Negative Absolute Temperature

by Isaac Woodard

Abstract – Temperature is a concept used in everyday life for things such as checking the weather and cooking food. In thermodynamics, though, temperature is defined formally as the partial derivative of internal energy with respect to entropy with particle number and system volume held fixed. Entropy is a never-decreasing value which is found from the multiplicity of a system's macrostate. In energy unbounded systems, entropy increases as more energy is put into a system. However, in systems where energy is bounded, entropy decreases as the system approaches its energy saturation limit. This results in the possibility of negative absolute temperatures for energy bounded systems. If a system's hotness is defined as being able to give off heat energy to its surroundings, then a negative temperature system is hotter than any positive temperature system. A simple example of a negative temperature system is a two-state paramagnet set in a uniform magnetic field. The magnetic dipoles have a high energy state and a low energy state. The total energy is hence bounded by the number of dipoles and the system exhibits negative temperatures when more than half of the dipoles are in the high energy state. Another example of a negative temperature system is the electron gas in the lasing medium of a laser. Lasers operate by exciting electrons in a lasing medium to emit photons. To create the laser beam, a very large number of electrons must be excited into higher states. In thermal equilibrium, less than half of the electrons in a system can be in excited states, but in a laser enough electrons are excited to create a population inversion where the majority of the electrons are excited and a negative temperature system is created. Negative temperature systems have few practical uses, but the concept is useful for theoretical modeling of exotic systems where it is possible for entropy to decrease with increasing internal energy.

There are several different ways temperature can be defined, some intuitive and some precise. An intuitive way temperature is often understood is by how “hot” an object is. The hotter the object is, the higher the temperature. This definition has limitations, though, because the idea of “hot” is only correlated to temperature while it is directly tied to the flow of heat between an object and its surroundings. A more precise way to define temperature is simply as the value given by a thermometer. This definition works essentially by default. While it is simple, though, it depends on having a thermometer that works in the necessary temperature range and environment.

A definition of temperature which has both intuitive and precise meaning is the proportionality between temperature and the average kinetic energy of the atoms or molecules in an object: $T \propto KE_{ave}$. This is likely the most common definition of temperature in the science classroom. Another way to express this idea is that temperature is proportional to an object’s total internal energy, $T \propto U$, where in the typical case the internal energy comes from the kinetic energy of the individual atoms or molecules in an object. Unfortunately, this last definition has limitations as well. In particular, it can’t be used to explain negative absolute temperatures. To get a working definition for negative temperatures, there are a few additional concepts which need to be addressed first.

The first of these concepts is multiplicity. Here multiplicity refers to the number of different ways to arrange the individual members of a system to get the same overall system. The specific arrangements are known as microstates while the overall arrangement is known as a macrostate. Multiplicity, then, is the number of different microstates for a given macrostate.[1] As an example, consider a grocery list with ingredients for several meals. This list can be viewed as a macrostate. Another list with the same ingredients but with items listed in a different order would be considered the same macrostate. However, the microstate of the list changes. There is a different microstate for each specific arrangement of the items on the grocery list.

The next concept to consider is entropy. Entropy is directly defined from multiplicity in the second law of thermodynamics. The second law of thermodynamics defines entropy as the product of Boltzmann’s constant and the natural logarithm of multiplicity.[2]

$$S = k \ln \Omega \tag{1}$$

This relationship means that as multiplicity increases, so does entropy, and conversely as multiplicity decreases entropy decreases as well. For systems of particles on the order of

Avogadro's number, multiplicities are very large. As a consequence, most of a system's microstates are held by a small number of macrostates. These few macrostates have an overwhelmingly higher probability of describing the system than any other macrostate, so much so that it is virtually impossible for the multiplicity of the system to decrease. This means that it is also virtually impossible for entropy to decrease. The third law of thermodynamics expresses the non-decreasing nature of entropy. In particular,[1]

$$\Delta S \geq 0 \tag{2}$$

This statement holds true for the sum of the change in entropy of a system and its surroundings. While the third law can be viewed as a statement of probability, in practice it is an immutable fact.

With the concept of entropy it is possible to give a formal definition for temperature. Temperature can be defined as the reciprocal of the change in entropy of a system with respect to the change in its internal energy, [3, 4]

$$\frac{1}{T} \equiv \left(\frac{\partial S}{\partial U}\right) \tag{3}$$

This can be re-written as the change in internal energy with respect to entropy,

$$T = \left(\frac{\partial U}{\partial S}\right)_{N,V} \tag{4}$$

where the subscripts denote that the relation is only valid as long as the number of things in the system, *N*, and the volume of the system, *V*, don't change.[1] These expressions allow temperature values to be interpreted from the slope of graphs of entropy and internal energy. Such a graph can be seen in Fig. 1.

It is now possible to describe the conditions under which negative absolute temperatures can arise. Absolute temperature refers to temperatures measured on the Kelvin scale. This distinction is important because negative temperatures are quite familiar on the Celsius and Fahrenheit scales. For reference, absolute zero is equal to about -273^{o} C and -460^{o} F. Negative absolute temperature is fundamentally different from negative temperatures on non-absolute scales. This difference lies in the energy-entropy relation of negative absolute temperature systems. Most of the systems encountered in the world can be described with positive absolute temperature. This is because entropy usually increases with increasing internal energy. As can be seen in the graph on the left in Fig. 1, this results in a positive temperature value. However, some systems have an inverse relationship between energy and entropy. This can be seen in graph on the right in Fig. 1. For these systems, entropy decreases once a certain threshold for the internal energy is reached. This results in a negative slope and thus a negative absolute temperature.

The strange energy-entropy relation for negative temperature systems likely raises the question of how heat would flow into or out of such as system. To understand this, let us first consider how heat flows for positive temperature systems. In general, positive temperature systems are considered "hot" if heat flows out of them into their surroundings. This flow of heat is due to a difference in temperature. A positive temperature system with a higher temperature will give off heat to a positive temperature system with a lower temperature. This process is governed by the third law of thermodynamics and occurs because it increases the total entropy of the two systems. While the high temperature system loses entropy by giving off heat, the low temperature system gains entropy by receiving the heat. The gain is greater than the loss because entropy changes more dramatically at lower positive temperatures.

Using the ability to give off heat as the definition of "hot", negative temperature systems can be viewed as infinitely hot compared to any positive temperature system.[5] Due to the inverse energy-entropy relation for negative temperature systems, they are able to increase their own entropy by giving off heat. When a negative temperature system is put into thermal contact with a positive temperature system, the total entropy of the two systems is increased when the negative temperature system gives off heat to the positive temperature system. In the situation where two different negative temperature systems are put into thermal contact with each other, the systems will compete for which can gain more entropy by giving off heat. Referring to the graph on the right in Fig. 1, the negative temperature system with a temperature closer to absolute zero will give off heat.

The inverse entropy-energy relation for negative temperature systems comes from one main requirement. Negative temperature systems are only possible for systems where the internal energy is bounded.[6] This bound makes it possible for an increase in internal energy to cause a decrease in entropy. Systems capable of exhibiting negative temperatures will first exhibit positive temperatures as their internal energy is increased from its minimum. Past a certain threshold, though, adding more energy decreases the system's entropy and the temperature becomes negative.

Most of the matter that makes up the world around us exhibits positive temperatures for any amount of internal energy because typically there is no upper bound on a system's internal energy. The contrast between how energy and entropy change for systems capable of exhibiting negative temperatures and systems which only exhibit positive temperatures can be seen in Fig. 2. The figure compares the distribution and temperature of occupied states in a lattice and a spin system for increasing amounts of internal energy.

A specific system capable of exhibiting negative absolute temperatures is a two-state paramagnet. A two-state paramagnet is a collection of magnetic dipoles where each dipole has an up-spin and a down-spin orientation. When the paramagnet is placed in a uniform magnetic field the two orientations take on different energy values. The orientation that points with the magnetic field takes on a low energy equal to $-\mu B$, where μ is a constant and B is the strength of the uniform magnetic field. The orientation that points against the magnetic field takes on a high energy equal to $+\mu B$. The number of dipoles which point against the field can be expressed as $N_\uparrow$ and the number of dipoles which point against it can be expressed as $N_\downarrow$. If the magnetic field points down and the high energy orientation points up the total energy of the paramagnet can be expressed as

$$U_{tot} = \mu B(N_\uparrow - N_\downarrow) \tag{5}$$

which is the sum of the energies of the individual dipoles. Notably, the zero point for the paramagnet's energy occurs when half of the dipoles point up and half point down. Minimum energy occurs when all the dipoles point down and maximum energy occurs when all the dipoles point up.

The negative temperature behavior of this system arises from its inverse energy-entropy relation past a certain energy threshold. The cause of this behavior can be seen by inspecting the multiplicity of the system. The multiplicity is given by simple combinatorics for a two state system, in particular[1]

$$\Omega = \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow! N_\downarrow!} \tag{6}$$

For a given number of dipoles, the multiplicity is maximized when half of the dipoles point up and half point down. The multiplicity is minimized when all of the dipoles point either up or down. The minimum value of the multiplicity is one for any number of magnetic dipoles. The maximum value of the multiplicity corresponds to the energy threshold where the system exhibits negative temperatures. The minimum values correspond to the bounds on the energy of the system.

If the two-state paramagnet begins at minimum energy with all of the dipoles pointing down, the multiplicity and thus the entropy are both at a minimum value. As energy is added to the system, its energy-entropy relation is positive and it exhibits positive temperature. This continues until half of the dipoles are flipped to point up. At this point this system can be described with an infinite positive temperature.[5] If the system takes on more internal energy the temperature will flip from positive infinity to negative infinity. The system now loses entropy as it gains entropy and its temperature is negative. This continues until all of the dipoles in the system are flipped up and the system has reached the upper bound for its internal energy. A graph of the energy-entropy relation for this process can be seen in the graph on the right in Fig 1.

An experiment was conducted to cause a two-state paramagnet to exhibit negative temperature by Purcell and Pound in 1950.[7] The lithium nuclei in a lithium-fluoride crystal were used as a nuclear paramagnet. The crystal was initially placed in a strong magnetic field of 6376 gauss. It was then transferred to a solenoid with a field of 100 gauss. Current was discharged through the solenoid to reverse the field to -100 gauss. The crystal was then removed from the solenoid and its magnetization was measured. The strong magnetic field served to align nearly all of the dipoles in the crystal with its field. When the crystal was placed in the solenoid and the field of the solenoid was reversed, most of the dipoles in the crystal were suddenly pointed against the magnetic field of the solenoid. In this sense, more than half of the dipoles had a high energy spin orientation and the two-state paramagnet could be described with a negative temperature. The duration of the negative temperature state lasted for about five minutes. Periodic sampling of the crystal’s magnetization can be seen in Fig 3. The peaks below the x-axis correspond to when the paramagnet had negative temperature.

A more complete description of the energy of the nuclear paramagnet used in this experiment includes spin-spin interactions and spin-lattice interactions.[2]

$$U_{tot} = -\boldsymbol{h} \cdot \mu \boldsymbol{B} + W_{ss} + W_{sl} \tag{7}$$

The ability of the system to have bounded internal energy and to exhibit negative absolute temperature requires the spin-spin and spin-lattice interactions to be negligible. The spin-lattice interactions are negligible so long as the relaxation time of the interactions is long enough to ignore them on small time scales. The spin-spin interactions can be ignored so long as they are negligible compared to the energy of the magnetic dipole moments.[2]

Another system capable of exhibiting negative absolute temperature can be found in the operation of a laser. The basic components of a laser are the lasing medium and parallel mirrors that bound the optical cavity.[8] The lasing medium is situated in between the mirrors. In solid-state lasers the lasing medium is a solid but liquid and gaseous lasing mediums also exist. The mirrors typically have a reflectivity of about 99% to minimize optical loss.[8] In addition a laser has some mechanism which pumps energy into the lasing medium to excite electrons. In solid state lasers a bulb known as a flashlamp is wrapped around the lasing medium to "pump" energy via light into the lasing medium.

Laser light comes from the relaxation of excited photons from an excited state back to the ground state. In practical lasers a three-level or four-level excitation and emission process takes place but a two-level process with just a ground state and one excited state gives sufficient theoretical understanding for our purposes.[9] A diagram of three-level and four-level processes can be seen in Fig. 4. The frequency of the emitted laser light is given by

$$E = hf \tag{8}$$

In the two-level process the difference in energies between the ground state and the excited state, ΔE, is equal to the energy of the emitted light. This in turn is equal to Planck's constant, h, times the frequency of the light, f. The emission process can be seen in Fig. 5 where an electron is first excited by incoming light from a flashlamp or other exciting source and then relaxes back to the ground state by emitting a photon. The emitted light travels back and forth in the optical cavity as it reflects off of the parallel mirrors. This creates standing waves of monochromatic light in the laser. Allowed wavelengths of light are half integer multiples of the length of the optical cavity

$$L = \frac{\lambda n}{2} \tag{9}$$

As photons travel back and forth through the lasing medium, they stimulate emission of additional photons. For a coherent laser beam to develop, sometimes referred to as lasing, it is necessary for the laser to reach a certain threshold gain in the density of photons to offset optical losses.[10]

The phenomenon which makes it possible for many lasers to reach the necessary threshold gain is known as a population inversion.[11, 12] A population inversion can be viewed as an inversion of the expected probability distribution from the Boltzmann distribution[6]

$$P = \frac{1}{Z} e^{-\frac{E}{kT}} \tag{10}$$

The Boltzmann distribution gives the probability of an electron being in a certain energy level at thermal equilibrium. This probability decays exponentially for energy levels above the ground state. For a system in thermal equilibrium, if we consider the ground state and the first excited state, an electron will always have a higher probability of being in the ground state than in the excited state. In other words the ratio between the two states will always be greater than one.

$$\frac{P_1}{P_0} = \frac{e^{-E_1/kT}}{e^{-E_0/kT}} > 1 \tag{11}$$

However, by putting extra energy into the system so it is not in thermal equilibrium it is possible to give the electron a higher probability of being in the excited state. In this case the ratio between the two states is less than one.

$$\frac{P_1}{P_0} = \frac{e^{-E_1/kT}}{e^{-E_0/kT}} < 1 \tag{12}$$

In this case a population inversion has taken place.

The electron gas in the lasing medium of a laser can be viewed as its own system within the laser. It is this system which is capable of exhibiting negative temperature. The point at which the electron gas reaches a negative temperature is the same as the point where a population inversion is reached. While the laser is off, the electrons in the lasing medium are in thermal equilibrium with their environment. When the laser is turned on the flashlamp pumps extra energy into the lasing medium so that a majority of the available electrons are in excited states and a population inversion takes place. At this point, attempting to describe the probability distribution of the electrons with Boltzmann factors, $\exp\,(-E/kT)$, shows that the temperature of the electrons must be negative.[13] Rather than exponentially decaying, the probability of electron occupation increases with increasing energy. This is only possible if the temperature value is negative and the exponential becomes positive.

The theory of negative absolute temperature has some implications both for practical and hypothetical use. While there is some debate over whether negative absolute temperature is an artifact of inappropriate definitions for entropy,[2, 3, 6, 13] if the definition given here for entropy is accepted then negative absolute temperature is useful for describing exotic systems with an upper bound on their internal energy. This usefulness comes from the nature of such systems to decrease in entropy as their internal energy is increased past a certain threshold. As for the hypothetical, a gas of attracting atoms can be kept from collapsing on itself if the gas exhibits a negative absolute temperature.[14, 15] This raises parallels to the role dark energy is hypothesized to play in preventing the universe from contracting due to the force of gravity.[14] In addition, negative absolute temperature systems raise the question of whether a Carnot heat engine with 100% or greater efficiency could be constructed.[2, 14] A Carnot heat engine operates between two different temperature reservoirs. The efficiency of a Carnot heat engine is given by

$$e \leq 1 - \frac{T_c}{T_h} \tag{13}$$

where T_c and T_h are the temperatures of the cold and hot reservoirs respectively.[1] A possible Carnot cycle for a heat pump using a two-state paramagnet as the working substance is described in Fig. 6.

In summary, negative absolute temperatures are possible for systems with an upper bound on their internal energy. Two systems were discussed which can exhibit negative absolute temperature: a two-state paramagnet and the electron gas system in the lasing medium of a laser. For the paramagnet, the internal energy was bounded by the number of magnetic dipoles and the energies of their two spin orientations within a uniform magnetic field. The point at which half of the dipoles pointed up and half pointed down marked the threshold where an increase in internal energy caused a decrease in entropy. Past this point the system exhibited negative absolute temperature. The electron gas in a two-level laser can be described similarly if the ground state is taken as the low energy orientation and the excited state is taken as the high energy orientation. In this case, the internal energy is bounded by the number of available electrons and the difference in energy of the ground state and excited state. Similarly to the case with the two-state paramagnet, a negative temperature is reached once more than half of the available electrons in the lasing medium are in the excited state. A population inversion is an equivalent way to describe this phenomenon.

Additional systems which have been found to exhibit negative absolute temperature include a gas of ultracold attracting bosons[15] and two dimensional Onsager vortex clusters which can form in quantum fluids.[4] At present, the theory of negative absolute temperature has limited practical use, but it has application in describing systems where entropy can decrease with increasing internal energy.

References

1. D. V. Schroeder, *An Introduction to Thermal Physics*, 1st ed. (Addison Wesley, San Francisco, 2000)

2. E. Abraham and O. Penrose, Phys. Rev. E **95** (1), 012125 (2017), doi: 10.1103/PhysRevE.95.012125

3. D. V. Anghel, EDP Sci. **108**, 02007 (2016), doi: 10.1051/epjconf/201610802007

4. G. Gauthier, M. T. Reeves, Y. Xiaoquan, A. S. Bradley, M. Baker, T. A. Bell, H. Rubinsztein-Dunlop, M. J. Davis and T. W. Neely, arXiv, 1 (2018). doi: arXiv:1801.06951

5. W. G. Proctor, Sci. Amer. **239** (2), 78 (1978), doi: 10.1038/scientificamerican0878-90

6. R. J. de Assis, C. J. Villas-Boas and N. G. de Almeida, Jour. of Phys. B-Ato. Mol. and Opt. Phys. 52 (6) (2019).

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

8. D. J. Klotzkin, *Introduction to Semiconductor Lasers for Optical Communications: An Applied Approach*, 1st ed. (Springer, New York, 2014), 11

9. J. O. White, Ieee Jour. of Quan. Ele. 45 (10), 1213 (2009).

10. G. Bjork, A. Karlsson and Y. Yamamoto, Phys. Rev. A **50** (2), 1675 (1994), doi: 10.1103/PhysRevA.50.1675

11. Z. K.-H. Chu, arXiv, 1 (2009). doi arXiv:0902.0421

12. S. G. Pavlov, N. Dessmann, B. Redlich, A. F. G. van der Meer, N. V. Abrosimov, H. Riemann, R. K. Zhukavin, V. N. Shastin and H. W. Hubers, Phys. Rev. X **8** (4), 041003 (2018), doi: 10.1103/PhysRevX.8.041003

13. J. Dunkel and S. Hilbert, Nat. Phys. **10** (1), 67 (2014), doi: 10.1038/nphys2815

14. A Temperature Below Absolute Zero, https://www.mpg.de/research/negative-absolute-temperature.

15. S. Braun, J. P. Ronzheimer, M. Schreiber, S. S. Hodgman, T. Rom, I. Bloch and U. Schneider, Sci. 339 (6115), 52 (2013).

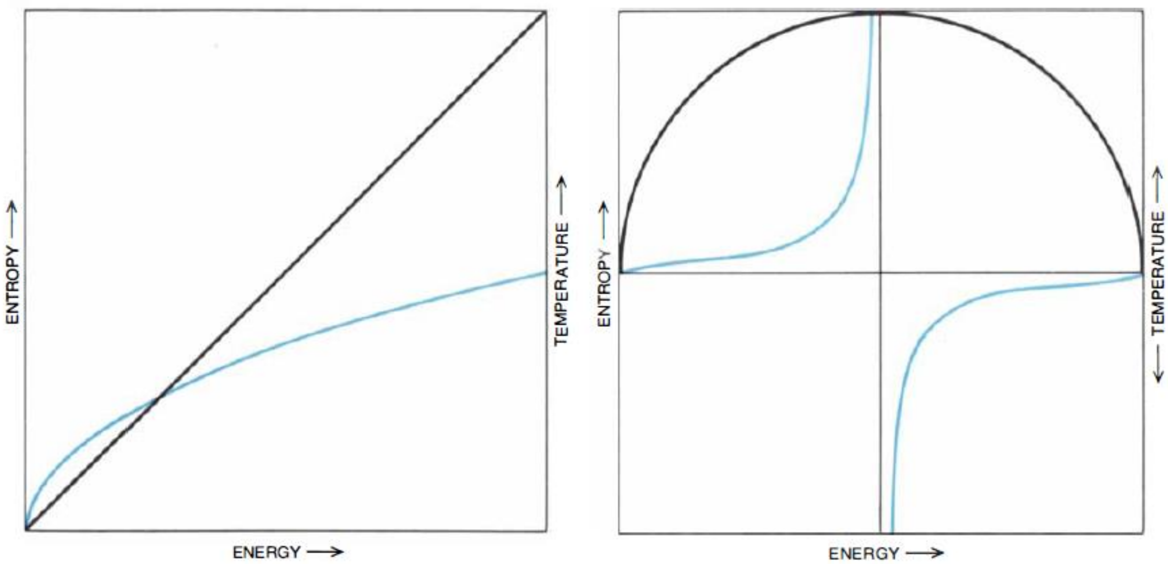

Fig. 1. “Energy and entropy are the basic elements in a definition of temperature in which negative values arise naturally: Temperature measure the amount of energy that must be added to a system to yield a given change in entropy. Here entropy (black curves) and temperature (colored curves) are both graphed as functions of energy. In a vibrational system (left) an increase in energy invariably brings an increase in entropy, and so the temperature is always positive. In the spin system, however (right), the entropy has a maximum possible value; at that point the change in the entropy is zero, and so the temperature is infinite. With each further increase in energy the entropy is reduced, and so the sign of the relation changes: the temperature becomes negative and at the maximum energy reaches minus zero.” W. G. Proctor, Sci. Amer. **239** (2), 78 (1978), doi: 10.1038/scientificamerican0878-90

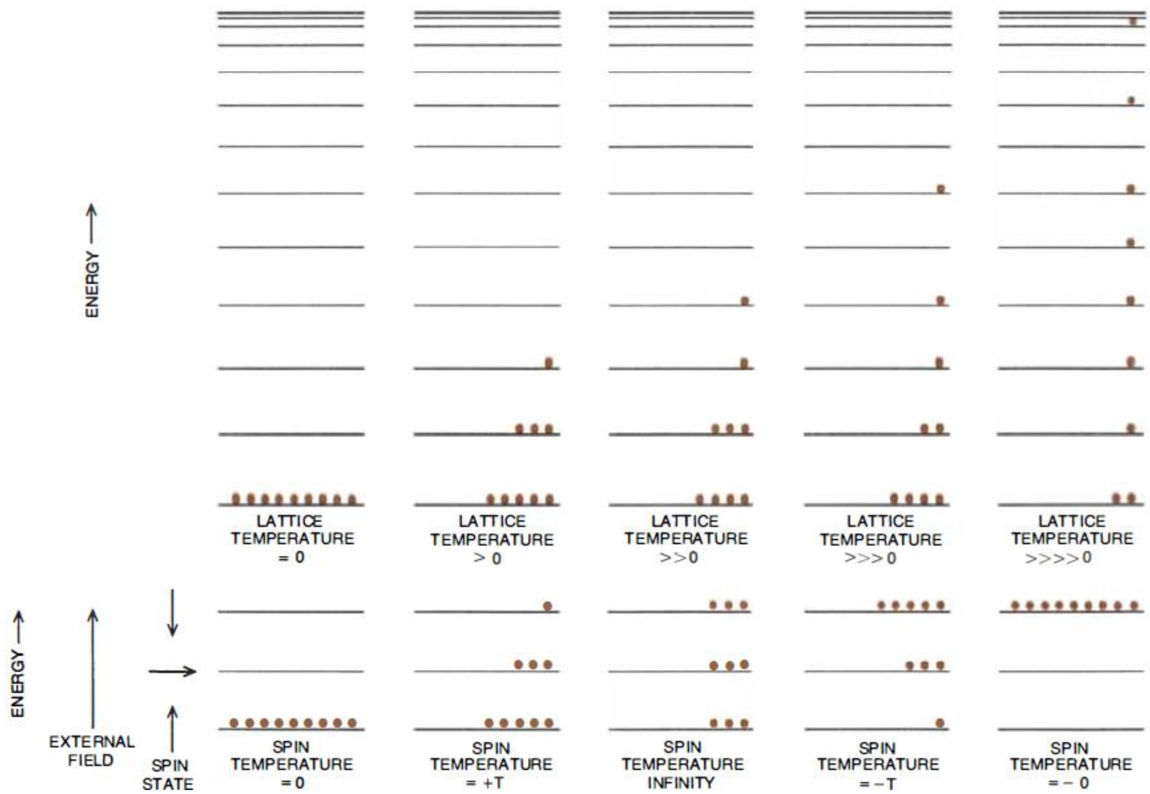

Fig. 2. A diagram of the distribution of members in a lattice system and a spin system amongst available energy states. As the lattice temperature increases the distribution becomes more even but the ground state remains the most occupied. For the spin system the energy is bounded and negative temperature is reached once the lowest energy spin state is less occupied than the other spin states. W. G. Proctor, Sci. Amer. **239** (2), 78 (1978), doi: 10.1038/scientificamerican0878-90

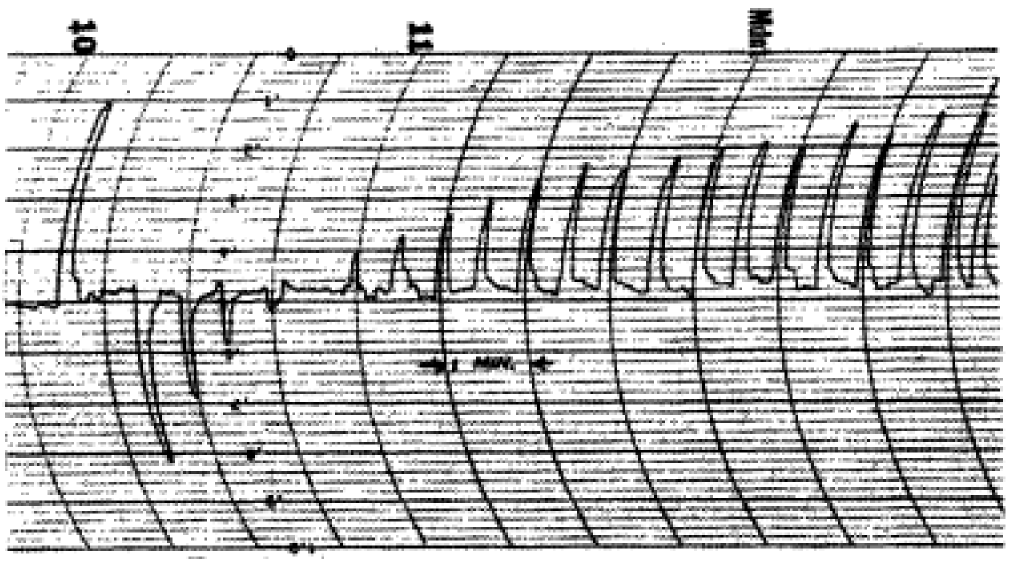

Fig. 3. “A typical record of the reversed nuclear magnetization. On the left is a deflection characteristic of the normal state at equilibrium magnetization (T about 300oK), followed by the reversed deflection (T about -350o K), decaying (T goes to – infinity) through zero deflection (T=infinity) to the initial equilibrium state.” E. M. Purcell and R. V. Pound, Phys. Rev. **81**, 279 (1951)

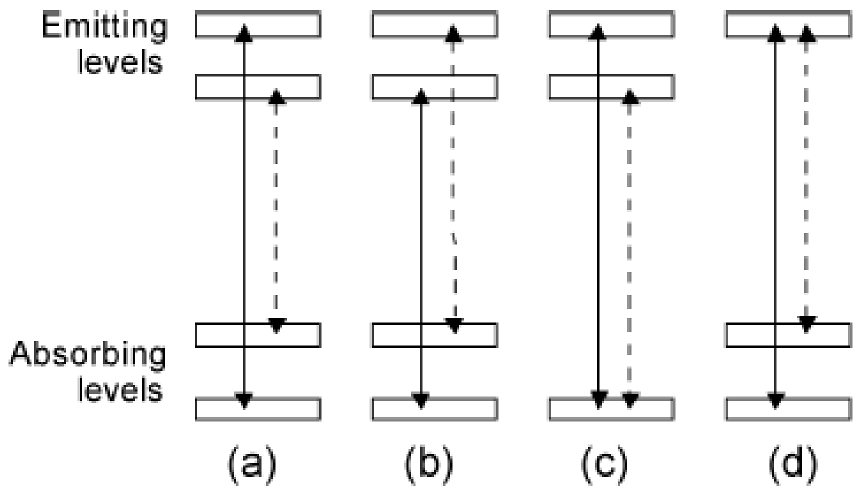

Fig. 4. “Different possibilities for four and three-level systems, showing pump (solid) and laser (dashed) transitions. All four cases can be quantitatively compared, on the basis of the “system level”, *l*.” J. O. White, Ieee Jour. of Quan. Ele. 45 (10), 1213 (2009).

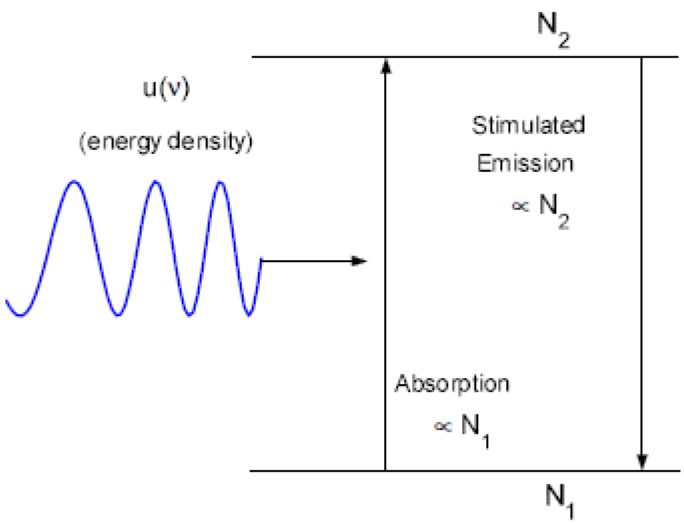

Fig. 5. “Schematic 2-level system for absorption and stimulated emission transitions (atoms with two energy levels).” Z. K.-H. Chu, arXiv, 1 (2009). doi arXiv:0902.0421

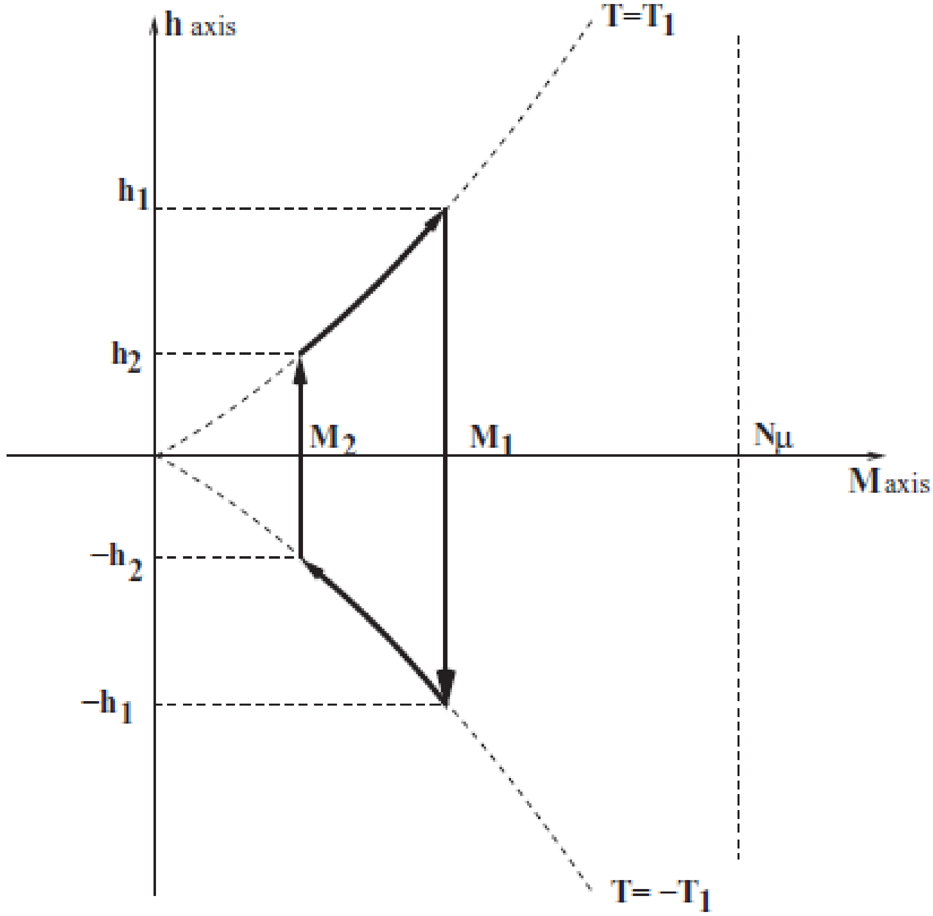

Fig. 6. "“Carnot” cycle for a heat pump using negative temperatures. The area enclosed by the loop equals the total energy transferred per cycle. For the nuclear spin system, the equation of the temperature-*T* isotherm is $h = (kt/\mu)\text{arc tanh}(M/N\mu)$. The vertical line at $M = N\mu$ is an asymptote 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." E. Abraham and O. Penrose, Phys. Rev. E **95** (1), 012125 (2017), doi: 10.1103/PhysRevE.95.012125