Entropies of Statistical Mechanics and Disorder Versus the Entropy of Thermodynamics and Order

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The prevailing beliefs in the scientific and engineering literature are that: (i) thermodynamics is explained and justified by statistical mechanics; (ii) entropy is a statistical measure of disorder; and (iii) for given values of energy, volume, and amounts of constituents, the largest value of entropy corresponds to both a thermodynamic equilibrium state and the ultimate disorder. In this paper, we provide: (i) a summary of the beliefs as stated by some eminent scientists; (ii) experimental evidence that casts serious doubt about the validity of the beliefs; (iii) an outline of a nonstatistical unified quantum theory of mechanics and thermodynamics; (iv) an outline of a nonquantal, nonstatistical exposition of thermodynamics, valid for all systems (both macroscopic and microscopic), and for all states (both thermodynamic equilibrium and not thermodynamic equilibrium); (v) the definition and analytical expression of the entropy of thermodynamics; (vi) the interpretation of entropy as both a measure of the quantum-theoretic spatial shape of a molecule, and an indicator of order; and (vii) nonstatistical answers to the questions that motivated the introduction of statistical mechanics. [DOI: 10.1115/1.1368122]

1 Introduction

Ever since the unrefined enunciation of the first and second laws of classical thermodynamics by Clausius [1], the question of the relation between thermodynamics and mechanics has been the subject of intense investigations and controversy. Invariably, Maxwell's [2] seminal ideas prevail, that is '' . . . the molecules in a vessel full of air at uniform temperature are moving with velocities by no means uniform . . . '', and ''In dealing with masses of matter, while we do not perceive the individual molecules, we are compelled to adopt what I have described as the statistical method of calculation, . . . ''. Though deeply rooted in classical mechanics, these ideas play a major role in conventional quantal explanations as well.

One of the consequences of Maxwell's seminal ideas is that the overwhelming majority of scientists and engineers share and promulgate the almost religious belief that entropy is not a fundamental scientific concept. Instead, they view it as a measure of ignorance or lack of information about a macroscopic system and a monotonic indicator of disorder.

Statistical theories of thermodynamics yield many correct and practical numerical results about thermodynamic equilibrium states [3,4]. Despite these successes, the almost universal efforts to compel thermodynamics to conform to statistical explanations is not justified in the light of many accurate, reproducible, nonstatistical experiences, and is out of step with the responses of the scientific community to the considerations that resulted in modifications of classical mechanics. Examples of such modifications are the theory of relativity, and the theory of quantum mechanics.

Over the past three decades, intrigued and challenged by the prevalent misunderstandings about thermodynamics, a group of us has proposed a resolution of the dilemmas and paradoxes created by statistical explanations. The resolution differs from all statistical interpretations of thermodynamics, in general, and from Maxwell's [2] explanation, in particular. The purposes of this paper are: (*i*) to review the statistical ideas and disorder; (*ii*) to present experimental evidence that contradicts the statistical entropies; (*iii*) to summarize a unified quantum theory of mechanics and thermodynamics which leads to the demonstrable conclusion that thermodynamics is a general, nonstatistical theory of physical phenomena; this theory admits mechanics (either classical or conventional quantum) as one limiting case (zero entropy physics), and classical thermodynamics as another limiting case (largest entropy physics); moreover, it is shown that entropy is a well-defined and mathematically precise monotonic indicator of order; the indicator is a measure of the quantum-theoretic shape of the constituents of a system, in the same sense that, in classical mechanics, $mv^2/2$, and not some other expression, is a measure of the kinetic energy of a particle; (*iv*) to sketch a nonquantal, novel exposition of thermodynamics that is almost equivalent to and results in the same conclusions as the unified theory; and (*v*) in the light of the unified theory and the new exposition, to evaluate the beliefs of and respond to the questions raised by many eminent scientists and engineers.

It is noteworthy that, in the unified theory, irreversibility—spontaneous entropy increase—is associated with the spontaneous change of the shapes of the molecules as they try to conform with both the externally applied and the intermolecular forces of the system. An example of external forces are those exerted by the walls of a container.

The paper is organized as follows. Summaries of the beliefs of a number of eminent scientists about both the necessity for a statistical explanation of thermodynamics, and the relation between entropy and disorder are presented in Section 2, and experiments that cast doubt about the validity of the statistical interpretation in Sections 3 to 5. A brief discussion of the novel, interwoven and fully documented new nonstatistical developments is outlined in Section 6. In the light of the new developments, comments about the relation between statistical mechanics and thermodynamics are discussed in Section 7, and concluding remarks in Section 8.

2 Entropies of Statistical Mechanics and Disorder

Newton's enunciation of the three laws of classical mechanics in 1666 is one of the greatest achievements of the human mind [5]. Their advent met with unprecedented success in a broad spectrum of applications from stars and planets, such as the solar system, to molecules and radiation. This success was so impressive and overwhelming that scientists were convinced that every natural phenomenon could and should be regularized by use only

of the laws and theorems of classical mechanics. So, two centuries after Newton's time, when the laws of classical thermodynamics were enunciated by Clausius [1], it was only natural that scientists felt compelled to explain these laws and their theorems by using classical mechanics.

2.1 Maxwell's Demon and the Statistical Method. Maxwell [2] is one of the great scientists who believed that all physical phenomena are mechanical, but numerical difficulties with macroscopic systems force us to abandon the mechanical explanation and resort to the statistical method. He said: ''One of the best established facts in thermodynamics is that it is impossible in a system enclosed in an envelope which permits neither change of volume nor passage of heat, and in which both the temperature and the pressure are everywhere the same, to produce any inequality of temperature or of pressure without the expenditure of work. . . . But if we conceive a being whose faculties are so sharpened that he can follow every molecule in its course, such a being, whose attributes are still as essentially finite as our own, would be able to do what is at present impossible to us. For we have seen that the molecules in a vessel full of air at uniform temperature are moving with velocities by no means uniform, though the mean velocity of any great number of them, arbitrarily selected, is almost exactly uniform. Now let us suppose that such a vessel is divided into two portions A and B, by a division in which there is a small hole, and that a being, who can see the individual molecules, opens and closes this hole, so as to allow only the swifter molecules to pass from A to B, and only the slower ones to pass from B to A. He will thus, without expenditure of work, raise the temperature of B and lower that of A, in contradiction to the second law of thermodynamics.'' And then, he continued: ''In dealing with masses of matter, while we do not perceive the individual molecules, we are compelled to adopt what I have described as the statistical method of calculation and to abandon the strict dynamical method, in which we follow every motion by the calculus.''

It is noteworthy that the statistical method of calculation implies irreversibility, whereas the strict dynamical model does not. The reason is that the concept of entropy plays a decisive and important role in classical thermodynamics, whereas it neither exists nor is necessary in classical mechanics.

Maxwell's sharp-witted being was subsequently nicknamed ''Maxwell's intelligent demon'' by Thomson [6], and created what Thomson called the reversibility paradox [7], that is, raised the question: ''How can irreversibility result from molecular motions and collisions which are themselves (according to Newton's laws of motion) reversible in time?''

2.2 Boltzmann, Entropy, and Disorder. Boltzmann began his lifelong, pioneering, and creative study of the atomic theory of matter as a doctoral candidate [8]. He tried to explain the second law of thermodynamics, misconstrued as $dS > 0$, by using classical mechanical principles, but concluded that such an explanation could not be completed without the statistical approach introduced by Maxwell. Upon adopting the statistical approach, Boltzmann made trailblazing contributions that are pre-eminent to date, and that include the Boltzmann equation and the H-theorem. As is well known, the H-theorem implies an expression for entropy [9].

In 1876, Boltzmann's professor, Loschmidt [8], brought the reversibility paradox to the attention of Boltzmann, and he quickly converted the apparent difficulty into a new conceptual advance. He asserted that ''systems tend to pass from ordered to disordered states, rather than the reverse, because the number of disordered states is so much greater than the number of ordered states . . . .''

This explanation suggested to Boltzmann that entropy—previously a rather mysterious quantity—should be interpreted as a measure of disorder, and the tendency toward larger values of entropy as a tendency toward greater disorder. Moreover, he specified an expression for entropy S given by the relation

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

where Ω is the number of microscopic configurations corresponding to a given macroscopic state, and k Boltzmann's constant. This expression is famous and is incised on Boltzmann's tombstone.

2.3 Brillouin and Information. In addressing the question of entropy, Brillouin [10] states: ''Entropy is usually described as measuring the amount of disorder in a physical system. A more precise statement is that *entropy measures the lack of information* about the actual structure of the system. This lack of information introduces the possibility of a great variety of microscopically distinct structures, which we are, in practice, unable to distinguish from one another. Since any one of these different microstructures can actually be realized at any given time, the lack of information corresponds to actual disorder in the hidden degrees of freedom.''

''This picture is clearly illustrated in the case of the ideal gas. When we specify the total number *n* of atoms, their mass *m*, their degeneracy factor *g*, and the total energy *E*, we do not state the positions and velocities of each individual atom. This is the lack of information leading to the entropy. Since we do not specify the positions and velocities of the atoms, we are unable to distinguish between two different samples of the gas, when the difference consists only in different positions and velocities for the atoms. Hence we can describe the situation as one of disordered atomic motion.''

Nuances in terminology notwithstanding, it is noteworthy that the information-theoretic approach is the underlying key idea of all statistical explanations of thermodynamics, in general, and the interpretations of various entropies, in particular. In view of the enormous and impressive empirical evidence about the objective reality, accurate reproducibility, and permanent impact of thermodynamic phenomena on our resources and our environment, it is amazing that so many people continue to try to understand the subject through statistical measures of ignorance. With some hindsight, such an attitude is like saying that no child will ever look like his parents because we do not know the details of the genome.

2.4 Feynmann, the Laws of Physics, and Disorder. In trying to understand entropy and irreversibility, Feynmann [11] considers the mixing of white and black molecules, and comments: ''Gradually the whites worm their way, by accident, across into the space of blacks, and the blacks worm their way, by accident, into the space of whites. If we wait long enough we get a mixture. Clearly, this is an irreversible process in the real world, and ought to involve an increase in the entropy.''

''Here we have a simple example of an irreversible process which is completely composed of reversible events. . . . So we have an irreversibility which is based on reversible situations. But we also see the *reason* now. We started with an arrangement which is, in some sense, *ordered*. Due to the chaos of the collisions, it becomes disordered.''

''So far as we know all the fundamental laws of physics, like Newton's equations, are reversible. Then where does irreversibility come from? It comes from order going to disorder, but we do not understand this until we know the origin of the order.''

Though indeed all the *known* fundamental laws of physics are reversible, it is noteworthy that neither Feynmann nor almost all other scientists ever pose the legitimate question: ''are the known fundamental laws of physics correct but incomplete?'' In Section 5, we will see that the so-called known fundamental laws of physics are correct, but incomplete, and that completion of these laws opens new scientific vistas that resolve the inconsistencies about thermodynamics and broaden the realm of quantum theory.

2.5 Penrose, Disorder, and Lack of Specificity of the Definition of Entropy. Among many other recent publications, the issue of entropy and disorder is addressed by Penrose [12]. He writes: ''Why is it that in the world in which we happen to live, it is the causes which actually *do* precede the effects; or to put things in another way, why do precisely coordinated particle mo-

tions occur only *after* some large-scale change in the physical state and not *before* it. In order to get a better physical description of such things, I shall need to introduce the concept of *entropy*. In rough terms, the entropy of a system is a measure of its manifest *disorder*. ... But what precisely *is* the entropy of a physical system? We have seen that it is some sort of measure of manifest disorder, but it would appear, by my use of such imprecise terms as 'manifest' and 'disorder', that the entropy concept could not really be a very clear-cut scientific quantity.''

''Thus, irreversibility seems to be merely a 'practical' matter. We cannot *in practice* unscramble an egg, though it is a perfectly allowable procedure according to the laws of mechanics. Does our concept of entropy depend upon what is practical and what is not?''

''Recall ... that the physical concept of *energy*, as well as momentum and angular momentum, *can* be given precise mathematical definitions in terms of particle positions, velocities, masses, and forces. But how can we be expected to do as well for the concept of 'manifest disorder' that is needed for making the concept of entropy mathematically precise? Surely, what is 'manifest' to one observer may not be so to another.''

Penrose's remarks are very puzzling in view of the universal, overwhelming, and extremely important empirical evidence that cries for a rational, complete, noncircular, and unambiguous explanation. Such an explanation is discussed in Section 5.

The preceding (Sections 2.1 to 2.5) are a few of the comments made by a number of eminent scientists about the statistical explanation of thermodynamics. Admittedly, the list is very short, and the comments selected. Nevertheless, they are a representative sample about the entropies of statistical mechanics and disorder, and reflect the views of almost all scientists and engineers. In the next two sections, we describe two typical numerical examples which purport to quantify the meanings of Boltzmann's entropy and disorder at the macroscopic and microscopic levels.

3 Mixing of Colored Batteries

In both scientific and popular discussions of statistical mechanics, one illustration of entropy is by means of mixtures of colored balls [13]. To facilitate the experimental verification of our conclusions, instead of balls we consider four flashlight batteries painted white, and four flashlight batteries painted black, and configure them in a flat container. Each white battery is denoted by A and each black by B. In one configuration, all white batteries A are to the left of the dotted line P (Fig. 1), and all black batteries B are to the right. It is clear that there is only one configuration of the type shown in Fig. 1, and therefore

$$\Omega_{4:0} = 1 \qquad (2)$$

where $\Omega_{i:j}$ stands for the number of configurations in which there are i A batteries to the left and j to the right of P.

Next, we consider a configuration in which there is one A to the right and one B to the left of P (Fig. 2). The A battery can be placed in any one of the four right-hand sites, and the B battery in any one of the four left-hand sites. So the number of configurations
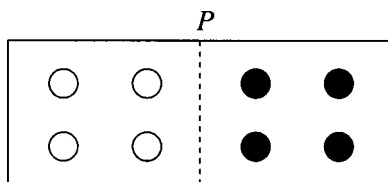
$$\Omega_{3:1} = 16 \qquad (3)$$

Fig. 1 Configuration of four white (*A*) and four black (*B*) flashlight batteries on each side of the line *P*
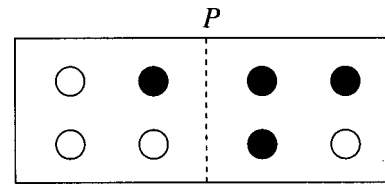

Fig. 2 One of the configurations with three white (*A*) and one black (*B*) batteries to the left of line *P*, and three black and one white batteries to the right of line *P*

Table 1

Batteries to the left of P	Batteries to the right of P	Number of configurations
$4A$	$4B$	1
$3A + B$	$A + 3B$	16
$2A + 2B$	$2A + 2B$	36
$A + 3B$	$3A + B$	16
$4B$	$4A$	1

Continuing this kind of configuring, and calculating the number of configurations of different types we find the results listed in Table 1. We see that the total number of configurations is 70, and that the most likely (36 out of 70) is the one corresponding to two A and two B on each side adjacent to P. According to Boltzmann's definition of entropy, the configuration with the most possibilities prevails, and its entropy is

$$S_{2:2} = k \ln 36 \qquad (4)$$

Next, we examine whether the preceding results conform to empirical evidence. For given values of the energy, the volume, and the amounts of constituents of a system, a very well-established and universally recognized thermodynamic experience is that the higher the value of the entropy, the less the ability of the system to do work. So the question must be raised: Does $S_{2:2}$ reflect this universal empirical fact? The answer to the question is an unqualified *no*! The reason is that each battery is a system, that is, both its spatial coordinates and its probabilistic features are separable from and uncorrelated with the spatial coordinates and probabilistic features of any other battery, respectively, [14]. Moreover, none of the instantaneous values of the properties of any of the batteries is affected by the volume of either the flat container or any of its sites. So no matter which configuration we consider at any instant in time, the amount of work that can be done either by each battery or by all the batteries collectively is the same for each of the 70 configurations. Because both the shape and the state of each battery are unaffected by its spatial location within the flat container, it follows that neither the value of any $S_{i:j}$ nor of $S_{2:2}$ is relevant to any thermodynamic considerations. More precisely, none of the values of $S_{i:j}$ affects the adiabatic availability[1] [15] of any of the batteries, individually or collectively.

This indisputable conclusion can be readily verified experimentally. All we need is 280 type A identically prepared batteries painted white, and 280 type B identically prepared batteries painted black. At any instant in time, we can create the 70 configurations listed in Table 1, and check the work that each configuration can do. Upon performing the experiments, we find that the work is the same for all configurations.

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[1]The adiabatic availability is defined as the largest work that can be done by a system A in a given initial state while the change of A does not involve net changes of the values of either the volume or the constituents, or both.

If the budget permits it, we can also check the effect of entropy generated by irreversibility as a result of the spontaneous internal discharge of each battery. To this end, we arrange many groups of 70 configurations, and check the work that can be done by one or more members of each group at a different instant in time. Upon performing this experiment, we find that the work decreases and, therefore, the entropy increases spontaneously regardless of configuration because the entropy increase is due to the internal discharge of each battery and not to the configuration.

In closing, it is noteworthy that all the conclusions just cited are true for any number of colored batteries, and would continue to be valid even if the colored batteries were moving randomly within the stationary flat container, provided we consider only the electricity from each and all batteries. Said differently, here the disorder defined by Boltzmann has no effect whatsoever on the entropy of the system.

4 Mixing of Ideal Gases

Next, we consider the isothermal mixing of two distinguishable, chemically noninteracting gases, say A consisting of n_A molecules of argon, and B consisting of n_B molecules of butane. This mixing has many similarities to the mixing of colored batteries, but also some fundamental differences.

Prior to mixing, A is in a container of volume V_A at temperature T and pressure p, and B in a container of volume V_B and at T and p. Temperature T is sufficiently high, and pressure p sufficiently low so that each gas behaves as ideal[2]. Upon mixing, each gas occupies the same volume $V = V_A + V_B$, and the mixture is at temperature T, pressure p, and has an experimentally verifiable thermodynamic entropy $S_A + S_B + S_{irr}$, where S_{irr} is the entropy of mixing generated spontaneously and given by the relation

$$S_{irr} = n_A \, k \ln \frac{V}{V_A} + n_B \, k \ln \frac{V}{V_B} \tag{5}$$

and S_i and n_i are the entropy prior to mixing and the number of molecules of gas i, respectively.

If viewed superficially, Eq. (5) may appear paradoxical compared to the results discussed in the previous section. The reason is as follows. Because the behavior of each of the gases is ideal, each gas molecule is a system, that is, both the spatial coordinates and the probabilistic features of each molecule are separable from and uncorrelated with the spatial coordinates and probabilistic features of any other molecule, respectively. Moreover, if we adopt the apparently innocuous classical mechanics view that each molecule can be visualized as a body of rigid shape, then there would be no difference between mixing argon and butane molecules and mixing of colored batteries discussed in Section 3. And yet, in contrast to the batteries which experience no entropy of mixing, here the mixing of molecules does result in the spontaneous generation of entropy by each molecule—$k \ln(V/V_A)$ by an A molecule, and $k \ln(V/V_B)$ by a B molecule. Moreover, the entropy increase per molecule is independent of whether the number of molecules is large or small, including unity.

Some authors try to justify the entropy increase (Eq. (5)) by arguing that the larger the volume the larger the number of microstates. In view of the behavior of the mixed batteries, this argument is unconvincing because, in the case of the batteries, the results show that the entropy is independent of the volume of the flat container. Moreover, if viewed classically, the number of microstates of each molecule of the mixture is infinite both for the initial volume and for the final volume. So, which infinity is larger? It is clear that a much more rational and rigorous explanation is required. We discuss a quantum-theoretic explanation in Section 6.7.

5 Remarks About the Entropies of Statistical Mechanics

In the preceding sections, comments by eminent scientists are cited to illustrate the widely held beliefs that entropy is a statistical, monotonic measure of disorder, and that disorder represents the number of microstates that are most likely to occur in a macroscopic system. In addition, two experiments are discussed which have practically identical classical mechanical features and yet yield results contrary to the premises and predictions of statistical classical mechanics and the empirical evidence about thermodynamics. Though the discussion of the experimental evidence has been based solely on k ln Ω, other expressions of entropies of statistical mechanics lead to identical contradictions.

In view of this background which is as old as the subject itself, it behooves us to ask whether the beliefs are consistent both with the correct laws and theorems of thermodynamics and the rich totality of the empirical evidence. If we take the view that thermodynamic phenomena represent a physical reality independent of the evolution of homo sapiens, then we must conclude that the empirical evidence is beyond the realm of mechanics, either classical or conventional quantum, because entropy is beyond the realm of these two sciences. This conclusion is analogous to the approach taken regarding the geocentricity versus heliocentricity of the solar system. After many millennia, the issue was decided not solely on the basis of appearances and accuracy of numerical results, but also on the basis of logical consistency and breadth of experiences.

6 Roadmap Through Recent Developments

6.1 A Unified Quantum Theory of Mechanics and Thermodynamics. Hatsopoulos and Gyftopoulos [16–19] have proposed a nonstatistical resolution of the dilemmas and paradoxes that have preoccupied generations of physicists over more than a century in their attempts to rationalize the relation between mechanics and thermodynamics. The resolution is based on a unified quantum theory of mechanics and thermodynamics which without modification encompasses all systems (both macroscopic and microscopic, including systems with only one particle), and all states (both thermodynamic or stable equilibrium and not stable equilibrium).

The key for the elimination of all statistical explanations is the discovery that the only quantum-mechanical density operators $\rho > \rho^2$ that are subject to the laws of physics (quantum-theoretic and thermodynamic) are those that can be represented by a homogeneous ensemble[3] [19]. In such an ensemble, every member is assigned the same ρ as any other member (Fig. 3), and experimentally (in contrast to algebraically), ρ cannot be decomposed—is unambiguous or irreducible—into a statistical mixture of either projectors or density operators different from ρ. The impossibility of decomposition is analogous to von Neumann's [20] conclusion that a wave function or projector ($\rho_i = \rho_i^2$) cannot be decomposed into a statistical mixture of states of classical mechanics. Moreover, and perhaps more importantly, the extension of the concept of homogeneity to density operators $\rho > \rho^2$ is accomplished without radical modifications of the quantum-theoretic postulates and theorems about observables, measurement results, values of observables, and densities or probabilities of measurement results.

Key concepts—definitions, postulates, and theorems—of the unified theory are discussed also by Gyftopoulos and Çubukçu [21], and Gyftopoulos [22].

6.2 Equation of Motion. Hatsopoulos and Gyftopoulos [18] observed that Newton's, Schroedinger's, and equivalent von

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[2]Ideal gas behavior means that none of the molecules of the gases interacts with any other molecule.

[3]In quantum theory, measurements of any property, such as energy, on an ensemble of identical systems, identically prepared yield a spectrum of values. Associated with each value is a nonstatistical probability—a probability that cannot be eliminated by increased or more accurate knowledge. The density operator ρ represents all the probabilities for measurements of all properties at an instant in time.
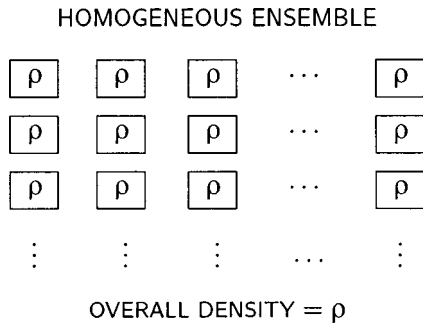
Fig. 3 Representation of a homogeneous ensemble

Fig. 4 Energy versus entropy graph of a system with fixed values of amounts of constituents and volume, and without upper bound on energy

Neumann's equations of motion are correct, but incomplete. More specifically, Schroedinger's equation describes only reversible adiabatic processes that are unitary. However, not all reversible adiabatic processes are unitary, and not all processes are reversible. Moreover, von Neumann's equation [23] for unitary transformations of ρ in time is not acceptable because both his ρ are a statistical average of wave functions or projectors, and the statistical weight of each wave function is independent of time.

In response to these observations, Hatsopoulos and Gyftopoulos [16] postulated a von Neumann-like equation for the unitary evolution in time of unambiguous or irreducible ρ's, and Beretta et al. [24,25] proposed equations of motion that involve no statistics associated with lack of information or ignorance, or macroscopic justifications, and that account for both all reversible and all irreversible processes.

It is noteworthy that, of all the equations of motion that differ from the Schroedinger equation and that have been proposed in the literature, Kossh and Steffen [26] and Çubukçu and Gyftopoulos [27] prove that the equations proposed by Beretta et al. [24,25] are the only ones that comply with all the criteria that must be satisfied by an equation that accounts for all reversible and all irreversible processes.

6.3 A Novel, Nonquantal Exposition of Thermodynamics. Gyftopoulos and Beretta [28] have composed a novel, nonstatistical exposition in which all concepts of thermodynamics are defined completely and without circular and tautological arguments in terms of only the concepts of space, time, and force or inertial mass. Though the intellectual underpinning is the unified quantum theory cited earlier, the new exposition evolves without any reference to quantum-theoretic concepts, postulates, and theorems. So it can be studied without knowledge of quantum theory.

The order of introduction of concepts, postulates, and theorems is: system (types and amounts of constituents, forces between constituents, and external forces or parameters, such as volume); properties at an instant in time; states; the first law (without the concepts of energy, work, and heat); energy (without work and heat); energy balance; classification of states in terms of time evolutions; thermodynamic or stable equilibrium states; second law (without temperature, heat, and entropy but as an assertion of *existence of one and only one stable equilibrium state for each set of values of energy, volume, and amounts of constituents*); generalized available energy; entropy of any state, stable equilibrium or not, in terms of energy and generalized available energy (and not in terms of temperature and heat); entropy balance; fundamental relation which exists for stable equilibrium states only; temperature, pressure and total potentials in terms of energy, entropy, volume, and amounts of constituents, valid for stable equilibrium states only; the third law; work in terms of energy only; heat in terms of energy, entropy, and temperature only; other interactions; various applications. All concepts and postulates are valid for all systems (both macroscopic and microscopic), and all states (both stable equilibrium and not stable equilibrium).
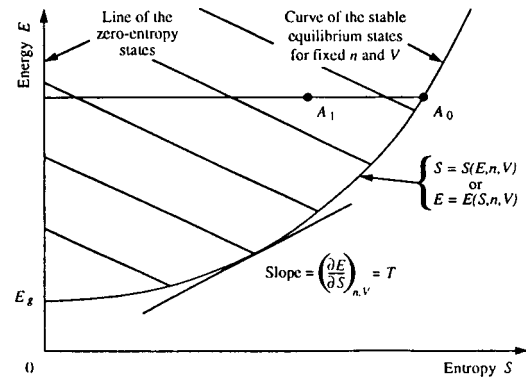
In this exposition, no statistical considerations whatsoever are required either by any definition or by any postulate or by any theorem.

6.4 Definition of Entropy. The definition of entropy in the novel exposition [21,29,30] differs from and is more general than that in any other exposition of thermodynamics. The new definition: (*i*) applies to all systems, both macroscopic and microscopic, including one-particle systems; (*ii*) applies to all states, both stable equilibrium and not stable equilibrium; (*iii*) most certainly is not statistical; and (*iv*) satisfies about ten reasonable and readily understandable criteria.

6.5 Energy Versus Entropy Graph. One result of the novel exposition of import to the purposes of this paper is a graph of energy E versus entropy S [31].

At an instant in time, the *state* of a system is defined by the values of the amounts of constituents n, the value of the volume V, and the values of a complete set of independent properties, and can be represented by a point in a multidimensional space with one axis for volume, for each amount of constituent, and for each independent property. Such a representation, however, is unwieldy because the number of independent properties of any system, even a system consisting of one particle only, is infinite. Nevertheless, useful information can be captured by first cutting the multidimensional state space by a hypersurface corresponding to given values of the volume and of each of the amounts of constituents, and then projecting the cut on an energy versus entropy plane. For a system A without upper bound on energy, we prove that the projection must have the shape of the cross-hatched area in Fig. 4.

A point either inside the cross-hatched area or on any line of the surface $S = 0$ represents the projections of an infinite number of states. Each such state has the same values of n, V, E, and S, but differing values of other properties, and is not a stable or thermodynamic equilibrium state. In particular, the surface $S = 0$ represents all the states encountered in purely mechanical theories of physical phenomena. On the other hand, by virtue of the second law of thermodynamics, each point on the convex curve represents one and only one stable equilibrium state. Said differently, on the convex curve the value of every property, including entropy, is determined solely by the values of E, n, and V, or the value of every property, including energy, is determined solely by the values S, n, and V.

For all classes of states, stable equilibrium or not stable equilibrium, it is clear that entropy is a property of the constituents of the system and not a statistical measure of ignorance, lack of information, inability to perform detailed calculations, or disorder. More specifically, in dilute systems (ideal gas behavior) each molecule has its own private entropy in the same sense that it has its
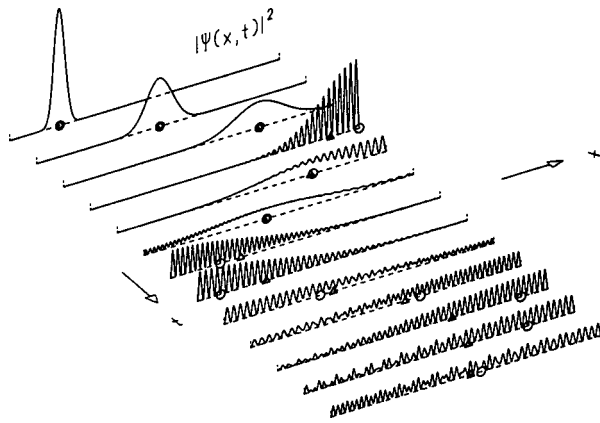
Fig. 5 Time evolution of the shape of a wave packet in an infinitely deep, one-dimensional potential well [32]

own private energy and its own private momentum. The importance of this interpretation of entropy and the conceptual difference of the interpretation from all others in the literature cannot be overemphasized.

6.6 Analytical Expression for Entropy. It is self-evident that any explicit analytical expression purporting to represent the concept of entropy must satisfy the criteria resulting from its definition. Gyftopoulos and Çubukçu [21] prove that none of the expressions existing in the literature, including $k \ln \Omega$, conform with these criteria, except for

$$S = -k \, \text{Tr}[\rho \ln \rho] \tag{6}$$

provided that ρ is a density operator that cannot be decomposed into other operators, that is, an operator which is represented by a homogeneous ensemble (Fig. 3), where Tr stands for the trace of the operator that follows,[4] and k is Boltzmann's constant.

Though it looks identical to a relation proposed by von Neumann, Eq. (6) differs from von Neumann's relation for a fundamental reason of paramount importance. In the von Neumann relation, ρ is a statistical average of wave functions or projectors. Accordingly, not all members of the ensemble representation of such a ρ are characterized by the same projector. In Eq. (6), ρ is an unambiguous or irreducible operator that can be represented only by a homogeneous ensemble (Fig. 3). If ρ is ambiguous—operationally can be decomposed into a statistical combination of two or more different density operators—Eq. (6) does not represent the entropy of thermodynamics, and neither ρ nor S are subject to the fundamental laws of physics.

6.7 Entropy as a Measure of the Quantum-Theoretic Shape of Constituents. In many textbooks [32,33], the probability density function of the spatial coordinates is interpreted as the shape of the constituents of a system. An illustration is provided by the wave packet and its evolution in time depicted in Fig. 5. Gyftopoulos [22,30] observed that the same interpretation of the spatial shape can be applied to the probabilities derived from a density operator $\rho > \rho^2$.

It follows that the entropy of thermodynamics (Eq. (6)) is a measure of the quantum-theoretic spatial shape of constituents, in the same sense that $mv^2/2$, and not some other expression, is the measure of the kinetic energy of a molecule.

For given values of the energy E, volume V, and amounts of constituents n, the values of the special measure S range from zero to a largest value. For all density operators that are projectors, $\rho_i = \rho_i^2$, such as the wave packet in Fig. 5, the value of $S = 0$. For

all other density operators, $\rho > \rho^2$, $S > 0$ and reaches the largest value for the density operator ρ^0 that corresponds to the unique stable equilibrium state dictated by the second law of thermodynamics for the given values E, V, and n. For example, for any stable equilibrium state of an electron in a spherically symmetric Coulomb field (hydrogen atom), the shape of ρ^0 is a perfect sphere.

With this interpretation in mind, we can think of the spontaneous increase of entropy in the course of irreversible processes as a natural tendency of an atom, molecule, or other system to adapt the shape of its state to the nest of internal and external forces of the system until no further reshaping is possible, that is, for given values of E, V, and n, until the unique ρ^0 and the largest value of S are achieved. The adaptation to the internal and external forces is always in the direction of nondecreasing entropy, and is beautifully exemplified by considering the spontaneous expansion of an amount of colored gas squirted in a corner of a transparent glass container. During the expansion, the shapes of the molecules change as illustrated by the wave packet in Fig. 5. Another example is the change of shape of a hydrogen atom from an initial arbitrary shape to a spherical ρ^0.

6.8 Velocity of Any Particle of a System in a Stable Equilibrium State. For a system in a stable equilibrium state, Gyftopoulos [22,30] proves that the quantum-theoretic value of the velocity of any particle—nucleon, electron, atom, or molecule—equals zero. This zero is the value of the velocity of the particle in question and not an average over velocities of different particles moving in different directions. In other words, if a system is in a thermodynamic or stable equilibrium state, every motion has ceased, nothing moves.[5]

6.9 Entropy of Thermodynamics and Perfect Order. For a system with given values of E, V, and n, in the unified theory and in the novel exposition we have established the following results: (i) there exists one and only one stable equilibrium state that cannot be decomposed into a statistical combination of other states; (ii) in the stable equilibrium state, the entropy has the largest value, and all velocities are null; and (iii) there is an infinite number of states for each value of the entropy smaller than the largest value. In view of these results, we are compelled to conclude that the stable equilibrium state is more orderly than any other state which is turbulent or nonequilibrium, or said differently, that thermodynamic or stable equilibrium represents perfect order rather than disorder. Interestingly enough, because of the uniqueness of the stable equilibrium state for each set of values E, V, and n, the conclusion about order is reached even if we use the definition of disorder proposed by Boltzmann!

This completes the brief description of the roadmap through the interwoven recent developments about thermodynamics and quantum theory, and the definition, analytical expression, and pictorial interpretation of the entropy of thermodynamics. In the next section, we examine the beliefs about statistics and disorder in the light of these developments.

7 Review of Beliefs About Statistical Mechanics

7.1 Maxwell's Views (Section 2.1). Maxwell is correct in asserting that if one accepts the classical atomic-kinetic viewpoint, entropy and irreversibility cannot be parts of an absolute law of nature. Viewed from that perspective, molecules have fixed shapes, and do not have entropy as a private property as they do have inertial mass and energy as private properties. As discussed in Section 4, however, the theoretical and empirical evidence with

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[4]If an operator is written in matrix form, the trace is the sum of the diagonal elements of the matrix.

[5]In quantum theory, the value of an observable is the expectation value of the operator that represents the observable. A complete set of expectation values of linear operators of independent observables defines one and only one ρ and, conversely, each ρ defines one and only one set of values of such observables. It is noteworthy that the momentum operator is linear, whereas its square is not. Again, the Hamiltonian operator is linear, whereas its square and any higher power are not.

gases under conditions of ideal behavior is contrary to Maxwell's conclusion. If we abandon the premise that molecules have fixed shapes and accept the quantum-theoretic idea that molecules have a variable shape, we can overcome the contradiction. The variable shape is even more elegantly illustrated by our current understanding of the electromagnetic field in a thermodynamic or stable equilibrium state. It is shown [34] both that each mode of fundamental frequency ν has its own private energy, entropy, and pressure—behaves as each molecule of an ideal gas—and that the integral of each of these three properties over all fundamental frequencies yields the respective calculated and measured property of the blackbody. Moreover, and perhaps more importantly, the pliability of the modes to adapt from one volume to another is easier to visualize and comprehend in terms of electromagnetic waves than in terms of molecules. Of course, the quantization of either a particle with nonzero inertial mass or of the electromagnetic field, and the nonclassical explanation of molecular structures and blackbody radiation were not known at the time Maxwell proposed his statistical theory. The contemporary evidence, however, suggests that the visualization of molecules as bodies with fixed shapes is neither necessary nor sufficient to regularize thermodynamic phenomena. The discussions in Sections 6.4, 6.6, and 6.7 eliminate the classical mechanics premise, and yield results that are consistent with both our understanding of quantum theory, and with all the empirical evidence.

Again, Maxwell is correct in asserting that a being with "fine tactile and perceptive organization"—a demon—could separate fast molecules from slow molecules in a container without performance of work, in violation of the second law of thermodynamics. Here too, his premise is the notion that, at the microscopic level, molecules do not have entropy as a private property. More than 300 publications [35] discuss the feasibility of the demon by using different specific devices (pistons, photons, ratchets and pawls, and computers), and all conclude that the demon is not feasible because each device of the schemes just cited generates entropy, and at the end of each scheme the entropy change is positive, and so the second law remains intact.

Upon careful study, I find that practically all the refutations about the demon are flawed for three fundamental reasons. First, none of the authors of these refutations addresses the problem posed by Maxwell, that is, that the demon must accomplish his task without any energetic and/or entropic cost to him whatsoever. In each refutal, the specific devices contribute either energy or entropy, or both and, therefore, do not operate as specified by Maxwell. Second, in each of these refutations, the demon is proven infeasible by showing that the entropy increases and so, the authors conclude, the second law is not violated. But this is not correct reasoning. The laws of thermodynamics require that the entropy increase only in irreversible adiabatic processes, but these laws do not require that all adiabatic processes be irreversible. Third, and perhaps most importantly, each of these refutations overlooks one of the most elegant and most universal results of thermodynamics, that is, limiting conditions must be and always are established for a reversible process, and not for any particular gizmo for the implementation of the process, because for a given task all reversible processes are equivalent. For example, the Carnot coefficient $(T_1 - T_2)/T_1$ is independent of the engine and its cycle, and an excellent illustration of the remark just cited.

One definitive exorcism of the demon [36] is achieved by an analysis of his demonic act in terms of the graph in Fig. 4. This graph can be regarded as representing the states of the air molecules in the vessel discussed by Maxwell. The air is system A in thermodynamic or stable equilibrium state A_0. The demon is asked to sort the air molecules into swift and slow without any contribution either by him or the environment. If this were possible, the final state of A would be A_1, that is, a state with the same values E, V, and n and less entropy than A_0; but, in the novel exposition of thermodynamics, entropy is not introduced because "we are compelled to adopt the statistical method of calculation" but because it is proven to be a well-defined, nonstatistical, and nondestructible property of each molecule. Accordingly, the demon cannot reduce this molecular entropy without compensation no matter how "fine his tactile and perceptive organization" is. It is clear that this impossibility has nothing to do with either spontaneous entropy generation (irreversibility), or shortcomings of the procedures the demon has at his disposal, or both.

Equivalently, if the demon is regarded as a perpetual motion machine of the second kind [37], then his ultimate goal is to extract energy only—make the system do work only—starting from state A_0. But, under Maxwell's specifications, it is clear from the graph in Fig. 4 that, inherently, each state of energy smaller than E_0 of A_0 has also smaller entropy than S_0. And again, because entropy is a well-defined, nonstatistical, and nondestructible property of each molecule, the demon cannot accomplish his assignment because he is forbidden from compensating for the entropy reduction. If either he were allowed to extract both energy and entropy, or if entropy were not a property of each molecule, the demon's task would be very easy. All he would have to do is cool the air to a temperature smaller than T_0 or extract only energy.

A second definitive exorcism is achieved by an analysis based on the quantum-theoretic results summarized in Section 6.8. To establish the quantum-theoretic value of the velocity of each molecule, the demon must perform measurements on homogeneous ensembles that represent the stable equilibrium state density operator ρ^0. As a result, he finds that the value of the velocity of each molecule—not the average of the velocities of many molecules—equals zero.[6] So he concludes that there are no swift and slow molecules to be sorted out. Though he would continue to venerate the imaginative and creative intellect of his father, he regrets that quantum theory was not recognized earlier so that he could have been spared the century-long search for a solution of a problem that does not exist.

7.2 Boltzmann's View (Section 2.2). On the occasion of the 150th anniversary of Boltzmann's birthday, in a recent essay Lebowitz [38] reminds us of how richly Boltzmann deserves to be admiringly commemorated for the originality and importance of his ideas, discusses the success of Boltzmann's statistical approach in explaining the observed irreversible behavior of macroscopic systems in a manner consistent with their reversible microscopic dynamics, and finds it surprising that there is still so much confusion about the problem of irreversibility.

I could not agree more with the debt we owe to Boltzmann for his trailblazing, stimulating, and fertile contributions to physics. However, both our current theoretical understanding, and empirical evidence suggest that Boltzmann's views about thermodynamics are not indisputable (see Sections 3 and 4).

In Sections 6.4 and 6.6, we show that entropy is not statistical, and that k ln Ω cannot represent the entropy of thermodynamics because it does not satisfy the criteria that must be met by an analytical expression that purports to represent entropy. In Section 6.2, we provide arguments for the need of a complete equation of motion which describes both all reversible processes and irreversible processes, and propose nonstatistical equations that satisfy these criteria. Moreover, Gyftopoulos [36] has shown that the Boltzmann equation that describes the evolution in time of a density function of space and time, even if valid, applies only to very dilute gases, that is, states for which the expectation value of the number of particles is less than unity.

In Section 6.9, we prove that both the novel exposition and the unified theory require that each thermodynamic or stable equilib-

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[6]Despite the fact that the value of the velocity is zero, many scientists claim that the kinetic energy of each molecule cannot be zero because the expectation value of the square of the momentum operator is always positive. There are at least a dozen arguments which prove that the reasoning just cited is not valid.

rium state must be unique because that is the content of the second law of thermodynamics. So, even if we use Boltzmann's criterion of disorder, we must conclude that a thermodynamic equilibrium state represents perfect order.

An empirical result that contradicts the idea that a spontaneous entropy increase implies an increase of disorder is the spontaneous crystallization of an agitated and turbulent fluid. It is hard to argue that an agitated and turbulent fluid is more orderly than a perfect crystal.

Another empirical result is discussed by Bridgman (Denbigh [13]). He refers to the spontaneous crystallization of a supercooled liquid which results in entropy increase, and for which again is difficult to claim that there has been an increase in disorder. Nevertheless, Denbigh [13] argues that: " . . . though there is a decrease of configurational entropy, consequent on the more orderly arrangement of the lattice as compared to the liquid, there is a more than compensating increase in *thermal energy*, due to the randomization of the liberated potential energy over the vibrational motions of the atoms in the crystal.''

There are several objections to Denbigh's insistence to explain the spontaneous entropy increase by invoking a connection between thermodynamic equilibrium and disorder. For example, thermal energy—heat—is not a property of a system. Thermal energy refers to the entities that are exchanged between two systems in the course of a heat interaction. Again, we have proved (Section 6.8) that, in any thermodynamic equilibrium state, the quantum-theoretic value of the velocity of any individual particle equals zero. So there are no vibrational motions in a crystal in a thermodynamic equilibrium state.

In view of these observations, we must conclude that neither Boltzmann's expression for the entropy of thermodynamics, nor his association of entropy with disorder are justified either by quantum theory or by the empirical evidence.

7.3 Brillouin's View (Section 2.3). Brillouin and other scientists [39–41] propose a statistical interpretation of thermodynamics, and an informational explanation of entropy. They argue that the better informed an observer is about the state of a system, the lesser the entropy that he assigns to that state. In the light of both the unified theory, and the empirical evidence, both the informational interpretation of thermodynamics, and the informational explanation of entropy cannot be correct. Given a system, its state is uniquely determined by a density operator ρ or by a complete set of values of independent properties, provided each property is represented by a linear operator and not any power of the operator, such as the momentum operator and not its square. Moreover, the performance of the system is dictated exclusively by the values of the concepts just cited and not by the degree of information of an observer. For example, if the system is in a stable equilibrium state, the operator is ρ^0, the entropy is the largest of the entropies of all the states that share the same values E, V, and $\mathbf{n}$, and no amount of additional information affects either ρ^0 or $(-k \operatorname{Tr} \rho^0 \ln \rho^0)$. Again, let us consider two identical electricity storage batteries, each having the same value of energy, but one being fully charged and the other fully discharged internally and spontaneously. A universal experience is that every observer, who knows nothing about thermodynamics, information theory, entropy, and batteries, will find that one battery powers a flashlight, whereas the other does not. Similar comments can be made about a myriad of other systems in either a thermodynamic equilibrium state or not in such a state. So the statistical interpretation of thermodynamics, and the concomitant informational explanation of entropy, cannot be correct.

In addition, Brillouin associates lack of information, entropy, and disorder with lack of specificity of the positions and velocities of the molecules of an ideal gas. As we discussed in Sections 3 and 4, however, this association leads to inconsistencies.

7.4 Feynmann's Views (Section 2.4). Feynmann wonders how we get irreversibility out of the equations of mechanics which describe only reversible phenomena, and associates entropy with disorder.

Our answer to Feynmann's perceptive comments is that the equations of motion of mechanics are correct but incomplete, and that an appropriate proposal for their completion has been made (Section 6.2). Unfortunately, because most scientists believe that all questions about thermodynamics have been answered by statistical mechanics, very few individuals recognize that there remain important questions to be answered, and that the discovery of the complete equation of motion of physics is one of them.

Our position about disorder is discussed in Section 7.2.

7.5 Penrose's Views (Section 2.5). Penrose as well as many other eminent physicists associate the increase of entropy with the arrow of time. Despite the almost universal agreement about this association, I believe that its validity is not correct; but full discussion of this issue is beyond the scope of this paper.

Next, Penrose asserts that entropy could not be a ''very clearcut scientific concept.'' I could not disagree more with this assertion because, in the novel exposition, the definition of entropy is as explicit, complete, noncircular, and precise as that of any other important concept of physics (Section 6.4).

Next, Penrose questions the importance of conceiving concepts, such as irreversibility, that are ''practical.'' I have two responses to this kind of questioning. First, thermodynamic thinking plays a very important role in cosmology. Second, our ability to control entropy generation—to use processes that are as close to reversible as we can afford—is of paramount importance to the protection of our environment, and the wise use of our limited resources of energy and materials. I would be very surprised if there were many scientists who feel that physics should not be concerned with the well-being of humanity.

Finally, Penrose claims that entropy does not have an analytical expression as do energy, momentum, and angular momentum. The discussions in Sections 6.6 and 6.7, and many relations of classical thermodynamics contradict this claim, and provide incontrovertible evidence that the concept of entropy not only has an analytical expression, but it is as well founded as any other well-defined concept of physics including energy, momentum, and angular momentum.

8 Conclusions

The brief summaries and the references listed in Section 6, provide a lot of information for study. The main message is that thermodynamics is a well-defined, nonstatistical general theory that includes mechanics, conventional quantum mechanics, and classical thermodynamics as special cases.

The conclusions in Section 7 contradict the beliefs about thermodynamics, statistical mechanics, and entropy discussed in Sections 2 to 4, but are consistent with the empirical evidence. In particular, entropy is shown to be a measure of the quantumtheoretic spatial shape of the molecules of a system. For given values of E, V, and $\mathbf{n}$, the value of this measure increases from zero to a maximum, and the latter value corresponds to a unique state which is the most ordered of all the states that have the same values E, V, and $\mathbf{n}$.

Nomenclature

E = energy
k = Boltzmann's const
$\mathbf{n}$ = vector of amounts of constituents
n_i = amount of ith constituent
p = pressure
S and S_i = entropy and entropy of system i
$S_{i:j}$ = entropy that corresponds to $\Omega_{i:j}$
T = temperature
Tr = trace of operator that follows

V and V_i = volume and volume of system i

ρ = quantum mechanical density operator

ρ_i = ith quantum-mechanical projector; represents quantum-mechanical wave function

ρ^0 = quantum-mechanical density operator that corresponds to one and only one thermodynamic equilibrium state

Ω = no. of microscopic configurations that correspond to given macroscopic state

$\Omega_{i:j}$ = no. of microscopic configurations that correspond to arrangement with i systems A and j systems B

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