On the Definition of Entropy
for Non-Equilibrium States

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In this paper it is demonstrated how the mathematical theory of stability of motion can be applied to kinetic equations, describing irreversible processes in an isolated, homogeneous system. It turns out that functions having all the properties of entropy exist throughout the domain of definition of the kinetic equations. Since the kinetic equations depend only on variables defined outside equilibrium thermodynamics, it is possible to define entropy far beyond the range of validity of the thermodynamics of irreversible processes. It is shown that the commonly assumed properties of entropy are not sufficient, however, to single out just one entropy function.

1. Introduction

The theory of thermodynamic equilibrium, for which sometimes also the name thermostatics has been proposed, is a well-established macroscopic theory. Although it has been understood better on the basis of a microscopic statistical theory, thermostatics does not have to be justified by statistical mechanics. This situation is very similar to that in other classical macroscopic theories, as e.g. mechanics of continuous media, where also the knowledge of the underlying microscopic processes deepens our understanding considerably, but is not necessary for the logical and self-consistent development of the macroscopic theory.

This situation is essentially different for the thermodynamics of irreversible processes where some of the intensive variables can be defined for non-equilibrium states, if at least "local equilibrium" is assumed. Local equilibrium, however, is explained in microscopic terms: For each sufficiently small, although still macroscopic volume element in the phase space, spanned by the extensive variables, the deviation of the probability distribution over its microscopic states from a Gibbs distribution is negligibly small. In cases, where this is not guaranteed, only the statistical approach is considered as justified. It seems, therefore, not to be possible to establish in this way a pure macroscopic theory of irreversible phenomena with its own inner logic and consistency. One of the reasons for this is certainly the fact that one seeks to generalize the theory starting from a theory of equilibrium. This procedure is opposed to that in all other macroscopic theories, where first a dynamic
theory is set up and a theory of equilibrium results from it in a quite natural way.

In this paper we discuss the possibility of relating in a direct way the fundamental quantities of the thermodynamics of irreversible processes, entropy and entropy production, to the kinetic equations governing the evolution of a system. To the author's knowledge this relation was recognized for the first time by Wei and was investigated further by Coleman and Mizel. The basic idea is to apply the mathematical theory of motions to these kinetic equations and to work out certain consequences which can be related to physical concepts. In order to avoid difficulties in dealing with partial differential equations, which would arise in consequence of the occurrence of spatial gradients we confine our study to the equations of evolution for an isolated homogeneous system. In principle, it is possible, however, to discuss more general systems with the same method.

In the macroscopic theory of irreversible processes it is assumed that non-equilibrium states can be characterized by the same quantities (functions of states) as the equilibrium state. This is a consequence of the assumption of local equilibrium. In this case the Gibbs relation

$$dS = T^{-1}(dE + pdV - \sum_{i} \mu_i d n_i)$$  \hspace{1cm} (1.1)

holds defining entropy as a function of $E$, $V$, $n_1$, ..., $n_k$, apart from an additive constant $S_0$, i.e. its value at equilibrium. Introducing as new coordinates the relative deviations $\alpha_i$, $i=1$, ..., $k+2$ of the coordinates from their equilibrium values (Onsager coordinates), the entropy difference $s=S-S_0$ becomes, at least near the equilibrium, a negative definite function of the variables $\alpha_i$

$$s(\alpha_1, ..., \alpha_{k+2}) = S - S_0 \leq 0,$$  \hspace{1cm} (1.2)

where the equality holds only for all $\alpha_i=0$. Assuming an isolated system, the Second Law requires that for our system during its motion towards equilibrium the entropy production must always be positive and zero at equilibrium, i.e. positive definite:

$$\dot{s} = \sum_{i} \frac{\partial s}{\partial \alpha_i} \dot{\alpha}_i \geq 0.$$  \hspace{1cm} (1.3)