Classical Axiomatics with Extension to Nonequilibrium Thermodynamics

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An attempt is made to reorganize the axiomatics of classical thermodynamics as written by Carathéodory in 1909 and to extend it to nonequilibrium systems. The three thermodynamic laws are derived from axioms and the entropy appears as the constant of integration of the Pfaffian equation with a suitably chosen integrating factor. Transition to nonequilibrium systems is shown to require an extension of the phase space to include the gradients of temperature and velocity as additional coordinates. Accessible states then have to comply with a system of momentum equations and any departure from these restrictions leads to inaccessible states.

KEY WORDS: classical axiomatics; entropy; nonequilibrium systems; thermodynamics.

1. INTRODUCTION

An analysis of Carathéodory's study of the axiomatics of thermodynamics in the year 1909 [1] shows that there are many facets of thermodynamics which were not covered in that study. The present paper is an attempt to reorganize the axiomatics of classical thermodynamics and to extend it to nonequilibrium systems. From the three "axioms" which describe the physics of the thermodynamic process, we derive the three thermodynamic "laws." A classification of the latter leads to Carathéodory's concept of "inaccessible states," which is discussed in Section 5 and derived without introducing Carathéodory's Axiom 1. The corresponding Pfaffian differential equation and its solutions are the subject of Sections 6 and 7; their

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constraints on the possible constitutive equations are shown in Section 8, together with the only condition under which negative absolute temperatures may occur. This condition is due to a unique correlation between macroscopic axiomatics and Planck's characteristic function of statistical thermodynamics. The entropy is shown to appear as the constant of integration of the Pfaffian equation in Section 10, with a suitably chosen integrating factor.

Transition to nonequilibrium systems requires a reexamination of the inaccessible states and is discussed in Section 11. These states have now become functions of the temperature and velocity gradients. Up to this point, we have constructed an "axiomatic formalism," i.e., a structure of rules which is independent of the particular substance about which we desire information. Such specific information can be obtained by considering the "constitutive equations" of the bodies involved. However, constitutive equations are not part of this study.

2. THE AXIOMS

The axioms which govern the energy transfer in systems with nonuniform temperature are as follows.

2.1. Axiom 1

"Transient energy $d\varepsilon/dt$ appears in the form of heat input $dq/dt$ as well as work input $dw/dt$":

$$\frac{d\varepsilon}{dt} = \frac{dq}{dt} + \frac{dw}{dt}$$

(1)

2.2 Axiom 2

"The energy input required to bring a body from state $C_1$ to state $C_2$ is independent of the nature of the energy chosen, and independent of the traversed intermediate states":

$$[\varepsilon]_1^2 = U(C_2, C_1)$$

(2)

such that

$$U(C_2, C_1) = u(C_2) - u(C_1)$$

(3)

or, abbreviated,

$$U(C_2, C_1) = u_2 - u_1$$

(4)