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Thermodynamics of Non-Differentiable Systems

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Abstract

An axiomatisation of classical thermodynamics previously proposed for a somewhat restricted class of systems whose state spaces are differentiable manifolds is extended to systems whose state spaces are arbitrary connected separable topological spaces. It turns out that such systems need not obey Carathéodory's principle, although they do obey a form of Kelvin's principle.

1. *Introduction*

In three earlier papers (Boyling, 1972, 1973a and 1973b), hereafter referred to as I, II and III respectively, an axiomatic formulation of classical thermodynamics was presented, in which attention was confined essentially to systems whose state spaces are differentiable manifolds.

Not all systems are of this type. For example, for a system made up of two identical subsystems in thermal contact, each subsystem being a cylinder fitted with a smooth piston and filled with a single chemically stable substance, the state space is not a manifold. In the neighbourhood of a state in which the substance in each cylinder is at its triple point, the state space is four-dimensional; elsewhere it is three-dimensional. Nor is it a manifold with boundary, since the four-dimensional part is not dense

We therefore wish to extend our previous results to systems whose state spaces are arbitrary connected separable topological spaces. It will still be necessary to assume the existence of thermometers (I), whose state spaces are differentiable manifolds. But, provided there are enough of these to cover all possible temperatures, it is possible to extend to non-differentiable systems all the results proved in I, II and III.

The basic postulates for non-differentiable systems are listed and discussed in Section 2. Entropy and absolute temperature are constructed for such systems in Section 3. In Section 4, the entropy so constructed is shown to be additive. In Section 5, it is shown that non-differentiable systems (with or without internal adiabatic partitions) obey the principle of increase of entropy and its converse (III). A notion of quasi-static transition for such systems is introduced in Section 6, in such a way as to give a meaning to the differential relation $đQ = T\,dS$, Clausius' inequality and Kelvin's principle. It turns out from the postulates that, although they obey Kelvin's principle, non-differentiable systems do not in general obey Carathéodory's principle (cf. Landsberg, 1964; Dunning-Davies, 1965).

2. *Basic Assumptions*

We shall assume postulates I–V of I and assumptions (i) and (ii) of II, in so far as they concern general thermodynamic systems and thermometers. In place of the simple systems (Carathéodory, 1909) of I, we shall consider the wider class of *generalised simple systems* M with the following properties (where, as in I, no distinction is made between a system and the set of all its states):

(1) Given x and y in M, then either $x \leqslant y$ or $y \leqslant x$ (or both), where $\leqslant$ is the relation of (adiabatic) accessibility.

(2) Given x in M, there exist y and z in M such that $z < x < y$ (where $x < y$ means $y \nleqslant x$).

(3) M is a connected separable topological space.

(4) $\leqslant$ is a closed relation on M, i.e. its graph G is a closed subset of the topological product $M \times M$.

(5) The mutual accessibility classes of M (i.e. equivalence classes of the equivalence relation $\equiv$ on M defined by $x \equiv y$ if and only if $x \leqslant y$ and $y \leqslant x$) are connected subsets of M.

(6) The adiabatic work function (I) is a continuous real-valued function on the subspace G of $M \times M$.

(7) The equivalence relation $\sim$ (equality of temperature) on states of simple systems may be extended to states of all generalised simple systems. Its equivalence classes will again be known as *isothermals* and those of its restriction to the states of a particular generalised simple system as the *isotherms* of that system.

(8) Every isothermal contains a state of some thermometer.

(9) If M is a generalised simple system, N a thermometer, and V any open set in N, then

$$\{x \in M; x \sim y \text{ for some } y \text{ in } V\}$$

is a (possibly empty) open subset of M.

(10) Let $M_1, M_2, \ldots, M_n$ be generalised simple systems, M their product. If the subspace

$$\{(x_1, \ldots, x_n) \in M; x_1 \sim x_2 \sim \cdots \sim x_n\}$$

of M is non-empty, when we say the M_i are (mutually for $n > 2$) *compatible*, then each connected component of this subspace represents a generalised simple system, called a *composite* of the M_i, for which the relation $\leqslant$ and the adiabatic work function are the appropriate restrictions of those of M.

(11) If M is a generalised simple system, N a thermometer compatible with M, and $L \subset M \times N$ a mutual accessibility class of a composite of M and N, then the image $\mathrm{pr}_1(L)$ of L under the first projection pr_1 of the topological product $M \times N$ is an open subset of M.

Comparison of the above assumptions with the postulates of I shows that it is consistent to assume that every simple system is a generalised simple system. Assumptions 1–6 constitute the analogue for generalised simple systems of postulate II of I for simple systems. Assumptions 7 and 8 extend the zeroth law (postulate IV of I) to generalised simple systems. The first law has already been assumed, in the shape of postulate I of I, which applies to arbitrary thermodynamic systems. There is no need to extend the second law to generalised simple systems or their products. Indeed, Carathéodory's principle need not hold for such systems (cf. Section 6). For our purposes it will be sufficient to assume the second law (postulate III or III′ of I) for thermometers alone. Assumption (i) of II (first proposed by Cooper, 1967) then ensures (cf. corollary to lemma 1 of II) that it holds also for all products of thermometers. The auxiliary assumptions 9, 10 and 11 above correspond roughly to postulate V of I for simple systems, though 10 also embraces an extension of assumption (ii) of II. A composite of generalised simple systems M_i is to be viewed physically as consisting of the M_i in mutual thermal contact. Comparing 10 with postulate V of I, we see that, if M and N are compatible thermometers, then they have only one composite, itself a thermometer, called their *sum* $M + N$. An inductive argument shows that a family of n mutually compatible thermometers $M_1, \ldots, M_n$ has just one composite $\sum_{i=1}^{n} M_i$, which is itself a thermometer. From 10, we also deduce the following lemma:

Lemma. Suppose $M_1, \ldots, M_n$ are generalised simple systems, I_α for $\alpha = 1, \ldots, m$ disjoint non-empty subsets of the set $I = \{1, \ldots, n\}$ of the first n positive integers, such that

$$\bigcup_{\alpha=1}^{m} I_\alpha = I$$

Then a generalised simple system C is a composite of the M_i ($i = 1, \ldots, n$) if and only if it is a composite of systems C_α for $\alpha = 1, \ldots, m$, where C_α is a composite of the M_i with i in I_α (or just M_i itself if I_α happens to consist of the single element i).

Proof. By abuse of language, we write

$$M = \prod_{i=1}^{n} M_i = \prod_{\alpha=1}^{m} M_\alpha$$

where

$$M_\alpha = \prod_{i \in I_\alpha} M_i$$

and denote by pr_α the natural projection of M onto M_α. We also write

$$N = \{(x_1, \ldots, x_n) \in M; x_1 \sim \cdots \sim x_n\}$$

$$N_\alpha = \{(x_i)_{i \in I_\alpha} \in M_\alpha; x_i \sim x_j \text{ for } i, j \in I_\alpha\}$$

Suppose first that C is a composite of the M_i, i.e. a component of N. Then $\mathrm{pr}_\alpha(C)$ is a connected subset of N_α. Let C_α be the component of N_α containing $\mathrm{pr}_\alpha(C)$. Then

$$C \subset \left(\prod_\alpha C_\alpha\right) \cap N$$

As C is a maximal connected subset of N, it is also a maximal connected subset of $(\prod_\alpha C_\alpha) \cap N$, i.e. C is a composite of the C_α.

Conversely, suppose there exists for each α a composite C_α of the M_i with i in I_α, such that C is a composite of the C_α. Then C is a component of $(\prod_\alpha C_\alpha) \cap N$. Let C' be any connected subset of N containing C. Then $\mathrm{pr}_\alpha(C')$ is a connected subset of N_α intersecting C_α. Since C_α is a maximal connected subset of N_α, it follows that $\mathrm{pr}_\alpha(C') \subset C_\alpha$. Hence

$$C' \subset \left(\prod_\alpha C_\alpha\right) \cap N$$

As C is a maximal connected subset of $(\prod_\alpha C_\alpha) \cap N$, it follows that $C = C'$. Thus C is a maximal connected subset of N, i.e. C is a composite of the M_i.

3. *Absolute Temperature and Entropy*

It was shown in I that postulate I implies the existence for every thermodynamic system M of a real-valued function U (determined to within an additive constant) called the *internal energy*, such that

$$W(x, y) = U(x) - U(y) \qquad \text{for } (x, y) \in G$$

where W is the adiabatic work function. If U_i is the internal energy of M_i for $i = 1, \ldots, n$, then the internal energy U of $M = \prod_{i=1}^n M_i$ is given (to within an additive constant) by

$$U(x_1, \ldots, x_n) = \sum_{i=1}^{n} U_i(x_i)$$

If M is a thermometer, then U is a C^∞ function with no critical points. Assumption 6 implies that the internal energy of a generalised simple system is continuous.

The construction of the *absolute temperature scale* in I enables us to associate with each thermometer M a positive-valued C^∞ function T_M on M with no critical points, in such a way that, if x and y are states of thermometers M and N, then $x \sim y$ if and only if $T_M(x) = T_N(y)$. This temperature scale (unique to within a positive multiplicative constant) has the (defining) property that the heat form of each thermometer M is of the form $\psi_M = T_M\, dS_M$, where S_M is a C^∞ function on M with no critical points (determined to within an additive constant) called the *entropy*. The function S_M is an *empirical entropy*, i.e. it satisfies the condition that $S_M(x) \leqslant S_M(x')$ if and only if $x \leqslant x'$. It is also *addi-*

tive, in the sense that the entropy S of the sum of the mutually compatible thermometers $M_1, \ldots, M_n$ is given by

$$S(x_1, \ldots, x_n) = \sum_{i=1}^{n} S_i(x_i) + \text{constant} \tag{3.1}$$

where S_i is the entropy of M_i.

The results of II and III show that, if the entropy of a product of thermometers $M = \prod_{i=1}^{n} M_i$ is *defined* by

$$S_M(x_1, \ldots, x_n) = \sum_{i=1}^{n} S_i(x_i) \tag{3.2}$$

where S_i is the entropy of M_i, then S_M is an empirical entropy for M.

Assumptions 7 and 8 enable us to extend the absolute temperature scale to generalised simple systems in an obvious way, by defining the absolute temperature $T_M(x)$ of a state x of a generalised simple system M to be $T_N(y)$ for any state y of any thermometer N such that $x \sim y$. Assumption 9 ensures that the positive-valued function T_M on M so defined is continuous.

The construction of the entropy of a generalised simple system is not quite so easy. We proceed by first using assumption 11 to construct local entropies for M, and then piecing these together using the known existence (implied by assumptions 1-5; cf. Buchdahl & Greve, 1962; Cooper, 1967; Boyling, 1968) of a continuous empirical entropy σ for M.

Let M be a generalised simple system, N a thermometer compatible with M, $L \subset M \times N$ a mutual accessibility class of a composite of M and N. By 11, $\mathrm{pr}_1(L)$ is an open subset of M, and, by 8, the sets $\mathrm{pr}_1(L)$ for varying (N and) L constitute an open covering of M. We define a local entropy S_L for M on $\mathrm{pr}_1(L)$ by

$$S_L(x) = -S_N(y) \tag{3.3}$$

for any y in N such that $(x, y) \in L$, where S_N is the (already defined) entropy of the thermometer N. This is a meaningful definition, i.e. the right-hand side of (3.3) is independent of the choice of y. For suppose $(x, y') \in L$. Then, as L is a mutual accessibility class of a composite of M and N, we have $(x, y) \equiv (x, y')$ for that composite, and hence, by 10, also for the product system $M \times N$. It follows by assumption (i) of II that $y \equiv y'$ for N, whence $S_N(y) = S_N(y')$, since S_N is an empirical entropy for N.

We now show that S_L is a local empirical entropy (Boyling, 1968) for M on $\mathrm{pr}_1(L)$. Let x and x' be any two points of $\mathrm{pr}_1(L)$. Then

$$S_L(x') - S_L(x) = S_N(y) - S_N(y')$$

where (x, y) and (x', y') both belong to L, so that

$$(x, y) \equiv (x', y') \qquad \text{for } M \times N$$

If $x \leqslant x'$, then

$$(x', y') \leqslant (x, y) \leqslant (x', y)$$

and so $y' \leqslant y$ by assumption (i) of II, whence

$$S_N(y') \leqslant S_N(y)$$

and

$$S_L(x) \leqslant S_L(x')$$

Conversely, if $S_L(x) \leqslant S_L(x')$, then $S_N(y') \leqslant S_N(y)$, $y' \leqslant y$, and so

$$(x, y) \leqslant (x', y') \leqslant (x', y)$$

whence $x \leqslant x'$ by assumption (i) of II.

Next we observe that S_L must be continuous. For its range

$$S_L \circ \mathrm{pr}_1(L) = -S_N \circ \mathrm{pr}_2(L)$$

is an interval I of the real line, since L is connected and S_N (and pr_2) continuous. Since the preorder relation $\leqslant$ on M is closed, the topology of the quotient space of $\mathrm{pr}_1(L)$ by the equivalence relation $\equiv$ is stronger than its order topology under the (total) ordering induced by $\leqslant$. Now the function S_L, being a local empirical entropy, passes to the quotient to define an order isomorphism $\hat{S}_L$ of the above quotient space onto I. But an order isomorphism of totally ordered sets becomes a homeomorphism if each set carries its order topology (see e.g. Kowalsky, 1965, 16.2, p. 117). It follows that $\hat{S}_L$ is continuous, and therefore so is S_L.

Now there exists (Boyling, 1968) a continuous empirical entropy σ on M, and, since S_L and the restriction σ_L of σ to $\mathrm{pr}_1(L)$ are both continuous local empirical entropies on $\mathrm{pr}_1(L)$, it follows that $S_L = f_L \circ \sigma_L$, where f_L is a strictly increasing continuous real-valued function on the interval $I_L = \sigma \circ \mathrm{pr}_1(L)$ of the real line.

The functions f_L for varying L have the property that, if any two of them have a common domain of definition, then they differ by a constant (at most) on that common domain. For suppose

$$I_L \cap I_{L'} \neq \emptyset, \qquad t_1, t_2 \in I_L \cap I_{L'}$$

Then, if N and N' are the thermometers corresponding to L and L', there exist states (x_1, y_1) and (x_2, y_2) in $L \subset M \times N$ and states (x_1', y_1') and (x_2', y_2') in $L' \subset M \times N'$ such that

$$\sigma(x_1) = \sigma(x_1') = t_1, \qquad \sigma(x_2) = \sigma(x_2') = t_2$$

Clearly $x_1 \equiv x_1'$ and $x_2 \equiv x_2'$ for M, $(x_1, y_1) \equiv (x_2, y_2)$ for $M \times N$, and $(x_1', y_1') \equiv (x_2', y_2')$ for $M \times N'$. Therefore, for $M \times N \times N'$, we have

$$(x_1, y_1, y_2') \equiv (x_2, y_2, y_2') \equiv (x_2', y_2, y_2') \equiv (x_1', y_2, y_1') \equiv (x_1, y_2, y_1')$$

whence

$$(y_1, y_2') \equiv (y_2, y_1') \qquad \text{for } N \times N'$$

by assumption (i) of II. Since N and N' are thermometers, the entropy of $N \times N'$ (defined by 3.2) is an empirical entropy, and so

$$S_N(y_1) + S_{N'}(y_2') = S_N(y_2) + S_{N'}(y_1')$$

whence

$$S_{L'}(x_1') - S_L(x_1) = S_{L'}(x_2') - S_L(x_2)$$

i.e.

$$f_{L'}(t_1) - f_L(t_1) = f_{L'}(t_2) - f_L(t_2)$$

Next we prove that there exists a strictly increasing continuous function f on the open interval $\sigma(M)$ which differs by a constant from each f_L on its domain of definition. This we do by applying Zorn's lemma to the set $\mathscr{F}$ of all (strictly increasing) continuous functions f on subintervals I of $\sigma(M)$ with the property that f and f_L differ by a constant on $I \cap I_L$ for every L. Clearly $\mathscr{F}$ is non-empty, since $f_L \in \mathscr{F}$ for each L. If $\mathscr{F}$ is partially ordered by $f \leqslant f'$ if and only if f' is an extension of f, then it is clear that $\mathscr{F}$ satisfies all the conditions of Zorn's lemma. It therefore contains at least one maximal element f. The domain I of this function f must be the whole of $\sigma(M)$. For suppose this is not so. Then at least one end point of I belongs to $\sigma(M)$. Suppose $t_0 = \sup I \in \sigma(M)$. Then there exists at least one L such that σ takes the value t_0 and values greater than t_0 on $\mathrm{pr}_1(L)$. For otherwise each point x of the mutual accessibility class $\sigma^{-1}(t_0)$ would have an open neighbourhood of the form $\mathrm{pr}_1(L)$ on which σ never exceeds t_0. The non-empty set

$$\{x \in M; \sigma(x) \leqslant t_0\}$$

would thus be both open and closed in the connected space M, and therefore equal to the whole of M, contradicting assumption 2. Thus there exists an L such that $t_0 \in I_L$, $\sup I_L > t_0$. Similarly, there exists an L' such that $t_0 \in I_{L'}$, $\inf I_{L'} < t_0$. Since f and $f_{L'}$ differ by a constant on $I_{L'} \cap I$, it follows that $f(t)$ tends to a finite limit l as t tends t_0 from below, with $l = f(t_0)$ if $t_0 \in I$. Defining the function f^* on the interval $I^* = I \cup I_L$ by

$$f^*(t) = \begin{cases} f(t) & \text{for } t \in I \\ f_L(t) - f_L(t_0) + l & \text{for } t \in I_L \end{cases}$$

we see that

$$f^* \in \mathscr{F}, \qquad f \leqslant f^*, \qquad f \neq f^*$$

contradicting the maximality of f. Similarly, the assumption that $\inf I \in \sigma(M)$ also leads to a contradiction. We conclude that $I = \sigma(M)$. The maximal function f clearly has all the required properties, and these determine it to within an arbitrary additive constant.

We now define (also to within an additive constant) the *entropy* of the generalised simple system M to be the function $S_M = f \circ \sigma$. Clearly S_M differs by a constant from each local entropy S_L on its domain of definition $\mathrm{pr}_1(L)$. Since f is a strictly increasing continuous function and σ a continuous empirical entropy, it follows that S_M is a continuous empirical entropy. If M happens to be a thermometer, then this newly defined entropy coincides (to within an additive constant) with the entropy already defined on M, as follows at once from the additivity property (3.1) of entropy for thermometers.

4. *The Additivity of Entropy*

This additivity property will now be extended to generalised simple systems. To get a concise statement of it, we first *define* (to within an additive constant) by analogy with (3.2) the entropy of a product $M = \Pi_{i=1}^n M_i$ of generalised simple systems M_i by

$$S_M(x_1, \ldots, x_n) = \sum_{i=1}^{n} S_i(x_i) \tag{4.1}$$

where S_i is the entropy of M_i (as constructed in Section 3). Additivity of entropy for generalised simple systems then states that, if the generalised simple system C is a composite of the generalised simple systems M_i, then the entropy S_C of C differs by a constant from the restriction S_C' to C of the entropy S_M of the product system M.

Since C is a connected subspace of M, it will be sufficient to prove that the function $S_C - S_C'$ is *locally* constant. Let $x = (x_1, \ldots, x_n)$ be any point of C, L_i a mutual accessibility class of a composite of M_i with a thermometer N_i, such that $(x_i, y_i) \in L_i$ for some y_i in N_i. We prove that $S_C - S_C'$ is constant on the open neighbourhood

$$V = C \cap \prod_{i=1}^{n} \mathrm{pr}_1(L_i)$$

of x in C.

Let $x' = (x_1', \ldots, x_n')$ and $x'' = (x_1'', \ldots, x_n'')$ be any two points of V. Choose y_i' and y_i'' in N_i such that (x_i', y_i') and (x_i'', y_i'') are both in L_i. Then

$$S_i(x_i'') - S_i(x_i') = \hat{S}_i(y_i') - \hat{S}_i(y_i'')$$

where S_i and $\hat{S}_i$ are the entropies of M_i and N_i respectively. Summing on i gives

$$S_M(x'') - S_M(x') = S_N(y') - S_N(y'') \tag{4.2}$$

where N is the *sum* of the (clearly mutually compatible) thermometers $N_1, \ldots, N_n$, and y' and y'' are the states of N in which N_i is in the state y_i' and y_i'' respectively ($i = 1, \ldots, n$). Now $(x_i', y_i') \equiv (x_i'', y_i'')$ for some composite of M_i and N_i, and therefore also (by 10) for $M_i \times N_i$. Hence

$$(x', y') \equiv (x'', y'') \qquad \text{for } \prod_{i=1}^{n} M_i \times \prod_{i=1}^{n} N_i$$

and therefore also for some composite of the M_i and the N_i, which must (by the lemma of Section 2) be a composite of some composite of the M_i with some composite of the N_i. Since $x', x'' \in C$ and N is the only composite of the N_i, it follows that $(x', y') \equiv (x'', y'')$ for some composite of C and N, whence

$$S_C(x'') - S_C(x') = S_N(y') - S_N(y'') \tag{4.3}$$

by construction of S_C. Comparing (4.2) and (4.3), we see that

$$S_C(x'') - S_M(x'') = S_C(x') - S_M(x')$$

i.e.

$$S_C(x'') - S'_C(x'') = S_C(x') - S'_C(x')$$

i.e. $S_C - S'_C$ is constant on V, as we sought to prove.

5. *The Principle of Increase of Entropy*

The principle of increase of entropy and its converse are satisfied by generalised simple systems by construction, since the entropy of Section 3 was seen to be an empirical entropy. We shall now show that the same is true of *generalised compound systems*, i.e. products of generalised simple systems, in the sense that the entropy defined by (4.1) for such a system is an empirical entropy.

Suppose $M = \prod_{i=1}^n M_i$, where the M_i are generalised simple systems, and let $x = (x_1, \ldots, x_n)$ and $x' = (x'_1, \ldots, x'_n)$ be any two states of M. We must show that $x \leqslant x'$ if and only if $S_M(x) \leqslant S_M(x')$.

Let $\mathscr{V}$ be the open covering of M by sets of the form $\prod_{i=1}^n \mathrm{pr}_1(L_i)$, where L_i is a mutual accessibility class of a composite of M_i with some thermometer N_i. Then, since M is connected, there exists a finite sequence $V_0, V_1, \ldots, V_m$ of sets of $\mathscr{V}$ such that:

$$x \in V_0, \qquad x' \in V_m$$
$$V_{k-1} \cap V_k \neq \emptyset \qquad \text{for } k = 1, \ldots, m$$

Suppose $V_k = \prod_{i=1}^n V_{ki}$, where $V_{ki} = \mathrm{pr}_1(L_{ki})$ for some mutual accessibility class L_{ki} of a composite of M_i with a thermometer N_{ki}, and choose

$$\xi_k = (\xi_{k1}, \ldots, \xi_{kn}) \in V_{k-1} \cap V_k \qquad \text{for } k = 1, \ldots, m$$

Define $\xi_0 = x$, $\xi_{m+1} = x'$. Then, for $i = 1, \ldots, n$, $k = 0, \ldots, m$, there exist y_{ki} and y'_{ki} in N_{ki} such that (ξ_{ki}, y_{ki}) and $(\xi_{k+1,i}, y'_{ki})$ both belong to L_{ki}. Let S_i be the entropy of M_i, S_{ki} that of N_{ki}. By construction of S_i, we have

$$S_i(\xi_{k+1,i}) - S_i(\xi_{ki}) = S_{ki}(y_{ki}) - S_{ki}(y'_{ki})$$

Summing on k and i gives

$$S_M(x') - S_M(x) = S_N(y) - S_N(y') \tag{5.1}$$

where

$$N = \prod_{ki} N_{ki}$$

$$y = (y_{ki}), \qquad y' = (y'_{ki})$$

Also $(\xi_{ki}, y_{ki}) \equiv (\xi_{k+1,i}, y'_{ki})$ for the system $M_i \times N_{ki}$ for each i and k. Therefore, for the system $M_i \times \prod_k N_{ki}$, we have $(x_i, y_{0i}, y_{1i}, \ldots, y_{mi}) \equiv (\xi_{1i}, y'_{0i}, y_{1i}, \ldots, y_{mi}) \equiv \ldots \equiv (\xi_{mi}, y'_{0i}, \ldots, y'_{m-1,i}, y_{mi}) \equiv (x'_i, y'_{0i}, \ldots, y'_{mi})$, so that

$$(x, y) \equiv (x', y') \qquad \text{for } M \times N \tag{5.2}$$

Suppose now that $x \leqslant x'$ for M. Then (5.2) gives

$$(x', y') \leqslant (x, y) \leqslant (x', y) \qquad \text{for } M \times N$$

whence $y' \leqslant y$ for N, by assumption (i) of II. But N is a product of thermometers, and therefore its entropy, defined by (3.2), is an empirical entropy (cf. II and III). Hence $S_N(y') \leqslant S_N(y)$, and so $S_M(x) \leqslant S_M(x')$, by (5.1).

Conversely, suppose that $S_M(x) \leqslant S_M(x')$. Then $S_N(y') \leqslant S_N(y)$ and so $y' \leqslant y$. Therefore, by (5.2),

$$(x, y) \leqslant (x', y') \leqslant (x', y)$$

whence $x \leqslant x'$ by assumption (i) of II.

6. *Quasi-Static Transitions*

We wish to investigate the possibility of extending to generalised simple systems the result $\psi_M = T_M\, dS_M$ proved for simple systems in I. This relation is meaningless as it stands unless M is a differentiable manifold. To get a result which can be extended to generalised simple systems, we apply both sides of the equation to the unit tangent vector $\dot{\gamma}$ of a C^∞ curve γ representing a quasi-static transition of the simple system M. This gives

$$\psi_M(\dot{\gamma}) = T_M\, dS_M(\dot{\gamma})$$

or

$$\frac{dQ_\gamma(t)}{dt} = T_M \circ \gamma(t) \frac{d}{dt} \{S_M \circ \gamma(t)\} \tag{6.1}$$

where Q_γ (only defined to within an additive constant) has the property that $Q_\gamma(t_2) - Q_\gamma(t_1)$ is the amount of heat absorbed by the system in the 'time' interval $t_1 < t < t_2$.

In order for this to make sense for a quasi-static transition of a generalised simple system M, represented by a continuous map γ of an open interval I into M, it is clearly necessary to impose some condition on γ to ensure that the continuous function $S_M \circ \gamma$ is differentiable. We therefore admit as allowable quasi-static transitions of a generalised simple system only those γ which satisfy the conditions of the following definition:

Definition. A continuous map γ of an open interval I into M is a *quasi-static transition* of the generalised simple system M if and only if I can be covered by open subintervals J such that, for each J, there is a thermometer N compatible with M and a continuous map $\Gamma : J \to M \times N$ into a single mutual accessibility class of a composite of M and N, such that $\mathrm{pr}_1 \circ \Gamma$ is the restriction of γ to J and $\mathrm{pr}_2 \circ \Gamma = \gamma' : J \to N$ is of class C^1.

Clearly, if M is a thermometer, then any C^1 curve is a quasi-static transition in this sense.

We now *assume* that it is possible to associate with each quasi-static transition $\gamma : I \to M$ of a generalised simple system M a continuous real-valued function W_γ on I in such a way that:

(A) $\gamma(I)$ is contained within a single mutual accessibility class of M if and only if

$$W_\gamma(t_2) - W_\gamma(t_1) = \begin{cases} W[\gamma(t_1), \gamma(t_2)] & \text{if } \gamma(t_1) \leqslant \gamma(t_2) \\ -W[\gamma(t_2), \gamma(t_1)] & \text{otherwise} \end{cases}$$

for all t_1 and t_2 in I, where W is the adiabatic work function of M.

(B) If C is a composite of the generalised simple systems $M_1, M_2, \ldots, M_n$ and $\gamma : I \to C$ is defined by $\gamma(t) = (\gamma_1(t), \ldots, \gamma_n(t))$, where $\gamma_i : I \to M_i$ is a quasi-static transition of M_i (in which case γ must be a quasi-static transition of C), then

$$W_\gamma(t) = \sum_{i=1}^{n} W_{\gamma_i}(t) + \text{constant}$$

(C) If M is a thermometer and $\gamma : I \to M$ is a C^1 curve, then

$$W_\gamma(t_2) - W_\gamma(t_1) = \int_{t_1}^{t_2} \omega\{\dot{\gamma}(\tau)\}\, d\tau$$

for all t_1 and t_2 in I, where ω is the (C^∞) work form of M.

The physical interpretation of W_γ is that $W_\gamma(t_2) - W_\gamma(t_1)$ represents the work done by the system in the 'time' interval $t_1 < t < t_2$. It is clear that the above conditions only determine W_γ to within an arbitrary additive constant.

It will be noted that the two equivalent conditions of A are both satisfied if the quasi-static transition γ is adiabatic, assuming that the reverse of such a transition is also adiabatic. However, not all quasi-static transitions satisfying these conditions are physically realisable adiabatic transitions of the system M. For example, suppose M is the system mentioned in the introduction. Consider a quasi-static transition of M at constant total entropy through states in which the volume of each cylinder remains fixed and the substance in each cylinder remains at its triple point. Such a transition satisfies both of the conditions of A, but it is not adiabatic, since there is no purely mechanical way of making heat pass gradually from one cylinder to the other. For this reason we shall make no further mention of adiabatic quasi-static transitions, using instead the wider class of quasi-static transitions mapping into single mutual accessibility classes.

If $\gamma : I \to M$ is a quasi-static transition of a generalised simple system M, we define the real-valued function Q_γ on I to within an arbitrary additive constant by the condition that

$$Q_\gamma(t_1) - Q_\gamma(t_2) + W_\gamma(t_2) - W_\gamma(t_1) = \begin{cases} W[\gamma(t_1), \gamma(t_2)] & \text{if } \gamma(t_1) \leqslant \gamma(t_2) \\ -W[\gamma(t_2), \gamma(t_1)] & \text{otherwise} \end{cases}$$

for t_1 and t_2 in I. The physical significance of Q_γ is that $Q_\gamma(t_2) - Q_\gamma(t_1)$ represents the heat absorbed by the system in the 'time' interval $t_1 < t < t_2$. In terms of Q_γ, assumptions A, B and C above take the alternative forms:

(A′) $\gamma(I)$ is contained within a single mutual accessibility class of M if and only if Q_γ is constant.

(B′) If γ is a quasi-static transition of a composite of the generalised simple systems $M_1, \ldots, M_n$ given by $\gamma(t) = (\gamma_1(t), \ldots, \gamma_n(t))$, where γ_i is a quasi-static transition of M_i, then

$$Q_\gamma(t) = \sum_{i=1}^{n} Q_{\gamma_i}(t) + \text{constant}$$

(C′) If M is a thermometer and $\gamma : I \to M$ is a C^1 curve, then

$$Q_\gamma(t_2) - Q_\gamma(t_1) = \int_{t_1}^{t_2} \psi\{\dot{\gamma}(\tau)\}\, d\tau$$

for all t_1 and t_2 in I, where ψ is the (C^∞) heat form $\omega + dU$ of M.

We shall now prove that, if $\gamma : I \to M$ is any quasi-static transition of a generalised simple system M, then $S_M \circ \gamma$, $T_M \circ \gamma$ and Q_γ are C^1 functions on I satisfying (6.1).

In view of our definition of a quasi-static transition, we may assume without loss of generality that $\gamma = \mathrm{pr}_1 \circ \Gamma$, where Γ is a continuous map of I into a single mutual accessibility class of a composite C of M with a thermometer N, such that $\gamma' = \mathrm{pr}_2 \circ \Gamma$ is a C^1 curve in N.

First we note that $S_M \circ \gamma$ and $T_M \circ \gamma$ are both C^1 functions. For γ' is of class C^1, and

$$S_M \circ \gamma = -S_N \circ \gamma' + \text{constant} \tag{6.2}$$

$$T_M \circ \gamma = T_N \circ \gamma' \tag{6.3}$$

Next we observe that γ' is a quasi-static transition of N and Γ a quasi-static transition of C, so that

$$Q_\Gamma(t) = Q_\gamma(t) + Q_{\gamma'}(t) + \text{constant}$$

by B′. Since $\Gamma(I)$ is contained within a single mutual accessibility class of C, we conclude from A′ that Q_Γ is constant, whence

$$Q_\gamma(t) = -Q_{\gamma'}(t) + \text{constant} \tag{6.4}$$

Now, since N is a thermometer, it follows from C′ that

$$Q_{\gamma'}(t_2) - Q_{\gamma'}(t_1) = \int_{t_1}^{t_2} \psi_N\{\dot{\gamma}'(t)\}\,dt \tag{6.5}$$

where ψ_N is the heat form of N. Combining (6.4) and (6.5), we see that Q_γ and $Q_{\gamma'}$ are C^1 functions satisfying

$$\frac{dQ_\gamma(t)}{dt} = -\frac{dQ_{\gamma'}(t)}{dt} = -\psi_N\{\dot{\gamma}'(t)\} \tag{6.6}$$

But $\psi_N = T_N\,dS_N$, so that

$$\psi_N\{\dot{\gamma}'(t)\} = T_N \circ \gamma'(t)\frac{d\{S_N \circ \gamma'(t)\}}{dt} \tag{6.7}$$

(6.1) now follows from (6.6), (6.7), (6.2) and (6.3).

We remark at this point that a continuous map $\gamma : I \to M$ for a generalised simple system M is a quasi-static transition if and only if the functions $T_M \circ \gamma$ and $S_M \circ \gamma$ are both of class C^1. This simple characterisation of quasi-static transitions is not suitable as a definition, since it involves the concepts of entropy and absolute temperature, which are derived from the postulates rather than assumed *a priori*.

Armed with the above notion of quasi-static transition for generalised simple systems, one may now use (6.1) to prove an obvious extension to generalised compound systems of the version of Clausius' inequality for compound systems proved in II.

One may also show that generalised (simple or) compound systems satisfy a form of Kelvin's principle analogous to postulate III′ of I:

Kelvin's Principle

Suppose $M = \Pi_{i=1}^{n} M_i$, where the M_i are generalised simple systems, and let $\gamma : I \to M$ be such that, for each i, $\gamma_i = \mathrm{pr}_i \circ \gamma$ is a quasi-static transition of M_i for which Q_{γ_i} is a strictly increasing function. Then $\gamma(t_2) \nless \gamma(t_1)$ when $t_1 < t_2$.

Proof. For each i, (6.1) gives

$$T_{M_i} \circ \gamma_i(t) \frac{d}{dt}\{S_{M_i} \circ \gamma_i(t)\} = \frac{dQ_{\gamma_i}(t)}{dt} > 0$$

and therefore

$$\frac{d}{dt}\{S_M \circ \gamma(t)\} = \sum_{i=1}^{n} \frac{d}{dt}\{S_{M_i} \circ \gamma_i(t)\} > 0$$

by (4.1). The result now follows, since S_M is an empirical entropy for M.

In the case of (differentiable) simple and compound systems, it was found (cf. Landsberg, 1964, Dunning-Davies, 1965) that Kelvin's principle implied Carathéodory's principle (postulate III of I). This is no longer the case for generalised simple and compound systems. Indeed, a generalised simple system need not obey Carathéodory's principle at all, since it could happen that its entropy S_M is constant on an open subset V of M, in which case every state in V would be accessible from every other state in V. We know of no experimentally observed violations of Carathéodory's principle, but, if there were any such (necessarily involving non-differentiable systems), then they could be accommodated within the present scheme. It will be seen that, although Carathéodory's principle is more economical than Kelvin's principle for differentiable systems, Kelvin's principle is preferable as a general statement of the second law of thermodynamics, since it has a wider range of validity (when quasi-static transitions have been suitably defined).

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