Some positive thoughts about Negative Absolute Temperature

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Abstract

It is now widely accepted that the concept of negative absolute temperature is real one and not just theoretical curiosity. In this brief report, by combining the formalism used in the statistical mechanics and thermodynamics, we have explained some aspects of negative temperature (both mathematically and graphically) in the two level system. We believe that these simple calculations may give useful and concrete insights about the negative absolute temperature to the undergraduate students.

1 Introduction

Traditionally the temperature of an ideal gas, consisting of point mass particles, is explained by establishing its relation with average kinetic energy. For a crystalline solid, the temperature is connected to the vibratory motion of nuclei about their mean positions. These connections have opened up a door to link the thermodynamic properties to a microscopic atomic structure. Further important insight of microscopic world can be obtained by Boltzmann definition of entropy. This established an association of the observable quantities of the macroscopic world (Thermodynamics) with the microscopic one (Statistical mechanics) through a relation

$$S = k_B \, ln \, \Omega$$

Here entropy, S, is a macroscopic parameter written in term of microscopic quantity called multiplicity of a state (Ω) and k_B is the Boltzmann constant. In thermal physics, the concept of temperature is introduced as the relationship between the entropy (S) and the internal energy (U).

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$$

Where N and V are number of particles and volume respectively. Hence by using the above definition,

the temperature can be rewritten as

$$\frac{1}{T} = k_B \left(\frac{\partial ln\, \Omega}{\partial U} \right)_{V,N}$$

The temperature remains positive if entropy is an increasing function of internal energy i.e gas consisting of free particles. In this type of physical system there is a lower bound on the energy and the lower level is more populated than the upper level.This can be understood from the fact that occupation number of each level is proportional to the Boltzmann factor

$$N_i \propto e^{-\epsilon_i / k_B T}$$

So the normalization factor for these N_i , popularly known as partition funtion, converges only if there is a lower bound on the ϵ_i for positive temperature state. There exists another class of physical systems where the entropy decreases with the increase in the internal energy *hence the temperature becomes negative*. In this type of system, there is a finite upper bound to the energy spectrum and the higher energy state are more populated than the lower energy state again to facilitate the convergence of partition function. This concept of negative absolute temperature is known since the work done by Onsager on vortices present in the 2-dim. hydrodynamics[1]. But experimentally the negative temperature was first observed in magnetic nuclear spin system by Purcell and Pound in the year 1951[2]. Recently it has been achieved in the ultra cold bosons in the optical lattices[3]. For the complete history of negative temperature and its implications on the thermodynamics, controversies and recent developments etc. , see the following ref's [4, 5, 6, 7, 8, 9, 10, 11, 12].

Motivated by the previous work in the literature about the negative temperature, in this paper we elaborate two important issues related to negative temperature. First, evaluate the entropy and internal energy of a finite level system when the population of the energy levels changes(we consider two levels in this work). The idea is to check what would happen to the temperature of such a system with the gradual change in the number of particles of the two levels. The second objective is to obtain the general expression of S (entropy) in terms of U (internal energy) and N (number of particles) by using the Lagrange interpolation method. We also believe that the above mentioned points related to the negative temperature have not been addressed adequately in the literature.

The outline of the paper is as follows: In section 2, we describe the set of equations for calculating the entropy of a two level system in various configurations of particle distributions. The Lagrange interpolation method along with its application to finite level system is presented in section 3. Finally, the results are discussed in section 4.

2 Entropy, S(U), of a finite level system

In this section we obtain the expressions of entropy and internal energy at various configurations of states defined by the distribution of particles in the two level system. We start with first case A; when the lower level of energy ϵ_1 is fully populated with $N_1 = N$ particles and upper level of energy ϵ_2 is completely vacant, $N_2 = 0$. Subsequently, we obtain both S and U for different cases when the population of lower level keep on decreasing and occupancy of high level goes on increasing. In other words we start with the case when $N_1 = N$ and $N_2 = 0$ and cover the entire range of variation of particles till $N_1 = 0$ and $N_2 = N$. The variation of entropy w.r.t. internal energy is plotted in Figure 1 and corresponding various configuration of particles in two levels are plotted in the Figure 2. Furthermore, a glance on Figure 1 shows that it is symmetric about the point U_D which corresponds to the maximum entropy of the given system. In this work we have assumed two level system with energy $\epsilon_1 < \epsilon_2$ and $N_1 + N_2 = N$. The details of calculations of S and U for various distribution of particles are as follows:

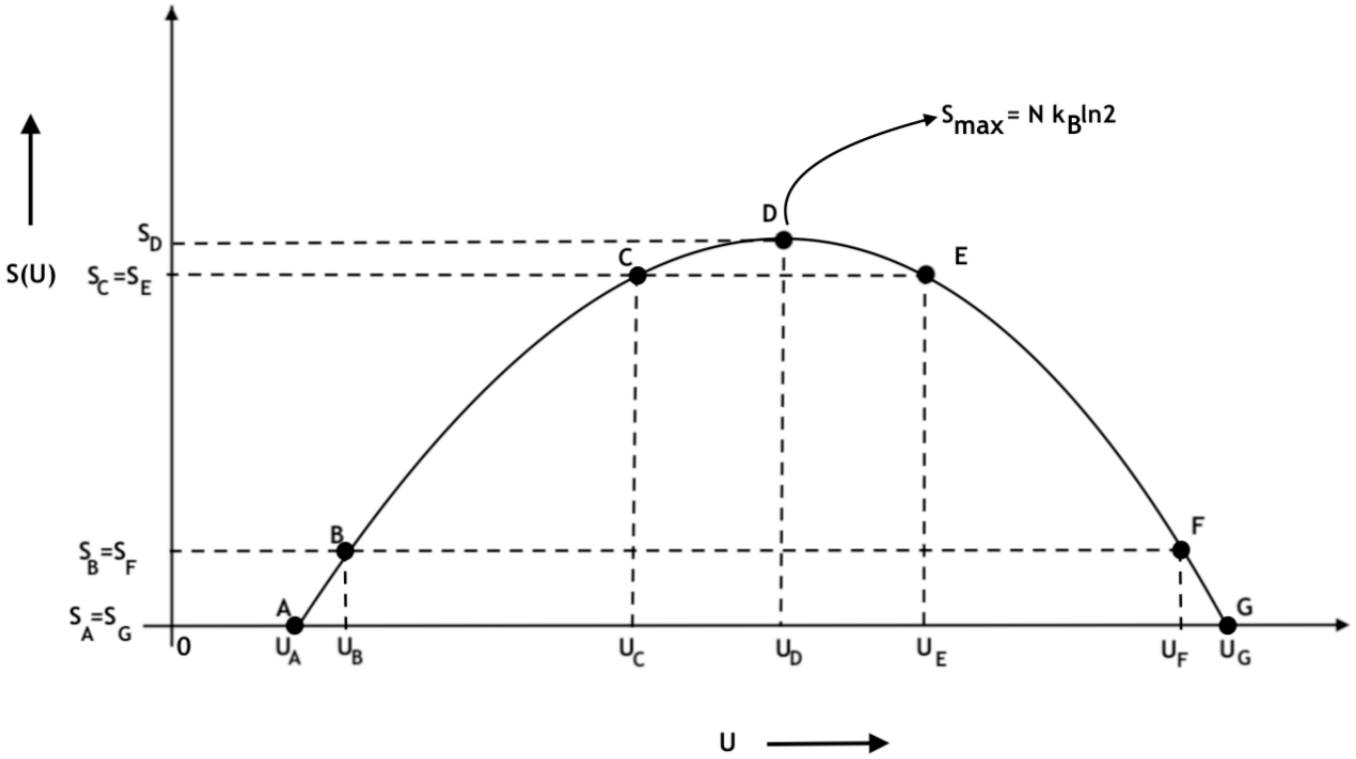

Figure 1: S versus U in a two level system

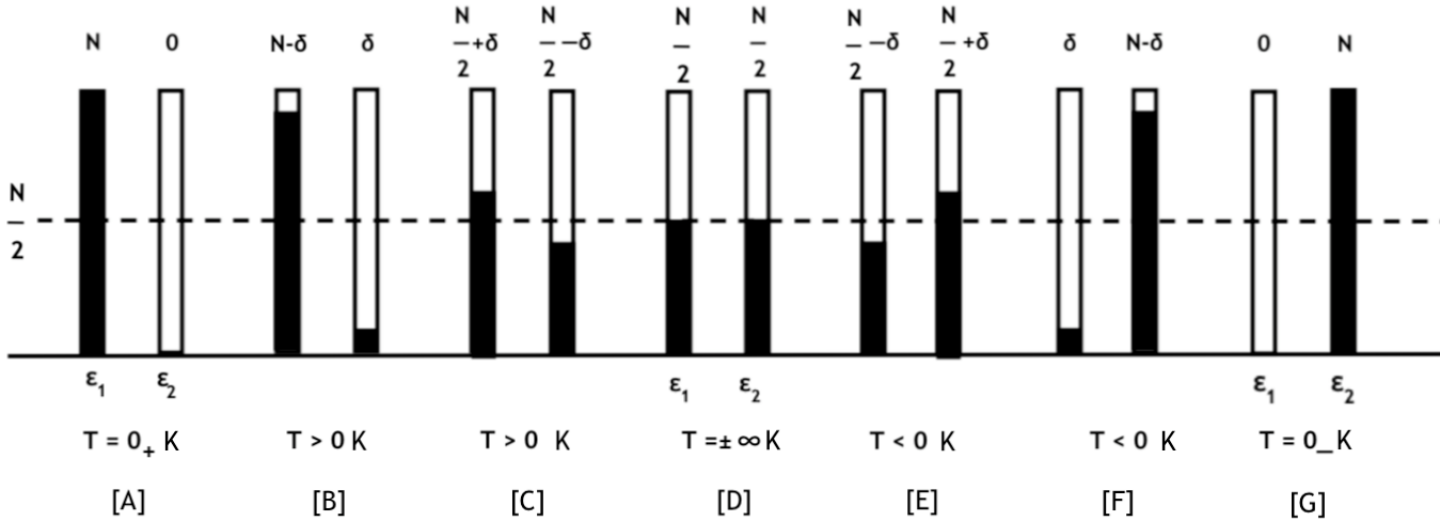

Figure 2: Distribution of particles in a two level system where $\epsilon_1 < \epsilon_2$

Case A: Minimum entropy

$N_1 = N$ and $N_2 = 0$, Internal energy is $U_A = N\epsilon_1$

The entropy at point A can be expressed as:

$$S_A = k_B \ln \Omega = k_B \ln \frac{N!}{N_1!\, N_2!} = k_B \ln \frac{N!}{N!\, 0!} = k_B \ln (1) = 0$$

Case B: Evaluation of S and U at a point close to minimum entropy configuration

$N_1 = N - \delta$ and $N_2 = \delta$,

Internal energy , $U_B = (N-\delta)\epsilon_1 + (\delta)\epsilon_2 = N\,\epsilon_1 \,+\, \delta(\epsilon_2 - \epsilon_1)$

The entropy at point B is equal to :

$$S_B = \, k_B \, ln \, \frac{N!}{(N-\delta)!\,(\delta)!} = k_B \, [\, N \, ln \, N - \, N - \, (N-\delta) \, ln \, (N-\delta) + (N-\delta) \,]$$

Since $\delta << N$, so $ln\,\delta!$ is negligible compare to $ln\,(N-\delta)!$ and $ln\,N!$.
On solving the above equation , we get :

$$S_B \, = \, k_B \left[\delta \, ln \, N - \frac{\delta^2}{2N} \right] \, = \, k_B \, \delta \, ln \, N - \frac{k_B \, \delta^2}{2N}$$

Case C: Evaluation of S and U at a point close to maximum entropy configuration

$N_1 = \frac{N}{2} + \delta$ and $N_2 = \frac{N}{2} - \delta$,

Internal energy , $U_C = (\frac{N}{2} + \delta)\epsilon_1 + (\frac{N}{2} - \, \delta)\epsilon_2 = \frac{N}{2}\,(\epsilon_1 + \epsilon_2) \, + \, \delta(\epsilon_1 - \epsilon_2)$

The entropy at point C is equal to :

$$S_B = \, k_B \, ln \, \frac{N!}{(\frac{N}{2}+\delta)!(\frac{N}{2}-\delta)!} = k_B \, \left[N \, lnN - \, (\frac{N}{2} + \delta) \, ln \, (\frac{N}{2} + \delta) - (\frac{N}{2} - \delta) \, ln \, (\frac{N}{2} - \delta) \right]$$

Using the approximation $\delta \, << \, \frac{N}{2}$, we get:

$$S_C \, = \, k_B \left[N \, ln \, N \, - N \, ln \frac{N}{2} - 2\frac{\delta^2}{N} \right] = \, k_B \, ln \, 2^N \, - 2 \, k_B \, \frac{\delta^2}{N}$$

Case D: Maximum entropy configuration

$N_1 = \frac{N}{2}$ and $N_2 = \frac{N}{2}$

Internal Energy, $U_D = \frac{N}{2}\,(\epsilon_1 \, + \epsilon_2)$

Entropy at D: $S_D = \, S_{max} = \, k_B \, ln \, 2^N$

Case E: Evaluation of S and U at a point close to maximum entropy configuration

$N_1 = \frac{N}{2} - \delta$ and $N_2 = \frac{N}{2} + \delta$,

Internal energy , $U_E = (\frac{N}{2} - \delta)\epsilon_1 + (\frac{N}{2} + \, \delta)\epsilon_2 = \frac{N}{2}\,(\epsilon_1 + \epsilon_2) \, + \, \delta(\epsilon_2 - \epsilon_1)$

The entropy at point E is equal to :

$$S_E \, = \, k_B \, ln \, \frac{N!}{(\frac{N}{2}-\delta)!(\frac{N}{2}+\delta)!} = k_B \, \left[N \, lnN - \, (\frac{N}{2} + \delta) \, ln \, (\frac{N}{2} + \delta) - (\frac{N}{2} - \delta) \, ln \, (\frac{N}{2} - \delta) \right]$$

Using the approximation $\delta \, << \, \frac{N}{2}$, we get:

$$S_E \, = \, k_B \left[N \, ln \, N \, - N \, ln \frac{N}{2} - 2\frac{\delta^2}{N} \right] = \, k_B \, ln \, 2^N \, - 2 \, k_B \, \frac{\delta^2}{N} = \, S_C$$

Case F: Evaluation of S and U at a point close to minimum entropy configuration

$N_1 = \delta$ and $N_2 = N - \delta$,

Internal energy , $U_F = N\epsilon_2 - \delta(\epsilon_2 - \epsilon_1)$

The entropy at point F is equal to :

$$S_F = k_B \, ln \, \frac{N!}{(\delta)! \, (N-\delta)!} = k_B \, [\, N \, ln \, N - \, N - \, (N-\delta) \, ln \, (N-\delta) + (N-\delta) \,]$$

On solving the above equation , we get :

$$S_F \, = \, k_B \, \left[\delta \, ln \, N - \frac{\delta^2}{2N} \right] \, = \, S_B$$

Case G: Minimum entropy

$N_1 = 0$ and $N_2 = N$, Internal energy is $U_G = N\epsilon_2$

The entropy at point G can be expressed as:

$$S_G = k_B \, ln \, \Omega = \, k_B \, ln \, \frac{N!}{N_1! \, N_2!} = k_B \, ln(1) \, = \, 0 = \, S_A$$

The results obtained above are mentioned in the Table 1. One can clearly observe that as we move from point A to D, the entropy increases from zero to its maximum value at point D and after that it decreases continuously as we move from D to the point G. On the other hand, the internal energy U, keeps on increasing continuously from Point A to G.

Another interesting feature of this calculation is the change in the magnitude of the entropy of the system with the variation of number of particles occupying the two levels of the system. In the vicinity of the minimum entropy position (point A or G), the change in the entropy is maximum when we move from A to point B (assume $\delta = 1$) or from F to G. Similarly the change in entropy is minimum in the vicinity of maximum entropy position. (For example when move from point C to D or from D to E and assume $\delta = 1$). Hence the variation of entropy is steep with the change in the number of particles close to the minimum position. Furthermore the variation of S slows down and becomes almost flat at the maximum position. This behaviour of entropy is symmetrical and hence one can easily co-relate this variation with the inverted parabola graph.

3 General expression of S(U, N)

In the previous section we obtained the values of entropy for a two level system for various distribution of particles in it. In this section we will focus on the construction of a smooth polynomial (Here S(U)) by using the data obtained in the form of (S_i, U_i) in the previous section. We use Lagrange interpolation method to find the general form of entropy as a function of internal energy. In this method the n^{th} order polynomial is constructed by using $n+1$ data points. This can be further written as

$$S_{ip}(U) = \sum_{i=1}^{n} L(U_i) S_i = L(U_1) \, S_1 + L(U_2) \, S_2 + \, L(U_3) \, S_3 + ... + \, L(U_n) \, S_n$$

Here S_{ip} is known as interpolating polynomial of degree n. The points $U_1, U_2, ...U_n$ are interpolation points and $L(U)$ is known as Lagrange polynomial. As mentioned in the previous section, the graph

Case	N_1	N_2	Internal Energy (U)	Entropy (S)
A	N	0	$N\,\epsilon_1$	0
B	$N-\delta$	δ	$N\,\epsilon_1 + \delta(\epsilon_2-\epsilon_1)$	$k_B\,\delta\,ln\,N - k_B\frac{\delta^2}{2N}$
C	$N/2+\delta$	$N/2-\delta$	$\frac{N}{2}\,(\epsilon_1+\epsilon_2) - \delta(\epsilon_2-\epsilon_1)$	$k_B\,ln\,2^N - 2\,k_B\,\frac{\delta^2}{N}$
D	N/2	N/2	$\frac{N}{2}\,(\epsilon_1+\epsilon_2)$	$k_B\,ln\,2^N$
E	$N/2-\delta$	$N/2+\delta$	$\frac{N}{2}\,(\epsilon_1+\epsilon_2) + \delta(\epsilon_2-\epsilon_1)$	$k_B\,ln\,2^N - 2\,k_B\,\frac{\delta^2}{N}$
F	δ	$N-\delta$	$N\,\epsilon_2 - \delta(\epsilon_2-\epsilon_1)$	$k_B\,\delta\,ln\,N - k_B\,\frac{\delta^2}{2N}$
G	0	N	$N\,\epsilon_2$	0

Table 1: Brief summary of the parameters obtained in the two level system

between S and U is an inverted parabola so we assume S to be a second order polynomial and hence use the three data points. This parabolic variation between S and U is also supported by Masthay and Fannin [13]. The three data points used to obtain the general form of S are (U_A, S_A),(U_C, S_C) and (U_G, S_G) at the points A, C and G respectively [1]. For more details of this method see [14].

Now the general form of $S_{ip}(U, N)$ in this case becomes:

$$S_{ip}(U,N) = L(U_A)S_A + L(U_C)S_C + L(U_G)S_G \tag{1}$$

as both $S_A = S_G = 0$, hence $S_{ip}(U) = L(U_C)S_C$

By definition, the basis polynomial, $L(U_C)$ is written as:

$$L(U_C) = \frac{(U-U_A)(U-U_G)}{(U_C-U_A)(U_C-U_G)}$$

After substituting the values of U_A, U_C, U_G and S_C in the eq.1, we finally get:

$$S_{ip}(U,N) = S_C\left[\frac{(U-N\epsilon_1)\,(U-N\epsilon_2)}{(\frac{N}{2}(\epsilon_1+\epsilon_2)+\delta(\epsilon_1-\epsilon_2)-N\epsilon_1)\left(\frac{N}{2}(\epsilon_1+\epsilon_2)+\delta(\epsilon_1-\epsilon_2)-N\epsilon_2\right)}\right]$$

$$\boxed{S_{ip}(U,N) = \left[k_B\,ln\,2^N - \frac{2\,k_B\,\delta^2}{N}\right]\left[\frac{U^2 - N(\epsilon_1+\epsilon_2)U + N^2\epsilon_1\epsilon_2}{(\delta^2-\frac{N^2}{4})(\epsilon_1-\epsilon_2)^2}\right]} \tag{2}$$

[1] one can also obtain the general form of S(U) by assuming any three points as shown in Figure 1.

One can easily check that the above expression (eq.2) reduces to the entropy at point D ($S = S_D = N\,k_B\,ln2$) in the limit $\delta \to 0$. Similarly as expected, we can also recover the entropy at point A , C and G with the general expression of entropy. We further checked the eq.2 for the two level magnetic system in which each spin dipole has energy levels $\epsilon_1 = -\epsilon$ and $\epsilon_2 = \epsilon$. The entropy for such a system can be written as:

$$S(U,N) \;=\; \left[k_B\,ln\,2^N \;-\; \frac{2\,k_B\,\delta^2}{N}\right]\left[1 \;-\; \frac{U^2}{N^2\epsilon^2}\right]\left[1 -\; \frac{4\delta^2}{N^2}\right]^{-1} \tag{3}$$

4 Discussion

We investigated two issues related to the negative absolute temperature which have not been highlighted explicitly in the literature. Hence the importance of this study is twofold:

First, We show the behaviour of entropy close to the maxima point when population in both the levels is equal. Similarly the values of entropy are obtained close to the minima point when one of the level is fully occupied while the other one is vacant. It clearly indicates that the graph between entropy and internal energy is symmetrical in nature. The internal energy increases continuously from the point A to G while entropy increases only from the point A to D and hence we obtain positive temperature in this region. While as we move from D to G, the entropy starts decreasing (see Fig.1) but internal energy is still increasing , hence the temperature becomes negative in this right half of the graph. The concept of positive and negative absolute temperature can be understood from the Figure 1 by invoking Boltzmann distribution. In the left half of the curve ADG, the ratio of the number of particles in the two levels given by : $N_2/N_1 = exp[(\epsilon_1 - \epsilon_2)/k_BT] < 1$ and hence the temperature is positive. Similarly in the right half of the curve ADG, $N_2/N_1 > 1$ and therefore the temperature becomes negative.

Second , To establish the general mathematical relation between the entropy and the internal energy for the two level system by using Lagrange interpolation method.

• It is important to note that one can obtain the *maximum magnitude of absolute temperature* in this finite level system by analysing the transition from $[\frac{N}{2}+1, \frac{N}{2}-1]$ to $[\frac{N}{2}, \frac{N}{2}]$ or from $[\frac{N}{2}, \frac{N}{2}]$ to $[\frac{N}{2}-1, \frac{N}{2}+1]$. In other words, the system attains the maximum value of the temperature when it reaches to the state of maximum entropy [N/2 , N/2].

For example, in case C, by assuming $\delta = 1$ we are close to maximum entropy state. So during transition from $[\frac{N}{2}+1, \frac{N}{2}-1]$ to $[\frac{N}{2}, \frac{N}{2}]$ or from case C to case D, the change in entropy is

$$S_D - S_C = \frac{2\,k_B}{N}$$

and change in internal energy is given as

$$U_D - U_C = \epsilon_2 - \epsilon_1$$

and hence the maximum magnitude of the temperature in this system is

$$T = \frac{(\epsilon_2 - \epsilon_1)}{2k_B/N}$$

In the limit , $N \to \infty$, the maximum magnitude of the temperature approaches $T = +\infty$.

Similarly during the transition from $[\frac{N}{2}, \frac{N}{2}]$ to $[\frac{N}{2}-1, \frac{N}{2}+1]$ or from case D to case E, one can easily obtain $T = -\infty$ in the limit when $N \to \infty$.

• Another interesting feature of such system is that the *minimum magnitude of absolute temperature* exist at the minimum entropy configuration. This can be easily understood when the system undergoes transition from the state [N, 0] to [N-1, 1] or from [1, N-1] to [0, N]. Hence in Case B, If we assume $\delta = 1$, we are close to the minimum entropy position (Case A). If the system moves to [N-1, 1] state from [N,0] state or transition from case A to B , the change in entropy is given as:

$$S_B - S_A = k_B \, lnN \, - \frac{k_B}{2N}$$

and change in internal energy is given as

$$U_B - U_A = \epsilon_2 - \epsilon_1$$

and hence the minimum temperature of such system is

$$T = \frac{(\epsilon_2 - \epsilon_1)}{k_B \, lnN \, - \, \frac{k_B}{2N}}$$

In the limit, $N \to \infty$, the minimum magnitude of the temperature approaches $T = 0_+$.

Similarly during the transition from $[1, N-1]$ to $[0, N]$ or from case F to case G, one can easily obtain $T = 0_-$ in the limit when $N \to \infty$. This is incidentally the maximum temperature one can obtain in a two level system.

To conclude, in this article we explore the behaviour of entropy close to the points where the entropy is either maximum or minimum in a finite level system. Furthermore we also obtain the general expression of entropy as function of internal energy of the given two level system. We hope that this simple calculation is going to provide very useful insight to undergraduate students in understanding the concept of negative absolute temperature.

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