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What is the Third Law?[*]

We discuss entropies of systems at very low temperatures or, equivalently, the third law of thermodynamics. We conclude that definitive values of such entropies can be established only by experiments on systems with very few degrees of freedom, such as one-particle systems. [DOI: 10.1115/1.4026380]

1 Introduction

In contemporary experiments, temperatures of a few nanokelvins have been measured [1], and single ions have been trapped and laser-cooled within suitable electrodes [2]. Such experiments call for a theoretical understanding of the behavior of systems with very few particles, and at very low entropies and temperatures.

In most expositions of thermodynamics, entropy is defined only for systems that consist of a very large number of particles in equilibrium states [3], the third law is stated in the form either "the entropy vanishes at zero temperature" [4] or "the entropy at zero temperature depends on the ground-energy degeneracy" [5–10] without reference to the statement of the second law, and opinions differ about whether the third law is useless [11] or useful [12,13]. For a system with a large number of particles, the difference between the two forms of the third law is negligible.

In our exposition [14], entropy is defined for all systems, including a system consisting of one particle only, and for all states, including nonequilibriúm states; the third law is useful and certain of its aspects are direct consequences of the second law; and the precise form of these aspects can be decided only by experiments on systems with very few particles.

In this paper, we present the third law in the context of our exposition. The statement of the second law is discussed in Section 2, absolute entropy in Section 3, the third law in Section 4, the quantum-theoretic underpinning of the third-law in Section 5, a modified statement of the second law in Section 6, and conclusions in Section 7. Complete definitions of terms, and elaborate proofs of many assertions herein are found in Ref. 14.

2 The Second Law

The essence of the second law of thermodynamics is contained in the 1824 pioneering study by the French physicist Nicolas Leonard Sadi Carnot (1796–1832) entitled "Refléxions sur la puissance motrice du feu," the study that gave birth to the science of thermodynamics.

Of the many correct statements of the second law, the most notable are those of the German mathematical physicist Rudolf Julius Emanuel Clausius (1822–1888), the English physicist William Thomson, Lord Kelvin (1824–1907), the German physicist Max Karl Ernst Planck (1858–1947), the Greek mathematician Constantin Carathéodory (1873–1950), and the American mechanical engineers George Nicholas Hatsopoulos (1926-) and Joseph Henry Keenan (1900–1977).

In their pioneering textbook "Principles of General Thermodynamics," Wiley (1965), Hatsopoulos and Keenan argue that all correct statements imply the existence of a stable equilibrium state for each set of values of energy, amounts of constituents, and parameters—an implication that they take to be the essential element of the second law. In our work, we adopt a statement of the second law which is an outgrowth of the Hatsopouios-Keenan statement, and prove explicitly that among its implications are the Clausius, the Planck-Kelvin, and the Carathéodory statements.

We state the second law as follows: "*Among all the states of a system that have a given value E of the energy, and are compatible*[1] *with a given set of values n* $(=\{n_1, n_2, \ldots, n_r\})$ *of the amounts of the r constituents, and β* $(=\{\beta_1, \beta_2, \ldots, \beta_s\})$ *of the s parameters, there exists one and only one stable equilibrium state. Moreover, starting from any state of a system it is always possible to reach a stable equilibrium state with arbitrarily specified values of amounts of constituents and parameters by means of a reversible weight process.*"

For systems in which all internal mechanisms capable of changing the values of the amounts of constituents and the parameters are disallowed, the only states that are compatible with given values n and β are the states that have the given values. For these systems, the first part of the second law can be restated in a simpler but equivalent form, namely, "*Among all the states of a system with given values of the energy, the amounts of constituents, and the parameters, there exists one and only one stable equilibrium state.*" For simplicity, we restrict our discussion here to these systems. Moreover, we assume that the value of the energy of a system can be increased without limit.

The existence of stable equilibrium states for various conditions of matter has many theoretical and practical consequences. It is a major augmentation of the principles of mechanics, essential to understanding and explaining many phenonena, including the behavior of systems with very few degrees of freedom, such as a system consisting of one particle only.

The second part of the statement of the second law is an indispensable premise of the exposition of thermodynamics. Its validity is essential to that of most basic results, such as the existence of entropy as a property of any state, be it stable equilibrium or not, and of temperature as a property of stable equilibrium states only. Yet, in traditional expositions, this part has never been recognized explicitly.

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[1] The concept of compatibility of a state with a given set of values of amounts of constituents and parameters plays a special role in the statement of the second law. It is defined as follows. A state A_1 with values $(n)_1$, $(\beta)_1$, $(P)_1$, where $(P)_1$ denotes the set of values of all the properties of the system, is *compatible with a given set of values n of the amounts of constituents and β of the parameters* if the two sets $(n)_1$, $(\beta)_1$ and n, β are compatible. Two sets of values of amounts of constituents and parameters $(n)_1$, $(\beta)_1$ and $(n)_2$, $(\beta)_2$ are *compatible* if the change from one set to the other can occur as a result of the allowed internal mechanisms of the system, such as chemical reactions, interconnections, and internal forces. For example, if a system has two compartments of volumes V' and V'', respectively, interconnected so as to satisfy the constraint $V' = V'' = \mathit{constant}$, then the two sets of values V'_1, V''_1 and V'_2, V''_2 are compatible if $V'_1 + V''_1 + V'_2 + V''_2$ because then the internal interconnection between the two volumes allows the change from one set of values, say, $V'_1 = 3\ m^3$ and $V''_1 = 5\ m^3$, to the other set of values, say, $V'_2 = 2\ m^3$ and $V''_2 = 6\ m^3$. The same two sets of values would not be compatible if the two compartments were not interconnected.

Among the implications of the second law are its traditional statements. In terms of the concepts of stable equilibrium state and temperature, these statements can be expressed as follows:

- Clausius' statement (1850): "No process is possible in which the sole net effect is the transfer of energy from a system in a stable equilibrium state at a given temperature to a system in a stable equilibrium state at a higher temperature."
- Planck's statement (1897), which is similar to one of several statements given by Kelvin: "It is impossible to construct an engine which will work in a complete cycle, and produce no effect except the raising of a weight and the transfer of energy out of a system in a stable equilibrium state." This statement is known also as the impossibility of a perpetual-motion machine of the second kind, impossibility of a PMM2.
- Carathéodory's statement (1909): "In the neighborhood of any given stable equilibrium state there exist stable equilibrium states that cannot be reached by any weight process that starts from the given state."

Additional implications of the second law are related to the notions of creation, annihiliation. and formation reactions. Another important implication is that for each given set of values of the amounts of constituents and the parameters there is one and only one ground-energy state. This state is stable equilibrium, and has a value of entropy that is independent of the values of n and β and can be taken equal to zero. In traditional expositions, this implication of the second law is stated as part of the third law.

What does not follow from the second law is that each of the ground-energy stable equilibrium states has a temperature equal to zero. We discuss zero temperature in Section 4.

3 Absolute Entropy

Prior to discussing zero temperature, we introduce a new and very useful graphical representation of the states of a system on an energy versus entropy graph [14]. For given values of the amounts of constituents and the parameters, we project the multidimensional state space of a system on the energy versus entropy plane. This projection of states includes both stable equilibrium states and other states that are either nonequilibrium or nonstable equilibrium. It is not to be confused with the standard graphical representations of thermodynamic relations which are strictly applicable to stable equilibrium states only.

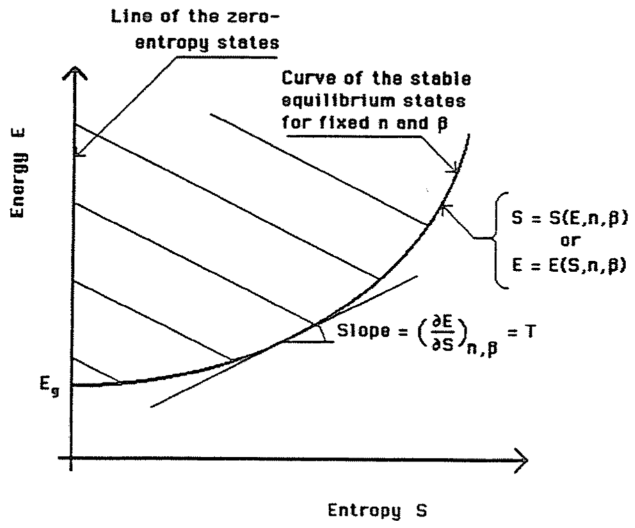

Fig. 1 Schematic representation of the projection of the states of a system with given values of the amounts of constituents and the parameters on the energy versus entropy plane

For any system, the projection has the shape of the cross-hatched area shown in Figure 1, namely, all the states that share the given values of the amounts of constituents and the parameters have property values that project on the area between the vertical line denoted as the line of the zero-entropy states, and the curve of the stable equilibrium states.

A point either in the cross-hatched area or on the vertical line $S = 0$ represents a large number of states. Each such state has the same values of amounts of constituents, parameters (such as the volume V), energy E, and entropy S, but differing values of other properties, and is not a stable equilibrium state. It can be any type of state except a stable equilibrium state.

A point on the convex curve of the stable equilibrium states represents one and only one state. For each such state, the value of any property is uniquely determined only by the values of the amounts of constituents, the parameters, and the pair (E, S) of the point on the curve. The temperature T, defined only for these states, is represented graphically by the slope of the convex curve of the stable equilibrium states.

For the same values of the amounts of constituents but a different value of one of the parameters, say, the volume V, the projection of the multidimensional state space onto the E versus S plane is again an area bounded by the zero entropy line and a convex curve, but the convex curve is shifted in the vertical direction. For example, for two values of volume V_1 and V_2, and such that $V_1 < V_2$, the relative position of the two convex curves is as shown in Figure 2*a*. The two projections may also be presented on different planes of a three-dimensional space with axes E, S and V, as shown in Figure 2*b*.

For stable equilibrium states having values of energy and entropy that may be both increased and decreased without net changes in the values of amounts of constituents and parameters, we show in Ref. 14 that the stable-equilibrium energy versus entropy relation is indeed convex, and that temperature is positive. We prove also that the value of the entropy of a ground-energy state, that is, a state for which the value of the energy may be increased but not decreased (without net changes in the values of amounts of constituents and parameters) can be taken equal to zero. The proof is completed by showing that: (1) among all the stable equilibrium states with given values of the amounts of constituents n and the parameters β, the ground-energy stable equilibrium state has the lowest entropy and the lowest temperature; (2) the value S_g of this lowest entropy is the same for all values of n and β of a system and, hence, it is the same for all ground-energy states of all systems; and (3) no other state of the system has entropy lower than S_g. Conclusions (2) and (3) do not hold if we adopt the modified statement of the second law discussed in Section 6.

In Ref. 14, we first define entropy in terms of an arbitrary reference value, and then we choose this value by setting $S_g = 0$. We can do so not only because the value of S_g is common to all the ground-energy states of all systems and is the lowest possible value of the entropy, but also because the choice is consistent with quantum-theoretic considerations (Section 5). In other words, in view of the conclusions (1), (2), and (3) just cited, we can set

$$S_g = 0 \quad \text{for all values of } n \text{ and } \beta \tag{1}$$

and in the definition of entropy we can choose a reference state A_g that is a ground-energy state so that the resulting entropy values are nonnegative. Entropy values thus obtained are called *absolute*.

4 Third Law

In Section 5, we use quantum-theoretic concepts and show that the temperature T_g of a ground-energy stable equilibrium state is equal to zero. However, such concepts are beyond the scope of a traditional exposition of thermodynamics. Short of quantum theory, the temperature of each ground-energy stable equilibrium state cannot be deduced from the first and second laws. It must be

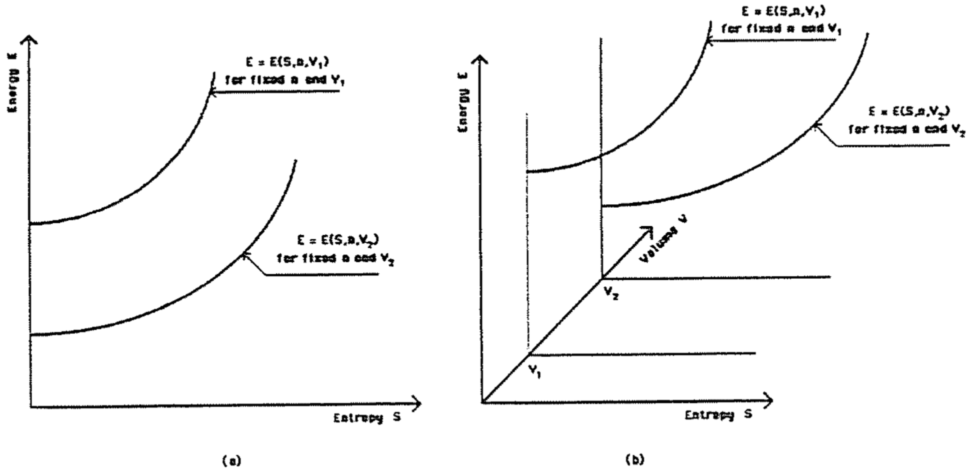

Fig. 2 Projections of the states of a system with given values of amounts of constituents, and two different values of the volume. V_1 and V_2 (*a*) Projection on the same *E* versus *S* plane; and (*b*) projections on two different planes in *E-S-V* space.

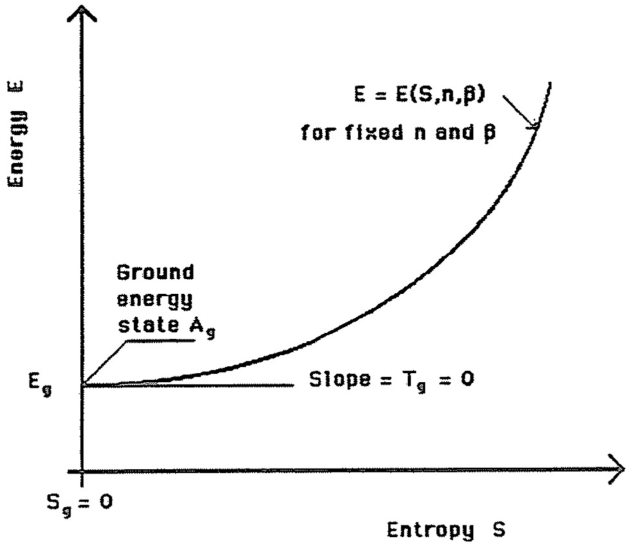

Fig. 3 Schematic representation of the energy versus entropy relation for stable equilibrium states with given values of *n* and *β* at low temperatures

introduced as an additional fundamental law, the *third law of thermodynamics*.[2] For systems with energy that can be increased without limit, we state the third law as follows: "*For each given set of values of the amounts of constituents and the parameters, there exists one stable equilibrium state with zero temperature.*"

For given values of n and β of a system with energy that can be increased without limit, the temperature is nonnegative and its lowest value occurs at the ground-energy stable equilibrium state. So, we readily conclude that the stable equilibrium state with zero temperature required by the third law is the ground-energy state. As shown in Figure 3. for given n and β, the least energy E_g corresponds to a unique stable equilibrium state at zero entropy and zero temperature.

The energy E_g is the least energy for which the system can exist with the given values of n and β, but it varies as n and β vary. Nevertheless, for all values of the amounts of constituents and the parameters, the ground-energy state is always a stable equilibrium state at zero entropy and zero temperature.

5 Quantum-Theoretic Considerations

Within the mathematical framework of quantum theory [15], the third law cited in Section 4 follows as a theorem. To see this clearly, we consider a system for which the energy E, entropy S, and temperature T of the stable equilibrium states are related by the canonical formulas

$$E(T;n,\beta) = \mathrm{Tr}\,\frac{H(n,\beta)\exp[-H(n,\beta)/kT]}{\mathrm{Tr}\exp[-H(n,\beta)/kT]} \tag{2}$$

and

$$S(T;n,\beta) = -k\mathrm{Tr}\,\frac{\exp[-H(n,\beta)/kT]}{\mathrm{Tr}\exp[-H(n,\beta)/kT]}\ln\frac{\exp[-H(n,\beta)/kT}{\mathrm{Tr}\exp[-H(n,\beta)/kT]} \tag{3}$$

where $H(n,\beta)$ is the Hamiltonian operator, Tr the trace functional on the Hilbert space of the system, and k the Boltzmann constant. For such a system, the Hamiltonian operator is a function of the amounts of constituents n and the parameters β. For example, if the system consists of structureless particles in a box. the Hamiltonian is a function of the number of particles and the geometrical characteristics of the box. We emphasize that all that we say holds even if the number of particles is unity, that is, even if it consists of a single particle.

The spectral expansion of the Hamiltonian operator can be written in general as

$$H(n,\beta) = \sum_{j=0}^{\infty}\epsilon_j(n,\beta)P_j(n,\beta) \tag{4}$$

where $\epsilon_j(n,\beta)$ is the jth eigenvalue, and $P_j(n,\beta)$ the projection operator onto the corresponding eigenspace. Without loss of generality, we assume that the eigenvalues are listed in increasing order with respect to the index j, that is, $\epsilon_0 < \epsilon_1 < \cdots \epsilon_j < \cdots$. The dimensionality of each eigenspace $D_j(n,\beta) = \mathrm{Tr}\,P_j(n,\beta)$. It is called the *multiplicity* or *degeneracy* of the corresponding eigenvalue. Alternatively, for given values of n and β we say that the jth energy eigenvalue ϵ_j is either D_j *fold degenerate* (or, simply, *degenerate)* if $D_j\,(n,\beta) > 1$, or *nondegenerate* if $D_j\,(n,\beta) = 1$.

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[2] In some expositions, the third law is referred to as Nernst's principle.

In terms of the spectral expansion, and for a given set of values of n and β, we can write

$$\frac{\exp[-H(n,\beta)/kT]}{\mathrm{Tr}\exp[-H(n,\beta)/kT]} = \frac{P_0 + \sum_{j=1}^{\infty} P_j \exp[-(\epsilon_j - \epsilon_0)/kT]}{D_0 + \sum_{j=1}^{\infty} D_j \exp[-(\epsilon_j - \epsilon_0)/kT]} \tag{5}$$

where, for simplicity, we drop the explicit dependences but recall that P_j, ϵ_j, D_j for $j = 0, 1, 2, \ldots, \infty$ are, in general, all functions of n and β.

Substituting Eqs. (4) and (5) into Eq. (2), and using the property of orthonormality of the projectors P_j, that is, the fact that $P_i P_j = \delta_{ij} P_j$, we find

$$E(T;n,\beta) = \frac{\epsilon_0 D_0 + \sum_{j=1}^{\infty} \epsilon_j D_j \exp[-(\epsilon_j - \epsilon_0)/kT]}{D_0 + \sum_{j=1}^{\infty} D_j \exp[-(\epsilon_j - \epsilon_0)/kT]} \geq \epsilon_0(n,\beta) \tag{6}$$

where δ_{ij} is the Kronecker delta, the inequality follows from the fact that $\epsilon_j > \epsilon_0$ for any $j > 0$ and, therefore, $\epsilon_0 D_o + \sum_{j=i}^{\infty} \epsilon_j D_j \exp[-(\epsilon_j - \epsilon_0)/kT \geq \epsilon_0 D_0 + \sum_{j=i}^{\infty} \epsilon_0 D_j \exp[-(\epsilon_j - \epsilon_0)/kT] = \epsilon_0(D_0 + \sum_{j=i}^{\infty} D_j \exp[-(\epsilon_j - \epsilon_0)/kT])$, and the equality obtains for $T = 0$, that is, $E(0;n,\beta) = \epsilon_0(n,\beta)$. Thus we conclude that, for given values of n and β, the lowest energy equals the lowest eigenvalue of the Hamiltonian operator, that is, $E_g(n,\beta) = \epsilon_0(n,\beta)$, and that the stable equilibrium state with lowest energy has temperature $T = 0$. These conclusions are equivalent to the implications of the third law given in the preceding section. But within the quantum-theoretic context, the third law is a theorem and not an independent postulate.

Another important theorem regards the heat capacity at constant volume and other parameters C_V at $T = 0$. Starting from Eq. (2), we can readily verify that[3]

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{n,\beta} \to 0 \quad \text{as} \quad T \to 0 \tag{7}$$

In addition, for $T = 0$ Eq. (5) becomes

$$\frac{\exp[-H(n,\beta/kT)}{\mathrm{Tr}\exp[-H(n,\beta)/kT]} = \frac{P_0}{\mathrm{Tr}P_0} = \frac{P_0}{D_0} \tag{8}$$

and, therefore, Eq. (3) yields

$$\begin{aligned} S(0;n,\beta) &= -k\mathrm{Tr}\frac{P_0}{D_0}\ln\frac{P_0}{D_0} = -k\frac{\mathrm{Tr}P_0\ln P_0}{D_0} + k\frac{\mathrm{Tr}P_0}{D_0}\ln D_0 \\ &= k\ln D_0(n,\beta) \end{aligned} \tag{9}$$

because $\mathrm{Tr}\,P_0 \ln P_0 = 0$ and $\mathrm{Tr}\,P_0 = D_0$. If $D_0(n,\beta) > 1$, the value of the entropy[4] of the ground-energy stable equilibrium state $S(0;n,\beta) = k\ln D_0(n,\beta) \neq 0$. This conclusion is in conflict with the second law—more precisely, with conclusions (2) and (3) listed in Section 3. One way to avoid the conflict is by asserting that every system has a Hamiltonian operator with a nondegenerate lowest energy eigenvalue, that is,

$$D_0(n,\beta) = 1 \quad \text{for all values of } n \text{ and } \beta \tag{10}$$

because only then

$$S(0;n,\beta) = 0 = S_g(n,\beta) \tag{11}$$

However, many authors [6–8] question the generality of Condition (10) because of lack of conclusive experimental evidence. As a result, they suggest that, in general, $D_0(n,\beta) \geq 1$.

In our exposition, the question of degeneracy of the lowest energy eigenvalue concerns neither the statement of the third law given in Section 4, nor the first part of the statement of the second law. The possibility that $D_0(n,\beta) > 1$ is in conflict only with the part of the statement of the second law which avers that "*Starting from any state of a system it is always possible to reach, a stable equilibrium state with arbitrarily specified values of amounts of constituents and parameters by means of a reversible weight process.*" In the next section we show how a slight modification of this part eliminates the conflict with the possibility that $D_0(n,\beta) > 1$ without affecting any of the major implications of the second law, such as the existence of entropy as a property of any state.

6 Modified Statement of the Second Law

To account for the existence of a system with a Hamiltonian operator such that $D_0(n,\beta) > 1$ for some or all sets of values of n and β, we express the second part of the statement of the second law as follows: "*Starting from any state of a system it is always possible to reach* either *a stable equilibrium state* or a ground-energy state *with arbitrarily specified values of amounts of constituents and parameters by means of a reversible weight process.*" In this form, the second law is consistent with the possibility that for a given set of values of amounts of constituents and parameters a system admits many ground-energy states, that is, many states with energy equal to the lowest eigenvalue of the Hamiltonian operator for the given values of n and β. Of course, the first part of the statement of the second law remains unchanged and implies that even among all these ground-energy states one and only one is stable equilibrium. Moreover, by virtue of either the quantum-theoretic treatment or the statement of the third law, the temperature of the ground-energy stable equilibrium state is equal to zero.

Indeed, with the modified statement of the second law. we conclude that the curved boundary of the projection onto the E versus S plane can take the shape shown in Figure 4, rather than the shape shown in Figure 3. Specifically, the horizontal line $E_g A_g$ represents the E versus S relation for all the states that are not stable equilibrium but have the ground-state energy E_g, and the curve $A_g A_{E1}$ the E versus S relation for the stable equilibrium states. Each point on the line $E_g A_g$, except A_g, represents the projection of many states none of which is stable equilibrium and, hence, none of which has a temperature, whereas each point on the curve $A_g A_{E1}$ represents only one state—a stable equilibrium state.

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[3] Indeed,

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{n,\beta} = \frac{1}{kT^2}\left[\frac{\sum_{j=0}^{\infty}\epsilon_j^2 D_j \exp[-\epsilon_j/kT]}{\sum_{j=0}^{\infty} D_j \exp[-\epsilon_j/kT]} - \left(\frac{\sum_{j=0}^{\infty}\epsilon_j D_j \exp[-\epsilon_j/kT}{\sum_{j=0}^{\infty} D_j \exp[-\epsilon_j/kT}\right)^2\right]$$

$$= \frac{D_0\sum_{j=1}^{\infty}(\epsilon_j - \epsilon_0)^2 D_j \exp[-(\epsilon_j - \epsilon_0/kT]/kT^2}{\left(D_0 + \sum_{j=1}^{\infty} D_j \exp[-(\epsilon_j - \epsilon_0)/kT]\right)^2}$$

$$+ \frac{\sum_{i=1}^{\infty}\sum_{j=1}^{\infty}(\epsilon_i - \epsilon_j)^2 D_i \exp[-(\epsilon_i - \epsilon_0)/kT] D_j \exp[-(\epsilon_j - \epsilon_0)/kT]/kT^2}{2\left(D_0 + \sum_{j=1}^{\infty} D_j \exp[(\epsilon_j - \epsilon_0)/kT\right)^2}$$

Because $\epsilon_j - \epsilon_0 > 0$ for every $j \geq 1$, and $\exp(-a/T)/T^2 \to 0$ for $a > 0$ and $T \to 0$, we readily verify Relation 7.

[4] As we discuss in Section 7, we are especially concerned with systems with few particules. Accordingly, the discussions in Refs. [8] to [10] about taking the limit as the number of particules goes to infinity are not germaine to our purposes.

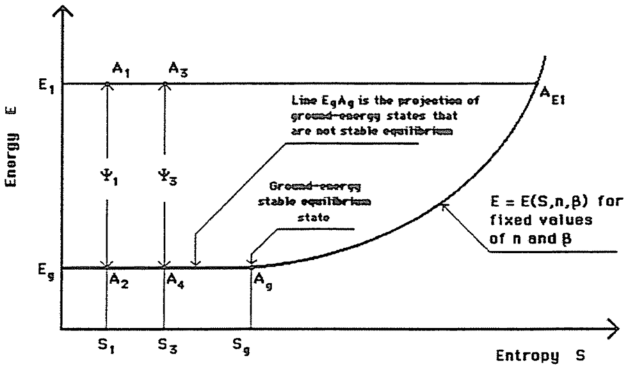

Fig. 4 Shape of the energy versus entropy diagram consistent with the statement of the second law modified to account for the possibility that for a given set of values of *n* and *β* a system admits more that a single ground-energy state.

To verify the last assertion, we note that given a set of values of n and β for which A_g is the ground-energy stable equilibrium state, a reversible weight process starting from a state A_1 can reach either a stable equilibrium state if the entropy S_1 of A_1 is greater than or equal to the entropy S_g of A_g, or a ground-energy state with energy $E = E_g$ if the entropy $0 \leq S_1 < S_g$. In the latter case, the final state is not a stable equilibrium state because its entropy is smaller than the largest value corresponding to the given values E_g, n, β.

Whereas the zero slope of the stable-equilibrium-state curve $E = E(S, n, \beta)$ at state A_g corresponds to a zero value of the temperature, the slope of the horizontal line E_gA_g for $0 \leq S < S_g$ is zero but does not correspond to a temperature because no single-valued relation of the form $E = E(S, n, \beta)$ exists for the states represented by points on this line.

The modified statement of the second law results in an interesting exception to our general understanding of irreversibility. Starting from any state A_1 with entropy $S_1 < S_g$, and using a reversible weight process we can reach a ground-energy state A_2 that is not stable equilibrium (Figure 4). The amount of energy that can be transferred to a weight in a reversible weight process is represented by the length $\Psi_1 = A_1A_2$. Similarly, starting from any state A_3 with energy $E_3 = E_1$ and entropy $S_1 < S_3 < S_g$, and using a reversible weight process we can reach a state A_4 that is not stable equilibrium. Now, the energy transferred to the weight is the same as in the weight process starting from A_1, and is represented by the length $\Psi_3 = A_3A_4$. But state A_1 can evolve spontaneously into A_3, and the increase in entropy $S_3 - S_1$ is generated by irreversibility. Thus, for the states with entropy between zero and S_g, we conclude that irreversibility does not reduce the value of the energy that can be transferred to a weight—a conclusion that is an exception to our general understanding of the adverse effects of irreversibility.

This exception does not contradict any experimental observation. As such it is not sufficient to dismiss the existence of degenerate ground-energy eigenvalues. Rather, the exception should stimulate further theoretical and experimental investigations.

7 Conclusions

The third law can be stated in a manner consistent with the second law. This can be done for all systems, including one that consists of very few particles. A question that remains unresolved is: Is there any experimental evidence that can be rationalized only in terms of a Hamiltonian operator with a degenerate lowest eigenvalue? If the answer is yes, then the modified statement of the second law should be adopted, and the exception cited in Section 6 better understood.

Should Condition 10 be satisfied by all systems? We have seen that neither the formalism of quantum theory nor the laws of thermodynamics forbid to model a system with a Hamiltonian operator that has a degenerate lowest eigenvalue, thus violating Condition 10. The question is whether such a system describes something that exists in nature and, therefore, can only be resolved experimentally.

Though presented in different terms, the question has been long debated [6–13]. Invariably, with various justifications [9,10], the question is analyzed for systems with a very large or infinite number of particles N. In this limit, however, the entropy per particle varies as $(1/N)k \ln D_0(n, \beta)$ and is negligible and hardly measurable if the dependence of $D_0(n, \beta)$ on N is weaker than $(1 + a)^N$, where a is of the order of unity [10]. In addition, the Hamiltonian operator must be necessarily based on an oversimplified model of the interactions between the many particles, otherwise the model is intractable. So, in our view, the question cannot be resolved by studying systems with many particles.

We suggest that the question is more likely to find a resolution from experimental studies of systems with very small values of the amounts of constituents, that is, systems with very few particles. Then, the entropy $S_g(n, \beta) = k \ln D_0(n, \beta)$ is nonnegligible unless $D_0(n, \beta) = 1$. In view of the experimental achievements mentioned in the introduction [1–2], we believe that such a study is feasible with current techniques. But, of course, the study requires that it be fully understood that the laws of thermodynamics hold for all systems, including one that consists of a single particle [15].

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