TITLE: Maxwell`s and Boltzmann`s Triumphant Contributions to and Misconceived Interpretations of Thermodynamics

AUTHORS: Elias GYFTOPOULOS

PAGES: 9-19

Int.J. Applied Thermodynamics,
Vol.1 (No.1-4), pp.9-19, 1998

ISSN 1301-9724

Maxwell's and Boltzmann's Triumphant Contributions to and Misconceived Interpretations of Thermodynamics

Elias P. GYFTOPOULOS
Massachusetts Institute of Technology
Room 24-111, Cambridge, MA 02139 - USA
Tel. No. (617) 253 3804, Fax No. (617) 258 7437

Abstract

The statistical interpretation is discussed and found to be inadequate to explain thermodynamic phenomena. Two alternative approaches to the statistical interpretation are summarized, one purely thermodynamic, and the other quantum-theoretic and thermodynamic.

Keywords: Finite time reversibility, Maxwell's demon; Microscopic systems, Nonstatistical entropy.

1. Introduction

The scientific and engineering communities are and must be most appreciative of Maxwell's and Boltzmann's imaginative, trail-blazing, and pregnant contributions to the statistical interpretation of thermodynamics. In their respective works, they developed a set of theorems and methods which have become a standard part of the training of all modern physicists, theoretical chemists, and engineering scientists, and have been recognized to play an indispensable role in all atomic theories of matter. Thousands of books, scientific articles, engineering applications, and philosophical treatises have been stimulated and guided by the Maxwell-Boltzmann distribution of velocities in a system with an infinite number of molecules and in a thermodynamic equilibrium state, and by the Boltzmann equation which describes both the evolution of the distribution function from a nonequilibrium state to a thermodynamic equilibrium state, and a concomitant monotonic increase of the entropy function conceived by Boltzmann.

The complete and detailed discussion of the voluminous literature by and about Maxwell and Boltzmann and their impact on the scientific and engineering communities is beyond the scope of this brief article. Two informative and well-documented sources are Klein (1973a), and Brush (1976).

For our purposes, we can refer to Hertz who said (Klein 1973b): "All physicists agree that their goal is the explanation of the natural world in mechanical terms." This goal is also the prevailing fundamental premise of the explanation of thermodynamic phenomena. However, because in thermodynamics we deal with massive amounts of matter, Maxwell (1871) argued that we cannot perceive the individual molecules and are compelled to adopt the statistical method of calculation and to abandon the strict mechanical method in which we follow every motion by calculus.

Moreover, Boltzmann quantified our inability to make detailed calculations by introducing a statistical measure called entropy, and showed that, as our information becomes blurred or more chaotic, the value of the Boltzmann entropy increases, that is, the phenomenon we analyze appears to be irreversible. This increase is contrary to the mechanical premise which requires that all phenomena be reversible.

Over the past more than hundred years, many scientists have raised serious objections, both theoretical and experimental, to the statistical interpretation of thermodynamics. Yet the interpretation is prevailing and vehemently reasserted by almost all scientists and engineers. The recurring reassertion is puzzling in the light of our experiences about the importance and nonvirtuality of irreversibility, and the many changes that we have accepted in our interpretations of physical reality. For example, no one has ever succeeded in erasing the detrimental effects of irreversibility without a penalty greater than the gain achieved by the erasure. Again, after millenia of successful correlations of observations on the basis of the idea that the solar system is geocentric, we now accept that it is heliocentric. Again, despite the overwhelming and triumphant successes of Newtonian mechanics, we now recognize the validity of both special relativity and quantum theory.

The purpose of this paper is to revisit two questions: (i) "is thermodynamics a statistical theory valid only for macroscopic systems in thermodynamic equilibrium?"; and (ii) "is entropy a statistical measure of our ignorance about the exact and actual mechanical state of a system?"

We will discuss these two questions in connection with the feasibility of Maxwell's demon, Boltzmann's equation, and reversibility and the age of the universe. More than anything else, the demon illustrates Maxwell's misconception that, in principle, all physical phenomena obey the laws of mechanics and not a broader theory that includes mechanics as a special case. Similarly, Boltzmann's equation and the problem of reversibility illustrate Boltzmann's misinterpretation of well-established and universally understood conclusions of thermodynamics.

Our discussions will be guided by two related contemporary theoretical developments, one purely thermodynamic, and the other quantum-theoretic and thermodynamic. The seminal ideas of the first development could have been deduced from the works of Clausius and Gibbs but until now have been overlooked by practically every scientist and engineer. The second development could not have been pursued until the discovery and flourishing of quantum mechanics.

The paper is organized as follows. Maxwell's demon and his nonmechanical exorcism are discussed in Part 2, comments about Boltzmann's equation and irreversibility in Part 3, and concluding remarks in Part 4.

2. Maxwell's Demon

2.1 Brief history

A very informative collection of articles and commentary on Maxwell's demon was edited by Leff and Rex (1990). They review briefly about 300 references that appeared in the scientific literature over a period of twelve decades and reprint fully about 30 of the seminal publications, all pertaining to the demon. The demon (or god) is Maxwell's brain child, and is defined as follows (Maxwell 1871):

"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. This is the second law of thermodynamics, and it is undoubtedly true as long as we can deal with bodies only in mass, and have no power of perceiving or handling the separate molecules of which they are made up. 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."

"This is only one of the instances in which conclusions which we have drawn from our experience of bodies consisting of an immense number of molecules may be found not to be applicable to the more delicate observations and experiments which we may suppose made by one who can perceive and handle the individual molecules which we deal with only in large masses."

"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."

Maxwell's sharp-witted being was subsequently nicknamed "Maxwell's intelligent demon" by Thomson (1874).

It is noteworthy that Maxwell's system is initially in what we call today a thermodynamic equilibrium or stable equilibrium state. If brought about by the demon without any effects on himself or the environment, only certain changes of such states would constitute violations of the laws of thermodynamics. Changes beginning from a state that is not stable equilibrium are possible, but they are not included in Maxwell's definition of the demon and do not constitute violations of the laws of thermodynamics.

Many authors have addressed the feasibility of the demon. In each case, a specific device or procedure is proposed, such as a piston (Szilard, 1929), or energetic photons (Brillouin, 1971; Gabor, 1964), or digital computers (Landauer, 1961; Bennett, 1982). Practically every author assumes that the second law is a statement of increase of entropy, and concludes that the second law is not violated because entropy generated by the demon in the environment of the molecules is always more than whatever entropy reduction occurs as a result of the separation of the molecules into swift and slow.

Even if correct, all the attempts to exorcise the demon reviewed by Leff and Rex (1990) are not germane to the issue at hand, that is, whether there exist microscopic phenomena which violate the laws of thermodynamics. They are not germane for at least three reasons. The first is the well-known and powerful fact that thermodynamics specifies limits on the performance of a system in terms of its initial and final states and the flows at its boundary, that is, with reference to a process and not with reference to the specific procedures and equipment that may be used to achieve the process. Moreover, the limiting process is always a reversible process (any reversible process) consistent with the specifications, and not one that involves a minute or a large amount of entropy generated spontaneously by irreversibility. Neither any of the articles reviewed by Leff and Rex (1990), nor their extensive comments conform to this important and powerful characteristic of thermodynamics.

A simple and well-known illustration of the powerful facet just cited is a work-producing cyclic engine operating between two reservoirs at fixed temperatures T_1 and T_2. Because T_1 is fixed, an energy flow Q_1 into the engine must be concurrently accompanied by an entropy flow (Q_1/T_1). Because it produces only work — transfers only energy through the shaft — the cyclic engine must dispose of at least the entropy (Q_1/T_1) at temperature T_2. But such disposition is accompanied unavoidably by a concurrent energy transfer $[T_2(Q_1/T_1)]$. So regardless of the type of engine and regardless of the type of cycle, the energy that remains for transfer across the shaft is $[Q_1-T_2(Q_1/T_1)]$, the well-known seminal result of Carnot.

To be sure, any particular engine and any particular cycle may have all sorts of deficiencies of their own and may generate entropy that must be discarded at temperature T_2 together with (Q_1/T_1). Then the energy discarded at T_2 is larger than $[T_2(Q_1/T_1)]$ and what remains for the shaft is less than $[Q_1-T_2(Q_1/T_1)]$, that is, less than the ultimate thermodynamic limit. However, the ultimate limit is independent of any and all deficiencies of the engine and its cycle.

In order to find a definitive solution to the problem posed by Maxwell, we must analyze it by considering solely the properties of the molecules, and by excluding any contribution by the demon and the environment.

The second reason the attempts are not germane to the issue at hand is entropy itself. Without exception, for both many-molecule and one-molecule (Szilard 1929) systems, each and every refutation of the demon that has ever been published relies on an entropic argument. In each of these publications, entropy is defined as a nonmechanical, statistical measure of ignorance or of lack of information, that is, as a subjective rather than a physical concept. But if it is not a physical concept — not a property of each molecule like inertial mass, or momentum, or energy — why should it play any role in deciding what a mechanical system can or cannot do, and why should it prevent an omniscient and omnipotent demon from accomplishing his task at no cost?

So arguments about the demon based on a statistical interpretation of entropy are internally inconsistent. They start with the assertion that the entropy concept is not valid at the molecular level — the behavior of the air at that level is exclusively mechanical — and then falsify the assertion by using entropic arguments that involve both the air and the demon.

One way to escape from this conundrum is to abandon the idea that entropy is a statistical measure of either ignorance or lack of information, and instead investigate whether it is a *bona fide* property of each molecule of a system. Perhaps, such an investigation may lead us to a new frontier of physics that up to now has remained unexplored.

Finally, the third reason the attempts may not be germane to the problem is Maxwell's assertion that air molecules in a vessel and in a thermodynamic equilibrium state move with velocities by no means uniform." To be sure, this assertion is valid in the context of classical mechanics. However, because classical mechanics is a special case of quantum theory, it is reasonable to ask: "Does the assertion continue to be valid in the quantum theoretic context?" Such a question is never discussed in any of the articles devoted to the demon, and yet the answer may reveal unexpected and surprising conclusions.

Over the past few decades, we have addressed the issues raised in the preceding paragraphs in two new but related developments. The first is an exposition of the laws of thermodynamics and their theorems and corollaries without logical inconsistencies, incomplete and ambiguous definitions, circular arguments, and unwarranted restrictions, and without reference to quantum theory (Gyftopoulos and Beretta, 1991a). The result is a nonstatistical theory of physical phenomena, valid for all systems (both macroscopic and microscopic) and all states (both thermodynamic equilibrium and not thermodynamic equilibrium). One of the proven theorems of the theory is the existence of a state function or property of a system in any state that cannot be destroyed and that is called entropy. It is a property of any state in the same sense that inertial mass is a property of any state. Another proven theorem is that the demon cannot perform his task because he is asked to extract only energy from air in a vessel under conditions that require the extraction of both energy and entropy. A brief discussion of the new exposition, and a definitive exorcism of the demon are presented in Sections 2.2 to 2.5.

The second development is a unified quantum-theoretic interpretation of mechanics and the thermodynamics just cited. In the context of the unified theory, among the many novel results is the theorem that each molecule of a system in a thermodynamic equilibrium state has zero values of both momentum and angular momentum, that is, each molecule is at a standstill and, therefore, there are no molecules to be sorted as swift and slow. Said differently, if Maxwell were cognizant of quantum theory, he would not have conceived of the idea of the demon. It is noteworthy that the zero value of momentum is not the result of averaging over different momenta of many molecules. Under the specified conditions, it is the quantum-theoretic value of the momentum of any one molecule, and the same result is valid even if the system consists of only one molecule. A brief discussion of the unified theory, and the quantum-theoretic exorcism of the demon are presented in Sections 2.6 and 2.7.

2.2 Thermodynamic considerations

Many scientists and engineers have expressed concerns about the completeness and clarity of the usual expositions of thermodynamics. In response to such concerns and questions, Gyftopoulos and Beretta (1991a) have composed an exposition of thermodynamics in which all concepts are defined completely and without circular arguments in terms of only the mechanical ideas of space, time, and inertial mass or force. A brief summary of this exposition is given by Gyftopoulos and Çubukçu (1997). The new exposition conforms to the three laws, the first, the second, and the third (see Appendix). Some theorems are as follows: (i) Any system A in any state A_1 (stable equilibrium or not stable equilibrium) has a property called entropy with a value denoted by S_1. The procedures for finding the value S_1 are discussed by Gyftopoulos and Beretta (1991a), and by Gyftopoulos and Çubukçu (1997); (ii) The entropy obeys a balance equation

$$(S_2 - S_1)_{system} = S^{\leftarrow} + S_{irr} \qquad (1)$$

that is, a change of entropy $(S_2 - S_1)$ system as the system goes from state A_1 to state A_2 must be accounted for by an entropy flow $S^{\leftarrow}$ at the boundary of the system, plus an amount of entropy S_{irr} generated spontaneously within the system, entropy generated by irreversibility. The entropy $S^{\leftarrow}$ is positive if entropy flows into the system, and the spontaneously generated entropy S_{irr} is nonnegative; (iii) The laws of thermodynamics do not require that processes be reversible or irreversible; this little appreciated fact is illustrated by two universally accepted but usually ignored theorems: (a) if an adiabatic process is reversible, the entropy of the system is invariant, and (b) if an adiabatic process is irreversible, the entropy of the system increases; (iv) If a system has r different constituents with amounts denoted by $\beta = \{n_1, n_2,\ldots, n_r\}$, s different (external) parameters denoted by $\beta = \{\beta_1, \beta_2,\ldots, \beta_r\}$, where $\beta_1 = V$ = volume, and is in a stable equilibrium state, only then the entropy of the system is given by the fundamental relation, that is, an analytic function of the form

$$S = S\,(E, n, \beta)\,; \qquad (2)$$

(v) For stable equilibrium states only, the following definitions apply

$$T = \frac{1}{\left(\partial S/\partial E\right)_{n,\beta}} = \text{temperature} \; ; \qquad (3)$$

$$\mu_i = \frac{1}{\left(\partial S/\partial n_i\right)_{E,n,\beta}} = \begin{array}{c}\text{total potential of}\\ \text{i - th constituent;}\end{array} \qquad (4)$$

$$p = \frac{1}{\left(\partial S/\partial V\right)_{E,n,\beta}} = \text{pressure}\,. \qquad (5)$$

For states that are not at stable equilibrium, the definitions of T, μ_i, and p are meaningless; (vi) The fundamental relation is concave with respect to each of its independent variables; in particular

$$\left(\partial^2 S/\partial V^2\right)_{n,\beta} \le 0 \qquad (6)$$

(vii) The minimum value of entropy is zero; (viii) Work, heat and other interactions are defined by Gyftopoulos and Beretta (1991a), and Gyftopoulos et al (1994).

Neither the statements of the three laws nor the proofs of the theorems require either any considerations about statistical measures of ignorance (or lack of information), or any restrictions to systems of either specific sizes or specific numbers of degrees of freedom, and to states of specific types. An exception to the last assertion is theorems proven solely for specific classes of states. So a *statistical interpretation of thermodynamics is unwarranted and misconceived.*

In particular, entropy is a nonstatistical property of any system in any state. This property adds a most important dimension to the property space of a system, a dimension that distinguishes the phenomena regularized by thermodynamics from the phenomena that can be encompassed solely by either classical mechanics or conventional quantum mechanics without any thermodynamic concepts.

In the light of the new definition of entropy as a nonstatistical property valid at both the macroscopic and the microscopic levels, an unavoidable issue is whether the demon's actions are restricted differently at one versus the other level. It will be shown that they are not. The general importance and implications of the entropic dimension and its role in the thermodynamic exorcism of the demon can be illustrated by means of a novel energy versus entropy graph (Gyftopoulos and Beretta 1991b).

2.3 An energy versus entropy graph

At an instant in time, the *state* of a system is defined by the values of the amounts of constituents, the values of the parameters, such as volume, and the values of a complete set of independent properties. Without any modification, this definition of state is valid in any paradigm of physics.

A state can be represented by a point in a multidimensional space with one axis for each amount of constituent, parameter, and independent property. Such a representation, however, would be 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 each of the amounts of constituents and each of the parameters, and then projecting the cut on an energy versus entropy plane. For a system A without upper bound on energy, and volume as the only external parameter, it is proven (Gyftopoulos and Beretta, 1991b) that the projection must have the shape of the cross-hatched area in *Figure 1*.

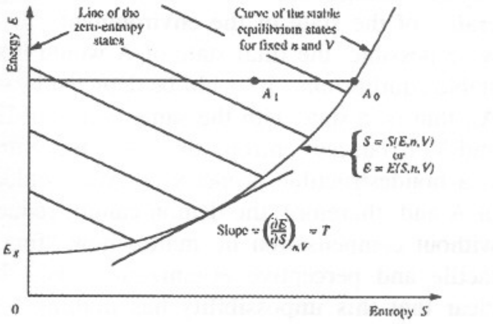

Figure 1. Energy versus entropy graph of a system with fixed values of amounts of constituents and volume, and without upper bound on energy.

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 amounts on constituents **n**, volume V, energy E, and entropy 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.

Each point on the convex curve represents one and only one stable equilibrium state. For any such state (see equation 2), the number of independent variables is only r+2, where r is the number of different constituents. Said differently, for each stable equilibrium state only, the value of any property is determined solely by the values of the energy, the r amounts of constituents, and the volume of that state. For all classes of states, it is clear that entropy is a property of the constituents of the system and not a measure of ignorance, lack of information, or inability to perform detailed calculations. The importance of this interpretation of entropy and the conceptual difference of the interpretation from all others in the literature cannot be overemphasized.

2.4 A thermodynamic exorcism of the demon

The graph in *Figure 1* can be regarded as representing the states of the air molecules in the vessel discussed by Maxwell in connection with his demon. 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 by the environment and, therefore, without any changes in the values of the energy, the amount, and the volume of the air, and without any change either of his state or, more generally, of the state of the environment. If this were possible, the final state of A would not be stable equilibrium. It would be depicted by state A_1, that is, a state with the same values of E, **n**, and V as but less entropy than A_0. But entropy is a nondestructible property of every molecule of A and, therefore, the demon cannot reduce it without compensation no matter how "fine his tactile and perceptive organization" is. It is clear that this impossibility has nothing to do with either entropy generated by irreversibility, or shortcomings of the demon's procedures and equipment, or both. It is also clear that this impossibility is not a paradox because here entropy is equally valid at the microscopic or molecular level as it is at the macroscopic level.

Equivalently, if the demon is regarded as a cyclic perpetual motion machine of the second kind (PMM2), then his ultimate task is to extract only energy from system A and, thus, change state A_0 to a state of smaller energy than that of A_0. But under the specified conditions — fixed value of the amount of air, and fixed volume — the graph in *Figure 1* shows that each state of energy smaller than that of A_0 has also smaller entropy. And again, because entropy is a nondestructible property, the demon cannot accomplish his assignment because he is asked to reduce the entropy without compensation. Here also it is clear that this impossibility has nothing to do with either entropy generated by irreversibility, or shortcomings of the demon's procedures and equipment, or both. It is dictated by the laws of thermodynamics and not the tactile and perceptive abilities of the demon.

Of course, if the initial state of A is not stable equilibrium and, therefore, lies somewhere within the cross-hatched area and not on the stable-equilibrium state curve of the graph in *Figure 1*, even an incompetent demon, let alone a smart one, could either extract only energy from A or change the state of A at constant energy without violating the laws of thermodynamics. For we see from the graph that an infinite number of states exists with lower or equal energy and equal or larger entropy than the energy and entropy of an initial state A_1.

2.5 Comments

The conception of the demon was motivated solely by Maxwell's conviction that, at the microscopic level, air molecules in a container obey exclusively the laws of classical mechanics, and need not be assigned statistical measures of ignorance, such as the entropy of statistical mechanics.

Despite this explicitly stated conviction, over the past about 130 years, all refutations of Maxwell's demon by hundreds of scientists, including Szilard, von Neumann, Prigogine, and Feynman, are based on some kind of statistical entropic argument that includes either both the air molecules and the demon or only the demon and not, as specified by Maxwell, solely the air molecules. Therefore, all these refutations address neither the problem posed by Maxwell, nor the strange implication of statistics that the degree of information of an observer can influence the ultimate course of physical phenomena. Another common premise of existing refutations is that entropy always increases. As we discussed in Section 2.2 this is a misrepresentation of the laws and theorems of thermodynamics.

The first and second laws of the exposition used in this paper do not include the concept of entropy. Entropy is derived as a theorem of the two laws, and is proven to be a nonstatistical property of any system in any state. Thus, it is possible to provide a thermodynamic exorcism of the demon by addressing directly the problem posed by Maxwell. This exorcism is based exclusively on limitations imposed by the air molecules in a fixed-volume container, and not any additional restrictions that may arise from the demon's clumsiness, and the ineffectiveness of procedures and equipment at his disposal.

2.6 A unified quantum theory of mechanics and thermodynamics

Ever since the enunciation of the first and second laws of classical thermodynamics by Clausius more than 130 years ago, the question of the relation between thermodynamics and mechanics has been the subject of intense investigations and controversy. Invariably, Maxwell's (1871) 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.

Statistical theories of thermodynamics yield many correct and practical results. For example, they yield the canonical, grand-canonical, Boltzmann, Bose-Einstein, and Fermi-Dirac distributions, and predict the equality of temperatures of systems in mutual stable equilibrium, the Maxwell relations, and the Gibbs equation (McQuarrie, 1973; Callen, 1985).

As pointed out by Schroedinger (1936), Park (1968) and (1988), Jancel (1963), and Wehrl (1978), however, the conceptual foundations of statistical interpretations of thermodynamics are not on solid ground. For example, they seem to require abandonment of the concept of state of a system, a cornerstone of traditional physical thought. Again, they foreclose opportunities for the development of a sound theory of nonequilibrium.

Though the successes of mechanics, equilibrium thermodynamics, and the *mathematical formalism* of statistical mechanics leave no doubt about the validity of the numerical results, the need for a coherent physical theory capable of encompassing these same results within a sound unified conceptual framework continues to be an interesting challenge.

Intrigued by the experiences, ideas, and concerns just cited, Hatsopoulos and Gyftopoulos (1976a-d) have proposed a resolution of the dilemmas that have preoccupied generations of physicists over more than a century in their attempts to rationalize the relation between mechanics and thermodynamics. The resolution differs from all statistical interpretations of thermodynamics, in general, and from Maxwell's explanation, in particular. It eliminates the need for statistics, and is the quantum-theoretic underpinning of the exposition of thermodynamics summarized in earlier sections, that is, the exposition which asserts that thermodynamics is a general, nonstatistical theory of all physical phenomena. The basis of the resolution is a unified quantum theory of mechanics and thermodynamics which without modification encompasses all systems (both microscopic and macroscopic), and all states (both stable or thermodynamic equilibrium and not stable equilibrium).

The key for the elimination of the statistics is the recognition that the only quantum-theoretic 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. In such an ensemble, every member is assigned the same ρ as any other member, and procedurally (in contrast to algebraically) ρ cannot be decomposed into a statistical mixture of either projectors or density operators different from ρ. The impossibility of decomposition is analogous to von Neumann's conclusion that a projector ($\rho=\rho^2$) 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 probabilities of measurement results.

Key concepts — definitions, postulates, and theorems — of the unified theory are discussed by Hatsopoulos and Gyftopoulos (1976a-d). For the purposes of this paper, we need to emphasize two results. To this end, we consider a system A in a stable equilibrium state A_0 with energy E, number of molecules $n \geq 1$,and volume V. For such a state, we prove that: (i) the value of the momentum $\langle p_k \rangle$ of any one molecule in any arbitrary spatial translational direction x_k equals zero (see also Section 3.2); and (ii) the value of the angular momentum of the internal structure of each molecule equals zero. It is noteworthy that each of the two values just cited is not an average over translational momenta and angular momenta of many molecules. Each value refers to a single molecule, regardless of whether the system consists of one, two, or many molecules.

2.7 A quantum-theoretic exorcism

In order to establish the momenta or velocities of the molecules of Maxwell's air in the context of the unified quantum theory of mechanics and thermodynamics, the demon must perform measurements on homogeneous ensembles, each member of which is assigned a density operator that corresponds to a stable equilibrium state. By doing so, he will establish that each molecule has a value of translational momentum equal to zero, and a value of angular momentum equal to zero. As a result, the demon will conclude that there are no swift and slow molecules to be sorted out. Though he will continue to venerate the imaginative and creative intellect of his father, he will regret that quantum theory was not recognized earlier so that he could have been spared the 130 year long efforts to solve a problem that does not exist!

3. Boltzmann's Computations

In a recent essay, Lebowitz (1993) reminds us of how richly Boltzmann deserves to be admiringly commemorated for the originality and importance of his ideas on the occasion of the 150th anniversary of his birth. In particular, the author 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."

In this paper, we will comment on two aspects of Boltzmann's computations, the microscopic versus macroscopic behavior of systems, and reversibility and the age of the universe. We will find that Boltzmann's explanations are not as definitive as the essay just cited suggests.

3.1 Microscopic versus macroscopic behavior

The essay quotes Schroedinger as saying: "Boltzmann's ideas really give an understanding of macroscopic behavior." However, later on Schroedinger (1954) also stated: "The older and more naive application is to N actually existing physical systems in actual physical interaction with each other, e.g., gas molecules or electrons. . This original point of view is associated with the names of Maxwell and Boltzmann, and others. But it suffices only for dealing with a very restricted class of physical systems — virtually only with gases. It is not applicable to a system which does not consist of a great number of identical constituents with private energies. … Hence a second point of view, which we owe to Willard Gibbs, has been developed." In fact, even the latter comment by Schroedinger does not capture all the limitations of Boltzmann's ideas about irreversibility. We can verify this fact, by reviewing the Boltzmann equation (Cercignani 1988, and Rose and Clark 1961).

Assuming that the Boltzmann equation is a valid description of irreversible processes and scrutinizing its terms, we reveal that it is applicable only if the value (expectation value) of the number of molecules of the gas in each elementary volume of phase space is smaller than unity. To see this clearly, we recall that the Boltzmann equation is given by the relation

$$\frac{\partial f}{\partial t} + \nabla_{\mathbf{r}} \cdot \mathbf{v}f + \nabla_{\mathbf{v}} \cdot \mathbf{a}f = \text{collision integral} \qquad (7)$$

In the left-hand side of the equation, f(**r**,**v**,t) d**r**d**v** represents the (expected) number of molecules of a system in phase-space volume d**r**d**v**, and the normalized sum of the three terms is the time derivative of this number, (df/dt) d**r**d**v**, where **r** denotes the Cartesian coordinates of a molecule, and **v** the velocity of the molecule. In the collision integral, f(**r**,**v**, t) d**r**d**v** enters as the probability that upon measurement at time t, a molecule of the system within the volume between **r** and **r** + d**r** is found to have velocity between **v** and **v** + d**v**. The circumstance for which a number is both a number of molecules and a probability occurs only if the number is smaller than unity. So Boltzmann's equation is applicable not to macroscopic systems with very large numbers of molecules but to systems so dilute as to have an expected number of molecules less than unity.

An excellent application of Boltzmann's equation is to neutrons in a nuclear power reactor. At full power, the number of neutrons is less than 10^{18} #/m^3 or less than unity per cube of a side of 10^{-6} m. This side is huge compared to the neutron diameter (about 10^{-15} m).

3.2 Reversibility and the age of the universe

Lebowitz (1993) states: "We can expect to see unusual events such as gases unmixing themselves, only if we wait for times inconceivably long compared with the age of the universe." This statement has its origin in a calculation made by Boltzmann (1896) in response to objections to the statistical interpretation of irreversibility raised by Poincaré (1890), and Zermelo (1896). It perpetuates a fallacy that has plagued the debate about statistical mechanics for over a century because it overlooks both the thermodynamic definition of reversibility, and fundamental results of quantum theory.

Even if valid, the inconceivably long time calculated by Boltzmann (1896) describes only one reversible process, the spontaneous return to initial conditions via intermolecular collisions. However, such a calculation ignores the thermodynamic definition of reversibility. According to this definition, a process is reversible if both the system and its environment can be restored to their respective initial states (Tolman, 1966; Gyftopoulos and Beretta, 1991c; and Haase, 1969) along any path of states and not exclusively along the path of intermolecular collisions. Moreover, a process is irreversible if, upon restoring the system to its initial state, an irreducible permanent effect is left on the environment. The permanent effect is experienced even if the restoration of the system is achieved with perfect machinery.

In light of the definitions just cited, the age of the universe is interesting but not germane to the issue at hand. Three universally and daily observed examples illustrate this conclusion: (i) Initially, a well insulated bucket of water consists of half hot and half cold water. If they are allowed to interact only with each other, the two water halves reach mutual stable equilibrium (thermodynamic equilibrium), all the water is lukewarm and, of course, the process experienced by the water is irreversible. It is irreversible because we can always restore the hot and cold parts over a very short period of time by means of cyclic machinery, but such restoration leaves a permanent effect on the environment — increases the entropy of the environment — even if the machinery is thermodynamically perfect. Moreover, the minimum permanent effect is independent of the speed with which the initial state is restored; (ii) Initially, a high quality electricity storage charged battery is wrapped in excellent insulation and left idle on a shelf. After a few years, the battery is found to be dead because of internal discharge at constant energy. At that time, we can restore the initial state of the battery (by first cooling and then recharging) over a period of time much shorter than the time required for the completion of the spontaneous internal discharge. The spontaneous discharge is irreversible because the restoration to the charged state increases the entropy of the environment even if the cooling and the recharging processes are perfect, and regardless of whether it is done over a short or long time; and (iii) A third example is the chemical reaction $2H_2 + O_2 = 2\ H_2O$ in an isolated oxidation chamber. The reaction is irreversible but the electrolytic reformation of H_2 and O_2 can be accomplished very quickly, and always at least a minimum permanent effect is left on the environment.

In the three examples, plus innumerable other irreversible processes, there is practically no difficulty in restoring the initial state of the system over a period of time that is short or long but has no connection to the age of the universe. Moreover, regardless of the time interval, each restoration consumes no energy (principle of energy conservation) but dissipates natural resources (coal, oil, natural gas, nuclei, or solar radiation), that is, materials with the same energy but higher entropy than the corresponding initial values are accumulated in the environment. This accumulation occurs even if the restoration devices are perfect.

Apart from innumerable experiences, there is a fundamental theoretical objection to both the validity of the inconceivably long time calculated by Boltzmann and the recurrence of the initial state via velocity reversals. The objection arises from a basic result of quantum theory, has no classical analogue, and is very often overlooked. It asserts that, in thermodynamic equilibrium the value of the velocity of each and every molecule is zero. Accordingly, neither the collisions invoked by Boltzmann nor velocity reversals can restore the initial state over either a short or a long period of time because every molecule is at a standstill.

In support of the assertions just cited, and to simplify the algebra, we can consider a system A having a value of the amount of each constituent equal to an eigenvalue of the corresponding number operator, a fixed volume, and nondegenerate energy eigenstates. The most general description of the thermodynamic or stable equilibrium states of A is quantum-theoretic not only because classical mechanics is a special case of quantum physics, but, more importantly, because there exist quantal aspects which can be neither represented classically nor overlooked. For example, the question of stability of molecular energy levels cannot be answered by means of classical mechanics. Again, the concept of entropy as a property of each individual molecule cannot be accommodated without quantum theory.

As it is very well known, the energy E, entropy S, and quantum-mechanical canonical probabilities x_i associated with a thermodynamic equilibrium state of the system under consideration are given by the relations

$$E = \sum_i x_i \varepsilon_i ; \quad S = -k \sum_i x_i \ln x_i ; \qquad (8)$$
$$x_i = \frac{\exp(-\beta\varepsilon_i)}{\sum_i \exp(-\beta\varepsilon_i)}$$

where ε_i is the ith energy eigenvalue, k the Boltzmann constant, β a coefficient determined solely by the value of the energy E, and the energy eigenvalues satisfy the eigenvalue problem

$$\hat{H}\Psi_j = \varepsilon_j \Psi_j \qquad (9)$$

Regardless of the number of molecules of the constituents of the system, any position operator $\hat{x}_k$ and the momentum operator $\hat{p}_k$ along the direction of the coordinate $\hat{x}_k$ of a molecule of mass m satisfy the commutator relation

$$\left[x_k, \hat{H}\right] = i\frac{\hbar}{m}, \hat{p}_k \qquad (10)$$

and the Heisenberg uncertainty relation (Jauch, 1968):

$$\Delta x_k \Delta E \geq \frac{\hbar}{2m} \left| \langle \hat{p}_k \rangle \right| \qquad (11)$$

where Δx_k and ΔE are the standard deviations (fluctuations) of measurement results of the observables $\hat{x}_k$ and $\hat{H}$, respectively.

For any stationary energy eigenstate ψ_j of a system with finite dimensions

$$\Delta x_k < \infty \qquad (12)$$

$$(\Delta E)^2 = \left\langle \Psi_j^* \hat{H}^2 \Psi_j \right\rangle - \left\langle \Psi_j^* \hat{H} \Psi_j \right\rangle^2 = \varepsilon_j^2 - \varepsilon_j^2 = 0 \qquad (13)$$

and, therefore, relation (11) yields $\left| \langle \hat{p}_k \rangle \right| = 0$. It follows that each stationary energy eigenstate corresponds to a zero value of momentum of any molecule in any direction, and that the same must be true for a canonical combination of such eigenstates (see equations 8). Accordingly, starting from a thermodynamic equilibrium state, neither collisions nor velocity reversals can restore the system to its initial state over a short or a very long period of time because all molecules are at a standstill. Said differently, the classical mechanics picture "that the molecules in a vessel full of air at uniform temperature are moving with velocities by no means uniform" is not valid in quantum theory.

4. Concluding Remarks

Maxwell's and Boltzmann's contributions to thermodynamics have had and continue to have profound, stimulating, and productive influences on science and engineering, but they are colored by the conviction that, in principle, all physical phenomena obey only the laws of mechanics. Recent understanding of thermodynamics casts serious doubts about the conviction just cited, and provides newer opportunities for expanding the frontiers of both mechanics and thermodynamics. Though it differs from that of Maxwell and Boltzmann, the newer understanding does not diminish the greatness and importance of the contributions of scientific giants such as Maxwell and Boltzmann. In fact, it makes their contributions even more valuable because without them no progress would have been made.

Appendix

For quick reference, we repeat here the statements of the three laws of thermodynamics.

The *first law* asserts that any two states of a system may always be the initial and final states of a weight process. Such a process involves no net effects external to the system except the change in elevation between z_1 and z_2 of a weight, that is, solely a mechanical effect. Moreover, for a given weight, the value of the expression $Mg\,(z_1 - z_2)$ is fixed only by the end states of the system, where M is the mass of the weight, and g the gravitational acceleration.

The statement of the *second law* is as follows (simplified version): Among all the states of a system with a given value of energy, and given values of the amounts of constituents and the parameters, there exists one and only one stable equilibrium state.

The *third law* is: For each given set of values of the amounts of constituents and the parameters of a system, there exists one stable equilibrium state with zero temperature.

References

Bennett, C.H., 1982, *Int. J. Theor. Phys.*, **21**, pp. 905–940.

Boltzmann, L., 1896, *Ann. Phys. (Leipzig)*, **57**, p. 773; translated and reprinted in Brush, S.G., 1966, *Kinetic Theory 2*, Pergamon, Elmsford, New York, pp. 218–228.

Brillouin, L., 1971, *Science and Information Theory*, Second Edition, Academic Press, New York.

Brush, S.G., 1976, "The Kind of Motion We Call Heat," Vols. 1 and 2, North Holland, Personal Library, New York.

Callen, H.B., 1985, *Thermodynamics and an Introduction to Thermostatics*, 2nd edition, John Wiley and Sons, New York.

Cercignani, C., 1988, *The Boltzmann Equation and Its Applications*, Springer-Verlag, New York.

Gabor, D., 1964, *Progress in Optics*, **1**, pp. 111–153.

Gyftopoulos, E.P. and Beretta, G.P., 1991a, *Thermodynamics: Foundations and Applications*, Macmillan, New York.

Gyftopoulos, E.P. and Beretta, G.P., 1991b, *op. cit.*, Chapter 13.

Gyftopoulos, E.P. and Beretta, G.P., 1991c, *op. cit.*, p. 59.

Gyftopoulos, E.P. and Çubukçu, E., 1997, *Phys. Rev. E*, **55**, **4**, pp. 3851–3858.

Gyftopoulos, E.P., Flik, M.I., and Beretta, G.P., 1994, *J. of Energy Resources and Technology*, **116**, pp. 136–139.

Haase, R., 1969, *Thermodynamics of Irreversible Processes*, Addison-Wesley, Reading, Massachusetts, p. 2.

Hatsopoulos, G.N. and Gyftopoulos, E.P., 1976a, *Found. Phys.*, **6**, **1**, pp. 15–31.

Hatsopoulos, G.N. and Gyftopoulos, E.P., 1976b, *Found. Phys.*, **6**, **2**, pp. 127–141.

Hatsopoulos, G.N. and Gyftopoulos, E.P., 1976c, *Found. Phys.*, **6**, **4**, pp. 439–455.

Hatsopoulos, G.N. and Gyftopoulos, E.P., 1976d, *Found. Phys.*, **6**, **5**, pp. 561–570.

Jancel, R., 1963, *Foundations of Classical and Quantum Statistical Mechanics*, Pergamon Press, Oxford, England, p. xxxi.

Jauch, J.M., 1968, *Foundations of Quantum Mechanics*, Addison-Wesley, Reading, Massachusetts, pp. 160–163.

Klein, M.J., 1973a, "The Development of Boltzmann's Statistical Ideas" in *The Boltzmann Equation: Theory and Applications*, edited by Cohen, E.G.D., 1973, Springer-Verlag, New York, pp. 53–106.

Klein, M.J., 1973b, *op. cit.*, p. 56.

Landauer, R., 1961, *IBM J. Res. Dev.*, **5**, pp. 183–191.

Lebowitz, J.L., 1993, *Phys. Today*, September, pp. 32–38.

Leff, H.S. and Rex, A.F., eds., 1990, *Maxwell's Demon, Entropy, Information, Computing*, Princeton University Press, Princeton.

Maxwell, J.C., 1871, *Theory of Heat*, Longmans, Green and Co., London, Chapter 12.

McQuarrie, D.A., 1973, *Statistical Thermodynamics*, Harper and Rowe, New York.

Park, J.L., 1968, *Amer. J. Phys.*, **36**, pp. 211–226.

Park, J.L., 1988, *Found. Phys.*, **18**, **2**, pp. 225–244.

Poincaré, H., 1890, *Acta Math.*, **13**, **1**; translated and reprinted in Brush, S.G., 1966, *Kinetic Theory 2*, Pergamon, Elmsford, New York, pp. 194–202.

Rose, D.J. and Clark, Jr., M., 1961, *Plasmas and Controlled Fusion*, MIT Press, Cambridge, Massachusetts, pp. 58–60.

Schoedinger, E., 1957, *Statistical Thermodynamics*, Cambridge University Press, London, pp. 2–3.

Schroedinger, E., 1936, *Proc. Cambridge Philos. Soc.*, **32**, p. 446.

Szilard, L., 1929, *Z. f. Physik*, **53**, pp. 840–856.

Thomson, W., 1874, *Nature* **9**, pp. 441–444..

Tolman, R.C., 1966, *Relativity, Thermodynamics, and Cosmology*, Oxford University Press, London, p. 121.

Wehrl, A., 1978, *Rev. Mod. Phys.*, **50**, pp. 221–260.

Zermelo, E., 1896, *Ann. Phys. Leipzig*, **57**, 485; translated and reprinted in Brush, S.G., 1966, *Kinetic Theory 2*, Pergamon, Elmsford, New York, pp. 208–217.