Negative Temperatures

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It is shown by an example how the concept of negative temperature finds a natural place in the approach to thermodynamics which was originated by Carathéodory.

1. INTRODUCTION

THE concept of spin temperature does not so far seem to have been discussed from the point of view of Carathéodory's principle in thermodynamics. A brief discussion of alternative signs for the absolute temperatures of equilibrium systems is, however, contained in an attempt to extend the approach originated by Carathéodory.[1] The purpose of this note is to show explicity how a negative temperature finds a natural place in this system of ideas. The results derived here are therefore to some extent contained in, or simple corollaries from, the approach developed in I. But they are difficult to obtain from I without working through the whole paper, so that the present exposition may be of use.

Consider a spin system which is decoupled from the lattice, and whose thermodynamic equilibrium state can be described by specifying the strength H of a uniform applied magnetic field, and the temperature $\tau \equiv -1/T$, where T is the absolute temperature. From a statistical mechanical analysis, the phase space may be taken to be the (S,τ) plane. Curves of constant magnetic field have then the form shown in Fig. 1. These have been drawn for the high-temperature approximation, when

$$M = -CH\tau, \tag{1}$$

$$U = C(H^2+B^2)\tau, \tag{2}$$

$$S = A - C(H^2+B^2)\tau^2/2, \tag{3}$$

where A, B, and C are constants. M is the average value of the magnetic moment in the direction of the applied field, and U is the mean internal energy. B is determined by the interaction among the spins. The proof of Eqs. (1) to (3) is straightforward, the main formulas having been given by Abragam and Proctor[2] (see Appendix for additional derivations).

The above example shows incidentally that the usual definition of an ideal paramagnetic material by $M = f(H/T)$ is too broad, since this law can also be obtained for interacting spins. The following additional restrictions may be suitable for the ideal paramagnetic material: (i) $H=0$ implies $M=0$, and conversely; (ii) the internal energy in zero field is independent of temperature. With this definition the system specified by Eqs. (1) to (3) is an ideal paramagnetic system only if $B=0$.

2. ANALYSIS OF THE PHASE SPACE

The thermodynamic state of any system must be specified by at least two independent variables (I, p. 365). One may chose T and S (as above), or T and another variable x, say the magnetic field. If one has only one independent variable, x and T cannot be independent. The theory of the thermodynamic equilibrium of such systems should therefore be derivable from the theory of equilibrium with respect to the variable x. For instance, the condition $T_1 = T_2$ for thermal equilibrium can then be stated by using only the variable x (i.e., the magnetic field). From this observation one obtains, as a special case, a remark by Abragam and Proctor (reference 2, p. 1444), who note with respect to systems satisfying Curie's Law that conclusions about the magnetic moment of the system can be derived "without bothering about spin temperature at all."

There is therefore little thermodynamic interest in considering a spin system which is subject to quasistatic adiabatic processes only, since this has only one independent variable. It will therefore be assumed that it is possible to link adiabatically the states represented by any two points in the phase space of Fig. 1—unless the contrary can definitely be established for specific points of this space. The concepts of I can then be applied, and one has two independent variables in T and S, or T and H. The question as to the validity of this assumption focusses attention on the search for the irreversible adiabatic processes which may be possible with spin systems. (For example, the above assumption would be invalid if no irreversible adiabatic processes were possible for spin systems.)

The set β.—Denote by β the set of points which has the property that the states represented by any two

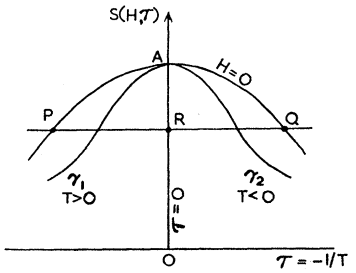

FIG. 1. Thermodynamic phase space of spin system.

[1] P. T. Landsberg, Revs. Modern Phys. **28**, 363 (1956), to be referred to as I. A more detailed exposition is contained in a forthcoming book on thermodynamics which is being published by Interscience Publishers, Inc., New York.
[2] A. Abragam and W. G. Proctor, Phys. Rev. **109**, 1441 (1958).

points of β can be linked adiabatically, and that no points which can be in the set are excluded (I, p. 371). Note that points such as R are outside β. For at infinite absolute temperature the entropy has the value A for all finite fields. R can be approached indefinitely, even in a quasistatic adiabatic manner, by raising the field, but it cannot be attained with finite fields. Thus no point on the $\tau=0$ axis can lie in β, excepting the point for which $S=A$.

The set $F(\beta)$.—This is the set of points which constitutes the "frontier" of β (I, p. 376), i.e., it contains all boundary points of β. $F(\beta)$ consists of the curve $H=0$, part of the axis $\tau=0$, and we shall regard it as open in the direction of the axis $S=0$, since the theory leading to Eqs. (1) to (3) ceases to apply in any case as the low entropy values are approached. The part AR of the $\tau=0$ axis, including the point $S=A$, belongs to $F(\beta)$. The assertion that a point lies in $F(\beta)$ does not mean, of course, that the point belongs to β. Which of the points of $F(\beta)$ belong to β must be decided by a separate argument. The criterion to be used is that, if a point of $F(\beta)$ belongs to β, then the state which this point represents must be adiabatically linked with the rest of β. If it does not belong to β, it is not adiabatically linked with the rest of β.

The set γ.—One can take one further step without deciding which points of $F(\beta)$ belong to β. Consider the set of those points of $F(\beta)$ which do in fact lie in β, and remove them from β. One is then left with two disconnected sets, to be denoted by γ_1 and γ_2, which lie respectively to the left and to the right of the axis $\tau=0$. Each set is an open set, i.e., it consists of internal points only, because it contains no boundary points. As in I, p.376, if a set γ is referred to in the sequel, either one of these open connected subsets of β is meant. Each point of γ_1 possesses a neighborhood, every point of which lies also in γ_1, and the same holds for γ_2.

3. EXISTENCE OF TWO SUBSETS γ: GENERALIZATIONS

The fact that the set β contains *two* sets γ holds clearly for all systems having a finite number of energy levels [and is not a property of the specific model leading to Eqs. (1) to (3)].[3] For such systems it is a fact of statistical mechanics that the entropies at $T=0$ and $\tau=0$ are independent of external parameters. However, critical values of such parameters may exist for which the entropy jumps abruptly from one value to another, for example, if a degeneracy is split by a magnetic field at absolute zero. It follows that on a plot such as that of Fig. 1, the set β can have only isolated points [which lie in $F(\beta)$ and therefore outside γ] on the $\tau=0$ axis. In an analogous plot of entropy against absolute temperature, the set β can have only isolated points on the $T=0$ axis. It follows that *whenever positive and negative temperatures have been defined for a set β, which refers to a system having a finite number of energy levels, that set contains (at least) two disconnected sets γ.*

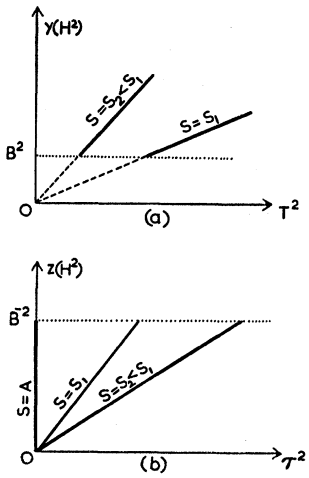

FIG. 2. Alternative forms of the phase space. "Reduced" representation which does not distinguish between positive and negative temperatures. [$y\equiv H^2+B^2$, $z\equiv(H^2+B^2)^{-1}$].

An even more general conclusion of this kind can be derived from thermodynamics. That an integrating factor of $d'Q$ is the absolute temperature T, holds in general only for a set γ, since no troubles can arise in these sets from the existence of boundary points. In such a set it may be possible to approach the hypersurface $T=0$ and $\tau=0$ as closely as desired (and it may also be possible to define these sets by a limiting process, as discussed in I, p. 379). However, they cannot be reached in γ, since the mathematical processes which enabled one to define the absolute temperature T as an integrating fact of $d'Q$, presume that T is finite and nonzero. Hence one can conclude that *the sets γ cannot actually attain or cross the hypersurfaces $T=0$ and $\tau=0$.*

4. THERMODYNAMIC CONSIDERATIONS

In the preceding sections we have started with statistical mechanics and hence introduced the thermodynamic phase space together with its simplest topological properties. It is instructive to invert this procedure. Given the thermodynamic properties of the system in the form of Eqs. (1) to (3), what can one say about the limitations of the treatment which gave rise to them?

The second law will be used in the following form: All points of γ are i-points. By an i-point is meant a point y of γ such that every γ-neighborhood of it contains a point which is adiabatically inaccessible from y [I, (D11)]. Let this law be applied to Fig. 2(a), assuming $B=0$. It is clear that the point 0 cannot be adiabatically linked with the points of the set β. For if it were, one could pass from any point in γ to all neighboring points, by choosing paths along adiabatics and going through 0. Hence the points of γ would not be i-points. This argument, which applies to ideal paramagnetic systems, shows that at low temperatures *and* low fields such systems cannot exist. If $B\neq 0$ it is, of course, clear from Fig. 2(a) that the system cannot exist at low tem-

[3] It holds also for an infinity of levels, provided there exist both an upper and a lower bound to the energy. See also N. F. Ramsey, Phys. Rev. **103**, 20 (1956).

peratures. A similar argument, applied to the origin of Fig. 2(b), shows that this point is adiabatically unlinked with the rest of the points of γ (whether $B=0$ or $B\neq 0$). The removal of one point from the set β must mean that physically also the immediate neighborhood of this point does not correspond to true states of the system. The origin of Fig. 2(b) corresponds to infinitely high temperatures *and* infinitely high fields. Thus thermodynamics suggests that the theory of Sec. 1 is either a high-temperature low-field theory, or else a low-temperature high-field theory. The first possibility is in fact the correct one.

It may be argued that at points such as 0 one has physically no means available of chosing one adiabatic rather than another on which to leave 0. In the present method of presenting thermodynamics, however, such questions do not arise, since any curve which lies in a set β and consists of adiabatics represents a quasistatic adiabatic linkage of two states. The possibilities of such linkages depends exclusively on the topology of the thermodynamic phase space.

To a high-temperature theory the third law of thermodynamics in its conventional form cannot be applied. In a more general formulation, the third law is a statement which asserts which of the boundary points $F(\beta)$ of a set γ may be regarded as adiabatically linked with the rest of γ, and are therefore to be regarded as also belonging to the set β. In general, all boundary points $F(\gamma)$ which do not correspond to a state at the absolute zero of temperature can be included in a set β. By this principle all points of the curve $H=0$ of Fig. 1 are to be regarded as part of the set β. This applies also to the state of maximum entropy A. This conclusion is in agreement with the result obtained from the assumption stated at the beginning of Sec. 2.

It is only for a set γ that the second law asserts the existence of an entropy and an absolute temperature. In the present example, therefore, it tells us that there exist an entropy S_1 and an absolute temperature T_1 for the set γ_1, and similarly that there exist functions S_2, T_2 for γ_2. Since the equation $d'Q=TdS$ remains valid under the transformation $T\rightarrow CT$, $S\rightarrow C^{-1}S$, however, there is still some arbitrariness in the definitions. If one set γ is considered by itself, for example, the choice of sign is still available, and this gives rise to various types of thermodynamics, as considered in I.

In the present example the signs chosen for T and S in γ_1 and in γ_2 are also arbitrary from the thermodynamic point of view. It is only if one considers the relation between the two sets that additional restrictions can be brought into play. For instance, one can use the statistical mechanical result that for a given field one can have two physically distinct states of the same entropy. It then becomes very convenient to choose opposite signs for the absolute temperatures in γ_1 and γ_2, and to choose the additive constants in the entropy in such a way that the entropies are positive in both γ_1 and γ_2.

ACKNOWLEDGMENT

I am indebted to Professor M. Fierz for correspondence.

APPENDIX

Using the notation of Abragam and Proctor,[2] the Hamiltonian of the system is $W=H_0+H_1$, where

$$\mathrm{Tr}(H_0)=\mathrm{Tr}(H_1)=\mathrm{Tr}(H_0H_1)=0.$$

The mean internal energy in the high-temperature approximation is, with $\beta\equiv 1/kT$,

$$\bar{U}=\mathrm{Tr}(We^{-\beta W})/\mathrm{Tr}(e^{-\beta W})\cong\mathrm{Tr}(W-\beta W^2)/\mathrm{Tr}I.$$

The mean magnetic moment in the direction of the field is

$$\bar{M}=\mathrm{Tr}(Me^{-\beta W})/\mathrm{Tr}(e^{-\beta W})\cong\mathrm{Tr}(M-\beta MW)/\mathrm{Tr}I.$$

Since $H_0=-MH$, where H is the magnetic field,

$$\bar{U}\cong -C(H^2+B^2)/T,\quad \bar{M}\cong CH/T, \tag{A1}$$

where

$$C\equiv\mathrm{Tr}(M^2)/k\mathrm{Tr}I,\quad B^2\equiv\mathrm{Tr}(H_1^2)/\mathrm{Tr}(M^2).$$

In the text U and M have been written for $\bar{U}$ and $\bar{M}$.

The relation $TdS=dU+MdH$ becomes, upon using H and T as variables,

$$dS=CT^{-3}(H^2+B^2)dT-CHT^{-2}dH.$$

Hence the entropy can be taken in the form

$$S=A-\tfrac{1}{2}CT^{-2}(H^2+B^2). \tag{A2}$$

This yields Eqs. (1) to (3) of the text.