*(ii)* $z<1$

Using an expansion for $\ln\Gamma(z)$ in powers of $z$, we can find

$$f(z)=\frac{1}{z}+2\ln z+(C-1+\ln 2\pi)+\mathcal{O}(z),\quad z<1 \qquad \text{(I.22)}$$

$$-\psi(z)=\frac{1}{z}+C+\mathcal{O}(z),\quad z<1 \qquad \text{(I.23)}$$

where $C$ is the Euler-Mascheroni constant. This region of $z$ is seen to be pertinent to $B\gg B_1$, where we derive

$$\frac{\lambda^2 M}{\mu_0}=\ln(B/B_1)\times\left\{1-\frac{2\ln\{(e/2\pi)^{\frac{1}{2}}[\ln(B/B_1)-C]\}}{\ln(B/B_1)}+\cdots\right\}, \qquad \text{(I.24)}$$

and thence Eq. (5.19).

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# Conditions for Equilibrium at Negative Absolute Temperatures*

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In the classical phenomenological thermodynamic theory of Gibbs, equilibrium is defined as the state of maximum entropy at constant energy, and a theorem is proved (*the energy theorem*) which asserts that the equilibrium state is the state of minimum energy at fixed entropy. This theorem is not true for systems at negative absolute temperatures. By examining a familiar statistical model which can exhibit negative absolute temperatures we find the correct form of the energy theorem. It turns out that at negative absolute temperatures the state of equilibrium of a system with a given entropy is that in which the system has its highest energy.

## INTRODUCTION

THE nuclear spin experiments done by Purcell and Pound[1] on a pure LiF crystal which exhibited long spin-lattice relaxation times[2,3] have shown that it is possible to induce negative absolute temperatures in systems which are thermally insulated and which have the property that each element of the system has an upper limit to its energy. In a recent analysis, Ramsey[4,5] has shown that the Kelvin-Planck formulation of the second law of thermodynamics must be revised if it is to be applicable to systems capable of negative absolute temperatures. In the present article, we shall discuss, in terms of a simple and now familiar statistical model, some consequences of the existence of negative absolute temperatures for the classical thermodynamic theory of Gibbs.

Gibbs starts his development of phenomenological thermodynamics[6,7] with a variational definition of equilibrium as the state of maximum entropy at fixed energy. This definition is used to derive general conditions which must be fulfilled by hypothetical states if they are to be equilibrium states.[8]

Often in classical thermodynamics,[9] instead of applying the definition of stable equilibrium directly, one uses its main consequence, which we shall call the *energy theorem;* i.e., the theorem which asserts that the state of equilibrium of a system with a given entropy is that in which the system has its *lowest* energy. Using the statistical model, we shall show that this theorem must be modified when negative absolute temperatures are possible. We shall show that at negative temperatures the equilibrium state of a system with a given entropy is that in which the system has its *highest* energy. In order to obtain a satisfactory formulation of the energy theorem it will be necessary to examine carefully certain points which are usually tacitly taken for granted in texts on statistical mechanics.

## I. THE MODEL

We consider a thermodynamic system consisting of a large number $N$ of distinguishable localized elements;

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

[2] R. V. Pound, Phys. Rev. **81**, 156 (1951).

[3] N. F. Ramsey and R. V. Pound, Phys. Rev. **81**, 278 (1951).

[4] N. F. Ramsey, Ordnance **40**, 898 (1956).

[5] N. F. Ramsey, Phys. Rev. **103**, 20 (1956).

[6] J. W. Gibbs, Trans. Conn. Acad. **3**, 108–248, 343–524 (1875–1878), or see reference 7.

[7] *The Collected Works of J. Willard Gibbs* (Yale University Press, New Haven, 1957), Vol. 1, pp. 55–372.

[8] Examples of the derived necessary conditions for equilibrium are the statements that the temperature must be uniform and the heat capacity must not be negative.

[9] See reference 7, pp. 55–62.

e.g., the lattice points of a crystal in a magnetic field. Following Ramsey,[5] we assume that the Hamiltonian $\mathfrak{H}$ of the system can be split into two parts

$$\mathfrak{H}=\mathfrak{H}_0+\mathfrak{H}_{\text{int}}, \tag{1.1}$$

where $\mathfrak{H}_{\text{int}}$ is the portion of $\mathfrak{H}$ arising from the interaction of the elements of the system, while

$$\mathfrak{H}_0=\sum_{j=1}^{N}\mathfrak{H}_j \tag{1.2}$$

is the sum of those portions $\mathfrak{H}_j$ of $\mathfrak{H}$ that depend only on the individual elements. We assume that $\mathfrak{H}_{\text{int}}$, compared to $\mathfrak{H}_0$, makes only a negligible contribution to the observed total energy, so that the $N$ elements are nearly independent. The portion $\mathfrak{H}_{\text{int}}$ plays a role in inducing those transitions by which the different elements exchange energy; but the details of this exchange are not considered here. It is assumed, however, that the exchanges take place often enough to make the concepts of equilibrium and temperature physically meaningful.

We assume that each of the $\mathfrak{H}_j$ has only a *finite number* of equally spaced eigenvalues,

$$\epsilon_i=i\epsilon, \quad i=1, 2, \cdots m. \tag{1.3}$$

In particular, we assume that $m\ll N$, and that the energy levels $\epsilon_i$ are independent of $j$; i.e., of the element. For example, the $\epsilon_i$ may correspond to the spectroscopic spin energies of a system of identical nuclei at the lattice points of a cyrstal in a magnetic field. Note that, from the present point of view, a change in the applied field produces a new system.

A *state* $a$ of the system is defined by an $m$-tuple $\{n_1^a, n_2^a, \cdots n_m^a\}$ of integers $n_i^a$ subject to the conditions

$$0\leqslant n_i^a\leqslant N, \quad \sum_{i=1}^{m} n_i^a=N. \tag{1.4}$$

The integer $n_i^a$ is the number of elements in the $i$th energy level, $\epsilon_i$.

The *internal energy* $E$ of the system is a function of the state $a$ and is given by

$$E=E(a)=\sum_{i=1}^{m} n_i^a\epsilon_i. \tag{1.5}$$

We neglect the contribution from $\mathfrak{H}_{\text{int}}$.

The *entropy* $S$ of the system, also a function of the state $a$, is proportional to the logarithm of the number of ways in which the $N$ elements can be divided among the $m$ energy levels $\epsilon_i$ such that the population of the $i$th level remains equal to $n_i^a$ for $i=1, 2, \cdots m$. We have

$$S=S(a)=k\ln(N!/\prod_{i=1}^{m} n_i^a!). \tag{1.6}$$

## II. EQUILIBRIUM

We are now ready for our main *definition:*

A state $b$ of the system is called a *state of equilibrium* if for all states $a$, $a\neq b$, such that

$$E(a)=E(b), \tag{2.1}$$

the inequality

$$S(a)<S(b) \tag{2.2}$$

holds.

In other words, a state is an equilibrium state if it has maximum entropy among all states with equal energy.

It is clear from Eq. (1.5) that the energy $E$ of the system is bounded; i.e.,

$$E_l\leq E\leq E_g, \tag{2.3}$$

where

$$E_l=N\epsilon_1=N\epsilon, \quad E_g=N\epsilon_m=Nm\epsilon. \tag{2.4}$$

If a value of $E$ between $E_l$ and $E_g$ is prescribed and if $E$ is a multiple of $\epsilon$, then there are finitely many states $a$ such that

$$E=E(a). \tag{2.5}$$

We denote the class of states which satisfy Eq. (2.5) by $\mathfrak{C}_E$. The maximum of the entropy for the states $a$ in $\mathfrak{C}_E$,

$$\operatorname*{Max}_{\mathfrak{C}_E} S(a)=S(E), \tag{2.6}$$

exists and is attained for some state $b$ in $\mathfrak{C}_E$, so that $S(E)=S(b)$.

We show that this maximal state $b$ has the property that $n_i^b\neq 0$ for all $i=1, 2, \cdots m$. If we had, for example, $n_1^b=0$, then we could construct a new state $a$ in $\mathfrak{C}_E$ by changing $n_1^b=0$ into $n_1^a=2$ and by making appropriate changes in the populations of highly populated energy levels in such a manner that $E$ would remain the same; i.e., $E(a)=E(b)$. It is clear from Eq. (1.6) that the change from $n_1^b=0$ to $n_1^a=2$ would amount to increasing $S$ by $k\log 2$, while the changes in the highly populated levels would affect $S$ but slightly. Thus, we would have $S(a)>S(b)$ in contradiction to the assumption that $b$ is the state of maximum entropy at fixed energy. Hence, $n_i^b\neq 0$ for all $i$.

As is customary in statistical mechanics we now replace the $n_i^a$ by continuous variables and approximate the entropy in Eq. (1.6), with the help of Stirling's formula, by

$$S(a)=k\{N\ln N-\sum_{i=1}^{m} n_i^a\ln n_i^a\}. \tag{2.7}$$

The class $\mathfrak{C}_E$ corresponds to those points in the space of $m$-tuples $\{n_1^a, n_2^a, \cdots n_m^a\}$ which satisfy Eqs. (1.4) and (2.5). These points fill a portion of a hyperplane in the $n_i^a$ space. $S(a)$ attains its maximum in the *interior* of this portion (not on the boundary) because

$n_i^b \neq 0$ for the maximal state $b$, as we have seen above. Hence, by a known theorem from calculus, the first variation of $S(a)$, subject to the constraints $N(a)=N$ and $E(a)=E$, must vanish for $a=b$. This means that the derivatives $\partial\Omega/\partial n_i^a$ of the function

$$\Omega(a)=S(a)+\lambda N(a)+\mu E(a) \tag{2.8}$$

must vanish for $a=b$; i.e., for $n_i^a=n_i^b$. Here $\lambda$ and $\mu$ are Lagrange multipliers. The usual derivation gives

$$n_i^b=Ae^{\beta\epsilon_i}, \tag{2.9}$$

where $A=e^{\lambda/k}$ and $\beta=\mu/k$.

We now show that the numbers $A$ and $\beta$ are *uniquely* determined by $N$ and the prescribed energy $E$. Substituting Eq. (2.9) into Eqs. (1.4) and (2.5), we obtain

$$N=A\sum_{i=1}^{m} e^{\beta\epsilon_i}, \tag{2.10}$$

and

$$E=E(\beta)=N\sum_{i=1}^{m} \epsilon_i e^{\beta\epsilon_i}/\sum_{i=1}^{m} e^{\beta\epsilon_i}. \tag{2.11}$$

We compute the derivative of $E(\beta)$ with respect to $\beta$ and get

$$\begin{aligned}\frac{1}{N}\frac{dE(\beta)}{d\beta}\Big(\sum_{i=1}^{m} e^{\beta\epsilon_i}\Big)^2 &= \Big(\sum_{i=1}^{m} \epsilon_i^2 e^{\beta\epsilon_i}\Big)\Big(\sum_{j=1}^{m} e^{\beta\epsilon_j}\Big)-\Big(\sum_{i=1}^{m} \epsilon_i e^{\beta\epsilon_i}\Big)^2 \\ &= \tfrac{1}{2}\sum_{i=1}^{m}\sum_{j=1}^{m} (\epsilon_i-\epsilon_j)^2 e^{\beta(\epsilon_i+\epsilon_j)},\end{aligned} \tag{2.12}$$

which shows that $dE/d\beta$ is always positive. Hence $E(\beta)$ is a strictly increasing function of $\beta$ and thus has a single valued, strictly increasing, inverse function:

$$\beta=\beta(E). \tag{2.13}$$

Once $\beta$ has been found from Eq. (2.13), Eq. (2.10) yields a unique value for $A$.

We summarize: In the class of states $\mathcal{C}_E$ (defined by the condition that $a$ is in $\mathcal{C}_E$ if and only if $E(a)=E$) there is *one state* $b$ for which the first variation of $S(a)$ vanishes. This state $b$ must be that state for which $S$ has a maximum, because we have shown that the maximum is attained at an interior point, and hence the first variation does vanish at the maximum. Thus, $b$ is a state of equilibrium. The $n_i^b$ are given by Eq. (2.9) where $\beta$ and $A$ are the unique solutions of Eqs. (2.10) and (2.11). Each equilibrium state is characterized by its energy $E$, which can vary between the values $E_l$ and $E_g$ given by Eq. (2.4). Since $E(\beta)$ is an increasing function of $\beta$, we can also characterize the equilibrium states by their corresponding values of $\beta$. It follows from Eq. (2.11) that

$$\lim_{\beta\to+\infty} E(\beta)=N\epsilon_m=E_g, \quad \lim_{\beta\to-\infty} E(\beta)=N\epsilon_1=E_l. \tag{2.14}$$

Hence $\beta$ varies between $-\infty$ and $+\infty$ as $E$ varies between $E_l$ and $E_g$. The equilibrium states form a one parameter family and either $E$, $(E_l\leq E\leq E_g)$, or $\beta$, $(-\infty\leq\beta\leq+\infty)$, may be used as the parameter. Let $E_0$ be the value of $E$ at $\beta=0$; we note that

$$E_0=(N/m)\sum_{i=1}^{m} \epsilon_i. \tag{2.15}$$

We remark that it is not very hard to give a rigorous mathematical justification for replacing the integers $n_i^a$ by continuous variables and for using the asymptotic formula of Eq. (2.7) instead of the precise entropy function of Eq. (1.6). Such a justification is based on the fact that Eq. (2.7) is not only an asymptotic approximation for Eq. (1.6), but also the derivatives of Eq. (2.7) approximate the derivatives of Eq. (1.6) with $n_i^a!$ replaced by $\Gamma(n_i^a+1)$ for nonintegral $n_i^a$. This follows from the known limit

$$\lim_{x\to\infty}\left(\frac{d}{dx}\ln\Gamma(x+1)-\ln x\right)=0.$$

## III. THE ENERGY THEOREM

For equilibrium states, the entropy $S$ may be regarded as a function of either the energy $E$ or the parameter $\beta$. We investigate the nature of the function $S=S(\beta)$.

Substituting Eqs. (2.9), (2.10), and (2.11) into Eq. (2.7) we find

$$S(\beta)=k\Big\{N\ln\Big(\sum_{i=1}^{m} e^{\beta\epsilon_i}\Big)-\beta E(\beta)\Big\}. \tag{3.1}$$

Differentiation of Eq. (3.1) with respect to $\beta$ gives

$$\frac{dS(\beta)}{d\beta}=k\left\{N\sum_{i=1}^{m} \epsilon_i e^{\beta\epsilon_i}/\sum_{i=1}^{m} e^{\beta\epsilon_i}-E(\beta)-\beta\frac{dE(\beta)}{d\beta}\right\}.$$

Hence, by Eq. (2.11)

$$\frac{dS(\beta)}{d\beta}=-k\beta\frac{dE(\beta)}{d\beta}. \tag{3.2}$$

Since $dE(\beta)/d\beta$ is always positive, it follows that $dS(\beta)/d\beta$ has the same sign as $-\beta$. Hence, we have

$$\begin{aligned} dS(\beta)/d\beta>0 &\quad \text{if} \quad -\infty\leq\beta<0, \\ dS(\beta)/d\beta<0 &\quad \text{if} \quad 0<\beta\leq+\infty, \\ dS(\beta)/d\beta=0 &\quad \text{if} \quad \beta=0. \end{aligned} \tag{3.3}$$

An investigation of Eq. (3.1) shows

$$\lim_{\beta\to+\infty} S(\beta)=\lim_{\beta\to-\infty} S(\beta)=0, \tag{3.4}$$

$$S(0)=S_0=kN\ln m. \tag{3.5}$$

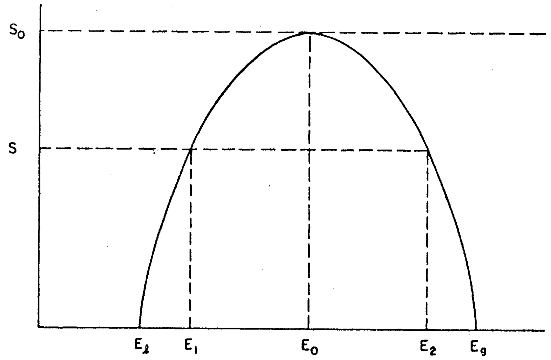

FIG. 1. Entropy *versus* energy at equilibrium.

Since $E(\beta)$ is a strictly increasing function of $\beta$, it follows from Eqs. (2.14), (3.3), and (3.4) that the graph of $S$ *versus* $E$, for equilibrium states, has the form indicated in Fig. 1, where $E_l$, $E_g$, $E_0$, and $S_0$ are given by Eqs. (2.14), (2.15), and (3.5).[10] It is clear that $S$ has an absolute maximum $S=S_0$ for $E=E_0$; i.e., $\beta=0$. The left branch ($E<E_0$) of the curve corresponds to negative values of $\beta$, the right branch to positive values of $\beta$. If we define the *temperature* $T$ of an equilibrium state by

$$T=-k/\beta, \tag{3.6}$$

we see that the left branch of the curve corresponds to positive temperatures, while the right branch corresponds to negative temperatures. The maximum point corresponds to $T=\pm\infty$, and the endpoints correspond both to $T=0$. The states of negative temperature all have higher total energy than the states of positive temperature.

We can now state the *energy theorem:* Let a value $S$ of the entropy be prescribed such that $0\leq S<S_0$. Consider the class $\mathcal{C}_S$ of all states $a$ such that

$$S(a)=S. \tag{3.7}$$

Then there are *two* equilibrium states $b_1$ and $b_2$ in $\mathcal{C}_S$, and

$$E(b_1)<E(a)<E(b_2) \tag{3.8}$$

for all states $a$ in $\mathcal{C}_S$ different from $b_1$ and $b_2$.

In other words, the equilibrium states have *minimum or maximum* energy among all states with equal entropy.

*Proof.*—We have already established the first part of the theorem, for we have proved that for equilibrium states the function $S=S(E)$ has the graph shown in Fig. 1, and it is clear from Fig. 1 that there are precisely two equilibrium states $b_1$ and $b_2$ with the prescribed entropy $S$. Now, let the energies of these two equilibrium states be $E_1=E(b_1)$ and $E_2=E(b_2)$. Consider an arbitrary nonequilibrium state $a$ in $\mathcal{C}_S$. Denote its energy by $E=E(a)$. There is precisely one equilibrium state $b$ in $\mathcal{C}_E$; i.e., there is one equilibrium state for which $E(b)=E=E(a)$. By the inequality (2.2), we must have $S(b)>S(a)$. Hence the state $b$ corresponds to a point on the curve of Fig. 1 which is above the line $S=\text{constant}=S(a)$. It follows that the corresponding energy $E(b)=E(a)$ must be between $E_1$ and $E_2$. This proves the inequality (3.8).

The equilibrium states which correspond to minimum energy at constant entropy are on the left branch of the curve of Fig. 1 and hence have positive temperatures. The equilibrium states which correspond to maximum energy at constant entropy have negative temperatures.

We observe that the points $(E,S)$ corresponding to non-equilibrium states lie above or on the $E$ axis and below the curve of Fig. 1. It follows that no nonequilibrium states are possible for $S=S_0$.

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[10] Of course, this graph has the same form as that exhibited by Ramsey in references 4 and 5 for the case $m=4$. Incidentally, from Eq. (2.7) on, all our arguments are independent of the equal spacing of energy levels $\epsilon_i$.