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LETTER TO THE EDITOR

On the sign of d^2H/dt^2

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Abstract. For a system with a given energy that has N different possible states, the H function (of thermodynamics) satisfies $d^2H/dt^2 > 0$ if $N \leq 3$, but d^2H/dt^2 may be both positive and negative if $N \geq 5$. The case of $N = 4$ remains undetermined.

1. Introduction

For a system with a given energy, which has N different possible states, the H function is given by

$$H = \sum_{p=1}^{N} f_p \ln f_p, \tag{1}$$

where f_p is the probability for the system to be in the pth state. Also we have

$$\dot{f}_p \equiv \frac{df_p}{dt} = \sum_q T_{pq}(f_q - f_p). \tag{2}$$

T_{pq} is the transition probability per unit time between the states p and q and ‡

$$T_{pq} \geq 0, \tag{I}$$

$$T_{pq} = T_{qp}. \tag{3}$$

It is well known that $dH/dt < 0$. Recently, there has been interest in the higher derivatives of H, especially the second derivative given by

$$\ddot{H} = \sum_p f_p^{-1}\dot{f}_p^2 + \sum_{p,q,r} T_{pq}T_{pr}(f_p - f_r)\ln\left(\frac{f_p}{f_q}\right). \tag{4}$$

Simons (1976) has proved that if

$$T_{pq} = T \qquad \text{for } p \neq q \tag{5}$$

then one must have

$$\ddot{H} \equiv \frac{d^2H}{dt^2} \geq 0. \tag{II}$$

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‡ Throughout this Letter Roman numerals stand for inequalities and Arabic numerals for equations.

Simons then asked whether (II) could be proved only from (I), (2) and (4) without using (5). However, this is possible if $N \leqslant 3$ and is not possible if $N \geqslant 5$; as we shall see here. The case when $N = 4$ remains undetermined.

2. The case when $N = 3$

Consider f_p, $\dot{f}_p$, T_{pq} and $\ddot{H}$ at any given time t. Without loss of generality, we can set

$$f_1 \geqslant f_2 \geqslant f_3. \tag{III}$$

From (2) and (3) we get, after a little simplification,

$$\ddot{H} = I_1 + I_2, \tag{6}$$

where

$$I_1 = aT_{12}^2 - bT_{12}T_{23} + cT_{23}^2,$$

with

$$a = (f_1 - f_2)^2\left(\frac{1}{f_1} + \frac{1}{f_2}\right) + 2(f_1 - f_2)\ln\left(\frac{f_1}{f_2}\right),$$

$$b = \frac{2(f_1 - f_2)(f_2 - f_3)}{f_2} + (f_1 - f_2)\ln\left(\frac{f_2}{f_3}\right) + (f_2 - f_3)\ln\left(\frac{f_1}{f_2}\right),$$

$$c = (f_2 - f_3)^2\left(\frac{1}{f_2} + \frac{1}{f_3}\right) + 2(f_2 - f_3)\ln\left(\frac{f_2}{f_3}\right),$$

and

$$\begin{aligned} I_2 = {} & \frac{2T_{12}T_{13}(f_1 - f_2)(f_1 - f_3) + T_{13}^2(f_1 - f_3)^2}{f_1} \\ & + \frac{2T_{13}T_{23}(f_1 - f_2)(f_2 - f_3) + T_{13}^2(f_1 - f_3)^2}{f_3} \\ & + 2T_{13}^2(f_1 - f_3)\ln\left(\frac{f_1}{f_3}\right) + T_{12}T_{13}\left[(f_1 - f_2)\ln\left(\frac{f_1}{f_3}\right) + (f_1 - f_3)\ln\left(\frac{f_1}{f_2}\right)\right] \\ & + T_{13}T_{23}\left[(f_1 - f_3)\ln\left(\frac{f_2}{f_3}\right) + (f_2 - f_3)\ln\left(\frac{f_1}{f_3}\right)\right]. \end{aligned} \tag{7}$$

It is obvious that

$$a \geqslant 0, \quad b \geqslant 0, \quad c \geqslant 0, \quad I_2 \geqslant 0. \tag{IV}$$

I_1 can be negative only if it is possible to choose f_1, f_2, f_3 such that

$$b^2 - 4ac > 0. \tag{V}$$

However, from (7) we get, after a little calculation,

$$b^2 - 4ac = (f_1 - f_2)^2 J_1 + (f_2 - f_3)^2 J_2 - J_3, \tag{8}$$

where

$$J_1=\left[\ln\left(\frac{f_2}{f_3}\right)\right]^2-\frac{4(f_2-f_3)^2}{f_2f_3}-\frac{4(f_2-f_3)}{f_2}\ln\left(\frac{f_2}{f_3}\right),$$

$$J_2=\left[\ln\left(\frac{f_1}{f_2}\right)\right]^2-\frac{4(f_1-f_2)^2}{f_1f_2}-\frac{4(f_1-f_2)}{f_2}\ln\left(\frac{f_1}{f_2}\right),$$

$$J_3=\frac{4}{f_1f_3}(f_1-f_2)^2(f_2-f_3)^2+\frac{8(f_1-f_3)^2(f_2-f_3)}{f_1}\ln\left(\frac{f_2}{f_3}\right)$$
$$+\frac{8(f_1-f_2)(f_2-f_3)^2}{f_3}\ln\left(\frac{f_1}{f_2}\right)+14(f_1-f_2)(f_2-f_3)\ln\left(\frac{f_1}{f_2}\right)\ln\left(\frac{f_2}{f_3}\right). \quad (9)$$

Obviously $J_3>0$. We shall show that $J_1<0, J_2<0$ and hence $b^2-4ac<0$.

If possible, let $J_1>0$. In view of (9), this can hold only if

$$\left[\ln\left(\frac{f_2}{f_3}\right)\right]^2>\frac{4(f_2-f_3)}{f_2}\ln\left(\frac{f_2}{f_3}\right), \quad \text{(VI)}$$

$$\left[\ln\left(\frac{f_2}{f_3}\right)\right]^2>\frac{4(f_2-f_3)^2}{f_2f_3}. \quad \text{(VII)}$$

However, since $\ln(f_2/f_3)>0$, (VI) is equivalent to

$$\ln\left(\frac{f_2}{f_3}\right)>\frac{4(f_2-f_3)}{f_2},$$

i.e.

$$\ln x+\frac{4}{x}-4>0 \qquad \text{where } x=\frac{f_2}{f_3}>1. \quad \text{(VIII)}$$

Using simple properties of maxima and minima, we see that (VIII) can be true only if

$$x>\gamma,$$

where γ is a numerical constant given by

$$\ln\gamma+\frac{4}{\gamma}-4=0$$

and

$$\gamma>1.$$

It may be noted that $\gamma\simeq 50$.

However, considering the function

$$(\ln x)^2-\frac{4(x-1)^2}{x}$$

for $x>\gamma$, it is easy to see that (VII) cannot be satisfied. Therefore $J_1<0$. Similarly, $J_2<0$. Thus $b^2-4ac<0$. Hence $I_1\geqslant 0$ and, as before, $I_2\geqslant 0$. Thus $\ddot{H}\geqslant 0$ for $N=3$. This holds for any given time t, i.e. it holds for all time. Also, since the case for $N=2$ is a particular case of $N=3$, it is obvious that $\ddot{H}\geqslant 0$ holds for $N=2$.

3. The case when $N = 5$

Here we shall see that (II) is not true in general. If at a particular time t we have

$$f_1 > f_2 > f_3$$

and

$$f_3 = f_4 = f_5$$

and the matrix T_{pq} as

$$T_{pq} = \begin{bmatrix} T_{11} & T_{12} & 0 & 0 & 0 \\ T_{12} & T_{22} & T_{23} & T_{24} & T_{25} \\ 0 & T_{23} & T_{33} & 0 & 0 \\ 0 & T_{24} & 0 & T_{44} & 0 \\ 0 & T_{25} & 0 & 0 & T_{55} \end{bmatrix}, \tag{10}$$

i.e. the only non-vanishing elements are the diagonal elements and those elements T_{pq} for which one of the indices p and q is equal to 2. Further,

$$T_{12} \neq T_{23} \qquad \text{and} \qquad T_{23} = T_{24} = T_{25}.$$

Then we get from (4)

$$\ddot{H} = AT_{12}^2 - BT_{12}T_{23} + CT_{23}^2, \tag{11}$$

where

$$\begin{aligned} A &= (f_1 - f_2)^2\left(\frac{1}{f_1} + \frac{1}{f_2}\right) + 2(f_1 - f_2)\ln\left(\frac{f_1}{f_2}\right), \\ B &= 3\left[\frac{2(f_1 - f_2)(f_2 - f_3)}{f_2} + (f_1 - f_2)\ln\left(\frac{f_2}{f_3}\right) + (f_2 - f_3)\ln\left(\frac{f_1}{f_2}\right)\right], \\ C &= 9\frac{(f_2 - f_3)^2}{f_2} + 3\left[\frac{(f_2 - f_3)^2}{f_3} + 2(f_2 - f_3)\ln\left(\frac{f_2}{f_3}\right)\right]. \end{aligned} \tag{12}$$

From (I),

$$A \geqslant 0, \quad B \geqslant 0, \quad C \geqslant 0 \tag{IX}$$

(11) can be rewritten as

$$\ddot{H} = AT_{23}^2\left(\frac{T_{12}}{T_{23}} - \alpha\right)\left(\frac{T_{12}}{T_{23}} - \beta\right),$$

where

$$\alpha = \frac{B + (B^2 - 4AC)^{1/2}}{2A}, \qquad \beta = \frac{B - (B^2 - 4AC)^{1/2}}{2A}.$$

Thus if α and β are real and distinct, i.e. if $B^2 > 4AC$, one can choose T_{12}/T_{23} such that $\beta < T_{12}/T_{23} < \alpha$, to get $\ddot{H} < 0$. Such a choice of T_{12}/T_{23} is also consistent with (I) since, in view of (IX), $B > (B^2 - 4AC)^{1/2}$ and thus $\beta > 0$.

That by suitable choice of f_1, f_2 and f_3 we can have $B^2 > 4AC$ is seen as follows. From (12)

$$B^2 - 4AC = f_2 I,$$

where

$$I = 9\left[\left(2\frac{f_1}{f_2}-1\right)\left(1-\frac{f_3}{f_2}\right)+\left(\frac{f_1}{f_2}-1\right)\ln\left(\frac{f_2}{f_3}\right)+\left(1-\frac{f_3}{f_2}\right)\ln\left(\frac{f_1}{f_2}\right)\right]^2$$
$$-4\left[\left(\frac{f_1}{f_2}-1\right)^2\left(\frac{f_2}{f_1}+1\right)+2\left(\frac{f_1}{f_2}-1\right)\ln\left(\frac{f_1}{f_2}\right)\right]\left\{9\left(1-\frac{f_3}{f_2}\right)^2\right.$$
$$\left.+3\left[\frac{f_2}{f_3}\left(1-\frac{f_3}{f_2}\right)+2\left(1-\frac{f_3}{f_2}\right)\ln\left(\frac{f_2}{f_3}\right)\right]\right\}. \tag{13}$$

Therefore $f_2>0$, $B^2-4AC\gtrless 0$ according as to whether $I\gtrless 0$.

In equation (13), we note that I depends only on f_1/f_2 and f_3/f_2. However, if we keep f_3/f_2 fixed and make f_1/f_2 bigger and bigger, for sufficiently large value of f_1/f_2, the sign of I will be determined by the coefficient of $(f_1/f_2)^2$, since the terms with f_1/f_2 and $f_1/f_2\ln(f_1/f_2)$ will be much smaller. Thus, for sufficiently large value of f_1/f_2, we can have $B^2-4AC>0$, if

$$9\left[2\left(1-\frac{f_3}{f_2}\right)+\ln\left(\frac{f_2}{f_3}\right)\right]^2-4\left\{9\left(1-\frac{f_3}{f_2}\right)^2+3\left[\frac{f_2}{f_3}\left(1-\frac{f_3}{f_2}\right)+2\left(1-\frac{f_3}{f_2}\right)\ln\left(\frac{f_2}{f_3}\right)\right]\right\}>0$$

or simplifying

$$12\frac{f_2-f_3}{f_2}\ln\left(\frac{f_2}{f_3}\right)+9\left[\ln\left(\frac{f_2}{f_3}\right)\right]^2-12\frac{(f_2-f_3)^2}{f_2f_3}>0. \tag{X}$$

(X) can be satisfied by a suitable choice of f_2/f_3. For example, $f_2/f_3=1\cdot1$ satisfies (X). Hence, inequality (II) does not hold for $N=5$. Since $N=5$ is a special case of $N=6$ and so on, it follows that (II) does not hold for any $N\geqslant 5$.

4. Conclusion

We see that (II) holds only when the number of states (all with the same energy) are very few; at most three or four. Thus, it could hold when the different states referred to are different spin states of an elementary particle or perhaps different orbital angular momentum states. It does not hold if the number of possible states is five or more. It may appear that the example given above is artificial. However, it is obvious from this example that for a larger value of N (commonly, N is of the order of 10^{23}), there will be a much wider range of values of T and f, which will give $\ddot{H}\leqslant 0$. It is unlikely that all of them will be unphysical.

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