1969

On the mathematical foundation of classical thermodynamics

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ON THE MATHEMATICAL FOUNDATION OF CLASSICAL THERMODYNAMICS

by

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Report 69-26

May, 1969
1. **Introduction**

Since Caratheodory's pioneer work on the foundation of thermodynamics, many authors (e.g. [3,4,7]) have written on this subject from a similar viewpoint. However, in most of these expositions, there lacks a clear separation between the mathematical theory and the physical consideration. As a consequence, many mathematically technical points are either overlooked or ignored. It is the purpose of this paper to construct a mathematical model which rectifies these shortcomings and at the same time brings out clearly all the mathematical hypotheses that are required in order to draw the desired conclusions. In this regard, the present investigation is influenced by the work of Aren [1] and Carter [6]. Also, instead of following a traditional approach in proving the existence of entropy and absolute temperature, we give a somewhat different and refined proof, in §4, for simple thermodynamic systems. Roughly speaking, simple thermodynamic systems are those systems whose states are specified by two thermodynamic variables, e.g. pressure and volume. The development in this section can be easily generalized to include more complicated systems.

In ^2, we first introduce the notion of a quasi-thermodynamic system. By imposing additional conditions on it, we arrive at the concept of a thermodynamic system. A basic property for the thermodynamic system, namely, its "heat form" has local integrating factors, is summarized in Theorem 2.5. Since we restrict our attention later to simple systems, we describe a proof only for
such simple cases.

Although multi-temperature systems have been discussed recently by several authors, we elect to follow the traditional line in considering only single temperature systems. The characterization of such systems is given in §3.

In the last section, we discuss the principle of increase of entropy during an irreversible adiabatic process for those simple systems whose constant entropy submanifolds are connected. We first identify the irreversible adiabatic processes with a certain subset of the set of ordered pairs of states. By generalizing the Carathéodory's principle, we are able to show that, for an irreversible adiabatic process, the entropy of the final state is strictly greater than that of the initial state.

Throughout this paper, the notations and terminologies borrowed from differential geometry follow closely with those used in [2,10]. By a differentiable manifold, we mean a separable, Hausdorff topological space together with a family of compatible coordinate systems defined on it. For a precise definition and many other basic facts in differential geometry which are used in our discussion, we again refer readers to [2,10].
2. Thermodynamic Systems

A quasi-thermodynamic system \((S, \mathcal{E}, w)\) consists of a \(C^2\)-differentiable manifold \(S\) of dimension \(n^2\) together with a differential 1-form \(w\) of class 1 on \(S\) and a real-valued \(C^2\)-function \(\mathcal{E}\) defined on the product manifold \(S \times S\) such that

\[
\forall s_1, s_2, s_3 \in S, \quad \mathcal{E}(s_1, s_2) + \mathcal{E}(s_3, s_2) = \mathcal{E}(s_1, s_3).
\]

(2.1)

The members of \(S\) are called the states, and the real-valued functions defined on \(S\) are called state functions. We will interpret \(\mathcal{E}(s_1, s_2)\) as the energy which must be added or taken away from the system in going from state \(s_1\) to \(s_2\). It follows from equation 2.1 that we have, for all \(s_1, s_2 \in S\), \(\mathcal{E}(s_1, s_2) = 0\) and \(\mathcal{E}(s_1, s_2) = -\mathcal{E}(s_2, s_1)\). The 1-form \(w\) is called the work form of the system.

2.2 Theorem. For each quasi-thermodynamic system \((S, \mathcal{E}, w)\), there exists a state function \(e\), unique up to an additive constant, such that

\[
\mathcal{E}(s_1, s_2) = e(s_2) - e(s_1)
\]

for all \(s_1, s_2 \in S\). Moreover, \(e\) is a \(C^2\)-function.

Proof: Choose any \(s_0 \in S\) and define \(e: S \rightarrow \mathbb{R}\) by

\[
e(s) = \mathcal{E}(s_0, s).
\]

Clearly, \(e\) is a \(C^2\)-function. Since \(\mathcal{E}(s_1, s_2) = -\mathcal{E}(s_2, s_1)\), we have
\[ \Delta e(s_1, s_2) = \Delta e(s_1, s_0) + \Delta e(s_0, s_2) \]
\[ = e(s_2) - e(s_0) \]
for all \( s, s_0 \in S \).

Now suppose \( e' \) is another such function. Then \( fe(s_0, s) = e'(s) - e'(s_0) = e(s) \). Hence, \( e'(s) - e(s) = e'(s_0) \) for all \( s \in S \).

We shall call \( e \) an internal energy function of the system.

The 1-form \( q \) defined on \( S \) by the equation
\[ q = de + w \]
is called the heat form of the system. Equation 2.3 is the statement of the first law of thermodynamics.

Let \( I \) be a closed and bounded interval of the reals. A function \( \mathcal{E}: I \to S \) is called a \( C^1 \)-curve if it is the restriction of a \( C^1 \)-function defined on some open interval containing \( I \), and if \( d\mathcal{E}(t) \neq 0 \) for all \( t \in I \). A piecewise differentiable curve is a continuous function \( \mathcal{E}: I \to S \) together with a subdivision of \( I \) on whose closed subintervals \( \mathcal{E} \) is a \( C^1 \)-curve. By a process (or quasi-static process) we mean a piecewise differentiable curve in \( S \). The restriction of a process \( \mathcal{E}: I \to S \) to any closed subinterval of \( I \) is called a subprocess of "\( \mathcal{E} \). The amount of work done by the system in traversing a process \( \mathcal{E}: [a, b] \to S \) is given by
\[ \int w = \int_a^b \mathcal{E}^*w. \]

The amount of heat added to the system in going along \( \mathcal{E} \) is equal to
\[ \int q = e(s_2) - e(s_1) + \int w \]
where $s_1 = \xi(a)$ is the initial state and $s_2 = \xi(b)$ the final state. A process $\xi$ is said to be an adiabatic process if $jq = 0$ for every subprocess $\xi$ of $\xi$. A state $s_1$ is adiabatically connected to $s_2$ if there exists an adiabatic process $\xi: [a, b] \to S$ such that $\xi(a) = s_1$ and $\xi(b) = s_2$.

2.4 Definition. A thermodynamic system is a quasi-thermodynamic system which satisfies the following additional conditions:

(2.4.a) The heat form $q$ of the system is nowhere zero.

(2.4.b) In every neighborhood of a given state $s$, there exist states which are not adiabatically connected to $s$.

The second condition is a mathematical statement of the second law of thermodynamics, commonly known as the Carathéodory's principle. As a consequence of (2.4.a) and (2.4.b), we have the following result:

2.5 Theorem. Let $(S, \langle A, w \rangle)$ be a thermodynamic system. For each state $s \in S$, there exist an open neighborhood $U$ of $s$ and two real-valued functions $A, a$ defined on $U$ such that $A$ is a positive $C^1$-function, $a$ is a $C^2$-function, and $Aa$ is equal to the restriction of $q$ to $U$.

In the usual axiomatic treatment of thermodynamics [3,4,5,11] the above theorem provides a basic tool in establishing the existence of entropy and absolute temperature. However, for our later discussion, a restricted version of this theorem to the cases where $S$ has dimension two is sufficient. In this case, the
proof does not depend on condition (2.4.b), and we argue as follows: Given any state \( s \in S \), let \((V, \phi)\) be a coordinate system about \( s \). Then the heat form \( q \) can be written locally as

\[
q = \left( \frac{\partial}{\partial x_1} (e) + w_1 \right) dx_1 + \left( \frac{\partial}{\partial x_2} (e) + w_2 \right) dx_2.
\]

Let us denote \( \frac{\partial}{\partial x_1} (e) + w_1 \) by \( a_1 \) and \( \frac{\partial}{\partial x_2} (e) + w_2 \) by \( a_2 \), respectively, and let \( y \) be an \( \mathcal{O} \)-form on \( V \). The 1-form \( -y \) is exact iff \( y \) satisfies the following partial differential equation:

\[
a_2 \frac{\partial}{\partial x_2} (y) - a_1 \frac{\partial}{\partial x_1} (y) = \left( \frac{\partial}{\partial x_2} (a_1) - \frac{\partial}{\partial x_1} (a_2) \right) y.
\]

Since \( a_1, a_2 \) are \( C^1 \)-functions and not simultaneously equal to zero, the local existence of solutions for equation 2.6 is guaranteed by the theorem on p. 59 [9]. Moreover, we may assume that \( y > 0 \).

Thus, there exists a \( C^1 \)-function or such that \( da = yq \) or \( q = Ada \) at some neighborhood \( U \subset V \) of \( s \).

We will call \( A \) an integrating factor, \( \alpha \) an integrator, and \((A, \alpha)\) an integrating pair of the heat form \( q \) about \( s \).

3. Single Temperature Systems
Let $U$ denote the class of all thermodynamic systems. A family of single temperature thermodynamic systems is a subclass $U$ of $3^*$ which satisfies the four conditions listed below.

(3.1.a) For each member $(S,e,w)$ of $U$, $S$ is simply connected and $dw(s) > 0$ for all $s \in S$.

(3.1.b) Given any two members $S_1, S_2$ of $U$, there exists a certain distinguished subset $S_1^*, S_2^*$ of $S_1 \times S_2$ such that

(i) for each $s_1 \in S_1$, there exists an $s_2 \in S_2$ such that $(s_1, s_2) \in S_1^* \times S_2^*$,

(ii) if $(s_1, s_2) \in S_1^* \times S_2^*$ then $(s_1 s_2) \in S_2^* \times S_1^*$ and

(iii) if $(s_1 s_2, s_3) \in S_1^* \times S_2^* \times S_2^*$ and $(s_2, s_3) \in S_2^* \times S_3^*$, then

If $(s_1, s_2) \in S_1^* \times S_2^*$, we say that $s_1$ and $s_2$ have the same temperature. Now suppose $s \in S$. By (i), there exists an $s_1 \in S$ such that $(s, s_1) \in S^*S$. Hence, by (ii), $(s_1, s) \in S^*S$. It then follows from (iii) that $(s, s) \in S^*S$. Thus, the above condition defines an equivalence relation on each $S$ of $\{|i,\}$, and the equivalence classes of $S$ are called isothermals. A temperature function $J^*$ of $S$ is a state function which is constant on each isothermal, and is a different constant on different isothermals. A temperature scale is a collection $\{\}$ of temperature functions, one for each $S \in U$, such that if $\{\}$, $\{\}$, and $\{\}$ are the temperature functions for the systems $S_1$ and $S_2$, respectively, then $\{\}(s_1) = \{\}(s_2)$ iff $(s_1, s_2) \in S_1^*S_2$. We point out here that it follows from 3.1.b and the fact that each $S \in 3^*$
is separable that one can always construct a temperature scale for U. However, such a temperature scale does not, in general, possess the desired smoothness. For this reason, we impose the next condition on U.

(3.1.c) There exists a temperature scale $\Omega_0$ for $\mathcal{U}$ with the property that each temperature function $\theta \in \Omega_0$ is a $C^2$-function. Furthermore, if $(A, \alpha)$ is an integrating pair as described in Theorem 2.5, and if $\theta \in \Omega_0$ is the corresponding temperature function for the system, then $d\theta(\eta)A\alpha(\eta) > 0$ for all $\eta \in \text{dom}(\alpha)$.

If the dimension of $\mathcal{S}_1 \times \mathcal{S}_2$ are $m$ and $n$ respectively, then it follows from condition (3.1.c) that $\mathcal{S}_1 \times \mathcal{S}_2$ is a $m+n-1$ dimensional $C$-submanifold of $\mathcal{S}_1 \times \mathcal{S}_2$. We will show next that $\mathcal{S}_1 \times \mathcal{S}_2$ can be made naturally into a quasi-thermodynamic system. To this end, let $A_{i1}, A_{i2}$ be the functions induced on $(\mathcal{S}_1 \times \mathcal{S}_2) \times (\mathcal{S}_1 \times \mathcal{S}_2)$ by $\ell_1$ and $\ell_2$, respectively, and let $\omega_1, \omega_2$ be the 1-forms induced on $\mathcal{S}_1 \times \mathcal{S}_2$ by $\omega_1$ and $\omega_2$, respectively. We denote the restriction of $A_{i1} + A_{i2}$ to $(\mathcal{S}_1 \times \mathcal{S}_2)$ by $(\mathcal{S}_1 \times \mathcal{S}_2)$ by $\omega_{i1}, \omega_{i2}$, and the restriction of $\omega_{i1} + \omega_{i2}$ to $\mathcal{S}_1 \times \mathcal{S}_2$ by $\omega_i$.

Then $(\mathcal{S}_1 \times \mathcal{S}_2, A_{i1}, \omega_i)$ is clearly a quasi-thermodynamic system, and is called the composite system of $\mathcal{S}_1$ and $\mathcal{S}_2$.

(3.1.d) For each pair $\mathcal{S}_1 \times \mathcal{S}_2 \in \mathcal{U}$, the composite system $\mathcal{S}_1 \times \mathcal{S}_2$ is a thermodynamic system.

To save writing, we will denote a single temperature system by $(\mathcal{S}, \ell_1, \eta, \omega, \theta)$ where $\theta$ is the corresponding temperature function for $\mathcal{S}$ in $\Omega_0$.
3.2 Theorem  Let $\Theta_0$ be a temperature scale for $\mathfrak{li}$ as described in (3.1.c). Then all the members of $\Theta_0$ have the same range and the range is an open interval in $\mathbb{R}^1$.

Proof: Let $\theta_1$, $\theta_0$ be members of $\Theta$, which correspond to the systems $S_1$ and $S_2$, respectively. For each $s_1 \in S_1$, by (3.1.b) and (3.1.c), there exists an $s_2 \in S_2$ such that $e^{s_1} = 6_2(s_2)$. Hence, range($\theta_1$) $\subseteq$ range($\theta_0$). Similarly, one can show the other inclusion. Thus, all the members in $\Theta_0$ have the same range.

Since $\theta_1$ is continuous and $S_1$ is connected, the range of $\theta_1$ is clearly connected. To show that it is open, we observe that at each state $s \in S_1$, $d\theta_1(s) > 0$ according to (3.1.c). This implies that $\theta_1$ cannot achieve maximum or minimum. Hence, range($\theta_1$) is an open interval in $\mathbb{R}^1$. 
4. **The Existence of Entropy and Absolute Temperature for Simple Systems**

A simple system is defined to be a single temperature system $(S, \mathcal{E}, \omega, Q)$ where $S$ has dimension two. Henceforth, we will restrict our discussion to simple systems, and will establish, in this section, the existence of global entropy function and absolute temperature for such systems.

Let $(S_1, \mathcal{E}_1, \omega_1, Q_1)$, $(S_2, \mathcal{E}_2, \omega_2, Q_2)$ be two simple systems, and let $(S, S_1, \mathcal{E}, \omega)$ be the corresponding composite system. For any two given states $s_1 \in S_1$ and $s_2 \in S_2$, let $(\alpha_1, \gamma_1)$ be an integrating pair of the heat form $q_1$ about $s_1$ and let $(\alpha_2, \gamma_2)$ be a similar pair for $q_2$ about $s_2$. It follows from (3.1.c) that there exist neighborhoods $V_{1\prime}$ of $s_1$ and $V_{2\prime}$ of $s_2$ such that the function $\omega_{\alpha_1, \gamma_1} : V_{1\prime} \to \mathbb{R}$ defined by $\omega_{\alpha_1, \gamma_1}(s) = (\alpha_1(s), \gamma_1(s))$ forms a coordinate system about $s_1$ and the function $\omega_{\alpha_2, \gamma_2} : V_{2\prime} \to \mathbb{R}^2$ defined by $\omega_{\alpha_2, \gamma_2}(s) = (\alpha_2(s), \gamma_2(s))$ forms a coordinate system about $s_2$. We call such coordinate systems $\omega_{\alpha_1, \gamma_1}$, $\omega_{\alpha_2, \gamma_2}$, the "preferred" coordinate systems. We denote $\alpha_1[V_1]$, $\gamma_1[V_1]$, $\alpha_2[V_2]$ and $\gamma_2[V_2]$ by $M_1$, $N_1$, $M_2$ and $N_2$, respectively. Also, we adopt the following notational convention: if $p$ is a differential form on $S_1$ or $S_2$, then by $\%$ we mean the form induced on $S_1 \times S_2$ by $p$. In this notation, the function $(D : V_1 \times V_2 \to \mathbb{R}^4$ given by $\langle (s_1, s_2) = (\alpha_1(s_1, s_2), \gamma_1(s_1, s_2), \alpha_2(s_1, s_2), \gamma_2(s_1, s_2)) \rangle$ forms a coordinate system about $(s_1, s_2)$ and the range of $w$ is $M_1 \times N_1 \times M_2 \times N_2$. The set $V = (V_1 \times V_2)(S \times S)$
is a nonempty open set in $S - j^\wedge$ iff $N^{K^\wedge} j^6$. In this case the restriction of $<p$ to $V$ induces a coordinate system

$$i\|: V \to \mathbb{R}^3 \text{ of } S_j^* S_j^* \text{ given by } \chi(s, s') = (c_f \wedge s, c_f \wedge s', \gamma(s, s')) \text{ where } \gamma = e_j \wedge = \chi \wedge. \text{ The range of } \chi \text{ is } M_1 \times M_2 \times (N_1, HNU).$$

From our construction of the composite system, the heat form $q$ of $S_j S_{0}$ is simply equal to the restriction of $q = \chi c$ to $S_j S_{2}$. Thus, for all $(s, s') \in V$, we have

$$q_c(s, s') = \chi_1(s, s') d\sigma_1(s, s') + \chi_2(s, s') d\sigma_2(s, s').$$

The induced form $(ib^{-1})^* q_c$ on $lyL \times N \times (N_1, PN_2)$ is given by

$$(ib^{-1})^* q_c = \chi_1^2 d\sigma_1 + \chi_2^2 d\sigma_2.$$}

Note that it follows from the definition of $A_1^\wedge$ and $W$ that we have

$$(4.1) \wedge i^\wedge 0^\wedge (a p \wedge f_2 \wedge x) = A_1^\wedge (c_f \wedge x) \wedge (a, \wedge e),$$

and

$$(4.2) \wedge (a p \wedge e_2) = A_2^\wedge (a x e_2) \wedge (a),$$

for all $(a, a, \wedge e) \in M_1 \times M_2 \times (N_1 \times N_2)$.

4.3 Lemma Let $(S, \wedge_j \wedge, e_1)$, $(S, \wedge_j \wedge, e_2)$ be two simple systems, and let $(A, \wedge j, \wedge e)$ be an integrating pair of $q$ about $s^\wedge \in S^\wedge$ and let $(A_2, a_2)$ be an integrating pair of $q_2$ about $s_2 \in S_2$. Suppose $(V^\wedge c^\wedge x e^\wedge$ is a "preferred" coordinate system about $s_1$ and $(V, c_r x e_2)$ is a "preferred" coordinate system about $s_2$ such that $\wedge [V \wedge n 6_t V] \wedge j b$. Then the
ratio \( \frac{H^{-1}J^{6}}{\left( g^{I}V \right)^{-1}} \) defined on \( A_{2}o(a_{2}xe_{2})^{-1}(T_{2},e) \) \( (G_{t}V_{t})n_{e_{2}}[V_{2}] \), is independent of \( 9 \).

Proof Let us denote \( A_{0}((T_{2}x_{6}) \) by \( A_{1} \) and \( \left( T_{2}x_{6} \right) \) by \( A_{2} \). Suppose the ratio \( \frac{1}{-1} \) is not independent of \( 9 \).

Then there exists a point \( (C{T}_{1}^{1},C{T}_{2},9^{0}) \in a^{1}V^{1}Xa_{2}[V_{2}]X(Q_{t}[V_{1}]n_{9_{2}}[V_{2}] \)

such that

\[
\frac{\partial}{\partial \theta} \lambda_{1}(\theta^{0},\theta^{0}) = 0.
\]

Let \( M_{1}XM_{2}XNC{T}_{1}[V_{1}]Xc_{2}[V_{2}]X(9_{1}tV_{1})n_{9_{2}}[V_{2}] \) be a compact neighborhood of \( (a_{2},a_{2},9^{0}) \). For each \( 9 \in N \), consider the following differential systems:

\[
(i) \quad \frac{d\sigma_{1}}{dt} = \frac{1}{W fil \quad \text{at } tfc = 0}
\]

\[
(ii) \quad \frac{da_{2}}{dt} = \frac{x}{A_{2}(Cf_{n}9)}
\]

From the existence theorem in the theory of ordinary differential equations, we know that there exists a \( T > 0 \), independent of \( 9 \), such that (i) and (ii) have unique solutions in \( M_{1}x[0,T] \) and \( IV^{xt0}jt] \), respectively. The solutions of (i) and (ii) can be written as
(iii) \[ \text{Ej}(t,e) = \alpha^0_1 + \int_0^t \frac{1}{\lambda_1^*(\Sigma_1(t',\theta),\theta)} \, dt' \]

and

(iv) \[ \text{So}(t,e) = a^? + \int_0^t \frac{1}{\lambda_2^*(\Sigma_2(t',\theta),\theta)} \, dt' \]

For each \( T, 0 < T < T \), we calculate the determinant of the Jacobian of the transformation \( \alpha_r, = \gamma^\prime(t, e), \) \( a_2 = \gg(t, e) \) at \((T, 9^°)\). Clearly, \( \gamma^\prime(9^°) = (-1)^{i+1} I^{o} + o(1) \) for \( i = 1,2 \). Also, from (iii) and (iv), one can show that

\[ \frac{\partial}{\partial \theta} \gamma^\prime(9^°) = \frac{t}{[A_1(c_1^0, e^0)]^2} \gamma^\prime(a^?, e^0) + O(T) \]

for \( i = 1,2 \). Thus,

\[ \det \left( \begin{array}{cc} \frac{\partial \Sigma_1}{\partial \theta} & \frac{\partial \Sigma_2}{\partial \theta} \\ \frac{\partial \Sigma_1}{\partial t} & \frac{\partial \Sigma_2}{\partial t} \end{array} \right) = \frac{t}{A_1(c_1^0, e^0)} \lambda_1^o(c_1^0, e^0) + O(T) \]

which is different from zero for sufficiently small \( T \). For such a \( r, \) let \( \frac{1}{r_1} = \gamma^\prime(T, 9^°) \) and \( \frac{1}{r_2} = T y(t, e^0) \). It follows from the inverse function theorem that there exist a neighborhood \( \text{AXB} \) of \((T, 0^°)\) and a neighborhood \( \text{CxD} \) of \((c^0_1, c^0_2)\) such that the transformation \( \alpha_r, = \gamma^\prime(t, e) ; \) \( j_0 = v_0(t, e) \) maps \( \text{AXB} \) 1-1 onto \( \text{CxD}. \) Thus, every point \((a_0^-, a_2^e) \in \text{CxDxN}\) can be connected to \( (c_1^0, c_2^0) \) by the following piecewise differentiable curve in \( \text{CxDxN}: \)

Let \((T^*, e^*)\) be the inverse image of \((c_1^0, c_2^0)\). Then
\[
\begin{align*}
\alpha(t) &= \begin{cases} 
\left(\sigma_1^2, \sigma_2^2, (1+t)^2, \theta^* - t \theta^0 \right), & -1 \leq t \leq 0 \\
\left(\Sigma_1(\tau^* - t, \theta^0), \Sigma_2(\tau^* - t, \theta^*), 0 \right), & 0 \leq t \leq T^* \\
\left(\sigma_1^0, \sigma_2^0, (1+\tau^* - t)^2, \theta^* + (t-T^*)e^0 \right), & T^* \leq t \leq T^* + 1 \\
\left(\Sigma_1(t-\tau^*-1, \theta^0), \Sigma_2(t-\tau^*-1, \theta^*), 0 \right), & T^*+1 \leq t \leq T^*+T+1
\end{cases}
\end{align*}
\]

which, in view of equations 4.1 and 4.2, satisfies that \( (S_{-1}^1)_{\pi^x}(c_\theta(s(t))) = 0 \) for all \( t \in [-1, T^*+T+1] \). This, of course, implies that every state in the neighborhood \( \psi^{-1}[1 \times 1 \times N] \) of \( \psi^{-1}[C_x \times N] \) is adiabatically connected to \( i^T \) \( a_{-1} \), \( Q_{-1} \), \( a_{-1} \), \( Q_{-1} \) which contradicts 3.1.d.

**4.4 Lemma** Let \((S, A, \pi, \pi)\) be a simple system and let \((A, \pi)\) be an integrating pair about \( s \in S \). Suppose \((V, \pi)\) is a "preferred" coordinate system about \( s \). Then there exist \( \mathcal{C}^1 \)-functions \( f > 0 \) on \( \pi[V] \) and a \( \mathcal{C}^1 \)-function \( g > 0 \) on \( \pi[V] \) such that

\[
\lambda^*(\sigma \pi \theta)^{-1}(\sigma, \theta) = f(\pi)g(\theta).
\]

If \((f', g')\) is any other such pair, then \( g' = cg \) and

\[
f' = \frac{1}{c}f \text{ for some positive constant } c.
\]

**Proof:** Setting \( S_1 = S_2 = S \) and \( A_1 = A_2 = A \) in Lemma 4.3, we obtain

\[
\frac{\lambda^*(\sigma_1, \theta)}{\lambda^*(\sigma_2, \theta)} = F(\sigma_1, \sigma_2) > 0
\]

for all \((\sigma_1, \sigma_2) \in [\pi[V] \times \pi[V]]\). Now fixing \( a_2 = \pi^2 \pi \in \pi[V] \), we have

\[
A^*(o_{-1}, e) = F(\sigma, \sigma_2^0)\lambda(\sigma_2^0, \theta) = f(x)g(e).
\]

Clearly, \( f \) and \( g \) are positive \( \mathcal{C}^1 \)-functions.
Suppose \((f, g')\) is another pair of such functions. Then we have 
\[ f(x)g(e) = f'(cx)g'(e) \quad \text{or} \quad f^f = f^1 \]
for all \((a, Q) \in a[V]x6[V]\). Thus, there exists a constant \(C > 0\) such that \(g' = eg\) and \(f' = \frac{1}{f}\).

4.5 Lemma Let \(A^cC^cQ^c\), \(A^o(o_2x6_2)\) be a pair of functions as described in Lemma 4.3. Suppose \(A^c(o(cr^G^c)) \quad (a^c 6^c) = (\theta_2)\)
\[ f_1(a_1)g_1(e_1) \quad \text{on} \quad cr_1[V_1]xe_1[V^c] \quad \text{and} \quad A^o(a_2xe_2) \quad (ct_2, 6_2) = f_2(cr_2)g_2 \]
on \(cr_0[V_0]x6_0[V_0]\). Then there exists a constant \(C > 0\) such that \(g_1(e) = cg_2(e)\) on \(e^cV^c ne_2[V_2]\).

Proof: By Lemma 4.3,
\[ \frac{f_1(cr_1)g_1(e)}{f_2(cr_2)g_2(e)} \]
for all \((a_1a_2, Q) \in a_1[V_1]xa_2tv_2]x(e_1[V_1] ne_2[V_2])\). Hence, the result follows.

4.6 Theorem Let \(0\) be a temperature scale for \(li\) as described in (3.1.c) and let \(J\) be the common range for all members of \(\Theta_0\). Then there exists a \(C\)-function \(T\) defined on \(J\) such that for each \(A \in(ax9)\) as described in Lemma 4.4, we have
\[ Ao(crxe)x^{-1} = T(6)F(or) \]
for some \(F\). The function \(T\) is unique up to a multiplicative constant and if \(T\) is fixed then \(F\) is uniquely determined. Moreover, \(T08\) is a temperature function.

Proof: Let us index the set of all integrating factors for the simple systems by \(A\). For each \(i \in A\), let \(h_i = log g_i\) where \(g_i\) is a factor of \(A_i\) as in Lemma 4.4. By Lemma 4.5,
\[ h_i h_j = \text{constant on their common domain.} \] Thus the 1-form \( \omega \) defined on \( J \) by \( p(e) = dh^e \) where \( e \in \text{dom}(h_i) \) is exact, i.e. \( p = dh \) where \( h \) is a real-valued \( C^1 \)-function defined on \( J \). The function \( T = \exp h \) clearly has all the properties as stated in the theorem except possibly the fact that \( T_0 \) is a temperature function.

To shew that \( T_0 \) is a temperature function, it suffices to show that 
\[
\frac{d}{de} T(e) \neq 0 \quad \text{for all } e \in J.
\]
Since \((\text{exp}_9)^{-1}(a, e) = \lambda^*(\sigma, \theta) \) \( \) \( \delta \) 
\[
T(e)P(\alpha) \delta_T = \left[ \cdot S e \circ \langle \text{exp}_9 \rangle^{-1}(\alpha, 6) + w_\alpha (\text{CT} \circ 9)^{-1}(\alpha, 6) \right] \delta \alpha + 
\]
\[
\left( \int_0^a \exp(aX9)^{-1}(a, \theta) + w_\alpha (\text{CT} \circ 9)^{-1}(\alpha, 6) \right) d\alpha,
\]
we have

\[(4.7) \quad T(e)P(\alpha) = \exp(ab9)^{-1}(a, \theta) + w_\alpha (\text{CT} \circ 9)^{-1}(\alpha, 6) \]

and

\[(4.8) \quad 0 = \exp(ab9)^{-1}(a, \theta) + w_\alpha (\text{CT} \circ 9)^{-1}(\alpha, 6) \cdot \]

Differentiating equation (4.7) with respect to \( e \) and equation (4.8) with respect to \( a \) and subtracting the two, we obtain

\[
F(\sigma)^{-1} T(\alpha) = \exp(ab9)^{-1}(\alpha, \theta) - \exp(ab9)^{-1}(\sigma, \theta)
\]

which, by 3.1.a, is different from zero. Thus, \( dT(e) \neq 0 \) for all \( e \in J \).

The function \( T_0 \) is called an **absolute temperature function** of the system.

**4.9 Theorem** For each simple system \((S, \alpha, w, 9)\), there exists a global entropy function \( r \) such that

\[ q = T_0 d\eta. \]
Proof. As shown in Theorem 4.6, locally, $q(s) = T(e(s))F(a(s))d_a(s) = T(e(s))da_0a(s)$, where $a_{(ct)} = \int F(cr)dcr$.

If $q(s) = T(e(s))da'o a'(s)$ is another such local representation of $q$ then $d(ctocr - a'o a'^1) = 0$ on the overlap. Thus, we can define a 1-form $p$ on $S$ by

$$p(s) = d(aoff)(s) \quad \text{if} \quad s \in \text{dom}(aocr)$$

Clearly, $p$ is closed. Since $S$ is simply connected, $p$ is exact. Hence, there exists a $C^2$ function $r$ defined on $S$ such that $q = T_{oQ} drj$.

4.10 Corollary. For each closed quasi-static process $\xi$,

$$\int_{\xi} \frac{q}{T_{oQ}} = 0$$

(A closed quasi-static process is a process $\xi: [a,b] \to S$ such that $A(a) = f(b)$).

Finally, it is worth noting that all the propositions in this section can be generalized to single temperature systems of higher dimension. One starts, in this case, from Theorem 2.5, and then uses this fact to prove Lemma 4.3 in a usual manner.
5. **Irreversible Processes and the Principle of Increase of Entropy.**

The theory we have developed so far deals strictly with physical systems which are in "thermal equilibrium". However, one would like to draw some conclusions from it in regard to irreversible processes such as free expansion of gases, etc. Although such processes do not fall into our definition of quasi-static processes, nevertheless, the initial and final state of such processes lies in the equilibrium states. Therefore, for an irreversible process where "no exchange of heat" takes place, one would like to conclude that the entropy of the final state is strictly greater than that of the initial state. To show this, we first restrict our attention to those simple systems which have the following property: Let \( r \) be an entropy function of the simple system \((S, \epsilon, e, w, \delta)\). Then the constant entropy submanifolds \( \{s \in S: r(s) = \text{constant} \} \) are connected. We denote a class of such simple systems by \( \mathcal{S} \), and prove that

5.1 Lemma Let \((S, \epsilon, e, w, \delta) \in \mathcal{S} \), and let \( \gamma \) be an entropy function of \( S \). Two states \( s, s' \in S \) are adiabatically connected iff \( r(?)(s) = r(?)(s') \).

**Proof:** Suppose \( s, s' \) are connected by an adiabatic process \( f: [a, b] \to S \). Then \( T_U(t) \) is constant for all \( a \leq t \leq b \). For if not, let \( t, t' \in [a, b] \) such that \( r_(f(t_1)) (t) \neq U(t_2) \) and \( t_1 < t_2 \). Let \( C_0 = \min(T(6; f(t)): t - t \leq t) \). We have
\[ t_2 = t_2 = t_2 \]

\[ \int_{t_1}^{t_2} q = \int_{t_1}^{t_2} T(e(Mt))d\eta(t) = \int_{t_1}^{t_2} \eta(f(t_2)) - \eta(f(t_1)) \neq 0 \]

which contradicts the fact that \( t \) is an adiabatic process.

Now suppose \( r(s_1) = r(s_2) \). Then \( s_1, s_2 \) is arcwise connected [2, Proposition 1.5.2]. Moreover, by a similar argument as to Proposition 1.5.1 [2], one can construct a piecewise differentiable curve connecting \( s_1, s_2 \) in the submanifold \( \{ s \in S : T(s) = r(s) \} \). Clearly, such a process is an adiabatic process.

Next we identify the irreversible adiabatic processes for a simple system \( (S, \mathbb{A}, w, 9) \in \mathcal{S} \) with a subset \( j \) of \( S \times S \) which has the following properties:

5.2. a If \( (s_1, s_2) \in j \), then \( s_1 \) is not adiabatically connected to \( s_2 \).

5.2. b If \( (s_1, s_2) \in j \) and if \( s_1 \) is not adiabatically connected to \( s_2 \), then \( (s_2, s_1) \in j \).

5.2. c If \( (s_1, s_2) \in j \) and \( s_2 \notin j \), then \( (s_1, s_2) \in j \).

5.2. d For each state \( s \in S \), the set \( K = \{ s : (s, s_1, s_2) \in j \} \) or \( s_1 \) is adiabatically connected to \( s \} \) and its complement are connected.

The above four conditions together with Lemma 5.1 imply that

5.3 Lemma Let \( s_1, s_0, s_2 \in S \). If \( s_0 \in K \) and \( s_1, s_2 \in K \), then \( s_0, s_1, s_2 \in K \).
A state $s_1$ is said to be **adiabatically and irreversibly** connected to $s_0$ if $(s_1, s_0) \in \Theta$. By generalizing the Caratheodory's principle 2.4.b to include the irreversible adiabatic processes as well, we have

**5.4 Lemma** Let $(S, \mathcal{E}, \omega, e) \in \mathcal{S}$ and let $77$ be an entropy function of $S$. Then for each $s \in S$, we have either $r/(s) \leq \tau(s_1)$ for all $s_1 \in \mathcal{K}$ or $77(s) \leq TjCs$ for all $s \in \mathcal{K}$.

**Proof** For each $s \in S$, by 5.2.d, $\tau^* s_1$ is an interval in $R^1$. Suppose $\tau^*(s)$ belongs to the interior of this interval. Then there exists an open interval $J$ such that $\tau(s) \in J \subset 77[K]$. Let $(V, \tau^* X \delta)$ be a coordinate system about $s$. Then every state in the neighborhood $U = (\tau^* X \delta) \cap (\tau V) \subset X \delta[V]$ can be connected to $s$ as follows: Suppose $s_1 \in U$. Then there exists a state $s_2 \in \mathcal{K}$ such that $\tau(s_2) = 77(s_0)$. By Lemma 5.1, $s_2 \in \mathcal{K}$. Hence, by Lemma 5.3, $s_2 \in \mathcal{K}$ which contradicts the generalized Caratheodory's principle. Since $s \in \mathcal{K}$, $\tau(s)$ must be an end point of the interval $\tau[K]$.

**5.5 Lemma** Let $(S, \mathcal{E}, \omega, 0) \in \mathcal{S}$ and let $77$ be an entropy function of $S$. Suppose $s \in S$ is such that $\tau(s) \leq \tau(s_0)$ for all $s \in \mathcal{K}$. Then every state $s_2 \in S$ with $\tau(s) < i \tau(s_2)$ belongs to $\mathcal{K}$. A similar result holds if the inequalities are reversed.

**Proof** Suppose there exists a state $s_0 \in S$ such that $\tau(s_0) \leq \tau(s')$ and $s_0 \in \mathcal{K}$. In view of Lemmas 5.1 and 5.3, we must have $\nu(s') < \tau(s_0)$ for all $s' \in \mathcal{K}$. But this would imply
that $71_{\text{s}}$ is not connected which contradicts 5.2.d.

**5.6 Lemma** Let $(S, \mathcal{E}, w, 6) \in I$ and let $\tau$ be an entropy function of $S$. Then either $\tau(s^1) < \tau(s^0)$ for all $(s^1s^j) \in \mathcal{J}$ or $\tau(s^1) > \tau(s^0)$ for all $(s^0s^j) \in \mathcal{J}$.

**Proof:** First we show that either $T(S) > I\tau(s^0)$ for all $s \in S$ and $s' \in K$, or $T(S) > I\tau(s^0)$ for all $s \in S$ and $s' \in K$.

Suppose not. Let $s^1, s^0 \in S$ such that $\tau(s^1) < \tau(s^0)$ for all $s \in K$ and $\tau(s^0) > \tau(s^1)$ for all $s \in K$. We consider the following three cases:

**Case 1** $\tau(s^1) < \tau(s^0)$. By Lemma 5.5, we have $s^1, s^0 \in K$. Thus $(s^1s^j) \in \mathcal{J}$ and $(s^1s^j) \in \mathcal{J}$ which, by 5.2.c, implies that $(s^1, s^0) \in \mathcal{J}$. But this contradicts 5.2.a.

**Case 2** $\tau(s^2) < \tau(s^1)$. Let $s^2 \in S$ be such that $\tau(s^2) < \tau(s^1) < \tau(s^0)$. Then $(s^2, s^1)$ and $(s^0, s^1) / \mathcal{J}$. By 5.2.b, we have $(s^0, s^1) \in \mathcal{J}$ and $(s^0, s^1) \in \mathcal{J}$. This implies that $\tau(s^0)$ belongs to the interior of $\tau(K)$ which was shown impossible.

**Case 3** $\tau(s^1) - \tau(s^0)$. This case again contradicts Lemma 5.4.

Finally, the strict inequality follows from 5.2.a which completes the proof.

By a proper choice of the sign of the absolute temperature, we obtain our principle result of this section.

**5.7 Theorem** Let $(S, \mathcal{E}, w, 6) \in I \mathcal{S}$. There exists an entropy function $\tau$ of the system such that if $(s^1, s^0) \in \mathcal{J}$, then $T(s^1) < \tau(s^0)$. 
Acknowledgement

This research is conducted while the author is a post-doctoral fellow at Carnegie-Mellon University. It is a pleasure here to thank Dr. Kolodner and the Department of Mathematics for providing this opportunity. Also, the author wishes to thank Dr. Duffin and Dr. Jensen for their valuable advice.
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