On H Buchdahl's project of a thermodynamics without empirical temperature as a primitive concept

1989 J. Phys. A: Math. Gen. 22 341

(http://iopscience.iop.org/0305-4470/22/3/018)

J. Phys. A: Math. Gen. **22** (1989) 341-342. Printed in the UK

COMMENT

On H Buchdahl's project of a thermodynamics without empirical temperature as a primitive concept†

Johann Walter

Institut für Mathematik, Rhein-Westfälische Technische Hochschule Aachen, Templergraben 55, D-5100 Aachen, Federal Republic of Germany

Received 25 November 1987, in final form 8 February 1988

Abstract. As a consequence of an elementary quantification-theoretical analysis, in the present comment I maintain that formulations in the spirit of Carathéodory of the second law are dependent on the zeroth law. Any attempt to show the redundancy of the zeroth law on the basis of formulations of this kind of the second law is, therefore, bound to fail.

In his paper 'On the redundancy of the zeroth law of thermodynamics' Buchdahl (1986) makes a very daring effort to develop a thermodynamics in which the so-called zeroth law is no longer an assumption in its own right but only a consequence of the first and second laws of thermodynamics. The concept of empirical temperature (so absolutely intertwined with the basis of what we call 'thermo'-dynamics) is thus degraded from a primitive notion to a derived one. It is clear that, in order to attain this goal, one has to use formulations of the first and second laws, which in their turn are independent of the zeroth law or, in the author's words, are 'manifestly free of any explicit or implicit reference to temperature' (Buchdahl 1986, p L561).

A formulation of the second law which (at first sight at least) seems to be independent of the zeroth law has been given by Carathéodory (1909, p 363). Specialised for quasistatic processes, this formulation says:

(i) 'in every arbitrarily close neighborhood of a given initial state there exist states that cannot be approached arbitrarily closely by quasistatic adiabatic processes' (Kestin 1976, p 236).

Buchdahl's thesis of the redundancy of the zeroth law now stands and falls with the truth of the assumption that Carathéodory's formulation (i) is an assertion which, on the one hand, rephrases correctly the contents of the second law and is, on the other hand, 'manifestly free of any explicit or implicit reference to temperature'. This assumption, however, which is not rigorously substantiated by Buchdahl (1986) is evidently false.

The delicate character of the situation described thus far can be gathered from the fact that Carathéodory's formulation (i) (if taken literally) is no 'well-formed formula' in the sense of quantification theory (Andrews 1986, p 45) because of the vagueness of the underlying model of the 'set of all thermodynamical systems' (the 'domain of discourse' of quantification theory (Andrews 1986, p 47)) and is, therefore, one of those assertions which, in Lord Kelvin's words (Thomson 1880, p 556), 'escape the merit of being false by having no assignable meaning'. Prior to trying to assess the correctness of the above assumption we have, therefore, to clear up the quantification-theoretic status of (i). For reasons from the conventions regulating the use of the

† The present comment is a shortened version of a more detailed manuscript (Walter 1987).

0305-4470/89/030341+02$02.50

'universal quantifier' one has to pass from the quantification-theoretically incomplete formulation (i) to the following formulation (intended, of course, by Carathéodory).

(ii) 'For every system $\Sigma \in \mathfrak{U}$ it is true that in every arbitrarily close neighborhood of a given initial state of Σ there exist states of Σ that cannot be approached arbitrarily closely by quasistatic adiabatic processes of Σ'.

Formulation (ii) differs from (i) mainly by the occurrence of the additional set-valued variable $\mathfrak{U}$ addressing the mathematical model of the 'set of all thermodynamical systems' underlying the discussion. Evidently, without a precise knowledge of the set $\mathfrak{U}$ a reliable judgement on the dependence or independence of (ii) on the zeroth law is not possible. Because of the unfortunately rather confused character of Carathéodory's writing the determination of the model set $\mathfrak{U}$ intended by Carathéodory is a rather troublesome task. In Walter (1978) I have given a mathematically coherent reconstruction of the central part of Carathéodory's theory in which, for the first time, the algebraic structure impressed by Carathéodory upon his model set $\mathfrak{U}$ (with 'diathermal composition' as its 'algebraic composition') is worked out in a systematic way. Because of the sequence (naturally emerging during this reconstruction) of introducing the various building blocks into the argument where the notion of the empirical temperature comes in *prior to* and is used *in an essential way* within the formulation of the first and second law, Buchdahl's assumption that the second law is independent of the zeroth law is definitely excluded.

As a résumé of the above analysis I want to state that the thesis (so contrary to the usual physical intuition) of the redundancy of the zeroth law cannot be considered as proven because the assumption that Carathéodory's formulation (i) of the second law be 'manifestly free of any explicit or implicit reference to temperature' (on which the proof of this redundancy hinges) does not find support in Carathéodory's text.

References

Andrews P B 1986 *An Introduction to Mathematical Logic and Type Theory: To Truth through Proof* (New York: Academic)

Buchdahl H 1986 *J. Phys. A: Math. Gen.* **19** L561-4

Carathéodory C 1909 *Math. Ann.* **67** 355-86

Kestin J (ed) 1976 *The Second Law of Thermodynamics* (Stroudsburg, PA: Dowden, Hutchinson & Ross)

Thomson W 1880 *Encyclopaedia Britannica* (ninth edn) **XI** 554-89

Walter J 1978 *Proc. R Soc. Edin.* A **82** 87-94

—— 1987 Logical frictions in the tradition of Carathéodory's thermodynamics *Preprint*