Spin Temperature

(Seminar)

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Absolute temperature is in general positive value. Last definition of temperature is based on the second law of thermodynamics and a system with a finite number of energy levels or upper limit of energy the absolute temperature can be negative. 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. At negative temperature systems posses more energy than at positive temperature so we can define that negative temperatures are hotter than positive. The statistical mechanics of such systems are discussed and the results are applied to nuclear spin systems.

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1. Introduction

The temperature of a system, consisting of a large number of particles, may conveniently be regarded as a parameter which determines the distribution of energy among the particles. When the temperature is small the probability of finding a particle with large energy is also small. In certain systems it can happen that the probability of a large energy is greater than the probability of a small energy; the temperature may then be regarded as negative.

Negative temperature was first theoretically studied for spin systems in magnetic field, which has been experimentally realized using pure Lithium Fluoride crystals (LiF) [1],[2],[3]. The temperature of such a system is usually called the "spin temperature" to distinguish it from the temperature of the solid, in which the spins are embedded, which, as we shall see, may be quite different.

The concept of absolute temperature is based on the second law of thermodynamics. In general absolute temperatures can only be positive values. However, in a finite number of energy levels, the absolute temperature can be negative values, theoretically and experimentally. Although it may be impossible to reach absolute zero temperature, this does not preclude the possibility that negative absolute temperatures exist. The inability to attain absolute zero may result from the impossibility of a transition from positive to negative absolute temperatures. However we will see that negative temperature is not obtained from cooling below 0 °K, as someone may think.

Of course 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 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.

Before we start studying systems with negative temperature, we must first define what the temperature is. In the past, scientists developed various quantitative definitions of temperature. First definition was based on linear expansion liquids (glass thermometers). But because expansion has not been perfectly linear, scientists developed (19'th century) new definition of temperature, which says that temperature of an ideal gas is the average kinetic energy of random translation motion per molecule.

As we will see in next chapter, the last definition of temperature $T$ is that it expresses a relationship between the change in the internal energy, $U$, and the change in the entropy, $S$, of a system:

$$
\frac{1}{T} = \frac{\delta S}{\delta U}.
$$

(1)
1.1 Temperature

To get things started, we need a clear definition of "temperature". Our intuitive notion is that two systems in thermal contact should exchange no heat, on average, if and only if they are at the same temperature. Let's call the two systems $S_1$ and $S_2$. The combined system, treating $S_1$ and $S_2$ together, can be $S_3$. The important question, consideration of which will lead us to a useful quantitative definition of temperature, is "How will the energy of $S_3$ be distributed between $S_1$ and $S_2$"? [4].

With a total internal energy $U_3$, system has many possible internal states (microstates). The atoms of $S_3$ can share the total energy in many ways. Let's say there are $N$ different states. Each state corresponds to a particular division of the total energy in the two subsystems $S_1$ and $S_2$. Many microstates can correspond to the same division, $U_1$ in $S_1$ and $U_2$ in $S_2$. A simple counting argument tells us that only one particular division of the energy will occur with any significant probability [5]. It's the one with the overwhelmingly largest number of microstates for the total system $S_3$. That number, $N_3(U_1, U_2)$ is just the product of the number of states allowed in each subsystem

$$N_3(U_1, U_2) = N_1(U_1) \cdot N_2(U_2). \quad (2)$$

Since $U_1 + U_2 = U_3$, $N(U_1, U_2)$ reaches a maximum when $N_1 \cdot N_2$ is stationary with respect to variations of $U_1$ and $U_2$ subject to the total energy constraint. That is,

$$\delta [N_3(U_1, U_2)] = \delta [N_1(U_1) \cdot N_2(U_2)] = 0 \quad \text{and} \quad \delta U_1 + \delta U_2 = 0.$$

This leads to the condition:

$$\frac{\partial \ln(N_1(U_1))}{\partial U_1} = \frac{\partial \ln(N_2(U_2))}{\partial U_2}. \quad (3)$$

We prefer to frame the question in terms of the logarithm of the number of microstates $N$, and call this the entropy. In statistical mechanic, entropy is defined as:

$$S = k_b \ln( N(U) )$$

and $k_b$ is the Boltzmann constant.

Since $S \propto \ln N$, we can easily see from the above that two systems are in equilibrium with one another when

$$\frac{\partial S_1}{\partial U_1} = \frac{\partial S_2}{\partial U_2}. \quad (4)$$

The rate of change of entropy, $S$, per unit change in energy, $U$, must be the same for both systems. Otherwise, energy will tend to flow from one subsystem to another as $S_3$ bounces randomly from one microstate to another, the total energy $U_3$ being constant, as the combined system moves towards a state of maximal total entropy. We define the temperature, $T$, by

$$\frac{1}{T} = \frac{\partial S}{\partial U}, \quad (5)$$

so that the equilibrium condition becomes the very simple $T_1 = T_2$. 


This statistical mechanical definition of temperature does in fact correspond to our intuitive notion of temperature for most systems. As long as \( \frac{\partial S}{\partial U} \) is always positive, \( T \) is always positive. For common situations, like a collection of free particles, or particles in a harmonic oscillator potential, adding energy always increases the number of available microstates, increasingly faster with increasing total energy. So temperature increases with increasing internal energy, from zero to positive infinity. But as we will see in next chapter, when system of elements in thermal equilibrium is such that each element of the system has an upper limit of possible energy, \( \frac{\partial S}{\partial U} \) can be negative and system can have negative temperature.

2. Negative Temperatures

2.1 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 function of \( U \) becomes negative, the temperature is negative since the temperature is related to:

\[
\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_X
\]

(6)

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 \( T dS \) and \( dU \).

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. 2.2 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 \( (\frac{\partial S}{\partial U})_X \). 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 number of microstates and 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 \( U \).

The maximum of the entropy curve discussed in the preceding paragraph corresponds to \( (\frac{\partial S}{\partial U})_X=0 \) and hence to infinite temperature. The region of negative \( (\frac{\partial S}{\partial U})_X \) corresponds
to negative temperature. Hence it is apparent that in cooling from negative to positive
temperature such a system passes through $\pm \infty^\circ K$ instead of through absolute $0^\circ K$ (Fig. 1).

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. (6) is a consequence, 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. (6) 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.
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 $+0^\circ K, \ldots, +300^\circ K, \ldots, +\infty^\circ K, \ldots, -300^\circ K, \ldots, -0^\circ K$. "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 $+1000^\circ K$, for example, is intermediate between $+300^\circ K$ and $-300^\circ K$. 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 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.

![Diagram](image)

Fig. 2: In thermal contact heat flows from system with negative temperature to system with positive temperature and so we can define that system with negative temperature is hotter than system with positive temperature.
2.2 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.

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 $m$-th state for one element of the system, then in thermal equilibrium the number of elements in the $m$-th state is proportional to the Boltzmann factor $\exp(-W_m/k_bT)$. 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.

For simple example, let assume a system that can have two levels of energy, $E(hi)$ and $E(lo)$: the particles either have energy or they have not. When the system is heated, energy is transferred to it; the particles must somehow accommodate this energy. In this model, this can only happen if some change from a low to a high energy state.

The number of particles that will be on the $i$-th energy level is given as we mentioned by the Boltzmann distribution:

\[
N(i) = C \cdot \exp \left( -\frac{E(i)}{k_bT} \right) \tag{7}
\]

where:

- $C$ a constant (at a given temperature)
- $N(i)$ the number of particles with energy $E(i)$
- $E(i)$ is the energy portion
- $k_b$ the Boltzmann constant
- $T$ absolute temperature

For only two levels of energy the ratio of the population of these levels is:

\[
\frac{N(hi)}{N(lo)} = \exp \left( -\frac{\Delta E}{k_bT} \right) \tag{8}
\]
where

$$\Delta E = E(hi) - E(lo) \quad (9)$$

Solving this equation for \( T \):

$$T = \frac{-\Delta E / k_B}{\ln[N(hi) / N(lo)]} \quad (10)$$

For bodies at thermal equilibrium \( N(lo) > N(hi) \), it is not possible to populate the high energy level more by adding heat to a body. Thus for usual systems the logarithm is negative and temperature is positive. If heat is added, more and more particles change from the low energy level to the high energy level. The number of particle with high energy, \( N(hi) \), grows and \( N(lo) \) decreases so the logarithm becomes less negative and temperature rises. The energy of the whole ensemble rises because now there are more particles on the high energy level.

On the other hand, if energy is withdrawn from a body, \( E(lo) \), the low energy level, is populated at the cost of \( E(hi) \). The value of the logarithm becomes more and more negative and temperature goes towards zero.

If both levels are equally populated, \( N(hi) = N(lo) \) and the logarithm vanishes, so that

$$\lim_{N(hi)\to N(lo)} \left[ \frac{-\Delta E / k_B}{\ln[N(hi) / N(lo)]} \right] = \infty \quad (11)$$

The value of the temperature becomes infinite. Since number of particles are always finite, only an finite amount of energy is needed to get infinite temperature in this model. Infinite temperature cannot be reached anyway by heating, although not because of the energy needed, but because heat flows from high temperature to low temperature. To heat a body, a hotter body is required.

As soon as the high energy level is populated more that the low energy one, we have negative absolute temperature. The formula (10) shows that a state of matter to which negative absolute temperature can be attributed has more energy than the states at usual temperatures, because more particles are at high energy level than at low energy level. Thus one has to add energy to get negative absolute temperature. It has been emphasized that such states cannot be reached by adding heat to a body.

To get a rough idea of the subject, let us look at magnetism due to electron spin. Each electron can have only two orientations in an external magnetic field, namely parallel to the field and antiparallel to it. If an external field is applied, the energy of the parallel state is lowered and energy of the antiparallel state goes up. Population of high and low energy state can be described also with infinite and negative temperature as we see on Fig. 3.

Looking at the limits of this two level model may help to elucidate further the concept of temperature. First, each level must be populated enough to avoid random fluctuations of particle number. Keep in mind that the systems are dynamic, particles exchanging energy continually. So the model fails when there are only a few particles on each level.
In the normal discussions 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 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 $H$ of the system can be expressed as:

$$ H = H_0 + H_{int} $$

(12)
where
\[ H_0 = \sum_{k=1}^{N} H_{0k} \] (13)

and \( H_{0k} \) is the portion of the Hamiltonian that depends only on the \( k \)th element of the system while \( H_{\text{int}} \) 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 \( H_{\text{int}} \) is comparable to or larger than that associated with \( H_0 \) as when \( H_{\text{int}} \) is small. On the other hand, the procedures are much more complicated in the former case and involve the complications of cooperative phenomena.

For this reason, the present discussion will be limited to cases where the average energy associated with \( H_0 \) is very large compared to that associated with \( H_{\text{int}} \). 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.

It will now be assumed for simplicity that the eigenstates of \( H_{0k} \) 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 \( H_{\text{int}} \) 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 energy of an element of the thermodynamic system and that the number of elements \( N \) is Avogadro's number.

With the foregoing assumptions, with \( \beta = 1/k_B T \), and with the normal procedure for summing a geometric series, the partition function \( Z \) [8] becomes:

\[
Z = \frac{\sinh(nW\beta/2)}{\sinh(W\beta/2)}
\]

(14)

Someone may ask, can we use Boltzmann distribution also at negative temperature. Answer is yes, because if we look a proof that in thermal equilibrium (when entropy reach maximum) distribution is Boltzmann, we see that we do not need assumption for positive temperature. Thus Partition function can be used at positive and at negative temperature.

From this, the internal energy \( U \) (taken as the sum of \( W_m \)) the entropy \( S \), and the specific heat \( C_V \) may readily be calculated with the result that
\[ U = \left( \frac{\partial [ \beta F ]}{\partial \beta} \right)_x = -\frac{NW}{2} \left[ n \coth \frac{nW\beta}{2} - \coth \frac{W\beta}{2} \right], \]

\[ S = k\beta^2 \left( \frac{\partial F}{\partial \beta} \right)_x = R \ln \left[ \left( \sinh \frac{nW\beta}{2} \right) \left( \sinh \frac{W\beta}{2} \right)^{-1} \right] - \frac{RW\beta}{2} \left[ n \coth \frac{nW\beta}{2} - \coth \frac{W\beta}{2} \right], \]

\[ C_x = -k\beta^2 \left( \frac{\partial^2 [ \beta F ]}{\partial \beta^2} \right)_x = R \left( \frac{W\beta}{2} \right)^2 \left[ \csc h^2 \frac{W\beta}{2} - n^2 \csc h^2 \frac{nW\beta}{2} \right] \quad (15) \]

Numerical values for these expressions have been evaluated in the case of \( n=4 \) and the results are plotted in Figs. 5. Figure 4 shows the entropy as a function of the internal energy. As discussed qualitatively in Sec. 2.1, 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. (6), the region of negative slope for this curve corresponds to negative temperature.

![Graph showing entropy as a function of internal energy.](image)

Fig. 4. The entropy is plotted as a function of the internal energy for a system of which each element has four equally spaced energy levels.
In Fig. 5 the internal energy, the entropy and the specific heat are plotted as functions of \(-1/T\) measured in units of \(k/W\) for the same system as Fig. 4. As discussed in Sec. 2.1 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 specific heat \(C_x\).

Fig. 5. The internal energy, the entropy and the specific heat are plotted as functions of \(-1/T\). As discussed in Sec. 2.1, 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 \(+0^\circ K\) and \(-0^\circ K\) 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 \(\infty^\circ K\) drops to zero for a different reason: the temperature changes greatly in the vicinity of \(\infty^\circ K\) for only a small change in configuration and internal energy.

It should be noted that \(+0^\circ K\) and \(-0^\circ K\) 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 \(+0^\circ K\) since it can give up no more of its energy. It cannot become hotter than \(-0^\circ K\) because it can absorb no more energy.
3. Nuclear spin systems

It has been recognized that spin systems often form thermodynamic systems which can appropriately be described by a temperature. However, almost all the doubts 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.

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. 2.2, 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. So energy levels must be equidistant among each other as we mentioned in precedent section. Zeeman Effect equally splits energy levels of spins in external magnetic field but spins interact among themselves and because of the influence of others effects (quadrupole moment, effects of electrons on nucleus), we have local magnetic field at every nucleus and we don’t have equally separated energy levels. In strong external magnetic field we can neglect those effects although we do not need perfectly equidistant levels because of the uncertainty principle. Transitions can accrue between levels with unequal energy differences thus probability is greatly decreases when this difference is large.

This spin-spin process is the one often characterized by the relaxation time designated $T_2$, 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 $T_1$. 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.

It has been 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 [10]. 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.

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. 2.2 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. 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. 2.2 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.

As discussed in Sec. 2.2, if the energy $W_m$ of the magnetic moment in the field $H$ is taken to be the spectroscopic energy and if $U$ is taken to be the sum of $W_m$ over one mole, then

$$TdS=dU+M\cdot dH$$  \hspace{1cm} (16)$$

and$$T=(\partial S/\partial U)_{H}^{-1}$$  \hspace{1cm} (17)$$
as in Eq. (6). The statistical mechanical results of Sec. 2.2 and Figs. 4 and 5 all apply to the nuclear spin case with the addition that, for nuclei of moment $\mu$ and spin $I$, the $W$ of Sec. 2.2 becomes $W=|\mu H/I|$.

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

The double nuclear spin systems were studied in a very pure crystal of $LiF$ [2]. In these experiments were 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. It was 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 [2]. All results of these experiments are completely consistent with the interpretations of the present paper.

4. Conclusion

In any thermodynamic system for which \( \left( \frac{\partial S}{\partial U} \right)_X \) may be negative, the temperature of the system may be negative by Eqs. (6). 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.

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-temperature systems are intrinsically amplifiers just as ordinary resistance networks at positive temperatures are attenuators. Example are 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. 3, 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.

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 \( \left( \frac{\partial S}{\partial U} \right)_X \) is 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 \( \left( \frac{\partial S}{\partial U} \right)_X \) is 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.

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.
5. Sources