"Negative Temperature", a Necessary and Sufficient Condition for Entropy Decrease in an Isolated System

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Negative temperature is based on the Kelvin scale and the condition dU>0 and dS<0. Conversely, there is also negative temperature for dU<0 and dS>0. When the derivation of negative temperature is examined, it necessarily requires a decrease in entropy. The concept of negative temperature contradicts the usual meaning of 'temperature,' as well as contradicting some basic concepts of physics and mathematics. Negative temperatures can be shown to occur only in a system which is not in thermodynamic equilibrium. It is here proposed that the decrease of entropy is possible due to magnified fluctuations and internal interactions in some isolated systems. Further, a necessary and sufficient condition for the decrease of entropy is discussed quantitatively. In addition, some possible tests for the decrease of entropy in isolated systems are proposed. They should be confirmed by many stable states in nature.

1. Restatement of Negative Temperature

In thermodynamics the concept of negative temperature is a well-known idea proposed and expounded by Ramsey [1] and Landau [2], et al. Ramsey discussed the thermodynamics and statistical mechanics of negative absolute temperatures in a detailed and fundamental manner [1]. He proved that "*if the entropy of a thermodynamic system is not a monotonically increasing function of its internal energy, it possesses a negative temperature whenever* $(\partial S/\partial U)_X$ *is negative. Negative temperatures are hotter than positive temperature.*" He pointed out that, from a thermodynamic point of view, the only requirement for the existence of a negative temperature is that the entropy S should not be restricted to a monotonically increasing function of the internal energy U. In the thermodynamic equation relating TdS and dU, a temperature is

$$T = \left(\frac{\partial S}{\partial U}\right)_X^{-1} \tag{1}$$

The assumption that entropy S increases monotonically with U is not necessary in the derivation of many thermodynamic theorems. In this regard, negative temperatures are hotter than infinite temperatures. The term 'negative temperature' is unfortunate and misleading. If the temperature function had been chosen as $-1/T$, then

1. the coldest temperature would correspond to $-\infty$ for this function,
2. positive infinite temperatures on the conventional scale would correspond to 0, and
3. negative temperatures on the conventional scale would correspond to positive values of this function.

Ramsey proposed: "*One of the standard formulations of the second law of thermodynamics must be altered to the following: It is impossible to construct an engine that will operate in a closed cycle and prove no effect other than (a) the extraction of heat from a positive-temperature reservoir with the performance of an equivalent amount of work or (b) the rejection of heat into a negative-temperature reservoir with the corresponding work being done on the engine. A thermody-*

namic system that is in internal thermodynamic equilibrium, that is otherwise essentially isolated" [1]. Negative temperatures are applied to some mutually interacting nuclear spin systems. Klein justified Ramsey's criteria for systems capable of negative absolute temperatures [3]. The only premise of Ramsey's statement is the definition of Kelvin temperature in equation (1). Even Klein implied that entropy might decrease with U, i.e., in an original definition of temperature

$$T = \frac{\partial U}{\partial S} \tag{2}$$

when $dU > 0$ and $dS < 0$, $T < 0$.

Intuitively, the physical meaning of temperature is that it describes whether a body is "hot or cold" [4]. Maxwell defined the absolute thermodynamic temperature scale as being proportional to the quantity of heat. His definition is that the temperature of a body is its thermal state in reference to its ability to transfer heat to other bodies. This definition was adopted substantially unchanged by Planck and Poincare [5]. However, in microscopic thermodynamics temperatures are related to the states of molecular motions. Kelvin temperature scale is defined by the relationship given in equation (1).

Landau's definition of negative temperature is a little different. In his book, **Statistical Physics** [2], negative temperature was dealt with by considering: some peculiar effects related to the properties of paramagnetic dielectrics. Here the interaction of these magnetic moments brings about a new magnetic spectrum, which is superposed on the ordinary spectrum. From this the entropy is

$$S_{\mathrm{mag}} = N \ln g - \frac{1}{2T^2}\left\langle \left(E_n - \bar{E}_n\right)^2 \right\rangle \tag{3}$$

where N is the number of atoms, g is the number of possible orientations of an individual moment relative to the lattice, E_n are the energy levels of the system of interacting moments, and $\bar{E}_n$ is the average as the ordinary arithmetic mean. Here the atomic magnetic moments are considered to be fixed at the lattice sites and interacting with one another as a single isolated system.

There is a further interesting result that the system of interacting moments may have either a positive or a negative temperature. "*At $T = 0$, the system is in its lower quantum state, and its entropy is zero*" [2]. In fact, the temperature $T = 0$ (absolute zero) is impossible to achieve. "*As the temperature increases, the energy and entropy of the system increase monotonically. At $T = \infty$, the energy is $\bar{E}_n$ and the entropy reaches its maximum value $N \ln g$; these values correspond to a distribution with equal probability over all quantum states of the system, which is the limit of the Gibbs distribution as $T \to \infty$.*" This statement regarding original negative temperature is based on the two premises: first, that the entropy of the system increases monotonically, and second, that the Gibbs distribution holds. From this some strange arguments [2] are obtained:

1. "*The temperature $T = -\infty$ is physically identical with $T = \infty$; the two values give the same distribution and the same values of the thermodynamic quantities for the system.*" According to the general definition, temperature cannot be infinite, since the quantity of heat or molecular motion all cannot be infinite. Negative temperature, even negative infinite temperature is stranger. Importantly, and in contradistinction, and in the same book *Statistical Physics*, Landau proved that temperatures must be positive: $T > 0$ [2]. Moreover, it must be noted that $T = \infty = -\infty$ is excluded by mathematics.

2. "*A further increase in the energy of the system corresponds to an increase in the temperature from $T = \infty$*", and "*the entropy decreases monotonically.*"

3. "*At $T = 0^-$ the energy reaches its greatest value and the entropy returns to zero, the system then being in its highest quantum state.*" This obeys Nernst's theorem, but in which the quantity of heat is zero at $T = 0$, while at $T = 0^-$ it possesses highest quantum state! I do not know whether $T = 0 = 0^-$ holds or not.

4. "*The region of negative temperature lies not below absolute zero but above infinity*", i.e., "*negative temperatures are higher than positive ones*".

2. Negative Temperature and Entropy Decrease

In a previous paper [6-8], we proved that since fluctuations can be magnified due to internal interactions under certain conditions, the equal probability and the standard equations do not hold. The laws of entropy and thermodynamics are usually applied to closed systems. This is how the previous equations should be used. If various internal complex mechanism and interactions cannot be neglected, a state with smaller entropy (for example, self-organized structures) will be able to appear. In these cases, the statistics and the second law of thermodynamics should be different, and decrease of entropy due to internal interactions in isolated system is caused possibly. In these cases a modification of the previous equations is necessary. A decrease in entropy due to internal interactions in an isolated system is one possible example. This possibility is researched for attractive process, internal energy, system entropy and nonlinear interactions, etc [6-8].

We think negative temperature necessarily derives from a decrease in entropy [9]. "$T = \infty = -\infty$" is only a finite threshold temperature T_c, which corresponds to a value of entropy from increase to decrease, and this entropy has a maximum of $N \ln g$. According to the basic equation of thermodynamics, i.e., Euler equation [10],

$$S = \frac{U}{T} - \frac{YX}{T} - \sum_i \frac{\mu_i N_i}{T} \tag{4}$$

If energy is invariant, the corresponding temperature should be

$$T = \frac{1}{S}\left(U - YX - \sum_i \mu_i N_i\right) \le \frac{E}{N \ln g} \tag{5}$$

This value should be testable and measurable. As temperature and energy increase continuously, entropy decreases to a minimum, but cannot be zero. In this process, energy passes necessarily from "negative temperature system" to positive temperature system.

Next, the Gibbs distribution is

$$w_n = Ae^{-E_n/T} \tag{6}$$

This means that "*the probability w_n of a state of the whole system such that the body concerned is in some definite quantum state (with energy E_n), i.e., a microscopically defined state*", and is acceptable provided that "*the system is assumed to be in equilibrium*" [2]. As long as it is assumed that the Gibbs distribution always holds, negative temperatures necessarily result.

There are several things which should be noticed at this point:

1. In both the above example as well as with lasers the related states are already in unstable or metastable equilibrium with higher energies.

2. Bodies of negative temperature are also completely unstable and cannot exist in nature [2].

3. The entropy of a body is a function only of its internal energy [2].

4. In states with negative temperature, a crystal can be magnetized in a strong magnetic field; then the direction of the field ~~is~~ can be reversed so quickly that the spins cannot follow it [2]. This system is in a non-equilibrium state, and its internal energy and entropy are different.

5. Lasers should also result in ~~be~~ an ordering process with a decrease of entropy.

Generally, the Gibbs distribution for a variable number of particles is [2]

$$w_{nN} = Ae^{(\Omega + \mu N - E_{nN})/T} \tag{7}$$

where Ω is the thermodynamic potential. The energy $E_{nN} = \Omega + \mu N$ corresponds to $T = \pm\infty$, and $E_{nN} < \Omega + \mu N$ corresponds to $T < 0$. Here the distributions are different for the number N of particles. The number N should be different in magnetic fields with reversed directions.

The above statement of "negative temperature" only proves that entropy is able to decrease with internal interactions in an isolated system. The experimental study requires that the spin system be well isolated from the lattice system [1]. This isolation is possible if the ratio of spin-lattice to spin-spin relaxation times is large [2]. This may describe in the following figure, which is taken from Fig.1 [1] and Fig.10 [2], in which the finite threshold value T_c corresponds to only a maximum point $dS/dE = 0$ [9, 11].
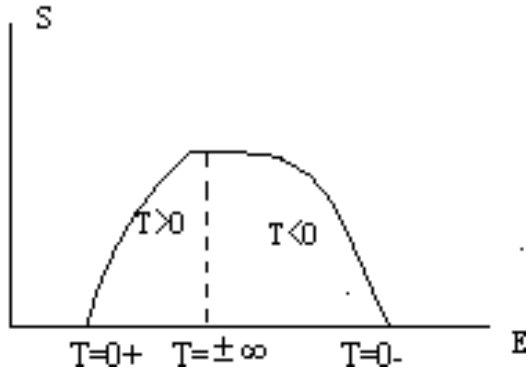
Fig. 1. "Negative temperature"

According to Eq. (1) or Eq.(2), when the condition $dU > 0$ and $dS < 0$ hold, a negative temperature will be obtained. Conversely, if $dU < 0$ and $dS > 0$, a negative temperature will also be obtained. But, Eq. (2) originates from Clausius entropy $dS = dQ/T$, so the question is, do the above conditions hold or not?

According to Eq. (5), $YX + \sum_i \mu_i N_i = 0$, T=U/S. In Fig.1, however, since $U > 0$ ($E > 0$) and $S > 0$, then $T > 0$. As a result, then we cannot obtain negative temperature, and $T_c = E_c / N \ln g$.

In another book, **Principles of General Thermodynamics** [5], Kelvin temperature (from Eq. (1)) of thermodynamic system may be either positive or negative. This depends on whether, as the system passes through stable states with fixed parameters, the entropy increases or decreases with increasing energy. This is different from Landau's statement. In fact, it seems to imply that the negative temperature is unnecessary, so long as the entropy decreases with increasing energy. "*A normal system can assume only positive Kelvin temperatures.*"

"*A system at a negative Kelvin temperature is in a special state. For if this were not true we could, by definition, do work on the system adiabatically and prove that the system was at a positive Kelvin temperature. A system is capable of attaining negative Kelvin temperatures if for some of its stable states the entropy decreases for increasing energy at fixed values of the parameters.*"

Further, for example, the entropy for a monatomic gas is given by

$$S = \frac{3}{2} R \ln T - R \ln \rho + S' \tag{8}$$

Based on this, T and the density ρ cannot be negative. If pure lithium fluoride (LiF) is considered, the system being considered is one of nuclear spin. In this case, the crystal spin lattice relaxation times are as long as 5 minutes at room temperature while the spin-spin relaxation time was less than 10^{-5} seconds. The systems lose internal energy as they gain entropy, and the reversed deflection corresponds to induced radiation. The sudden reversal of the magnetic field produces a negative temperature when the Boltzmann distribution is considered [12]. Next, this book [5] discusses heat flow between two systems, A and B, at unequal temperatures, and derives

$$dQ_A \left(\frac{1}{T_A} - \frac{1}{T_B} \right) > 0 \tag{9}$$

If we allow a heat quantity dQ_A to flow into A from B, there should be $T_B > T_A > 0$, which is also consistent with inequality (9). Further, according to an efficiency of heat engines

$$\eta = 1 - \frac{T_2}{T_1} \tag{10}$$

Thus, if either temperature is negative, the efficiency will be greater than unity. "*The results arrived at for negative temperatures which are strange to our intuition have no practical significance in the field of energy production.*" But, "*systems at negative Kelvin temperatures obey the second law and its many corollaries.*" Of course, "*it would be useless to consume work in order to produce a reservoir at a negative temperature which can be used to operate a very efficient heat engine*" [5]. Therefore, this seems to imply that negative temperature is introduced only in order to obey the second law of thermodynamics.

There is the same efficiency of a Carnot engine applied by Ramsey [1]:

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1} \tag{11}$$

Here, in order to avoid contradicting the principle of increasing entropy, various results regarding the behavior of this engine are discussed.

For an equal-temperature process, there is a simple result:

$$dS = \frac{1}{T}(dU + PdV) \tag{12}$$

where U is the internal energy of system. A general case is $dU + PdV > 0$, $dS > 0$ for usual temperature $T > 0$; $dS < 0$ if $T < 0$. Further, if $T > 0$ and $dU + PdV < 0$, for example, a contractive process is $dV < 0$, and $dS > 0$ is possible [6-8].

In fact, so long as $dS < 0$, the negative-temperature is unnecessary [9, 11]. In a word, negative temperature is a remarkable postulate -- it can only occur in nonequilibrium thermodynamics. It is a fallacy. From the Kelvin scale one obtains both infinite temperature and negative temperature, which is inconsistent with other definitions of temperature, as well as with some basic concepts of physics and mathematics. Moreover, "negative temperature" is confused easily with an absolute zero, which is usually defined as negative 273.16C.

3. A Necessary and Sufficient Condition for Decrease of Entropy in Isolated Systems

Recently, the universality of the second law of the thermodynamics has been questioned. The statistical basis for thermodynamics is the basic principle of statistical independence. The state of one subsystem does not affect the probabilities of various states of the other subsystems, due to the weak interactions among the different subsystems [2]. Therefore various interactions among these subsystems should not be considered. However various internal complex mechanisms and interactions cannot be neglected, because a state with smaller entropy (for example, a self-organized structure) will be able to appear under some conditions. In this case, statistics and the second law of thermodynamics may possibly diverge [6-8]. Since there can be a de-

crease in entropy in an isolated system because of internal interactions, statistical independence may be invalidated.

Specifically, this presents a possibility for attractive processes, internal energy, system entropy, etc. Therefore, a necessary condition of decrease of entropy in isolated system is the existence of internal interactions. The internal interactions are often nonlinearly related [7].

For any isolated system we proposed the following generalized formula [8]:

$$dS = dS^a + dS^i \qquad (13)$$

where dS^a is an additive part of entropy and is always positive, and dS^i is an interacting part of entropy and can be positive or negative. Eq. (13) is similar to a well known formula:

$$dS = d_i S + d_e S \qquad (14)$$

which is found in the theory of dissipative structure proposed by Prigogine. Two formulae are then applicable for internal or external interactions, respectively. Based on Eq. (13), the necessary and sufficient condition for entropy decrease in an isolated system will be:

$$0 > dS^i > -dS^a, \text{ i.e. } |dS^i| > dS^a \text{ (for negative } dS^i) \qquad (15)$$

In usual cases, the condition corresponds to that found in isolated systems where there are some stronger internal attractive interactions [12].

If we add a decrease of entropy, entropy with the arrow of time will resume symmetry. Thus the complete formulation should be the following symmetrical structure:

$$\text{Entropy} \begin{cases} \text{increase} \\ \text{decrease} \begin{cases} dS = d_i S + d_e S \\ dS = dS^a + dS^i \end{cases} \end{cases} \qquad (16)$$

Here decrease of entropy may be the dissipative structure ~~for~~ in an open system, or it may involve internal interactions in an isolated system.

We researched the fractal-dimensional and complex dimensional mathematics and the physics, and discussed the fractal relativity, which connects with self-similarity of the Universe and an extensive quantum theory. Combining the quaternion, etc., the high dimensional time $ict \rightarrow ic_1 t_1 + jc_2 t_2 + kc_3 t_3$ is introduced. The arrow of time and irreversibility are then derived. When the fractal dimensional time is obtained, space and time then possess complete symmetry. There can be a preliminary construction of a higher dimensional, fractal, complex and super-complex space-time theory covering all possibilities. We propose a generalized Noether's theorem, where the irreversibility of time should correspond to non-conservation of a certain quantity. Possible reversibility of time and decrease of entropy are discussed [13].

4. Some Possible Tests for Entropy Decrease in Isolated Systems

Fort and Llebot proved that classical entropy does not increase monotonically for an isolated fluid, and considered that generalized entropy of extended irreversible thermodynamics is more suitable for this fluid [14]. Erez, et al., discussed thermodynamic control by frequent quantum measurements, and the corresponding entropy and temperature of both the system and the bath are found to either decrease or increase depending only on the rate of observation, and contrary to the standard thermodynamical rules that hold for memory-less (Markov) baths [15]. They obtained a total Hamiltonian of the system [15]:

$$H_{tot} = H_S + H_B + H_{SB} \qquad (17)$$

in which $H_{SB} = SB$ is the system-bath interaction Hamiltonian. From this Eq. (13) may be derived, and it is associated with non-addition and nonlinearity. Moreover, $H_{SB} < 0$ corresponds to an attractive force. Entropy as a function of state should connect with internal interactions and the structure of the system. We proposed that the necessary condition of decrease of entropy in isolated systems is the existence of internal interactions, which is the weak system-bath coupling in this case [15]. If any interaction is external, this system will be not isolated. Therefore, Eq. (13) should be a universal formula.

When probability changes with time, entropy would be defined as:

$$S(t) = -k \sum_r P_r(t) \ln P_r(t) \qquad (18)$$

From this or $S = k \ln \Omega$ in an internal condensed process, the possible decrease of entropy can be calculated [8].

In experiments, Halperin, et al., found that the solid-He entropy decreases by 80% in an interval at $T = 1.17$ mK [16]. Xie, et al., found that the entropy discontinuity decreases ($\Delta S = 0.13R \ln 2$) as the magnetic field increases, and thermodynamic data not previously available are obtained [17]. The entropy of the quantized massless spinor field in the Schwarzschild space-time [18] is:

$$\Delta S = \frac{7\pi}{k} \begin{bmatrix} \frac{8}{9}x^{-3} + \frac{8}{3}x^{-2} + 8x^{-1} - \frac{16}{9} - \frac{200}{21}x \\ -8x^2 + \frac{488}{63}x^3 + \frac{128}{7}\ln x \end{bmatrix} \qquad (19)$$

in which $x = 2M/r$. Then

$$\frac{d(\Delta S)}{dx} = \frac{7\pi}{k} \begin{bmatrix} -\frac{8}{3}x^{-4} - \frac{16}{3}x^{-3} - 8x^{-2} - \frac{200}{21} \\ -16x + \frac{488}{21}x^2 + \frac{128}{7}x^{-1} \end{bmatrix} \qquad (20)$$

The equation $d(\Delta S)/dx = 0$ has six critical points, in which there is necessarily the limiting point x_0. So when $x > x_0$ or $x < x_0$, ΔS increases or decreases.

In chemical thermodynamics, the entropy of formation varies with pressure [4]. In general, any chemical reaction is reversible. Therefore some ordering processes with decrease of entropy are possible in an isolated system for various complex chemical oscillations, condensations, catalysis, self-organization and so on [19, 20]. The oscillatory component of the non-Markovian quantum relaxation [15] may extend to various oscillations. The Belousov-Zhabotinski reaction shows a period change automatically, at least at certain times.

Moreover, we researched a decrease of entropy in an isolated system in the quantum region, in particular for some Bose systems [21], and calculated quantitatively the decrease of entropy by the known formulas in the ordering phenomena and nucleation of the thermodynamics of microstructures [12]. Since various evolutions from astronomy to biology and social systems cannot be due to only an increase of entropy, we discussed possible decreases of entropy in astronomy, biology, psychology, some social systems and so on. We then obtained a mathematical expression for a moderate degree of input of negative entropy flow (which is a universal scientific law) [22].

The auto-control mechanism in an isolated system may produce a degree of order. If it does not need the input of energy, at least in a given time interval, the auto-control will act like a type of Maxwell demon [7], which is just a type of internal interaction. The demon may be a permeable membrane. For the isolated system, it is possible that a catalyst and other substances are mixed to produce a new order substance with smaller entropy [6-8]. Ordering is the formation of a structure through self-organization from a disordered state. Of course, a spontaneous process usually increases entropy, but an opposite process is also possible under some conditions [6-8]. In evolutionary processes and phase transformations, the systems cannot be in thermal equilibrium; this is true for various systems in biology and society [6-8].

In a word, according to the second law of thermodynamics, all systems in Nature will tend toward "heat death." This means the production of more complex systems will be impossible. However, gravitational interactions produce various ordered stable stars and celestial bodies. Electromagnetic interactions produce various crystals and atoms. Atomic stability is determined by electromagnetic interaction. According to the second law of thermodynamics, atoms should be unstable but strong interactions produce various stable nuclei and particles. Theses stabilities depend mainly on various internal interactions and self-organizations. These attractive interactions correspond to decrease of entropy in our theory [6-8]. Any stable objects and their formations from particles to stars are accompanied with internal interactions inside these objects, which have implied a possibility of decrease of entropy [7, 9, 22].

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