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Physics of negative absolute temperatures

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Negative absolute temperatures were introduced into experimental physics by Purcell and Pound, who successfully applied this concept to nuclear spins; nevertheless, the concept has proved controversial: a recent article aroused considerable interest by its claim, based on a classical entropy formula (the "volume entropy") due to Gibbs, that negative temperatures violated basic principles of statistical thermodynamics. Here we give a thermodynamic analysis that confirms the negative-temperature interpretation of the Purcell-Pound experiments. We also examine the principal arguments that have been advanced against the negative temperature concept; we find that these arguments are not logically compelling, and moreover that the underlying "volume" entropy formula leads to predictions inconsistent with existing experimental results on nuclear spins. We conclude that, despite the counterarguments, negative absolute temperatures make good theoretical sense and did occur in the experiments designed to produce them.

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I. INTRODUCTION

The concept of negative absolute temperature, first put forward by Onsager [1,2] in the context of two-dimensional turbulence, fits consistently into the description of various experimental findings. In 1951, Purcell and Pound [3], by rapidly reversing the magnetic field applied to nuclear spins in LiF crystals, produced a state displaying negative magnetic susceptibility, which lasted for several minutes. In 1957, Abragam and Proctor [4,5] performed experiments, also on LiF, which they described as "calorimetry ... at negative temperature". In 1997, a group from Helsinki [6,7], using a similar procedure, brought the nuclear spins in silver to temperatures measured to be around -2 nK, and in 2013, Braun *et al.* [8] brought a system of interacting bosons in an optical lattice to a state exhibiting Bose-Einstein condensation into the single-particle state of highest, rather than lowest, energy. Nevertheless, the negative absolute temperature concept has proved controversial: Berdichevsky *et al.* [9] argued that Onsager's use of it was flawed, and a recent article [10] argued that the negative-temperature concept was inconsistent with basic thermodynamic principles. Subsequently, a number of articles have appeared on both sides of the argument [11–22].

In Secs. II and III of this paper, we present an argument based on the second law of thermodynamics, which confirms the negative-temperature interpretation of the nuclear-spin experiments mentioned above. In Sec. IV, we examine the statistical mechanics argument which has been held to rule out negative temperatures; we find that this argument is not logically compelling, and moreover (Sec. IV D) that it leads to predictions inconsistent with known experimental results.

II. MACROSCOPIC BEHAVIOR AND TIME SCALES

The Purcell-Pound experiment uses a system of nuclear spins located on a crystal lattice in a uniform magnetic field $\mathbf{h}$. The energy of this system can be written

$$E = -\mathbf{h}\cdot\mathbf{M} + W_{\mathrm{ss}} + W_{\mathrm{sl}}, \tag{1}$$

where $\mathbf{M}$ is the magnetic moment vector, W_{ss} is the spin-spin interaction, and W_{sl} is the spin-lattice interaction.

At sufficiently low temperatures, the spin-lattice interaction acts very slowly; the relevant relaxation time τ_{sl} can be of the order of minutes [23] or even hours [6]. On shorter time scales, we can, following Abragam (Chap. 5 of Ref. [24]), neglect W_{sl} and treat the spin system as isolated apart from the effect of changes in $\mathbf{h}$. If we perturb the spin system by changing $\mathbf{h}$, and then leave it alone for a time that is short compared to τ_{sl}, it may come to a (transient) internal equilibrium under the action of the spin-spin interaction, at a "spin temperature" [4,5,24], which can differ from that of the lattice. The lifetime of this transient equilibrium state, being of order τ_{sl}, is much greater than the relaxation time τ_{ss} for approaching it, which can [23] be less than 0.1 s. In such a state, the magnetic moment $\mathbf{M}$ must (assuming $\mathbf{h} \neq \mathbf{0}$) be parallel or antiparallel to the applied field $\mathbf{h}$, otherwise the Larmor precession would cause the vector $\mathbf{M}$ to rotate about $\mathbf{h}$.

The energy of any such transient equilibrium state can be found from (1), which, provided that $\mathbf{h}\cdot\mathbf{M}$ is large enough to justify neglecting[1] W_{ss}, simplifies to

$$E \approx -\mathbf{h}\cdot\mathbf{M}, \tag{2}$$

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[1] Although we neglect the contribution of W_{ss} to the energy, we do not neglect its dynamical effect, which is what brings the spin system to internal equilibrium. There is an analogy with the kinetic theory of gases, where the effect of the molecular interactions on the energy may be neglected even though their effect on the time evolution is crucial.

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where the sign $\approx$ means that the difference between the quantities it separates is negligible when $|W_{\rm ss}| \ll E$. The transient equilibrium states can conveniently be labeled by their values of the energy E and magnetic field $\mathbf{h}$. Their magnetic moments are determined by these two parameters, since $\mathbf{M}(E,\mathbf{h})$ has to be parallel or antiparallel to $\mathbf{h}$, and therefore it equals the only scalar multiple of $\mathbf{h}$ satisfying (2), namely

$$\mathbf{M}(E,\mathbf{h}) \approx -\mathbf{h}E/|\mathbf{h}|^2. \tag{3}$$

III. USING THE ENTROPY INCREASE PRINCIPLE

The procedure used by Purcell and Pound in their quest for negative temperatures was to bring the system to equilibrium at a very low (positive) temperature in a strong magnetic field and then reverse the field rapidly, in a time much less than the period τ_L of the Larmor precession, so that the magnetic moment has no time to change. Assuming that $\mathbf{M}$ and $\mathbf{h}$ were parallel in the old state, the new magnetic field is in the opposite direction to the magnetic moment, so that there is no Larmor precession in the new state. The new state is therefore also a transient equilibrium state. By Eq. (2), the energy of the new state is the negative of the old. If the energy of the old state was negative, that of the new one is positive.

To obtain thermodynamic information about these transient equilibrium states, we shall use the second law of thermodynamics. An integral part of this law is[2] the principle of increase of entropy (or, more precisely, nondecrease of entropy), which asserts ([26], p. 77) that *the entropy of the final state of any adiabatic transition is never less than that of its initial state.*[3] Here "adiabatic transition" means a process during which no heat enters or leaves the system—that is, one during which any change in the energy of the system is equal to the work done on it by external mechanisms. To avoid misunderstandings, we emphasize that (i) the word "adiabatic" is *not* being used here to mean "infinitely slow" (i.e., quasistatic), as in the adiabatic theorem of mechanics discussed in Sec. IV C below, nor (as in Ref. [16], p. 12) as a synonym for "isentropic"; (ii) (as noted explicitly in Ref. [26]) there is no requirement for the system to be isolated; and (iii) although the initial and final states are equilibrium states (otherwise their entropies would not be defined), there is no need for the states passed through during the process to be equilibrium states, not even approximately.

So long as $\mathbf{M}$ remains constant, the field-reversal process considered here satisfies the definition of "adiabatic transition", for it follows from (2) that

$$dE = -\mathbf{M}\cdot d\mathbf{h} - \mathbf{h}\cdot d\mathbf{M} \tag{4}$$

so that, with $\mathbf{M}$ constant (i.e., $d\mathbf{M} = \mathbf{0}$), the change in E is $-\mathbf{M}\cdot d\mathbf{h}$, which, as shown, for example, in Reif's textbook ([28], pp. 440–444),[4] is equal to the work done by external mechanisms in changing $\mathbf{h}$ so that the process is indeed an "adiabatic transition" as defined above. It follows, from the entropy increase principle, that neither of the two states with opposite $\mathbf{h}$ but the same $\mathbf{M}$ can have greater entropy than the other, i.e., their entropies are equal. But by (2) these two states have equal and opposite energies, and so if the entropy is written as a function of E and $\mathbf{h}$, the function $S(E,\mathbf{h})$ has the property

$$S(E,\mathbf{h}) = S(-E,-\mathbf{h}). \tag{5}$$

We define the reciprocal temperature θ (usually denoted $1/T$, or else $k\beta$) by

$$\theta := \frac{\partial S(E,\mathbf{h})}{\partial E}. \tag{6}$$

The physical significance of this definition is that if a small amount of energy is transferred from a body with a lower θ to one with a higher θ, then the total entropy will increase. Moreover, if the two bodies are in thermal contact (i.e., if energy can pass by heat conduction from one to the other), then at equilibrium their θ values must be equal. In everyday language, the body with lower θ is [23] "hotter" than the other. In particular, a body with negative temperature (negative θ) is "hotter" than any body with positive temperature. An example of this is the experiment of Abragam and Proctor discussed in more detail below (Sec. IV D), where a spin system with positive energy (corresponding to a negative temperature, i.e., $\theta < 0$) gave up energy to another spin system with zero energy (corresponding to an infinite temperature, i.e., $\theta = 0$).

Defining the temperature $T := 1/\theta$, it follows from (5) and (6) that

$$T(E,\mathbf{h}) = -T(-E,-\mathbf{h}). \tag{7}$$

Thus, when the magnetic field is reversed, the temperature T changes sign along with E, in agreement with the interpretation given by Purcell and Pound [3], by Abragam and Proctor [4,5], and by the Helsinki group [6,7] that the states they obtained by magnetic-field reversal had negative thermodynamic temperatures.

The negative-temperature interpretation has, however, been challenged [10], using a statistical mechanics argument. This argument is considered in the next section.

IV. STATISTICAL MECHANICS AND NEGATIVE TEMPERATURES

A. The "Boltzmann" entropy

When we come to apply statistical mechanics to negative absolute temperatures, the first question to consider is what ensemble to use. The canonical ensemble, based on the Gibbs canonical distribution $\exp(-\beta\mathcal{H})$, where $\mathcal{H}$ is the Hamiltonian and β is a parameter specifying the reciprocal temperature, seems natural, but it has the disadvantage that this distribution describes a system in thermal contact with a heat bath whose temperature is treated as something already given, rather than

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[2] This is what Campisi [25] calls "part B" of the second law.

[3] An alternative to the formulation in Ref. [26] is the entropy principle used by Lieb and Yngvason [27] in their axiomatic formulation of thermodynamics.

[4] An alternative to Reif's argument is to imagine the magnetic field acting on the system to be produced by movable permanent magnets so that the work done on the system in changing $\mathbf{h}$ equals the mechanical work done in moving these magnets.

being expressed in terms of more "fundamental" concepts whose meaning is unequivocal.

For this reason, our discussion here will be based on the microcanonical rather than the canonical ensemble. The main conceptual problem is how best to extend the notion of entropy, originally a thermodynamic concept, into the realm of mechanics. There is no unique solution to this problem; the choice of entropy definition is partly a matter of taste, so long as the chosen definition agrees with the thermodynamic entropy when applied to macroscopic systems.

Traditionally, the microcanonical definition of entropy has been based on Boltzmann's principle,[5]

$$S = k \log W, \tag{8}$$

where W is the number of quantum states constituting the microcanonical ensemble. For our spin system, the energy levels are highly degenerate, and a microcanonical ensemble can be set up for each energy level, comprising all the states with that energy. In that case, Eq. (8) gives, for all E in the energy spectrum for the given value of $\mathbf{h}$,

$$S = S_B(E,\mathbf{h}) := k \log \omega(E,\mathbf{h}), \tag{9}$$

where k is Boltzmann's constant, and $\omega(E)$ is the multiplicity of the energy level E. If E is not in the energy spectrum, Boltzmann's principle gives no clear guidance; the usual procedure is to use a convenient interpolation formula. For more general systems, where the energy levels may not be degenerate at all, the ensemble can be defined [30] to comprise all the states whose energies lie in a specified interval, say $(E-\epsilon,E]$, where ϵ is a parameter that is large in comparison with the energy level spacing but small in comparison with E itself; the corresponding entropy formula would be

$$S_{B\epsilon} = k \log\left(\Omega(E,\mathbf{h}) - \Omega(E-\epsilon,\mathbf{h})\right), \tag{10}$$

where $\Omega(E,\mathbf{h})$ denotes the number of energy levels with energies not exceeding E. In Refs. [10,16,19], the formula (10) is approximated as

$$S_{B\epsilon} = k \log[\epsilon \varpi(E)], \tag{11}$$

in which $\varpi(E)$, the "density of states", is the derivative of a differentiable approximation to $\Omega(E)$.

For a system of N spin-$\frac{1}{2}$ particles in a magnetic field $\mathbf{h}$, the energy levels are given by the formula

$$E = (2n - N)\mu|\mathbf{h}|, \tag{12}$$

where n is the number of spins pointing along the negative $\mathbf{h}$ direction, and μ denotes the magnetic moment of one spin. Each energy level has a definite magnetic moment along or against the direction of $\mathbf{h}$, whose component in the direction of $\mathbf{h}$ is

$$M = (N - 2n)\mu \tag{13}$$

$$= -E/|\mathbf{h}|. \tag{14}$$

The vector $\mathbf{M}$ is given in terms of E and $\mathbf{h}$ in Eq. (3).

A standard combinatorial formula gives, using (13),

$$\omega(E,\mathbf{h}) = \frac{N!}{n!(N-n)!} = \frac{N|}{\left(\frac{N}{2} - \frac{M}{2\mu}\right)!\left(\frac{N}{2} + \frac{M}{2\mu}\right)!}. \tag{15}$$

From (14) and (15) it follows that $\omega(E,\mathbf{h})$ is an even function of E at constant $|\mathbf{h}|$, so that the "Boltzmann" entropy defined by (9) has the symmetry property (5). The temperature T_B associated [via Eq. (6)] with this entropy definition therefore has the antisymmetry property (7) and is negative for the states reached by magnetic-field reversal. Thus the consequences of the "Boltzmann" entropy formula in this case are consistent with the thermodynamic argument leading to (7) and with the negative-temperature interpretation of the magnetic-field reversal experiments.

B. The thermostatistical consistency condition

Some authors [10,12,14,16,18,19] have challenged the negative-temperature interpretation of the experiments described above. In their argument, originally due to Berdichevsky *et al.* [9], the microcanonical entropy is defined not by (9) but by

$$S = S_G := k \log \Omega(E), \tag{16}$$

where $\Omega(E)$ [or more precisely $\Omega(E,\mathbf{h})$] is the number of energy levels with energies not exceeding E. The classical analog of (16) was used by Gibbs ([31], p. 170) and so S_G is often called the "Gibbs" entropy. Since the function $\Omega(E)$ is manifestly nondecreasing, the "Gibbs temperature", defined in analogy with (6) as $T_G := (\partial S_G/\partial E)^{-1}$, cannot be negative; thus the definition (16) implies that negative absolute temperatures are impossible.

The principal argument given in Refs. [9,10] and elsewhere in support of the "Gibbs" entropy definition (16) makes use of a "thermostatistical consistency" condition [10], which for spin systems using the microcanonical ensemble reads

$$T\, dS(E,\mathbf{h}) = dE + \langle \mathcal{M} \rangle_{E,\mathbf{h}} \cdot d\mathbf{h}, \tag{17}$$

where

$$\mathcal{M} := -\partial \mathcal{H}/\partial \mathbf{h} \tag{18}$$

is the magnetic moment operator, defined in terms of the Hamiltonian operator $\mathcal{H}$ in which $\mathbf{h}$ is a parameter, and $\langle \cdots \rangle_{E,\mathbf{h}}$ denotes a microcanonical average at energy E and magnetic field $\mathbf{h}$. Equation (17) ensures that the statistical mechanics formula $\langle \mathcal{M} \rangle_{E,\mathbf{h}}$ for the magnetic moment agrees with the thermodynamic formula for the same quantity, which can be written $-\partial E(S,\mathbf{h})/\partial \mathbf{h}$. As shown in the supplementary material of Ref. [10], the "Gibbs" entropy (16) exactly satisfies (17), whereas the "Boltzmann" entropy as defined in (10) does not. The conclusion drawn in Ref. [10] is that the "Boltzmann" entropy is inherently unsatisfactory and should never be used.

What this argument ignores, however, is that for spin systems there is an alternative, simpler, definition of "Boltzmann" entropy, namely (9), and that this simpler definition does exactly satisfy thermodynamic consistency. To see this, we use the fact, evident from (15), that $\omega(E,\mathbf{h})$ can be written as a function of the single variable M. It follows that differentiation holding S_B fixed is equivalent to differentiation holding M

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[5] See, for example, p. 170 of Ref. [29].

fixed, so that[6]

$$\left(\frac{\partial E}{\partial \mathbf{h}}\right)_{S_B} = \left(\frac{\partial E}{\partial \mathbf{h}}\right)_M \tag{19}$$

$$= -\mathbf{M} \text{ by (4).} \tag{20}$$

By a standard calculus formula, it follows that

$$\frac{\partial S_B(E,\mathbf{h})/\partial \mathbf{h}}{\partial S_B(E,\mathbf{h})/\partial E} = \mathbf{M} \tag{21}$$

and hence that

$$T_B dS_B = T_B\left(\frac{\partial S_B}{\partial E}dE + \frac{\partial S_B}{\partial \mathbf{h}}\cdot d\mathbf{h}\right)$$

$$= dE + \mathbf{M}\cdot d\mathbf{h}, \tag{22}$$

where T_B is the "Boltzmann" temperature, defined in analogy with (6) by

$$T_B = \left(\frac{\partial S_B(E,\mathbf{h})}{\partial E}\right)^{-1}. \tag{23}$$

But by its definition [see (13)], $\mathbf{M}$ is the microcanonical expectation of the magnetic moment, and so our result (22) confirms that the Boltzmann entropy, as defined in (9), satisfies the thermostatistical consistency condition (17)—not only in the thermodynamic limit, as shown, for example, in Ref. [21], but for finite systems as well.

Thus for the nuclear spin system, the thermostatistical consistency criterion is neutral between the "Gibbs" and "Boltzmann" entropies, giving no reason to disbelieve our result obtained earlier that the magnetic-field reversal experiments produced negative absolute temperatures, even though such temperatures are incompatible with the "Gibbs" formula (16).

C. "Gibbs" entropy and the adiabatic theorem of mechanics

An important strand in the rationale behind the "Gibbs" entropy formula (16) is [10,32] the adiabatic theorem of classical mechanics [33]. This theorem tells us how energy varies with time for any system whose Hamiltonian contains a parameter such as $\mathbf{h}$, when that parameter is varied extremely slowly (the type of process known in thermodynamics as quasistatic). The theorem states that, provided certain further conditions are satisfied, the energy E will vary with time in such a way that $\Omega(E,\mathbf{h})$ is invariant. The most important of these conditions is that, as $\mathbf{h}$ changes, the phase-space region inside a given closed energy surface must always be transformed into the region inside, rather than outside, the new energy surface. Since the thermodynamic entropy is also invariant in any quasistatic process, this theorem supports the claim that $k \log \Omega(E,\mathbf{h})$ equals the thermodynamic entropy—*provided* that the energy surfaces satisfy the condition just mentioned.

For quantum systems, the corresponding necessary condition is that the energy levels near E should not cross during the process. For the Hamiltonian of the spin system,

$$\mathcal{H} := -\mathbf{h}\cdot\mathcal{M}, \tag{24}$$

this condition is satisfied if and only if $\mathbf{h}$ does not pass through the value zero during the process. Thus, for all the equilibrium states that can be reached quasistatically with $\mathbf{h} \neq \mathbf{0}$ throughout, the entropy formula (16) is a good one. The catch is that $\mathbf{h}$ does pass through zero in the field reversal process used to reach positive values of E, thus the necessary condition is not satisfied and the theorem does not require $\Omega(E,\mathbf{h})$ to be invariant during this process. Our contention that $k \log \Omega(E,\mathbf{h})$ is not the thermodynamic entropy for the (transient) equilibrium states reached by field reversal is therefore compatible with the theorem.

Some other arguments that have been put forward in favor of using S_G rather than S_B are considered in Appendix C.

D. An experimental test of the entropy formulas

Consider an experiment in which two spin systems, each comprising N nuclei with magnetic moment μ, are brought into thermal contact. Such an experiment was carried out by Abragam and Proctor [4,5], the two spin systems being the Li nuclei in an LiF crystal and the F nuclei in the same crystal. Initially, both systems are in thermal equilibrium, one having energy 0 and the other having maximum positive energy, $E_{\max} := N\mu|\mathbf{h}|$. How will this energy be apportioned between the two systems when the new equilibrium is reached? For the spin system, a standard calculation based on applying Stirling's approximation to Eq. (15) gives, using (9),

$$S_B(E) \cong -Nk[x\log x + (1-x)\log(1-x)], \tag{25}$$

where $x := n/N = (E + E_{\max})/2E_{\max}$ with $E_{\max} := N\mu|\mathbf{h}|$, and the symbol $\cong$ signifies that the difference between the expressions it separates is thermodynamically negligible, or more precisely that $1/N$ times this difference tends to 0 in the *thermodynamic limit* where $N,E \to \infty$ at constant E/N and constant $\mathbf{h}$.

From (25) we have, for a spin system,

$$S_B(0) \cong Nk\log 2 = 0.69\ Nk,$$
$$S_B\left(\tfrac{1}{2}E_{\max}\right) \cong Nk[2\log 2 - (3/4)\log 3] = 0.56\ Nk,$$
$$S_B(E_{\max}) = 0.$$

If N spins with energy 0 and N spins with total energy $E_{\max}$ are brought into thermal contact, their initial Boltzmann entropy of $(0 + 0.69)k$ per spin can increase to $(0.56 + 0.56)k = 1.12k$ per spin if they share their energy equally. Thus the Boltzmann entropy formula (9) predicts that in the new equilibrium state, the energy will be shared between the two groups of spins.[7] And that is just what happened in the experiments of Abragam and Proctor [4,5,35].

Now consider the predictions of the "Gibbs" entropy formula (16). Since $\Omega(E)$ increases monotonically with E, the entropy increase achieved by giving energy E_1 to one

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[6] The notation $\partial/\partial\mathbf{h}$ denotes a gradient in $\mathbf{h}$ space.

[7] This may be thought of as an application of Callen's "entropy maximum postulate" [34], which asserts that at equilibrium the available energy will be distributed between the subsystems in the way that maximizes the total entropy. The entropy-maximizing energy apportionment is the one that equalizes the reciprocal temperatures of the two groups of spins and hence also, by (6), their energies.

subsystem and E_2 to the other, where $E_1 + E_2 = E_{\max}$, has the following upper bound:

$$\begin{aligned}
&[S_G(E_1) + S_G(E_2)] - [S_G(0) + S_G(E_{\max})] \\
&\quad \leqslant S_G(E_{\max}) - S_G(0) \\
&\quad = k \log\left(\frac{\Omega(E_{\max})}{\Omega(0)}\right) \\
&\quad = k \log\left(\frac{\Omega(E_{\max})}{\frac{1}{2}(\Omega(E_{\max}) + \omega(0))}\right) \\
&\quad < k \log 2,
\end{aligned} \tag{26}$$

where we have used first the monotonicity of $S_G(E)$, which implies that $S_G(E_1) + S_G(E_2) \leqslant 2S_G(E_{\max})$, and afterwards the symmetry of the energy spectrum about $E = 0$, which implies that the number of energy levels with negative energy, namely $\Omega(0) - \omega(0)$, is equal to the number with positive energy, namely $\Omega(E_{\max}) - \Omega(0)$, so that $\Omega(E_{\max}) + \omega(0) = 2\Omega(0)$. The inequality (26) shows that the composite system cannot significantly increase its "Gibbs" entropy by transferring energy from one subsystem to another; consequently, if the Gibbs entropy is the same as the thermodynamic entropy, one might expect the energy of each subsystem to perform some kind of random walk after the two subsystems are brought into thermal contact, but never to settle down at any definite "equilibrium" value.[8] But this prediction is inconsistent with the experimental results of Abragam and Proctor [4,5], who found that the energy apportionment went to a definite value, not far from that which maximizes the "Boltzmann" entropy of the composite system. One is led to the conclusion that the "Gibbs" entropy formula (16), whatever its other virtues, is not a secure foundation for the discussion of systems capable of negative absolute temperatures.

V. DISCUSSION

A. Negative temperatures in a system of particles

The discussion given so far shows that negative absolute temperatures make thermodynamic sense and are necessary for a coherent description of nuclear spin experiments, but negative absolute temperatures can also arise in other types of experiment. One such experiment, described by Braun *et al.* [8], involves ^{39}K atoms in an optical lattice. The system was first brought to equilibrium at a positive temperature and then manipulated by changing the experimental parameters in a way that, in essence, reversed the sign of the Hamiltonian. As with the magnetic-field reversal for nuclear spin systems, this manipulation can bring the atomic system to a state in which the negative temperature concept is appropriate. A more detailed analysis is given in the Appendix.

B. Negative temperatures in other systems

It is sometimes stated, e.g., in Refs. [13,23,35], that negative absolute temperatures can arise in any system whose energy spectrum is bounded above. Even without any specific mechanism, such as magnetic-field reversal, for bringing the system on its own to a negative temperature, such a claim still makes sense because the system can, in principle, be placed in a negative-temperature heat bath consisting of nuclear spins. By a standard result of statistical mechanics (see, for example, Chap. 11 of Ref. [35]), the system's probability distribution at equilibrium would then be canonical at the temperature of the heat bath. If the energy spectrum of the original system is bounded above, its partition function is a convergent sum when the temperature is negative, and so this system can come to equilibrium with a negative-temperature heat bath. In that situation, it would be reasonable to describe the system itself as being at a negative absolute temperature.

C. Gibbs versus Boltzmann

The debate about negative absolute temperatures tends to take the form of a contest between the "Gibbs" and "Boltzmann" formulas for the microcanonical entropy; for example, it is argued in Refs. [10,16,18] that the "Boltzmann" formula is flawed and that the "Gibbs" formula should always be used, whereas Refs. [11,13,17,21,22] take the opposite view. Our work suggests, however, that there is no definitive way to decide in advance which entropy formula should be used—the choice between them can depend on what system is being considered, and even on what state that system is in. For spin-$\frac{1}{2}$ systems at positive energies ($T_B < 0$), the "Gibbs" entropy definition is unsatisfactory (see Sec. IV), but at negative energies ($T_B > 0$) there is little to choose between the two definitions. Additionally, for classical systems of particles, the "Gibbs" definition has some advantages [10,31], which include the fact that no arbitrary parameter ϵ appears in it.

Incidentally, this parameter ϵ is not quite as innocent as it may look. Although its contribution $k \log \epsilon$ to the entropy is macroscopically negligible, the way it is chosen can make the difference between thermostatistical consistency and inconsistency. In Ref. [18], the choice $\epsilon =$ const in (11) leads to a formula for magnetization that is thermodynamically inconsistent [it disagrees with (2)], but by choosing $\epsilon \propto \mu|\mathbf{h}|$ instead, the inconsistency can be removed (see the calculation in Sec. IV B). The reader may like to investigate whether or not an equally effective choice of ϵ is always possible.

D. Superefficient Carnot engines?

It is sometimes asserted [8,23] that negative temperatures make Carnot engines of efficiency greater than 1 possible. This paradoxical assertion seems to stem from an uncritical application of the standard formula $1 - T_2/T_1$ for the efficiency of a reversible Carnot engine operating between positive temperatures T_1, T_2 with $T_1 > T_2$. A more careful treatment [11,36] shows, however, that the standard formula does not apply if one of the temperatures is negative. Denoting the increases in entropy of the working substance at the temperatures T_1, T_2 by $\delta S_1, \delta S_2$ per cycle, the amounts of heat taken in at the two temperatures are $T_1 \delta S_1$ and $T_2 \delta S_2$. If T_1 and T_2 have opposite signs, then, since $\delta S_1 + \delta S_2 = 0$ in a reversible cycle, the amounts of heat taken in at the two

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[8] This is an illustration of the unphysically large fluctuations sometimes predicted, according to Ref. [22], by the "Gibbs" entropy formula.

temperatures have the same sign; therefore, the work done by the engine per cycle is equal to the total heat taken in: no heat is wasted and the efficiency is 1. An efficiency of 1 is remarkable enough, but there is no mysterious creation of mechanical energy coming from nowhere.

Such a Carnot-type engine might be useful working in reverse, as a heat pump [36] that would take in mechanical energy and pump out some of it as heat into a negative-temperature system, thereby helping to maintain that system at a desired negative temperature against the inevitable loss of heat to its "cooler" positive-temperature surroundings. A possible cycle for such a device is described in the Appendix.

VI. SUMMARY AND CONCLUSIONS

The aim of this paper is to clarify the current controversy, in which it has been claimed, on the one hand, that certain experimental procedures produce negative absolute temperatures and, on the other hand, that negative temperatures are incompatible with basic thermodynamic principles.

These experimental procedures involve reversing the magnetic field acting on a system of nuclear spins in a crystal whose initial temperature is so low that the interaction of the spin system with crystal lattice vibrations can be neglected. Using the thermodynamic principle of entropy increase, we show that the magnetic-field reversal does not change the entropy, and hence, since the energy of the spin system is reversed, that S is an even function of E so that the temperature $(\partial S/\partial E)^{-1}$, initially positive, is negative after field reversal.

The challenge to the negative T concept has been mainly based on the claim that it is incompatible with the "thermostatistical consistency condition" (17), since the most obvious entropy definition satisfying that condition, the "Gibbs" formula (16), implies $T \geqslant 0$. Here we show that there is in fact no incompatibility, since (for spin systems) the "Boltzmann" entropy, as defined in (9), also satisfies thermostatistical consistency and yet permits negative temperatures. To confirm that the Gibbs formula is not the right entropy definition for nuclear spin systems, we also show that it is incompatible with the experimental results of Abragam and Proctor [4,5] on the way that energy is shared between spin systems in thermal contact.

In conclusion, we have shown that negative absolute temperatures arise naturally in the analysis of certain experiments on spin systems, and that for those systems the Gibbs entropy definition gives misleading results, whereas the Boltzmann definition does not.

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APPENDIX A: NEGATIVE TEMPERATURES IN A SYSTEM OF PARTICLES

The experiment described by Braun *et al.* [8] involves a system of ^{39}K atoms in an optical lattice. They modeled this system using a Hamiltonian of "Bose-Hubbard" type, which can be written in the form

$$\mathcal{H}_1 := c_1 \sum_{\mathbf{k},\mathbf{l}} (a_{\mathbf{k}}^\dagger - a_{\mathbf{l}}^\dagger)(a_{\mathbf{k}} - a_{\mathbf{l}}) + c_2 \sum_{\mathbf{k}} a_{\mathbf{k}}^\dagger a_{\mathbf{k}}^\dagger a_{\mathbf{k}} a_{\mathbf{k}} + c_3 \sum_{\mathbf{k}} r_{\mathbf{k}}^2 a_{\mathbf{k}}^\dagger a_{\mathbf{k}}, \tag{A1}$$

where c_1,c_2,c_3 are positive constants, the indices $\mathbf{k},\mathbf{l}$ label the lattice sites, the double sum goes over all nearest-neighbor pairs of sites, $a_{\mathbf{k}}$ is the operator annihilating a particle at lattice site $\mathbf{k}$, the dagger indicates a Hermitian conjugate, and $r_{\mathbf{k}}$ is the distance from the lattice site $\mathbf{k}$ to a fixed origin. In the experiment, the system was started in equilibrium at a positive temperature T, with Hamiltonian $\mathcal{H}_1$, and then manipulated by changing the parameters c_1,c_2,c_3 until the Hamiltonian became (essentially) $-\mathcal{H}_1$. To study what happens to the thermodynamic entropy during such a process, consider the family of Hamiltonians

$$\mathcal{H}_\lambda := \lambda \mathcal{H}_1 \quad (-1 \leqslant \lambda \leqslant 1) \tag{A2}$$

and consider a thought experiment in which the (time-dependent) Hamiltonian is $\mathcal{H}_\lambda$, with λ being controlled so that its value starts at 1 and ends at -1. The system starts in equilibrium, modeled by a microcanonical ensemble at energy $E = E_1$. Since the operator $\mathcal{H}_1$ commutes with the time-varying Hamiltonian $\mathcal{H}_\lambda$, its expectation $\langle \mathcal{H}_1 \rangle$ is an invariant and therefore preserves its initial value, E_1, thus the energy, i.e., the expectation of $\mathcal{H}_\lambda = \lambda \mathcal{H}_1$, is equal to λE_1 throughout and finally reaches the value $-E_1$. The final ensemble is again microcanonical and therefore describes a new equilibrium state, this time with energy $-E_1$. Moreover, the process can be reversed, bringing us back to the original equilibrium state with $\lambda = 1$ and energy E_1. Hence, by an argument similar to the one used in deriving (5), the entropy as a function of energy and λ must satisfy[9]

$$S(-E,-\lambda) = S(E,\lambda), \tag{A3}$$

and it follows, as in the discussion of (5), that

$$T(-E,-\lambda) = -T(E,\lambda), \tag{A4}$$

confirming the interpretation made in Ref. [8] that the equilibrium state reached by reversing the signs of c_1,c_2,c_3 does have a negative absolute temperature.

The Hamiltonian $\mathcal{H}_1$ is not bounded above; therefore, the reversed Hamiltonian $\mathcal{H}_{-1} := -\mathcal{H}_1$, used here to model the "inverted" state produced in the experiment, is not bounded below. This fact has the consequence that $\Omega(E)$ is not defined for the reversed Hamiltonian, so that it does not have a "Gibbs" entropy, nor a "Gibbs" temperature. One could instead work with the "complementary Gibbs entropy" defined [13,16] in terms of the number of energy levels above, rather than below, the actual energy of the system. The ramifications of this possibility will not be explored further here.

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[9] It does not matter that the density matrix when $\lambda = 0$ is not microcanonical and therefore does not describe an equilibrium state—as noted in Sec. III, the entropy increase principle does not require the intermediate states to be equilibrium states.

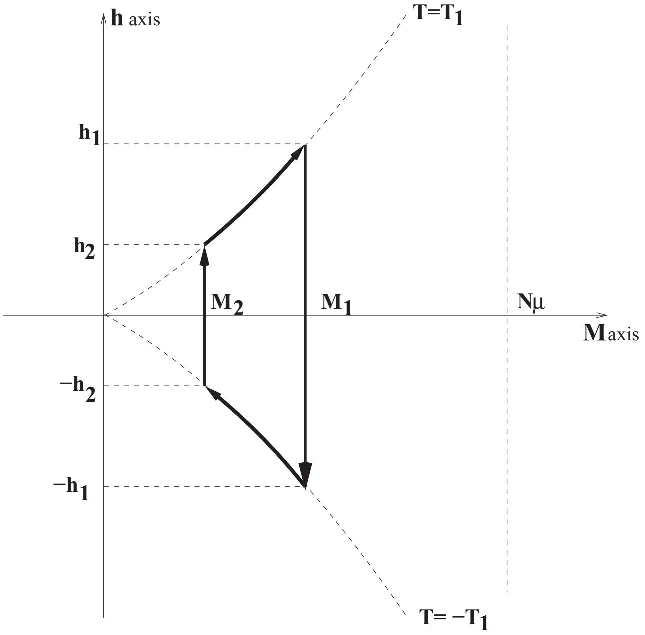

FIG. 1. “Carnot” cycle for a heat pump using negative temperatures. The area enclosed by the loop equals the total energy transferred per cycle. For the nuclear spin system, the equation of the temperature-T isotherm is $h = (kT/\mu)\text{arc}\tanh(M/N\mu)$. The vertical line at $M = N\mu$ is an asymptote of all the isotherms, both for positive and negative temperatures. M_1 and M_2 are the magnetization values at which the magnetic field is suddenly reversed. $N\mu$ is the maximum value the magnetization can acquire.

APPENDIX B: A POSSIBLE NEGATIVE-TEMPERATURE MAINTENANCE CYCLE

The engine might operate as follows (see Fig. 1)[10]

(i) As in Sec. III: the working substance starts in equilibrium at temperature $T_1 > 0$ with magnetic field h_1 and magnetic moment M_1 both in the positive z direction, so that [by (1)] the energy is $E = -h_1 M_1 < 0$ initially. The magnetic field is then quickly reversed (to $-h_1$); the energy increases from $-h_1 M_1$ to $+h_1 M_1$, the temperature changes to $-T_1$, but the entropy and magnetic moment stay constant.

(ii) The working substance is placed in contact with the (relatively large) object that is to be maintained at temperature $-T_1$ in the face of energy losses to its environment. Heat is taken from the working substance isothermally so that $|h|$ and M both decrease but the reciprocal temperature, which for the spin systems considered earlier can be shown[11] to be equal to $(k/\mu h)\text{arc}\tanh(M/N\mu)$, remains constant; the magnetic field decreases (in magnitude) from $-h_1$ to $-h_2$ and the energy decreases from $h_1 M_1$ to $h_2 M_2$, with $h_2 < h_1, M_2 < M_1$; the entropy of the working substance increases by $\Delta E/T = (h_2 M_2 - h_1 M_1)/(-T_1) > 0$ (i.e., it takes entropy out of the object).

(iii) The magnetic field is again quickly reversed (from $-h_2$ to $+h_2$); the magnetic moment stays at M_2 but the temperature goes back to T_1; the energy decreases from $h_2 M_2$ to $-h_2 M_2$.

(iv) The working substance is placed in contact with a heat sink at temperature T_1 and gives out heat isothermally. The magnetic field returns to h_1 and the magnetic moment returns to M_1, the energy of the working substance decreases [see (1) from $-h_2 M_2$ to $-h_1 M_1$], and the entropy of the working substance increases by $\Delta E/T = (-h_1 M_1 + h_2 M_2)/T_1 < 0$ (i.e., it gives up entropy to the heat sink).

An important difference from positive-temperature Carnot cycles is that steps (i) and (iii) are not quasistatic, so that the system need not pass through equilibrium states and does not have a well-defined temperature throughout. In particular, when the magnetic field passes through the value zero, the system is not in equilibrium and so there is no violation of the third law of thermodynamics, even though the representative point in the (M,h) plane crosses isotherms belonging to arbitrarily small temperatures.

APPENDIX C: REPLIES TO SOME OTHER ARGUMENTS FOR USING S_G

An argument sometimes given for preferring the “Gibbs” to the “Boltzmann” entropy definition is [16,19] that “only S_G obeys the second law” in the sense that S_G always increases when two systems, both previously in equilibrium but separated, are brought together, whereas $S_{B\epsilon}$ [defined in (10)] may decrease slightly (depending on the value of ϵ). The Boltzmann entropy S_B as defined here [see (9)] does, however, obey the second law in this sense.

An ingenious argument due to Campisi [18,37] depends on the fact that all exact solutions of (17) have the form $S(E) = g[\Omega(E)]$; it is argued that, if the function g is known for one system [such as the classical ideal gas, for which $g(x) = k \log x$], then “it has to be one and the same for all systems ...because by adjusting the external parameters ...one can transform any Hamiltonian into any other”. However, it is not self-evident that the change from one system to another can always be accomplished by a mere adjustment of external parameters. The change from classical to quantum mechanics is the most obvious example, and the change from a system with an unbounded energy spectrum to one with a bounded spectrum, or even the magnetic-field reversal considered in Sec. III, also involves discontinuous changes in the properties of the system, which may require a corresponding discontinuous change in the function $g(\cdot)$.

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[10] A very similar diagram, with more isotherms, is given in Ref. [11].

[11] See, for example, Eq. (6.3.3) on p. 207 of Ref. [28], or Eq. (15) of Ref. [11].

[1] L. Onsager, Nuovo Cimento **6**(Suppl. 2), 279 (1949).
[2] G. Eyink and K. R. Sreenivasan, Rev. Mod. Phys. **78**, 87 (2006).
[3] E. Purcell and R. Pound, Phys. Rev. **81**, 279 (1951).
[4] A. Abragam and W. Proctor, Phys. Rev. **106**, 160 (1957).
[5] A. Abragam and W. Proctor, Phys. Rev. **109**, 1441 (1958).
[6] P. J. Hakonen, K. K. Nummila, R. T. Vuorinen, and O. V. Lounasmaa, Phys. Rev. Lett. **68**, 365 (1992).
[7] A. Oja and O. Lounasmaa, Rev. Mod. Phys. **69**, 1 (1997).

[8] S. Braun, J. Ronzheimer, M. Schreiber, S. Hodgman, T. Rom, I. Bloch, and U. Schneider, Science **339**, 52 (2013).
[9] V. Berdichevsky, I. Kunin, and F. Hussain, Phys. Rev. A **43**, 2050 (1991).
[10] J. Dunkel and S. Hilbert, Nat. Phys. **10**, 67 (2014).
[11] D. Frenkel and P. Warren, Am. J. Phys. **83**, 163 (2015).
[12] J. Dunkel and S. Hilbert, arXiv:1403.6058.
[13] U. Schneider, S. Mandt, A. Rapp, S. Braun, H. Weimer, I. Bloch, and A. Rosch, arXiv:1407.4127.
[14] J. Dunkel and S. Hilbert, arXiv:1408.5392.
[15] J. Vilar and J. Rubi, J. Chem. Phys. **140**, 201101 (2014).
[16] S. Hilbert, P. Hänggi, and J. Dunkel, Phys. Rev. E **90**, 062116 (2014).
[17] R. H. Swendsen and J.-S. Wang, Phys. Rev. E **92**, 020103(R) (2015).
[18] M. Campisi, Phys. Rev. E **91**, 052147 (2015).
[19] P. Hänggi, S. Hilbert, and J. Dunkel, Philos. Trans. R. Soc. London, Ser. A **374**, 20150039 (2016).
[20] R. Swendsen and J.-S. Wang, Physica A **453**, 24 (2016).
[21] J. Poulter, Phys. Rev. E **93**, 032149 (2016).
[22] D.-V. Anghel, EPJ Web Conf. **108**, 02007 (2016).
[23] N. F. Ramsey, Phys. Rev. **103**, 20 (1956).
[24] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, Oxford, 1961).
[25] M. Campisi, Stud. Hist. Philos. Mod. Phys. **36**, 275 (2005).
[26] H. Buchdahl, *The Concepts of Classical Thermodynamics* (Cambridge University Press, Cambridge, 1966).
[27] E. Lieb and J. Yngvason, Phys. Rep. **310**, 1 (1999).
[28] F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill Kogakusha, Tokyo, 1965).
[29] O. Penrose, *Foundations of Statistical Mechanics* (Dover, New York, 2005).
[30] R. B. Griffiths, J. Math. Phys. **6**, 1447 (1965).
[31] J. W. Gibbs, *Elementary Principles in Statistical Mechanics* (reprinted by OxBow Press, Woodbridge, CT, 1981).
[32] P. Hertz, Ann. Phys. (Leipzig) **338**, 225 (1910).
[33] T. Kasuga, Proc. Jpn. Acad. **37**, 366 (1961).
[34] H. Callen, *Thermodynamics* (Wiley, New York, 1960).
[35] C. Kittel, *Elementary Statistical Physics* (Wiley, New York, 1961).
[36] P. T. Landsberg, J. Phys. A **10**, 1773 (1977).
[37] M. Campisi, Phys. Rev. E **93**, 039901(E) (2016).