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Carathéodory's Principle and the Existence of Global Integrating Factors

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Abstract. A proof is given of a theorem on the integrability of Pfaffian forms which is used in Carathéodory's approach to thermodynamics. It is pointed out that Carathéodory's original proof of the existence of entropy and of absolute temperature is incomplete, since it fails to take into account the local nature of this theorem. By combining the theorem with the results of BUCHDAHL and GREVE on the existence of continuous empirical entropy functions, it is shown that the First and Second Laws of Thermodynamics imply the existence of a globally defined differentiable empirical entropy function for every simple thermodynamic system. This result supplies the missing step in Carathéodory's argument and makes a separate proof of the principle of increase of entropy unnecessary.

1. Introduction

It has been pointed out by BERNSTEIN [1] that Carathéodory's proof [2] of the existence of entropy and of absolute temperature is incomplete, since the local nature of a certain theorem on the integrability of Pfaffians is not fully taken into account. The theorem in question [3, 4] runs as follows:

Theorem. *Let M be a C^∞ differentiable manifold* [5] *(finite-dimensional and without boundary), ψ an everywhere non-vanishing C^∞ differential 1-form on M. Then the following three conditions are equivalent:*

(i) *Given x in M, there exists an open neighbourhood V of x in M such that each neighbourhood W of x in V contains a point y which cannot be connected to x by a piece-wise C^∞ path γ in V which satisfies $\psi\{\dot{\gamma}(t)\} = 0$ whenever $\dot{\gamma}(t)$ is defined.*

(ii) $\psi \wedge d\psi = 0$.

(iii) *Given x in M, there exists an open neighbourhood V of x in M such that the restriction $\psi | V$ of ψ to V is of the form $\psi | V = f dg$, where f and g are C^∞ functions on V.*

For the sake of completeness, a proof of this theorem is given in the appendix.

Carathéodory's form of the Second Law of Thermodynamics (Carathéodory's Principle) implies that a certain everywhere non-vanishing differential 1-form ψ on the thermodynamic configuration space M of a