International Journal of Theoretical Physics, Vol. 13, No. 2 (1975), pp. 143–148

The Converse of the Entropy Principle for Compound Systems

J. B. BOYLING

School of Mathematics, University of Leeds, Leeds, England, LS2 9JT

Received: 13 *October* 1974

Abstract

On the basis of postulates laid down in two previous papers, it is shown that, if a compound system, i.e. a system consisting of several simple systems separated from one another by adiabatic partitions, has greater entropy (in the wide sense) in the state x' than in the state x, then the system is capable of undergoing an adiabatic transition from the state x to the state x'.

1. *Introduction*

In an earlier paper (Boyling, 1972), hereafter referred to as I, it was pointed out that the converse of the entropy principle (or principle of increase of entropy) does not in general hold for systems with non-uniform temperature, i.e. their entropies need not be empirical entropies (Buchdahl & Greve, 1962; Boyling, 1968). This means that, if such a system has a pair of states x and y, of which y has the greater entropy (in the wide sense), then it does not automatically follow that the system can pass adiabatically from the state x to the state y. An example was given of a pair of states x and y of a system consisting of two identical closed calorimeters adiabatically separated from each other, such that no adiabatic transition was possible either from x to y or from y to x. These two states had equal entropy, since one could be obtained from the other by interchanging the states of the two component calorimeters.

We shall now show that this sort of behaviour is in a sense atypical, since the converse of the entropy principle does hold for a very wide class of systems with non-uniform temperature, namely for compound systems, i.e. systems consisting of several simple systems (Carathéodory, 1909) separated from one another by adiabatic partitions.

This is perhaps not altogether surprising, since the example cited above is a rather artificial one. The system has no mechanical degrees of freedom, since the calorimeters each have constant volume. A more realistic system can be obtained by replacing the two closed calorimeters by two identical cylinders of gas fitted with pistons. Let x and y be states of the individual cylinders such that $T(y) > T(x)$, where T denotes the absolute temperature. Consider the state $z = (x, y)$ of the composite system in which the first cylinder is in the state x and the second in the state y, and the state $z' = (y, x)$ obtained from z by reversing the roles of the two cylinders. If the pistons on the two cylinders were immovable, then, as in the case of the two closed calorimeters, there would be no way of passing adiabatically from the state z to the state z'. However, if we imagine that the two pistons may be moved freely and without friction, then the system can undergo a quasi-static adiabatic transition from the state z to the state z' (or from z' to z).

To see how this comes about, we introduce states x' and y' of the individual cylinders defined as follows: x' is the point of intersection of the isothermal through x and the adiabatic through y; y' is the point of intersection of the isothermal through y and the adiabatic through x. Suppose the system is initially in the state z, so that the first cylinder is in the state x and the second in the state y. Then we can change its state adiabatically to z' in three stages. First we compress the first cylinder adiabatically until it reaches the state y', when its temperature will be equal to that of the second cylinder (which has been left in its original state y). Next we allow the two cylinders to exchange heat by temporarily removing the thermal insulation between them. By simultaneously expanding one cylinder and contracting the other at suitable rates, we can make the whole system pass adiabatically and isothermally at temperature $T(y) = T(y')$ to a state in which the first cylinder is in the state y and the second cylinder in the state y'. Finally, we replace the thermal insulation and expand the second cylinder adiabatically until it reaches the state x, leaving the first cylinder in the state y.

The mode of passing adiabatically from the state z to the state z' in this simple example suggests a line of attack for the general problem of proving the converse of the entropy principle for an arbitrary compound system, to which we now turn. The axiomatic basis for our proof will be the set of postulates laid down in I, supplemented by assumptions (i) and (ii) of a subsequent paper (Boyling, 1973), hereafter referred to as II. The definitions and notations of I and II will be used throughout without further explanation.

The first step in the proof of the converse of the entropy principle for the product $M = \Pi_i M_i$ of the simple systems M_i is taken in Section 2, where it is shown that the isentropics (i.e. level surfaces of entropy) of the system M are connected. In Section 3 the converse of the entropy principle is shown to be equivalent to a certain local result, which is then proved with the aid of Carnot engines, whose existence was established in II.

2. *The Connectedness of the Isentropics*

Let L be any isentropic of $M = \Pi_{i=1}^n M_i$, where the M_i are all simple. Then L has an equation of the form $S(x) = \text{constant}$, where the entropy S of M is defined in terms of the entropies S_i of the M_i by

$$S(x_1, x_2, \ldots, x_n) = S_1(x_1) + S_2(x_2) + \cdots + S_n(x_n)$$

Since each S_i is a C^∞ function with everywhere non-vanishing differential, it is clear that the function S on M also enjoys these properties, so that L is a closed C^∞ submanifold (without boundary) of M of codimension 1. In particular, L is locally path-connected (see, for example, Spanier, 1966). It is therefore connected if and only if it is path-connected, i.e. if and only if xCx' for any x and x' in L, where xCx' means that there exists a path γ in L joining x to x', i.e. a continuous function $\gamma : [0, 1] \to L$ such that $\gamma(0) = x$ and $\gamma(1) = x'$. Clearly C is an equivalence relation on the points of L. To prove that L is connected, we must show that C has only one equivalence class.

Let $x = (x_1, \ldots, x_n)$ and $x' = (x'_1, \ldots, x'_n)$ be any two points of L, so that $S(x) = S(x')$, i.e. $\Sigma_i S_i(x_i) = \Sigma_i S_i(x'_i)$. We must prove that xCx'. Let J_i be the closed interval with end-points $S_i(x_i)$ and $S_i(x'_i)$. Since the differential dS_i of the C^∞ function S_i on M_i is nowhere zero, it follows that, for any number s in J_i, there exists an open rectangular (I) coordinate neighbourhood V_i in M_i on which S_i is one of the (C^∞) local coordinates, such that $s \in S_i(V_i)$. As s varies over J_i, the corresponding open intervals $S_i(V_i)$ form an open covering of the compact metric space J_i. Let δ_i be a Lebesgue number (see, for example, Hilton & Wylie, 1960, Lemma 1.8.2) for this open covering, and let N be any integer greater than every one of the n quantities $\delta_i^{-1} |S_i(x'_i) - S_i(x_i)|$. Then, if J_i is divided into N equal closed subintervals, each of these will be contained in an open interval of the form $S_i(V_i)$, where V_i is an open rectangular coordinate neighbourhood of M_i on which S_i is one of the (C^∞) local coordinates. Let V_{ik} be the neighbourhood corresponding to the kth subinterval of J_i, where the counting of subintervals begins at the end-point $S_i(x_i)$ of J_i. Then, for each i and k, we can find a pair of points $x'_{i,k-1}$ and x_{ik} in V_{ik} such that

$$S_i(x'_{i,k-1}) = \left(\frac{N-k+1}{N}\right) S_i(x_i) + \left(\frac{k-1}{N}\right) S_i(x'_i)$$

$$S_i(x_{ik}) = \left(\frac{N-k}{N}\right) S_i(x_i) + \frac{k}{N} S_i(x'_i)$$

Defining $x_{i0} = x_i$ and $x'_{iN} = x'_i$, we see that

$$\sum_i S_i(x_{ik}) = \sum_i S_i(x'_{ik}) = \sum_i S_i(x_i) = \sum_i S_i(x'_i)$$

for $k = 0, 1, \ldots, N$, so that the states $\xi_k = (x_{1k}, x_{2k}, \ldots, x_{nk})$ and $\xi'_k = (x'_{1k}, x'_{2k}, \ldots, x'_{nk})$ of M belong to L for all k. Since $S_i(x_{ik}) = S_i(x'_{ik})$ for all i and the isentropics of a simple system are (path-) connected, it is clear that $\xi_k C \xi'_k$ for $k = 0, 1, \ldots, N$. Also $\xi'_{k-1} C \xi_k$ for $k = 1, 2, \ldots, N$. For $x'_{i,k-1}$ and x_{ik} are both in V_{ik}. As V_{ik} is an open rectangular coordinate neighbourhood on which S_i is one of the (C^∞) local coordinates, we may construct a C^∞ path $\gamma_i : [0, 1] \to V_{ik}$ such that $\gamma_i(0) = x'_{i,k-1}$, $\gamma_i(1) = x_{ik}$,

$$S_i\{\gamma_i(t)\} = (1-t) S_i(x'_{i,k-1}) + t S_i(x_{ik})$$

(e.g. the path represented in terms of the local coordinates on V_{ik} by the straight line segment joining the points representing $x'_{i,k-1}$ and x_{ik}). Clearly $\gamma : [0, 1] \to M$ defined by $\gamma(t) = (\gamma_1(t), \gamma_2(t), \ldots, \gamma_n(t))$ is a (C^∞) path in L joining ξ'_{k-1} to ξ_k. Successive application of the results $\xi_k C \xi'_k$ and $\xi'_{k-1} C \xi_k$ for various values of k now shows that $\xi_0 C \xi'_N$, i.e. that xCx'.

3. *Proof of the Converse of the Entropy Principle*

We first observe that it is sufficient to prove that $x \leqslant x'$ whenever x and x' lie on the same isentropic of M. For suppose that this result holds. Let $x = (x_1, \ldots, x_n)$ and $x' = (x'_1, \ldots, x'_n)$ be any two states of M satisfying $S(x) \leqslant S(x')$, i.e. $\Sigma_i S_i(x_i) \leqslant \Sigma_i S_i(x'_i)$. Then we can find states x''_i of M_i such that $S_i(x''_i) \leqslant S_i(x'_i)$ for all i and $\Sigma_i S_i(x''_i) = \Sigma_i S_i(x_i)$. For the range $S_i(M_i)$ of the function S_i is an open interval (a_i, b_i), where a_i may take the value $-\infty$ (and b_i may take the value $+\infty$). If the a_i are all finite, then we choose x''_i such that

$$S_i(x''_i) = \left\{\frac{S(x) - \sum_j a_j}{S(x') - \sum_j a_j}\right\} S_i(x'_i) + \left\{\frac{S(x') - S(x)}{S(x') - \sum_j a_j}\right\} a_i$$

If $a_i = -\infty$ for some i, then we choose the corresponding x''_i such that $S_i(x''_i) = S_i(x'_i) + S(x) - S(x')$, and take $x''_j = x'_j$ for $j \neq i$. The result we have assumed now implies that the state $x'' = (x''_1, \ldots, x''_n)$ satisfies $x \leqslant x''$. On the other hand $x'' \leqslant x'$, since $x''_i \leqslant x'_i$ for each i. Hence $x \leqslant x'$ by transitivity.

Next we note that, as the isentropics of M are connected, it will be sufficient to prove the following localised version of the above result:

There exists an open covering $\mathscr{V}$ of M such that $x \leqslant x'$ whenever x and x' lie on the same isentropic and are both contained in a single set v of $\mathscr{V}$.

For suppose that this local result holds. Let x and x' be any two states of M belonging to the same isentropic L. Then, as the sets $V \cap L$ for $V \in \mathscr{V}$ form an open covering for the connected topological space L, there exists (see, for example, Hocking and Young, 1961, Theorem 3-4) a finite sequence of sets V_k in $\mathscr{V}$ and points x_k in L such that

$$x \in V_1, \qquad x' \in V_N, \qquad x_k \in V_k \cap V_{k+1} \qquad \text{for } k = 1, 2, \ldots, N-1$$

By the local result assumed above, we have

$$x \leqslant x_1 \leqslant x_2 \leqslant \cdots \leqslant x_{N-1} \leqslant x'$$

whence $x \leqslant x'$ by transitivity.

The remainder of this section will be devoted to proving the above local result. In fact we shall show that this result holds if the open covering $\mathscr{V}$ consists of all topological products of the form $V = \Pi_i V_i$, where V_i is a non-empty open set in M_i of the form $T_i^{-1} T_i^*(W_i) \cap S_i^{-1}(J_i)$ for some thermometer N_i, where T_i is the absolute temperature for M_i, T_i^* and S_i^* are the absolute temperature and entropy for N_i, W_i is a standard neighbourhood (I) for N_i, and J_i is some translate of the open interval $S_i^*(W_i)$. We must prove that, for any such $V, x \leqslant x'$ whenever $S(x) = S(x')$ and x and x' both belong to V.

Suppose $x = (x_1, \ldots, x_n)$ and $x' = (x'_1, \ldots, x'_n)$. The definition of V_i in terms of the thermometer N_i ensures that we can find states y_i, y'_i, y''_i of N_i in W_i such that

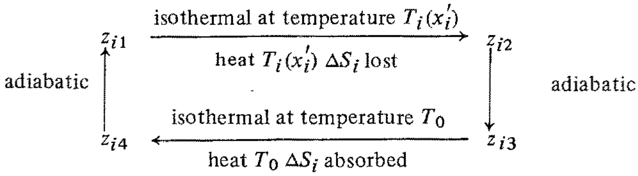
$$T_i^*(y_i) = T_i(x_i), \qquad T_i^*(y'_i) = T_i^*(y''_i) = T_i(x'_i)$$
$$S_i^*(y_i) = S_i^*(y''_i) = S_i^*(y'_i) + \Delta S_i$$

where

$$\Delta S_i = S_i(x'_i) - S_i(x_i)$$

Now $x_i \sim y_i$ and $x'_i \sim y'_i$, so (x_i, y_i) and (x'_i, y'_i) may both be regarded as states of the sum $M_i + N_i$. Since these two states have the same entropy and $M_i + N_i$ is a simple system, it follows that $(x_i, y_i) \leqslant (x'_i, y'_i)$ for $M_i + N_i$ and therefore also for $M_i \times N_i$ (cf. assumption (ii) of II).

We now introduce for each i a Carnot engine C_i capable of executing a Carnot cycle between the temperature $T_i(x'_i)$ and some fixed temperature T_0 less than all of the $T_i(x'_i)$, the entropy difference between the two adiabatics of the cycle being precisely ΔS_i. The existence of such Carnot engines is guaranteed by the results of II. We shall assume that the Carnot cycle of C_i proceeds as follows:



(with an obvious change of wording in the event that ΔS_i is negative). The Carnot engine C_i is a product of thermometers, and only one of these, that called the head in II, changes state in the transition from z_{i1} to z_{i2}. Since the entropies of the states (y'_i, z_{i1}) and (y''_i, z_{i2}) of $N_i \times C_i$ are equal, the same applies to the corresponding states of the product of N_i and the head of C_i, states in which these two systems both have temperature $T_i(x'_i)$. Arguing as in the proof of $(x_i, y_i) \leqslant (x'_i, y'_i)$ above, we now deduce that $(y'_i, z_{i1}) \leqslant (y''_i, z_{i2})$ for $N_i \times C_i$. The same sort of argument shows that the states $z_3 = (z_{13}, z_{23}, \ldots, z_{n3})$ and $z_4 = (z_{14}, z_{24}, \ldots, z_{n4})$ of $C = \Pi_i C_i$ satisfy $z_3 \leqslant z_4$, since they have the same entropy and only one component of each C_i, that called the foot in II, changes state in the transition from z_3 to z_4, and that isothermally at temperature T_0 (cf. the similar argument in Section 3 of II).

Combining the above results, writing $\Pi_i N_i = N$, and using an obvious notation for states of product systems, we see that the system $M \times N \times C$ satisfies

$$(x, y, z_1) \leqslant (x', y', z_1) \leqslant (x', y'', z_2) \leqslant (x', y, z_3)$$
$$\leqslant (x', y, z_4) \leqslant (x', y, z_1)$$

Appealing to assumption (i) of II, we now conclude that $x \leqslant x'$.

4. *Conclusion*

We have shown that, as far as compound systems are concerned, $S(x) \leqslant S(x')$ is not only a necessary but also a sufficient condition for the existence of an adiabatic transition from the state x to the state x', i.e. $x \leqslant x'$ if and only if $S(x) \leqslant S(x')$, so that S is an empirical entropy. In particular, this means that, given any pair of states x and x' of a compound system, then one or other (or both) of the relations $x \leqslant x', x' \leqslant x$ must hold. This was only *assumed* to be the case for *simple* systems in I. We have now *proved* from the postulates that it is also true for compound systems. If attention were confined to (simple and) compound systems, it would therefore be legitimate to postulate this property for all systems (cf. Cooper, 1967). The approach used in I has the advantage that it is more economical and applies to a wider class of systems.

The above results should not lead one to suppose that the entropy plays exactly the same role for compound as for simple systems. The heat form of a simple system has an integrating factor (namely the reciprocal of the absolute temperature) converting it to the differential of the entropy. A quasi-static transition represented by a smooth curve is adiabatic if and only if its tangent vector is everywhere annihilated by the heat form, or, equivalently, if and only if the entropy is constant along it. However, the heat form of a compound system has in general no integrating factor. Moreover, the annihilation by the heat form of all of its tangent vectors is not a sufficient condition for a smooth curve to represent a quasi-static adiabatic transition of a compound system. Again not every smooth curve on which the entropy is constant represents a quasi-static adiabatic transition of such a system. Admittedly, since the entropy is an empirical entropy, it is true that every state on the curve can be reached from every other state on the curve by an adiabatic transition of some sort. However, even if this adiabatic transition is quasi-static, it need not follow the original curve between the two states.

References

Boyling, J. B. (1968). *Communications in Mathematical Physics*, **10**, 52.
Boyling, J. B. (1972). *Proceedings of the Royal Society (London)*, **A329**, 35.
Boyling, J. B. (1973). *International Journal of Theoretical Physics*, **7**, 291.
Buchdahl, H. A. and Greve, W. (1962). *Zeitschrift für Physik*, **168**, 386.
Carathéodory, C. (1909). *Mathematische Annalen*, **67**, 355.
Cooper, J. L. B. (1967). *Journal of Mathematical Analysis and Applications*, **17**, 172.
Hilton, P. J. and Wylie, S. (1960). *Homology Theory*. Cambridge University Press.
Hocking, J. G. and Young, G. S. (1961). *Topology*. Addison-Wesley, Reading, Mass.
Spanier, E. H. (1966). *Algebraic Topology*. McGraw-Hill, New York.