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Negative Absolute Temperatures

The concept of negative absolute temperatures, a matter of some initial controversy (1) only a few years ago, is now a regular topic in recent texts (2). I hope to show in this discussion how easily this concept may be accommodated by thermodynamics and elementary statistical mechanics in an aesthetically satisfying way.

Let us first consider phenomenologically a schematic system that can exhibit negative temperatures. Take an assembly of tiny magnetic moments (arising from nuclear spins), each moment considered localized at certain lattice sites (the positions of ^{7}Li nuclei in a LiF lattice for example). The moments can interact with each other but are isolated from the rest of the universe in the sense that the spin-spin relaxation time (a kind of half-life for an average spin to exist unaffected by interaction with any other nuclear spin) is very short compared to any other relaxation time, in particular that of spin-lattice interaction. In practice the spin-spin relaxation time is of the order of 10^{-5}–10^{-6} sec, while the spin-lattice relaxation time is of the order of 1–10 min. Only if we have this operative spin interaction can we discuss a spin temperature differing from the temperature of the lattice. The interaction with the lattice corresponds to leakage through vacuum bottle walls in ordinary calorimetry. It is also important to note that the spin system is decoupled thermally from the internal motions of the nucleons, for any nucleus would disintegrate at temperatures far

below those achieved by the nuclear spins even before these latter reached the negative absolute temperature range. Negative absolute temperatures are hotter than infinite temperature in the sense that if a spontaneous flow of heat is possible between a negative temperature system and a system at infinite temperature, it is the system at negative temperature that loses heat. We can express the fundamental equation of thermodynamics in the form:

$$dE = TdS - \sum_i x_i dX_i \qquad (1)$$

with E the energy and S the entropy. The pairs of variables (x_i, X_i) are conjugate state variables of mechanics, electromagnetic theory, etc. One is intensive and one is extensive in each pair such that they represent work terms in a reversible process (3), for example, PdV, or $-\gamma dA$, or $-B_e dM$ for compression, surface, and magnetic work (4) terms, respectively. (P is the pressure of the system, V its volume, γ its surface tension, A its surface area, M its total magnetic moment, and B_e the magnitude of the external magnetic force vector bathing it.) We note that the absolute temperature of a system is then given by:

$$T = \left(\frac{\partial E}{\partial S}\right)_{X_i} \qquad (2)$$

Consider now a large space enclosed by adiabatic walls subjected to an external magnetic force B_e and inside of which is suspended a box of nuclear spins. At time $t_0 - \Delta t$ (Fig. 1a) an equilibrium has been reached such that the net numbers of spins in the spin box aligned in the direction of the external field is represented by four upward pointing arrows. The net magnetic force in the enclosure B_{n_a} is $B_e + B_s$ where B_s is the added magnetic field strength due to the net field aligned spins. At time t_0 (Fig. 1b) the direction of the external magnetic force is reversed in a time interval much less than the spin-spin relaxation time. The way that this may be done is described in the literature (5–7) and need not detain us here. The net force field in the enclosure, B_{n_b}, is then $B_e - B_s$. At time $t_0 + \Delta t'$ where $\Delta t'$ is much less than the spin-lattice relaxation time, but greater than the spin-spin relaxation time (10^{-5} sec), some of the net spins which opposed the reversed external field at time t_0 have flipped and lined up with the new direction of the external field. This is shown schematically in Figure 1c by three upward pointing arrows and one downward pointing arrow. The net field in the enclosure becomes $B_{n_c} > B_{n_b}$. During the time $\Delta t'$ we may say phenomenologically that a catalyst in the spin box has
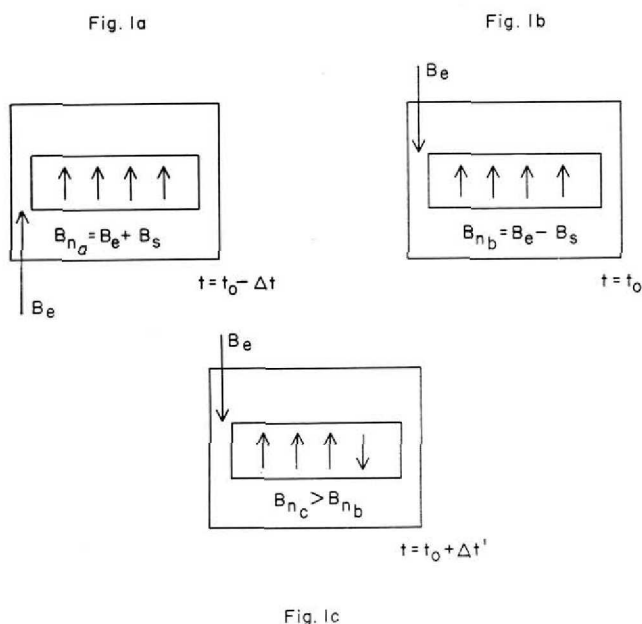
Fig. 1a

Fig. 1b

Fig. 1c

Figure 1a. Box of nuclear spins subjected to an external magnetic force B_e at time $t_0 - \Delta t$ which in b. at time t_0 is reversed such that the nuclear spins are partially relaxed in c. at time $t_0 + \Delta t'$.

reversed some spins such that $\Delta S_{sb} > 0$ since an isolated system (here the spin box denoted by subscript sb plus the field in the enclosure) must undergo an entropy increase and clearly part at least of this entropy increase is localized in the spin box due to the disordering process underway within it. In addition $\Delta E_{sb} < 0$ since some spins have fallen into lower energy states as they line up with the reversed external field. We see then, making changes infinitesimal that:

$$\left(\frac{\partial E_{sb}}{\partial S_{sb}}\right)_M < 0 \qquad (3)$$

This means by reference to eqn. (2) that the absolute (spin) temperature of the spin box must be negative. The energy lost by the spin box is taken up by the magnetic field of force in the large enclosure surrounding it since $B_{n_e} > B_{n_b}$. This magnetic field is at some positive absolute temperature and we see that the spin box at negative temperature loses energy (heat) to its surroundings (here, the net field in the region of the enclosure) at positive temperature. This means that negative absolute temperatures must be "hotter," not colder than positive absolute temperatures! More generally if we suppose that we have any isolated pair of systems, one at a negative absolute temperature T_n and one at a positive absolute temperature T_p exchanging a quantity of heat Q irreversibly (since T_n and T_p differ by a finite amount) the overall ΔS is:

$$\Delta S = \left(\frac{Q}{T_n} + \frac{(-Q)}{T_p}\right) > 0$$

or

$$Q\left(\frac{-1}{|T_n|} - \frac{1}{T_p}\right) > 0$$

meaning that Q must be negative and it is the system at T_n that gives off heat spontaneously.

A Statistical Mechanics View

Next let us consider the assembly of localized nuclei discussed above from the standpoint of statistical mechanics. We assume they all have nuclear spin $1/2$ such that only two magnetic energy levels exist in the presence of an external magnetic force field, B_e. Of the total of N nuclei, N_1 are in level one with $E_1 = 0$ and N_2 are in level two with $E_2 = \epsilon$. Denoting the fraction of nuclei in level i by X_i, the total magnetic energy is:

$$E = NX_2\epsilon \qquad (4)$$

while the entropy is given by:

$$S = k \ln \Omega_{cl}(\bar{N}_i) \qquad (5)$$

where $\Omega_{cl}(\bar{N}_i)$ is the total number of micro-ways the assembly can be realized as a function of the $\bar{N}_i$ which are the Boltzmann set of occupation numbers that maximize Ω_{cl}. The subscript cl indicates that uncorrected Boltzmann (classical) counting of states is used since the spins are localized (8). Actually

$$\Omega_{cl} = \sum_{N_i} W_{cl}(N_i) \qquad (6)$$

where the summation is carried out over all distributions of N nuclei having N_1 in level one and N_2 in level two, subject to the two restrictions:

$$N_1 + N_2 = N \qquad (7a)$$
$$N_2\epsilon = E \qquad (7b)$$

The a priori weight of any such distribution is $W_{cl}(N_i) = N!/(N_1!N_2!)$ since there are $N!$ ways of picking out the spin carriers to put them on their lattice sites and permutations of the like nuclei bearing the same energy level are not distinguishable. As we show below (since logarithms are involved) the sum in eqn. (6) can be replaced by the single term that is the maximum term. Thus:

$$\ln \Omega_{cl} \cong \ln W_{cl}(\bar{N}_i) \qquad (8)$$

where the $\bar{N}_i$ are the occupation numbers that maximize $\ln W_{cl}$ subject to the two restrictions (7a) and (7b). In order to be sure that our conditions (7a) and (7b) are satisfied we add to the ordinary condition of maximization:

$$d\ln W_{cl} = 0 \qquad (9)$$

the identity:

$$\alpha dN - \beta dE = 0 \qquad (10)$$

introducing thereby the Lagrangian parameters α and β. Using Stirling's approximation for the logarithm of the factorial of a large number:

$$\ln N! = N \ln N - N \qquad (11)$$

the sum of eqns. (9) and (10) becomes:

$$(-\ln \bar{N}_2 + \alpha - \beta\epsilon)\, d\bar{N}_2 + (\alpha - \ln \bar{N}_1)\, d\bar{N}_1 = 0 \qquad (12)$$

where now the variations of $d\bar{N}_2$ and $d\bar{N}_1$ are entirely independent. Since the only way for eqn. (12) to hold is for each coefficient to be identically zero we find:

$$\bar{N}_2 = e^\alpha e^{-\beta\epsilon} \qquad (13a)$$
$$\bar{N}_1 = e^\alpha \qquad (13b)$$

From eqn. (7a) we find:

$$e^\alpha = \frac{N}{1 + e^{-\beta\epsilon}} \qquad (14)$$

and from eqn. (7b) we have:

$$E = \frac{N\epsilon e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}} \qquad (15)$$

Substituting into eqn. (5) for the entropy and using Stirling's approximation once more we have

$$S = k[N \ln N - N\alpha + N_2\beta\epsilon] \qquad (16)$$

Use of eqn. (14) and eqn. (4) gives

$$S = kN \ln(1 + e^{-\beta\epsilon}) + k\beta E \qquad (17)$$

From eqn. (17) we can find at once the physical meaning of β by use of eqn. (2)

$$\left(\frac{\partial S}{\partial E}\right)_{N,M} = \frac{1}{T} = k\beta + k\frac{\partial}{\partial\beta}[N \ln(1 + e^{-\beta\epsilon}) + \beta E]\frac{\partial\beta}{\partial E} \qquad (18)$$

The second term on the right of eqn. (18) vanishes by virtue of eqn. (15) so that we find

$$\beta = \frac{1}{kT} \qquad (19)$$

Before going on we should justify our replacement of Ω_{cl} in eqn. (6) by the one maximum term $W_{cl}(\bar{N}_i)$ in the sum. Suppose that there are indeed m other values of $W_{cl}(N_i)$ essentially equal to $W_{cl}(\bar{N}_i)$ while

all the rest of the terms put together are negligible. Then:

$$S = k \ln \Omega_{el} = k \ln W_{el}(\bar{N}_i) + k \ln m \qquad (20)$$

and even if m were as large as N the added term in eqn. (20) is entirely negligible compared to the first term which as we see from eqn. (17) contains N as a factor.

Putting together the above results we have for the mole fractions of nuclei in the two levels:

$$X_2 = \frac{1}{1 + e^{\epsilon/kt}} \qquad (21a)$$

$$X_1 = 1 - X_2 = \frac{e^{\epsilon/kt}}{1 + e^{\epsilon/kt}} \qquad (21b)$$

while the entropy assumes a simple entropy of mixing form:

$$\frac{S}{Nk} = -X_1 \ln X_1 - X_2 \ln X_2$$

$$= -\left\{ \left(1 - \frac{E}{N\epsilon}\right) \ln \left(1 - \frac{E}{N\epsilon}\right) + \left(\frac{E}{N\epsilon}\right) \ln \left(\frac{E}{N\epsilon}\right) \right\} \quad (22)$$

Hence

$$\left(\frac{\partial S}{\partial E}\right) = \frac{1}{T} = \frac{-k}{\epsilon} \ln \left(\frac{E/N\epsilon}{1 - [E/N\epsilon]}\right) = \frac{-k}{\epsilon} \ln \left(\frac{X_2}{X_1}\right) \quad (23)$$

For $X_2 > X_1$, which means more nuclei in the higher energy state than in the lower energy state, the absolute temperature of the spin system is negative. Negative temperatures are exhibited by those assemblies whose energy level populations have been inverted. This is entirely in accord with our previous discussion. In Figure 2 (S/Nk) is plotted against $E/N\epsilon = X_2$. There is a single maximum in S at $T = \pm \infty$ where $E = N\epsilon/2$ corresponds to equal occupancy of the two energy levels. For energies greater than this amount $X_2 > X_1$, and the entropy decreases as the energy increases corresponding to the negative temperature region. Note in particular that $T = +\infty$ is coincident with $T = -\infty$ since both these temperatures give identical nuclear distributions and identical values for all the thermodynamic properties of the spin system. Temperatures of minus a finite number are hotter than $T = -\infty$, and the temperature of zero at the far limit of
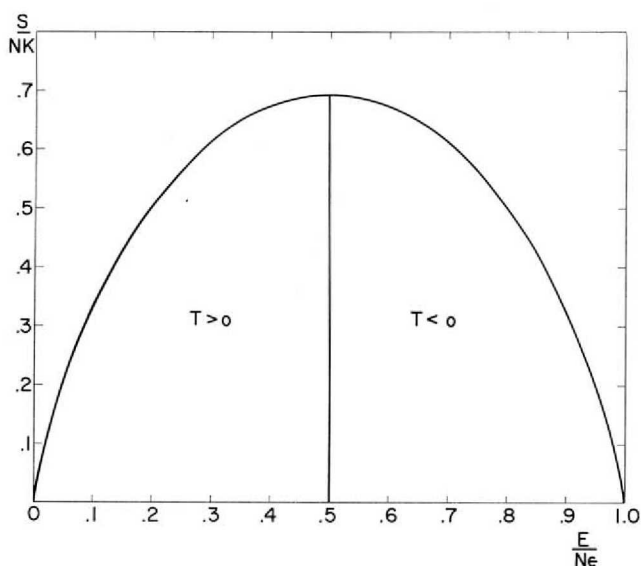

Figure 2. Entropy as a function of energy for a two level spin system of N nuclei with a maximum total energy of $N\epsilon$.

the negative region $(0-)$ is the hottest temperature of all. This temperature is just as unattainable as the ordinary absolute zero $(0+)$. This ordering comes about because the physically significant parameter is not T but $\phi \equiv (-1/T)$ as, for example, in the usual Boltzmann factors, $\exp +(\phi E_i/k)$. Thus ϕ varies from $-\infty$ at one extreme through zero (at $T = \pm\infty$) to $+\infty$ at the other extreme.

Another important insight can be gained by considering the heat capacity (C_M) at constant magnetic moment M,

$$C_M = \left(\frac{\partial E}{\partial T}\right)_M$$

$$= \frac{\partial}{\partial T}(NX_2\epsilon) = \frac{\partial}{\partial T}\left(\frac{N\epsilon}{1 + e^{\epsilon/kt}}\right) \quad (24)$$

or

$$\left(\frac{C_M}{Nk}\right) = \left(\frac{1}{T^*}\right)^2 \frac{e^{1/T^*}}{[1 + e^{1/T^*}]^2} \quad (25)$$

where

$$T^* = \frac{kT}{\epsilon} \quad (26)$$

This C_M is zero at $T = \pm 0$ and also at the single point $T = \pm\infty$. This latter zero value means that one can heat up the system to infinite temperature by putting in only a finite amount of energy such that equal occupancy of levels is achieved. Then one can add still more energy and pass into the negative temperature region. This property of zero heat capacity as $T \to \infty$ is crucial for the existence of an assembly with negative temperatures and is only realized if there is a finite upper bound to the energy spectrum (just ϵ in our very simple case) of the assembly. If there were not a finite upper bound to the spectrum no finite energy input could drive the assembly into the state of infinite temperature. Note that C_M is positive also in the negative temperature region. It exhibits two maxima, at $T^* = \pm 0.42$, of equal value, namely

$$\left(\frac{C_M}{Nk}\right)_{Max} = 0.44.$$

From eqn. (23) we can express the temperature explicitly in terms of the total energy E, namely

$$T = \frac{\epsilon}{k}\left[\ln\left[\frac{(1 - [E/N\epsilon])}{(E/N\epsilon)}\right]\right]^{-1} \quad (27)$$

showing that fixed E means fixed T. Referring to Figure 2 we note that any non-equilibrium curve of the entropy at the same temperature (meaning thus at the same total energy) must lie below the equilibrium curve there drawn, since in any non-equilibrium situation the entropy must be less than that on the equilibrium curve. Considering then spontaneous processes at fixed entropy we must move toward the left, i.e., to minimize the energy in order to reach the equilibrium curve if we are in a positive temperature state and toward the right, i.e., to maximize the energy in order to reach the equilibrium curve if we are in a negative temperature state! This is a special case of the general result (9) that the ordinary thermodynamic potentials tend to increase rather than to decrease in spontaneous processes in negative temperature assemblies.

There is no need to modify the statement of the second law of thermodynamics in its modern postula-

tional form due to Born (10) because of the possible existence of assemblies exhibiting negative temperatures. This postulational form is simply that the state function entropy (S) exists defined by the equality:

$$dS = \frac{dQ}{T} \tag{28}$$

for reversible paths and exhibiting the inequality

$$dS > \frac{dQ}{T} \tag{29}$$

for all real (irreversible) paths. Certain modifications of some of the historically earlier, but certainly presently outmoded, heat engine formulations (due to Clausius and Kelvin-Planck) of the second law are necessary. These modifications have been discussed adequately elsewhere (11, 12).

Negative temperatures have been observed in the laboratory (6, 7) but are quite a special case of the temperature concept. Nevertheless as in many other fields of science the special, even paradoxical, situation serves particularly well in illuminating what we mean by the general concept.

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