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ON THE DEDUCTION OF CARATHÉODORY'S AXIOM FROM KELVIN'S PRINCIPLE

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Synopsis

Landsberg recently proved that Carathéodory's axiom is a logical consequence of Kelvin's principle. His proof is here modified, so that the consequences of an implicit assumption become apparent. The result may be summarised as follows: *Purely mechanical systems are the only systems that obey Kelvin's principle but not Carathéodory's axiom.*

1. *Introduction.* One of the controversial points in the history of thermodynamics concerns the derivation of the second law, i.e. the proof of the existence of entropy and absolute temperature. For such derivations two different starting points have been used. The first one is Kelvin's principle[1]), which states the impossibility of devising an engine which, working in a cycle, produces no other effect than the extraction of an amount of heat from a reservoir and its complete conversion into mechanical work. It is clearly a generalisation of an experimental fact, the impossibility of the perpetuum mobile of the second kind.

The second approach is due to Carathéodory[2]). He starts from the axiom: in the immediate neighbourhood of any point in thermodynamical space there are points which cannot be reached from the given point by means of an adiabatic process. As was noted for instance by Planck[3]) this statement cannot be considered as a generalization of experimental facts. It is sometimes argued that Carathéodory's axiom is a consequence of Kelvin's principle. Born[4]) shows this for a special system and Mrs. Ehrenfest-Afanassjewa[5]) sketches a more general proof without going into details. In a recent textbook[6]) the question was even left as an exercise to the reader. A general proof, however, was not available until recently.

In a recent note[7]) Landsberg proved that Carathéodory's axiom follows from Kelvin's principle. In doing so he makes an assumption concerning the system. We shall here show that this assumption is not necessary for the proof.

As a result of this result, the classical treatment of thermodynamics and Carathéodory's method can no longer be considered as essentially different.

Rather, Carathéodory's treatment can be regarded as an alternative derivation of the classical results from Kelvin's principle.

2. *Description of the system.* We consider a system with n mechanical degrees of freedom, described by means of the variables $x_1, \ldots, x_n$. The thermal equilibrium states of this system are assumed to be completely characterized by the values of $x_1, \ldots, x_n$ plus one additional variable, the empirical temperature ϑ. The empirical temperature is chosen such that two systems are in thermal equilibrium with one another if and only if their temperatures are equal. These thermal equilibrium states can be represented as points in the $(n + 1)$-dimensional thermodynamical space, with coordinates $x_1, \ldots, x_n, \vartheta$. Conversely it is assumed that to each point in a certain domain of thermodynamic space corresponds one thermal equilibrium state of the system.

A quasistatic process is a process carried out in such a way that the system remains in thermal equilibrium. We must now choose the empirical temperature in such a way that it varies continuously during a quasistatic process, as do the variables $x_1, \ldots, x_n$. In this case each quasistatic process can be represented by means of a continuous curve or path in phase space; by assumption the converse is also true.

During a quasistatic process the system can do mechanical work on and absorb heat from external bodies. The amount of mechanical work $đA$ done by the system when each of the x_i varies by $\mathrm{d}x_i$ is

$$đA = \sum_{i=1}^{n} A_i(x_i, \ldots, x_n, \vartheta)\, \mathrm{d}x_i. \tag{1}$$

The generalized forces A_i must be completely determined by the state of the system, owing to the definition of thermal equilibrium states. The amount of heat absorbed during the same process is

$$đQ = \sum_{i=1}^{n} Q_i(x_1, \ldots, x_n, \vartheta)\, \mathrm{d}x_i + Q_0(x_1, \ldots, x_n, \vartheta)\, \mathrm{d}\vartheta. \tag{2}$$

We shall say that this differential form vanishes identically at a point, $đQ \equiv 0$, if all coefficients $Q_1, \ldots, Q_n, Q_0$ vanish at this point. We shall write $đQ = 0$ if (2) vanishes at a point for a given set of differentials $(\mathrm{d}x_1, \ldots, \mathrm{d}x_n, \mathrm{d}\vartheta)$. A process is called adiabatic when $đQ = 0$ along the whole path.

According to the first law there exists a quantity $U(x_1, \ldots, x_n, \vartheta)$ such that $đQ = \mathrm{d}U - đA$, or

$$Q_i = \frac{\partial U}{\partial x_i} - A_i, \quad Q_0 = \frac{\partial U}{\partial \vartheta}. \tag{3}$$

Landsberg uses $x_1, \ldots, x_n, U$ as coordinates in thermodynamic space.

This implies the assumption that $\partial U/\partial\vartheta$ never vanishes. Our purpose is to modify his proof in such a way that this assumption is avoided.

3. *Proof of Landsberg's theorem.* Suppose Carathéodory's axiom is not fulfilled; in other words, there is a point $P^0 = (x_1^0, \ldots, x_n^0, \vartheta)$ with a neighbourhood D, such that each point in D can be connected with P^0 by an adiabatic path. Note that then also any two points of D are mutually connected by an adiabatic path. Now either $đQ \equiv 0$ in all points of D, or there is at least one point where $đQ \not\equiv 0$. We show that the latter case is incompatible with Kelvin's principle.

Suppose that $đQ \not\equiv 0$ in P^0. Then it is possible to select a point P^1 in D such that $\mathrm{d}Q > 0$ along the straight line P^0P^1. We construct a closed cycle by returning from P^1 to P^0 along the adiabatic path, along which $đQ = 0$. Clearly during this cyclic process heat is only absorbed by the system, no heat is given off to the surroundings. According to the first law an equal amount of work is done by the system. Hence the net result is that heat is converted entirely into work, which violates Kelvin's principle. This completes the proof that Carathéodory's axiom is implied by Kelvin's principle.

We still have to consider the exceptional case $đQ \equiv 0$ throughout D. Then $đA = \mathrm{d}U$, where U is a function of $x_1, \ldots, x_n$, but depends no longer on ϑ, as shown by (3). Thus the variable ϑ has become spurious and our system is a purely mechanical system. On the other hand, it is clear that mechanical systems do obey Kelvin's principle. It is also clear that they do not obey Carathéodory's axiom. In fact, every set of values $x_1, \ldots, x_n$ (in a certain domain) can be reached by a mechanical, and therefore adiabatic process. Subsequently the temperature ϑ may be varied, which is also an adiabatic process, as $\partial U/\partial\vartheta = 0$.

4. *Discussion.* It is interesting to note that Landsberg's assumption $\partial U/\partial\vartheta \neq 0$ was also implied by Carathéodory[2]) in his definition of a simple system (einfaches System). It is used in his derivation of the concept of entropy from his axioms. However, by means of a procedure similar to the one given above, his treatment can be modified in order to avoid this assumption.

The statement that $\partial U/\partial\vartheta$ be positive everywhere is a connection between the concepts of temperature and internal energy, which is by no means implied by the assumptions preceding it. Systems for which $\partial U/\partial\vartheta$ vanishes and changes sign are considered by Giles[8]). These states are no equilibrium states in the usual sense, but it may be argued that nevertheless thermodynamics may be applied to them[8]) [9]).

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