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Negative Absolute Temperatures: Plausible or Impossible – A Clarification

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Abstract—Negative absolute temperatures were shown to be achievable in the nuclear spin systems in a pure LiF crystal in 1950's. The nuclear spin system can adequately be considered as a thermodynamic subsystem describable by a temperature, and the various nuclear spins must interact among themselves in such a way that thermodynamic equilibrium is achieved rapidly. However, these findings and interpretations might lead to a misperceived generalization of the idea to, for instance, in the same pure crystal, the lattice subsystem capable of lattice vibrations (phonons) with a stable equilibrium distribution of the vibrations. The lattice subsystem can be assigned a separate temperature. Only the latter system is a thermal subsystem capable of heat transfer for which achievability of negative absolute temperatures is an impossibility. This article attempts to clarify the thermodynamics of the negative absolute temperatures that may be plausible or impossible for subsystem constructs in the same material.

Index Terms—Negative absolute temperature, thermodynamics at negative temperatures, nuclear spin subsystem, phonon subsystem, pure LiF crystal.

I INTRODUCTION

The necessary condition for the concept of temperature to be defined is the following postulate of thermodynamics. "In processes for which there is no net effect on the environment, all systems (simple and composite) with given internal restraints will change in such a way that they approach one and only one stable equilibrium state for each "subsystem". In the limiting condition, the entire system is said to be at equilibrium [1]." In order to appropriately assign a temperature to a subsystem the following conditions must be met [2]:

(1) The elements (i.e. particles) of the subsystem must reach their stable thermodynamic equilibrium distribution among themselves fast.
(2) The approach to the thermodynamic equilibrium between the subsystem and the rest of the composite system must take place slowly enough to enable satisfactory measurements to be made.

The concept of subsystem deserves clarification for the rest of the discussions in the report. A subsystem is a spatial and/or functional subset of a composite (or complex) system. For example, in pure crystals the atomic species form a lattice subsystem capable of lattice vibrations (phonons) with a stable equilibrium distribution of the vibrations, and hence the lattice subsystem can be assigned a temperature. The same atomic species also form a nuclear spin subsystem in which the magnetic spins are capable of aligning in any given external magnetic field with a stable equilibrium distribution of alignments, and hence can be assigned a separate temperature.

The fundamental property relationship for systems capable of pressure-volume changes only is given by [3]:

$$dU = TdS - PdV \tag{1}$$

For magnetic spin systems capable of magnetic energy exchange only, the fundamental property relationship is given by [4]:

$$dU = TdS - \vec{M}.d\vec{H} \tag{2}$$

where M is the magnetic moment of the nuclear spins, and H is the external magnetic field strength.

The thermodynamic temperature is, therefore, defined for the former system from Eqn. 1 as,

$$T = (\partial U/\partial S)_V \tag{3}$$

and for the latter system from Eqn. 2 as,

$$T = (\partial U/\partial S)_H \tag{4}$$

The sign of thermodynamic temperature, that is, of absolute temperature depends on the sign of $(\partial U/\partial S)_x$. In classical thermodynamics $(\partial U/\partial S)_x > 0$ is implicitly assumed for all the physical phenomena, and indeed it is the case for almost all of the physical processes.

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In this article the theoretical possibilities, and the practical situations that $(\partial U/\partial S)_x < 0$ are discussed. For instance, a nuclear spin system in a pure LiF crystal can adequately be considered as a thermodynamic subsystem describable by a temperature, and the various nuclear spins must interact among themselves in such a way that thermodynamic equilibrium is achieved rapidly, and the plausibility of negative absolute of such a defined temperature arises in experimental setups. However, the findings and interpretations that belong to the nuclear spin subsystem might lead to a misperceived generalization of the idea to the lattice subsystem capable of lattice vibrations (phonons) with a stable equilibrium distribution of the vibrations in the same pure crystal. The lattice subsystem can be assigned a separate temperature. Only the latter system is capable of heat transfer for which achievability of negative absolute temperatures is an impossibility. This article attempts to clarify the thermodynamics of the negative absolute temperatures that may be plausible or impossible for subsystem constructs in the same material, as a review.

II THERMODYNAMIC TEMPERATURE SCALE

The postulate of thermodynamics “if the sets of systems A, B and A, C each have no heat interaction when connected across nonadiabatic walls, there will be no heat interaction if systems B and C are also so connected [1]” is referred to as the zeroth law of thermodynamics. This law puts the concept of temperature on a firm basis by the definition that all the systems which have no heat interaction between any two pairs when in thermal contact, are in thermal equilibrium, and have the same temperature. If they are not in thermal equilibrium they have different temperatures, and heat interaction takes place.

The second law of thermodynamics is a consequence of the observed fact that all spontaneous processes proceed in such a way that the entropy of the universe never decreases. The corollary of this statement is that the heat will be transferred from the system with a higher value of $(\partial U/\partial S)_x$ to the lower one, since by the heat transfer, an equivalent amount of change of internal energy in the lower value $(\partial U/\partial S)_x$ system brings about a higher increase in the system entropy than the decrease in the entropy of the higher value $(\partial U/\partial S)_x$ system, and hence overall the entropy of the universe increases. This is equivalent to the expression that the rate of change of entropy with internal energy is higher for lower values of $(\partial U/\partial S)_x$.

The thermodynamic temperature scale is so selected that heat spontaneously flows from the system with the higher algebraic value of temperature to the lower one. This selection is in conformity with the definition of temperature by the fundamental property relationship (Eqn. 3, 4). Therefore, heat is transferred from higher value of $T=(\partial U/\partial S)_x$ to the lower, or from hotter to the cooler system.

The consequences of this result are also seen in the Carnot heat engine, a reversible cyclic process for heat-work conversion, and the second law of thermodynamics is rephrased as:

1. The Kelvin-Planck statement: It is impossible to construct a cyclic process whose only effect is to absorb heat at a single temperature and convert it to an equivalent amount of work.
2. The Clausius statement: It is impossible to construct a cyclic process whose only effect is to transfer heat from a lower temperature to a higher one. (This statement can be derived from the first one.)

The thermodynamic temperature scale so defined has the lower limit as “+0”, which constitutes the third law of thermodynamics that the entropy of perfect crystals at absolute zero of temperature are zero. At absolute zero of temperature there is only one possible microstate of atomic arrangements, and hence entropy defined by Eqn. 5 is zero.

$$S_i = k \ln \Omega_i \tag{5}$$

where k is the Boltzmann constant, Ω_i is the microstates in the i macrostate.

However, there is no upper limit to the thermodynamic temperature. Increasing the internal energy of a system by transferring energy in various ways, will increase the number of available energy levels for the particles of the system, that is, the number of higher energy level microstates will increase, and from Eqn. 5 the entropy of the system increases. Therefore, entropy is a monotonically increasing function of internal energy and the absolute temperature always positive.

The Maxwell-Boltzmann distribution of particles on energy levels is given by [5],

$$n_i/N = e^{-\varepsilon_i/kT}/P_{MB} \tag{6}$$

where n_i is the number of particles at the ε_i energy level, and P_{MB} is the Maxwell-Boltzmann partition function. Eqn. 6 can be used to express the quotient of the number of particles between two subsequent energy levels as follows [2],

$$n_2/n_1 = e^{-(\varepsilon_2-\varepsilon_1)/kT} \tag{7}$$

Eqn. 7 states that as the higher energy level (ε_2) particles increases (n_2), temperature increases, but n_2 is always less than n_1 for finite temperatures. In other words, no energy level ever gets more populated than the one below it that is, n_2/n_1 is always less than unity for positive finite temperatures. As the internal energy increases the number of particles populating higher energy levels and the temperature increases indefinitely. Matter at temperatures higher than 10 million degrees would radiate away its energy in a time as short as the time taken by light to travel from its center to the surface. It is practically impossible to heat matter to a temperature higher than this for any appreciable time except in regions of high density such as the centers of stars. Above 10 million degrees empty space behaves like a wet sponge, having an inexhaustible capacity for absorbing energy without greatly increasing in temperature [6].

At T=∞, $n_2=n_1$ which means that all energy levels are equally populated, and the entropy attains its maximum value of $S_{max}=Nk\ln P$ from Eqn. 6. The rate of change of S with U decreases as T increases by the definition given by Eqn. 3. At very high temperatures the increase in internal energy alters entropy only slightly, with the limiting case of T=∞ in which the change in entropy is zero with increasing temperature. At T=0, $n_2/n_1=0$ which implies that the only possible distribution is the lowest possible energy level is populated by all the particles as discussed above where entropy is assigned the value of zero.

III THE POSSIBILITY OF NEGATIVE ABSOLUTE TEMPERATURES

As indicated by Eqn. 3 or 4, thermodynamically the only requirement for the existence of a negative absolute temperature is the decrease of entropy by the increasing internal energy,

$$T=(\partial U/\partial S)_X<0 \tag{8}$$

The conditions and consequences of this to be realized are discussed below. From Eqn. 7 it can be seen that if T<0 then $n_2>n_1$, that is, higher energy levels are more populated than the lower energy levels. The only physically possible case for which this can be achieved is the existence of a finite number of energy levels for a given system or subsystem. The simplest system, the case can be described, comprises N particles, and two available energy levels 0 and ε. The possible distributions of particles between these two energy levels is shown in Fig. 1.

In Fig. 1 (a) all the particles populate the zero (the lower) energy level which is a state of minimum internal energy, and minimum entropy (disorder), in fact the situation correspond to T=0. If the internal energy of the system is increased as in Fig. 1(b) the number of particles populating the higher energy level and hence the entropy increases. Therefore, $T=(\partial U/\partial S)_x$ is positive as also indicated by Eqn. 7 for $n_2/n_1<1$. When the internal energy of the system is further increased the number of particles populating the two energy levels becomes equal ($n_2=n_1$) as in Fig. 1(c), and entropy reaches its maximum value. $(\partial S/\partial U)_x$ is zero since entropy is maximized at that internal energy, and $T=(\partial U/\partial S)_x=\infty$ (for $n_2/n_1=1$, T=∞ from Eqn. 7).

When the internal energy is further increased the number of particles occupying the higher energy level surpasses the number in the lower energy level as in Fig.1(d). The order and hence the entropy decrease as the internal energy increases which is the condition for the existence of a negative absolute temperature. Again Eqn. 7 yields the same result of negative temperature for $n_2/n_1>1$. When the system reaches its maximum attainable internal energy all the particles reside in the upper energy level, a maximum order, and hence minimum (zero) entropy situation. This corresponds to $n_2/n_1=\infty$ and the temperature from Eqn. 7 is $T=0^-$ (minus zero).

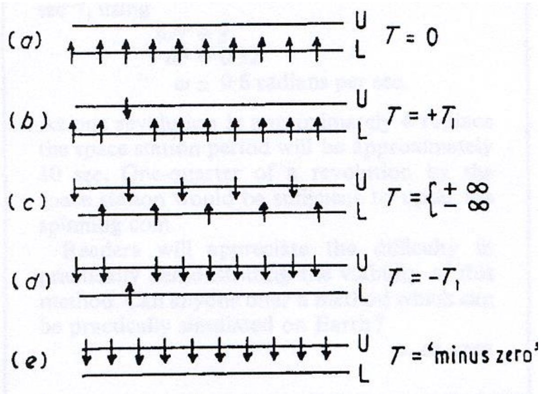

Figure 1. Distribution of spins between two possible energy states [7].

The variation of entropy and temperature with internal energy in a system with two possible energy levels are shown in Fig. 2. Also, the change of entropy with internal energy for a system with no upper energy level limit is shown. As described previously, for the case of two possible energy levels for the system the entropy increases from a minimum (zero) value monotonically with internal energy (positive temperatures), passes through a maximum (infinite temperature), and beyond entropy decreases monotonically with increasing internal energy from (negative temperatures from -∞ to -0). Finally, the entropy again is reduced to its minimum value (zero).

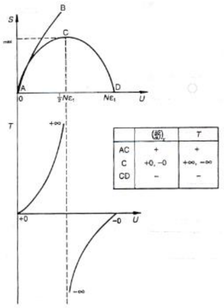

Figure 2. Variation of internal energy, entropy, and temperature in a system with two possible energy levels [8].

The temperature scale range including negative values varies from cold to hot in such a way that the minimum temperature is +0 K (coldest), it increases through positive values (e.g. +300 K) to +∞ K, swings to -∞ K, passes through negative values (e.g. –300 K), reaching –0 K the highest temperature (hottest). Therefore, negative temperatures are hotter than any positive temperature including infinite temperature in the sense that heat would be transferred from the systems at negative temperatures to the systems at positive temperatures.

If the thermodynamic temperature scale has been defined as –1/T, the algebraic order and the order from cold to hot would be identical [4]. The plot of internal energy, entropy, and specific heat as a function of –1/T, for four available energy levels for nuclear spin systems, is shown in Fig. 3. The minimum and the coldest of the scale is -∞ (corresponds to +0 K), passes through minus values (corresponds to positive absolute temperatures) and a zero point –0 and +0 (corresponds to -∞ K, and +∞ K), and passes through plus values (corresponds to negative absolute temperatures), and reaches asymptotically to +∞ the hottest temperature (corresponds to –0 K).

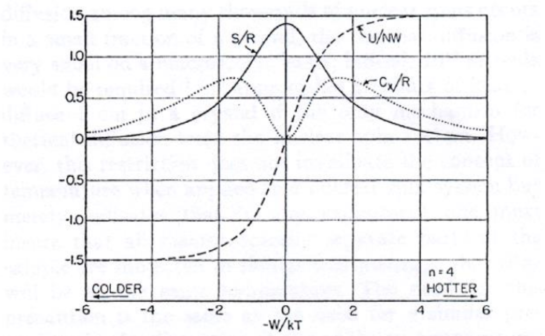

Figure 3. The internal energy, the entropy and the specific heat are plotted as a function of -1/T measured in units of k/W [2].

IV PLAUSIBILITY OF NEGATIVE ABSOLUTE TEMPERATURES

The necessary and sufficient conditions for a thermodynamic subsystem to be capable of negative absolute temperatures are [4]:

(1) There must be an upper limit to the possible energy levels allowed of the thermodynamic subsystem.

(2) The elements of the thermodynamic subsystem must come to thermodynamic equilibrium among themselves rapidly.

(3) The subsystem must come to equilibrium with its surroundings slowly enough to enable measurements to be made.

Pound [9-11], Purcell [11], and Ramsey [10,12] studied experimentally the various properties of the nuclear spin systems in a pure LiF crystal including the demonstration of negative absolute temperatures. In order that the nuclear spin system can adequately be considered as a thermodynamic subsystem describable by a temperature, the various nuclear spins must interact among themselves in such a way that thermodynamic equilibrium is achieved rapidly. This occurs by virtue of 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 potential energy relative to an external field increased while the other's decreased by the same amount, as is also the case of collisions between molecules in a gas. This spin-spin process is characterized by the relaxation time of the order 10^{-5} seconds. It is this process which brings the nuclear 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. The foregoing discussion justifies the assignment of a thermodynamic temperature to the nuclear spin systems.

In the LiF crystals there are two separate sets of nuclear spins and these "magnets" can have four different energy levels when in a magnetic field. The nuclear magnets may align themselves either in the same direction as the field, or opposite the direction of the field, a state of higher energy as shown in Fig. 4.

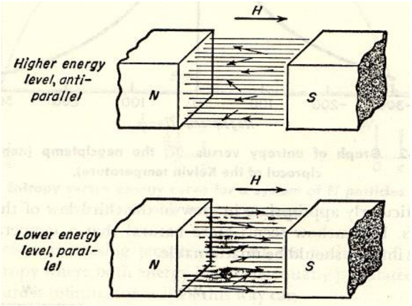

Figure 4. Nuclear magnets pointing opposite the magnetic field (upper) have more energy than those in the same direction (lower) [2].

Under ordinary circumstances, there are fewer nuclear magnets in the upper energy level than in the lower. The nuclear spin subsystem is in equilibrium with itself and also with the rest of the lattice, so that both the subsystem and its surroundings have the same positive temperature.

Purcell [11] and Pound [9, 11] in their experimental study quickly reversed the direction of the external field, that the nuclear magnets are unable to follow the change of direction of the field. The larger number of magnets which were formerly in the direction of the field (and in the lower energy level) are oriented opposite to the field and therefore in the upper energy level. The few nuclear magnets formerly in the upper state are now in the lower one. There has been a population inversion. After a small and rapid reorientation, the nuclear magnets attain a Boltzmann distribution of the higher energy state. As described previously the temperature of the nuclear spin subsystem is negative.

This temperature is not to be confused with the lattice temperature of the Boltzmann distribution of phonon energy (lattice vibrations) which is described by a different temperature. The interaction of these two separate subsystems, that is, spin-lattice interaction is characterized by a relaxation time of several minutes (5 to 30 minutes). Therefore, there is sufficient time for spin-spin subsystem temperature measurements. The nuclear spin subsystem cools off and comes to equilibrium with the rest of the lattice and regains its former positive temperature.

The population inversion is followed up by a beam of microwave passed through the crystal. The beam is attenuated when more of the nuclear spins occupy the lower energy level and excited to the upper. However, when the higher energy level is more populated the beam is amplified by the nuclei lowered in energy level emitting radiation in phase with the radiation that forced it down (microwave amplification through stimulated emission of radiation).

V THERMODYNAMICS AT NEGATIVE ABSOLUTE TEMPERATURES

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 by the ratio of heats absorbed and rejected. However, no means is available by which a Carnot cycle can be operated between positive and negative temperatures. By adiabatic magnetization of a spin system the temperature can be raised as high on the positive scale as desired, but it cannot be made to cross over to negative values.

Equally valid at positive and negative temperatures the efficiency of a Carnot engine is given by

$$\eta = 1 + (Q_L/Q_H) = 1 - (T_L/T_H) \tag{9}$$

where L corresponds to the reservoir at lower temperature while H corresponds to the higher temperature reservoir. For negative temperature reservoirs $T_L/T_H > 1$, and the η is negative and can be very large. 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, if such a Carnot cycle is operated in the opposite direction work is produced while heat is transferred from a colder reservoir to hotter one. If the heat transferred to the hotter reservoir by this cycle is allowed to flow back to the colder reservoir, the net effect of the overall cyclic process is to absorb heat at a single temperature and convert it to an equivalent amount of work. This is in violation of the Kelvin-Planck statement of the second law of thermodynamics. Therefore, the Kelvin-Planck statement of the second law must be modified to:

It is impossible to construct a cyclic process whose only effect is (1) to absorb heat at a from a positive temperature reservoir with the performance of an equivalent amount of work, (2) to reject heat into a negative temperature reservoir with the corresponding work being done on the system.

Nevertheless, the Clausius statement is unaltered. Besides, such a process is not in contradiction to the principle of increasing entropy for spontaneous changes, since as is apparent from Fig. 2 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). The statement that the entropy of a system is a state function and the entropy of an isolated system never decreases.

VI CONCLUSIONS

In any thermodynamic system for which $(\partial U/\partial S)_x < 0$, the temperature of the system is negative. If there is an upper limit to the energy levels that can be attained by the elements of the system, $(\partial U/\partial S)_x$ becomes less than zero when the internal energy of the system is increased over a certain value. The negative absolute temperatures are hotter than infinite temperature and hence all the positive temperatures. The thermodynamic temperature scale including negative temperatures changes from the coldest temperature +0 K, through positive temperatures to +∞, then to -∞, through negative values of temperatures to –0 K the hottest temperature.

The negative absolute temperatures were first physically achieved by Pound and Purcell [9, 11], in nuclear spin subsystems of a LiF crystal capable of attaining only four energy levels. The crystal was placed in an external magnetic field which is quickly reversed to render most of the nuclear spins to the higher energy levels. The spin-spin relaxation time is about 10^{-5} seconds while spin-lattice relaxation time is above 5 minutes allowing measurements of the reversed population of nuclear spin energy levels in the external magnetic field, and hence the confirmation of negative absolute temperatures by microwave amplification passed through the crystal.

However, these findings and interpretations might lead to a misperceived generalization of the idea to, for instance, in the same pure crystal, the lattice subsystem capable of lattice vibrations (phonons) with a stable equilibrium distribution of the vibrations. The lattice subsystem can be assigned a separate temperature, which is a thermal subsystem capable of heat transfer for which achievability of negative absolute temperatures is an impossibility.

REFERENCES

[1] Modell M., Reid R. C., "Thermodynamics and Its Applications", second ed., Prentice-Hall, Inc., Englewood Cliffs, N.J., 1983.

[2] Zemansky M. W., "Temperatures Very Low and Very High", Dover Publications, Inc., New York, 1964.

[3] Balzhiser R. E., Samuels M. R., Eliassen J. D., "Chemical Engineering Thermodynamics, The Study of Energy, Entropy, and Equilibrium", Prentice-Hall, Inc., Englewood Cliffs, N.J., 1972.

[4] Ramsey N. F., Thermodynamics and Statistical Mechanics at Negative Absolute Temperatures, Physical Review, **103**, 20-28, 1956.

[5] DeHoff R. T., "Thermodynamics in Materials Science", McGraw-Hill, Inc., New York, 1993.

[6] Dyson F. J., What is Heat?, Scientific American, September, 58-63,1954.

[7] Lowell J., Negative Absolute Temperatures, Physics Education, **2**, 154-155, 1967.

[8] Wisniak J., Negative Absolute Temperatures, a Novelty, Journal of Chemical Education, **77**, 4, 518-522, 2000.

[9] Pound R. V., Nuclear Spin Relaxation Times in Single Crystals of LiF, Physical Review, **81**, 156, 1951.

[10] Ramsey N. F., Pound R. V., Nuclear Audiofrequency Spectroscopy by Resonant Heating of the Nuclear Spin Systems, Physical Review, **81**, 278, 1951.

[11] Purcell E. M., Pound R. V., A Nuclear Spin System at Negative Temperature, Physical Review, **81**, 279, 1951.

[12] Ramsey N. F., Electron coupled interactions between nuclear spins in molecules Physical Review, 91: 303-307, 1953.

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