An axiomatic thermodynamics of open systems

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Abstract The axiomatic thermodynamics of Giles is extended in such a way that direct applications to open systems are possible. The Helmholtz and other generalised Massieu function representations of thermodynamics are discussed without specialising to equilibrium. Quasi, 'ordinary', and absolute Helmholtz and generalised Massieu functions are introduced and shown to exist. 'Uniqueness' theorems for these quantities are established. A fundamental theorem is proved for each of the above representations of thermodynamics. This theorem provides quantitative conditions which are necessary and sufficient for one arbitrary state of a system A to be accessible from another arbitrary state of A in a natural process which involves not only A but also certain reservoirs. It is verified that, when the theory is specialised to equilibrium, the result is the well known partial Legendre transform 'picture' of the Helmholtz and Massieu function representations.

1. Introduction and summary

In this paper the axiomatic theory of thermodynamics developed by Giles (1964) is extended in such a way that direct applications to open systems are possible. Processes which can involve heat reservoirs and similar systems are investigated and this yields a set of alternative representations of thermodynamics. The theory is not restricted to equilibrium. The states which are allowed are quite general and are best thought of as corresponding to the mixed states, probability distributions, or density operators of statistical mechanics. The suitability of this notion of state for physical applications is thoroughly discussed by Giles. Several examples are studied (Giles 1964, pp 96–129). These include systems of variable volume and electric and magnetic systems. The possibility of constructing alternative formal representations of thermodynamics which are not restricted to equilibrium can be made plausible by reference to Landsberg (1961, pp 128–70). An interesting result here is table 24.2 (Landsberg 1961, p 162), which distinguishes the equilibrium theory as a special case.

The existence of various alternative representations of equilibrium thermodynamics is well known. One can learn from standard texts (e.g., Callen 1961, Landsberg 1961) that, given the entropy representation, alternative representations can be obtained by partial Legendre transformation. In these alternative representations Massieu functions play a central role. These functions are often related in a simple way to more familiar free energies. Physically, the entropy representation is appropriate for closed systems and the Massieu function representations are appropriate for open systems in contact with certain reservoirs. To give an example, suppose that one starts with the entropy representation of equilibrium thermodynamics and 'replaces' the energy by the inverse temperature $1/T$ via partial Legendre transformation. Then one effectively

obtains the Helmholtz representation—the Massieu function is $-F/T$ where F is the Helmholtz free energy. This representation is appropriate for a system in contact with a heat reservoir.

In the present work equilibrium is obtained as a special case and one of the principal results is the justification of the above picture on the basis of general considerations. Equilibrium thermodynamics, including Legendre transformation, is derived from the extended version of Giles' theory and this gives the equilibrium theory a firm theoretical basis.

The other main result is not restricted to equilibrium. Suppose that one writes $a \rightarrow b$ whenever the state b of a system of interest is accessible from the state a in a natural process which may involve certain reservoirs. It is established below that there exist a quasi Massieu function Ψ and a set $\mathcal{W}$ of components of content with the property that the condition $\Psi(a) \leqslant \Psi(b)$ and $X(a) = X(b)$ for all $X \in \mathcal{W}$ is necessary and sufficient for $a \rightarrow b$. The quantity Ψ—which is non-decreasing—and the quantities X which are conserved are real-valued functions on the state space. They are also additive in a sense described below. A close connection between quasi Massieu functions and their entropic analogues, quasi-entropies, is established. This underlies the connection via Legendre transform mentioned above which holds at equilibrium.

The plan of the rest of the paper is as follows. In § 2, Giles' theory of the entropy representation is reviewed. In § 3, processes which can involve heat reservoirs are investigated and the theory is extended to the Helmholtz representation. In § 4, more general reservoirs and associated quasi Massieu function representations of thermodynamics are discussed.

2. The entropy representation

The theory of the entropy representation presented by Giles (1964) provides not only firm foundations on which the proposed extension to other representations might be based but also a model which suggests how a large part of the new structure might be built. Consequently, this section is devoted to the task of establishing some of the central ideas of Giles' theory. To save space proofs of theorems will be omitted. These can be found in Giles' book.

Giles presents thermodynamics as an axiomatic mathematical theory of states and processes together with certain 'rules of interpretation' which award a physical meaning to each primitive term (and therefore, indirectly, to each derived term) of the theory. The primitive terms of the theory correspond to the notions 'state', 'composition of states' and 'natural process'. *States* are denoted a, b, c, etc and the space of all (equilibrium and non-equilibrium) states is written $\mathcal{S}$ and assumed to be non-empty. The *composite state* consisting of the arbitrary states a and b is written $a + b$. One writes $a \rightarrow b$, where a and b are arbitrary states, if and only if b is accessible from a in a *natural process*.

The main difficulty is with the notion 'state' and, in particular, with the fact that it is not restricted to equilibrium situations. Giles' rule of interpretation is, roughly speaking, 'a state is a method of preparation'. Since non-equilibrium states can unquestionably be prepared, it follows from this rule that the theory should certainly include them. In this context the model provided by statistical mechanics proves instructive for a method of preparation clearly yields a mixed state which, in general, is not at equilibrium.

The axioms should correspond—via the rules of interpretation for 'etate', '+', and '→'—to 'simple' assertions about physics. Thus Giles (p 30) starts with the following assertions which do have simple physical interpretations.

Axiom. For any states a, b and c:

$$a + b \in \mathcal{S} \tag{2.1a}$$

$$a + b = b + a \tag{2.1b}$$

$$(a + b) + c = a + (b + c) \tag{2.1c}$$

$$a \to a \tag{2.1d}$$

$$a \to b \text{ and } b \to c \Rightarrow a \to c \tag{2.1e}$$

$$a + c \to b + c \Leftrightarrow a \to b \tag{2.1f}$$

and

$$a \to b \text{ and } a \to c \Rightarrow b \to c \text{ or } c \to b. \tag{2.1g}$$

This axiom has a number of interesting consequences for the theory of (*formal*) *processes*. Such processes are identified as ordered pairs of states. They can be added and any process has an inverse (Giles 1964, p 32). A process is *possible* if it is natural in one direction or the other. Giles shows (p 35) that axiom (2.1) implies that the set of all possible processes forms a subgroup of the group of all processes. This allows him (p 42) to define an *irreversibility* function and to show that, if such a function exists, it is unique up to a positive multiplier. Irreversibility functions are intimately connected with the crucial idea of entropy. It is useful to use the term '*function of state*' to denote any real-valued function on $\mathcal{S}$ and to refer to such functions F as *additive* if and only if

$$F(a + b) = F(a) + F(b) \tag{2.2}$$

for all states a and b. This allows one (Giles 1964, p 57) to introduce a notion which is very nearly that of entropy as follows.

Definition. A function of state S will be called a *quasi-entropy* if and only if it is additive and such that, for all states a and b,

$$a \to b \text{ and } b \to a \Rightarrow S(a) = S(b) \tag{2.3a}$$

and

$$a \to b \text{ and } b \not\to a \Rightarrow S(a) < S(b). \tag{2.3b}$$

Giles also introduces (p 37) conserved quantities as follows.

Definition. A function of state X will be called a *component of content* if and only if it is additive and such that, for all states a and b,

$$a \to b \Rightarrow X(a) = X(b). \tag{2.4}$$

The connection between irreversibility functions and quasi-entropies then leads to the following 'uniqueness' theorem (Giles 1964, p 199).

Theorem. If S is a quasi-entropy and S' is a function of state, then S' is also a quasi-entropy if and only if there exists a component of content X and a positive real number λ such that

$$S' = \lambda S + X. \tag{2.5}$$

This shows that there really is quite a lot of latitude in the choice of quasi-entropies and leads one to enquire whether the same is true of *entropies*. Giles (p 56) distinguishes these from quasi-entropies by the additional requirement that they vanish on a certain subset $\mathcal{M}$ of $\mathcal{S}$. This subset consists of mechanical states and, by awarding it certain reasonable properties, Giles shows (p 57) that the entropy satisfies a version of (2.5) in which X must vanish on $\mathcal{M}$. The set $\mathcal{M}$ is to some extent arbitrary and *absolute entropies* are distinguished from entropies by the device of using the 'maximal' $\mathcal{M}$. Giles shows (p 69) that absolute entropies are unique up to a positive multiplier. (The proof of this depends on an extra axiom which is not really a central part of the theory.)

The following axiom (Giles 1964, p 31)—which in some sense asserts the continuity of thermodynamic properties—allows one to make important progress with the theory.

Axiom. Let '*na*' denote the sum of n states a. Given any states a and b, if there exist states x and y such that for arbitrarily large positive integers n

$$na + x \to nb + y \qquad \text{then } a \to b. \tag{2.6}$$

In the presence of this axiom, the following fundamental theorem of the entropy representation of thermodynamics can be proved (Giles 1964, p 59).

Theorem. There exist a quasi-entropy S and a set $\mathcal{W}$ of components of content with the property that, for arbitrary states a and b,

$$a \to b \Leftrightarrow S(a) \leqslant S(b) \qquad \text{and} \qquad X(a) = X(b) \qquad \text{for all } X \in \mathcal{W}. \tag{2.7}$$

Any set of components of content with the property ascribed to $\mathcal{W}$ in (2.7) will be called *sufficient*. The theorem asserts that the set of all components of content is sufficient. It is easy to prove that this set is a vector space and that any linearly independent subset of a sufficient set is also sufficient. In practical cases there is a finite linearly independent set. The claim that theorem (2.7) is fundamental needs to be justified. This is done thoroughly by Giles on page 59 of his book.

Giles (pp 60–3) introduces the notion of 'physical acceptability' for functions of state via the following sequence of ideas.

Definition. The state b will be said to be *greater in content* than the state a—so that $a \subset b$—if and only if a positive integer n and a state c exist such that

$$na + c \to nb \qquad \text{or} \qquad nb \to na + c. \tag{2.8}$$

Definition. The *magnitude* of the state x relative to the state e is $\|x\|$ where

$$\|x\| = \inf\{n/m : m, n \text{ are positive integers and } mx \subset ne\}. \tag{2.9}$$

Axiom. There exists an *internal state e*. This has the property that, given any state x, one can find a positive integer n such that

$$x \subset ne. \tag{2.10}$$

To ensure that all states have finite magnitudes one restricts one's choice of 'e' in (2.9) to internal states. The following property of boundedness is independent of this choice.

Definition. An additive function of state F will be said to be *bounded* if and only if there exists a real number k such that, for all states x,

$$|F(x)| \leqslant k\|x\|. \tag{2.11}$$

The view taken is that functions of state are physically acceptable if and only if they are bounded. One can prove quite directly that the requirement of boundedness leaves the

forms of the uniqueness theorems for the quasi-entropy, entropy and absolute entropy unchanged.

The real problem is to prove that theorem (2.7) remains true when only bounded functions of state are admitted. This requires a more sophisticated axiom of continuity than (2.6). The following axiom (Giles 1964, p 66)—which relegates (2.6) to the status of a theorem—proves suitable.

Axiom. Given states *a* and *b*, if there exists a state *c* such that, for any positive number ϵ, one can find positive integers *m* and *n* and states *x* and *y* with the property that $m/n < \epsilon$, $x \subset mc$, $y \subset mc$ and $x + na \to y + nb$, then

$$a \to b. \tag{2.12}$$

In the presence of this axiom the fundamental theorem is true even if only bounded components of content and quasi-entropies are allowed. This is Giles' central result. (Actually, the existence of a bounded *absolute* entropy is ensured in Giles' theory.)

Giles (pp 82–9) obtains some interesting results for specifically equilibrium thermodynamics. These rely on the following idea.

Definition. Any state *a* is an *equilibrium state* if and only if there is no state *b* such that

$$a \to b \qquad \text{and} \qquad b \not\to a. \tag{2.13}$$

This definition has the consequence that *a* is an equilibrium state if and only if it is a state of maximum quasi-entropy *S* for the given values of a sufficient set of components of content. (Clearly, this condition is independent of the choice of *S*.) The set of all bounded components of content forms a vector space. Suppose that $(X_1, \ldots, X_n)$ is a basis for this space so that—by previous results—it is a sufficient set. Let *S* be a fixed bounded quasi-entropy. Despite the abuse of notation, let $S(X_1, \ldots, X_n)$ denote the least upper bound of the values obtained by the function of state *S* for all states such that $X_1(a) = X_1, \ldots, X_n(a) = X_n$. Then it follows directly that *a* is an equilibrium state if and only if $S(a) = S(X_1(a), \ldots, X_n(a))$. Furthermore, the values $S(X_1, \ldots, X_n)r$ give rise to an equilibrium quasi-entropy function *S* with the property that $-S$ is *subadditive* (Giles 1964, p 84).

If one makes suitable assumptions about the equilibrium quasi-entropy *S*, *components of potential* ϕ_i— which are quantities conjugate to the X_i—can be introduced via

$$\phi_i = -\partial S/\partial X_i. \tag{2.14}$$

In particular, if the energy *U* appears amongst the X_i, then the temperature *T* can be identified via the conjugate potential and one has $1/T = \partial S/\partial U$. As Giles shows (pp 84–9), the components of potential introduced in this way have the expected properties.

3. The Helmholtz representation

According to Giles, systems are identified via the set of all their states and a particular system is said to be *involved* in a given process if and only if its initial and final states differ. The theory of the entropy representation given in § 2 is particularly useful for closed systems and processes which involve just the system of interest. Attention will now be turned to the Helmholtz representation of thermodynamics and to the study of open systems and processes which involve both the system of interest and a heat

reservoir. To save space, proofs of many of the results obtained below will be omitted, sometimes without comment.

The properties usually ascribed to heat reservoirs can be formalised as follows.

Definition. Let U be a component of content called the energy. A subset $\mathscr{R}$ of $\mathscr{S}$ will be said to be a *heat reservoir* if and only if the following apply. First, there exists a sufficient set $\mathscr{V}$ of components of content which contains U and has the property that

$$X(r) = X(r') \qquad \text{for all } r, r' \in \mathscr{R} \tag{3.1a}$$

and all $X \in \mathscr{V}$ except U. Second, for all $a, b \in \mathscr{S}$ and $r \in \mathscr{R}$, there exists $r' \in \mathscr{R}$ such that

$$U(a) + U(r) = U(b) + U(r'). \tag{3.1b}$$

Third, for all $r, r' \in \mathscr{R}$ and for each absolute entropy S,

$$S(r) - S(r') = (1/T^{\mathscr{R}})(U(r) - U(r')), \tag{3.1c}$$

where $T^{\mathscr{R}}$ is a positive quantity, called the reservoir temperature, which depends only on S and $\mathscr{R}$. Note that $(3.1c)$ is consistent with the uniqueness theorem for the absolute entropy.

The symbol '$\rightsquigarrow$' will be used to denote the relation 'can go to in a natural process involving the heat reservoir $\mathscr{R}$' in the following way.

Definition. For arbitrary states a and b,

$$a \rightsquigarrow b \Leftrightarrow a + r_1 \rightarrow b + r_2 \qquad \text{for some } r_1, r_2 \in \mathscr{R}. \tag{3.2}$$

One needs to construct a theory of '$\rightsquigarrow$' which is similar to the theory of '$\rightarrow$' described in § 2. The following powerful theorem allows one to do this.

Replacement theorem. Axioms $(2.1), (2.6), (2.10)$ and (2.12) remain true when '$\rightarrow$' is replaced by '$\rightsquigarrow$' in the statements of these axioms and in the definitions of any derived terms that they contain.

In order to establish the truth of the proposition obtained from one of the axioms by the replacement procedure one needs to use the axiom itself and axioms preceding it. Definitions (3.1) and (3.2) are also needed. The following is one consequence of (3.1) which is particularly useful.

Lemma. For any states a and b and any states $r_1, r_2, r_3, r_4 \in \mathscr{R}$,

$$a + r_1 + r_2 \rightarrow b + r_3 + r_4 \Rightarrow a + r \rightarrow b + r' \qquad \text{for some } r, r' \in \mathscr{R}$$

$$\Leftrightarrow a \rightsquigarrow b. \tag{3.3}$$

It follows from the replacement theorem that, since '$+$' plays the same role here as it does in § 2, all the consequences of $(2.1), (2.6), (2.10)$ and (2.12) also remain true when '$\rightarrow$' is replaced by '$\rightsquigarrow$'. This means that one has a 'ready-made' theory of '$\rightsquigarrow$'. To generate this new theory from the one given in § 2, all that is necessary is to insert the adjective 'open' or the phrase 'open analogue of' in definitions in which '$\rightarrow$' is replaced by '$\rightsquigarrow$'. (One speaks, for example, of 'open components of content'.) After this one has only to use the new names of the derived terms in the theorems. In this way one obtains, from (2.5), the following uniqueness theorem for the open analogue of the quasi-entropy. This additive function of state will be called a *quasi Massieu function* in order to allow contact with traditional usages to be easily made.

Theorem. If Ψ is a quasi Massieu function and Ψ' is a function of state, then Ψ' is also a quasi Massieu function if and only if there exist an open component of content and a

positive real number λ such that

$$\Psi' = \lambda \Psi + X. \tag{3.4}$$

The above procedure applied to (2.7) yields the following form of the fundamental theorem of the Helmholtz representation.

Theorem. There exist a quasi Massieu function Ψ and a set $\mathcal{W}$ of open components of content with the property that, for arbitrary states a and b,

$$a \to b \Leftrightarrow \Psi(a) \leqslant \Psi(b) \qquad \text{and} \qquad X(a) = X(b) \qquad \text{for all } X \in \mathcal{W}. \tag{3.5}$$

The remarks about sufficient sets $\mathcal{W}$ remain much as before. In practice one expects a finite linearly independent sufficient set. The sequence of results obtained from (2.8)–(2.12) by replacement allows one to conclude that the fundamental theorem (3.5) remains true when only physically acceptable functions of state are admitted. In addition, one can conclude that this requirement leaves the form of the uniqueness theorem (3.4) unchanged. As a matter of notational convenience in investigations of physical acceptability it is useful to use $\subset\!\!\!\!\cdot$ and $\|\quad\|_0$ respectively to denote the open analogues of $\subset$ and $\|\quad\|$.

The entropy and Helmholtz representations are connected in ways which are not contained in the replacement theorem. It is, for example, easy to prove the following results.

Theorem. The open components of content constitute a subspace of the space of all components of content.

Theorem. The function of state Ψ is a quasi Massieu function if and only if it is such that

$$\Psi = S - U / T^{\mathcal{R}} \tag{3.6}$$

where S is an allowable quasi-entropy and U is the energy. Allowable quasi-entropies are of the form $S_a + X$ where S_a is an absolute entropy—with corresponding reservoir temperature $T^{\mathcal{R}}$—and X is an open component of content. In practice, one expects that the space of all components of content will consist of the direct sum of the subspace generated by the energy and the space of all open components of content. One can prove directly from (3.1) and (3.2) that $\mathcal{V} - \{U\}$ is a sufficient set of open components of content. The existence, first, of a set $\mathcal{V}$ which satisfies (3.1) and which is a basis for the space of all components of content and, second, of an open natural process in which U changes is sufficient to ensure the direct sum property. As far as boundedness is concerned, the above results remain true when the obvious modifications are made. Furthermore, one can prove that 'boundedness' in the sense implied by the replacement procedure ensures 'boundedness' in the sense of § 2. One may continue to use the boundedness of § 2 as a criterion of physical acceptability.

Two consequences of (3.6) are worthy of mention. First, this equation suggests that a quasi Massieu function should be called a *Massieu function* or an *absolute Massieu function* whenever the corresponding quasi-entropy is an entropy or absolute entropy, respectively. Second, it allows one to rewrite the theory of the present section using not the quasi Massieu function Ψ, but the Helmholtz free energy

$$F = -T^{\mathcal{R}} \Psi \tag{3.7}$$

where $T^{\mathcal{R}}$ is the reservoir temperature of (3.6).

Attention can now be concentrated on equilibrium thermodynamics. Let r be a heat reservoir state. Using the sufficiency of $\mathcal{V} - \{U\}$ and other previous results, one can

show that $a + r$ is an equilibrium state if and only if the state a maximises any quasi Massieu function for the given values of any sufficient set of open components of content. (This condition is independent of the choices one makes.) The above holds for any reservoir state r so that one talks of states in *equilibrium with heat reservoirs*. It follows that the state a is in equilibrium with the given heat reservoir if and only if there is no state b such that $a \rightsquigarrow b$ while $b \not\rightsquigarrow a$. When one compares this result with (2.13), one sees that it extends the scope of the replacement procedure. In this way, given any basis of the space of all open components of content and any quasi Massieu function, one can—by analogy with § 2—construct an equilibrium quasi Massieu function whose negative is subadditive.

Equation (3.6) can lead to an important connection between equilibrium functions. Let $(X_2, \ldots, X_n)$ be a basis for the space of bounded open components of content. Despite the abuse of notation, let Ψ denote the equilibrium function corresponding to the quasi Massieu function $\Psi = S - U/T^{\mathcal{R}}$ of (3.6). Then

$$\Psi(T^{\mathcal{R}}, X_2, \ldots, X_n) = \sup_{a \in \mathcal{A}} (S(a) - U(a)/T^{\mathcal{R}}) \tag{3.8}$$

where $\mathcal{A} = \{a : X_2(a) = X_2, \ldots, X_n(a) = X_n \text{ and } a \in \mathcal{S}\}$ and the dependence on the temperature has been emphasised. It follows directly that

$$\Psi(T^{\mathcal{R}}, X_2, \ldots, X_n) = \sup_{U \in \mathcal{E}} (S(U, X_2, \ldots, X_n) - U/T^{\mathcal{R}}) \tag{3.9}$$

where the supremum is over all values of U and S is the equilibrium quasi-entropy of § 2. (In practical cases, U extends $(X_2, \ldots, X_n)$ to a basis for the space of all bounded components of content.)

Given differentiability, (3.9) is equivalent to partial Legendre transform. If one uses the definition $\partial S/\partial U = 1/T$ of the inverse temperature, one finds that a value of U which maximises $S(U, X_2, \ldots, X_n) - U/T^{\mathcal{R}}$ satisfies $1/T = 1/T^{\mathcal{R}}$. Thus a state in equilibrium with a heat reservoir is at the temperature of the reservoir and T can be used in place of $T^{\mathcal{R}}$. Suppose that one has a function whose values $U(T, X_2, \ldots, X_n)$ maximise $S(U, X_2, \ldots, X_n) - U/T$ for varying U with T and $X_2, \ldots, X_n$ fixed. Then

$$\Psi(T, X_2, \ldots, X_n) = S(U(T, X_2, \ldots, X_n), X_2, \ldots, X_n) - U(T, X_2, \ldots, X_n)/T, \tag{3.10}$$

and it follows from the chain rule that

$$\partial \Psi/\partial X_i = -\phi_i, \qquad i \in \{2, \ldots, n\} \tag{3.11}$$

while

$$\partial \Psi/\partial(1/T) = -U. \tag{3.12}$$

These are standard results and the discussion of Legendre transform is complete.

4. Generalised Massieu function representations

The above theory can easily be generalised in such a way as to make it apply to processes which involve both the system of interest and a system which acts as a reservoir for several linearly independent components of content (or for a single component of content other than the energy). This yields a set of alternative representations of thermodynamics.

First, one needs to generalise the concept of a heat reservoir.

Definition. Let $\mathcal{X}$ be a subspace of the space of all components of content. A subset $\mathcal{R}$ of $\mathcal{S}$ will be said to be an $\mathcal{X}$ *reservoir* if and only if the following apply. First, there exists a sufficient set $\mathcal{V}$ of components of content which contains $\mathcal{X}$ in its span and which has the property that

$$X(r) = X(r') \qquad \text{for all } r, r' \in \mathcal{R} \tag{4.1a}$$

and all X in $\mathcal{V}$ which are not in $\mathcal{X}$. Second, for all $a, b \in \mathcal{S}$ and $r \in \mathcal{R}$, given any $X \in \mathcal{X}$, one can find $r' \in \mathcal{R}$ such that

$$X(a) + X(r) = X(b) + X(r'). \tag{4.1b}$$

Third, for all $r, r' \in \mathcal{R}$ and for each absolute entropy S,

$$S(r) - S(r') = \sum_{i=1}^{m} F_i^{\mathcal{R}} (X_i(r) - X_i(r')) \tag{4.1c}$$

where the $F_i^{\mathcal{R}}$ are constants for fixed $\mathcal{R}$ and S and a fixed basis $(X_1, \ldots, X_m)$ of $\mathcal{X}$. The form of (4.1c) is consistent with the uniqueness theorem for the absolute entropy and with transformations induced by a change of basis in $\mathcal{X}$.

Clearly, one needs to generalise '$\leadsto$'. All that is necessary is to adopt (3.2) but allow $\mathcal{R}$ to be an $\mathcal{X}$ reservoir. The replacement theorem then remains true and all its consequences can be taken over to the present case. The existence of generalised quasi Massieu functions satisfying the uniqueness theorem (3.4) is ensured. The existence of a sufficient set of generalised open components of content is also guaranteed. The fundamental theorem (3.5) thus remains true.

The nature of quasi Massieu functions and open components of content can differ from case to case. Any result of § 3 which mentions the energy U explicitly needs modification. Theorem (3.6) becomes the following.

Theorem. The function of state Ψ is a quasi Massieu function if and only if

$$\Psi = S - \sum_{i=1}^{m} F_i^{\mathcal{R}} X_i \tag{4.2}$$

where S is an allowable quasi-entropy and $(X_1, \ldots, X_m)$ is a basis for $\mathcal{X}$. Allowable quasi-entropies are of the form $S_a + X$ where S_a is an absolute entropy—corresponding via the X_i to the constants $F_i^{\mathcal{R}}$ of (4.1c)—and X is an open component of content. Again one expects that the space of all components of content will be the direct sum of $\mathcal{X}$ and the space of all open components of content. One can prove directly that $\mathcal{V} - \mathcal{V} \cap \mathcal{X}$ is a sufficient set of open components of content. Conditions which ensure the direct sum property are easy to obtain. They are obviously parallels of those given in § 3. Theorem (4.2) allows some representations of thermodynamics to be expressed in terms of the 'quasi free energy' $F = -T^{\mathcal{R}}\Psi$, where $T^{\mathcal{R}}$ is a reservoir temperature, as well as the quasi Massieu function Ψ.

The discussion of boundedness and some aspects of the discussion of equilibrium differ little from the specific case of § 3. However, the last two paragraphs of § 3 do need modification. Let $(X_{m+1}, \ldots, X_n)$ be a basis for the space of bounded open components of content. The appropriate generalisation of (3.8) is

$$\Psi(F_1^{\mathcal{R}}, \ldots, F_m^{\mathcal{R}}, X_{m+1}, \ldots, X_n) = \sup_{a \in \mathcal{A}} \left(S(a) - \sum_{i=1}^{m} F_i^{\mathcal{R}} X_i(a) \right) \tag{4.3}$$

where $\mathscr{A} = \{a : X_{m+1}(a) = X_{m+1}, \ldots, X_n(a) = X_n \text{ and } a \in \mathscr{S}\}$ and the dependence on the constants $F_i^{\mathscr{R}}$ of (4.1) has been emphasised. It follows directly that

$$\Psi(F_1^{\mathscr{R}}, \ldots, F_m^{\mathscr{R}}, X_{m+1}, \ldots, X_n) = \sup_{(X_1, \ldots, X_m) \in \mathscr{E}} \left(S(X, \ldots, X_n) - \sum_{i=1}^{m} F^{\mathscr{R}} X_i \right) \tag{4.4}$$

where the supremum is over all values of $X_1, \ldots, X_m$ and S is the equilibrium quasi-entropy of § 2. (In practical cases $(X_1, \ldots, X_m)$ extends $(X_{m+1}, \ldots, X_n)$ to a basis for the space of all bounded components of content.) Given differentiability, (4.4) again implies Legendre transform. The appropriate generalisations of (3.11) and (3.12) can easily be seen to be

$$\begin{aligned}
\partial\Psi/\partial X_i &= -\phi_i & i &\in \{m+1, \ldots, n\} \\
\partial\Psi/\partial\phi_i &= X_i & i &\in \{1, \ldots, m\}
\end{aligned} \tag{4.5}$$

where $\phi_i = -\partial S/\partial X_i$ is the component of potential of § 2. (To prove these results one needs the variables $F_1, \ldots F_m, X_{m+1}, \ldots, X_n$ to be independent. If $m = n$, one may quote the Gibbs–Duhem relation which expresses the dependence of the variables $F_1, \ldots, F_m$.)

References

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