We notice that according to Eq. (22) the initial deviation of $\langle m\rangle$ from its value in the equilibrium distribution decays to zero with a "relaxation time" given by $\tau 2R/(p+p')$.

As our final point we consider the time variation of the thermodynamic functions of our model. Since we are dealing with a system which is not isolated but is instead coupled to a heat bath at temperature T, we do not expect the entropy of the system itself to be a maximum at equilibrium. Instead, the entropy of the system plus that of the heat bath must be maximum, or, equivalently, the Helmholtz function of the system must be a minimum at equilibrium. Without giving the details, we mention that it can be proved by the methods we used in another paper,[6] that the Helmholtz function for this system decreases monotonically and attains its minimum value in the equilibrium state. Consequently in this respect, as in all others considered, the generalized Ehrenfest urn model is indicative of the behavior of a system which is kept at a fixed temperature.

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[6] M. J. Klein, Physica (to be published).

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Thermodynamics and Statistical Mechanics at Negative Absolute Temperatures

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The circumstances under which negative absolute temperatures can occur are discussed, and principles of thermodynamics and statistical mechanics at negative temperatures are developed. If the entropy of a thermodynamic system is not a monotonically increasing function of its internal energy, it possesses a negative temperature whenever $(\partial S/\partial U)_X$ is negative. Negative temperatures are hotter than positive temperatures. When account is taken of the possibility of negative temperatures, various modifications of conventional thermodynamics statements are required. For example, heat *can* be extracted from a negative-temperature reservoir with no other effect than the performance of an equivalent amount of work. One of the standard formulations of the second law of thermodynamics must be altered to the following: It is impossible to construct an engine that will operate in a closed cycle and provide no effect other than (1) the extraction of heat from a positive-temperature reservoir with the performance of an equivalent amount of work or (2) the rejection of heat into a negative-temperature reservoir with the corresponding work being done on the engine. A thermodynamic system that is in internal thermodynamic equilibrium, that is otherwise essentially isolated, and that has an energetic upper limit to its allowed states can possess a negative temperature. The statistical mechanics of such a system are discussed and the results are applied to nuclear spin systems.

I. INTRODUCTION

SEVERAL years ago Pound,[1–3] Purcell,[3] and Ramsey[2,4] studied experimentally various properties of the nuclear spin systems in a pure LiF crystal for which spin lattice relaxation times were as large as 5 minutes at room temperature while the spin-spin relaxation time was less than 10^{-5} second. With the nuclear spin systems of this crystal various experiments were carried out, including experiments with a spin system at negative temperatures.[3] In the present paper, the thermodynamical and statistical mechanical implications of negative absolute temperature are discussed. Since the theoretical analysis of the past experiments has been only briefly described,[1–4] there has been some misunderstanding[5] of them. For this reason and because of the thermodynamic significance of negative temperatures,[4,6] the present paper also contains a more detailed justification for the use of temperature as a description of suitable nuclear spin systems.

As discussed in Sec. III below, the conditions for the existence of a system at negative temperatures are so restrictive that they are rarely met in practice except with some mutually interacting nuclear spin systems. However, the thermodynamics and statistical mechanics of negative temperatures are more general than their application to a single type of system. Consequently, in the present paper, the thermodynamics and statistical mechanics of negative temperatures will be discussed first for a general system capable of negative temperatures, and only later will specific applications be made to spin systems.

II. THERMODYNAMICS AT NEGATIVE TEMPERATURES

From a thermodynamic point of view, the only requirement for the existence of a negative temperature is that the entropy S should not be restricted to a monotonically increasing function of the internal energy U. At any point for which the slope of the entropy as a

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[1] R. V. Pound, Phys. Rev. **81**, 156 (1951).

[2] N. F. Ramsey and R. V. Pound, Phys. Rev. **81**, 278 (1951).

[3] E. M. Purcell and R. V. Pound, Phys. Rev. **81**, 279 (1951).

[4] N. F. Ramsey, Ordnance **40**, 898 (1956).

[5] W. F. Giauque, J. Am. Chem. Soc. **76**, 5577 (1954); Time **46**, No. 26, 49 (1955).

[6] F. J. Dyson, Sci. American (September, 1954); F. Simon (private communication).

function of U becomes negative, the temperature is negative since the temperature is related to $(\partial S/\partial U)_X$ by the well-known thermodynamic relation[7]

$$T=(\partial S/\partial U)_X^{-1}, \tag{1}$$

where the symbol $(\;)_X$ indicates that for the partial differentiation one should hold constant the thermodynamic variables X that appear as additional differentials in the thermodynamic equation relating TdS and dU. Likewise $(\;)_Y$ indicates that for the partial differentiation one should hold constant the variables Y that appear as additional differentials in the thermodynamic equation relating TdS and the enthalpy H. In the latter case one may write[7]

$$T=(\partial S/\partial H)_Y^{-1}. \tag{2}$$

Ordinarily the assumption is not explicitly made in thermodynamics that S increases monotonically with U, and such an assumption is not necessary in the derivation of many thermodynamic theorems. Of course, even though there is no mathematical objection to S decreasing as U increases, there would be no physical interest to the subject if no thermodynamic system with such a property could be conceived of and if such systems were never realized in practice. However, such systems can be both theoretically devised and closely realized experimentally. In the discussions of statistical mechanics in Sec. III it will be shown that systems of elements in thermal equilibrium such that each element of the system has an upper limit to its maximum possible energy can have the characteristic of negative $(\partial S/\partial U)_X$. This may easily be seen, for example, if there are only two energy states available to each element of the system. Then the lowest possible energy is achieved with all elements in the lowest energy state, which is clearly a highly ordered state for the thermodynamic system and corresponds to $S=0$. Likewise the greatest energy is achieved with all elements in the highest state, which of course is also a highly ordered state of the system and corresponds to $S=0$. At intermediate energies, when some elements are in the high-energy state and others in the low-energy state, there is much greater disorder and a correspondingly greater entropy. Therefore, between the lowest and the highest energy states of the thermodynamic system, the entropy clearly passes through a maximum and then diminishes with increasing U. This is shown in Fig. 1 of Sec. III where the entropy of such a system is calculated by normal procedures of statistical mechanics.

The maximum of the entropy curve discussed in the preceding paragraph corresponds to $(\partial S/\partial U)_X=0$ and hence to infinite temperature. The region of negative $(\partial S/\partial U)_X$ corresponds to negative temperature. Hence it is apparent that in cooling from negative to positive temperature such a system passes through ∞ °K instead of through absolute 0°K; this characteristic is illustrated by the negative temperature cooling curves reported by Purcell and Pound.[3] In other words, negative temperatures are not "colder" than absolute zero but instead are "hotter" than infinite temperature. In view of this, it might well be argued that the term negative temperature is an unfortunate and misleading one. However, the thermodynamic definition of temperature, of which Eqs. (1) and (2) are consequences, was agreed upon long ago. As long as this standard definition is followed there is no choice but to use the term negative temperature when a thermodynamic system is in a condition such that the quantities occurring in Eqs. (1) and (2) are negative.

Since the assumption of a monotonic increase of S with U is not essential to the development of thermodynamics, the normal thermodynamic theorems and discussions apply in the negative as well as the positive temperature region, provided suitable modifications and extensions are made. However, the definitions of certain thermodynamical quantities must be clarified before discussing the theorems, since two alternative definitions are sometimes used which are compatible at positive temperatures but are not so at negative. The definitions[7] of "work" and "heat" will be taken to be the same at positive and negative temperatures.[7] In some respects this is a trivial statement but it is perhaps worth noting that the only means by which all of the various alternative statements of the second law of thermodynamics could be preserved unaltered would be by a reversed sign for both of these quantities at negative temperatures. With the above definitions the conventional formulations of the first law of thermodynamics are equally applicable at positive and negative temperatures.

The definitions of the terms "hotter" and "colder" are not obvious since various alternative definitions which agree at positive temperatures disagree at negative. One possible definition would be to define the "hotter" of two bodies to be the one with the greater algebraic value of T. In this case all positive temperatures would be hotter than negative ones, despite the fact discussed above that negative temperatures in the normal sense of the word are "hotter" than positive temperatures, as indicated by the fact that if a positive and negative-temperature system are in thermal contact heat will flow from the negative temperature to the positive. The definition which agrees best with the normal meaning and which will be adopted is that the "hotter" of two bodies is the one from which heat flows when they are brought into thermal contact while the "colder" is the one to which the heat flows. With this definition any negative temperature is hotter than any positive temperature while for two temperatures of the same sign the one with the algebraically greater temperature is the hotter. The temperature scale from cold to hot then runs +0°K, $\cdots$, +300°K, $\cdots$, $+\infty$ °K, $\cdots$, $-\infty$ °K, $\cdots$, −300°K,

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[7] M. Zemansky, *Thermodynamics* (McGraw-Hill Book Company, Inc., New York, 1951), third edition.

$\cdots$, -0°K. "Intermediate" temperatures should likewise be defined relative to such an order. With the above definitions, if two systems at different temperatures are brought into thermal contact they will reach some final temperature which is intermediate between the two starting temperatures. It should be noted, however, that $+1000$°K, for example, is intermediate between $+300$°K and -300°K.

It might at first sight appear that the necessity for ordering the temperature scale from cold to hot in the fashion of the preceding paragraph might be an argument against the validity of negative temperatures. However, the apparent artificialness of the above ordering is merely an accidental result of the arbitrary choice of the conventional temperature function. If the temperature function had been chosen as $-1/T$, then the coldest temperatures would correspond to $-\infty$ for this function, infinite temperatures on the conventional scale would correspond to 0, and the negative temperatures on the conventional scale would correspond to positive values of this function. For this temperature function the algebraic order and the order from cold to hot would then be identical. Such a $-1/T$ function is often used in thermodynamic discussions for the purpose of expanding the temperature scale in the vicinity of absolute zero. The function $\ln T$ is sometimes also used for the same purpose. The above discussion shows that, for the purposes of negative temperatures, the $-1/T$ scale in many ways is even more convenient than the T scale. On the other hand, the logarithmic scale is less convenient since the logarithm of a negative number is complex.

At negative temperatures various cyclic processes, such as magnetic Carnot cycles, can be operated. Just as with positive temperatures, the ratio between two different negative temperatures can be determined absolutely as the ratio of the heats absorbed and rejected by a Carnot cycle operating between the two temperatures.

It should be noted, however, that no means has yet been devised by which a Carnot cycle can be operated between positive and negative temperatures. By adiabatic magnetization of a spin system, for example, the temperature can be raised as high on the positive scale as one wishes but it cannot be made to cross over to negative values; a corresponding statement applies if one starts initially with the system at a negative temperature. As a result, the ratio of a positive temperature to a negative one has not been determined by operating a Carnot cycle between the two temperatures.

At positive and negative temperatures, the efficiency of a Carnot engine is given by

$$\eta = 1-(Q_2/Q_1) = 1-(T_2/T_1), \tag{3}$$

where Q_1 is the heat absorbed at temperature T_1 while Q_2 is the heat rejected at temperature T_2. If, as in the normal heat engine at positive temperatures, the heat is absorbed at the hotter temperature then, as discussed above, $T_2/T_1 > 1$ for negative-temperature reservoirs and the efficiency η is negative and can be very large. At first sight this may seem surprising. It means that instead of work being produced when a Carnot heat engine is operated with heat received at the hot reservoir, work must be supplied to maintain the cycle. Inversely, it means that if such a Carnot cycle is operated in the opposite direction work is produced while heat is transferred from a colder reservoir to a hotter. If the heat transported to the hot reservoir by this reverse cycle is allowed to flow back to the colder reservoir, there then exists an engine that will operate in a closed cycle and produce no other effect than the extraction of heat from a reservoir and the performance of an equivalent amount of work. Although the existence of such a machine is a contradiction of one of the conventional formulations of the second law of thermodynamics, it is not in contradiction to the appropriate reformulation of this form of the second law that is given below. The existence of such a machine is also not in contradiction to the principle of increasing entropy, since from Fig. 1 it is apparent that the extraction of energy from a system at negative temperature corresponds to an increase in the entropy of the system rather than a decrease, as at positive temperatures.

It should be noted that when the Carnot cycle is operated between two negative temperatures in such a way that work is done by the machine while heat is absorbed from the colder reservoir and rejected at the hotter, then the efficiency by Eq. (3) is not only positive but it is also less than unity. Thus at both positive and negative temperatures cyclic heat engines which produce work have efficiencies less than unity, i.e., they absorb more heat than they produce work.

Of the alternative conventional statements of the second law of thermodynamics, some are applicable without modification for negative temperatures while others must be modified. The entropy formulation remains unaltered: (a) The entropy of a system is a variable of its state and the entropy of an isolated system can never decrease. Likewise the Clausius statement[7] is unaltered: (b) It is impossible to construct a device operating in a closed cycle that will produce no other effect than the transfer of heat from a cooler to a hotter body. However, the Kelvin-Planck formulation[7] of the second law must be modified to: (c) It is impossible to construct an engine that will operate in a closed cycle and produce no effect other than (1) the extraction of heat from a positive temperature reservoir with the performance of an equivalent amount of work or (2) the rejection of heat into a negative-temperature reservoir with the corresponding work being done on the engine. The Carathéodory form of the second law is unaltered.

The first and second laws of thermodynamics can as easily be used at negative temperatures as at positive ones to derive other thermodynamic relations. However, in these, as in the above statements of the second law, it is apparent that the difficulty of heating a hot system at negative temperatures is analogous to the difficulty in cooling a cold system at positive temperature. This is illustrated by the experimental fact to be discussed later that a nuclear resonance absorption experiment at positive temperatures becomes a nuclear resonance emission experiment at negative temperatures, and also by the potential usefulness of negative temperature systems as amplifiers. The difference between positive temperatures and negative temperatures can be clarified by noting the physical reasons for which the Clausius statement (b) need not be modified whereas the Kelvin-Planck formulation (c) must be changed. One might attempt to violate the Clausius statement (b) by constructing a cyclic heat engine which would first extract heat from a colder reservoir and convert it into work with no other change being produced. Then this work could be converted into heat that is transferred to a hotter reservoir, in violation of the statement. At positive temperatures this two-stage process is impossible because the first step cannot be done. At negative temperatures, on the other hand, the first step for converting heat to work is easy, as discussed earlier, but the impossible step is the conversion of all the work into heat to be supplied to the hotter reservoir without producing any other change. That such should be the case is of course reasonable from Fig. 1, since at negative temperatures an increased internal energy corresponds to diminished entropy just as the reverse is true at positive temperatures.

The various statements of the third law of thermodynamics apply unaltered at negative temperature provided it is understood that the absolute zero of temperature means absolute zero of both positive and negative temperature. Thus the unattainability statement of the third law would be: It is impossible by any procedure, no matter how idealized, in a finite number of operations to reduce any system to the absolute zero of positive temperature or to raise any system to the absolute zero of negative temperature.

III. STATISTICAL MECHANICS AT NEGATIVE TEMPERATURES

The essential requirements for a thermodynamical system to be capable of negative temperature are: (1) The elements of the thermodynamical system must be in thermodynamical equilibrium among themselves in order that the system can be described by a temperature at all; (2) there must be an upper limit to the possible energy of the allowed states of the system; and (3) the system must be thermally isolated from all systems which do not satisfy both of the above conditions, i.e., the thermal equilibrium time among the elements of the system must be short compared to the time during which appreciable energy is lost to or gained from other systems. The temperature concept is applicable to the system only for time intervals far from either of the above time limits.

The condition (2) must be satisfied if negative temperatures are to be achieved with a finite energy. If W_m is the energy of the mth state for one element of the system, then in thermal equilibrium the number of elements in the mth state is proportional to the Boltzmann factor $\exp(-W_m/kT)$. For negative temperatures, the Boltzmann factor increases exponentially with increasing W_m and the high-energy states are therefore occupied more than the low-energy ones, which is the reverse of the positive temperature case. Consequently, with no upper limit to the energy, negative temperatures could not be achieved with a finite energy. Most systems do not satisfy this condition, e.g., there is no upper limit to the possible kinetic energy of a gas molecule. It is for this reason that systems of negative temperatures occur only rarely.

Systems of interacting nuclear spins, however, have the characteristic that under suitable circumstances they can satisfy all three of the above conditions, as discussed in the next section. The discussion in the present section, however, will not be explicitly limited to spin systems.

In the normal discussions[8] of statistical mechanics, no assumption is made as to whether the energy levels of the elements of the system have an upper bound; indeed, the methods of statistical mechanics are often conventionally applied[8] to systems such as idealized paramagnetic systems, whose elements do have an upper energy limit. As a result the normal statistical mechanics theorems and procedures, such as the uses of partitions functions, apply equally well to systems capable of negative temperatures.

Consider a thermodynamic system of N elements such that the Hamiltonian $\mathfrak{H}$ of the system can be expressed as

$$\mathfrak{H}=\mathfrak{H}_0+\mathfrak{H}_{\text{int}}, \tag{4}$$

where

$$\mathfrak{H}_0=\sum_{k=1}^{N}\mathfrak{H}_{0k} \tag{5}$$

and $\mathfrak{H}_{0k}$ is the portion of the Hamiltonian that depends only on the kth element of the system while $\mathfrak{H}_{\text{int}}$ is the portion of the Hamiltonian that cannot be separated into terms dependent upon only one element.

The procedures of statistical mechanics and the concept of temperature are of course equally applicable when the average energy associated with $\mathfrak{H}_{\text{int}}$ is comparable to or larger than that associated with $\mathfrak{H}_0$ as when $\mathfrak{H}_{\text{int}}$ is small. On the other hand, the procedures are much more complicated in the former case and involve the complications of cooperative phenomena.

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[8] D. ter Haar, *Elements of Statistical Mechanics* (Rinehart and Company, New York, 1954) and the other standard texts referred to by ter Haar.

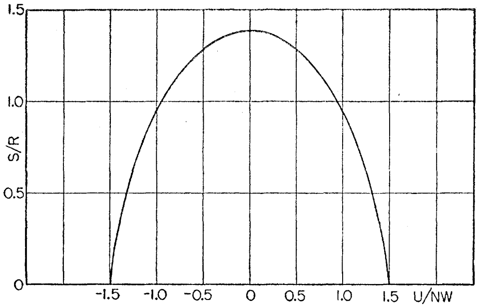

FIG. 1. The entropy is plotted as a function of the internal energy for a system of which each element has four equally spaced energy levels.

For this reason, the present discussion will be limited to cases where the average energy associated with $\mathfrak{H}_0$ is very large compared to that associated with $\mathfrak{H}_{\text{int}}$. It should be emphasized, however, that this assumption is only for the purpose of simplifying the discussion and does not imply that the concept of negative temperatures is limited by this condition or the other simplifying restrictions of the specific statistical mechanical model assumed below. Density-matrix procedures are useful in discussions of more complicated models.

It will now be assumed for simplicity that the eigenstates of $\mathfrak{H}_{0k}$ consist of n different levels of energy W_m spaced the same distance W from each other and with the zero of energy being selected midway between; therefore, $W_m = mW$ where m is an integer between $-(n-1)/2$ and $+(n-1)/2$. It will further be assumed that all N of the elements are identifiable and have the same energy level separations and that $\mathfrak{H}_{\text{int}}$ induces transitions in which one element has an upward transition while the other has a downward transition. The reason for assuming equal spacing of the levels is that the simplifying assumption of the preceding paragraph makes it unlikely, for energetic reasons with small n, that one element should make a downward transition which is energetically much different from the associated upward transition of the other element. It will also be assumed in the discussion immediately following that W_m is the spectroscopic[9,10] energy of an element of the thermodynamic system, i.e., the energy which governs the frequency of the emitted radiation from Bohr's frequency relation. The effects of departures from this last assumption will be discussed in the next section. It will also be assumed that the number of elements N is Avogadro's number.

With the foregoing assumptions, with $\beta = 1/kT$, and with the normal procedure for summing a geometric series, the partition function Z_μ and the Helmholtz function $A \equiv F$ become

$$Z_\mu = \exp(-A\beta/N) = \sum_{m=-(n-1)/2}^{+(n-1)/2} \exp(-mW\beta)$$

$$= \frac{\exp(nW\beta/2) - \exp(-nW\beta/2)}{\exp(W\beta/2) - \exp(-W\beta/2)} = \frac{\sinh(nW\beta/2)}{\sinh(W\beta/2)}. \tag{6}$$

From this, the internal energy U (taken as the sum of W_m) the entropy S, and the specific heat C_X may readily be calculated with the result that

$$U = \left(\frac{\partial[\beta A]}{\partial\beta}\right)_X = -\frac{NW}{2}\left[n\coth\frac{nW\beta}{2} - \coth\frac{W\beta}{2}\right],$$

$$S = k\beta^2\left(\frac{\partial A}{\partial\beta}\right)_X = R\ln\left[\left(\sinh\frac{nW\beta}{2}\right)\left(\sinh\frac{W\beta}{2}\right)^{-1}\right]$$

$$-\frac{RW\beta}{2}\left[n\coth\frac{nW\beta}{2} - \coth\frac{W\beta}{2}\right],$$

$$C_X = -k\beta^2\left(\frac{\partial^2[\beta A]}{\partial\beta^2}\right)_X = R\left(\frac{W\beta}{2}\right)^2$$

$$\times\left[\operatorname{csch}^2\frac{W\beta}{2} - n^2\operatorname{csch}^2\frac{nW\beta}{2}\right]. \tag{7}$$

Numerical values for these expressions have been evaluated in the case of $n=4$ and the results are plotted in Figs. 1 and 2. Figure 1 shows the entropy as a function of the internal energy. As discussed qualitatively in Sec. II, this form of curve is intuitively reasonable since the highest and lowest possible energies of the thermodynamic system correspond to the ordered array of all the elements of the system being in the same state. From Eq. (1), the region of negative slope for this curve corresponds to negative temperature.

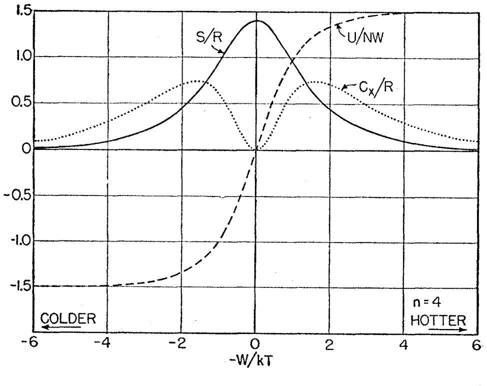

FIG. 2. The internal energy, the entropy and the specific heat are plotted as a function of $-1/T$ measured in units of k/W for the same system as Fig. 1. As discussed in Sec. II this choice of abscissa corresponds to the colder points being to the left of the hotter ones. The dashed curve (- - - - -) is for the internal energy U, the full curve (———) is for the entropy S, and the dotted curve (· · · · ·) is for the specific heat C_X.

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[9] L. J. F. Broer, Physica **12**, 49 (1946).

[10] C. J. Gorter, *Paramagnetic Relaxation* (Elsevier Publishing Company, Amsterdam, 1947).

In Fig. 2 the internal energy, the entropy and the specific heat are plotted as functions of $-1/T$. As discussed in Sec. II, this choice of scale makes the colder temperatures always appear to the left of the hotter ones. The internal energy can rise above zero, the average energy of the levels, because the Boltzmann factor $\exp(-W_m/kT)$ increases with increasing W_m at negative temperatures. The physical reason that the specific heat drops to zero at both +0°K and −0°K is that all elements of the system finally get into their lowest or highest energy state and no more heat can be removed or absorbed, respectively; on the other hand the specific heat at ∞°K drops to zero for a different reason: the temperature changes greatly in the vicinity of ∞°K for only a small change in configuration and internal energy.

It should be noted that +0°K and −0°K correspond to completely different physical states. For the former, the system is in its lowest possible energy state and for the latter it is in its highest. The system cannot become colder than +0°K since it can give up no more of its energy. It cannot become hotter than −0°K because it can absorb no more energy.

IV. NUCLEAR SPIN SYSTEMS

It has been recognized for some time that spin systems often form thermodynamic systems which can appropriately be described by a temperature.[10–14] However, almost all the doubts[5] that have been expressed as to the validity of negative temperature resolve into doubts as to the validity of any spin temperature. For this reason a few of the arguments in favor of the concept of temperature for a spin system will be briefly summarized here, though the reader should refer to the published literature[10–14] for more extensive discussions.

Although spin temperatures have been used and justified by a number of authors,[10–14] the most extensive justification of nuclear spin temperatures in a single article has been given by Bloembergen.[14] In order that the nuclear spin system can adequately be considered as a thermodynamic system describable by a temperature, it must satisfy the first condition of Sec. III, i.e., the various nuclear spins must interact among themselves in such a way that thermodynamic equilibrium is achieved. This occurs by virtue of the nuclear spin-spin magnetic interaction. As a result of this interaction nuclei can precess about each other's mutual magnetic field and undergo a transition whereby one nucleus has its magnetic quantum number relative to an external field increased while the other's is decreased the same amount. Since the energy absorbed by one nucleus is exactly equal to that released by the other, no additional energy need be added, as is also the case of collisions between molecules in a gas. This spin-spin process is the one often characterized by the relaxation time designated[14] T_2, which is approximately the period of the Larmor precession of one nucleus in the field of its neighbor. T_2 is of the order of 10^{-5} second. It is this process which brings the spin system into thermodynamic equilibrium with itself in a similar way to that in which molecular collisions bring about the thermodynamic equilibrium of a gas. Even if the initial distribution among the different spin orientation states were completely different from the Boltzmann distribution, the mutual spin reorientations from the spin-spin magnetic interaction would bring about a Boltzmann distribution. This process is quite distinct from the process characterized by the relaxation time[14] T_1. The latter depends upon the interaction between the spin system and the crystal lattice and is ordinarily dependent on the lattice vibrations, etc., whereas the spin-spin interaction is essentially independent. In the thermodynamics of spin systems the lattice interaction with relaxation time T_1 corresponds to leakage through the thermos bottle walls in ordinary heat experiments.

Bloembergen has theoretically calculated the thermal conductivity for such a spin system and has shown that many thousands of nuclear spins are brought into thermal equilibrium with each other in less than a tenth of a second. Consequently, it is legitimate to speak of a spin system as a thermodynamic system in essential equilibrium with itself, provided the relaxation time to the lattice is large compared with the aforementioned equilibrium time. This condition is ordinarily achieved and T_1 is often many minutes, which is very much greater than $T_2 \rightarrow 10^{-5}$ second and is even much greater than the above 10^{-1} second in which many thousands of nuclear spins are brought into thermodynamic equilibrium with each other.

One restriction on nuclear spin-temperatures should be noted. Although the thermal conductivities of nuclear spin systems are large on a microscopic scale and interdiffusion among many thousands of nuclear spins occurs in a small fraction of a second, the thermal diffusion is very small on a macroscopic basis; indeed, 10^{12} seconds would be required[14] for appreciable amounts of heat to diffuse 1 cm in a crystal if the only mechanism for thermal diffusion were the nuclear spin system. However, this restriction does not invalidate the concept of temperature when applied to a nuclear spin system but merely indicates that in any experiment one must insure that all macroscopically separate parts of the sample are subjected to similar treatments so that they will be at the same temperature. The need for this precaution is the same as the need for a similar precaution in the discussion of the ordinary temperatures of large subterranean rock samples.

Bloembergen[14] has produced strong experimental evidence in support of his spin diffusion calculations and of the concept of nuclear spin temperature. He has experimentally studied the effect of paramagnetic im-

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[11] H. B. G. Casimir and F. K. Du Pre, Physica **5**, 507 (1938).

[12] L. J. F. Broer, Physica **10**, 801 (1943).

[13] N. F. Ramsey, *Nuclear Moments* (John Wiley and Sons, Inc., New York, 1953).

[14] N. Bloembergen, Physica **15**, 386 (1949).

purities in bringing about equilibrium between the nuclear spin system and the crystal lattice. He finds that the experimental relaxation times T_1 to the lattice are as much as 10^4 times greater than could be expected by direct interaction between the paramagnetic impurity and individual nuclear spins. On the other hand, he finds excellent agreement between theory and experiment if he assumes the impurity ion first brings the nuclear spins in its immediate vicinity to the temperature of the lattice and that thermal diffusion within the nuclear spin system then brings the other nuclear spins to that temperature.

It should of course be noted that when the spin system and the lattice in a crystal are essentially isolated from each other and are of different temperatures it is improper to speak of the temperature of the substance. However, the spin system itself can be described by a temperature while the lattice system can also be described by a different temperature.

In order that condition (3) of Sec. III should be satisfied, it is necessary that the nuclear spin system be effectively isolated from all other systems which do not satisfy conditions (1) and (2) of that section. The above discussion shows that it is possible to obtain systems for which the relaxation time to the crystal lattice is sufficiently large for the nuclear spin system to be essentially isolated from it for macroscopic periods of time. However, in principle one should also consider the degree of isolation of the nuclear spin system from other systems as well. The radiation field corresponding to the black body radiation of the surrounding medium is one such system. However, the relaxation to this system is extremely long, as discussed in greater detail by Bloembergen and Pound.[15] This is further indicated by the fact that the oscillatory magnetic fields required to induce nuclear transitions in nuclear resonance experiments are far greater than those present at the appropriate frequency in black body radiation. For a negative-temperature experiment it is of course essential that the spin system be effectively isolated from the system of black body radiation, since such a system violates condition (2) of the preceding paragraph and is consequently incapable of being at a negative temperature. In this connection it should be noted that the nuclear spin-spin magnetic interaction which brings about the thermodynamic equilibrium of the spin system depends on the static magnetic field of the nuclei and not upon the radiation field. Another system from which the nuclear spin system is and must be decoupled is the system of internal motions of the nuclei; nuclei would disintegrate at temperatures far below those often achieved for nuclear spin systems.

Since a nuclear spin I can possess only $2I+1$ different orientation states, it is apparent from the foregoing discussion that some nuclear spin systems *can* satisfy all the requirements of Sec. III for the possible existence of a negative temperature. Of course, it should be emphasized that most nuclear spin systems don't satisfy these requirements. For example, in a molecular beam experiment, the molecules may be selected so that most of the nuclei are in the higher energy orientation states. Nevertheless, the nuclear spins in such a case cannot be described as at negative temperature since there is no internal thermodynamic equilibrium.

Since a nuclear spin system is an almost perfect paramagnetic substance, the various thermodynamic functions for the system in a magnetic field may readily be calculated at both positive and negative temperatures. Unfortunately, any discussion of the thermodynamics and statistical mechanics of magnetism is necessarily confused by the disagreement[9,10,16–18] that exists as to the definition of the internal energy of the system. In the two most frequently used procedures the roles of internal energy and of enthalpy are reversed. The disagreements are of course purely in matters of definitions and either procedure leads to the same physical results provided it is applied consistently. In particular, the temperature of a system is the same regardless of which procedure is used; the existence of negative temperatures is equally consistent with either procedure, but the designation of the thermodynamic variables in Figs. 1 and 2 are altered. Since this disagreement on matters of definition has sometimes led to a misunderstanding of negative spin temperatures, both alternatives are discussed in Appendix A, where it is shown that the temperature of a spin system is the same with either of the alternative procedures.

As discussed in Appendix A, if the energy W_m of the magnetic moment in the field $\mathcal{H}$ is taken to be the spectroscopic energy[9] and if U is taken to be the sum of W_m over one mole, then

$$T\,dS = dU + \mathbf{M}\cdot d\mathcal{H} \tag{8}$$

and

$$T = (\partial S/\partial U)_{\mathcal{H}}^{-1},$$

as in Eq. (1). The statistical mechanical results of Sec. III and Figs. 1 and 2 all apply to the nuclear spin case with the addition that, for nuclei of moment μ and spin I, the W of Sec. III becomes $W = |\mu\mathcal{H}/I|$.

In general, in strong magnetic fields the spins of two different kinds of nuclei form two separate spin systems that are thermally well isolated from each other since, as discussed in Sec. III, a mutual reorientation of spins between a pair of the nuclei of different kinds is not energetically possible. However, at weaker magnetic fields such that the differences in interaction energies with the external field are comparable with the mutual interaction energies, mutual reorientations become possible and the two spin systems come in thermal contact

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[15] N. Bloembergen and R. V. Pound, Phys. Rev. **95**, 8 (1954).

[16] C. G. B. Garrett, *Magnetic Cooling* (Harvard University Press, Cambridge, 1954).

[17] E. A. Guggenheim, Proc. Roy. Soc. (London) **A155**, 49 and 70 (1936).

[18] G. H. Livens, Proc. Cambridge Phil. Soc. **44**, 534 (1948).

with each other. This means for bringing two systems in and out of thermal contact can be used in various thermodynamical cyclic processes.

The nuclear spin systems studied by Pound, Purcell, and Ramsey[1–3] were those in a very pure crystal of LiF. In these experiments Pound and Ramsey[2] studied the spin-spin interactions which bring about thermal equilibrium of the spin system. They also observed effects of the mutual interactions of two different spin systems, as discussed in the preceding paragraph. Purcell and Pound[3] studied the means for bringing a nuclear spin system to a negative temperature and observed the cooling curve as a negative temperature spin system cooled to positive room temperature. All results of these experiments are completely consistent with the interpretations of the present paper. It was found for example that, when a negative temperature spin system was subjected to resonance radiation, more radiant energy was given off by the spin system than was absorbed.

V. SUMMARY AND CONCLUSIONS

In any thermodynamic system for which $(\partial S/\partial U)_X$ or $(\partial S/\partial H)_Y$ may be negative, the temperature of the system may be negative by Eqs. (1) and (2). The preceding discussion shows both that ideal systems can be theoretically devised with this property and that such ideal systems are closely realized experimentally by nuclear spin systems.

Systems at negative temperatures have various novel properties, of which one of the most intriguing is that a frequently quoted formulation of the second law of thermodynamics is easily violated at negative temperatures: a heat engine operating in a closed cycle *can* be constructed that will produce no other effect than the extraction of heat from a negative-temperature reservoir with the performance of the equivalent amount of work. On the other hand, it is impossible to construct a closed cycle machine on which work can be done with no other effect than the rejection of heat into a negative-temperature reservoir. This characteristic is experimentally observed in nuclear magnetic resonance experiments; for these the direction of the observed resonance deflection is reversed at negative temperature as a result of stimulated emission from the negative temperature spin system exceeding absorption.

The ease with which heat energy can be converted to work may provide an important practical application for negative-temperature systems. At negative temperatures most resistances are negative, and negative-temperarure systems are intrinsically amplifiers just as ordinary resistance networks at positive temperatures are attenuators. Townes[19] has used molecules with greater population of high-energy states than low-energy ones as the source of energy for a self-maintained oscillator. However, it should be noted, as in Sec. IV, that in such a molecular beam experiment there is no internal thermodynamic equilibrium within the spin system; consequently such a system cannot be described as being at negative temperature.

Nuclear spin systems at negative temperatures have several properties that are the reverse of those at positive temperatures. Adiabatic demagnetization heats the spin system instead of cooling it as at positive temperatures. Likewise for nuclear polarization experiments the nuclear spin system should be heated to the hottest possible negative temperature, whereas at positive temperatures the spin system should be cooled to the lowest possible temperature. The negative Curie temperature is such that for all hotter temperatures the system will be ferromagnetic (or antiferromagnetic). In addition, if the spin system is such that it is ferromagnetic when colder than the positive Curie temperature, it will be antiferromagnetic when hotter than the positive Curie temperature.

The need for modifying various standard statements of thermodynamics and statistical mechanics when the possibility of negative temperatures is recognized shows clearly how it is ordinarily implicitly assumed in the subject of thermodynamics that $(\partial S/\partial U)_X$ and $(\partial S/\partial H)_Y$ are positive even though neither of these is ordinarily introduced as an explicit assumption. If the minor complications of negative temperatures are to be validly avoided in discussions of thermodynamics, the assumption that $(\partial S/\partial U)_X$ and $(\partial S/\partial H)_Y$ are only positive should be explicitly introduced with the warning that this restrictive assumption is for simplification only and that it excludes a few valid, but rarely occurring thermodynamic systems.

In conclusion, it should be emphasized that although the phenomena of negative temperatures form fully valid portions of thermodynamics and statistical mechanics they are necessarily of much less practical importance than phenomena of positive temperatures. The occurrence of systems at negative temperatures will necessarily be relatively infrequent since a very special combination of rarely met requirements must be satisfied before negative temperatures are even a possibility for the system.

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APPENDIX A.

Unfortunately there has not been agreement in the definitions[9,10,16–18] of the thermodynamic functions of paramagnetic systems. In the two most frequently used procedures the roles of internal energy and enthalpy are reversed. In the present appendix it will be shown that the disagreements are purely in matters of definitions and that either procedure leads to the

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[19] Gordon, Geiger, and Townes, Phys. Rev. **95**, 282 (1954); **99**, 1264 (1955).

same temperature for the same physical system; the existence of negative temperature is equally consistent with either procedure.

As discussed by Broer[9] and others,[10] from the point of view of statistical mechanics it is most convenient to take the energy W_m of the magnetic moment in the field to be the spectroscopic energy.[9] This differs from the total energy W_m' by

$$W_m = W_m' - \boldsymbol{\mathcal{H}} \cdot \boldsymbol{\mu}_m, \tag{9}$$

since the work $\boldsymbol{\mathcal{H}} \cdot d\mathbf{M}$ done by the batteries when the magnetization is increased by $d\mathbf{M}$ is not available for radiation as it must be returned to the batteries again when the magnetization is reduced again by $d\mathbf{M}$. If the internal energy is taken to be U, the sum of W_m over one mole, in contrast to U', which is the sum of W_m', the average of Eq. (9) shows U and U' are related by

$$U = U' - \boldsymbol{\mathcal{H}} \cdot \mathbf{M}. \tag{10}$$

Since the heat TdS that must be supplied in a reversible process is equal to the change in total internal energy dU' minus the work done by the batteries,

$$TdS = dU' - \boldsymbol{\mathcal{H}} \cdot d\mathbf{M}. \tag{11}$$

From Eq. (10), the fundamental thermodynamic relation for U is then

$$TdS = dU + \mathbf{M} \cdot d\boldsymbol{\mathcal{H}}. \tag{12}$$

From Eq. (10) it is apparent that if U is taken as the internal energy, the quantity U' is just the enthalpy $H = U + \boldsymbol{\mathcal{H}} \cdot \mathbf{M}$. With this choice of U, the usual relations to the Helmholtz function A, the Gibbs function G, etc. apply. From Eq. (12) it is apparent that the temperature is given by Eq. (1).

The advantage of the above selection of W_m as the spectroscopic energy is that a system of interacting nuclear moments which is isolated except for a fixed external field will have all possible states of the microcanonical ensemble limited by

$$\sum W_m \delta n_m = 0, \tag{13}$$

where n_m indicates the number of nuclei in orientation state m. Since Eq. (13) is one of the equations used in the normal development of the Boltzmann factor in statistical mechanics and since the other relations are also unaltered, the normal results apply and the Boltzmann factor is $\exp(-W_m\beta)$. Likewise the partition function and its relation to F, U, S, and C_H is unaltered. The statistical-mechanical results of Sec. III and Figs. 1 and 2 then all apply, with the addition that the W of that section for nuclei of moment μ and spin I becomes $W = |\mu H/I|$. Since in this case $U = -\mathbf{M} \cdot \boldsymbol{\mathcal{H}}$, the enthalpy $H = U'$ vanishes identically and is represented by the horizontal axis of Fig. 2.

If, on the other hand, U' is taken as the internal energy, the fundamental thermodynamic relation is given by Eq. (11) instead of Eq. (12) and from Eq. (10) the previous quantity U becomes the enthalpy H'. Other thermodynamic relations and definitions follow in the usual way. However, from a statistical mechanics point of view the situation is more complicated. No longer does Eq. (13) hold, so the usual derivation of the Boltzmann factor in statistical mechanics no longer applies. If the derivation is suitably modified, the result is that the Boltzmann factor is $\exp[-(W_m' - \boldsymbol{\mu}_m \cdot \boldsymbol{\mathcal{H}})\beta]$, as of course it should be from the simpler approach of the preceding paragraph. If the sum of the Boltzmann factors is taken as the partition function Z_μ', it is immediately apparent by carrying out the differentiation that $-N(\partial/\partial\beta)(\ln Z')$ gives H' or U, and not U'. Likewise G' and not A' equals $-(N/\beta)\ln Z'$. From these, the other thermodynamic relations may be found. If U', H', S, and C_H are plotted as functions of the pressure, the results are exactly the same as Figs. 1 and 2 except that U is replaced by H' and H by U'. The latter step shows that U' vanishes, as is indeed reasonable since W_m also vanishes for a perfect paramagnetic nucleus in a magnetic field, since the mechanical work required to reorient a permanent magnet in a field is just exactly equal to the work that is done on the battery that maintains the current for the field. With these curves for the thermodynamical functions, $(\partial S/\partial U')_M$ is indeterminate; however, the temperature may be determined thermodynamically from Eq. (2). For a given physical system, the temperature determined in this way from Eq. (2) is clearly the same as from Eq. (1) with the definition of U used in the first part of this appendix.