ELSEVIER

Physica A 307 (2002) 405–420

PHYSICA A

www.elsevier.com/locate/physa

Maxwell's demon. (I) A thermodynamic exorcism

Elias P. Gyftopoulos *

Massachusetts Institute of Technology, Room 24-111, 77 Massachusetts Avenue, Cambridge, MA 02139, USA

Received 23 November 2001

Abstract

It is shown that Maxwell's demon is unable to accomplish his task not because of considerations related to irreversibility, acquisition of information, and computers and erasure of information but because of limitations imposed by the properties of the system on which he is asked to perform his demonic manipulations.

The limitations emerge from two recent but related developments of which Maxwell was completely unaware. One is an exposition of thermodynamics as a nonstatistical theory, valid for all systems, both large and small, including a system with only one degree of (translational) freedom, and for all states, both thermodynamic or stable equilibrium states and states that are not thermodynamic equilibrium, including states encountered in mechanics. In this theory, entropy is proven to be a nondestructible, nonstatistical property of any state in the same sense that inertial mass is a nonstatistical property of any state.

In Part I, the demon is shown to be incapable of accomplishing his task because this would be equivalent either to reducing the nondestructible and nonstatistical entropy of air in a container without compensation by any other system, including himself, or to extracting only energy from the air under conditions that require the extraction of both energy and entropy.

The second development is a unified, quantum-theoretic interpretation of mechanics and the thermodynamics just cited. In this theory: (a) the quantum-theoretic probabilities of measurement results are represented by a density operator ρ that corresponds to a homogeneous ensemble of identical systems, identically prepared; homogeneous is an ensemble in which every member is described by the same density operator ρ as any other member, that is, the ensemble is not a statistical mixture of projectors (wave functions); said differently, experimentally (as opposed to algebraically) the homogeneous ensemble cannot be decomposed into mixtures either of pure states or other mixtures; (b) the value $\langle A \rangle$ of any observable is not given by any particular measurement result but by the average of an ensemble of measurement results, that is,

* Tel.: +1-617-253-3804; fax: +1-617-258-7437.
E-mail address: epgyft@aol.com (E.P. Gyftopoulos).

PII: S0378-4371(01)00630-6

$\langle A\rangle=\sum_i a_i/N$, where A is the Hermitian operator representing the observable, a_i the measurement result of A from the ith member of the ensemble, and $N \to \infty$, that is, the number of members of the ensemble; and (c) in a thermodynamic equilibrium state, molecules do not move—each molecule has a zero value of momentum.

In Part II, the demon is shown to be incapable of accomplishing his task because this requires the sorting of air molecules into swift and slow and in thermodynamic equilibrium there are no such molecules—all the molecules are at a standstill. It is worth noting that this conclusion would not be generally valid if the ensemble for ρ were not homogeneous, that is, if the ensemble were a statistical mixture of different subensembles. But then, the ensemble would not be subject to the laws of physics.

PACS: 05.70−a; 05.70.Ln

Keywords: Nonstatistical thermodynamics; Nonstatistical entropy

1. Introduction

The purpose of this paper (Parts I and II) is to provide two rigorous exorcisms (!) of Maxwell's demon based on contemporary developments, one purely thermodynamic, and the other quantum-theoretic and thermodynamic. Both developments were completely unknown to Maxwell when he conceived of his demon.

The first development consists of an exposition of thermodynamics in which entropy is proven to be a nondestructible, nonstatistical property of any system, both large and small, in any state, both thermodynamic equilibrium and not thermodynamic equilibrium, in the same sense that inertial mass is a property of any state. In this exposition, it is shown that the demon cannot accomplish his task because he is asked either to reduce the entropy of a given amount of air without compensation or, equivalently, to extract only energy from air under conditions that require the simultaneous extraction of both energy and entropy. So, the insurmountable limitations on his actions are dictated neither by the procedures and equipment at his disposal nor by the effects of irreversibility. They result from the characteristics of the properties of the air on which he is asked to perform his demonic acts.

Maxwell did not consider the characteristics just cited because his universal paradigm of physics was classical mechanics (The word paradigm is used with the meaning coined by Kuhn [1]). Accordingly, he interpreted correctly statistics and entropy as necessary tools to bypass difficult dynamic calculations, and mistakingly restricted the use of these tools to macroscopic systems—in the case of classical mechanics, the possibility of applying statistical methods to a system having a small number of degrees of freedom was emphasized by Gibbs himself as well as by E.B. Wilson [2]. Thus, a limitation was created about the validity of the then prevailing statement of the second law of thermodynamics. In the new exposition, the limitation is eliminated because the laws of thermodynamics are part of the universal paradigm, classical mechanics is a special case, and the entropy theorem is nonstatistical and valid at all levels, both macroscopic and microscopic.

The second development is a unified quantum theory of mechanics and thermodynamics in which: (a) the probabilities represented by a density operator ρ ($\rho_i \geqslant \rho_i^2$) are exclusively quantal and not a mixture of quantal probabilities derived from projectors ($\rho_i = \rho_i^2$) and statistical (informational) probabilities α_i expressing lack of knowledge of the state of the system; said differently, ρ is represented by a homogeneous ensemble of identical systems, identically prepared; *homogeneous* is an ensemble in which every member is assigned the same density operator ρ as any other member, that is, experimentally (as opposed to algebraically) the ensemble cannot be decomposed into statistical mixtures of either projectors or other mixtures; (b) the value $\langle A \rangle$ of any observable is not any particular measurement result—any eigenvalue of the Hermitian operator A representing the observable—but the average of an ensemble of measurement results, that is, $\langle A \rangle = \sum_i a_i/N$, where a_i is the measurement result of A from the ith member of the ensemble, and $N \rightarrow \infty$, that is, the number of members of the ensemble; and (c) in a thermodynamic equilibrium state, molecules do not move—each molecule has a zero value of momentum.

In the context of the unified quantum theory, the demon is shown to be incapable of accomplishing his task because this requires the sorting of air molecules into swift and slow and, if the air is in a stable or thermodynamic equilibrium state, there are no such molecules. Of course, Maxwell was unaware of this quantal theorem. He thought of the air molecules in classical terms and, in classical mechanics, the only stable equilibrium state is that of zero momentum and lowest potential energy. In contrast, in the unified quantum theory, equilibrium states, in general, and one stable equilibrium state, in particular, exist at any value of the energy of the air.

The limitations emerging from the two relatively recent theoretical developments are, of course, facets of the same thermodynamic jewel. For present purposes, what is most noteworthy is that each depends solely on characteristics of a stable or thermodynamic equilibrium state, and is independent of any limitations inherent to the procedures and equipment available to the demon. This observation is universally true. No ultimate limit derived in thermodynamics depends on the specifics of the procedures and equipment used to approach it. To be sure, limitations inherent to any particular practical realization of a demon must be taken into account in addition to the ultimate limit imposed by the characteristic features of a system. But the latter are not as definitive and as decisive as the former.

The paper is organized as follows. Maxwell's definition of the demon and a brief history of his almost 130-year-old life are given in Section 2, the thermodynamic discussion is presented in Section 3, and conclusions are summarized in Section 4. The quantum-theoretic analysis is given in Part II.

2. Brief history

A very informative collection of articles and commentary was edited recently by Leff and Rex [3]. The editors 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 Random House Dictionary of the English Language (Second Edition, 1988) defines the demon as follows.

> Maxwell's demon: A hypothetical agent or device of arbitrarily small mass that is considered to admit or block selectively the passage of individual molecules from one compartment to another according to their speed, constituting a violation of the second law of thermodynamics.

This definition is so loosely stated as to include many processes that do occur every day and that do not violate any laws, let alone the second law of thermodynamics. For example, in a system with two counterflow beams of particles, the separation of the two beams occurs spontaneously. It involves neither interference by any hypothetical agent nor violation of any laws of physics.

Besides, the dictionary definition does not represent what Maxwell had in mind when he introduced a "being" with such sharp faculties that he could see individual molecules. Maxwell wrote [4]:

> Before I conclude, I wish to direct attention to an aspect of the molecular theory which deserves consideration.
>
> 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 to be made by one which 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 [5]. He wrote, "The definition of a demon, according to the use of this word by Maxwell, is an intelligent being endowed with free will and fine enough tactile and perceptive organization to give him the faculty of observing and influencing individual molecules of matter".

It is noteworthy that Maxwell's system is initially in what we call today a thermodynamic equilibrium or stable equilibrium state. It is only certain changes of such states that, if brought about by the demon without work done on the system, 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. For example, the external discharge of a charged electricity-storage battery, and the models discussed by Zhang and Zhang [6] are not included in Maxwell's definition, and do not constitute violations of the laws of thermodynamics because in each of these examples the initial state is not a thermodynamic equilibrium state.

Maxwell's and Thomson's references to intelligent beings left the strong impression that such beings are not subject to the same laws of physics as inanimate matter, an impression that is contrary to overwhelming contemporary scientific and engineering evidence.

Much later, Smoluchowski [7] tried to alleviate this impression by arguing that the demon could be conceived as a simple automatic apparatus, such as a trap door, and that the apparatus could not achieve the sorting of the molecules because of its own Brownian motion. But then he added [8], "As far as we know today, there is no automatic, permanently effective perpetual motion machine, in spite of molecular fluctuations, but such a device might, perhaps, function regularly if it were appropriately operated by intelligent beings".

There are two interesting notions in the last quotation. One is that the demon is a perpetual motion machine or, more precisely, a perpetual motion machine of the second kind (PMM2). In view of the current understanding of thermodynamics, the complete definition of such a machine for a system without upper bound on energy is as follows.

> A perpetual motion machine of the second kind (PMM2) is any system B undergoing a cyclic process that produces no external effects except the rise of a weight in a gravity field, and the change of another system A from an initial stable equilibrium state A_0 to a different final state A_1 corresponding to the same values of amounts of constituents and volume as state A_0. State A_1 may have the same energy as A_0, but then the rise of the weight is null.

In this definition, system A is the air, and system B the demon. As does the one given by Maxwell, here the definition excludes any contributions of the demon to any of the balances that must be satisfied because system B experiences a cycle and raises a weight. The rise of the weight can be replaced by any other mechanical effect, such as separation of electric charges, or change of speed of a point mass.

The demon is entirely equivalent to a PMM2. Upon sorting the air molecules which are initially in a thermodynamic equilibrium state A_0, he creates a state A_1 that is not thermodynamic equilibrium, and that has the same energy as A_0. From such a state, energy can be transferred out of A and lift a weight. The feasibility of a PMM2 is discussed in the next section.

The other notion introduced by Smoluchowski is the shift from the apparatus to the operator which is a distinction without a difference.

The apparent ability of intelligent beings to violate the laws of thermodynamics was addressed by Szilard in his famous paper [9] "On the Decrease of Entropy in a Thermodynamic System by the Intervention of Intelligent Beings". He argued that the act of measurement, by which the demon determines the velocity of the molecule, is necessarily accompanied by an entropy increase sufficient to compensate or overcompensate for the entropy decrease that accompanies the separation of the molecules into two types, fast and slow, and so no violation of the second law occurs. He was vague about which system experiences the entropy increase. Later on, it was assumed that the increase appears in the entropy of the universe. Szilard's ideas led to the concept of bit of information, and created a fertile ground for the development of information theory, cybernetics, and computing.

Brillouin [10] and Gabor [11] followed up on the thermodynamic cost of measurement by using the quantum nature of light, and appeared to have resolved the demon's puzzle. Brillouin wrote: "Is it actually possible for the demon to see the individual atoms? … The demon is in an enclosure at equilibrium at constant temperature,…, and it is impossible to see anything in the interior of a black body… . The demon would see thermal radiation and its fluctuations, but he would never see the molecules".

Next, Brillouin considers a dissipative measurement procedure in which the demon observes the molecules by using photons that are not in equilibrium with the air. He concludes that the demon must use photons more energetic than the photons comprising the thermal background and, therefore, must dissipate energy.

Later on, Landauer [12] introduced the concept of logical irreversibility in connection with information-discarding processes in computers. The work of Landauer was extended by Bennett [13] who argued that a computing automaton can be made logically reversible. However, Bennett's extension does not conform to Maxwell's specification of the demon because it requires a reservoir, and a reservoir involves heat interactions—energy and entropy flows—between the demon and the system.

Even if correct, all the preceding attempts to exorcise the demon plus many more discussed in detail in Ref. [3] 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) conforming to the specifications, and not one that involves a minute or a large amount of entropy generated spontaneously by irreversibility.

A simple and well-known illustration of the powerful fact 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, regardless of the working fluid, 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, any particular working fluid, 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.

Another example is the so-called available energy or exergy of 1 kg of methane, the largest work that can be done by the methane plus stoichiometric air in combination with the environment. It is determined solely by any reversible process of oxidation of the methane and equilibration of the products of oxidation with the environment, and not by the steam engine, fuel cell, gas turbine, or operator that may be used for that purpose.

The same ideas are in effect and must be considered in any discussion of the air molecules being observed by Maxwell's demon. A measurement and a computer manipulation may introduce detrimental effects of their own. However, these effects are in addition to whatever limitation is imposed by the thermodynamics of the air, and it is this latter limitation that the demon is asked by Maxwell to overcome "without expenditure of work".

As stated earlier, it is noteworthy that Maxwell's description of the air molecules is based solely on classical mechanics and, therefore, the only possible interactions are work. So, Maxwell's specification "without expenditure of work" means that the demon must contribute neither energy nor anything else to the separation of the swift molecules from the slow molecules. And yet, in many discussions the demon is treated as an active contributor of entropy as well as energy.

The second reason the attempts are not germane to the issue at hand is entropy itself. Without exception, for both many- and one-molecule [9] 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?

So arguments about the demon based on a statistical interpretation of entropy are internally inconsistent. They start with the hypothesis that the entropy concept is not valid at the molecular level—the behavior of the air at that level is mechanical. But then they falsify the hypothesis by using entropic arguments that involve both the air and the demon. A typical illustration of this inconsistency is the discussion of the ratchet and pawl by Feynman et al. [14].

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 it will be shown that the answer is negative.

One way to address the issues raised in the preceding paragraphs is through two new but related developments over the past few decades. 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 [15]. The result is a nonstatistical theory of physical phenomena, valid for all systems (both large and small) and all states (both thermodynamic equilibrium and not thermodynamic equilibrium). One of the proven theorems of the theory is the existence of a property of any system that cannot be destroyed and that is called entropy. It is a property of any system in the same sense that inertial mass, momentum, and energy are properties of any system. 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. The discussion of the thermodynamic issues is the subject of this manuscript.

The second development is a unified quantum-theoretic interpretation of mechanics and the thermodynamics just cited. This development is discussed in Part II.

3. Thermodynamic considerations

3.1. *Brief summary*

Many scientists and engineers have expressed concerns about the completeness and clarity of the usual expositions of thermodynamics. A few puzzling questions are: (i) Is thermodynamics a macroscopic, statistical theory valid only for thermodynamic equilibrium states? (ii) Is entropy a measure of the lack of information of scientists and engineers about the initial conditions and the actual mechanical state of a system, and a tool to avoid detailed but almost impossible calculations? (iii) Are the differences between mechanical and thermodynamic descriptions of physical phenomena reconcilable?

In response to such concerns and questions, Gyftopoulos and Beretta [15] 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. In addition to Ref. [15], a brief summary of this exposition appears in Ref. [16]. The reconciliation between mechanical and thermodynamic descriptions is discussed in Part II. For emphasis and clarity of meanings, a few important points of the exposition just cited are repeated here.

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 inertial mass of the weight, and g the gravitational acceleration. It is noteworthy that this statement involves neither the concept of energy nor the concepts of work and heat.

One theorem of the first law is that every system A in any state A_1 has a property called *energy*, with a value denoted by the symbol E_1. The energy E_1 can be evaluated by a weight process that connects A_1 and a reference state A_0 to which is assigned an arbitrary reference value E_0 so that

$$E_1 = E_0 - Mg(z_1 - z_0)\,. \tag{1}$$

Another theorem is that energy obeys a balance equation

$$(E_2 - E_1)_{\text{system}} = E^{\leftarrow} \tag{2}$$

that is, a change of energy of the system, $(E_2 - E_1)_{\text{system}}$, as it goes from state A_1 to state A_2 must be accounted for by an energy flow $E^{\leftarrow}$ at the boundary of the system, where $E^{\leftarrow}$ is positive if energy flows into the system.

The *second law* asserts (simplified version) that among all the states of a system with a given value of energy, and given values of the amounts of constituents and the (external) parameters (such as volume), there exists one and only one stable equilibrium state. The term *stable equilibrium state* is synonymous with but more precisely defined than what in classical thermodynamics is called a thermodynamic equilibrium state. It is noteworthy that the second law does not involve the concepts of temperature, heat, entropy, and perpetual motion machines.

Some theorems of the first and second laws are as follows: (i) Any system 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 in Refs. [15,16]; (ii) The entropy obeys a balance equation

$$(S_2 - S_1)_{\text{system}} = S^{\leftarrow} + S_{\text{irr}} \tag{3}$$

that is, a change of entropy of the system, $(S_2 - S_1)_{\text{system}}$, 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 which aver that, if an adiabatic process is reversible, the entropy of the system is invariant, and that, if an adiabatic process is irreversible, the entropy of the system increases; (iv) If a system has r different constituents with amounts denoted by $\boldsymbol{n}=\{n_1,n_2,\dots,n_r\}$, s different (external) parameters denoted by $\boldsymbol{\beta}=\{\beta_1,\beta_2,\dots,\beta_s\}$, 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

$$S=S(E,\boldsymbol{n},\boldsymbol{\beta})\ ; \tag{4}$$

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

$$T=1/(\partial S/\partial E)_{n,\beta}=\text{temperature}\ ; \tag{5}$$

$$\mu_i=-T/(\partial S/\partial n_i)_{E,n,\beta}=\text{total potential of the ith constituent}\ ; \tag{6}$$

$$p=T/(\partial S/\partial V)_{E,n,\beta}=\text{pressure}\ . \tag{7}$$

For states that are not 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

$$(\partial^2 S/\partial E^2)_{n,\beta}\leqslant 0\ ; \tag{8}$$

(vii) The minimum value of entropy is zero; (viii) Work, heat, and other interactions are defined in Refs. [15,17]; and (ix) The *third law* or the *Nerst principle* asserts that for each given set of values $\boldsymbol{n}$ and $\boldsymbol{\beta}$, there exists one stable equilibrium state with zero temperature.

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, both the laws and, in general, the theorems are nonstatistical, and valid for all systems and all states.

In particular, a property that is nonstatistical, applies to all systems and all states, and must be singled out is entropy. 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 both at 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 [18].

3.2. 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

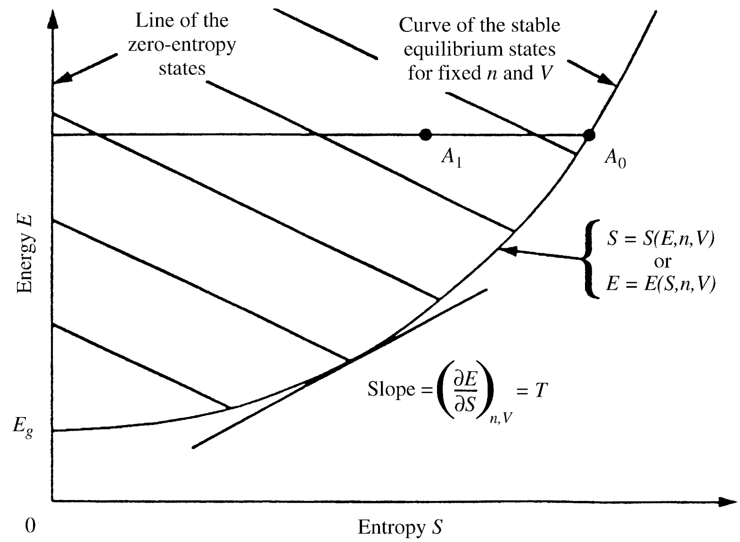

Fig. 1. Energy versus entropy graph of a system with fixed values of amounts of constituents and volume, and without upper bound on energy.

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 infinitely large. 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 limit on energy, and volume as the only external parameter, it is proven [18] that the projection must have the shape of the cross-hatched area in Fig. 1.

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 of such state has the same values of amounts of constituents $\boldsymbol{n}$, 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 mechanical theories of physical phenomena. So, classical mechanics and conventional quantum mechanics can be regarded as zero-entropy physics.

Each point on the convex curve represents one and only one stable equilibrium state. For any such state (see Eq. (4)), the number of independent variables is only r + 2, where r is the number of different constituents. Of course, specification of the function $S(E,\boldsymbol{n},V)$ requires an infinite number of values. 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, whereas specification of the surface $S(E, \boldsymbol{n}, V)$ requires specification of an infinite number of stable equilibrium states.

It is noteworthy that each stable equilibrium state is either the state of largest entropy among all the states with the same values of E, $\boldsymbol{n}$, and V, or the state of least energy among all the states with the same values of S, $\boldsymbol{n}$, and V. Moreover, for different sets of values $\boldsymbol{n}$ and V, the stable equilibrium state curves represent all the states encountered in classical thermodynamics. So classical thermodynamics can be regarded either as largest entropy physics or as least energy physics. In each of the interpretations just cited, 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.

3.3. A thermodynamic exorcism of the demon

The graph in Fig. 1 can be regarded as representing 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 on his behalf and, therefore, without any changes in the values of the energy, the amount, and the volume of the air. 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, $\boldsymbol{n}$, and V as but less entropy than A_0. But entropy is a nondestructible property 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 arises from the fact that, in the new exposition, entropy is equally valid at the microscopic level as it is at the macroscopic level.

Equivalently, if as suggested by Smoluchowski [8] the demon is regarded as a cyclic perpetual motion machine of the second kind – PMM2, then his ultimate task is to extract energy only 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 Fig. 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, if he did, he would have reduced 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 noteworthy that in practically all expositions of classical thermodynamics, the impossibility of a PMM2 is postulated as the second law. If this impossibility were used to exorcise the demon, then the argument would have been circular. In the new exposition for systems without upper bound on energy, the impossibility of a PMM2 is a proven theorem of the laws of thermodynamics, none of which includes any reference to a PMM2.

So, even if the demon were omnipotent and could measure and see molecules or record and erase information or do whatever he pleases at no cost to him whatsoever, he would not be able to accomplish his task because of limitations imposed by the characteristics of the system on which he is working. Altering the latter limitations requires a change of the laws of physics, laws which are independent of the demon's tactile and perceptive abilities.

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 Fig. 1, even a less competent 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. Accordingly, the demon can extract only energy from the system in a manner entirely consistent with the predicaments of the theorem that avers that entropy is a nonstatistical, nondecreasing property for each state of an isolated system.

A trivial illustration of the last two conclusions are two identical, electricity storage batteries, both having the same energy but one having been internally discharged and the other having just been charged. Clearly, even a child knowing only how to either press a small button (switch) or touch a spot with a wire gets no electricity from the discharged battery (stable equilibrium state) and lots of electricity from the charged battery (not a stable equilibrium state) without any cost to the child, and without any difficulty. [1]

The complete independence of the laws of thermodynamics from the theorem of the impossibility of a PMM2 can be further illustrated by considering systems with both a lower and an upper bound on energy, that is, systems which can be in stable equilibrium states with either positive or negative temperatures. For such systems, it can be proven (see inequality 8) that the projection of property space on the energy versus entropy graph has the shape of the cross-hatched area in Fig. 2. It is clear from this graph that the demon can extract only energy from any stable equilibrium state A_0 with a negative temperature because there exists an infinite number of states with energy smaller and entropy equal or larger than the energy and entropy of A_0, respectively. So, for states with negative temperatures the impossibility of a PMM2 differs from the impossibility of a PMM2 for states with positive temperatures. In fact, the former is the mirror image of the latter.

3.4. Comments

To some readers the exorcism of the demon given here may appear circular because I use the laws of thermodynamics to show that they cannot be violated. However,

[1] In principle, it is noteworthy that concepts derived for stable equilibrium states, such as temperature, pressure, and free energy, are not valid for states that are not stable equilibrium.

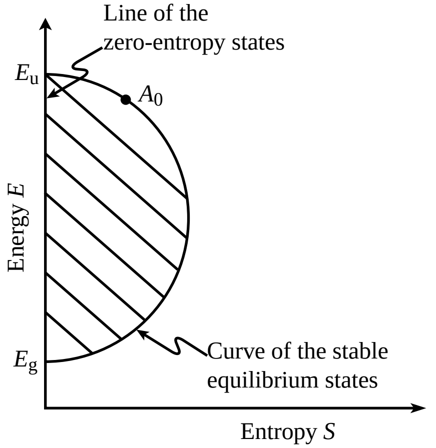

Fig. 2. Energy versus entropy graph of a system with fixed values of amounts of constituents and volume, and an upper bound on energy.

I am fully confident that the proof is not circular for the following reasons: (i) All theories of physical phenomena, including thermodynamics, are motivated by the desire to regularize experimental observations—perceptions in the language of Margenau [19]. I mention this premise because some scientists characterize thermodynamics as "a fact of experience" as if all other theories are not based on "facts of experience"; (ii) Innumerable experiences exist that cannot be regularized by the rules and conclusions of purely mechanical theories; (iii) Ref. [15] presents a nonstatistical exposition of thermodynamics that begins solely with the concepts of space, time, and inertial mass or force, and regularizes experiences with all types of states, thermodynamic equilibrium and not thermodynamic equilibrium, at both the microscopic and macroscopic levels; (iv) The definition of circularity in logic is that "conclusions are part of the premises". The exposition of thermodynamics in Ref. [15] is not circular because none of its premises—definitions and laws—includes any of its conclusions; (v) One of the proven theorems of the exposition is the existence of a nonstatistical, nondestructible property S valid for all the systems and all the states as the premises; (vi) The existence of property S does not automatically preclude the possibility of the demon for all states. The possibility is precluded only for stable or thermodynamic equilibrium states of systems without upper bound on energy because of the proven features of the energy versus entropy graph for such states; (vii) If despite these comments, some readers continue to believe that the proof given in this manuscript is circular, then I ask them to ponder the following example. Suppose that Newt Isaac is the world's expert on classical mechanics, and that quantum mechanics has not been invented yet. Next, assume that a young scientist claims to have discovered a new constant of the motion, $mv^2 + V(x)/2$, of a molecule having only one degree of freedom, and approaches Newt asking for an endorsement. Newt is impressed but, before endorsing the discovery, considers the postulates of classical mechanics, integrates the famous equation $m\mathrm{d}^2x/\mathrm{d}t^2 = -\mathrm{d}V/\mathrm{d}x$, finds that $(mv^2/2) + V(x)$ and not $mv^2 + V(x)/2$ is the proper constant, and declares the discovery invalid. Because he based it on the dynamical postulate of mechanics, is Newt's conclusion circular?

4. Conclusions

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 both the air molecules and 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.

The exposition of thermodynamics used in this paper reveals the existence of a property—the entropy—which is nonstatistical and valid for 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.

A quantum-theoretic exorcism is discussed in Part II of this work together with an interpretation of the meaning of entropy as a measure of the quantum-theoretic shape of either an individual molecule or a collection of molecules.

References

[1] T.S. Kuhn, The Structure of Scientific Revolutions, 2nd Edition, Chicago University Press, Chicago, 1970.
[2] E.B. Wilson, Ann. Math. 10 (1909) 129, 149.
[3] H.S. Leff, A.F. Rex, Maxwell's Demon, Entropy, Information, Computing, Princeton University Press, Princeton, 1990.
[4] J.C. Maxwell, Theory of Heat, Longmans, Green, and Co., London, 1871 (Chapter 12).
[5] W. Thomson, Nature 9 (1874) 441–444.
[6] K. Zhang, K. Zhang, Phys. Rev. A 46 (1992) 4598–4605.
[7] M. von Smoluchowski, Physik Z 13 (1912) 1069–1080.
[8] M. von Smoluchowski, Vorträge über die Kinetische Theorie der Materie und der Elekrizität, Teubner, Leipzig, 1914, pp. 89–121.
[9] L. Szilard, Z. Phys. 53 (1929) 840–856.
[10] L. Brillouin, Science and Information Theory, 2nd Edition, Academic Press, New York, 1971.
[11] D. Gabor, Prog. Opt. 1 (1964) 111–153.
[12] R. Landauer, IBM J. Res. Dev. 5 (1961) 183–191.
[13] C.H. Bennett, Int. J. Theor. Phys. 21 (1982) 901–940.
[14] R.P. Feynman, R.B. Leighton, M. Sands, The Feynman Lectures on Physics, Vol. I, Addison Wesley, Reading, MA, 1963, pp. 46-1–46-4.

[15] E.P. Gyftopoulos, G.P. Beretta, Thermodynamics: Foundations and Applications, Macmillan, New York, 1991.
[16] E.P. Gyftopoulos, E. Çubukçu, Phys. Rev. E 55 (1997) 3851–3858.
[17] E.P. Gyftopoulos, M.I. Flik, G.P. Beretta, J. Energy Resources Technol. 116 (1994) 136–139.
[18] E.P. Gyftopoulos, G.P. Beretta, Thermodynamics: Foundations and Applications, Macmillan, New York, 1991 (Chapter 13).
[19] H. Margenau, The Nature of Physical Reality, Oxbow Press, Woodbridge, CT, 1977.