

Pictorial visualization of the entropy of thermodynamics

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Abstract — The thermodynamic definition of entropy of a system and its quantum-theoretic expression are reviewed. The expression is interpreted as a measure of the spatial shape of the constituents of the system, and pictorial visualizations of the shapes associated with various states are presented. The generation of entropy (irreversibility) is attributed to the spontaneous change of the spatial shape of constituents as they try to conform to the external and internal forces of the system. The spontaneous change occurs until the entropy assumes its largest value, and the spatial shape of constituents yields zero values in any direction of both the translational momentum and the internal structure angular momentum of each constituent. © 1999 Éditions scientifiques et médicales Elsevier SAS.

entropy definition / entropy analytic expression / entropy visualization in 3 dimensions

Nomenclature

A	system	\mathbf{x}	Cartesian coordinates of all constituents of a system
A_i	i -th state of system A	α_i	statistical probability assigned to actual state
c_R	positive constant equal to temperature of reservoir R	ε_n	n -th energy eigenvalue of the electron in a hydrogen atom
E_{electron}	energy of the electron in a hydrogen atom	ρ	density operator
E_i	energy of state A_i	ρ_{electron}^0	density operator of the electron in a hydrogen atom and in a stable equilibrium state
g_n	degeneracy of n -th energy eigenstate of the electron in a hydrogen atom	ρ_i	projector associated wave function ψ_i ; in Dirac notation $\rho_i = \psi_i\rangle\langle\psi_i $
\hbar	Planck's constant divided by 2π	$ \psi_i\rangle$	ket, Dirac notation
H_{electron}	Hamiltonian operator of the electron in a hydrogen atom	$\langle\psi_i $	bra, Dirac notation
k	Boltzmann's constant	$\psi(x), \psi(\mathbf{x})$	wave functions $\psi(x) = \langle x \psi\rangle$ and $\psi(\mathbf{x}) = \langle \mathbf{x} \psi\rangle$ respectively
ℓ	quantum number of square of angular momentum of the electron in a hydrogen atom	Ω^R	generalized available energy of system A with respect to reservoir R
m	quantum number of z -component of angular momentum of the electron in a hydrogen atom	Ω_i^R	generalized available energy of state A_i with respect to reservoir R
n	quantum number of n -th energy eigenstate of the electron in a hydrogen atom		
\mathbf{n}	vector of amounts of constituents		
R	reservoir		
$S, S(\rho)$	entropy		
S_i	entropy of state A_i		
Tr	trace of operator that follows		
\mathbf{x}	Cartesian coordinate in one dimension		

1. INTRODUCTORY REMARKS

The term entropy was coined by Clausius [1]. He said: "I have felt it more suitable to take the names of important scientific quantities from the ancient languages in order that they may appear unchanged in all contemporary languages. Hence I propose that we

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call S the *entropy* of the body after the Greek word *τροπή*, meaning transformation. I have intentionally formed the word *entropy* to be as similar as possible to the word *energy* since the two quantities that are given these names are so closely related in their physical significance that a certain likeness in their names has seemed appropriate.”

In the scientific literature, Clausius’ perceptive and important observation that the energy and entropy of thermodynamics are closely related has not always been heeded. Since its inception, the concept of energy has been accorded a universal meaning that underlies our understanding of all physical phenomena. In contrast, the term entropy has been associated with many statistical concepts and mathematical expressions. Because these concepts and expressions differ from each other, the common name is a source of confusion [2, 3] and has confounded understanding of many issues not only about the relations among various entropies but, more importantly, about both the physical meaning of the entropy of thermodynamics and the idea of transformation.

In addition to the issues raised by the association of the term entropy with different concepts, many scientists and engineers have expressed concerns about the completeness and clarity of the usual expositions of thermodynamics. For example, Obert [4] writes: “Most teachers will agree that the subject of engineering thermodynamics is confusing to the student despite the simplicity of the usual undergraduate presentation.”

Intrigued and challenged by the issues and concerns just cited, over the past few decades we have made an attempt to clarify both the theoretical foundations of thermodynamics and the experimental evidence in support of these foundations, and have reached conclusions that differ from the interpretations presented in the scientific literature. We have discussed the new viewpoint first as a unified quantum theory of mechanics and thermodynamics in Refs. [5–10], and then as a non-quantal exposition of the foundations and applications of thermodynamics in [11].

In this paper, we recapitulate our findings about both the thermodynamic definition of entropy, and its quantum-theoretic expression. Then, we provide a pictorial visualization of entropy in terms of the quantum-theoretic probability density function in ordinary space, that is, in terms of the shape of the constituents of a system. Moreover, we show that the generation of entropy (irreversibility) is due to spontaneous changes or transformations of the shape of constituents as they try to conform to the external and internal forces of the system. The spontaneous changes can occur until the entropy assumes its largest value. At that condition, the spatial shape of the constituents yields zero values in any direction of both the translational momentum and the internal structure angular momentum of each atom, or molecule, or other particle. In other words, in thermodynamic equilibrium, all motions cease to exist — everything is at rest.

Many scientists and engineers interested in applications may feel that a general, rigorous, noncircular, and complete description of thermodynamics, and a quantum-theoretic explanation of the foundations of the subject are not important in solving practical problems. This view is only partially correct, and if insisted upon may deprive us of opportunities to make new discoveries and major practical contributions. Some of the reasons for the preceding comment are as follows: (i) The entropy of thermodynamics is a cornerstone of the profession of mechanical engineers as well as of all other engineering and scientific disciplines. For example, if it were not for the possible spontaneous increase of entropy, humanity would have no problems of exhaustion of natural resources of both energy and raw materials, no problems of pollution, and no need for so many professionals preoccupying themselves with such problems; (ii) The popular meaning of the word energy does not represent the concept of energy of thermodynamics but the concept of available energy or exergy, and available energy is decisively controlled by entropy rather than the energy defined in thermodynamics. So, understanding entropy is of paramount importance to all concerned about energy systems and processes; (iii) In our works we have expressed the laws of thermodynamics in terms of the concepts of space, time, and force or inertial mass only, and have proven many theorems of these laws without inconsistencies, incompleteness, circular arguments, and ambiguities. As a result, we have discovered that thermodynamics and quantum theory are facets of a new unified paradigm of physics, and that conventional quantum mechanics (the quantum mechanics taught to undergraduate students) is a special case of the unified theory (zero entropy physics); (iv) The rigorous exposition of thermodynamics helped us to discover that entropy is a nonstatistical property of the constituents of any system in any state. Moreover, the unified quantum theory of mechanics and thermodynamics helped us to determine the quantum-theoretic analytical expression for this important property; (v) As a result of the quantum-theoretic considerations, we have obtained both a pictorial visualization of the mathematical expression of entropy as a measure of the shape of the constituents of a system, and a correlation between spontaneous shape changes and entropy generation (irreversibility). Hopefully, the visualization and the correlation will stimulate interest in better understanding of the foundations of thermodynamics both without and with quantum theory; and (vi) Educators, practitioners, and students have a scientific and professional responsibility to pay more attention to the rigorous, noncircular, and nonconfusing understanding and practice of thermodynamics of all systems and all states. Such understanding and practice are lacking now. A wider and more frequent appreciation of both the beauty, generality, and power of thermodynamics, and the correct use of its fundamental principles is not a matter of presenting a new theory. It is an imperative that will help us address and solve many problems of great importance to humanity and its planet Earth.

2. THE ENTROPY OF THERMODYNAMICS

Among the many novel results of the nonquantal exposition [11] is the recognition that the entropy of thermodynamics is a nonstatistical property of a system, in the same sense that inertial mass, or energy, or momentum is a nonstatistical property of a system, and that this entropy is well-defined for all systems, both macroscopic and microscopic, and all states, both thermodynamic equilibrium and not thermodynamic equilibrium.

Because the nonquantal exposition is not widely known yet, a brief summary of the laws of thermodynamics and some of their theorems is presented in Appendix A, including the definition of entropy by the relation

$$S_2 - S_1 = \frac{1}{c_R} [(E_2 - E_1) - (\Omega_2^R - \Omega_1^R)] \quad (1)$$

where S_i and E_i are the entropy and energy of state A_i of system A , respectively, Ω_i^R is the generalized available energy of state A_i with respect to reservoir R , and c_R a well-defined positive constant.

Based on the characteristic features of E_i and Ω_i^R listed in Appendix A, we find that the entropy of thermodynamics must conform to the following criteria: (i) be well-defined for every system (both macroscopic and microscopic), and every state (both stable equilibrium and not stable equilibrium); (ii) be independent of the reservoir R ; (iii) be invariant in all reversible adiabatic processes, and increasing in all irreversible adiabatic processes; (iv) be additive; (v) be nonnegative, and vanish for all the states encountered in mechanics; (vi) for given values of energy, amounts of constituents, and (external) parameters, admit one and only one state that corresponds to the largest value of entropy; (vii) for given values of amounts of constituents, and parameters, the graph of entropy versus energy of stable equilibrium states be concave and smooth; (viii) for a composite C of two subsystems A and B , must be such that the constrained maximization procedure for C (criterion vi) yields identical thermodynamic potentials (for example, temperature, total potentials, and pressure) for all three systems A , B , and C ; (ix) for stable equilibrium states, must reduce to relations that have been established experimentally and that express the entropy in terms of energy, amounts of constituents, and parameters, such as the relations for ideal gases.

In due course, we prove that the preceding reasonable and relatively simple criteria reject all but one of the analytical expressions for entropy that have appeared in the scientific literature. In fact, even the one and only acceptable expression requires a profound and radical reinterpretation of its independent variables.

3. UNIFIED QUANTUM THEORY OF MECHANICS AND THERMODYNAMICS

In many textbooks on quantum mechanics, probabilities associated with measurement results are derived from a normalized wave function $\psi(\mathbf{x})$ or, equivalently, from either a Dirac ket $|\psi\rangle$ or a projector $|\psi\rangle\langle\psi|$, where \mathbf{x} are the spatial coordinates of the constituents of a system, and $\langle\psi|$ is the bra of ket $|\psi\rangle$ [12]. For example, for a system with one degree of spatial freedom x , the probability density function of measurement results of x is given by $|\psi(x)|^2 = \langle\psi|x\rangle\langle x|\psi\rangle = |\langle x|\psi\rangle|^2$.

In statistical quantum mechanics, probabilities associated with measurement results are derived from a density operator $\rho = \sum_i \alpha_i \rho_i$ which represents a mixture 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 which reflect the lack of information about some or all aspects of the state of a system.

In general, the foundations and theorems of the unified quantum theory of mechanics and thermodynamics differ from those of the ordinary expositions of quantum mechanics and statistical quantum mechanics. Among the many novel concepts and results, two deserve special emphasis at this point. (i) In contrast to statistical quantum mechanics, a novel concept of the unified quantum theory is that its postulates — quantum-theoretic and thermodynamic — do not apply to density operators that represent mixtures of quantal probabilities derived from projectors $\rho_i = |\psi_i\rangle\langle\psi_i|$, 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 a ρ that can be represented by a homogeneous ensemble 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 non-projector density operators. The concept of homogeneous ensemble was introduced by von Neumann [13]. 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 $\rho \geq \rho^2$. (ii) As already indicated, in contrast to the plethora of expressions for entropy that have been proposed in the scientific literature over the past fourteen decades, we find that only one satisfies the criteria listed in the preceding section. Because the unified quantum theory of mechanics and thermodynamics

is not widely known yet, a brief summary of both the quantum-theoretic postulates and some of their theorems is presented in Appendix B, including a discussion of the fact that, of the known expressions for entropy S , the only acceptable is

$$S = -k \text{Tr} [\rho \ln \rho] \quad (2)$$

where k is Boltzmann's constant, Tr stands for the trace of the operator that follows, and ρ is a density operator which can be represented solely by a homogeneous ensemble. It is noteworthy that, if ρ cannot be represented by a homogeneous ensemble, then $-k \text{Tr} [\rho \ln \rho]$ does not represent the entropy of thermodynamics.

For given values of energy, parameters, and amounts of constituents, if ρ is a projector (wave function) then $S = 0$, if ρ is not a projector but corresponds to a state which is not stable equilibrium (not thermodynamic equilibrium) then S has a positive value smaller than the largest possible for the given specifications, and if ρ corresponds to the unique stable equilibrium state, then S has the largest value of all the entropies of the system which share the given values of energy, parameters, and amounts of constituents.

4. PICTORIAL VISUALIZATION OF ENTROPY

In many textbooks, the probability density function associated with measurement results of the spatial coordinates of the constituents of a system is interpreted as the spatial shape of the constituents of the system [14,15], and the shape is used to calculate atomic, molecular, and ionic radii [16], and to explain the formation of various compounds. The probability density function of the spatial coordinates enters also in the evaluation of the entropy S (equation (2)) and, therefore, we can think of entropy as a measure of the spatial shape of the constituents of a system, and thus achieve a pictorial visualization of a concept that has been puzzling scientists and engineers over more than a century.

A few graphs of surfaces of constant probability density are shown in figures 1 to 3. They are derived from probability density functions which represent energy eigenfunctions (energy eigenprojectors) of the electron in a hydrogen atom. They have been calculated by Brandt and Dahmen [15]. In the notation ρ_{nlm} of each shape, ρ denotes the probability density function as a function of the Cartesian coordinates x, y, z of the electron, subscript n denotes the energy quantum number and appears in the energy eigenvalue relation

$$\varepsilon_n = -13.61/n^2 \text{ (eV)} \quad (3)$$

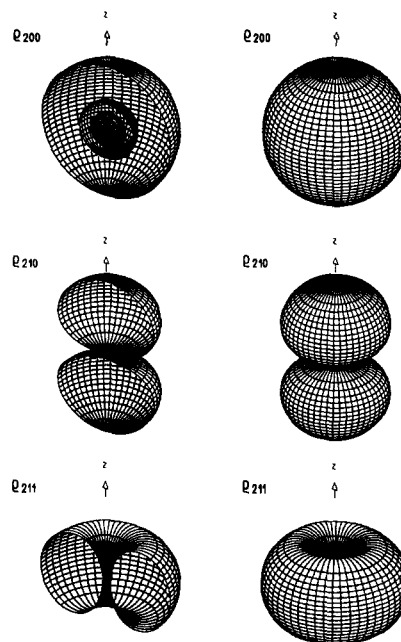


Figure 1. Surfaces of constant probability density $\rho_{2\ell m} = 0.02$ in full x, y, z -space of the electron in a hydrogen atom [15].

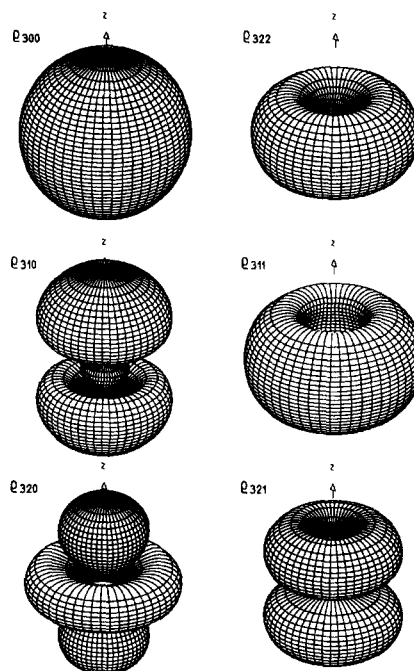


Figure 2. Surfaces of constant probability density $\rho_{3\ell m} = 0.0002$ in full x, y, z -space of the electron in a hydrogen atom [15].

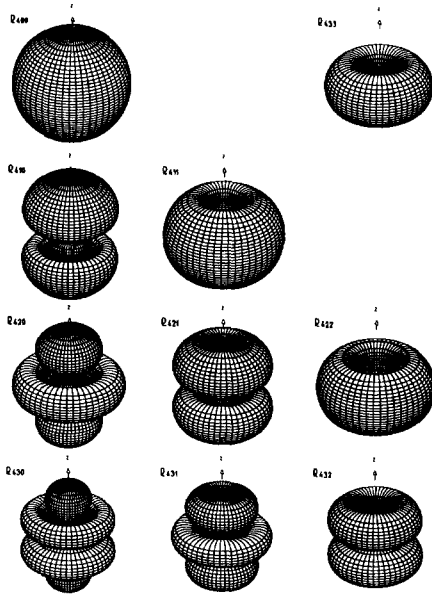


Figure 3. Surfaces of constant probability density $\rho_{4\ell m} = 0.00002$ in full x, y, z -space of the electron in a hydrogen atom [15].

subscript ℓ denotes the angular momentum quantum number ($0 \leq \ell \leq n-1$) and appears in the square of the total angular momentum eigenvalue relation

$$L^2 = \hbar^2 \ell(\ell + 1), \quad (4)$$

L^2 is the square of the total angular momentum, and \hbar Planck's constant divided by 2π , and subscript m denotes the z -component of the angular momentum quantum number ($-\ell \leq m \leq \ell$) and appears in the eigenvalue relation

$$L_z = m \hbar \quad (5)$$

where L_z is the z -component of the angular momentum. The probability density function equals the square of the absolute magnitude of the electron energy eigenfunction as a function of x, y, z .

If the normalized wave function $\psi(x, y, z)$ of the electron is not an energy eigenfunction, and has energy $E_{\text{electron}} = \langle \psi | H_{\text{electron}} | \psi \rangle$, then the probability distribution function in x, y, z -space is again given by $|\psi|^2$, and a graph of the electron shape can be made in a manner analogous to that described for energy eigenfunctions.

Regardless of whether a wave function is an eigenfunction of a Hamiltonian operator H , or another operator that represents an observable, or not an eigenfunction of any operator, the probability density function can be visualized as a shape in Cartesian space, and the value of the entropy S of any such shape equals zero.

For a nonzero value of S , we must consider a density operator which does not correspond to a projector $|\psi\rangle\langle\psi|$ or wave function ψ . The choices are infinite. For our purposes, we have selected ρ_{electron}^0 which corresponds to the stable equilibrium state of the electron of a hydrogen atom, at electron energy E_{electron} [17]. Because the energy eigenstates of the electron in a hydrogen atom are degenerate, the probability density function ρ_{electron}^0 of the electron in a stable equilibrium state of energy E_{electron} is given by the relation (see Appendix B)

$$\rho_{\text{electron}}^0 = \sum_n \rho_{nn}^0 \rho_n \quad (6)$$

where

$$\rho_{nn}^0 = \frac{g_n \exp(-\beta \varepsilon_n)}{\sum_n g_n \exp(-\beta \varepsilon_n)} \quad (7)$$

$$\rho_n = \frac{\sum_{\ell} \sum_m \rho_{n\ell m}}{g_n} \quad (8)$$

$g_n = n^2$ and is the degeneracy of the energy eigenvalue ε_n , β is determined by the energy by means of the relation

$$E_{\text{electron}} = \sum_n \rho_{nn}^0 \varepsilon_n \quad (9)$$

and $\rho_{n\ell m}$ is the probability density of the energy eigenstate with quantum numbers n, ℓ, m ($0 \leq \ell \leq n-1$ and $-\ell \leq m \leq \ell$). As shown in Appendix B, $\beta = 1/kT$, where T is the temperature of the electron. Because β is determined by E_{electron} , it follows that T is also determined solely by E_{electron} .

Using graphs such as in figures 2 and 3, we find

$$g_3 = 9; \quad \rho_3 = \frac{1}{9} (\rho_{300} + \rho_{310} + \rho_{320}) + \frac{2}{9} (\rho_{311} + \rho_{321} + \rho_{322}) \quad (10)$$

$$g_4 = 16; \quad \rho_4 = \frac{1}{16} (\rho_{400} + \rho_{410} + \rho_{420} + \rho_{430}) + \frac{2}{16} (\rho_{411} + \rho_{421} + \rho_{422} + \rho_{431} + \rho_{432} + \rho_{433}) \quad (11)$$

For the purposes of this paper, Dahmen and Stroh [18] graphed ρ_3 , ρ_4 and ρ_n for any value of n . As any quantum-thermodynamicist might have expected, ρ_n is spherically symmetric for $n = 1, 2, \dots$ (figure 4) and, therefore, the probability density function ρ_{electron}^0 or the corresponding electron shape around the proton is spherically symmetric. The spherical shape has at least two important implications. First, the angular momentum of the electron in any direction equals zero. Zero angular momentum means that the electron is not

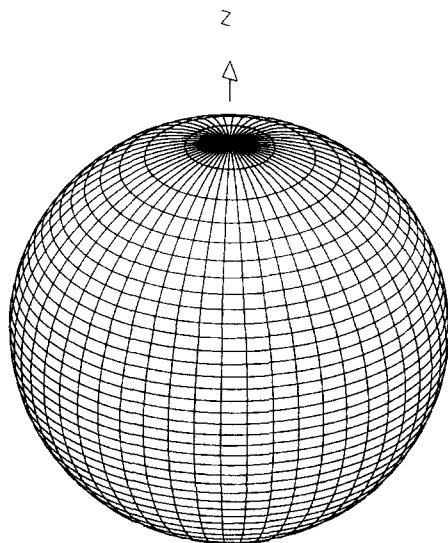


Figure 4. Surface of constant probability density ρ_n in full x, y, z -space of the electron in a hydrogen atom, arbitrary units for any value of n [18].

moving around the proton nucleus of the hydrogen atom, as the term stable equilibrium suggests and electromagnetic theory requires for equilibrium to be achieved. It is noteworthy that there exists an infinite number of spherical shapes of the electron around the proton which correspond to the same value E_{electron} of the energy but an upper limit of n in equation (6) smaller than infinity. Each such shape is an unstable equilibrium probability distribution function, and upon a minute perturbation tends spontaneously to the shape ρ_{electron}^0 .

The second important implication is that the value of the entropy that corresponds to the shape ρ_{electron}^0 is larger than that determined by any other density operator $\rho \neq \rho_{\text{electron}}^0$ and such that $\text{Tr } \rho H_{\text{electron}} = \text{Tr } \rho_{\text{electron}}^0 H_{\text{electron}}$ (see, however, Ref. 17).

If the change of shape from ρ to ρ_{electron}^0 occurs, the entropy change from a low value $S(\rho)$ to the largest value $S(\rho_{\text{electron}}^0)$ is spontaneous, and the process is irreversible. There are, however, spontaneous shape changes such as either from one wave function to another, or from ρ_1 to $\rho_2 \neq \rho_1$ but at constant values of energy ($\text{Tr } \rho_1 H_{\text{electron}} = \text{Tr } \rho_2 H_{\text{electron}}$), amounts of constituents, and parameters, for which $S(\rho_2) = S(\rho_1)$ and, then, the process is reversible.

Completion of the discussion of a hydrogen atom in a finite-size box requires also the consideration of the shapes arising from the translational degrees of freedom of the proton nucleus. The energy eigenvalues, eigenfunctions, and shapes of a structureless proton in a box, and the procedure for combining the translational shapes with the electron shapes are discussed in many texts, including Hatsopoulos and Gyftopoulos [19]. For

the sake of brevity, we will not repeat this discussion here except for only one comment. If the probability density function of the proton is derived from an energy eigenfunction, the value of the speed of the proton in any direction is zero (see Appendix B). So, in a stable equilibrium state, both the electron velocities and the proton velocities are all zero—nothing moves, that is, the concept of stable equilibrium in the unified theory is the same as the concept of stable equilibrium in classical mechanics. However, there exists an important difference between the two theories. Whereas in classical mechanics the stable equilibrium state of a system corresponds to the lowest energy of the system, in the unified theory there exists one stable equilibrium state for each set of values of energy, amounts of constituents, and parameters (see Appendix A).

5. CONCLUDING REMARKS

In closing, we wish to reiterate that the entropy of thermodynamics is: (i) a nonstatistical property of the constituents of a system, in the same sense that inertial mass is such a property; (ii) valid for any system, both macroscopic and microscopic, including a system with only one particle; (iii) valid for any state, thermodynamic equilibrium or not; and (iv) a measure of the geometric shape of the constituents of the system, even if the system consists of only one particle. Moreover, irreversibility is due to the spontaneous change of the shape of the constituents as they try to conform to the external and internal forces of the system.

Acknowledgements

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APPENDIX A

Thermodynamics

A.1. General remarks

Gyftopoulos and Beretta [11] have composed a novel exposition in which all basic concepts of thermodynamics are defined completely and without circular arguments in terms of the mechanical concepts of space, time, and force or inertial mass. Many of these definitions are new. The order of introduction of concepts and postulates is: system (types and amounts of constituents, forces between constituents, and external forces or parameters); properties; states; the first law;

energy (without work and heat); energy balance; classification of states in terms of time evolutions; stable equilibrium states; second law (without temperature, heat, and entropy); generalized available energy; entropy of any state, stable equilibrium or not, in terms of energy and generalized available energy and not in terms of temperature and heat; entropy balance; fundamental relation for stable equilibrium states only; temperature, total potentials, and pressure in terms of energy, entropy, amounts of constituents and parameters for stable equilibrium states only; the third law; work in terms of energy; and heat in terms of energy, entropy, and temperature. All concepts and postulates are valid for all systems (both macroscopic and microscopic), all states (both stable equilibrium and not stable equilibrium), and require no statistical probabilities.

A.1.1. Definition

We define general thermodynamics or simply thermodynamics as the study of motions of physical constituents (particles and radiations) resulting from externally applied forces, and from internal forces (the actions and reactions between constituents). This definition is identical to that given by Timoshenko and Young about mechanical dynamics [20]. However, because of the second law, the definition encompasses a much broader spectrum of phenomena than mechanical dynamics.

A.1.2. Kinematics: conditions at an instant in time

In kinematics we give verbal definitions of the terms system, property, and state so that each definition is valid without change in any physical theory, and involves no statistics attributable to lack of information. The definitions include innovations. To the best of our knowledge, they contradict neither any theoretical principle nor any experimental result.

A *system* is defined as a collection of *constituents* confined by a nest of *internal intermolecular forces* and *external forces* or *parameters*. Without modification, this definition applies to all paradigms of physics. The term paradigm is used in the sense of Kuhn [21].

Everything that is not included in the system is the *environment*.

For a system with r constituents, we denote their amounts by the vector $\mathbf{n} = \{n_1, n_2, \dots, n_r\}$. For a system with external forces described by s parameters we denote the parameters by the vector $\beta = \{\beta_1, \beta_2, \dots, \beta_s\}$. One parameter may be volume, $\beta_1 = V$.

At any instant in time, the amount of each constituent, and the parameters of each external force have specific values. We denote these values by \mathbf{n} and β with or without additional subscripts.

By themselves, the values of the amounts of constituents and of the parameters at an instant in time

do not suffice to characterize completely the condition of the system at that time. We also need the values of a set of independent properties at the same instant in time. The value of an independent property can be varied without affecting the values of other properties. Each *property* is an attribute that can be evaluated at any given instant in time (not as an average over time) by means of a set of measurements and operations that are performed on the system and result in a numerical value — the *value of the property*. This value is independent of the measuring devices, other systems in the environment, and other instants in time.

For a given system, the values of the amounts of the constituents, the values of the parameters, and the values of a complete set of independent properties encompass all that can be said about both the system at an instant in time, and the results of any measurements that may be performed on the system at that same instant in time. We call this complete characterization of the system at an instant in time the *state* of the system. This definition of state is novel and, without change, applies to any branch and any paradigm of physics.

A.2. Dynamics: changes of state in time

The state of a system may change in time either spontaneously due to the internal and external forces, or as a result of interactions with other systems, or both. The relation that describes the evolution of the state of an isolated system — *spontaneous changes of state* — as a function of time is the *equation of motion*. Certain time evolutions obey *Newton's equation* which relates the total force F on each system particle to its inertial mass m and acceleration a so that $F = ma$. Other evolutions obey the *time-dependent Schroedinger equation*, that is, the quantum-mechanical equivalent of Newton's equation. Other experimentally observed time evolutions, however, do not obey either of these two equations. So the equations of motion that we have are incomplete. The discovery of the complete equation of motion that describes all physical phenomena remains a subject of research at the frontier of science — one of the most intriguing and challenging problems in physics [2, 5, 8–10, 22–24]. Many features of the equation of motion have already been discovered. These features provide not only guidance for the discovery of the complete equation but also a powerful alternative procedure for analyses of many time-dependent, practical problems. Two of the most general and well-established features are captured by the consequences of the first and second laws of thermodynamics discussed later.

A.3. Energy and energy balance

Energy is a concept that underlies our understanding of all physical phenomena, yet its meaning is subtle and difficult to grasp. It emerges from a fundamental

principle known as the first law of thermodynamics. The *first law* asserts that any two states of a system may always be the initial and final states of a change (weight process) that involves no net effects external to the system except the change in elevation between z_1 and z_2 of a weight, that is, 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 main consequence of this 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 (Ref. [11], Sec. 3.4, pp. 32–33). The energy E_1 can be evaluated by means of 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

$$E_1 = E_0 - Mg(z_1 - z_0) \quad (\text{A-1})$$

Energy is shown to be an additive property (Ref. [11], Sec. 3.6, pp. 34–35), that is, the energy of a composite system is the sum of the energies of its subsystems. Moreover, it is also shown that energy has the same value at the final time as at the initial time if the system experiences a zero-net-effect weight process, or remains invariant in time if the process is spontaneous (Ref. [11], Sec. 3.7, pp. 35–37). In either of the last two processes, $z_2 = z_1$ and $E(t_2) = E(t_1)$ for time t_2 greater than t_1 , that is, energy is *conserved*. Energy conservation is a time-dependent result. In Ref. [11], this result is obtained without use of the general equation of motion.

Energy can be exchanged between systems by means of interactions. Denoting by $E^{A\leftarrow}$ the amount of energy exchanged between the environment and system A in a process that changes the state of A from A_1 to A_2 , we can derive the *energy balance*. This derivation is based on the additivity of energy and energy conservation (Ref. [11], Sec. 3.8, pp. 37–38), and reads

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

In words, the energy change of a system must be accounted for by the energy transferred across the boundary of the system. The energy $E^{A\leftarrow}$ crossing the boundary of A is positive if energy flows from the environment to system A .

A.4. Types of states

Because the number of independent properties of a system is infinite even for a system consisting of a single particle with a single translational degree of freedom — a single variable that fixes the configuration of the system in space — and because most properties can vary over a range of values, the number of possible states of a system is infinite. The discussion of these states is

facilitated if they are classified into different categories according to time evolutions. This classification brings forth many important aspects of physics, and provides a readily understandable motivation for the introduction of the second law of thermodynamics.

The classification consists of: unsteady states; steady states; non-equilibrium states; and equilibrium states (Ref. [11], Sec. 4.1, pp. 53–58). An *equilibrium state* is one that does not change as a function of time while the system is isolated — a state that does not change spontaneously. An *unstable equilibrium state* is an equilibrium state that may be caused to proceed spontaneously to a sequence of entirely different states by means of a minute and short-lived interaction that has only an infinitesimal effect on the state of the environment. A *stable equilibrium state* is an equilibrium state that can be altered to a different state only by interactions that leave net effects in the environment of the system. These definitions are identical to the corresponding definitions in mechanics but include a much broader spectrum of states than those encountered in mechanics. The broader spectrum is due to the second law discussed later.

Starting either from a nonequilibrium state or from an equilibrium state that is not stable, energy can be extracted from a system and affect a mechanical effect without leaving any other net changes in the state of the environment. In contrast, experience shows that, starting from a stable equilibrium state, no energy can be extracted from the system that would result in the mechanical effect just cited. This impossibility is one of the most striking consequences of the first and second laws of thermodynamics. It is consistent with innumerable experiences.

A.5. Generalized available energy

The existence of stable equilibrium states is not self-evident. It was first recognized by Hatsopoulos and Keenan [25] as the essence of all correct statements of the second law. Gyftopoulos and Beretta (Ref. [11], Ch. 4, pp. 53–66) concur with this recognition, and state the second law 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 existence of stable equilibrium states for the conditions specified and, therefore, the second law cannot be derived from the laws of mechanics. Within mechanics, the stability analysis yields that among all the allowed states of a system with fixed values of amounts of constituents and parameters, the only stable equilibrium state is that of lowest energy. In contrast the second law avers the existence of a stable equilibrium state for each value of the energy. As a result, for every system the second law implies the existence of a broad class of states in addition to the states contemplated by mechanics.

The existence of stable equilibrium states for various conditions of a system has many theoretical and practical consequences. One consequence is that, starting from a stable equilibrium state of any system, no energy is available to affect a mechanical effect while the values of both the amounts of constituents and the parameters of the system experience no net changes (Ref. [11], Sec. 4.5, pp. 64–65). This consequence is often referred to as the impossibility of a perpetual motion machine of the second kind (PMM2). In some expositions of thermodynamics, it is taken as the statement of the second law. In the new exposition, it is only one aspect of both the first and the second laws.

At fixed values of both the amounts of constituents and the parameters, another consequence is that not all states of a system can be changed to the state of minimum energy by means of solely a mechanical effect. This is a generalization of the impossibility of a PMM2, and is represented by a property called *adiabatic availability*, and denoted by Ψ (Ref. [11], Secs. 5.2 to 5.4, pp. 73–76). The concept of adiabatic availability can be generalized to the concept of *generalized adiabatic availability* (Ref. [11], Secs. 5.5 and 5.6, pp. 77–80). The latter represents the optimum amount of energy that can be exchanged between a system and a weight in a weight process in which the respective initial and final values of the amounts of constituents and/or the parameters differ. Generalized adiabatic availability differs from energy. Like energy, this property is well defined for any system in any state. Unlike energy, it is not additive (Ref. [11], Sec. 5.3.8, p. 75).

In striving to define an additive property that captures the important features of generalized adiabatic availability, Gyftopoulos and Beretta introduce a special reference system, called a *reservoir*, and discuss the possible weight processes that the composite of a system and the reservoir may experience. Thus, they disclose a third consequence of the first and second laws, that is, a limit on the optimum amount of energy that can be exchanged between a weight and a composite of a system and a reservoir R — the optimum mechanical effect. They call the optimum value *generalized available energy* (Ref. [11], Sec. 6.8, pp. 95–97), denote it by Ω^R , and show that it is additive (Ref. [11], Sec. 6.9.6, pp. 98–99). It is a generalization of the concept of motive power of fire first introduced by Carnot. It is a generalization because he assumed that both systems of the composite acted as reservoirs with fixed values of their respective amounts of constituents and parameters, whereas Gyftopoulos and Beretta do not use this assumption. The definition of a reservoir is given in Ref. [11], Sec. 6.3, pp. 87–88.

If the net exchanges between a system and its environment involve only energy, the process experienced by the system is called *adiabatic*. For an adiabatic process of system A only, it is shown that the energy change $E_1 - E_2$ of A and the generalized available energy change $\Omega_1^R - \Omega_2^R$ of the composite of A and reservoir R satisfy the relations (Ref. [11], Sec. 6.9, pp. 97–99):

if the adiabatic process of A is reversible:

$$E_1 - E_2 = \Omega_1^R - \Omega_2^R \quad (\text{A-3})$$

if the adiabatic process of A is irreversible:

$$E_1 - E_2 < \Omega_1^R - \Omega_2^R \quad (\text{A-4})$$

A process is *reversible* if both the system and its environment can be restored to their respective initial states. A process is *irreversible* if the restoration just cited is impossible.

It is noteworthy that energy and generalized available energy are defined for any state of any system, regardless of whether the state is steady, unsteady, equilibrium, nonequilibrium, or stable equilibrium, and regardless of whether the system has many degrees of freedom or one degree of freedom, or whether the size of the system is large or small.

A.6. Entropy and entropy balance

A system A in any state A_1 has many properties. Two of these properties are: energy E_1 , and generalized available energy Ω_1^R with respect to a given auxiliary reservoir R . These two properties determine a third property called *entropy*, and denoted by the symbol S . It is a property in the same sense that inertial mass is a property, or energy is a property, or momentum is a property. For a state A_1 , S_1 can be evaluated by means of an auxiliary reservoir R , a reference state A_0 , with energy E_0 and generalized available energy Ω_0^R , to which is assigned a reference value S_0 , and the expression

$$S_1 = S_0 + \frac{1}{c_R} [(E_1 - E_0) - (\Omega_1^R - \Omega_0^R)] \quad (\text{A-5})$$

where c_R is a well-defined positive constant that depends on the auxiliary reservoir R only. Entropy S is shown to be independent of the reservoir (Ref. [11], Sec. 7.4, pp. 108–112), that is, S is a property of system A and the reservoir is auxiliary and is used only because it facilitates the definition of S . It is also shown that S can be assigned absolute values that are nonnegative, and that vanish for all the states encountered in mechanics (Ref. [11], Sec. 9.8, pp. 137–138).

Because energy and generalized available energy satisfy relations (A-3) and (A-4), the entropy defined by equation (A-5) remains invariant in any reversible adiabatic process of A , and increases in any irreversible adiabatic process of A . These conclusions are valid also for spontaneous processes and for zero-net-effect interactions. The latter features are known as *the principle of nondecrease of entropy*. Both a spontaneous process and a zero-net-effect interaction are special cases of an adiabatic process of system A .

The entropy created during an irreversible process as a state changes in time is called *entropy generated by*

irreversibility. It is positive. The entropy nondecrease is a time-dependent result. In the exposition of thermodynamics in Ref. [11], this result is obtained without use of the general equation of motion. Because both energy and generalized available energy are additive, equation (A-5) implies that entropy is also additive (Ref. [11], Sec. 7.2.2, pp. 103–104).

Like energy, entropy can be exchanged between systems by means of interactions. Denoting by S^{A-} the amount of entropy exchanged between the environment and system A in the course of a process that changes the state of A from A_1 to A_2 , we derive a very important analytical tool, the *entropy balance* (Ref. [11], Sec. 7.3, pp. 106–108), that is,

$$(S_2 - S_1)_{\text{system } A} = S^{A-} + S_{\text{irr}} \quad (\text{A-6})$$

where S_{irr} is positive or at least zero and represents the entropy generated spontaneously within system A during the time interval from t_1 to t_2 required to affect the change from state A_1 to state A_2 . Spontaneous entropy generation within a system occurs if the system is in a state that is not stable and the system forces precipitate the natural tendency towards stable equilibrium. The entropy S^{A-} crossing the boundary of A is positive if entropy flows from the environment to system A . The dimensions of S depend on the dimensions of both energy and c_R . It turns out that the dimensions of c_R are independent of mechanical dimensions, and are the same as those of temperature. Temperature is defined later.

A.7. Stable equilibrium states

It is shown that among the many states of a system that have given values of the energy E , the amounts of constituents n , and the parameters β , the entropy of the unique stable equilibrium state that corresponds to these values is larger than that of any other state with the same values E, n, β (Ref. [11], Sec. 8.2, pp. 119–120). Moreover, the entropy of a stable equilibrium state must be a function solely of E, n, β , that is,

$$S = S(E, n, \beta) \quad (\text{A-7})$$

Equation (A-7) is called the *fundamental relation* (Ref. [11], Sec. 8.3, pp. 120–124). For states that are not stable equilibrium, S depends on more variables than E, n, β , that is, equation (A-7) is not valid.

The fundamental relation is concave with respect to energy (Ref. [11], Sec. 9.4, pp. 131–132), that is,

$$\left(\frac{\partial^2 S}{\partial E^2} \right)_{n, \beta} \leq 0 \quad (\text{A-8})$$

and analytic in each of its variables E, n, β (Ref. [11], Sec. 8.3, pp. 120–124).

Moreover, the fundamental relation is used to define other properties of stable equilibrium states, such as *temperature* T (Ref. [11], Ch. 9),

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{n, \beta} \quad (\text{A-9})$$

total potentials μ_i for $i = 1, 2, \dots, r$ (Ref. [11], Ch. 10, pp. 147–151)

$$\mu_i = -T \left(\frac{\partial S}{\partial n_i} \right)_{E, n, \beta} \quad \text{for } i = 1, 2, \dots, r \quad (\text{A-10})$$

and *pressure* p (Ref. [11], Ch. 11, pp. 157–162)

$$p = T \left(\frac{\partial S}{\partial V} \right)_{E, n, \beta} \quad \text{for } \beta_1 = V = \text{volume} . \quad (\text{A-11})$$

Detailed discussion of properties of stable equilibrium states are given in Ref. [11], Chapters 8–11.

A.8. Comment

The concept of entropy introduced here differs from and is more general than that in all textbooks except Ref. [11]. It does not involve the concepts of temperature and heat; it is not restricted to large systems; it applies to both macroscopic and microscopic systems, including a system with one spin, or a system with one particle with only one (translational) degree of freedom; it is not restricted to stable (thermodynamic) equilibrium states; it is defined for both stable equilibrium and not stable equilibrium states because energy and generalized available energy are defined for all states; and most certainly, it is not statistical — it is a property of matter and not a measure of the lack of information of an observer.

A.9. Interactions

Work, heat, bulk flow, and diffusion interactions, and their use in the balance equations are discussed in Refs. [11] and [26] and will not be repeated in this brief review.

APPENDIX B

Unified quantum theory of mechanics and thermodynamics

B.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 [27], 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 $\rho_i = |\epsilon_i\rangle\langle\epsilon_i|$, or from an energy eigenfunction ϵ_i , where $|\epsilon_i\rangle$ is an energy eigenket 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 [13], 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 (figure B-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 $S = -k \sum_i \alpha_i \ln \alpha_i$, where k is Boltzmann's constant.

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 [28, 29]. Mutual stable equilibrium is defined in Ref. [11], Sec. 6.2, pp. 86–87. Despite these successes, the

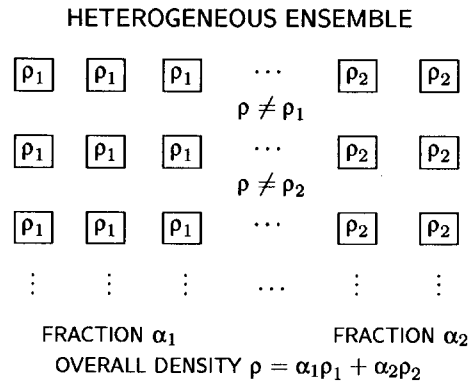


Figure B-1. Representation of a heterogeneous ensemble.

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 [30–32], 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. 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.

B.2. The unified theory

Intrigued by the experiences, ideas, and concerns just cited, Hatsopoulos and Gyftopoulos [5–8] 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 Appendix A, that is, the exposition which asserts that thermodynamics is a general, nonstatistical or noninformational 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 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 (*figure B-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 because of the emphasis that must be given to the concept of homogeneous or unambiguous ensemble.

B.3. Kinematics

The term *kinematics* refers to the definitions of the terms system, property, and state, all at an instant in time.

B.3.1. System

The meaning of the term *system* is discussed in Appendix A. The quantum-theoretic representation of a system is as follows.

B.3.2. System postulate

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

HOMOGENEOUS ENSEMBLE

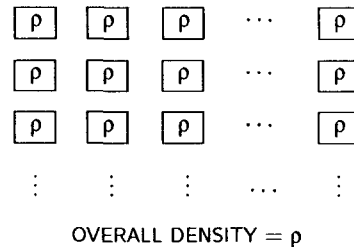


Figure B-2. Representation of a homogeneous ensemble.

Hilbert spaces \mathcal{H}^1 and \mathcal{H}^2 , respectively, is the direct product space $\mathcal{H}^1 \otimes \mathcal{H}^2$ [33].

B.3.3. Homogeneous or unambiguous ensemble

At an instant in time, an ensemble of identical systems is called *homogeneous* or *unambiguous* [8] 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.

B.3.4. Preparation

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

B.3.5. Property

The meaning of the term *property* is discussed in Appendix A. 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.

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

B.3.6. Observable

From the definition just cited, it follows that each property can be observed, that is, evaluated.

Traditionally, however, in quantum theory, a property is called an *observable* only if it conforms to the following mathematical representation.

B.3.7. Correspondence postulate

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 [33].

As explained by Park and Margenau, 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: (i) every Hermitian operator corresponds to a physical observable; and (ii) every observable has a Hermitian operator representative. Superselection rules introduced by Wick et al. [34] exclude certain Hermitian operators from being observable. By replacing the word *every* in statement (i) by the word *some*, superselection rules are satisfied. Compatibility of simultaneous measurements introduced by Park and Margenau [33] 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 (ii) 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.

B.3.8. 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 — error free — 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.

B.3.9. Mean-value postulate

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,

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

where a_i is the error-free measurement result of the measurement act applied to the i th member of the ensemble, and $\langle A \rangle$ another notation for $m(A)$ [33].

B.3.10. Mean-value theorem

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 [33]

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

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 [35] 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, nonnegative-definite, unit trace and, in general, not a projector [8, 22, 36], that is,

$$\rho > 0; \quad \text{Tr} \rho = 1; \quad \rho \geq \rho^2 \quad (\text{B-3})$$

B.3.11. 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

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

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

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

and $|\alpha_n\rangle$ the n th eigenket of operator A .

B.3.12. Measurement result theorem

The only possible result of a measurement act of the observable represented by A is one of the eigenvalues of A (equation B-5).

Though the statements of the mean-value postulate, and the probability and measurement result theorems are practically the same as those given by Park and Margenau [33], here the contents of the statements differ from those of Park and Margenau because of the restriction of ρ to a homogeneous ensemble. The importance and necessity of this restriction in the unified theory cannot be overemphasized.

B.4. Comment on the pictorial representation of a homogeneous ensemble

Because no conceivable decomposition of a homogeneous ensemble short of measurements can yield component subensembles with different measurement results — spectra of values and frequency of occurrence of

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 summarized in Appendix A.

It is noteworthy that the third law of thermodynamics is not needed because it is inherent in the quantum theoretic foundations.

B.4.5. Entropy

On the basis of the new exposition of thermodynamics presented in Ref. [11] and summarized in Appendix A, and the unified theory presented in Refs. [5–8], and summarized in this appendix, in Ref. [38] 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

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

provided that ρ is exclusively represented by a homogeneous ensemble. If ρ is represented by a heterogeneous ensemble, then equation (B-11) does not represent the entropy of thermodynamics.

For given values of energy, amounts of constituents, and parameters, 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 parameters. If, as it is usually done for projectors, we interpret a density operator ρ as the shape of constituents of a 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 parameters.

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 the Dirac delta function $\delta(\mathbf{q} - \mathbf{q}_0) \delta(\mathbf{p} - \mathbf{p}_0)$ of space coordinates \mathbf{q} and momenta \mathbf{p} . Though highly accurate, such an approximation would be inadequate because it does not include the concept of shape of the constituents of the system and, therefore, provides neither the mathematical representation for the concept of entropy as a property of the constituents, nor the possibility of change of this mathematical representation over a range of values. This is another aspect of the inadequacy of classical mechanics to accommodate the concepts of thermodynamics.

B.4.6. 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

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

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 [39]

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

where

$$H |\epsilon_i\rangle = \epsilon_i |\epsilon_i\rangle; \quad \rho_{ii}^0 = \exp(-\beta \epsilon_i) / \sum_i \exp(-\beta \epsilon_i)$$

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

$$\langle H \rangle = E = \operatorname{Tr} [\rho^0 H] = \sum_i \rho_{ii}^0 \epsilon_i$$

We can show that

$$\beta = [(\partial S / \partial E)_{\epsilon, n}]_0 / k \quad (\text{B-14})$$

where the subscript “ ϵ ” stands for fixed values of all the energy eigenvalues $\epsilon_1, \epsilon_2, \dots$, and the subscript “0” for state A_0 , that is, the partial derivative is taken along the stable equilibrium state locus for fixed values of parameters (fixed ϵ) and fixed amount of the constituent n at state A_0 . But for stable equilibrium states, the partial derivative $[(\partial S / \partial E)_{\epsilon, n}]_0$ is defined as the inverse temperature of A_0 . Accordingly

$$\beta = 1/k T_0 \quad (\text{B-15})$$

B.4.7. Translational velocity of a molecule

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

$$\begin{aligned} \langle p_k \rangle &= \operatorname{Tr} [\rho^0 p_k] = \sum_m \sum_n \rho_{nn}^0 \langle \epsilon_n | \epsilon_n \rangle \langle \epsilon_n | p_k | \epsilon_m \rangle \\ &= \sum_m \sum_n \rho_{nm}^0 \delta_{nm} \langle \epsilon_n | p_k | \epsilon_m \rangle \\ &= \sum_m \rho_{mm}^0 \langle \epsilon_m | p_k | \epsilon_m \rangle = 0 \end{aligned} \quad (\text{B-16})$$

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

$$\langle \epsilon_m | \epsilon_n \rangle = \delta_{nm} = \text{Kronecker delta} \quad (\text{B-17})$$

and the last equation from the relation

$$\langle \epsilon_m | p_k | \epsilon_m \rangle = 0 \quad \text{for all } k \text{ and } m \quad (\text{B-18})$$

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

$$[x_k, H] = i \hbar p_k / M \quad (\text{B-19})$$

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

$$(\Delta x_k)_m^2 = \langle \epsilon_m | x_k^2 | \epsilon_m \rangle - \langle \epsilon_m | x_k | \epsilon_m \rangle^2 \quad (\text{B-20})$$

$$(\Delta H)_m^2 = \langle \epsilon_m | H^2 | \epsilon_m \rangle - \langle \epsilon_m | H | \epsilon_m \rangle^2 \quad (\text{B-21})$$

we can readily prove that [40]

$$(\Delta x_k)_m (\Delta H)_m \geq \hbar |\langle \epsilon_m | p_k | \epsilon_m \rangle| / 2M \quad (\text{B-22})$$

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

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

and so equality (B-18) is proved.

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¹ There is an inconsistency between the calculation of the eigenstates of the proton and those of the electron of a hydrogen atom. The former are calculated for a proton confined in a finite size container, whereas the latter are calculated for a Coulomb potential extending over all space. As a result the operator ρ_{electron}^0 is not well defined because $\text{Tr} \exp(-\beta H_{\text{electron}})$ is unbounded, and the entropy of the electron is infinite.

Pictorial visualization of the entropy of thermodynamics

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