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Maxwell's demon. (II) A quantum-theoretic exorcism

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Abstract

In Part II of this two-part paper we prove that Maxwell's demon is unable to accomplish his task of sorting air molecules into swift and slow because in air in a thermodynamic equilibrium state there are no such molecules. The proof is based on the principles of a unified quantum theory of mechanics and thermodynamics.

The key idea of the unified theory is that von Neumann's concept of a homogeneous ensemble of identical systems, identically prepared, is valid not only for a density operator ρ equal to a projector (every member of the ensemble is assigned the same projector, $\rho_i = |\psi_i\rangle \langle\psi_i| = \rho_i^2$, or the same wave function ψ_i as any other member) but also for a density operator that is not a projector (every member of the ensemble is assigned the same density operator, $\rho > \rho^2$, as any other member). So, the latter ensemble is not a statistical mixture of projectors. The broadening of the validity of the homogeneous ensemble is consistent with the quantum-theoretic postulates about observables, measurement results, and value of any observable.

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 value of 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. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The definition of Maxwell's demon, a brief history of his more than 130 years life, and a novel, consistent, and noncircular thermodynamic exorcism of his existence are discussed in Part I of this two-part paper [1]. The novelty of the exorcism lies in: (i) a new exposition of thermodynamics which avers that the laws of thermodynamics are valid for all systems and all states, and are not statistical [2,3]; and (ii) the proof of a theorem asserting that each air molecule in the system proposed by Maxwell has a well-defined, nonstatistical property called entropy [3], in the same sense that it has other properties, such as inertial mass, momentum, and energy. The new exposition of thermodynamics and the theorem just cited differ diametrically from Maxwell's idea that entropy is a thermodynamic equilibrium statistical measure of information, inapplicable at the molecular or microscopic level.

The purpose of Part II is to present an exorcism of the demon based on a unified quantum theory of mechanics and thermodynamics. In contrast to statistical quantum mechanics, a key idea of the unified theory is that the laws of physics—quantum theoretic and thermodynamic—do not apply to density operators that represent mixtures of quantal probabilities derived from projectors $\rho_i = |\psi_i\rangle\langle\psi_i|$, for $i = 1, 2, \dots$, and statistical (informational) probabilities α_i that reflect the lack of information about some or all aspects of the state of a system. Instead, the unified theory avers that the laws of physics apply only to density operators each of which is construed as the seat of exclusively quantal probabilities, that is, only to density operators ρ that can be represented by homogeneous ensembles of identical systems, identically prepared. *Homogeneous* is an ensemble in which the probabilities of results of measurements on any member are represented by the same density operator ρ as those on any other member. Accordingly, experimentally (in contrast to algebraically) the ensemble cannot be decomposed into statistical mixtures of projectors or other nonprojector density operators.

The concept of homogeneous ensemble was introduced by von Neumann [4]. But he assumed that it applies only to projectors ($\rho_i = \rho_i^2$), whereas here the concept is extended to all self-adjoint, nonnegative definite, linear, unit trace density operators. Each such operator satisfies the relation $\rho \geq \rho^2$.

Using the unified theory, we prove that each molecule of a system in a thermodynamic equilibrium state has zero value of momentum, that is, each molecule is at standstill and, therefore, there are no molecules to be sorted as swift and slow. The zero momentum is not the result of adding vectors in different directions, each representing the momentum of a particular molecule. The quantum-theoretic value of the momentum of one molecule is equal to zero, even if the system consists of only one molecule in a thermodynamic equilibrium state.

The paper is organized as follows. The foundations and a few theorems of the unified theory are described briefly in Section 2, the quantum-theoretic exorcism and possible criticisms of this exorcism are discussed in Sections 3 and 4, and conclusions are summarized in Section 5.

2. Quantum theoretic considerations

2.1. Statistical descriptions

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 classical thermodynamics and mechanics has been the subject of intense investigations and controversy. Invariably, Maxwell's seminal ideas prevail [5], 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.

Specifically, in statistical quantum mechanics, the dominant view currently held about the physical significance of classical thermodynamics is based on the interpretation of a "thermodynamic equilibrium state" as a composite that best describes the knowledge of an observer possessing only partial information about the "actual state" of a macroscopic system.

The "ith actual state" at any instant in time is defined as the set of quantal probabilities derivable from an energy eigenprojector $\rho_i = |\varepsilon_i\rangle \langle \varepsilon_i|$, where $|\varepsilon_i\rangle$ is an energy eigenket (or from an energy eigenfunction ψ_i) of conventional quantum mechanics. Because observers are uncertain about the actual state, they consider all possible "actual states" and assign to each of them a statistical probability α_i . The assignment is achieved by using a hypothesis in addition to the laws of conventional quantum mechanics. The combination of the two types of probabilities is a mixture characterized by an overall density operator $\rho = \sum_i \alpha_i \rho_i$, where $\sum_i \alpha_i = 1$, and $\rho > \rho^2$.

The theories that have evolved pursuant to the view just cited are called informational, though the general idea is the foundation of each statistical interpretation of thermodynamics proposed to date.

If at an instant in time, ρ_i for $i = 1, 2, \dots$, and ρ are represented by ensembles of identical systems, von Neumann has shown that the ensemble for each ρ_i is and must be homogeneous [4], that is, each member of the ensemble is assigned the same ρ_i as any other member, whereas the ensemble for ρ is heterogeneous, that is, only a fraction α_i of the members of the ρ ensemble is assigned the projector ρ_i (Fig. 1).

In addition to representing the fractions of the ρ_i 's in ρ , the statistical probabilities α_i enter in the evaluation of an informational measure of uncertainty, a subjective entropy, such as $S = -k \sum_i \alpha_i \ln \alpha_i$.

Except for the probabilities represented by each energy eigenprojector ρ_i , the description of a thermodynamic equilibrium state in conventional statistical quantum mechanics appears to be a complete analogy to Maxwell's statistical classical mechanical description of the molecules. It will be seen later, however, that the appearance is misleading.

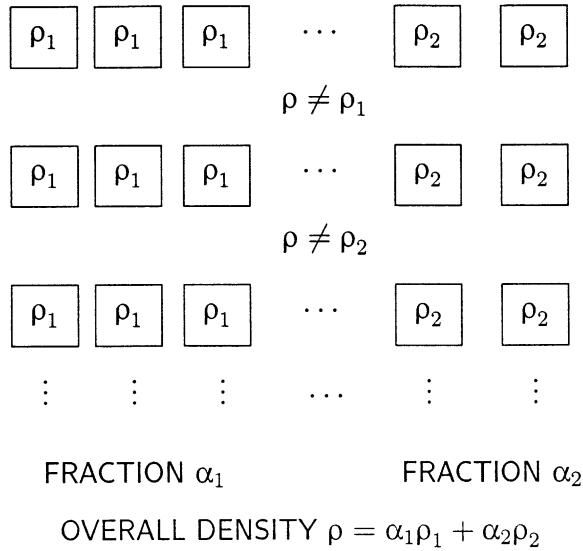


Fig. 1. Schematic of a heterogeneous ensemble of identical systems.

2.2. *Comments*

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 [6,7].

Despite these successes, the premise that entropy is a subjective characteristic of the knowledge of a partially informed observer rather than a property of a system leaves much to be desired in the light of many accurate, reproducible and nonstatistical experiences, such as the mixing of hot and cold substances, the characteristics of an internally discharging electricity storage battery, the Peltier effect, and chemical reactions. In all these experiences, entropy plays a dominant and decisive role which is entirely independent of whether an observer is informed or misinformed.

As pointed out by Schroedinger and others [8–11], 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. The reason for the foreclosure is that each statistical theory considers either Newton’s equation or Schroedinger’s equation as the relation that specifies the evolution of the “actual state” in time, but faces insurmountable conceptual difficulties to propose deterministic equations for the evolutions of the α_i ’s in time. In fact, any argument that considers the α_i ’s as indices of ignorance but proposes a deterministic evolution of this ignorance in time is an oxymoron.

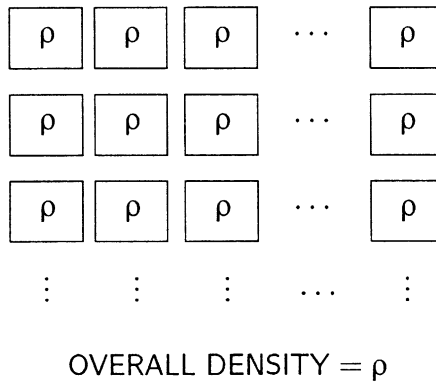


Fig. 2. Schematic of a homogeneous ensemble of identical systems.

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.

2.3. A new development

Intrigued by the experiences, ideas, and concerns just cited, Hatsopoulos and Gyftopoulos [12–15] have proposed a resolution of the dilemmas and paradoxes that have preoccupied generations of physicists over more than a century in their attempts to rationalize the relation between mechanics and thermodynamics. The resolution differs from all statistical interpretations of thermodynamics, in general, and from Maxwell's explanation, in particular.

This resolution eliminates the need for the statistical estimates α_i , and is the quantum-theoretic underpinning of the exposition of thermodynamics summarized in Part I [1], that is, the exposition which asserts that thermodynamics is a general, nonstatistical or noninformational theory of 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 thermodynamic equilibrium and not thermodynamic equilibrium).

The key for the elimination of the statistical probabilities α_i is the recognition that the only 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 (Fig. 2) and experimentally (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 cannot be decomposed into a statistical mixture of states of classical mechanics. Moreover, and perhaps more importantly, the extension of the concept of homogeneity to density

operators $\rho > \rho^2$ is accomplished without radical modifications of the quantum-theoretic postulates and theorems about observables, measurement results, values of observables, and densities or probabilities of measurement results.

Key concepts—definitions, postulates, and theorems—of the unified theory are discussed briefly below. They are included here rather than in an appendix because of the emphasis that must be given to the concept of homogeneous or unambiguous ensemble.

System. The meaning of the term *system* is discussed in Refs. [2,3]. It is a set of specified types and amounts of constituents, confined by a nest of internal and external forces. Without any modification this definition applies to all paradigms of physics [16]. The mathematical representation of a system is as follows.

System postulate [17]. To every system there corresponds a complex, separable, complete, inner product space, a Hilbert space \mathcal{H} . The Hilbert space of a composite system of two distinguishable subsystems 1 and 2, with associated Hilbert spaces \mathcal{H}_1 and \mathcal{H}_2 , respectively, is the direct product space $\mathcal{H}_1 \otimes \mathcal{H}_2$.

Kinematics. The term *kinematics* refers to a snapshot of a system at any instant in time. It includes the following concepts.

Homogeneous or unambiguous ensemble. At an instant in time, an ensemble of identical systems is called *homogeneous* or *unambiguous* [15] only if upon subdivision into subensembles in any conceivable way short of measurements, each subensemble yields in every respect measurement results—spectra of values and frequency of occurrence of each value within a spectrum—identical to the corresponding results obtained from the ensemble. For example, the spectrum of energy measurement results and the frequency of occurrence of each energy measurement result obtained from any subensemble are identical to the spectrum of energy measurement results and the frequency of occurrence of each energy measurement result obtained from an independent ensemble that includes all the subensembles.

Preparation. A *preparation* is a reproducible scheme used to generate one or more homogeneous ensembles for study.

Property. The meaning of the term *property* is discussed in Refs. [2,3]. It refers to any attribute of a system that can be quantitatively evaluated at an instant in time by means of measurements and specified procedures. All measurement results and procedures are assumed to be precise, and not to depend on either other systems or other instants in time.

Without any modifications the meanings of the concepts of homogeneous ensemble, preparation, and property are valid in all paradigms of physics.

Observable. From the definition just cited, it follows that each property can be observed. Traditionally, however, in quantum theory, a property is called an *observable* only if it conforms to the following mathematical representation.

Correspondence postulate [17]. Some linear Hermitian operators A, B, \dots , on Hilbert space \mathcal{H} , which have complete orthonormal sets of eigenvectors, correspond to observables of a system.

As explained by Park and Margenau [17], the content of this postulate is slightly different from that of its analogues in typical axiomatics inspired by the work of von Neumann. In its original form, the correspondence postulate included both of the following statements: (1) every Hermitian operator corresponds to a physical observable;

and (2) every observable has a Hermitian operator representative. Superselection rules introduced by Wick et al. [18] exclude certain Hermitian operators from being observable. By replacing the word *every* in statement (1) by the word *some*, superselection rules are satisfied. Compatibility of simultaneous measurements introduced by Park and Margenau [17] excludes certain observables from corresponding to Hermitian operators. In addition, in a unified theory of mechanics and thermodynamics other properties are observable, such as temperature, but correspond to no Hermitian operators. By replacing the word *every* in statement (2) by the word *some* the asymmetry between observables and operators is embraced. It is clear that the correspondence postulate as stated earlier accommodates both the asymmetry between operators and observables and the asymmetry between observables and operators.

Measurement act. A *measurement act* is a reproducible scheme of measurements and operations on a member of an ensemble. The result of such an act is a precise number associated with an observable.

If a measurement act is applied to each and every member of a homogeneous ensemble, the results conform to the following mathematical representation.

Mean-value postulate [17]. If a measurement act of an observable represented by Hermitian operator A is applied to each and every member of a homogeneous ensemble, there exists a linear functional $m(A)$ of A such that the value of $m(A)$ equals the arithmetic mean of the ensemble of A measurements, that is,

$$m(A) = \langle A \rangle = \sum_i a_i/N \quad \text{for } N \rightarrow \infty, \quad (1)$$

where a_i is the measurement result of the measurement act applied to the i th member of the ensemble, and $\langle A \rangle$ another notation for $m(A)$.

Mean-value theorem [17]. For each of the mean-value functionals $m(A)$ of a system at an instant in time, there exists the same Hermitian operator ρ such that

$$m(A) = \langle A \rangle = \text{Tr}[\rho A]. \quad (2)$$

The operator ρ is known as the *density operator* or the *density of measurement results of observables*.

The concept of the density operator was introduced by von Neumann [19] as a statistical average of projectors. In contrast, here ρ is restricted to homogeneous ensembles and, therefore, it is exclusively quantum-theoretic.

The operator ρ is proven to be Hermitian, positive semidefinite, unit trace and, in general, not a projector [15,20,21], that is,

$$\rho \geq 0, \quad \text{Tr } \rho = 1, \quad \rho \geq \rho^2. \quad (3)$$

Probability theorem. If a measurement act of an observable represented by operator A is applied to each and every member of a homogeneous ensemble characterized by ρ , the probability or frequency $W(a_n)$ that the results will yield eigenvalue a_n is given by the relation

$$W(a_n) = \text{Tr}[\rho A_n], \quad (4)$$

where A_n is the projection onto the subspace belonging to a_n , and

$$A|\alpha_n\rangle = a_n|\alpha_n\rangle \quad \text{for } n = 1, 2, \dots \quad (5)$$

Schroedinger picture is incomplete because it prescribes only a unitary evolution in time of a projector $\rho_i = \rho_i^2$ for $i = 1, 2, \dots$, and such an evolution corresponds to a reversible adiabatic process only. In a unified theory, the equation of motion must account for unitary changes in time of density operators that are not projectors ($\rho > \rho^2$), for reversible adiabatic processes that are not unitary and, of course, for irreversible processes.

Until a complete equation of motion is universally accepted by the scientific community, three postulates provide a partial substitute for the purposes of the unified theory. The substitute is partial because it covers only some of the requirements of the unified theory.

Limited dynamical postulate. Hatsopoulos and Gyftopoulos [12] postulated that unitary transformations of ρ in time obey the relation

$$\frac{d\rho}{dt} = -\frac{i}{\hbar} [H\rho - \rho H], \quad (7)$$

where H is the Hamiltonian operator of the system. The unitary transformation of ρ satisfies the equation

$$\rho(t) = U(t, t_0) \rho(t_0) U^+(t, t_0), \quad (8)$$

where, if H is independent of t ,

$$U(t, t_0) = \exp[-(i/\hbar)(t - t_0) H], \quad (9)$$

and if H is explicitly dependent on t ,

$$\frac{dU(t, t_0)}{dt} = -(i/\hbar) H(t) U(t, t_0) \quad (10)$$

and U^+ is the Hermitian conjugate of U .

Though Eq. (7) is well known in the literature as the von Neumann equation, here it must be postulated for the following reason. In statistical quantum mechanics [22], the equation is derived as a statistical average of Schroedinger equations, each of which describes the evolution in time of a projector in the statistical mixture represented by ρ , and each of which is multiplied by a time independent statistical probability. In the unified theory, ρ is not a mixture of projectors and, therefore, cannot be derived as a statistical average of projectors.

It is noteworthy that the dynamical postulate is limited or incomplete because all unitary evolutions of ρ in time correspond to reversible adiabatic processes. But not all reversible adiabatic processes correspond to unitary evolutions of ρ in time [14], and not all processes are reversible.

The first and second laws of thermodynamics. A partial relief to the limitations of the dynamical postulate just cited is provided by adding to Eq. (7) two more statements, the first law and the second law of thermodynamics. These statements are given in Refs. [2,3], and are not repeated here.

The quantum-theoretic postulates and theorems, and the two laws of thermodynamics provide the conceptual framework for the exposition of the unified quantum theory of mechanics and thermodynamics, a theory that applies to all systems and all states.

Moreover, the quantum-theoretic concepts lurk behind every aspect of the exposition of thermodynamics in Ref. [2].

Entropy. As discussed in Ref. [3], on the basis of the new exposition of thermodynamics in Ref. [2], and the unified theory in Refs. [12–15], we prove that, of all the expressions for entropy S that have been proposed in the literature, the only one that satisfies all the necessary criteria is given by the relation

$$S = -k \operatorname{Tr}[\rho \ln \rho]. \quad (11)$$

For given values of energy, amounts of constituents, and volume, if ρ is a projector then $S=0$, and if ρ corresponds to the unique stable equilibrium state required by the second law then S has the largest value of all the entropies of states that share the given values of energy, amounts of constituents, and volume. If, as it is usually done for projectors, we interpret a density operator ρ as the shape of an atom, a molecule, or an entire system, then the entropy of the system is a special measure of the shape with values ranging from zero to a maximum for each set of values of energy, amounts of constituents, and volume.

With this interpretation in mind, we can think of the spontaneous increase of entropy in the course of irreversible processes as a natural tendency of a system to adapt the shape of its state to the nest of internal and external forces of the system until no further reshaping is possible—largest value of S for given values of energy, amounts of constituents, and volume is achieved.

If we adopt the measure of shape interpretation for entropy, an interesting concomitant ensues. Let us assume that the paradigm of the unified quantum theory was conceived prior to that of classical mechanics, and that a physicist wished to approximate quantum-theoretic results by classical concepts. We can safely predict that he would have done an excellent job because for macroscopic systems with highly degenerate eigenkets, densities of measurement results of practically all observables can be approximated by Dirac delta functions $\delta(\mathbf{q} - \mathbf{q}_0) \delta(\mathbf{p} - \mathbf{p}_0)$. Though highly accurate, such an approximation would be inadequate because it does not include the concept of shape of an atom, or molecule, or entire system and, therefore, provides neither the mathematical representation for the concept of entropy as a property of the atom, the molecule, or the entire system, nor the possibility of changing this mathematical representative over a range of values.

Density operator of a stable equilibrium state. We can find the density operator ρ^0 of a thermodynamic or stable equilibrium state A_0 of system A by maximizing the entropy S subject to the constraints

$$\operatorname{Tr} \rho = 1 \quad \text{and} \quad \langle H \rangle = \operatorname{Tr}[\rho H] = \text{fixed} = E. \quad (12)$$

For simplicity, we assume that the system has only volume as a parameter, and only one constituent with an amount n equal to an eigenvalue of the number operator of the constituent. Moreover, we use a different subscript i even for orthonormal projectors that correspond to the same eigenvalue.

The constrained maximization solution is proven to be [23]

$$\rho^0 = \frac{\exp(-\beta H)}{\operatorname{Tr} \exp(-\beta H)} = \sum_i \rho_{ii}^0 |\varepsilon_i\rangle \langle \varepsilon_i|, \quad (13)$$

where

$$H|\varepsilon_i\rangle = \varepsilon_i|\varepsilon_i\rangle, \quad \rho_{ii}^0 = \frac{\exp(-\beta\varepsilon_i)}{\sum_i \exp(-\beta\varepsilon_i)}$$

and β is determined by the value of the energy E because

$$\langle H \rangle = E = \text{Tr}[\rho^0 H] = \sum_i \rho_{ii}^0 \varepsilon_i .$$

We can show that

$$\beta = \frac{[\partial S / \partial E]_{\varepsilon, n}^0}{k} , \tag{14}$$

where the subscript “ ε ” stands for fixed values of all the energy eigenvalues $\varepsilon_1, \varepsilon_2, \dots$, and the subscript “0” for state A_0 , that is, the partial derivative is taken along the stable equilibrium state locus for fixed volume V (fixed ε), and fixed amount n , at state A_0 . But for stable equilibrium states, the partial derivative $[\partial S / \partial E]_{\varepsilon, n}^0$ is defined as the inverse temperature of A_0 . Accordingly

$$\beta = 1/kT_0 . \tag{15}$$

3. A quantum-theoretic exorcism

With the results presented in the preceding section, we have all the quantum-theoretic tools to investigate the feasibility of a demon that can sort the molecules into swift and slow.

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, the value of the momentum of a molecule $\langle p_k \rangle$ in the spatial direction x_k is given by the relation

$$\begin{aligned} \langle p_k \rangle &= \text{Tr}[\rho^0 p_k] = \sum_m \sum_n \rho_{nn}^0 \langle \varepsilon_m | \varepsilon_n \rangle \langle \varepsilon_n | p_k | \varepsilon_m \rangle \\ &= \sum_m \sum_n \rho_{nn}^0 \delta_{nm} \langle \varepsilon_n | p_k | \varepsilon_m \rangle \\ &= \sum_m \rho_{mm}^0 \langle \varepsilon_m | p_k | \varepsilon_m \rangle = 0 , \end{aligned} \tag{16}$$

where the third of these equations results from the fact that the energy eigenkets are orthonormal and, therefore,

$$\langle \varepsilon_m | \varepsilon_n \rangle = \delta_{nm} = \text{Kronecker delta} \tag{17}$$

and the last equation from the relation

$$\langle \varepsilon_m | p_k | \varepsilon_m \rangle = 0 \quad \text{for all } k \text{ and } m . \tag{18}$$

The proof of Eq. (18) is straightforward. First, we observe that the Hamiltonian operator H of the system and the momentum operator p_k of the molecule satisfy the commutation relation

$$[x_k, H] = i\hbar p_k / M , \tag{19}$$

where M is the mass of the molecule. Next, upon defining for all k and m

$$(\Delta x_k)_m^2 = \langle \varepsilon_m | x_k^2 | \varepsilon_m \rangle - \langle \varepsilon_m | x_k | \varepsilon_m \rangle^2, \quad (20)$$

$$(\Delta H)_m^2 = \langle \varepsilon_m | H^2 | \varepsilon_m \rangle - \langle \varepsilon_m | H | \varepsilon_m \rangle^2 \quad (21)$$

we can readily prove that [21]

$$(\Delta x_k)_m (\Delta H)_m \geq \hbar |\langle \varepsilon_m | p_k | \varepsilon_m \rangle| / 2M. \quad (22)$$

But for a system with a finite extension L_k along the coordinate axis of x_k , and an energy eigenket $|\varepsilon_m\rangle$, we have

$$0 < (\Delta x_k)_m < L_k \quad \text{and} \quad (\Delta H)_m = 0 \quad (23)$$

and so equality (18) is proved.

In summary, 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, we see that his brainchild—the demon—must perform measurements on homogeneous ensembles, each member of which is assigned a density operator ρ^0 (Eq. (13)). By doing so, he will establish that each molecule has a value of momentum equal to zero and, therefore, 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 efforts to solve a problem that does not exist!

4. Discussion of criticisms

The main idea of this manuscript—in a system in a stable equilibrium state each molecule is at a standstill¹—has been the subject of criticisms by some scientists and engineers. Because other readers may have similar criticisms, I think it is purposeful to include here the opinions that I heard and my responses.

(i) Colleagues agree that in a stable equilibrium state, the expectation value of the momentum of each molecule vanishes. But they argue that “the expectation value is not what enters into a typical measurement or interaction with an external system”.

This criticism contradicts the mean-value postulate and the mean-value theorem. To be sure, one interaction that attempts to measure the velocity of a molecule yields a precise value of velocity—an eigenvalue proportional to one of the eigenvalues of the momentum operator (see measurement result theorem). In general, however, quantum theory does not assert that such a result represents the value of the velocity of the molecule prior to measurement. To make such an assertion, we need an ensemble of measurements on a homogeneous ensemble and then, only if the density operator of the state of the system is a momentum eigenprojector $|p\rangle\langle p|$, we have that the common result of the ensemble of measurement acts is the value of the momentum prior to measurement. Because the demon performs his measurements on a homogeneous

¹ It is noteworthy that each molecule is at a standstill even in a system that is in an equilibrium state which is not stable.

ensemble assigned a density operator $\rho^0 \neq |p\rangle\langle p|$ (Eq. (13)), the result consists of a spectrum of momentum values, and a frequency of occurrence of each value in the spectrum. So, he is faced with the question, “Which result accounts for the value of the momentum?” In quantum theory, the answer is not a matter of personal opinion or choice but the contents of the mean-value postulate and the mean-value theorem.

In addition, it is noteworthy that the lack of motion refers to an isolated system and not to what happens in an interaction with an external system, such as the demon. This remark notwithstanding, it is also noteworthy that, in interactions with an external system, the expectation values enter in the balances and not any particular eigenvalues that account for the effects. Examples illustrative of this remark are the theorems of energy conservation, mass conservation, and momentum conservation if applicable.

(ii) A chemist said, “In a day and age when spectroscopists can measure molecular velocity distributions, and have such elegant tricks as optical molasses to slow molecules, how can one possibly assert that in quantum mechanics molecular velocities, in equilibrium, must vanish?”

Again, the assertion is not a matter of personal opinion. It is a consequence of the postulates and theorems of quantum theory. Unless either the demon, or spectroscopists, or both can provide evidence that invalidates the premises and consequences of that theory, we must abide by it because so far it has been a triumphant and fertile paradigm of physics.

Besides, the quantum-mechanical result that, in equilibrium, molecular velocities vanish neither contradicts nor is mutually exclusive with the elegant, imaginative, and productive tricks of spectroscopists. All that the theory avers is that a measurement act on a member of a homogeneous ensemble assigned a density operator ρ^0 yields neither the value of an observable, nor the characterization of the member of the ensemble prior to measurement. It seems to me that physics is full of such distinctions and rightly so, no one objects to them. For example, because a photon is emitted in the course of deexcitation of an electron in a molecule, we do not claim that prior to the observation of the photon the molecule consisted of an electron and a photon, and that after deexcitation it has only an electron. Again, in the course of an interaction heat flows from one system to another, and yet, in view of our current understanding of heat, we do not say that prior to the interaction heat was contained in one or both of the interacting systems.

Finally, if molecules are observed to be moving, such an observation does not contradict any of the arguments just cited. All it implies is that the system is not in a thermodynamic equilibrium state. In contrast to other expositions of thermodynamics, states that are not thermodynamic equilibrium are part of the unified quantum theory.

(iii) Several chemists and physicists said, “Molecules do move and bounce into walls; that is why there is pressure”.

This criticism is not correct for at least three reasons. First, whereas pressure is defined for all systems that have volume as a (an external) parameter and that are in any stable equilibrium state [2,3], the calculation of pressure in terms of molecules that bounce into walls is a numerical coincidence that applies only to dilute systems that behave as ideal gases, and that obey the laws of classical mechanics. This calculation is not valid outside the range of validity of the ideal gas behavior.

Second, as discussed earlier, the broad class of states encompassed by the unified theory cannot be regularized by classical mechanics because the latter does not include any concepts that can account for entropy as a property of a molecule for systems with an arbitrary number of molecules, including one.

And third, and perhaps more importantly, pressure of any system in a stable equilibrium state can be evaluated at one instant in time based on results from measurements on a homogeneous ensemble. The basic elements of this calculation are given by ter Haar [24].

(iv) Many physicists, chemists, and engineers agree that

$$\langle \rho \rangle = \text{Tr}[\rho^0 \mathbf{p}] = 0 \tag{24}$$

for any number of atoms or molecules $n \geq 1$. However, they counterargue that

$$\langle \mathbf{p}^2 \rangle = \text{Tr}[\rho^0 \mathbf{p}^2] \neq 0 \tag{25}$$

and, therefore, that the atom or molecule with momentum represented by the operator \mathbf{p} has kinetic energy and is moving.

I believe that the counterargument is not correct for at least two reasons. First, I have searched the literature, and have found not even one calculation that evaluates evolution in time by using $\langle \mathbf{p}^2 \rangle$. In contrast, I find several examples based exclusively on $\langle \mathbf{p} \rangle$, such as

$$\frac{d\langle x \rangle}{dt} = \frac{\langle \mathbf{p}_x \rangle}{M}, \quad \frac{d\langle \mathbf{p}_x \rangle}{dt} = -\langle \partial V_p / \partial x \rangle, \quad M \frac{d^2\langle x \rangle}{dt^2} = \frac{d\langle \mathbf{p}_x \rangle}{dt}, \tag{26}$$

where V_p is the potential energy function, and M the mass.

Second, the expression for kinetic energy is not universal for all paradigms of physics. For one particle, it is $Mv^2/2$ in classical mechanics, $E - m_0c^2$ in the special theory of relativity, nonexistent in the general theory of relativity, and unknown in conventional quantum mechanics.

And third and, perhaps, more importantly, for the sake of mathematical simplicity let us consider one structureless molecule having only one translational degree of freedom x in a force free range $-a \leq x \leq a$ of a well of infinite depth, and a density operator $\rho = |\epsilon_n\rangle\langle\epsilon_n|$, where $|\epsilon_n\rangle$ is the n th energy eigenket of the Hamiltonian operator H . According to the measurement result theorem of the unified theory, an ensemble of energy measurement results yields the energy eigenvalue ϵ_n and a probability $W(\epsilon_n)=1$. On the other hand, an ensemble of momentum measurement results yields a continuous spectrum of momentum eigenvalues in the range $-\infty < p_x < \infty$ and a probability density function in the momentum language [24, pp. 3, 65].

$$\begin{aligned} W(p_x) &= \langle p_x | \epsilon_n \rangle \langle \epsilon_n | p_x \rangle \\ &= \frac{4n^2 \pi a \hbar^3}{(p_x^2 a^2 - n^2 \pi^2 \hbar^2)^2} \begin{cases} \cos^2(p_x a / 2\hbar) & \text{for odd } n, \\ \sin^2(p_x a / 2\hbar) & \text{for even } n. \end{cases} \end{aligned} \tag{27}$$

If the demon interprets $p_x^2/2M$ as kinetic energy of the molecule, then he will be faced with the monstrosity that an ensemble of direct energy measurement results yields only one eigenvalue with probability equal to unity, whereas an ensemble of indirect

energy measurement results—based on momentum measurements—yields a continuous spectrum of values from $-\infty$ to ∞ , and a probability density function given by Eq. (27). Because he is omniscient, he will recognize immediately that such a monstrosity is justified neither by the postulates nor by the theorems of quantum theory. Because the eigenvalue result is a cornerstone of the theory, he will abandon the interpretation of $p_x^2/2M$ as kinetic energy, and will use it only in the calculation of the variance of the distribution density $W(p_x)$. In doing so, he is consistent with other calculations, such as the value of energy $\langle H \rangle$ and the variance of an ensemble of energy measurement results $\langle H^2 \rangle - \langle H \rangle^2$.

5. Conclusions

For given values of energy E , volume V , and amounts of constituents \mathbf{n} , we can think of the molecules of a system as changing their shape as they tumble from a state in which quantum probabilities are described by a projector to quantum probabilities described by a density operator ρ^0 of the unique stable equilibrium state that corresponds to the values E , V , and \mathbf{n} . If the shape is ρ^0 , no further change is possible, and the (expectation) value of the momentum of each molecule vanishes. Accordingly, Maxwell's demon cannot think of the molecules in classical terms because the concept of molecular shape does not exist in classical mechanics, and cannot sort the molecules of air in a container into swift and slow because there are no such molecules.

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