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ON THE SIGN OF $\frac{d^2H}{dt^2}$ *

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ABSTRACT

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

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1. INTRODUCTION

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

$$H = \sum_{p=1}^N f_p \ln f_p \quad (1)$$

where f_p = probability for the system to be in p^{th} state. Also we have

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

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

$$T_{pq} \geq 0 \quad (I)$$

$$T_{pq} = T_{qp} \quad (3)$$

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

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

Simons(1976) has proved that if

$$T_{pq} = T \quad \text{for } p \neq q \quad (5)$$

then one must have

$$\ddot{H} \equiv \frac{d^2H}{dt^2} \geq 0 \quad (II)$$

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

*) Throughout the paper Roman numerals stand for inequalities and Arabic numerals for equations.

II. CASE OF 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

$$f_1 \geq f_2 \geq f_3 \quad (III)$$

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

$$\ddot{H} = I_1 + I_2 \quad (6)$$

where

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

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

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

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

$$I_2 = \frac{2T_{12}T_{13}(f_1 - f_2)(f_1 - f_3) + T_{13}^2(f_1 - f_3)^2}{f_1} + \frac{2T_{13}T_{23}(f_1 - f_2)(f_2 - f_3) + T_{13}^2(f_1 - f_3)^2}{f_3} + 2T_{13}^2(f_1 - f_3) \ln \frac{f_1}{f_3} + T_{12}T_{13} \left[(f_1 - f_2) \ln \frac{f_1}{f_3} + (f_1 - f_3) \ln \frac{f_1}{f_2} \right] + T_{13}T_{23} \left[(f_1 - f_3) \ln \frac{f_2}{f_3} + (f_2 - f_3) \ln \frac{f_1}{f_3} \right] \quad (7)$$

It is obvious that

$$a > 0 \quad , \quad b \geq 0 \quad , \quad c \geq 0 \quad , \quad I_2 \geq 0 \quad (IV)$$

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

$$b^2 - 4ac > 0 \quad (V)$$

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

$$b^2 - 4ac = (f_1 - f_2)^2 J_1 + (f_2 - f_3)^2 J_2 - J_3 \quad (8)$$

where

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

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

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

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

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

$$\left(\ln \frac{f_2}{f_3} \right)^2 > \frac{4(f_2 - f_3)^2}{f_2 f_3} \quad (VII)$$

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

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

i.e.

$$\left. \begin{array}{l} \ln x + \frac{4}{x} - 4 > 0 \\ \text{where } x = \frac{f_2}{f_3} > 1 \end{array} \right\} \quad (VIII)$$

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

$$x > \alpha \quad ,$$

where α is a numerical constant given by

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

and

$$\alpha > 1.$$

It may be noted that $\alpha \approx 50$.

However, considering the function

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

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

III. CASE OF $N = 5$

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

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

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,

$$T_{12} \neq T_{23}$$

and

$$T_{23} = T_{24} = T_{25}.$$

Then we get from (4)

$$\ddot{H} = AT_{12}^2 - B T_{12} T_{23} + C T_{23}^2, \quad (11)$$

where

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

From (I),

$$A \geq 0, B \geq 0, C \geq 0 \quad (IX)$$

(11) can be rewritten as

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

where

$$\alpha = \frac{B + \sqrt{B^2 - 4AC}}{2A},$$

$$\beta = \frac{B - \sqrt{B^2 - 4AC}}{2A}.$$

Thus if α and β are real and distinct, i.e. if $B^2 > 4AC$, one can choose

$\frac{T_{12}}{T_{23}}$ such that $\beta < \frac{T_{12}}{T_{23}} < \alpha$, to get $\ddot{H} < 0$. Such a choice of $\frac{T_{12}}{T_{23}}$ is also consistent with (I) since, in view of (IX), $B > \sqrt{B^2 - 4AC}$ 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

$$I = 9 \left[2 \frac{f_1}{f_2} - 1 \right] \left[1 - \frac{f_3}{f_2} \right] + \left(\frac{f_1}{f_2} - 1 \right) \ln \frac{f_2}{f_3} + \left(1 - \frac{f_3}{f_2} \right) \ln \frac{f_1}{f_2} \Bigg]^2$$

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

$$\left. + 3 \left\{ \frac{f_2}{f_3} \left(1 - \frac{f_3}{f_2} \right) + 2 \left(1 - \frac{f_3}{f_2} \right) \ln \frac{f_2}{f_3} \right\} \right] \quad (13)$$

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

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

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

or simplifying

$$12 \frac{f_2 - f_3}{f_2} \ln \frac{f_2}{f_3} + 9 \left(\ln \frac{f_2}{f_3} \right)^2 - 12 \frac{(f_2 - f_3)^2}{f_2 f_3} > 0 \quad (X)$$

(X) can be satisfied by a suitable choice of $\frac{f_2}{f_3}$. For example, $\frac{f_2}{f_3} = 1.1$ 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 $N \geq 5$.

IV. 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 ≥ 5 . 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 's and f 's, which will give $\dot{H} \leq 0$. It is unlikely that all of them will be unphysical.

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