^4S/\mathrm{d}t^4 \leqslant 0.$$

These results lead one to surmise that the full alternating property of S—inequality (2)—may perhaps hold for the present situation. The important question of whether or not inequalities (1) or (2) hold for the *general* case of non-linear interactions remains, of course, open.

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