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Negative Absolute Temperatures

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Ramsey's criteria for systems capable of negative absolute temperatures are justified. This is done by showing that a thermodynamic proof that the temperature must not be negative breaks down for systems satisfying Ramsey's conditions.

RAMSEY[1] has recently discussed the thermodynamics and statistical mechanics of negative absolute temperatures in a detailed and fundamental manner. It appears to the writer however, that Ramsey's argument in support of the correctness of the concept of negative temperature is inadequately stated at one point and therefore open to criticism. It is the purpose of this note to clarify the point and so to remove a possible objection to the use of this novel concept.

Ramsey says that the condition that the temperature T be nonnegative is postulated in thermodynamics,[2] although usually not explicitly, and that this postulate is not necessary for most of the theorems of thermodynamics.[3] There is, however, one important way of developing thermodynamics in which the statement $T \geq 0$ is a theorem and not a postulate.[4] In order to justify Ramsey's use of negative temperatures, it is therefore necessary to analyze the proof of this theorem and to show that the proof fails precisely when the system is capable of negative temperatures according to Ramsey's criteria.

The proof is based on the following postulates:

1. Every closed system evolves into a state of equilibrium in which, among other properties, internal macroscopic motions cease.
2. In this equilibrium state, the entropy S has its maximum value consistent with the given values of the energy and all other extensive variables of the system.
3. The thermodynamic temperature T is defined by the equation
$$1/T = (\partial S/\partial U)_x,$$
where U is the internal energy and x stands for all other extensive variables.

The proof is given in detail by Landau and Lifshitz, but the essential idea can be stated simply.[5] If the temperature were negative, then any process in which U decreased (at constant x) would have to be accompanied by an increase in S, the entropy. One such process is the conversion of the internal energy into kinetic energy of internal macroscopic motion, i.e., the reversal of the trend to equilibrium. Hence, if T were negative, and if the system could decrease U by conversion to kinetic energy, then the foregoing postulates 1 and 2 would be violated; therefore T cannot be negative.

This proof does not apply to systems which, on the basis of Ramsey's criteria, are capable of negative temperatures. Such systems must have an upper limit to the energy of their allowed states and must also be thermally isolated from all systems which do not have such an upper limit to their energy levels. Since kinetic energies do not have such an upper limit, Ramsey's systems cannot convert their internal energies into kinetic energy. Thus the argument used in the foregoing proof is inapplicable, and negative temperatures are possible for systems satisfying Ramsey's criteria.

[1] N. F. Ramsey, Phys. Rev. **103**, 20 (1956).
[2] See, for example, E. A. Guggenheim, *Thermodynamics* (Interscience Publishers, Inc., New York, 1949), pp. 11, 12.
[3] Ramsey discusses those aspects of thermodynamics which need revision when negative temperatures are used, e.g., the Kelvin-Planck form of the Second Law.
[4] L. Landau and E. Lifshitz, *Statistical Physics* (Oxford University Press, New York, 1938), Chaps. II, III, especially p. 29.
[5] This formulation is based on unpublished lecture notes by L. Tisza, 1946.