COMPARABILITY OF STATES AND THE DEFINITION OF ENTROPY

Jakob Yngvason

Faculty of Physics, University of Vienna, Boltzmanngasse 5, 1090 Vienna, Austria

EXTENDED ABSTRACT

In an axiomatic approach to equilibrium thermodynamics, developed more than a decade ago in collaboration with E.H. Lieb [1-4], the Second Law of Thermodynamics, understood as the increase of the entropy of equilibrium states in irreversible adiabatic processes, is derived from certain basic properties of the relation of adiabatic accessibility of states. This line of thought has its roots in the work of C. Carathéodory [5] that was taken up in subsequent work in the 1950's and 60's by P.T. Landsberg, H.A. Buchdahl, G. Falk, H. Jung and R. Giles [6-9], among others. In these earlier approaches it is usually taken for granted that two equilibrium states of the same chemical composition are always *comparable* with respect to the relation of adiabatic accessibility, i.e., that it is possible to transform at least one of the states into the other by means of a process whose only net effect on the surroundings is equivalent to the raising and lowering of a weight. By contrast, it is argued in [1-4] that this comparability is a highly nontrivial property and needs justification. In fact, the analytic backbone of the approach of [1-4] is its establishment starting from more plausible assumptions that include convex combinations of states, continuity properties of generalized pressure, and assumptions about thermal contact.

In the panel discussion it will be argued that adiabatic comparability is also of central importance for any attempt to extend the definition of entropy beyond thermodynamic equilibrium states. More specifically, we consider a situation where an (essentially unique) entropy function S is defined on a space Γ of equilibrium states that is contained in some larger space Γ^* of nonequilibrium states of the same system. We assume that any nonequlibrium state can be generated by an adiabatic process starting from some equilibrium state, and conversely, that any nonequilibrium state can be brought to equilibrium through such a process. Under these assumptions we show that any function S^* on the space Γ^* that extends the entropy S and is monotone under adiabatic state changes necessarily lies between two extremes, denoted S_- and S_+. These two functions coincide, leading to a unique entropy function on Γ^*, if and only if all states in Γ^* are adiabatically comparable. We also argue that *assuming* that this property holds in general is highly implausible. A comparison with the definition of entropy (for equilibrium *and* nonequilibrium states) via the concept of generalized availability as in the monograph of Gyftopoulos and Beretta [10] will also be commented on. Some further details are given in ref. [11].

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