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Heat, the Key to Understanding the Quantum

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Summary

The dynamics of the phase transition processes that occur in the vapor state of a pure simple substance is here addressed by resuming the research program proposed in 1876 by A. Bartoli. It allows derive the *Kinetic Theory* of an abstract thermodynamic system (the *Perfect Vapor*) composed of a large number of atoms and molecules (as conceived by the current tenets of chemistry) moving under the *taut constraints* imposed by special relativity, $|v| \leq c$, and the quantum conditions, $|\Delta p \Delta q| \geq h$.

Such theory reveals the precedence of special relativity over the foundations of quantum mechanics, thereby unveiling the elementary non-conservative forces involved in chemical reactions, and providing a first principles explanation of the time asymmetry of natural processes. Besides superseding the whole of statistical mechanics, it is shown to add the missing link required to complete the epistemological chain that connects thermodynamics to quantum mechanics.

Key Words

entropy — special relativity — ladder operators
statistical mechanics — indistinguishability principle
foundations of quantum theory

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Chapter 1

Introduction

> *There is no branch of mathematics, however abstract, which may not some day be applied to phenomena of the real world.*
> Lobachevsky

Numbers are mental abstractions which were early proven useful in everyday life: the notions of the magnitudes of length, area, or volume, give concretion to what can be universally understood as *reality*. With the invention of measuring instruments, different individuals can obtain the same numbers for the same magnitudes. A *measurement* is a procedure that, once established in a community, as much as words are established in its common language, give to *different* individuals the *same* numerical value measured. The operations of transposition and substitution of numbers by algebra extended the scope of applications that can be used to describe a larger variety of phenomena.

Numbers, the carriers of scientific knowledge

History has shown that the capacity of predicting phenomena became the main social function of scientific knowledge. Scientific theories are made by humans for humans. Civilized societies invented media and methods to *communicate* to future generations the past knowledge both to preserve and improve it by promoting the intellectual power of their members in the behalf of social and economic organization.

Although prone to ambiguities, context-sensitivity, or imprecision, natural *language* is the main carrier of knowledge in these communication processes. Its weaknesses might be graceful for poets, a curse for scientists, or powerful weapons for sophistic propaganda. Injudicious or malicious use of words might be misleading or harmful to society.

Among the main interests of mathematicians there is the need to improve the quality and precision of communication. This has been achieved by inventing a special language whose vocabulary and grammar are artificially designed. From its origins, numbers have been the universal carriers of “reality”, which allowed humans to share their knowledge with their contemporaries and perpetuate it to future generations.

Abstraction — that “distillation” process by whose means one gets rid of all the *superfluous* elements of speech until irreducible *essential* sentences are achieved — has been a persistent target aimed by mathematicians in history, which culminates in the extreme definition, thus expressed by Bertrand Russell:

> *“Mathematics may be defined as the subject in which we never know what we are talking about, nor whether what we are saying is true.”*

Treating Russell’s aphorism as a joke, the French mathematician Émile Borel argued [1]:

> *Cette boutade de Bertrand Russell tend à mettre en évidence le rôle fondamental que jouent en mathématiques les* définitions arbitraires. *On pourrait ailleurs dire tout aussi bien:* “Les mathématiques sont la seule science où l’on sait toujours exactement de quoi l’on parle et où l’on est certain que ce que l’on dit est vrai.” *En fait, si nous parlons des propriétés de la droite, le mot* ligne droite *n’a pas le même sens dans la géométrie d’Euclide, de Riemann ou de Lobatchefski; mais si la droite est conformément aux postulats de telle ou telle géométrie, nous saurons exactement de qui nous parlons et nous serons assurés de la vérité de tel ou tel théorème.*

The importance to physical science of Borel’s objection to Russel’s aphorism is in the *imperative condition* of *being true* he imposes on mathematical sentences[1]. Although superfluous for abstract systems of pure mathematics, it is essential for natural philosophy: while mathematicians are free to deal with any universe they choose, physicists are condemned to treat of *the particular universe they live in*.

If, in the communication of a theory, the *emitter* (an author, a speaker, or a teacher) treats reality as superfluous in its formulation, it becomes very difficult, if not impossible for the *receiver* to extract reality from it. Since a physical theory is not mere algorithm of calculus[2], it is a challenge for its emitter to provide the information by whose means the receiver can recover the reality content that has

---

[1] True is an attribute of sentences, a *logical* property of a message. The meaning of a sentence of a scientific theory must be shared by the community of *Science speaking* people.

[2] An algorithm can be arithmetic, geometric, algebraic, differential, integral or operational. In scientific communication an algorithm is supposed to be performable by any *science speaking human*, anytime, and anywhere, thereby endowed with the same communication universality and reliability of numbers.

been removed by distillation. Hence, such recovering process, usually referred to as *interpretation* becomes indeterminate.

In the formulation of a physical theory it is essential to endow its fundamental axioms with *evidence*, namely, the revelations obtained from the empirical processes of observation and experimentation.

Quantum theory suffers from Russell's syndrome

When we refer to wave functions, *we never know what we are talking about, nor whether what we are saying is true*.

A retrospective look at the prehistory of quantum theory reveals that the treatment of this disease was found by Bartoli, whose *research program* consists in applying Borel's medicine: to replace the unsatisfactory *definition* of heat, given by the first law of thermodynamics, by the more substantiated one, derived from electromagnetic theory.

Bartoli research program

Taking into account the revelation by Maxwell that electromagnetic radiation has the property of momentum, and thereby that radiation exerts pressure upon any surface it is exposed to, A. Bartoli concluded to be theoretically cogent to replace the notion of heat, as conceived by the first law of thermodynamics, by that given by electromagnetic theory [2]. His new characterization of heat, which literally *redefines* thermodynamics, can then be summarized as follows:

§ 1 (Bartoli Redefinition of Heat)
Thermal radiation is both a Bernoulli's discrete fluid*, and a* thermodynamic system.

From this definition the following corollary derives:

> *If constrained to undergo a Carnot's cycle, radiation will exhibit its thermodynamic properties and behavior.*

This corollary can be demonstrated by thermodynamic arguments applied to the following imaginary experimental arrangement, designated by *hollow*:

> *A* hollow *is a completely enclosed space empty of all ordinary matter and traversed by (electromagnetic) radiation energy.* [3].

It was this corollary which allowed Boltzmann to derive Stefan's law of radiation, used by Planck in his formulation of the quantum hypothesis. It also leads to the following thermodynamic formula that relates the radiation energy to its pressure,

$$\mathscr{E} = 3pV. \tag{1.1}$$

Heat is a fundamental element of a theory of matter

Bartoli's program significantly improved the explanatory and predictive power of thermodynamics. In spite of its importance to the epistemology of modern physics[3], specially in the revelation of the thermodynamic properties of radiation, it was inexplicably interrupted thereafter, and sunk into oblivion.

By thus reviewing the notion of heat, which adds momentum to its characterization, Bartoli program restates thermodynamics as the first *Theory of Matter-Radiation Interaction*, thus throwing some light on the interpretations of the quantum theories of radiation proposed later by Einstein and Dirac[4].

Revisiting the many inquiries on science of matter, specially in the chapters scattered by in the good text-books of physical-chemistry, we are persuaded that the underlying notion which pervades them is that of *heat*, and suggested to formulate the following conjecture:

> *Heat is the key to understanding modern physics, namely, special relativity and quantum mechanics.*
>
> *The wave function of any molecule of a chemical substance is, itself, a function of the thermodynamic properties. Hence, its quantum description is incomplete unless the environment that contextualizes the whole system is completely specified.*

Bernoulli's discrete fluid

Before proceeding with this Introduction, it is worthwhile recalling the notion of *discrete fluid*.

By showing that the mechanical pressure of air can be explained in terms of the impact of a system of particles in rapid motion against the walls of the container it is confined within, D. Bernoulli suggested the equivalence between such mechanical system and the air. This explanation leads to the following model of the gas:

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[3] It is remarkable the relativistic nature of the phase space of the perfect vapor, as shown in Sections 4.2.1 and 4.3.1.

[4] This issue will be discussed in Section 4.2.

§ 2 (The Discrete Fluid)
A gas is a system composed of a number $N \gg 1$ of identical particles with mass m, endowed with Newtonian degrees of freedom, namely, positions and velocities, moving inside a container of volume V.

The energy $\mathscr{E}$ of the discrete fluid was then shown to be given by the equation:

$$\mathscr{E} = \frac{3}{2}pV. \tag{1.2}$$

It is presumable that among the scientists of Bernoulli's time, many expected that the success of Newtonian mechanics in previewing the motion of certain systems of bodies[5] could be extended to predict the time evolution of the state of gases. This expectation led to a research program that can be thus formulated:

§ 3 *To derive the laws of thermodynamics from the mechanics of the discrete fluid.*

It is therefore justified to consider Bernoulli's model of the gas as the first promising attempt to establish a mechanical explanation of thermodynamic phenomena that is in the origins of the *Kinetic Theory of Gases*.

> *In Appendix A, some notions raised during the attempts to formulate a strictly classical kinetic theory of gases, which are important to the present approach, are reviewed.*
>
> *In Section 4.2.1 it will be shown that the mechanics referred to in* § 3 *is not classical, but relativistic.*

The intentional exclusion of radiation by Newton

The limitations that prevent the classical approach to Bernoulli's model to preview the thermodynamic properties of the gas in terms of classical mechanics can be found in the Definition **I** of Newton's *Principia*:

§ 4 (...) *I have no regard in this place to a medium, if any such there is, that freely pervades the interstices between the parts of the bodies.* (...)

It is accepted nowadays that this *medium*[6], identified with *thermal radiation*, is something that not only *pervades the interstices between the parts of the bodies*, but also, even inside a thermodynamic isolated system, *interacts* with them. Hence, to apply classical mechanics to explain the behavior of a thermodynamic system, certain amendments to its foundations are required, specially the recognition that its particles must be susceptible to heat radiation.

---

[5] This expectation persisted despite the formulation of the *Lunar Theory*, whose difficulties were well-known at the times of Euler [5].

[6] Once we realize that the space where the bodies move in is Minkowskian, the very notion of radiation must be reviewed.

Overview of the present approach

Besides seeking for the solution of proposition § 3, I decided inquiring also about the following complementary proposition:

§ 5 *To endow the mechanical model of a chemical substance with thermodynamic faculties.*

By subjecting the equations (1.1) and (1.2) to the constraints imposed by the second law, we obtain functional correlations that characterize the thermodynamic properties of the discrete fluid, thus revealing the differences between the gas of Planck resonators (black-body radiation), and the perfect vapor, composed of material atoms and molecules.

For pedagogical purposes, let us pretend rename *Electrothermodynamics* Bartoli's version of thermodynamics restated by Bartoli. In resuming his program we are then naturally suggested to rename its corresponding *Kinetic Theory* after the title given by Einstein to his first paper on special relativity, namely, *On the Electrodynamics of Moving Bodies*. With this metaphor, we can state one of our main propositions:

§ 6 *To show that, in the epistemological order of its formulation, quantum theory must be preceded by special relativity.*

It will also be shown why the corresponding kinetic theoretical representation of Bartoli thermodynamics requires a departure from the current tenets of statistical mechanics, and its replacement by a *stochastic mechanics*[7], which might sound heretical to the current canonic theory of quanta.

A quantum-relativistic kinetic theory

Once revealed that the mechanical representation of thermodynamic transformations are relativistic, we proceed in seeking for the solution of the following proposition:

§ 7 (Taut Constraints)
To determine the laws of motion of the molecules of a chemical substance subject to two taut constraints*, namely, $|v| \leq c$, imposed by special relativity, and the quantum conditions, $\Delta p \Delta q \geq h$.*

---

[7] Stochastic here refers to *time dependent* evolution of the probability distribution functions of population numbers, as opposed to equilibrium characterized by stationary, time invariant, statistics.

Amendment to quantum axioms

Suffering of acquired Russell's syndrome, the current formulation of the Axiom 3 does not specify which are the *natural* procedures that lead a dynamic variable of a system to one of its eigen-values. It postulates that this value becomes defined as a consequence of an artificial procedure identified with the *measurement* of a supposedly persistent degree of freedom.

This freedom of choice allows select, arbitrarily, the most convenient artificial procedure for calculus, thus introducing speculative noise in the unnatural formulation of some axioms of quantum theory, and in the foundational principles of statistical mechanics.

Time dependent probabilities

It is remarkable that quantum mechanics, itself, allows determine the conditional probabilities characteristic of the creation and annihilation processes, which, in their turn, will be shown to derive from their interaction with radiation.

In concrete instances, the factorization of the wave function [6],

$$\Psi(x,t) = \psi(x)\varphi(t),$$

of an ideal gas, allows give different, separate, physical meanings to the functions $\psi(x)$ and $\varphi(t)$.

In a previous paper [7], I replaced the meaning currently given to the time variable, which is incompatible with the predictions of the second law of thermodynamics, by the Minkowskian one, based on the revelation that the nature of the ladder operators[8] is relativistic. Such uncoupling of the wave function allows recognize in the automorphism[9] expressed in the *Amplitude Schrödinger Equation* $\psi(x)$, a rigorous definition of an equilibrium condition.

Without denying the practical importance of having artificial algorithms destined for the calculation by humans, to correctly interpret quantum theory, it is necessary to seek for the *natural algorithm* whose *elementary spontaneous processes* conduct the system towards its final state of equilibrium.

This approach was shown to be successful in the derivation of time dependent evolution of the Bose-Einstein and Fermi-Dirac occupation number from the representation of the ladder operators in terms of the *laws of change* of Markovian birth and death stochastic processes.

We will then assume that these eigen-values correspond to the equilibrium state of a many-body system under the influence of an electromagnetic field[10],

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[8] To be justified later, in Section 4.2.1.

[9] See Section B.4.

[10] In the absence of a field, the wave function of the system is stationary.

i.e., in a thermodynamic environment.

As opposed to the current tenets, it is here understood that this equilibrium is attained, not as the result of a single step process, but, instead, only in the *thermodynamic equilibrium*, after the consummation of a large number of absorption-emission elementary processes, described by the ladder operations, until its relaxation is attained. The system then proceeds fluctuating around one of these eigen-values, in an equilibrium stable or metastable thermodynamic state.

Chapter 2

Thermodynamics of a Discrete Fluid

One of the preferred approaches to describe the discrete fluid in terms of thermodynamic variables is to assume the *Principle of Molecular Chaos*. It requires the knowledge of the average kinetic energy $\langle \mathscr{E} \rangle$ of the particles expressed in terms of the temperature. The simplest way to obtain it is by substituting the product pV in equation (1.2) by its corresponding value given by the *Clapeyron* ideal gas law, $pV = RT$, giving [4],

$$\langle \mathscr{E} \rangle = \frac{3}{2} NkT. \tag{2.1}$$

Although suitable for the statistical description of the equilibrium state of the gas at high temperatures and low densities[1], this approach is a crude simplification of the behavior of real gases, for it conceals the subtle effects of heat on the states of motion of its particles, thus undermining the understanding of the phenomenon and impoverishing its subsequent analyses.

Instead of assuming equation (2.1), I therefore preferred to adopt equations (1.1) and (1.2) as the thermodynamic representatives of the discrete fluid, and seek for their macroscopic properties, by subjecting them to the laws of thermodynamics. For generality, we will consider the families of abstract substances defined by the following generic equation,

$$\mathscr{E} = \kappa p V, \qquad (\kappa \text{ is a rational number}) \tag{2.2}$$

as the representative of both these two families of gases.

2.1 The thermodynamic properties of a discrete fluid

To obtain the functional relations involving the thermodynamic variables of these two families of discrete fluids under the constraints imposed by the second law,

---

[1] The *molecular chaos* approach is briefly reviewed in § 43 of the Appendix A.

we subject equation (2.2) to the Maxwell relation[2],

$$\left(\frac{\partial \mathscr{E}}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p. \tag{2.3}$$

Substituting (2.2) in (2.3), we obtain the linear PDE of the first order,

$$T\left(\frac{\partial p}{\partial T}\right)_V - \frac{1}{\kappa}V\left(\frac{\partial p}{\partial V}\right)_T = \frac{1}{\kappa+1}p, \tag{2.4}$$

whose solution is given by any of the following expressions,

$$z = \Phi_p\left(T^\kappa V\right) = \Phi_V\left(\frac{p}{T^{\kappa+1}}\right) = \Phi_T\left[pV^{(\kappa+1)/\kappa}\right], \tag{2.5}$$

where $z = pV/RT$ and Φ_p, Φ_V, Φ_T are indeterminate functions. Some consequences of this derivation follow:

§ 8 (The Discrete Fluid is a Two-Phase System)
Being z a function of a single variable, according to the phase rule, equations (2.5) *refer to a two-phases thermodynamic system.*

Let us recall the following theorem[3]:

§ 9 *(A) hollow, at a given temperature, constitutes a simple thermodynamic system. If it is brought in contact with a heat reservoir of the same temperature, and its volume is in some way increased or diminished, heat will be taken from or given to the reservoir. The case is entirely analogous to a mixture of liquid and vapor enclosed in a cylinder with a moving piston* [3].

Theorem § 9 reveals that the discrete fluid exhibits condensation in equilibrium, a phenomenon previewed by Einstein for the gas of Bose particles[4].

The following corollary holds for every substance:

§ 10 *Any form of energy that depends exclusively on the temperature is discarded in the evaluation of the left hand side of equation* (2.3)*, no matter how important it is to the heat capacity of the substance.*

The following corollary derives from § 10:

§ 11 *Being functions of temperature only, the molecular energies of rotation and oscillation do not affect the equations of state* (2.5).

---

[2] The conditions imposed on the gas here are essentially the same obtained by Clapeyron in 1834 to derive equation $\frac{dp}{dT} = \frac{\Delta H}{T\Delta V}$, known as the first physicochemical application of the second law of thermodynamics [3].

[3] This theorem, was first stated by Planck in § 52 of [8].

[4] Consider the gaseous phase composed of electrons (fermions) removed by the photoelectric effect from the phase containing the electrons moving inside a metal [9]

2.1.1 The dimensionlessness requisite

Equations (2.5) give the arguments of the mathematically arbitrary functions Φ_p, Φ_V and Φ_T, but not their functional forms. We have some reason to assume that the argument of an arbitrary thermodynamic function cannot be dimensional: in fact, if Φ_p happens to be, say, a non homogeneous function, $\Phi_p(x) = 1/(1-x)$, and its argument x, a dimensional quantity such as length, then, in its power series expansion, $1+x+x^2+\ldots$, the first term is the pure number 1; the second has the dimension of length; the third the dimension of area; and so on. Whatever unforeseen use one can find for such function, it does not fit the current standards of thermodynamic practice. Hence, to assign a physical meaning to the argument of Φ_p, we impose on it the *dimensionlessness requisite*.

> *In the formulation of his hypothesis of the quantum, Planck paid special attention to Dimensional Analysis. With the universal constant h, required by imposing the dimensionlessness requisite on the argument of Boltzmann entropy, independently of its combinatorial character, Planck discovered the possibility of establishing a (non-arbitrary) natural system of units*[5]*, that acquired importance in cosmological theory, and is being increasingly adopted by many theoretical physicists* [10].

2.2 A family of abstract thermodynamic systems

In classical thermodynamics the entropy S of a simple pure substance is expressed as a function $S = F(\mathscr{E}, V, m)$ of three variables, namely, its energy $\mathscr{E}$, the volume V it occupies, and the amount of its substance, here represented by its mass m.

The Boltzmann principle of statistical mechanics, differently, states that the entropy of a physical system *in equilibrium* depends solely on the (thermodynamic) probability W, according to the formula $S = k\ln W$. If statistical mechanics fulfills the requirements to replace equilibrium thermodynamics in physical theory, then these two entropies must be identical:

$$F(\mathscr{E}, V, m) = k\ln W. \tag{2.6}$$

Equation (2.6) cannot be solved unless a detailed microscopic description of the substance is given in terms of the *equilibrium* occupancy number of quantum states, which, in their turn, are expressed in terms of the quantities $\mathscr{E}, V, m$.

Notwithstanding the indeterminacy of the function F, Boltzmann's definition of entropy establishes that the quantity W is an integer pure number. We can then

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[5] §164 of [8]

conclude that the argument of F is correspondingly a single, dimensionless, quantity. Hence, to assure mathematical consistency with the Boltzmann principle, we impose on the argument of the function F the *dimensionlessness requisite*.

To treat our problem by the methods of classical thermodynamics, it is advisable to introduce the abstract prototype Θ of a family of thermodynamic systems, whose entropy is given by the following definition,

§ 12 (The Family Θ of Thermodynamic Systems)
The entropy of a member of the family Θ of thermodynamic systems is given by a function $F(W)$ of the single dimensionless quantity W, given by the monomial,

$$W = \mathscr{E}^{\chi} V^{\beta} m^{\gamma} \varsigma. \tag{2.7}$$

where χ, β and γ are rational numbers, and ς is a dimensional constant, characteristic of the system, that renders W dimensionless.

Once ς is fixed, the values of χ, β and γ can be obtained by the methods of Dimensional Analysis. According to the chain rule for derivatives, the fundamental thermodynamic differential coefficients for the entropy give,

$$\begin{aligned} \left(\frac{\partial S}{\partial \mathscr{E}}\right)_{V,m} &= \frac{1}{T} = \frac{\chi}{\mathscr{E}} W F'(W), \\ \left(\frac{\partial S}{\partial V}\right)_{\mathscr{E},m} &= \frac{p}{T} = \frac{\beta}{V} W F'(W). \end{aligned} \tag{2.8}$$

Dividing the latter by the former and adopting the notation $\kappa = \chi/\beta$ we obtain the general energy law (2.2) of the members of the family Θ, that confirms that radiation (a gas of Bose particles) and the gas of fermions are members of the same family Θ.

> *The establishment of the functional form of the magnitude W in (2.7) cannot be obtained by purely thermodynamic methods. This issue will be treated in Chapters **8**, and **9**.*

2.3 Ideal substances defined by universal constants

Although the quantity ς can be any physical constant, we will concentrate here on the already known universal constants, and focus on those connected with thermodynamic phenomena, as revealed by the theories of thermal radiation, quantum mechanics, and electromagnetism[6], namely Planck's constant h, the speed of light c, and the charge of the electron e.

The family Θ defined by these constants can be subdivided into two main groups, according to the dependence of entropy on the mass of the particles.

---

[6] Although the gravitational constant G can be included among the fundamental constants of physics, considerations about gravitation are beyond the scope of this paper.

2.3.1 Mass-independent entropy

Kirchhoff's laws of black-body radiation and Wien's *Displacement Law* contributed to add *spectroscopy* to thermodynamics, which imposes the *Frequency Matching Principle*[7] to the analysis of matter-radiation phenomena.

Such revelation introduced another difficulty in the determination of the thermodynamic properties of chemical substances.

> *In a few cases of abstract substances, these properties could be derived from the introduction of strongly simplifying hypotheses about their spectra, to obtain their* Partition Functions *by the methods of* Operational Calculus.

§ 13 (Mass Independent behavior)
It is known that the electric charge e is connected to the constant hc by the fine structure constant α*, so that we can write* $u_{hc} = 2\pi\alpha u_e$*. The quantity* u_{hc} *characterizes a gas of massless particles (photons), and* u_e*, a gas composed of electrically charged particles whose behavior does not depend on their masses. Both these gases lead to* $\kappa = 3$.

The physical meaning of the fine structure constant is debatable. At least empirically, it is calculated with remarkable precision by the methods of QED, so to be safely acknowledged as a universal constant for practical purposes.

It is possible, however, to derive such constant from the following heuristic analysis of the expected frontal collision of one electron against one proton caused by Coulomb forces, that occurs at a supposedly distance λ between the particles, as follows:

> *We can depict such collision as analogous to a reverse photoelectric effect. It is described by an hydrogen ion absorbing an electron, thus acquiring an energy P, concomitantly emitting a photon of wavelength* λ*. Comparing the total energy of this process with the energy given by Coulomb's law, we obtain the value of hc in terms of the energies involved in the collision. Such phenomenon cannot be derived from electromagnetic theory. Besides, the resulting identity has the merit of revealing the existence of two elementary electric charges, proportional to* $\pm\sqrt{hc}$.

The partition functions of these substances, hence, their entropies, are known to be expressed in terms of a power series of the Boltzmann factor, $e^{-\varepsilon_\ell/kT}$, where ε_ℓ denotes the element ℓ of the energy spectrum of the gas, expressed in terms of its radiation spectrum wavelengths,

$$\lambda_\ell \propto \sqrt[3]{\frac{V}{N}}. \tag{2.9}$$

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[7] To be introduced in Chapter 9.

The lengths λ_ℓ were assumed by Wien in his derivation of the *displacement law* to be integer divisors of the linear dimensions of the geometry of the container.

2.3.2 Mass-dependent entropy

Chemical reactions involve relativistic change on the masses of the particles of reactants and products[8]. Mass relativistic variation occur in any system whose entropy depends on the masses of its constitutive components.

> *Gases defined in terms of $\varsigma = h$ lead to $\kappa = 3/2$. It is not possible to render dimensionless the argument $T^{3/2}V$ of the function Φ_p in* (2.5)*, unless we have recourse to Planck's constant. We therefore adopt the quantum magnitude,*
>
> $$\theta = \frac{h}{\sqrt{2m\pi kT}} \sqrt[3]{\frac{N}{V}}, \tag{2.10}$$
>
> *where m is the mass of a molecule of the gas, and N is the number of molecules of the substance contained in the volume V. The quantity θ can be recognized as the cubic root of the* degree of gas degeneration*, which is ubiquitous in statistical mechanics.*

It will be shown that the behavior of these gases depends on the relativistic variation of the masses of their particles, so that their thermodynamic functions depend, not on the Boltzmann factor $\exp\left(-\frac{\varepsilon}{kT}\right)$, as hitherto assumed by many authors, but on the magnitude θ.

> *Although Gibbs adopted the mass as a measure of the quantity of matter in each phase of heterogeneous substances* [11]*, his successors adopted, as the quantity of reactants and products in chemical reactions, the dimensionless stoichiometric numbers, instead. The adoption of the latter option in the definition* § 12*, has concealed the relativistic nature of chemical reactions.*
>
> *Substances composed of electrically charged material particles might exhibit a dual behavior, whether characterized by $\varsigma = e$, or by $\varsigma = h$. The latter occurs when the laws that cause the changes on state of motion of the particles are relativistic.*

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[8] While this fact has been long admitted in the treatises on chemistry, it has been neglected, either due to the undetectable variation of mass, or due to the then unknown mechanisms of mass-energy relativistic interconversion processes, previewed in Section 4.2.1.

Chapter 3

The Perfect Vapor

Introduction

> *Since, according to (Kirchhoff's) law, we are free to choose any system whatever, we now select from all possible* emitting and absorbing systems *the simplest conceivable one, namely, one consisting of a large number N of similar stationary oscillators* (...) [8]

It is important to emphasize that, in modeling the black-body radiation, the selection of the *system of resonators* is not imperative. It was a mere *choice* made by Planck to simplify the derivation of the chromatic distribution function.

In a certain sense, it was an unfortunate historical coincidence that the energy distribution of photons is isomorphic to that of a system of *Planck resonators*[1], for it led several pioneers of quantum theory to confuse the distribution of energy by atoms and molecules of a gas with that which holds for photons. This confusion is still found in some formulations of the partition functions of real gases, and in the incorrect adoption of Gibbs' canonical ensembles approach to systems involving relativistic phenomena, in particular, chemical reactions.

3.1 The Canonical distribution approach

Kinetic theory and statistical mechanics have been committed to the hypothesis of the canonical distribution of internal energies, that assumes that the probability p_n, of finding a particle of a gas at temperature T with energy ε_n, is proportional

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[1] In the first reading of Einstein's 1917 paper, I became confused when I realized that he was deriving, not the distribution of energy by the molecules of a chemical substance, but, instead, that he was treating of the black-body radiation, itself.

to the Boltzmann factor,

$$p_n \propto \exp\left(\frac{-\varepsilon_n}{kT}\right). \tag{3.1}$$

The canonical distribution hypothesis owes its general acceptance to the many cases in which the energy of the particles is potential, for instance, in the evaluation of the atmospheric pressure, given by the formula (3.1), for $\varepsilon_n = \mu g z$, where μ is the mass of the molecule, g is the acceleration of gravity and z is the height above sea level.

Recall that in his derivation of the Stefan law, the working fluid that Boltzmann submitted to a Carnot cycle, was not a chemical substance composed of atoms and molecules, but a system of *radiation particles* [12], the same "substance" which led Wien to his *displacement law* expressed in terms of the Boltzmann factors (3.1).

This hypothesis, however, does not hold when material particles (atoms and molecules) exchange heat with the environment, a faculty necessary to properly characterize thermodynamic and chemical systems.

3.1.1 The inadequacy of Gibbs' ensembles approach

Recall also that Gibbs' ensembles approach refers to the canonical distribution hypothesis. Our objections to the usual justification given to that approach are recorded in the two footnotes appended by me to the following citation:

> *From a quantum mechanical point of view, a closed system of n particles is characterized by its energy levels E_n. Suppose that from the system we single out a volume (subsystem) that can still be regarded as macroscopic. The number of particles in such a subsystem is still very large, whereas the interaction forces between the particles act at distances whose order of magnitude is that of atomic dimensions. Therefore,* apart from boundary effects[2], *we can regard the subsystem itself as closed, and characterized by certain* energy levels[3] *(for a given number of particles). Since the subsystem interacts with other parts of the closed system, it does not have a fixed energy, and a fixed number of particles, and in fact, it has a non zero probability of occupying any energy state.* [13]

---

[2] This hypothesis neglects, with Newton's definition I (§ 4), the existence of a medium (radiation) that *freely pervades the interstices between the parts of the bodies*, thereby interacting with them.

[3] It is necessary to differentiate the energy levels that can lead to canonic distributions (vibrations or rotations of molecules) from those (relativistic, such as chemical reactions or clustering) that cannot.

3.2 The perfect vapor

Theorem § 9 justifies adopting, as an abstract model of the vapor state of chemical substances, the thermodynamic system defined by equation (1.2), henceforward denoted by *perfect vapor*, whose equation of state can be written in terms of the indeterminate function ϕ_p of the single variable θ,

$$z = \phi_p(\theta). \tag{3.2}$$

3.2.1 The asymptotic behavior of the perfect vapor

Recall that the limit $\theta \to 0$ is usually invoked in kinetic theory as the condition under which the molecules of a gas can be treated as classical particles with rather well defined positions and momenta [14]. To improve the reality of equation (3.2), we subject it to the following asymptotic condition:

§ 14 (Asymptotic Behavior of a Chemical Substance)
The behavior of every known chemical substance in equilibrium, as $\theta \to 0$, *is given by the ideal gas law,* $z = 1$.

From § 14, we can express $\phi_p(\theta)$ in terms of the power series,

$$z = 1 - \theta\left(a_1 + a_2\theta + a_3\theta^2 + \ldots\right) = 1 - f_\sigma(\theta), \tag{3.3}$$

where the a_i's are constants and $f_\sigma(\theta)$ is a function that characterizes the indeterminate substance σ, of the single argument θ, that, expressed in terms of the thermodynamic variables, acquires the form,

$$pV + RT f_\sigma(\theta) = RT, \qquad f_\sigma(0) = 0, \tag{3.4}$$

The indeterminacy of the function $f_\sigma(\theta)$ suggests that each substance (or family of substances) σ has its own characteristic function.

3.2.2 The entropy of the perfect vapor

The entropy derived from § 12 for the case of relativistic variation of the mass of its particles, reveals the existence of a type of partial entropy, *hitherto ignored*, which leads to the departure $f_\sigma(\theta)$ of the EOS (3.3).

The above derivation of the thermodynamic properties of the perfect vapor, based on the Maxwell's relation (2.3), does not preview the expressions of its partial entropies.

To obtain the partial entropies of these two phases, denoted by the symbols $\mathfrak{G}$ and $\mathfrak{L}$, we subject the EOS (3.4), to another of Maxwell's relations, namely,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V, \tag{3.5}$$

which allows obtain a different PDE, whose solution $S = S_{\mathfrak{G}} + S_{\mathfrak{L}}$, reveals these partial entropies,

$$\begin{aligned} S_{\mathfrak{G}} &= -3R\ln\theta, && (3.6)\\ S_{\mathfrak{L}} &= -\frac{3}{2}Rf_\sigma(\theta) + 3R\int\frac{f_\sigma(\theta)}{\theta}d\theta. && (3.7)\end{aligned}$$

The magnitude $S_{\mathfrak{G}}$ reproduces the Sackur–Tetrode entropy of the *monatomic ideal gas*.

We can then assume that the $\mathfrak{G}$-phase corresponds to the *gaseous phase* of the perfect vapor, composed of mutually independent radicles, and behaving according to the laws of the perfect gas, whose entropy, as shown in Chapter 2, is given by the Sackur-Tetrode equation (3.6).

The $\mathfrak{L}$-phase, assumed to correspond to the liquid phase of the perfect vapor, will be treated as a system of *clusters*.

Chapter 4

Matter-Radiation Interaction

Introduction

This Chapter reveals that the thermodynamic interconversion processes of heat and work stem from the constraint imposed by special relativity on the motion of its particles, thus providing a kinetic theoretical proof of proposition § 6, thereby suggesting resume the research program § 3, whose purpose is to formulate a *Kinetic Theory of the Perfect Vapor*, according to the following proposition:

> *To derive the laws of thermodynamics from the mechanics of the discrete fluid, in the assumption that its particles move in the space of Minkowski.*

4.1 Principle of conservation of action

An emblematic instance of the equilibrium between matter and radiation is found in the vapor state of chemical substances, also referred to as phase transition or condensation phenomena, approached in thermodynamics by the following theorem:

§ 15 (Conservation of Entropy during Reversible Condensation)
"(when) a system, or any part of a system, undergoes an increase of entropy just in so far as it absorbs heat from the surroundings, resulting in an equal decrease of the entropy of the surroundings, and that the increase in entropy is equal to the heat so absorbed divided by the absolute temperature" [3],

$$dS = \frac{\delta q_{rev}}{T}. \tag{4.1}$$

If our thermodynamic system is composed of radiation (its surroundings) and the chemical substance, theorem § 15 states the *Principle of Conservation of Action*[1] for the matter-radiation equilibrium.

According to definition § 12, both the radiation and the perfect vapor are members of the family Θ, whose entropies are given, respectively, by the indeterminate functions, $F(u_{hc})$, and $F(\theta)$. The results obtained in the previous Chapters allow analyze the system

$$\mathsf{Radiation} + \mathsf{Perfect\ Vapor}. \tag{4.2}$$

Besides, from the standpoint of Bartoli thermodynamics, radiation is, itself, a thermodynamic system in its own right, so that the equilibrium between matter and radiation presupposes both the equilibrium of radiation and matter, separately, and the equilibrium of a three phase system,

$$\mathsf{Radiation} + \mathfrak{G}\text{-phase} + \mathfrak{L}\text{-phase}. \tag{4.3}$$

Recalling that u_{hc} characterizes the equilibrium of radiation, and θ, the equilibrium of the perfect vapor, then the equilibrium of the combined system (4.3), according to theorem § 15, is achieved when,

$$u_{hc} = \theta. \tag{4.4}$$

Substituting the proportionality relation (2.9) in (4.4) we obtain the expression,

$$kT \propto mc^2. \tag{4.5}$$

The result thus obtained is eloquent enough to persuade us to assume that the heat-work interconversion processes that characterize thermodynamics are relativistic, which allow assume the provisionally scalar relation $\Delta\varepsilon \propto \Delta mc^2$.

> *Proportionality* (4.5) *reveals a noteworthy faculty thermodynamics is endowed with, namely, to predict the occurrence of relativistic energy conversion processes in the perfect vapor.*
>
> *Both the suggestion by Roger Penrose that the missing gear of the machinery that imparts the sensation of the flux of time occurs during a quantum interaction; and the widespread belief that "in the elementary equations of the world, time's arrow appears only when heat is involved"*[2] *are strengthened by the revelation of the relativistic nature of thermodynamic phenomena.*

---

[1] This principle, applied to quantum systems, was heuristically formulated by Ehrenfest [15], and named by Einstein the *Adiabatic Hypothesis*.

[2] Second-hand citation from [16], p. 110.

4.2 On the complex nature of relativistic energy

In 1924, Dirac published his famous *Quantum Theory of Radiation*. In 1932, in a homonimous paper, Fermi wrote [17]:

> *Dirac's theory of radiation is based on a very simple idea; instead of considering an atom and the radiation field with which it interacts as two distinct systems,* he treats them as a single system whose energy is the sum of three terms*: one representing the energy of the atom, a second representing the electromagnetic energy of the radiation field, and a small term representing* the <u>coupling</u> <u>energy</u> of the atom and the radiation field. *If we neglect this last term, the atom and the field could not affect each other in any way; that is, no radiation energy could be either emitted or absorbed by the atom.*

A confrontation of Dirac's against Einstein's *Quantum Theory of Radiation* reveals the difficulty we face when we intend to establish the correspondence of thermodynamics with quantum mechanics:

> *It is in the way matter and radiation interact that we can identify the essential difference between Einstein's from Dirac's* Quantum Theory of Radiation*: while in Einstein's theory a quantum system (atom, molecule) interacts with the radiation field only when that system emits or absorbs radiation, in Dirac's theory, this interaction is permanent and stationary. Both theories are relativistic: in the former such character is determined by the particle's momentum*[3]*, ε/c, in the latter, it is the energy of the system that is relativistic, where the variables are represented by operators. As opposed to Dirac's assumptions, Einstein suggests that these interactive processes are stochastic and independent.*

4.2.1 The relativistic character of equilibrium

As is well known, Einstein unveiled the existence of the constraint $|v| < c$, imposed on the motion of material particles in his formulation of special relativity theory. Hence, it is natural to assume that the energy converted during an *elementary* thermodynamic transformation occurring in a material substance in the presence of an electromagnetic field (a thermodynamic system in contact with a heat reservoir) can be obtained from the relativistic equation,

$$\varepsilon^2 = m^2c^4 + c^2p^2. \tag{4.6}$$

Besides the well-know four dimensional Dirac's factorization of expression

$$\sqrt{m^2c^4 + c^2p^2}.$$

---

[3] Spin was discovered only in 1924 [4]; seven years after Einstein formulated his theory.

in terms of quantum operators, there is an elementary one, that, despite its importance, seems to have been hitherto neglected,

$$\varepsilon^2 = \left(mc^2 + \imath cp\right)\left(mc^2 - \imath cp\right). \tag{4.7}$$

Equation (4.7), which is justified by assuming that the particle with mass m moves in the Minkowski space, gives physical meaning in the following circumstances:

When a material particle of mass m interacts with electromagnetic radiation, its energy undergoes changes caused by the action of the *independent* elementary energy conversions processes[4] which occur inside chemical substances. Due to the stochastic *independence* of these processes, the energies $\Delta\varepsilon$ or $\Delta\varepsilon^*$ involved are expressed in terms of the *two separate* complex numbers, whose values are given, respectively, by the equations,

$$\begin{aligned} \Delta\varepsilon &= \Delta mc^2 + \imath c\Delta p, \qquad (4.8)\\ \Delta\varepsilon^* &= \Delta mc^2 - \imath c\Delta p. \qquad (4.9) \end{aligned}$$

> *It will be shown later, in Section 6.2, that the complex energies* (4.8) *and* (4.9) *correspond to the dimensionless complex actions in the mathematical representation of the ladder operators that act on the clusters that compose the* $\mathfrak{L}$*-phase of the perfect vapor. Its is noteworthy that these equations can be recognized to be consequences of the kinetic theory derived from Bartoli thermodynamics, thus providing a preliminary proof of proposition* § 6 *that will be shown to lead to the reformulation of the Boltzmann principle, and of Axiom 5 of quantum theory.*

4.2.2 The transient distinguishability of identical particles

In a previous paper [7] I showed the cogency of assigning, in the epistemological order of the axioms of the theory of quantum many-body systems, the precedence of the ladder operators over the indistinguishability and Pauli exclusion "principles". This hypothesis is justified by the very derivation of these operators in formal quantum mechanics, where from they can be obtained without any mention to these principles[5].

Further evidences, discussed in Appendix C, revealed by the properties of chemical substances undergoing large scale departures from equilibrium, as usual

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[4] These interconversion processes can be identified with the absorption and emission of radiation.

[5] Although usually derived for the particular case of the harmonic oscillator (See, for instance, § 41 of [18]), its derivation from special relativity is, as prescribed by Kirchhoff's law, independent of the nature of the material body considered.

in thermodynamic transformations, show that these principles cannot be acknowledged as necessary ontological characters of a substance, but instead, treated as conditions of *statistical equilibrium*.

> *A relativistic kinetic theory brings to sight the existence of certain force-like agents hidden behind the elementary processes of energy conversion, that cause non-potential changes on the state of motion of the particles that give rise to the internal pressure*[6] *of the substances.*

4.3 The reciprocity of heat exchange

We can depict the heat exchange between the thermal reservoir and the perfect vapor (the working substance in a Carnot cycle of a thermal engine), by regarding the photon as an entity that, when absorbed by (created in) the gas, is correspondingly emitted by (annihilated in) radiation. Conversely, when a photon is emitted by the gas, it is absorbed by radiation.

> *Instead of imagining a process where an entity is created from nothing or that it is annihilated to nothing, we depict these processes as an exchange, as it occurs in a commercial transaction, when two people give something to each other at the same time.*

This interpretation of the consequences of the elementary energy conversion process on the perfect vapor provides an adequate framework to analyze the kinetics of a *Multiple Component System*, where creation and annihilation are different names to describe the two-way quantum exchange processes: the chemical analysis of the vapor evidences that with the exchange of one quantum between radiation and the perfect vapor during an elementary energy conversion process, a concomitant exchange of radicles between the two phases of the vapor occurs.

> *It is usually assumed in spectroscopy that infra-red radiation acts only on the vibratory and rotational degrees of freedom of the molecules of a substance. According to theorem* § 8, *this hypothesis cannot explain the partial entropy* (3.7) *of the* $\mathfrak{L}$*-phase. The results obtained by the present approach allows conclude that the action of heat on the vapor state, whatever the region of the radiation spectrum where it occurs, imparts* chemical reactions *between the different chemical substances that compose the two phases of the perfect vapor.*

---

[6] The partial pressure p_i acquires physical meaning in the language of Chemical Physics, as the cause of the *internal work*, $dW_i = p_i dV$ exerted against internal forces in the gas [19].

4.3.1 The Newtonian space-time versus the Minkowskian timeless space

A thoroughgoing discussion of the meaning of time in physics[7] is beyond the scope of this paper. It is here exceptionally mentioned because the present approach seems to add more confusion to the conundrum of the role of time in our perception of the phenomenal world. It is worthwhile to consider the following interpretation raised by the foregoing discussion, which *opposes* the Minkowski representation of the square of the four dimensional *interval dS*,

$$ds^2 = x_1^2 + x_2^2 + x_3^2 + x_4^2 \tag{4.10}$$

to its corresponding Newtonian expression,

$$ds^2 = \underbrace{c^2t^2 - \overbrace{\left(x_1^2 + x_2^2 + x_3^2\right)}^{\text{Euclidean}}}_{\text{Newtonian}}. \tag{4.11}$$

that describes the relativistic *taut constraint* imposed on the motion of Newtonian particles.

The radical difference between the structures of the $\mathfrak{G}$ and $\mathfrak{L}$-phases, reveals that equations (4.10) and (4.11) are not *equivalent*, i.e., they describe different physical realities. While the former holds for the $\mathfrak{L}$-phase, which is identified with a many-body (many-radicle) quantum system, characterized by a single, timeless, non-observable stationary wave function defined in the Minkowsky purely-spatial domain, the latter, holds for the $\mathfrak{G}$-phase, that is perceived as a system of classical particles evolving in time, in the Euclidean space, that can, in principle, be observed in the *time-varying* chemical-thermodynamic domain of phenomena[8].

> *In classical mechanics it is implicit that the coordinates and momentum degrees of freedom are independent variables. There is, however, an imperative precondition which is so obvious that is frequently forgotten: these variables acquire physical meaning only when their values refer to the same instant of time. From the standpoint of special relativity independence is not a necessary, ontological, attribute of these degrees of freedom, but an accidental condition of simultaneity, which denies the very notion of independence.*

The timeless stationarity of a many-body quantum system can be broken when it is acted from the outside by an elementary energy conversion process, which is

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[7] For a discussion about this issue, see Rovelli [16].

[8] As far as I know, our sense organs are chemical "instruments", sensitive to quantum state transitions, which are characteristic of time-dependent, hence Newtonian, processes.

ruled by the laws of creation and annihilation. I therefore propose the following conjecture:

> *The change that occurs in a many-body system caused by the action of an elementary energy conversion process describes the phenomenon known as the* collapse of its wave function.

Chapter 5

The Meaning of the Quantum of Action

Introduction

After the revelation that the elementary energy conversion processes that occur in the perfect vapor are relativistic, we can state the purpose of the forthcoming Chapters, in terms of the following proposition:

§ 16 *To find the natural laws that rule the elementary processes that cause the changes of the* concentration *of the $\mathfrak{G}$-phase of the perfect vapor that conduct it towards the final state of thermodynamic equilibrium.*

The present Chapter is an intermediate contribution to the demonstration that the elementary relativistic energy conversion processes (4.8)-(4.9) are prerequisite for the kinetic theoretical description of these processes, further modified by the quantum constraints $\Delta p \Delta q \geq h$.

Henceforward renamed "*elementary processes of quantum exchange*", these elementary processes will be shown to occur in the perfect vapor during the chemical reactions, already mentioned in the Chapter 3, that characterize the subject of present approach, namely, the state transitions that occur in that abstract substance.

In the present Chapter, the reinterpretation of the heat-work relativistic interconversion processes, expressed in terms of equations (4.8)-(4.9), as consequences of the *taut constraint* $\Delta p \Delta q \geq h$, their connections with the Schrödinger equation, and a first approach to the understanding of their role in the explanation of chemical reactions, will be discussed. The central point of the present discussion can be summarized in the following definition:

§ 17 *The relation* (5.1) *describes a* taut constraint *imposed by radiation on the transmutation processes that act on the population of the phases of the perfect vapor.*

> *In Chapter 6 the description of these processes will be used in a new derivation of the creation-annihilation operators, in connection with inelastic collisions which, besides providing a cogent explanation of a chemical reaction, reveals the Minkowski structure of the phase space of the perfect vapor, that will eventually lead to a reinterpretation of the Boltzmann entropy in Chapter 8, and of the Axiom 5 of quantum theory in Chapter 10.*

5.1 The Old Quantum Theory Era

In the body of physical knowledge developed during the first quarter of the last century, also known as the Old Quantum Theory Era[1], Planck's constant appeared in several equations, with different meanings, given in terms of either line, or multiple integrals, as amendments to the classical definition of the mechanical action. In the attempts to describe certain thermodynamic, radiation or atomic phenomena, both of them were applied.

The numerical value of the constant h was first derived by Planck, himself, from the empirical chromatic distribution curve of the black-body radiation. Other theoretical approaches suggesting experiments to obtain this value, notably Einstein's theory of the photo-electric effect, followed. Although important, the knowledge of its numerical value does not give physical meaning to this constant, specially its role in the explanation of quantum phenomena, as stated in proposition § 16.

The Planck constant and the magnitude θ

It is not accidental that the interpretation of θ is connected with varied interpretations given to Planck's constant, and *vice-versa*. In fact, the well-known relation,

$$\Delta p \Delta q = \Delta \mathscr{E} \Delta t \geq h. \tag{5.1}$$

can be rewritten in the form,

$$\theta \leq 1. \tag{5.2}$$

As will be shown in the forthcoming Sections, it is the physical role played by the magnitude θ in the quantum explanation of the several thermodynamic phenomena that provides a more cogent interpretation of Planck's constant, not

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[1] In the forthcoming we will refer to this era by the acronym OQTE.

the opposite. In other words, it is thermodynamics that precedes quantum theory in the epistemological order of physical knowledge, not the inverse.

Let us recall the following thermodynamic variables expressed in terms of the magnitude θ:

1. According to Section 2.3.2, the entropy of the perfect vapor is given by a function of the single variable θ, which describes the argument of the partial entropies:
    (a) $S_{\mathfrak{G}}$ of the *gaseous* $\mathfrak{G}$*-phase*, given by equation (3.6), reproduces, for a gas of single radicles, the Sackur-Tetrode entropy of the monatomic gas;
    (b) $S_{\mathfrak{L}}$, of the liquid $\mathfrak{L}$-phase, whose mathematical expression (3.7), depends on the indeterminate function $f_{\sigma}(\theta,)$, describes a system of clusters. From the evidences exhibited in Appendix D we conclude that this quantity corresponds to the main departure of the entropy of real gases from the ideal gas law;
2. the mean value of the action (A13), developed by a particle traversing the space interval that separates two consecutive collisions;
3. the invariant quantity of the Brownian movement, defined as the distance traversed by a granule during two consecutive localizations [20].

5.2 Sommerfeld relations are taut constraints

One of the first interpretations given to Planck's constant was proposed by Sommerfeld, as a *constraint* imposed on the motion of a mechanical system [21],

$$\Delta p \Delta q = h. \tag{5.3}$$

Later Sommerfeld restated it in the following terms[2]:

§ 18 (Sommerfeld's Conjecture)
Planck's constant h (quantum of action) puts a lower limit to the size $p_\ell q_\ell$ *for every pair of degrees of freedom,* $\{p_\ell, q_\ell\}$*,*

$$\Delta p_\ell \Delta q_\ell = h \tag{5.4}$$

Conjecture § 18 allows translate the relation (5.1) into the language of set theory:

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[2] Ch. V, §28.7 [22].

§ 19 (Sommerfeld Redefinition of the Phase Space)
The inequality,

$$\Delta p_\ell \Delta q_\ell > h, \tag{5.5}$$

describes an open subset of the classical phase space, *whose* boundary set *is given by the equality* (5.4).

From this interpretation the following corollary derives:

> *Under the condition* (5.5)*, the processes that cause changes on the values of any degree of freedom, are classical.*
>
> *It is noteworthy that every process that affect the value of the degree of freedom ℓ of a system, determined by quantity $\Delta p_\ell \Delta q_\ell$, or its very elimination by the quantum condition expressed in the taut constraint* (5.4)*, causes, according to Boltzmann principle, a variation on the entropy of that system.*

5.3 Bohr's model of the hydrogen atom

Bohr's description of the energies exchanged between the atom and radiation during the absorption and emission of radiation processes, conjointly referred to as the *elementary processes of quantum exchange*. Section 5.8 gives complementary information about the elementary processes of energy conversion described by the relativistic equations (4.8)-(4.9).

Although superseded by the wave and matrix mechanics, the model of the hydrogen atom proposed by Bohr revealed the empirical foundations that spectral analysis imparts to the epistemology of quantum mechanics, namely, the derivation of the Balmer series, the theoretical calculus of the Rydberg constant, and the association of the Ritz *combination principle* with the absorption and emission processes in the hydrogen atom.

The discrete character of the energies involved in these processes revealed by *spectroscopy* implies in the assumption of the finite duration and discrete character of the elementary processes of quantum exchange between the material particles and electromagnetic radiation. Since all these quantities are obtained from spectroscopic measurements, Bohr's model of the hydrogen atom was *justified by its consequences*, the epistemological criterion universally (though unavoidably provisional) adopted to the acceptance of speculative theories. It is worthwhile to recall the second postulate of the supporting theory of Bohr's model:

$$\Delta \varepsilon_{mn} = \varepsilon_m - \varepsilon_n = h\nu_{mn}, \tag{5.6}$$

where ε_m and ε_n are the values of the energy in the states, $\{m,n\}$ under consideration.

The abbreviated form $\Delta\varepsilon = h\nu$ of expression (5.6), became known as the *Einstein-Bohr relation.*

> *To equate the variation of the energy given by* (5.6) *to the relativistic variations described by the equations* (4.8) *and* (4.9), *we must inquire, not on the meaning of Planck's constant, itself, but on the algebraic structure its existence imparts to the mathematical representation of quantum phenomena, namely, its influence on Schrödinger equation, on the laws of chemical change implicit in the ladder operators, and in the Axiom 5.*

The interpretation that implicitly derives from Bohr's second postulate is that of a *finite matter-radiation interaction process*, between an atom and heat, during which a finite amount of energy $\Delta\varepsilon$ is involved.

5.3.1 A heuristic description of Bohr's second postulate

Let us focus on the absorption and emission processes.

Equation (5.6) can be rewritten in terms of the period $\Delta\tau = 1/\nu$ of the oscillatory process with frequency ν,

$$\Delta\mathscr{E}\Delta\tau = h. \tag{5.7}$$

In the lack of a picture to visualize the processes involved in the exchange of one quantum of action between the atom and radiation, it might be helpful to speculate on a possible interpretation of the transformations that occur during their evolution, by comparing a frontal elastic collision of a ball against a wall with the behavior of the *Planck resonator*.

The reversion of the momentum the ball undergoes during such collision can be likened to the reflection of a periodic signal on a mirror, where the first half-period of the collision corresponds to the "absorption" of the momentum of the ball, immediately followed by its "emission" during the second half-period. The duration of both these processes is finite. The difference between them is in the time interval that separates an absorption from its subsequent emission: while in the mechanical system the emission starts when the momentum of the ball vanishes, in the case of radiation. that period is indeterminate, i.e., absorptions and emissions are stochastically independent.

5.3.2 Reinterpretation of heat

There are many evidences to assume that these processes, known as the absorption and the emission of one quantum of frequency ν, are elementary, stochastic, and mutually independent. In the Chapter 4 it was shown that the thermodynamic analysis of the equilibrium between the perfect vapor and electromagnetic radiation can be explained in terms of the relativistic equations equations (4.8) and (4.9). Confronting the amount of energy there expressed with the corresponding value given by equation (5.6), we conclude that the very notion of *heat* exchanged between matter and radiation, must be reviewed.

Furthermore, in the way to introduce the amendments required to improve the connection between thermodynamics and the quantum theory, it is imperative to remind that the nature of Carnot's abstract "*working substance*" is chemical, so that its corpuscles are neither Newtonian particles, nor Planck resonators, but atoms and molecules.

5.4 Algebraic approach to the Planck resonator

Let us assume momentarily, with classical mechanics, that the unit of action h is a scalar quantity. Justified by this provisional hypothesis we can apply the rules of ordinary algebra to combine relations (5.4)-(5.5), thus obtaining,

$$\Delta\mathscr{E}\Delta\tau = \Delta p_\ell \Delta q_\ell = h. \tag{5.8}$$

We can correspondingly rewrite (5.5) in the form,

$$\Delta\mathscr{E}\Delta\tau = \Delta p_\ell \Delta q_\ell > h, \tag{5.9}$$

> *While the character of equation* (5.4) *is corpuscular (expressed in terms of mechanical translational degrees of freedom), that of equation* (5.6)*, as opposed, is undulatory (expressed in terms of oscillatory degrees of freedom).*

5.4.1 The algebra of quantum exchange

Assuming that $\Delta q_\ell = \lambda_\ell$ in (5.8), where λ_ℓ is the wavelength of radiation, we have $\Delta p_\ell = h/\lambda_\ell$ which substituted in equations (4.8) and (4.9), gives the quantum-relativistic equations that describe the elementary processes of quantum exchange, namely, the absorption and emission processes of one quantum of radiation by atoms.

$$\Delta\varepsilon_\ell = \Delta m_\ell c^2 + \imath c \frac{h}{\lambda_\ell}, \tag{5.10}$$

$$\Delta\varepsilon_\ell^* = \Delta m_\ell c^2 - \imath c \frac{h}{\lambda_\ell}. \tag{5.11}$$

> *Equations* (5.10) *and* (5.11) *will be justified in Section 6.2, when the forces that act on the corpuscles (radicles) of the perfect vapor are shown to be described by the algebra of the* ladder operators.

According to the *Principle of Conservation of Action* (Section 4.1) we can state:

§ 20 (The Principle of Reciprocity)
The exchange of quanta between matter and radiation are reciprocal processes: to an absorption of one photon by a particle there corresponds the emission of one photon by radiation, and vice-versa.

In the phase transition processes triggered by the elementary processes of quantum exchange that occur in the perfect vapor, we can see a similarity with the three conservative principles of classical mechanics, namely, the invariance of energy, momentum and angular moment: during an elementary processes of quantum exchange, the energies involved are given by the quantum-relativistic equations (5.10)-(5.11), which establish the functional correlation of the degrees of freedom that describe these interaction processes, namely, the mass, the momentum, and the *spin*, the latter being the discrete quantum version of the angular momentum.

To the three conservative principles of classical mechanics, namely, the invariance of energy, momentum and angular moment, there correspond the invariant entities in the phase transition processes in perfect vapor. In the elementary processes of quantum exchange, the energies involved are given by the relativistic equations (4.8)-(4.9), where from the quantum-relativistic equations, (5.10)-(5.11), derive. These equations establish the functional correlation involving the degrees of freedom that describe these interaction processes, namely, the mass, the momentum and the *spin*, a discrete version of the angular momentum.

5.4.2 The Inadequacy of Liouville's Theorem

Being the entropies (3.6) and (3.7) exclusive functions of the thermodynamic variable θ, they are not invariant quantities, as previewed for potential systems of particles by Liouville's theorem[3]. Thermodynamic invariance occurs only in those processes in which θ is constant in a quantum-like condition, which was interpreted by Ehrenfest as *adiabatic* [15].

---

[3] This theorem was called *conservation of extension-in-phase*, by Gibbs in his definition of the microcanonic ensemble[23].

> *It is noteworthy that the elementary changes of entropy, described in thermodynamics by the variation* $T\Delta S$*, when translated into the microscopic representation of kinetic theory, has no limit for* $\Delta S \rightarrow 0$*, for they are bound*[4] *by the taut constraints relations* (5.4)-(5.5).
>
> *The algebra of Quantum Mechanics endows the complex numbers that represent dynamical variables with the faculties of operators, with the power to cause changes on the values of these variables. It will be shown in Section 6.2 that the operators that derive from equations* (5.10) *and* (5.11)*, describe the causes of change of the concentration of the* $\mathfrak{G}$*-phase of the perfect vapor.*

In fact, the volume of the phase space cannot be treated as a strictly scalar classical variable. As a complex variable, it varies in the Minkowski space, where it is endowed with thermodynamic faculties. Hence, a system of particles whose state of motion is susceptible to the action of heat (hence, to thermal radiation) does not satisfy Liouville's invariance theorem.

The foregoing considerations allow us to state:

5.4.3 The Algebra of Quantum Complex Numbers

Complex numbers are usually defined as members of a *Field*. Hence, for every complex number $u \neq 0$, there is its inverse u^{-1}. This is not true in quantum algebra, because the complex conjugate u^*, necessary to evaluate u^{-1}, corresponds to an elementary processes of quantum exchange which is *independent* of the elementary processes of quantum exchange represented by the complex *operator* u.

This evidence imposes a reinterpretation of the Axiom 3, for while it gives the algorithm necessary to *artificially* calculate the eigen-values of a given dynamic variable, it does not inform that the *natural* algorithm performed by real particles is the result of the composition of stochastic, mutually independent processes of absorption and emission of quanta, described by their corresponding quantum ladder operators.

> *The phenomenon that reveals that a mechanical system of particles is endowed with thermodynamic faculties is its susceptibility to* heat (radiation).
>
> *From the standpoint of classical mechanics, the variation of* θ *in the perfect vapor characterizes a non-conservative process.*

---

[4] See § 30.

5.5 Inelastic collisions and the quantum of action

A workable description of the motion of particles in a vapor can be obtained from a reinterpretation of the description of the motion of the molecules in the gas given by Maxwell:

§ 21 *During the great part of their course the molecules (of the gas) are not acted on by any sensible force, and therefore move in straight lines with uniform velocity. When two molecules come* within a certain distance of each other, a mutual action takes place between them (...). *Each molecule has its course changed, and starts a new path* [24].

In the present approach, differently, the relations (5.4)-(5.5) are interpreted, not as the manifestation of measurement uncertainties, but as the description of a *taut constraint*, that gives to Maxwell's *mutual action* a different meaning, namely, that of an *inelastic collision of finite duration*, in the course of which the mechanical action developed by the colliding particles is determined by the *quantum-relativistic laws* of absorption and emission of one quantum of action.

Maxwell's description § 21 refers to two processes: the inertial inter-collisions translation, and an inelastic collision, corresponding, respectively, to the edges (F) and vertexes (C) of the polygonal line that describes the Brownian movement, as reviewed in Section A.10.

5.6 Chemical reactions and entropy

The description of atoms and molecules that compose the chemical substances in terms of the laws of Dalton and Avogadro, as revealed by chemistry, are adequate for our analyses of the behavior of the perfect vapor.

A chemical reaction can be depicted as a finite process during which heat is absorbed or emitted according to Hess's law, thus allowing redefine his notion of *heat of reaction* in terms of the equilibrium of the elementary energies exchanged between the radiation and the individual molecules involved in a chemical reaction.

We can then assume, with kinetic theory, that each elementary quantum state transition in the perfect vapor is the result of the inelastic collision involving radicles and clusters. During an *endothermic* collision there occurs the

5.7 The second law and the taut constraints

Experience has shown that an adequate mechanical representation of the elementary processes of a chemical reaction are inelastic collisions, an assumption that allows depict the gas as a *mechanism* in which its *moving parts* (atoms and molecules) are constrained by a mechanical equivalent of the second law.

As revealed by Analytical Mechanics, the introduction of a certain class of *constraints* into a system of particles, or their removal from it, cause a change on the number of its degrees of freedom, hence, on its Boltzmann entropy. This fact allows regard a chemical reaction as the consequence of the *quantum-relativistic taut constraints* that impose, stochastically, restrictions on the motion of the molecules involved.

Note that, according to § 13, electrically charged particles can have two different behaviors, either strictly quantum or quantum-relativistic. In the latter, one cannot differentiate the motion of the particle under the influence of an electromagnetic field from its motion in a Minkowski space, a circumstance in which the description § 21 can be restated as follows:

§ 22 (Maxwell's Description in the Minkowski Space)
(...) when two molecules come within a certain "interval" from each other in the Minkowski phase-space-time, an elementary process of quantum exchange can be triggered, giving rise to a quantum-relativistic transition (an elementary chemical reaction).

5.8 How do degrees of freedom become conjugate?

Having verified that equation (5.8), and thereby, Planck's constant h, has also a vestigial meaning inherited from classical mechanics, we are suggested to seek, hidden behind the relations (5.4)-(5.5), the operative faculty that comes to sight only after the mentioned Newtonian degrees of freedom of a radicle *become* conjugate.

Equation (5.8) can be rewritten in the form of the work of a force well-known from classical mechanics,

$$\Delta\mathscr{E} = \frac{\Delta p_\ell}{\Delta\tau}\Delta q_\ell = h\nu. \tag{5.12}$$

If this algebraic manipulation is justified, we are allowed to adopt the equation (5.8) as the expression of a non-conservative process. The quantity $\frac{\Delta p_\ell}{\Delta\tau}\cdot\Delta q_\ell$ in equation (5.12) can be interpreted as the work exerted by radiation, either on some degree of freedom of the material medium that composes the gas during an absorption of a quantum, or *vice-versa* during an emission.

The connection between the pairs of degrees of freedom $\{p_\ell, q_\ell\}$, or between $\{\mathscr{E}, \tau\}$, can be justified when we realize that Planck's constant cannot be interpreted merely as a scalar magnitude. Due to the enigmatic nature of Planck's constant, the mathematical interconnection of these pairs of quantities were given in the formulation of wave mechanics, by a non-conventional treatment of the operators of calculus, as follows.

By rewriting equations (5.4)–(5.6), in the forms,

$$\Delta\mathscr{E} = \frac{h}{\Delta t}, \qquad \text{and} \qquad \Delta p = \frac{h}{\Delta q}, \tag{5.13}$$

the difference operators Δ, become interpreted, in wave mechanics, as the discrete version of the corresponding differential operators of energy and momentum, respectively,

$$\frac{h}{\Delta t} \to \hat{\mathscr{E}} = \frac{h}{2\pi\imath}\frac{\partial}{\partial t}, \qquad \text{and} \qquad \frac{h}{\Delta q} \to \hat{p}_x = \frac{h}{2\pi\imath}\frac{\partial}{\partial x}. \tag{5.14}$$

The correspondences (5.14), and the algebraic properties of the operators adopted in quantum mechanics, establish the rules required to formulate the PDEs that characterize atoms and molecules as many-body quantum systems. In an equation, these operators can be interpreted as “conjugators”, i.e., entities that replace the degrees of freedom, originally independent, into a single *conjugate* unit, imposed on them by the EPQE.

Furthermore, in these operators, the Planck constant h appears combined with the imaginary unit $\imath$. According to the rules of algebra above, they can be treated as a single symbol.

By assuming that the Planck constant is not a real, but an imaginary constant, we conclude in favor of proposition § 6, in conformity with the results obtained in Section 4.2.1.

The formulation of Schrödinger equation consists in translating the Hamiltonian that characterizes the mechanical system of particles involved in that process, into the language of these operators[5]. This authorizes one to assign to relations (5.4)-(5.5) the *operative faculties* that were hidden in the previous interpretations.

> *By operative faculty of an agent we understand its “power to cause a change” on the entity on which it acts. Although the notion of force has been criticized by some authors* [25]*, mathematicians borrowed its meaning from Newtonian physics to establish the way the notion of operator is to be interpreted.*

From the previous considerations we can conclude:

> *The motion of the molecules of the gas in the sub-phase-space* (5.9) *is classical, where the identity* (5.8) *refers to a finite elementary process whose duration is given by the period* $1/\nu$.

---

[5] To justify this procedure it was necessary to have recourse to an artificial *Principle of Correspondence*. The strange limit operation (5.14), should have a more sound foundation, concerning the mathematics of taut constraints.

5.9 On being and becoming

A chemical reaction can also be interpreted as an elementary exchange of heat and work that characterizes thermodynamics.

§ 23 (Destruction and Creation of Degrees of Freedom)
During a chemical reaction the degrees of freedom of the reactants are destroyed*, and the resulting products that are* created *acquire new degrees of freedom with unpredictable values.*

From § 23 derives the following corollary:

§ 24 *The classical degrees of freedom, namely, momentum and position of a particle of the perfect vapor,* pass away *as* independent *attributes when the particle moves from the $\mathfrak{G}$-phase, to enter into the $\mathfrak{L}$-phase thus* becoming *described by* conjugate differential operators *inside it, after undergoing the non-conservative process that takes place during a chemical reaction.*

Corollary § 24 enforces the understanding that "*conjugation*" is a previously non-existent *relation* between momentum and position, expressed by the Hamiltonian combination of the operators (5.14) in the composition of Schrödinger's equation. Such relation can be "*created*" (come to be) or "*destroyed*" (pass away) during the elementary processes of quantum exchange.

Hence, in quantum theory we cannot say that position and momentum are "something" that *always existed together* with the particle, a conclusion that raises a challenge to the interpretation of the uncertainty principle, and serious objection to its acceptance as a fundamental principle of physics.

> *The definitions of position and momentum, as fundamental degrees of freedom in classical mechanics, acquire meaning only if referred to the same instant of time, a notion that has a characteristic meaning in special relativity, expressed in terms of simultaneity and space-time interval. Note that relativistic simultaneity (zero length of space-time interval*[6]*) is a precondition for the consummation of the phenomenon* "becoming conjugate"*, as discussed in Section 5.8.*

The *principle of reciprocity* § 20, can then be naturally extended to the condensation phenomenon:

§ 25 *In the perfect vapor, the annihilation of one radicle in its $\mathfrak{L}$-phase, corresponds to its creation in the $\mathfrak{G}$-phase, and* vice-versa.

---

[6] This condition might be related with the notion of *entanglement*.

In current quantum mechanics the words *creation* and *annihilation* will be used according to the meanings given in § 4.3. With this understanding, statement § 25 describes a transaction, in which the words *creation* and *annihilation* acquire the complementary meanings of “death and birth (reincarnation)”, as metaphors of the reciprocal processes that correspond to the exchange of a radicle between two coexisting phases. This reinterpretation justifies having recourse to the Markovian theory of birth and death processes in Appendix C where from the kinetics of the population of the clusters in the $\mathfrak{L}$-phase derives.

5.10 The uncertainty principle

In spite of the variety of meaningful interpretations given to the relations (5.1) during the OQTE, much of the literature abandoned them in favor of the hitherto almost indelible Heisenberg’s *Uncertainty Principle* interpretation, renaming it *uncertainty relations*.

> *Being founded on the notion of measurements of the degrees of freedom of micro-particles, the uncertainty principle is unsuitable for the analysis of chemical*[7] *or thermodynamic phenomena. The hypothesis verification processes adopted in thermodynamic experiments (using measurement instruments such as thermometers, calorimeters, barometers, spectrometers, etc.) do not focus on the degrees of freedom of the particles of the system.*

I intend to show that, though compatible with the interpretations of the Planck constant proposed during the OQTE, including those derived from the conception of heat that stems from Bartoli thermodynamics, the definition § 17 is shown to be incongruous with the formulation of the uncertainty principle, an issue that will be discussed separately, in Appendix B.

5.11 Knowing without touching the bodies

Before Jules Verne no scientist would dare submit to a financial institution a project to launch rockets to *touch* an heavenly body. The remarkable theoretical results obtained by the ancient astronomers about the motion of celestial bodies were based on techniques of *passive observation*. The same happens in thermodynamic observation:

The results of the measurements performed to determine the values of macroscopic magnitudes <u>do</u> <u>not</u> <u>touch</u> <u>the</u> <u>particles</u>. Any influence of whatever (a) the

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[7] See § 23.

measurement equipment used, (b) its *operator* is, or (c) the proximity of any *observer*, are purposely discarded at the outset *by construction*[8], from their experimental arrangements.

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[8] In chemical and thermodynamic practice, care is taken in the establishment of *standard protocols* designed to minimize the effects that the interference of observation and measurement processes can cause on the state of the system.

Chapter 6

Taut Constraints

Summary

Except for Planck's constant itself, all quantities in the relations (5.4)-(5.5) are classical. It is therefore legitimate and insightful to analyze them from the Newtonian perspective. It will be shown in this Chapter that equation (5.8) can be adopted as the expression of an *stochastic taut constraint* that arises when the molecules of the gas interact with radiation.

The changes on the populations of the quantum states of the clusters in the $\mathfrak{L}$-phase of the perfect vapor, are caused by the *elementary processes of quantum exchange*, triggered by the taut constraints $|v| \leq c$, imposed by special relativity and $\Delta p \Delta q \geq h$, imposed by the quantum conditions. During these processes, known as *absorption or emission of radiation*, quanta are exchanged between the substance and radiation, and radicles are exchanged between the phases of the perfect vapor. Their relativistic nature was revealed in the derivation of the equations (4.8) and (4.9), and the variation of the momentum $\Delta p = \varepsilon/c$, was shown to correspond to the quantum expression, $\Delta p = h/\lambda$.

Henceforth, in the description of the phenomena involved in the perfect vapor, the two taut constraints are combined into a single representation, expressed in terms of non-commutative complex quantities which, in formal quantum mechanics are represented by the ladder operators[1] $\left\{\mathsf{a}, \mathsf{a}^\dagger\right\}$. We can then state the

§ 26 (Fundamental Problem of Kinetic Theory of Vapor)
To show that the taut constraints *imposed on the state of motion of the molecules of a chemical substance under the influence of an electromagnetic field, reproduce and detail the constraints imposed by the second law of thermodynamics on its behavior.*

---

[1] See §41 [18]

According to Analytical Mechanics, the introduction or elimination of a certain class of constraints changes the number of degrees of freedom of the phase-space of a system of particles.

Recall that according to § 23, the phenomena that cause changes on the number of degrees of freedom of reactants and products have been identified as chemical reactions. In the present approach, will focus on the changes imposed by the *taut constraint* $|\Delta p \Delta q| \geq h$ on the entropy formation in the perfect vapor.

Since state transitions are identified with chemical reactions, we will correspondingly assume the following proposition:

> *To show that the kind of constraint that arises when the particles of the perfect vapor interact with radiation, causes changes on the number of degrees of freedom of the phase-space occupied by its molecules.*

Instead of interpreting the variation Δp and Δq of the values of the conjugate quantities $\{p, q\}$ in relations (5.4)-(5.5) as *measurement uncertainties*, as prescribed by the uncertainty principle, in the forthcoming they will be treated as the *changes* the momentum and position a particle of the gas undergo during a finite time interval of length Δt under the action of a certain type of *force*, described in terms of the *difference operator* Δ.

> *This assumption is justified both by its thermodynamic consequences, and by their correspondences with the operators of wave mechanics, as shown in Section 5.8.*
>
> *Whatever the elementary processes that cause changes on the phase space where the corpuscles of the perfect vapor move, their collective effect is thermodynamic.*

6.1 Forces imposed by taut constraints

In Newtonian mechanics the work $\Delta\mathscr{E}$ performed by a force f is expressed by the equation,

$$\Delta\mathscr{E} = f \cdot \Delta q, \tag{6.1}$$

where Δq is the displacement traversed by the particle. Denoting by Δp the change of the linear momentum of the particle, equation (6.1) can be written in the form,

$$\Delta\mathscr{E} = \frac{\Delta p \cdot \Delta q}{\Delta t}, \tag{6.2}$$

where Δt is the period of time during which the momentum of the particle undergoes the variation Δp.

In Newtonian mechanics the meaning of force is usually assigned to the finite quantity $\Delta p/\Delta t$, and *exceptionally* to the derivative operation of Calculus,

$$f = \lim_{\Delta t \to 0} \frac{\Delta p}{\Delta t}. \tag{6.3}$$

Let us rewrite (6.2) in the form,

$$\Delta\mathscr{E}\Delta t = \Delta p \cdot \Delta q. \tag{6.4}$$

If the derivative (6.3) exists, then,

$$\lim_{\Delta t \to 0} \Delta\mathscr{E}\Delta t = \lim_{\Delta\mathscr{E} \to 0} \Delta\mathscr{E}\Delta t = 0. \tag{6.5}$$

To examine the physical meaning of (6.4) when the constraint (5.8) is added to mechanics, we invoke Bridgman's criterion[2]:

§ 27 *Nature imposes a lower bound on the products in* (6.4)*, so that the operation which gives them meaning is not* (6.5) *but, instead, the quantum constraints,* (5.8).

Recall that Newton's second law provides a general indeterminate equation that is completed with the special laws of forces that act on the motion of the bodies. When the quotients $\Delta p/\Delta t$ and $\Delta\mathscr{E}/\Delta q$ have, for a given motion of a body, well defined[3] limits for $\Delta t \to 0$ and $\Delta q \to 0$, then (6.4) can be rewritten as a second order ordinary differential equation whose solution, given its initial conditions, completely describes that motion.

When, as opposed, the influence of the quantum constraints cannot be neglected, a different system of "equations of motion" derived from a quantum-relativistic analysis must be considered. In either case, however, it is possible to assign, to $\Delta p/\Delta t$, at least symbolically, the Newtonian meaning of force and to reason, in the analysis of quantum phenomena, in terms of certain *force-like agents* that cause the change of the motion of the particles. The interpretation § 27 justifies the following assumption:

§ 28 (Taut Constraints)
The foregoing considerations suggest to treat the relations (5.1) *as* taut constraints *imposed on the motion of the molecules of the gas that arise only during the elementary processes of quantum exchange, when the molecules of the gas interact with radiation.*

---

[2] "*In dealing with physical situations, the operations that give meaning to our physical concepts should be the physical operations actually carried out*" [26].

[3] When the constraints imposed by the quantum constraints have negligible influence on the motion of the body.

> *Hypothesis* § 28 *allows adopt Sommerfeld's conjecture* § 18 *as the descriptor of an inelastic collision, and thereby of a chemical reaction (see Section 6.3).*

Taut (unilateral) constraints can be treated in Analytical Mechanics according to the following suggestion [27]:

> *"The motion of a system on which unilateral constraint is imposed may be divided into portions so that in certain portions the constraint is taut and the motion occurs as if the constraint were bilateral, and in other portions the constraint is not taut, and the motion occurs as if there were no such constraint. In other words, in certain portions a unilateral constraint is either replaced by a bilateral constraint or is eliminated altogether.'*

Hence, the motion of particles whose degrees of freedom satisfy the condition (5.5) must be treated as classical. The condition (5.4), differently, imposes on the particles involved, the behavior described in proposition § 26.

6.1.1 Mechanical consequences of the quantum taut constraints

Since according to the quantum constraints § 27, the limit operation $\Delta q \rightarrow 0$ does not exist, we conclude that:

> *The derivative*
>
> $$\lim_{\Delta q \rightarrow 0} \frac{\Delta \mathscr{E}}{\Delta q},$$
>
> *is undefined in the scope of quantum phenomena.*

According to a well known theorem of classical mechanics,

§ 29 *The forces that arise in the motion of a particle constrained by the quantum constraints are* non-conservative.

When the quantum constraints cannot be neglected, it is not only hopeless to search for an approximation for this process in terms of some suitably chosen (perturbation) potential, but specially misleading, for it conceals the existence of the elementary energy conversion processes and their intrinsic irreversibility, hindering the quantum nature of thermodynamic phenomena.

We also assume that the quantum constraints also imply that …

> *… if, in the treatment of any magnitude that is under the action of the quantum constraints, is described by a continuous and differentiable function, the former condition prevails over the latter.*

where from the following well known corollary derives:

> *The use of the* limit *operation of differential calculus must be reviewed under the quantum constraints.*

This proposition has far reaching consequences, for, by denying the existence of convergence processes that, acting on the degrees of freedom of a single particle, give rise to well defined limit values, the quantum constraints undermine the very foundations of differential calculus, thereby subverting the whole of Analytical Mechanics[4].

§ 30 *This condition should not be surprising, for, as already noted in* § 23 *and* § 24*, during a chemical reaction, when the molecules of the reactants become subject to the taut constraints* (5.4)-(5.5)*, their classical degrees of freedom are annihilated, loosing both their physical meaning (and their classical identities*[5]*), and new ones, with "unpredictable" values, are created with its products.*

6.1.2 Action representation of Hamilton's equations

According to § 21 the motion of a radicle in the 𝔊-phase is the alternation of two elementary motions, viz., a free path and a collision. To describe them we invoke the system of Hamilton equations,

$$\frac{dq}{dt} = \left(\frac{\partial H}{\partial p}\right)_q, \qquad \frac{dp}{dt} = -\left(\frac{\partial H}{\partial q}\right)_p. \tag{6.6}$$

The description of the former, being classical and conservative, is straightforward.

An inelastic collision, as opposed, is a non-conservative process requiring an *ad-hoc* treatment.

To describe the variation of the actions $\Delta\alpha_q$ and $\Delta\alpha_p$ of the two possible outcomes of a collision, we rewrite *Hamilton*'s equations (6.6) in their finite forms in the time interval of duration Δt,

$$\begin{aligned} \Delta\alpha_q &= (\Delta H)_q \Delta t = \ \ \Delta q \Delta p, \\ \Delta\alpha_p &= (\Delta H)_p \Delta t = -\Delta p \Delta q. \end{aligned} \tag{6.7}$$

---

[4] The way out this radical restriction imposed by the uncertainty principle is found in the *Law of Large Numbers*, which, applied not to a single particle, but to a large population of particles, provide the convergence processes that legitimate the use of the limit operator of Calculus in Statistical Mechanics, playing the role of an *asymptotic operator*.

[5] This phenomenon, that has nothing to do with the observation or measurement processes, has led to interpret expressions (5.4)-(5.5) as *uncertainty relations* by the uncertainty principle.

We can readily recognize in (6.7) the Newton's second law *prototypes* (5.1), and thereby assume the existence of two independent phenomena, described respectively by the variations α_q and α_p of the actions developed during the reaction, as already proposed in § 6.4.

Since we are focusing on the motion of an individual particle, abstracted from its environment, we must assume that the energy is not invariant, i.e., the Hamiltonian H_C of a collision is time-dependent, say, $\Delta H_C \neq 0$ during the time interval Δt (that corresponds to the classical expression $\partial H_C/\partial t \neq 0$), whence[6], the *phenomena* described respectively by $\Delta\alpha_q$ and $\Delta\alpha_p$, are independent.

We are then led to the following corollary:

§ 31 (The two elementary energy conversion processes)
*To describe the interaction of a particle with its environment (a "*quantum-relativistic reaction*") the two equations in* (6.7) *are uncoupled,* i.e., *they are mutually independent, corresponding to two different processes*[7] *of finite duration that cause the* quantum *changes of the state of the particle.*

As in Section 4.2.1, we here assume that these two processes are identified with absorption and emission of a photon by a system.

6.1.3 The environment as a requisite

The principle of conservation of energy imposes another requirement to describe the motion of particles under the quantum constraints. According to § 29 we must assume the existence of an *environment*[8] where the particles move and with which they interact, exchanging the non-conservative amounts of energy (heat) emitted or absorbed during these processes.

That the interaction of material particles with a certain kind of environment is a mechanical problem was recognized in the synthesis of the electromagnetic theory. While this theory can satisfactorily characterize the nature of the environment that is susceptible to interact with electrically charged particles and explain this interaction requiring no modification of Newtonian Mechanics, it cannot explain the behavior of the electrically charged particles involving atoms and the molecules [6]. Specially, it can explain neither how the environment causes

---

[6] This fact is more formally represented by the properties of the dynamic quantities, imposed by special relativity in equations (4.8)-(4.9).

[7] The assumption that there are two opposing processes was emphasized in the notation adopted in equation (6.7), where the subscripts q and p (usually neglected in the representation of Hamilton's equations), were imported from the partial derivatives in (6.6).

[8] Such environment is here identified with the *medium* referred to by Newton in the Definition I of his *Principia*, § 4.

changes on the behavior of the particles of a chemical substance, nor how they are reflected in their thermodynamic properties.

Thermodynamics identifies the environment with a *thermal bath* (*heat reservoir*) characterized by its temperature. Although the identification of the physical properties of this environment, together with the understanding of the way it interacts with material particles, are essential for the complete formulation of a kinetic theory, the revelation of the mechanical nature of heat was not considered a problem of thermodynamics before Bartoli thermodynamics.

6.2 Bose operators

Rewriting the actions (6.12) in the dimensionless form,

$$\frac{\Delta\alpha}{h} = \frac{\Delta p \cdot \Delta z}{h} + \imath \frac{\Delta p \times \Delta z}{h}, \tag{6.8}$$

$$\frac{\Delta\alpha^*}{h} = \frac{\Delta p \cdot \Delta z}{h} - \imath \frac{\Delta p \times \Delta z}{h}. \tag{6.9}$$

we obtain,

$$(\Delta\alpha - \Delta\alpha^*) = 2\imath(\Delta p \times \Delta z),,$$

thus recovering in $\Delta\alpha/h$, and $\Delta\alpha^*/h$, respectively, the *(quantum) complex algebra representation* of the creation and annihilation operators $\left\{\mathsf{a}^\dagger, \mathsf{a}\right\}$ that characterize the Bose–Einstein statistics.

6.3 The action developed during a binary collision

In classical mechanics a binary collision is usually treated as a two dimensional motion. Taking the origin of coordinates in the center of mass of the system composed of the two colliding particles, the *Lagrange* function of the motion in the plane formed by the vectors of the relative velocity of the system before and after the collision can be written in terms of complex variables,

$$\mathscr{L} = \frac{m}{2}(\Delta\dot{z})(\Delta\dot{z}^*), \tag{6.10}$$

where Δz is the vector that describes the trajectory traversed by the system, and Δz^*, its conjugate.

During the evolution of the collision a certain quantity of action $\Delta\alpha = \mathscr{L}\Delta t$ is developed. In the evaluation of this complex quantity, an indeterminacy arises, for pre-multiplication and post-multiplication of $\mathscr{L}$ by Δt give different results. It is known from experiment that the factors of the product,

$$\left(\Delta t\frac{\Delta z}{\Delta t}\right)\left(m\frac{\Delta z^*}{\Delta t}\right)\neq\left(m\frac{\Delta z}{\Delta t}\right)\left(\frac{\Delta z^*}{\Delta t}\Delta t\right), \tag{6.11}$$

correspond to different, independent phenomena, so that the "*algebraical cancellation law*" does not hold, implying in the non-commutative product of these quantities. We can then write,

$$\begin{aligned}\Delta\alpha &= \mathscr{L}\Delta t = (\Delta p)(\Delta z^*),\\ \Delta\alpha^* &= \Delta t\mathscr{L} = (\Delta z)(\Delta p^*).\end{aligned} \tag{6.12}$$

> *According to Section 4.2.1, this character of the Lagrange function can be ascribed to the constraint imposed by the laws of special relativity on the motion of the particles involved in this kind of inelastic collision.*

In agreement with § 31, we assume that the non-commutative character of the product (6.11) is due to the existence of two independent processes that cannot be confused, namely, absorption and emission, represented by two different mathematical expressions that are concealed in the classical interpretation of equation (6.10).

> *Axiom 5 of quantum mechanics takes for granted the non-commutativity of the products*
>
> $$\Delta p\Delta z\neq\Delta z\Delta p.$$
>
> *This implies recognize that* Q-complex numbers *(complex numbers in quantum theory) are not members of a* division algebra[9].
>
> *In fact, to be satisfied, the division operation,*
>
> $$\frac{z_1}{z_2}=z_3,\quad \text{if}\quad z_2z_3=z_1.$$
>
> *requires the existence of a solution for the following system of* <u>simultaneous</u> *equations,*
>
> $$\begin{aligned}x_2x_3-y_2y_3&=x_1,\\ x_2y_3+x_3y_2&=y_1.\end{aligned}$$
>
> *However, in nature, these equations are not* simultaneous. *Actually, they correspond to two* distinct *and* independent *phenomena, namely, the interchange (absorption or emission) of one quantum of action between matter and radiation. These two processes occur in* different, mutually exclusive, *instants of time*[10].

---

[9] This raises a problem to mathematicians: Are they members of an *associative algebra*?

[10] In considering this fact, we must take into account that *simultaneity* of two events is an accidental condition imposed by special relativity to be satisfied.

6.4 Causes of change of the volume of the phase-space

Equations (6.8) and (6.9) describe the changes that the dimensionless volume of the phase-space of the perfect vapor undergo under the action of the elementary processes of quantum exchange they describe, leading us to conclude:

§ 32 *The algebraic structure of the* phase space *of a system of particles interacting with radiation is Minkowskian.*

The revelation § 32, which allows eliminate the *ambiguity* already detected in Section 5.8, implies the need to reformulate the *Boltzmann Principle*, by adopting θ as a variable endowed with both thermodynamic and relativistic faculties.

By introducing the definition,

$$\Delta p \times \Delta z = -\imath \frac{h}{2}. \tag{6.13}$$

where h is Planck constant, we recover, in $\Delta\alpha/h$, and $\Delta\alpha^*/h$, the *complex number representation* of the creation and annihilation dimensionless operators $\{\mathsf{a}^\dagger, \mathsf{a}\}$ that characterize the Bose–Einstein statistics, and the stochastic indistinguishability that characterizes the thermodynamic equilibrium of a gas of Bose particles.

6.4.1 Ladder operators describe relativistic processes

As already pointed out in § 31, to give physical meaning to the motions characterized by $\Delta\alpha$ and $\Delta\alpha^*$, we introduce the following postulate:

> *There are in Nature two independent phenomena characterized respectively by the actions $\Delta\alpha$ and $\Delta\alpha^*$, corresponding, respectively, to the absorption and emission elementary processes.*

Such interpretation implies a revision on the observability of certain quantum phenomena:

§ 33 (Displacement in the Time Dimension)
We can regard the development of the imaginary part of the action caused by the kind of inelastic collision above discussed, as a torsion in the Minkowski plane*, that corresponds to a displacement of the particle in the time, towards the future or the past, depending on the arithmetic signal of the torsion.*

Statement § 33 explains why elementary particles might *become* non-observable.

6.4.2 Thermodynamic equilibrium

In the Axiom 3 of quantum theory, the *measured value* of a dynamic variable is given by the eigenvalue of its associated operator, as stated in its Axiom 3. However, being *Schrödinger's space alone equation* an automorphism[11], its solution describes an equilibrium condition, whose eigenvalues give, not the *measured* values of a dynamic variable at a given instant, but its values at the thermodynamic equilibrium (stable and *supposedly*[12] metastable), a conclusion that imposes an amendment to that axiom.

---

[11] Section B.4.

[12] Depending on further inquires on this issue.

Chapter 7

Molecular Mechanics

Summary

This Chapter details the model of the vapor state of a chemical substance, which allows explain the elementary quantum-relativistic laws that cause the thermodynamic changes on the structure and motion of its molecules during their interactions with radiation. The derivation of the partial entropy $S_{\mathfrak{L}}$ of the liquid phase of the vapor is also discussed.

Introduction

After the revelation by Bartoli that heat can be properly described by a discrete fluid, we can regard the vapor state of a chemical substance as a three phases thermodynamic system in persistent mutual interaction, as expressed in (4.3). It is known from thermodynamics and chemistry that the gaseous and liquid phases are two distinct chemical substances, which allows conclude that:

> *A phase transition is a chemical reaction.*

In Section 4.2.1 it was shown that this phenomenon is relativistic, and that the quantities of energy exchanged between matter and radiation are given by equations (4.8) and (4.9), which, after modified by the quantum taut constraints $\Delta p \Delta q \geq h$ led to equations (5.10)-(5.11). In Section 6.2 it was revealed that these equations reproduce the mathematical expressions of the *ladder operators* $\left\{\mathsf{a},\mathsf{a}^{\dagger}\right\}$ for bosons. With these results we are in condition to obtain the mathematical expression of the entropy $S_{\mathfrak{L}}$, and an explanation of the kinetics of the condensation and evaporation processes.

7.1 The chemical description of the vapor

The entropy of a chemical substance can be decomposed into several partial entropies, depending on the different nature of the degrees of freedom with which its molecules are endowed, e.g., rotations, oscillations, etc.

The existence of the two phases $\mathfrak{G}$ and $\mathfrak{L}$ in the perfect vapor was revealed in Section 2.2, based on very general hypotheses about its entropy S, whose partial entropies are given by,

$$S = S_{\mathfrak{G}} + S_{\mathfrak{L}},$$

expressed in equations (3.6) and (3.7), in terms of the same single argument θ.

In this and the following Chapters we will focus on the partial entropy $S_{\mathfrak{L}}$ of the liquid phase for the simple cases of substances that have a single equilibrium state, supposed to be attained when the perfect vapor is under the action of a *standard spectrum*, namely, that of the black-body radiation[1].

Before entering into this subject, let us remind that the evaporation and condensing processes, by whose means heat is exchanged between matter and radiation, depend on the set of frequencies to which the former is susceptible, and on the frequency spectrum of the latter. Although thermodynamics is concerned mainly with stable equilibrium, an incomplete frequency matching of spectra in the interaction processes might lead to metastable states, a subject of considerable importance to climatology.

> *In the previous Chapters it was shown that both the function $f_\sigma(\theta)$ in the* EOS, (3.3)*, of the perfect vapor, and its partial entropy $S_{\mathfrak{L}}$, are different descriptions of a regular departure from the ideal gas law. In Appendix D, the confrontation of the pVT data of steam against the* EOS *of the perfect vapor confirms that result.*

7.1.1 Radicles and Clusters

Chemistry has established that material substances are composed of atoms and molecules. A kinetic theory of the vapor must therefore be based on the physical characteristics of these entities. The chemical substances in the $\mathfrak{G}$ and $\mathfrak{L}$-phases are more appropriately described, not by atoms and molecules, but by *radicles* and *clusters*:

§ 34 (Radicles)
We will assume that during the conversion processes from gas to liquid, or vice-versa*, the molecules of the perfect vapor do not dissociate in smaller molecules.*

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[1] Note that the pVT data set of the steam table represented in fig. D.1 does not denounce any evidence of the metastable states known to exist in water.

Instead, during these phase transition processes, they are supposed to behave as indivisible units, as it happens with atoms in chemical reactions. The particles of the substances with this character were named radicles *by Berzelius* [28].

§ 35 (Clusters)
A cluster ℓ is a molecule, treated as a many-body quantum system, composed of a random number $\mathbf{r}_\ell(t)$ of radicles, thereby described by a single wave function, $\psi_\ell(\mathbf{r}_\ell(t))$. The PDFs[2]*, which describe the population dynamics of a cluster, is determined by the conditional probability laws that rule the elementary processes of creation and annihilation.*

We can think of a cluster as a polymer of radicles and, as usual in the conjectures about the structure of the liquid state, It is assumed to be a molecule with short life cycle.

According to the correspondence rules (5.14), the degrees of freedom of each constitutive radicle become *conjugated* by its wave function inside a cluster.

7.1.2 On the chemical structure of the phases

From the foregoing considerations we can represent the vapor by the *perfect vapor*, whose phases can be described as follows.

The $\mathfrak{G}$ and the $\mathfrak{L}$-phases, are assumed to be distinct *chemical substances*, whose interactions involve *chemical reactions*.

The $\mathfrak{G}$-phase, here interpreted as the *gas phase* of the vapor, is composed of a random number $\mathbf{N}_{\mathfrak{G}}$ of radicles, whose partial entropy is given by the quantity,

$$S_{\mathfrak{G}} = -\mathbf{N}_{\mathfrak{G}} k \ln(\theta),$$

which reproduces the Sackur-Tetrode entropy of the ideal monatomic gas.

The concentration of the $\mathfrak{G}$-phase is given by the quantity $\mathbf{N}_{\mathfrak{G}}/\mathbf{N}$.

The $\mathfrak{L}$-phase, here interpreted as the *liquid phase* of the vapor, is composed of an enumerable set of *clusters*[3]. As specified in § 35, the dynamic variable which characterizes the quantum state of a cluster ℓ, is its *population*, i.e., the random the number $\mathbf{r}_\ell(t)$ of radicles it contains.

---

[2] The acronym PDF will be adopted henceforward to designate a *Probability Distribution Function*.

[3] In fact, this description is a simplification. The $\mathfrak{L}$-phase is, itself, composed of a random number sub-phases, composed, in their turn, of groups of clusters with the same number of radicles.

7.1.3 On phase transitions

Phase transitions occur when the perfect vapor interacts with radiation. According to Prévost's *Law of Exchanges*, during these processes bursts of photons are exchanged between the thermal bath and the perfect vapor. We then introduce the following postulate, which will be shown to be in conformance to the *Laws of Change* determined by the quantum theorems on creation and annihilation:

> *To the exchange of one photon between the thermal bath and the substance, there corresponds the exchange of a radicle between the* $\mathfrak{G}$*-phase and one (unspecified) of the clusters in the* $\mathfrak{L}$*-phase*[4].

7.2 Molecular Mechanics

In this inquire we will focus on the processes occurring during the interaction between the clusters and radiation, adopting as paradigm the laws of Newton.

The description of an elementary quantum state transition can be expressed in terms analogous to Newton's first law:

§ 36 (The quantum version of Newton's First Law)
Every cluster continues in its state of (chemical) rest, described by a stationary wave function, unless it is compelled to change that state by forces impressed upon it.

In the previous Chapters it was shown that quantum-relativistic forces arise as consequence of the taut constraints, which arise when the clusters interact with electromagnetic radiation, thus causing the *collapse* of its wave function, and its replacement by another new one.

These interaction processes, identified with the phenomena of *emission* and *absorption* of radiation by the components of the perfect vapor, are referred to by the expression *elementary processes of quantum exchange*.

7.2.1 Entropy variation due to chemical reaction

According to the principle of conservation of action, equations (5.10)–(5.11) can be written in the form:

$$\begin{aligned} \Delta\alpha_\ell &= \Delta m_\ell c \Delta q + \imath h, \\ \Delta\alpha_\ell^* &= \Delta m_\ell c \Delta q - \imath h. \end{aligned} \tag{7.1}$$

---

[4] This simplification is justified by its consequences.

According to the Boltzmann principle, variation of entropy corresponds to change on the volume $\Delta\alpha$ of the phase space, which, according to equations (7.1), is not a scalar, but a complex entity. Hence, an elementary change of the entropy is expressed either by the expression $\mathrm{Ln}(\Delta\alpha_\ell)$, or $\mathrm{Ln}(\Delta\alpha_\ell^*)$, where Ln designates the complex logarithm function.

The variation of the volume of the phase space just described is discrete, occurring in increments or decrements h. When described in terms of dimensionless quantities, it changes in steps of one imaginary unit.

Note that the equations (7.1) reproduce the expressions of the operators of creation and annihilation of particles in a quantum state[5].

This allows conclude that the quantum-relativistic equations (7.1) describe the way an elementary process of quantum exchange induce the cluster of the $\mathfrak{L}$-phase to eject (destroy or annihilate) one radicle, which thereby is created in (becomes a member of) the $\mathfrak{G}$-phase, while it absorbs (creates) one quantum of radiation in that cluster. In the opposite phenomenon, a cluster (creates) "absorbs" one radicle from the $\mathfrak{G}$-phase, concomitantly emitting (annihilating) one quantum in radiation. Such explanation of an elementary quantum state transitions suggest the following conjecture:

> *The previous considerations describe a chemical reaction, It can be explained in terms of a different interpretation of the current tenets of quantum theory, where from the description of the creation and annihilation processes derive.*

7.3 On the equilibrium of the perfect vapor

The second quantization rules of annihilation and creation, respectively[6],

$$\hat{\mathsf{a}}_\ell\, \Psi_{N_1 N_2 \ldots N_\ell \ldots} \Rightarrow \sqrt{N_\ell}\, \Psi_{N_1 N_2 \ldots N_{\ell-1} \ldots} \tag{7.2}$$

$$\hat{\mathsf{a}}_\ell^+\, \Psi_{N_1 N_2 \ldots N_\ell \ldots} \Rightarrow \sqrt{N_\ell + 1}\, \Psi_{N_1 N_2 \ldots N_{\ell+1} \ldots} \tag{7.3}$$

does not describe an identity but a process, in fact, a quantum state transition in which we are not entitled to assume that a particle is added to the many-body system, coming from nothing. Instead we are allowed to assume that it comes from elsewhere. The same interpretation holds for the effect described by the annihilation operator.

> *In equations* (7.2)-(7.3) *I used the symbol* $\Rightarrow$*, instead of the identity symbol* "$=$" *adopted in the literature, to emphasize that action of the ladder operators* $\{\mathsf{a}, \mathsf{a}^\dagger\}$ *is not described by an identity* $a = b$*, as understood in ordinary*

---

[5] See §41 in [18].

[6] Eqs. (64,6) and (64,9), are transcribed, respectively, from §64 [29].

> *algebra, where it is said that we can interchangeably use either a or b in any equation. Instead, its meaning is similar to those symbols used in the description of chemical reactions. The wave functions at the left-hand side of the equations above are understood to collapse, giving rise to the new wave functions at their right-hand side. Furthermore, these processes are irreversible.*

Furthermore, according to Born's interpretation of the wave-function Ψ_ℓ, the quantum state transition, referred to by action of the ladder operators (7.2) and (7.3), describes a random event, which implies assuming that a dynamic variable (in this case, the state occupancy number $\mathbf{r}_\ell$) changes erratically under the action of the elementary processes of quantum exchange. We can then conclude that its eigen-value $\bar{\mathbf{r}}_\ell$, will not be attained as a consequence of a single step quantum state transition, but, according to the *Law of Large Numbers*, only after the consummation of a large number of stochastically independent recurrence of these elementary processes approaches the *relaxation time* characteristic of the substance in that thermodynamic state.

7.4 Elementary changes on dynamic variables

The distribution of the total number $\mathbf{N}$ of radicles in the perfect vapor, by the $\mathfrak{G}$-phase and the clusters of the $\mathfrak{L}$-phase, is an instance of the classical combinatorial problem of distributing balls in cells [30].

In our case, there is a compromise between the quantity $\mathbf{N}_{\mathfrak{G}}$ of radicles in the $\mathfrak{G}$-phase, and the energies ε_ℓ stored in the $\mathfrak{L}$-phase: which are bounded by the total energy E of the perfect vapor.

The current approach of statistical mechanics to the Bose and Fermi statistics is based this compromise. That approach is a two step procedure: first, the calculus of the volume of the phase space is performed, on which either the indistinguishability, or the Pauli's principle on depending on the nature of the particles, is imposed.

In the second step, the previous result is subjected to the (here objected) *Principle of Most Probable Configuration*, in which the maximum entropy is sought for a fixed number $\mathbf{N}$ of particles and a fixed amount of energy E [4]. If, instead, we seek for the minimum energy E for fixed $\mathbf{N}$ and fixed entropy S (assuming that indistinguishability and Pauli's exclusion determine equilibrium conditions), we would obtain exactly the same result. The formulation of the infinitesimal energy change in terms of the Lagrange's indeterminate multipliers method, allows both interpretations.

We will adopt here two different approaches. To calculate the equilibrium entropy in Chapter 8, we will state, in agreement with Einstein's hypotheses adopted for absorptions and emissions in his 1917 paper, and Prévost's law of exchanges, that emissions and absorptions must compensate each other in the thermodynamic equilibrium state.

To describe the state transition condensation or evaporation kinetics we will translate in Appendix C the conditional probabilities determined by quantum mechanics, which characterize the creation and annihilation processes, as the laws of change of Markovian birth and death stochastic processes, which give the time varying PDF of the random number of occupancy in quantum states of the clusters of the $\mathfrak{L}$-phase.

7.5 The laws of probability

The number of radicles in a chemical substance is too large to be handled by measurement or by calculus. It is therefore sensible to adopt the statistical approach described in § 43, in which the *Principle of Molecular Chaos* is replaced by Born's quantum mechanical interpretation of probability as the product $\psi\psi^*$ of the wave function ψ.

Since the radicles of the perfect vapor are grouped randomly into clusters, instead of inquiring about the instantaneous values of the $\mathbf{r}_\ell(t)$ of the individual degrees of freedom of the radicles, we will focus on the time evolution of their *probability distribution functions*[7].

7.5.1 Transmutation and radicles migration

The chemical changes a given cluster undergoes are expressed by the variation of the random number $\mathbf{r}_\ell(t)$. These changes are necessarily discrete, caused by the elementary processes of quantum exchange that act on the cluster ℓ. Since these changes are chemical reactions, they are relativistic.

We regard the rules imposed by the operators (7.2) and (7.3), as the trials of a combinatorial game of chance, whose outcomes, abstractly described in the § 37 and § 38, can be restated in terms of the following statements:

§ 37 (Emission of one Quantum of Action by a Cluster: Condensation)
When a cluster is compelled by the combined quantum taut constraint to emit one quantum of action*, the same magnitude is transferred from one radicle of the $\mathfrak{G}$-phase to radiation, and this radicle undergoes a transmutation process of time duration τ_e, during which it is incorporated into that cluster. The position and momentum degrees of freedom of the radicle, originally independent when in the $\mathfrak{G}$-phase, become* conjugated *inside the cluster, as the consequence of the action*

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[7] Henceforward we will adopt the acronym PDF to designate a probability distribution function.

of the elementary process of quantum exchange that causes the following change on its population,

$$\mathbf{r}_\ell(t) \Rightarrow \mathbf{r}_\ell(t+\tau_e)+1, \qquad \text{hence,} \qquad \mathbf{N}_{\mathfrak{G}} \Rightarrow \mathbf{N}_{\mathfrak{G}}-1. \tag{7.4}$$

It can be said that the radicle of the gas phase of the vapor decays to its liquid phase, in an elementary condensation process.

§ 38 (Absorption of one Quantum of Action by a Cluster: Evaporation)
When the cluster absorbs one quantum of action from radiation, one radicle of the $\mathfrak{L}$-phase is transferred to the $\mathfrak{G}$-phase though a process of duration τ_a. Its position and momentum degrees of freedom, originally conjugate, become independent *and unpredictable, according to the transmutation elementary process that causes the following change on its population,*

$$\mathbf{r}_\ell(t) \Rightarrow \mathbf{r}_\ell(t+\tau_a)-1, \qquad \text{hence,} \qquad \mathbf{N}_{\mathfrak{G}} \Rightarrow \mathbf{N}_{\mathfrak{G}}+1. \tag{7.5}$$

The transfer of one radicle from the liquid to the gaseous phase is known as an elementary process of evaporation.

In both of these cases, there occurs a process known as the *collapse of the wave function* ψ_ℓ, caused from the outside, when the cluster ℓ and a radicle “fall” into a *quantum taut constraint*.

The internal state of a cluster cannot be perceived by humans because it is a stationary configuration hidden inside the Minkowski subspace. Only its change, manifest in the variation of the $\mathfrak{G}$-phase *concentration* can be, in principle, observed by us, because it occurs in the observable Newtonian space-time we are biologically endowed to perceive.

7.6 The natural convergence to eigen-states

Creation-annihilation operators occur when a cluster interacts with radiation. A real cluster is not *endowed with the faculty* to perform by itself the convergence to its eigen-value (equilibrium) population. Its convergence to the final state of equilibrium is the result of the incessant action of the elementary processes of quantum exchange on its internal state.

In vitro, i.e. during the calculation by computer algorithms, that artificially implement the process prescribed by Axiom 3, the convergence to its eigen-value is attained. This axiom suggests the false idea that the convergence to the eigen-state is a single-step process.

In natura, instead, convergence is not a *single step* process. The phase transitions the $\mathfrak{L}$-phase undergoes are caused by the action of a large number of stochastic processes of creation-annihilation acting on its clusters, which are known to be mutually independent. As opposed to quantum particles, humans, after learning quantum theory, become endowed with the faculty to preview the eigen-states of a dynamical variable that characterizes equilibrium, by artificially performing the *algorithms* of calculus prescribed by the solution of Schrödinger's space alone equation.

Differently, a natural cluster evolves undergoing erratically the *recurrent stochastic processes* of *creation-annihilation* until the system attains its stationary state of statistical fluctuation around the equilibrium state.

7.7 Reinterpretation of Axiom 3

According to Axiom 3 of the current tenets of quantum mechanics, when the system is subject to a *measurement process* its wave-function collapses, and its dynamic variables are "forced" to assume the eigen-values of their corresponding operators. The dynamic variable of a cluster is its population $\mathbf{r}_\ell(t)$, whose value is determined by the combined action of the three above mentioned elementary stochastically independent processes.

The value of the population $\mathbf{r}_\ell(t)$ that is meaningful for thermodynamics is not that obtained as the result of a measurement made at the an arbitrary instant t, but the average asymptotic value $\bar{\mathbf{r}}$, for $t \to \infty$, that corresponds to the equilibrium state of the perfect vapor.

§ 39 (Equilibrium)
The equilibrium between a cluster ℓ and radiation is attained when,

$$\lim_{t\to\infty} \mathbf{r}_\ell(t) = \bar{\mathbf{r}}.$$

In practice, the asymptotic value $\bar{\mathbf{r}}$ is attained after elapsed the *relaxation time* characteristic of the clusters of the substance considered.

The values of the occupation random numbers $\mathbf{r}_\ell(t)$ are

> *The forces that cause the changes on the internal state of a cluster come from the outside, arising when it happens to be subject to the taut constraint $\Delta p \Delta q = h$, that "triggers" an elementary processes of quantum exchange.*

Hence, the actions $h\nu_{mn} = h\nu^*_{nm}$ were fused into certain *Hermitian* matrices of quantum theory. This expedient allowed the derivation, by humans, of *artificial algorithms* for the *calculation* of eigen-values or eigen-vectors. However, as already commented in Section 7.6, these artificial algorithms not necessarily represent the *spontaneous, intrinsic natural faculty* the perfect vapor is endowed with, by the relativistic nature of the elementary processes of quantum exchange, to move towards its equilibrium state.

The merge of creation and annihilation into a single matrix reflects the tacit, although false, assumption that they are not stochastically independent. The foregoing considerations led me to blame this merge for the mistaken conclusion that quantum theory is unable to preview the time asymmetry of such natural processes.

> *Statement* § 39 *differs from Axiom 3, in that it assumes that the value* $\bar{\mathbf{r}}_\ell$ *is the result, not of an instantaneous (or almost so) collapse of the wave function of the cluster in the case of an observation or of a measurement, but after being recurrently modified by the incessant action of stochastic absorptions and emissions elementary processes, which conduct the system erratically towards its equilibrium state, independently of its initial state.*

7.7.1 Statistical equilibrium

As I have already shown [7]:

> *It is the persistent action of the stochastic processes of absorption and emission that lead the quantum system to its equilibrium state.*

The variations (6.12) of the actions are assumed to correspond to the three mutually independent stochastic phenomena involved in the absorption and emission of a photon, or *vice-versa*, depending on the system in focus, whether radiation itself, or the gas of material particles, characterized respectively by the variation of their actions,

$$\Delta\alpha = \Delta\alpha_q \qquad \text{and} \qquad \Delta\alpha^* = \Delta\alpha_p,$$

Hence the effects of the elementary processes of quantum exchange on the state of motion of the gas will be neutralized only statistically, when the *average actions* accumulated during these processes compensate each other, i.e., when they attain the following condition of stochastic equilibrium, which, according to the Law of Large Numbers, is attained only after the relaxation time has elapsed:

$$\langle\Delta\alpha\rangle_{\text{Relax}} = \langle\Delta\alpha^*\rangle_{\text{Relax}}. \tag{7.6}$$

> *Since expression* (7.6) *describes the thermodynamic equilibrium, it will be used in Section 8.3 to evaluate the entropy of the perfect vapor.*

We can then summarize the results above:

> *The connection of Planck's constant h with the imaginary part of the complex representation of the variation of action, gives physical meaning to both the constants, h and the imaginary unit ı, revealing the quantum-relativistic character of the elementary processes of quantum exchange, that correspond to the absorption and emission of quanta by the material particles, mathematically described by the non-commutative operators of the creation and annihilation.*

7.7.2 The $\mathfrak{L}$-phase as a "gas" of clusters

From the previous considerations, we propose a tentative description of the $\mathfrak{L}$-phase of the perfect vapor as a *gas* of certain entities, imagined as many-body systems, composed, in their turn, of particles of the perfect vapor "*entangled*" with each other, thus forming a many-body system.

> *An image of the $\mathfrak{L}$-phase of the perfect vapor can then be depicted as a random number $\mathbf{L}$ of clusters, where the cluster ℓ is a many-body system composed of a random number $\mathbf{r}_\ell$ of radicles of the perfect vapor, characterized by a quantum number ℓ.*

> *To describe the formalization of the abstract system of bosons, in terns of the random variables $\mathbf{L}$ and $\mathbf{r}_\ell$, in agreement with de the description of the current tenets of statistical mechanics,* BEFORE *apply it to the perfect vapor.*

The number radicles in the $\mathfrak{L}$-phase, in each instant, is therefore a random number $\mathbf{S_L}$, given by the sum,

$$\mathbf{S_L} = \mathbf{r}_1 + \mathbf{r}_2 + \cdots + \mathbf{r}_\ell \cdots + \mathbf{r_L}. \tag{7.7}$$

> *Equation* (7.7) *characterizes a compound process. If we denote by $\beta(s)$ the generating function (*GF*) of the probability distribution function (*PDF*) of the random variable $\mathbf{r}_\ell$, and by $g(s)$ the* GF *of the* PDF *of the random variable, $\mathbf{S_L}$, then its compound* PDF *is given $g(\beta(s))$* [30].

Furthermore, according to the definition § 12, this function is an exclusive function of θ. Hence, for $s = \theta$, we have,

$$g(s) = g(\beta(\theta)). \tag{7.8}$$

Chapter 8

Ladder Operators and Entropy

Summary

In this Chapter the particles in Brownian Movement are considered to be in persistent interaction with a heat reservoir.

This approach depends on the extension of Boltzmann's entropy to properly reflect the relativistic nature of the interaction processes, that are ruled by the *laws of change* determined by the Bose character of the agents defined by equations (6.8) and (6.9), and shown that they are responsible for the changes caused on the volume of the phase space.

8.1 The Bose character of radiation

It can be verified that:

> *Equations* (6.8) *and* (6.9) *are the* complex algebra representatives *of the creation and annihilation dimensionless operators* $\{\mathsf{a}^{\dagger}, \mathsf{a}\}$ *that characterize the Bose–Einstein statistics.*

Equations can be derived from (4.8) and (4.9), can be rewritten in the dimensionless form,

$$\frac{\Delta\alpha}{h} = \frac{\Delta mc}{h} + \imath, \tag{8.1}$$

$$\frac{\Delta\alpha^*}{h} = \frac{\Delta mc}{h} - \imath, \tag{8.2}$$

which reveals that the elementary processes of quantum exchange increase or decrease the dimension of the phase space by one quantum unit.

8.2 The interaction {matter ⇔ radiation}

To properly represent the action developed during the elementary processes of quantum exchange, we will adopt the complex quantities (8.1) and (8.2) to express both the inner and outer products in a single mathematical unit. It provides a clear differentiation between the variation of the action during these processes from its corresponding classical, expressed by inequality (5.9).

The volume of the phase space of the gas is then revealed to be represented by a complex number, thus extending the definition of Boltzmann's entropy. For the particles moving in the classical subspace of the phase space, $\Delta\alpha_j > h$, the entropy is given by

$$S_j = \ln\left(\Delta p_j \cdot \Delta q_j\right).$$

Denoting by $\Delta\alpha\left(\mathrm{a}^{\dagger}\right)$ and $\Delta\alpha\,(\mathrm{a})$ the variation of the action, generated by the operators (6.8) and (6.9). We can write the variation of the entropy by substituting the scalar by the scalar the complex logarithmic function (`Ln`) in the Boltzmann principle[1], when the gas absorbs or emits one quantum,

$$\mathsf{S}_k = \begin{cases} \mathrm{Ln}\left[\Delta\alpha_k\left(\mathrm{a}^{\dagger}\right)\right] & = \mathrm{Ln}\left[(\Delta p_k \cdot \Delta q_k) - \imath\,(\Delta p_k \times \Delta q_k)\right], \\ \mathrm{Ln}\left[\Delta\alpha_k(\mathrm{a})\right] & = \mathrm{Ln}\left[(\Delta p_k \cdot \Delta q_k) + \imath\,(\Delta p_k \times \Delta q_k)\right]. \end{cases}$$

In summary,

$$S_j = \ln\left(\Delta p_j \cdot \Delta q_j\right), \qquad \text{for} \quad \left(\Delta\alpha_j > h\right), \tag{8.3}$$

$$\mathsf{S}_k = \left.\begin{cases} \mathrm{Ln}\left[\Delta\alpha_k\left(\mathrm{a}^{\dagger}\right)\right] & = \mathrm{Ln}\left[(\Delta p_k \cdot \Delta q_k) - \imath\,(\Delta p_k \times \Delta q_k)\right] \\ \mathrm{Ln}\left[\Delta\alpha_k(\mathrm{a})\right] & = \mathrm{Ln}\left[(\Delta p_k \cdot \Delta q_k) + \imath\,(\Delta p_k \times \Delta q_k)\right] \end{cases}\right\}, \qquad \text{for} \quad \left(\Delta\alpha_k = h\right), \tag{8.4}$$

8.3 Equilibrium formation processes

Since the elementary processes of quantum exchange involve *force-like agents* that cause the changes on the motions of the particles of the gas, we have some reason to believe that they are the main responsible for the processes of equilibrium formation in the perfect vapor. An amendment to Boltzmann principle, referring to the equilibrium condition, expressed in terms of the balance between absorptions and emissions of quanta by the particles of the perfect vapor, is here proposed.

---

[1] In the following expressions the superscripts c e q designate the classic e quantum behaviors, respectively. The signals of the equations (8.4) depend on the system to which they refer, if radiation or the gas.

The elementary processes of quantum exchange are the responsible for the variation of the *dimension* of the phase space. Since they are stochastic and independent, they cause a fluctuation of the volume of the phase space, that corresponds to the variation of the entropy of the perfect vapor.

> *The change of the entropy caused by the "combination" of the two opposite processes of absorption and emission, is given by the amount,*
>
> $$\mathrm{Ln}\left(\mathrm{a}_k^\dagger\right)-\mathrm{Ln}\left(\mathrm{a}_j\right)=\mathrm{Ln}\left[\frac{(p_k\cdot q_k)-\imath\,(p_k\times q_k)}{(p_j\cdot q_j)+\imath\,(p_j\times q_j)}\right]. \tag{8.5}$$

Denoting the quotient,

$$\vartheta=\frac{p\times q}{p\cdot q} \tag{8.6}$$

we can rewrite equation (8.5) in the dimensionless form,

$$\left(\frac{a_k^\dagger}{a_j}\right)=\frac{1-\imath\vartheta_k}{1+\imath\vartheta_j}. \tag{8.7}$$

Since the entropy of the perfect vapor is given by (3.2), equation (8.7) can be rewritten in terms of the single magnitude θ:

> *Both the quantities ϑ_k and ϑ_j are described by the same* PDF. *We can then replace the quotient $(1-\vartheta_k)\,/\,(\vartheta_j)$ by a function $g(\theta)$ of a single argument θ, and rewrite (8.7) in the form,*
>
> $$S=\imath\mathrm{Ln}\left(\frac{\langle a^\dagger\rangle}{\langle a\rangle}\right)=2\arctan\left(g(\theta)\right). \tag{8.8}$$

Equation (8.8) is insufficient to determine the entropy of the perfect vapor. As pointed out in Section 2.3.1, the functional form of $g(\theta)$ depends on the matching of two frequency spectra, namely, of radiation and of the characteristic of the chemical substance. Hence, we cannot predict the thermodynamic properties of the perfect vapor, unless the frequency spectrum of the radiation with which it interacts is given. To properly characterize its thermodynamic properties, it is convenient to establish, by *convention*, a *standard radiation* spectrum, an issue that is the subject of Chapter 9.

8.4 Potential Theory of the Equilibrium in the $\mathfrak{L}$-phase

According to Krönig's description of the motion of a particle in the gas, the trajectory of a particle between two consecutive elastic collisions is inertial, with length

Δq and constant momentum p. Such edge F of the polygonal line, $\cdots$ FCFCF $\cdots$, can be represented by a free (slide) vector, as in Perrin's analysis of the Brownian movement [20]:

> *Une autre vérification plus frappante encore, dont je dois l'idée à* Langevin, *consiste à transporter parallèlement à eux-mêmes, les déplacements horizontaux observés, de façon à leur donner une origine commune (...) Cela revient à considérer des grains qui auraient même point de départ.*

After sliding to the point $+\imath$ of the complex plane the origins of the free vectors corresponding to the actions developed by a particle immediately after the absorption of a quantum from radiation; and sliding to the point $-\imath$ of such plane the end points of the free vectors immediately before the emission of one quantum, we can recognize in equation (8.5) the representation of the flux of quanta in the perfect vapor, with a *source* in the point $+\imath$ and a *sink* in the point $-\imath$ of the complex plane.

> *The description of such flux can be seen in fig. 111, Ch* III *§2, p. 252* [31].

Chapter 9

Principle of Frequency Matching

Summary

This Chapter treats of the incapacity of *The Kinetic Theory of the Perfect Vapor* to provide a complete description of the vapor state of a chemical substance.

In the previous Chapters I showed that Bartoli's reformulation of thermodynamics allows obtain a relativistic kinetic theory of a system of material particles, denoted by the *Perfect Vapor*. The quantum hypothesis was then introduced as a consequence of the taut constraint $\Delta p \Delta q \geq h$, which allowed derive its thermodynamic representation in terms of the ladder operators. With the reinterpretation of the relativistic role of time in quantum theory it became possible to explain the time asymmetry in thermodynamic phenomena, and reveal the hidden forces involved in the entropy formation.

However, this approach does not provide the theoretical elements required to predict the set of clusters that compose the $\mathfrak{L}$-phase of any given chemical substance, i.e., its *liquid phase*. As can be easily seen, the variety of clusters existing in the $\mathfrak{L}$-phase, are given by the molecular structure of the radicle, itself, and of the variety of clusters it can engender.

The liquid phase is still largely a *terra incognita*. The entropy of a chemical substance can be, in principle, inferred from their absorption-emission spectra. However, the hypotheses proposed to explain the liquefaction processes, notably, clustering and nucleation, lead to different theories of entropy formation.

The analyses of rotations and vibrations of parts of the radicles and clusters constrained by the different articulation points formed inside the molecules, have been the main sources for predicting the absorption/emission spectra of the vapor. As pointed out in § 10, neither these procedures, nor the methods to calculate the contribution of nucleation, formulated by Kelvin and Gibbs, shown to be in conflict [32], can explain the origin of the term $f_\sigma(\theta)$ in the EOS of the perfect vapor.

9.1 Incompleteness of thermodynamics

With the development of spectroscopy the measurements of the frequencies or wavelengths of radiation became subject of intense examination, which led to the representation of the hydrogen series in terms of functions of integer numbers by Balmer. After Bohr proposed a theory of the hydrogen atom capable to derive the Rydberg well known formula, $\nu = cR\left(\frac{1}{n^2} - \frac{1}{k^2}\right)$ from few postulates, the empirical knowledge accumulated by spectroscopy found a speculative explanation, expressed in terms of the quantities in Bohr's theoretical redefinition of Rydberg constant, $R = \frac{m_H e^4}{4\pi c h^2}$, where m_H is the mass of hydrogen. The measurement of the numeric values of these constants, characteristic of atomic phenomena, were obtained by methods independent of spectroscopic analysis, thus representing a major breakthrough in the empirical foundations of quantum theory.

9.2 Varieties of Spectra

Except for the particular cases, such as the black-body radiation, we cannot preview the thermodynamic properties of an arbitrary radiation or of any given chemical substance, unless their respective frequencies spectra are given.

To characterize the thermodynamic properties of a chemical substance, a convention is required, by choosing a *standard*, for instance, the spectrum of the black-body radiation, as arbitrarily adopted in this Chapter.

The indeterminacy of the entropy of the perfect vapor persists even in the equilibrium equation (8.8), which remains unknown until the generating function $g(\theta)$, is given. As pointed out in Section 2.3.1, that function depends on the matching of the two frequency spectra that characterize the radiation and the chemical substance.

9.3 Frequency spectrum of a discrete fluid

Kirchhoff's approach to spectroscopy revealed that the character that differentiates one chemical element from the others in the periodic table is its frequency spectrum, which was later shown to be determined by the set of its quantum states.

This same character was shown to hold for chemical substances, i.e., the frequency spectrum is an individual identity of each substance. Hence, the description of the thermodynamic state of a chemical substance is incomplete until its *characteristic frequency spectrum* is known.

9.3.1 Metastable States

When black-body radiation interacts with a chemical substance the latter will be eventually conducted to its fundamental state of *stable* equilibrium, under the quantum taut constraint. The spectrum of a different radiation might neither cause any change in the thermodynamic system, nor lead it to its fundamental state of equilibrium. It can, instead, conduct the system to some state of *metastable equilibrium*.

> *The specification of the radiation spectrum is particularly important when the chemical substance can be found in a variety of metastable states, as it happens with clouds in the atmosphere. Meteorological observation revealed that dry air is transparent to most frequencies of solar radiation, though sensitive to the heat emitted from the surface of earth, that functions as a geographically distributed set of frequency transducers, thus leading to the multiplicity of metastable cloud formations observed.*

9.4 The principle of reciprocity

According to the *Principle of Conservation of Complex Action* (Section 4.1), we can conclude that the absorption and emission processes are reciprocal.

Besides justifying the Bose character of equations (6.8) and (6.9), this principle allows develop the analogical reciprocity between the $\mathfrak{L}$-phase of the perfect vapor and the quantum harmonic oscillator, which characterizes radiation.

However, due to its abstract character, we are allowed to specify neither the molecular structure of the radicles of the perfect vapor, nor the structure of the clusters they engender in the $\mathfrak{L}$-phase. Nevertheless, by assuming the hypotheses advanced by Einstein in his 1917 paper, we can conclude that the processes in which photons and the elements of its phases interact, are reciprocal, according to § 20.

> *Considering the mutual independence of the absorption and emission pro-*

> *cesses, equilibrium is settled only when the equation* (7.6) *is satisfied*[1],
>
> $$\frac{\langle \Delta\alpha \rangle}{\langle \Delta\alpha^* \rangle} \approx 1. \qquad (9.1)$$

With these considerations we can take a step towards the statistical equilibrium of the population of particles in the $\mathfrak{L}$-phase of the perfect vapor.

9.5 The principle of the frequency matching

The behavior of a chemical substance in a given environment can only be determined if both, the frequency spectrum characteristic of the substance, and that of the incident radiation, are given.

> *The thermodynamic characterization of radiation confined inside a fixed volume is given by Wien's displacement law (or equation* (2.5)*, derived in Chapter 2), expressed in terms of an indeterminate function* $f(u)$ *of the argument*
>
> $$u_{hc} = \frac{h\nu}{kT} = \frac{hc}{\lambda kT} \propto \frac{hc}{kT}\sqrt[3]{\frac{N}{V}}.$$
>
> *Note that Wien's formula suggests that thermodynamics predicts the existence of a variety of spectra described by the same argument* u_{hc}.

9.5.1 The algebra of frequency matching

By adopting the symbols of set theory algebra, let us denote by $\mathbb{R}$ the frequency spectrum of the environmental radiation, and by $\mathbb{L}$ the frequency spectrum of the chemical substance in consideration.

We then define the *susceptibility* $\mathbb{S}$ of the given substance to this particular radiation by the set *intersection*, $\mathbb{S} = \mathbb{R} \cap \mathbb{L}$.

When the $\mathbb{S} \neq \emptyset$, we say that the substance is *susceptible* to radiation $\mathfrak{R}$, otherwise, that it is *transparent* to it.

9.6 The black-body radiation as a standard

Recall that a *thermal reservoir* is defined in classical thermodynamics as a system endowed with infinite heat capacity, characterized exclusively by its temperature, which is maintained constant whatever the changes that occur in the system with

---

[1] The symbol "$\approx$" is here used to denote the fluctuation between the values of the quantities involved.

which it interacts. It is known, however, that the heating process of a chemical substance is determined, not only by the temperature of the heat source, but also by its sensitivity to the frequencies of the radiation spectrum.

Hence, to be complete, the definition of the *heat bath* in thermodynamics must specify its frequency spectrum. Thermodynamic practice therefore had, I presume, to adopt tacitly as the *standard radiation spectrum*, that of the *black-body radiation*.

9.6.1 The Indeterminate character of Wien displacement law

The argument u_{hc} plays the role of a *functional of the probability distribution function* of the environmental radiation. According to this formula the frequency spectrum of heat is indeterminate. Hence, it must be treated as arbitrary and specified for each particular case studied. Planck determined the functional form of $f(u_{hc})$, which is exclusive of the particular case of black-body radiation.

Being a functional of Wien's[2] chromatic distribution, except for the black-body, temperature alone cannot determine the frequency spectrum of radiation. However, I presume, it has been a common practice to *confuse* the electromagnetic radiation with the set of Planck's resonators, and to adopt its frequency spectrum as *paradigmatic* for the characterization of chemical elements and chemical substances in thermodynamic analysis.

9.6.2 The equations of the Planck resonator

The PDF of the occupancy number random variable $\mathbf{r}_\ell$ is well known from the description of radiation in terms of the quantum harmonic oscillator. Its generating function is usually expressed in the form of its partition function[3],

$$\beta(s) = \frac{1}{2}\,\mathrm{csch}\left(\frac{h\nu}{2kT}\right). \tag{9.2}$$

This implicit "standard", however, is unrealistic, for there is an infinite variety of radiation spectra, depending on the physical nature of their sources. A complete description of radiation for thermodynamical analysis requires the knowledge of the particular spectrum of the radiation with which the specific system under analysis interacts. Furthermore, no chemical substance is susceptible to the frequencies outside the set of the spectrum determined by its molecular structure.

---

[2] Planck's distribution is a limit instance of Wien's indeterminate spectrum.

[3] Recall Section 2.3, where it is shown that the characteristic argument of the entropy of radiation is $\varsigma = hc$, so that $s = \frac{h\nu}{2kT}$.

9.7 Migration of radicles between phases

In the finite time during which the perfect vapor exchanges a quantum with radiation, one of its molecules, under the action of the laws of the creation–annihilation operators, is exchanged between the phases $\mathfrak{G}$ and $\mathfrak{L}$. Such processes are recurrent, leading the perfect vapor to equilibrium, when absorptions and emissions compensate each other.

The interpretation of the creation-annihilation operators cannot therefore be taken literally as the agents of a process during which a particle is created from nothing, or annihilated to nothing, but the agents that cause the exchange of a particle between the $\mathfrak{G}$ and the $\mathfrak{L}$-phases (See § 23 and § 24).

In the exchange of heat between matter and radiation, the photon that is absorbed by the gas was emitted by the heat reservoir, and the photon emitted by the gas is absorbed by that reservoir. We can then conclude that the occupation of photons in quantum states of radiation correspond *reciprocally* to the occupation of particles of the gas in the $\mathfrak{L}$-phase, i.e., the form of the partition function for particles in the cluster of quantum number ℓ is the *same* for photons in the quantum state ℓ, however with a different argument s of the function $\beta(s)$ in (9.2), corresponding to particles with mass. We therefore put $s = \theta$, obtaining,

$$\beta(s) \Rightarrow \frac{1}{2}\,\mathrm{csch}\left(\frac{\theta}{2}\right), \tag{9.3}$$

as expected from definition § 12. Hence, the expression of the GF of the random variable $\mathbf{S_L}$ is given by,

$$g\left(\frac{1}{2}\,\mathrm{csch}\left(\frac{\theta}{2}\right)\right).$$

9.7.1 The compound generating function of the $\mathfrak{L}$-phase

The generating function $g(s)$ of the random variable $\mathbf{S_L}$, according to the theory of compound distribution processes, is given by the generating function of the $\mathfrak{L}$-phase of the perfect vapor, namely, the extended Boltzmann entropy, (8.8), discussed in Section 7.7.2.

Due to the equation (2.7) that defines the entropy of the perfect vapor for $\varsigma = h$, we conclude that the quantity ϑ, defined in (8.6), must be expressed in terms of a function $\vartheta(\theta)$ of θ. Hence, the relation (8.8) can be written in the form,

$$\arctan\left(\vartheta_j\right) = \arctan\left(\vartheta(\theta)\right).$$

In the particular case in which the perfect vapor is under the influence of blackbody radiation, the function $\vartheta(\theta)$ is given by (9.3), which gives the generating function of the thermodynamic properties of the perfect vapor's $\mathfrak{L}$-phase, that, in its turn, describes a compound process,

$$\frac{S_{\mathfrak{L}}}{k} = \left\{ \left(j + \frac{1}{2} \right) \pi - \arctan \left[2 \sinh \left(\frac{\theta}{2} \right) \right] \right\}, \tag{9.4}$$

where the integers $j = 1, 2, \cdots$ might represent the contribution of some yet unexplained phenomenon.

9.8 The equation of state of the perfect vapor

From the entropy (9.4) it was possible to derive the function,

$$f(\theta) = \frac{\theta}{2} \operatorname{sech} \left(\frac{\theta}{2} \right), \tag{9.5}$$

which appears in the equation of state (3.4).

As shown in Appendix D, after removing the influence of the supposedly contribution of the *nucleation processes* that give rise to the $\mathfrak{L}$ (liquid)-phase from steam pVT data, their adherence to a single curve in the $\theta \times \zeta$ plane (fig. D.2) is noteworthy. It is then justified to confront the theoretical expression (9.5) with these data.

Since the theoretical function $f(\theta)$ is an odd function[4], it can explain the remarkable half-turn symmetry observed in the vapor region of steam. Besides, it reveals that the observed adherence to a single curve, depends on the translation of the origin of (9.5) to the center $[\theta_m, \zeta_m]$ of symmetry in the experimental curve, localized in the mid-point of the segment AB. The non-negligible dispersion of points around the point $B = [\theta^*, \zeta^*]$, and the low accuracy method used for its determination impedes the accurate location of this point in the graphics.

With these empirical evidences, the entropy (9.4) of the perfect vapor, can be rewritten in the form,

$$\frac{S_{\mathfrak{L}}}{k} = \left\{ \left(j + \frac{1}{2} \right) \pi - \arctan \left[2 \sinh \left(\frac{\theta - \theta_m}{2} \right) \right] \right\},$$

where j is a constant whose presence, although mathematically justified, could not be explained by me.

---

[4] This finding might justify the notion of quasi-particles in dealing with certain many-body problems.

Chapter 10

Amendments to The Axioms of Quantum Mechanics

In this Chapter it is intended to show how the present kinetic theory of the perfect vapor can contribute to our understanding of the interaction of matter and radiation. Our purpose is to improve the empirical contents of the axioms of quantum theory to more properly support the speculative assumptions, and avoid confusion and controversy.

10.1 Epistemological order of physical knowledge

In the following we summarize our attempts to reorder the epistemological chain that connects observation to quantum theory, after the results hitherto obtained:

1. In Section 4.2.1 its was shown that the analysis of the equilibrium between the perfect vapor and radiation according to Bartoli thermodynamics reveals that its corresponding kinetic theory, constrained by the second law, is relativistic.

2. In Section 5.8 it was shown that the conjugation process, which takes place during an emission of quanta by a cluster, endows Planck constant with the faculties of a (Hilbertian) differential operator, which leads to restate the Axiom 5 of quantum theory in terms of these operators.

3. In Section 6.2 the relativistic energy conversion processes were shown to obey the ladder operators rules.

4. In Chapter 8 the main departure of the thermodynamic behavior of the perfect vapor from the ideal gas law was determined.

5. In Appendix C it was shown how the ladder operators determine the laws of change of the probability distribution functions of the occupancy numbers of the clusters that compose que $\mathfrak{L}$-phase of the perfect vapor.

6. Furthermore, the discrete nature of the taut constraints $\Delta p \Delta q \geq h$ imposed on the motion of the molecules, revealed by spectroscopy, must be added to complete both the thermodynamic and the kinetic theoretical description of the perfect vapor, a target still unattained.

10.2 The Axioms of quantum theory

Before presenting the amendments suggested by this approach to the axioms of quantum theory, let us recall their current formulations as proposed by Chpolski [18]:

> **Axiom 1** *Les états du système de la mécanique quantique se décrivent par de vecteurs* $|\psi\rangle$ *de l'espace hilbertien abstrait.*
>
> **Axiom 2** *Aux variables dynamiques de la mécanique quantique on fait correspondre des opérateurs linéaires et hermitiens* F *agissant dans l'espace hilbertien des vecteurs d'états.*
>
> **Axiom 3** *Les seuls résultats possibles des mesures de la variable dynamique donné dans l'état défini du sytème sont les valeurs propres de l'opérateur associé* F.
>
> **Axiom 4** *La probabilité* $W_\psi(f)$ *d'obtenir par mesure la variable dynamique* F *dans l'état* $|\psi\rangle$ *la valeur est donné par la formule* $W_\psi(f) = |\langle f\rangle|^2$ *où* f *est le vecteur propre de l'opérateur* F *appartenant à la valeur propre* f.
>
> **Axiom 5** *Aux coordonnées* x_j *et aux impulsions* p_j *(*j *étant le numéro du degré de liberté) correspondent dans le système de la mécanique quantique les opérateurs* $\mathscr{X}_j$ *et* $\mathscr{P}_j$ *satisfaisant aux relations de commutation*
>
> $$\mathscr{X}_j \mathscr{P}_k - \mathscr{P}_k \mathscr{X}_j = \imath\hbar\delta_{jk}\mathbf{I} \tag{10.1}$$
>
> *où* $\hbar$ *est la constante de Planck.*

10.3 The Amendments to the Axioms

The central point of the present reformulation is in the Axiom 5, where the three main foundational elements of quantum mechanics, namely, (a) the Planck constant, (b) the imaginary unit $\imath$, and (c) the commutation rule, are introduced. As shown in Section 4.2.1, both the imaginary unit and the commutation rule, essential to give thermodynamic and chemical meanings to the creation and annihilation operators, derive from special relativity. The only addition to the relativistic formulation prescribed in equations (4.8) and (4.9) required to introduce the Planck constant, is the *taut constraint*, $\Delta p \Delta q \geq h$, which enters together with the imaginary unit in (10.1).

From the above amendment to Axiom 5, Axiom 1 derives as a corollary.

Axiom 1 is necessary for the formulation of the differential equations of quantum mechanics. The above mentioned amendment to Axiom 5 introduces the most fundamental evidence (well confirmed by experience), that the universe where the elementary microscopic processes evolve, has the Minkowskian structure of space-time.

The wave function $\Psi(x,t)$, can always be decomposed into two [6], $\Psi(x,t) = \varphi(t)\psi(x)$. With the above interpretation, the functions $\varphi(t)$ and $\psi(x)$ acquire the following meanings:

> *The time variable function $\varphi(t)$, that is affected by the imaginary unit "$\imath$", will be here interpreted as mere manifestation of the relativistic nature of the state transition phenomenon of absorption and emission of radiation by the particles of the gas. The function $\phi(t)$ is then replaced by the equations of the Markovian birth and death stochastic processes, whose laws of change are derived from the conditional probabilities specified by the creation and annihilation operators, as is currently derived from coordinate alone Schrödinger equation of the harmonic oscillator.*

As shown in Chapter 3, the $\mathfrak{G}$-phase is defined in a time-varying Euclidean space, described by classical mechanics. The clusters in the $\mathfrak{L}$-phase were shown to be stationary systems, each one described by a single time-independent (space only) wave function, i.e., a *quantum many-radicle system*, defined in the Minkowski *timeless 4-space* domain, thereby non-observable.

Observable inferences about the internal structure of the quantum many-radicle system becomes possible only when a transient elementary processes of quantum exchange occurs, during which a chemical-like reaction takes place. Such process, ruled by the laws of absorption and emission, causes a change on the population of particles in the phases of the thermodynamic system. Since these processes cause corresponding changes on the thermodynamic state of the system, these phenomena become, in principle, observable.

This possibility exempts mechanics of molecular systems from having recourse to the interference of observers or instruments, provided experimentalists are entrusted to avoid their influences.

Axiom 2

This postulate is the consequence of the new type of limit introduced in Section 5.8. The mentioned *correspondence* is no longer stated dogmatically, but, instead, as the result of this new type of limit that has been implicitly smuggled to differential calculus by the current tenets of quantum mechanics.

The Taut Constraints

The *taut constraints*, defined by relations (5.4)-(5.5), are interpreted according to the unconventional limit transformations (5.14) that imply the existence of a PDE, namely, Schrödinger equation, that couples (conjugates) p with q.

The current understanding of a chemical reaction imposes on any theory of quantum phenomena to recognize that classical degrees of freedom, namely position and momentum, are not persistent: the reactants' degrees of freedom are destroyed and new ones, with *unpredictable* values, are created in their products (See § 23 and § 24). These processes give rise to statistical indistinguishability and Pauli exclusion rules in many-body quantum systems.

Axiom 3

The statement "*The only results of the measurement of the dynamic variable*" in this axiom, is replaced by "*The results of the measurements of the dynamic thermodynamic variable in the equilibrium*".

The current formulation of Axiom 3 refers to an unspecified artificial method of calculus of these values to be performed by physicists. It does not describes the real processes that occur in nature. In the latter, equilibrium formation is described by a natural nondeterministic procedure of calculus of eigen-values, that results of the reiteration of three stochastic, mutually independent, processes, described by the ladder operators which, in their turn, as expressed in terms of conditional probabilities. As I have shown [7], these uncorrelated processes lead the systems of Bose, Fermi, and Boltzmann particles to converge *asymptotically*, with Arrhenius rates, to the mentioned eigen-values, after elapsed a finite time known in thermodynamics as the *relaxation time*.

As a corollary of this axiom it follows that the indistinguishability and Pauli exclusion principles, hitherto assumed to be ontological properties of many-body quantum systems, can be reinterpreted as mere conditions of thermodynamic equilibrium. When a quantum system is removed from its equilibrium state, its particles can be transiently distinguished, and in a given quantum state more than one Fermi particle can transiently be found. We must refer to the equilibrium phenomena, not as that of absolute indistinguishability, but as *statistical indistinguishability* in persistent fluctuation.

Axiom 4

Similarly, this axiom should not be interpreted as the description of the phenomenon, but as of the artificial algorithm of calculus of the *conditional probabilities* whose asymptotic values are given by the mentioned eigen-values.

Further Comments on Axiom 5

Finally, in the amended version of Axiom 5, Planck's constant is redefined as an *imaginary* constant, whose empirical origin is determined by the intrinsically relativistic nature of the quantum phenomena, described in Minkowski formalism, thus giving a reliable empirical content that is missing in the current formulation of Axiom 1, whose amended version, here proposed, turns it a mere corollary of the amended Axiom 5.

The non commutative relation (10.1) impedes the acknowledgement the algebra of complex representation of ladder operators as a field, for the product $(x+\imath y)(x-\imath y)$ correspond to no natural process, as assumed in § 31, and in Section 6.3. It is introduced in quantum theory by the *new limit rule* (5.14) to describe the action of the *taut constraints*

$$\Delta p \Delta q \geq h, \quad \Delta E \Delta t \geq h, \tag{10.2}$$

on the state of motion of the particles of a chemical substance. The mathematical representation (6.8) and (6.9) of the ladder operators in terms of dimensionless complex numbers are derived in Section 6.2.

Appendix A

Classical Phase Space

Summary

Classical mechanics describes the motion of bodies in the Newtonian universe, which is devoid of electromagnetic radiation. During its motion, a system of particles preserves certain collective quantities, thereby important to be taken into account in the formulation of thermodynamics.

Liouville's theorem assumes that the Boltzmann principle is valid for hypothetical *classical motions*, thus leading to a faulty[1] definition of *entropy*, as an invariant magnitude characteristic of a system of particles.

Thermodynamics imposes on entropy the character of additivity, which requires the existence of an universal constant with the dimensions of action to render its argument dimensionless.

Furthermore, it states that the entropy of a gas is variable: its value changes according to the second law, when its material constituent particles interact with electromagnetic radiation. Thermodynamic phase transitions of chemical substances under the action of heat can only be explained by kinetic theory if it is assumed that the states of motion of its particles are, themselves, susceptible to heat.

A.1 Inadequacy of a Classical kinetic theory of gases

Chemical substances can be found in different metastable states. The varieties of atmospheric clouds and of snowflakes are evidences of the existence of such

---

[1] Some of the properties of entropy are shared with that which can be derived from Liouville's theorem. Although devoid of thermodynamic faculties, the definition here introduced might be useful for pedagogical purposes, mainly by showing how the logarithm function arises naturally.

states in water, and of the variety of their condensation and solidification paths. This fact has raised hypotheses about the existence of a *memory capacity* of water to retain the vestiges of the road it takes towards the state in which the substance is found in any equilibrium state, whether stable or metastable.

Observation has revealed that the evolution of the macroscopic state of a gas described by the thermodynamic magnitudes, such as pressure, volume, temperature, etc., culminates in a stationary state of *thermodynamic equilibrium*. In the formulation of the present theory, as has been usual in kinetic theory and statistical mechanics, we adopt the simplifying hypothesis according to which the discrete fluid considered has a single equilibrium state. With this assumption we can state:

§ 40 *The final state of the system of particles that compose the discrete fluid is* independent *of its initial state.*

Recall that the motion of the particles described by classical mechanics obeys the following principle:

§ 41 (Principe de Déterminisme de Newton)
L'état initial d'un système méchanique (l'ensemble des positions et des vitesses de ses points à une date quelconque) définit de façon unique *le futur de son mouvement* [33].

The striking contradiction between the empirical revelation § 40 and the theoretical principle § 41 evidences that classical mechanics cannot explain the motion of the particles of the gas towards its thermodynamic equilibrium. The generalization of this contradiction to substances liable to fall into metastable states of equilibrium is straightforward.

The principle of molecular chaos

To circumvent the incapacity of classical mechanics to describe thermodynamic phenomena, Maxwell and Boltzmann found that, by assuming the *Principle of Molecular Chaos*, and having recourse to probability theory, specially to the *Law of Large Numbers* and the *de Moivre-Laplace Theorem*, the average values of velocities and kinetic energies of the particles of a system could be obtained. This approach established another research program, known as *Statistical Mechanics*.

Comments on Order and Chaos

In commenting about the philosophical opposition of *Chaos* to *Order*, Bridgman pointed out that the notion of order requires an explicit reference to a *context*. It is timely to recall his citation [26]:

> ”*G. N. Lewis has justly pointed out that it could be possible to formulate the rules of some card game so that any arrangement of the cards whatsoever would be a regular arrangement from the point of view of that game*”.
>
> *In my opinion* [34]*, this philosophic issue is connected with the notion of* information*, where connection between an emitter and a receiver, required to give meaning to messages, substantiates the* context *as a necessity. It is remarkable that none of these notions has any meaning outside the biosphere, which led me to conclude that information is an epistemological primitive of Biology. In fact, no information processor is found outside the biosphere*[2]*. Neither Mathematics, nor Physics, can give it a cogent notion, capable to scan the variety of fields in which its meaning is required to characterize.*

The conundrum of entropy

An inquire on the kinetics of the perfect vapor is justified by the incapacity of statistical mechanics to give cogent definitions of temperature and heat, and particularly, by the debatable attempt to explain the asymmetry of time in terms of the ill-defined *Principle of the Most Probable Configuration*. Boltzmann, himself, objected to this formulation [22]:

> *“I do not think that one is justified in accepting this result without reservation as something evident, at least not until an exact definition of what we are to understand by the term ‘most probable distribution’ has been given”.*

The objection raised by Boltzmann is cogent. While it is possible to assign a meaning to the statement *most probable value* to a set of scalar quantities, defined by the values that a *variable* can take — in this case, a *random variable* — no cogent meaning can be assigned to the statement *most probable distribution*, for “distribution” describes the *von Mises sample space* of a statistical experiment [30]. The drawbacks of the *sample space approach* to endow a system of particles with thermodynamic faculties are discussed in Appendix B.

Such confusion led many physicists and philosophers of science to feel uneasy in acknowledging statistical mechanics as a fundamental theory, neither they seem to feel more comfortable in treating thermodynamics as a heretical theory to be banished from physics.

Conformity to the official canons, however, has exerted a strong influence in the support of the set of axioms on which statistical mechanics is founded, namely,

---

[2] To those critics who might argue: “But neither a computer, nor a robot are a living beings!”, I would answer: “Yes, but their ancestors are. Hence, they are members of the phylogenetic tree.”

the "principles" of *Boltzmann, Indistinguishability, Pauli's exclusion*, and the already mentioned *Principle of the Most Probable Configuration*. Such theoretical program, known as the *reduction of thermodynamics to statistical mechanics*, however, seems to be far from unanimity [35],[36]. A way out this conundrum, which requires slight amendments to the quantum axioms discussed in Chapter 10, is briefly reviewed in Appendix C.

A.2 The pioneer's approaches

Once convinced that there is no classical explanation of the equilibrium formation processes that occur in a real gas, the pioneers of the kinetic theory of gases — presumably inspired in the Atomistic Doctrine of the Greek philosophers Leucipus and Democritus, and propagated by Lucretius' poem *De Rerum Natura* — attempted to find an explanation of the equilibrium stationary state in terms of the notion of the *chaotic motion of atoms*.

The incorporation of the notion of chaos in kinetic theory opened a new road to the study of the properties of gases. Although useless to describe the transient processes that lead the gas to the state of thermodynamic equilibrium, it was shown to be specially appropriate for the study of equilibrium itself. The purpose of kinetic theory became, therefore, to seek not a detailed description of the trajectories of its particles, but, instead, the thermodynamic properties of gases (pressure, temperature, etc.), and their correlations, in the equilibrium.

The notion of chaotic motion presumably led Maxwell and Boltzmann to regard the particles of the gas as the *moving pieces* of a *game of chance*, such as dice throwing, coins tossing, or cards shuffling. They might have realized that taking this road it would be possible to apply the findings of Probability Theory to the study of the motion of particles in the thermodynamic equilibrium.

This approach led to the Boltzmann principle that equates the *phase space* of the mechanical system of particles to the *sample space* notion of Probability Theory, thereby anticipating the notion of entropy defined in statistical mechanics. This theory, however, does not explain how the imposition of the random behavior in it particles, endows the gas with susceptibility to radiation.

A.3 The Boltzmann principle

The Boltzmann principle presupposes the following hypotheses:

> *Sample Space.* In thermodynamic equilibrium the *phase space*, defined according to Liouville's theorem § 42, can be redefined as a

Sample Space of probability theory, thereby allowing, redefine the *entropy* of a system of particles in terms of classical magnitudes.

Asymptotic Conditions. Thermodynamic equilibrium is characterized by the asymtotic conditions established in proposition § 43.

Coordinates. (In the absence of a gravitational field), the PDF of the *coordinates* of a particle in any direction of the space is *uniform* in the whole of the extension of the volume V occupied by the gas.

Velocities. (In the absence of a gravitational field), the PDF of the *velocities* is characterized by the asymptotic behavior of the random processes, whose Gaussian distribution is given by the *de Moivre-Laplace* theorem, whose first moment is zero (the gas is assumed to be at rest in the laboratory) and its second moment is determined by the mean value of the energy (2.1) of the gas.

From the foregoing hypotheses Maxwell and Boltzmann could derive the following macroscopic (hence, thermodynamic) properties of the system of identical particles of mass m: (a) the density of the gas, given by $\frac{Nm}{V}$; (b) the average energy, $\mathscr{E}/N$; (c) the average momentum, $\sqrt{2\pi mkT}$; and (d) the *extension-in-phase* (or volume of the phase space), given by the integral [23].

$$\Omega = \int \cdots \int dp_1 \cdots dp_n dq_1 \cdots dq_n. \tag{A1}$$

The angular momentum of the elementary particles (atoms) is usually neglected, except in the case of polyatomic molecules, when they are expressed in terms of their classical moments of inertia.

A.3.1 The mechanical meaning of temperature

Statistical mechanics adopts, as an axiom, the Boltzmann principle, that defines the logarithm of the volume Ω of the phase space as the mechanical representative of the entropy of the system. Being the conjugate of entropy, one might be persuaded that temperature acquires thereby a mechanical meaning. It is here intended to show that, instead, the physical meaning of temperature is given by the way heat is defined.

Without any mention to heat, the very idea of temperature behind the Boltzmann principle is merely formal, devoid of physical meaning, for it does not lead to the same consequences previewed by the second law of thermodynamics, specially the spontaneous tendency of the gas to move towards its equilibrium state.

To circumvent this limitation, an amendment was added to the Boltzmann principle, namely, that the system moves towards its state of "Most Probable Distribution". In Appendix B an approach to the time-dependent equilibrium formation process, that is independent of the debatable *Most Probable Distribution Principle*, is proposed.

A.4 Many-body problem in classical mechanics

The inquiries on the theoretical methods to evaluate the thermodynamic properties of the gases started with the confirmation that the *discrete fluid* is an instance of the *problem of N bodies*, formulated in the beginnings of Newton's gravitation theory, then known as the *Lunar Theory*[3]:

> *To determine the trajectories of the Moon, the Earth and the Sun moving under mutual gravitational attraction.*

It was found possible to simplify the problem by approaching it with lesser ambition: instead of seeking for trajectories one might be satisfied with study the simpler case, namely, the thermodynamic equilibrium. In the development of Newtonian mechanics, four theorems referring to characteristic collective magnitudes — hence thermodynamic — of a system of particles have been proved. Three of them refer to the conservation of *energy*, *momentum*, and *angular moment*. The fourth, which is usually detached from these three in the treatises on Classical Mechanics, is *Liouville's theorem* that establishes the invariance of the volume Ω of the phase space of a system. Gibbs stated this theorem (without mentioning its author), in the following statement [23]:

§ 42 (Conservation of the Extension-in-Phase)
When the phases bounding any extension-in-phase vary in the course of time according to the dynamical laws of a system subject to forces that are functions of the coordinates either alone or with the time, the value of the extension-in-phase thus bounded remains constant. In this form the principle may be called the principle of conservation of extension-in-phase.

The notion of *phase space* might have suggested to Boltzmann that a definition of entropy can be derived from Liouville's theorem[4] (Statement § 16 in [33]),

---

[3] Though sought by the most eminent mathematicians, no exact finite algorithm was found to describe these trajectories.

[4] There are doubts about the original author of this theorem [37].

reveals the existence of an *invariant magnitude* in the motion of Newtonian particles in a *space devoid of electromagnetic radiation*, namely, the volume Ω of the *phase space* of that system.

Despite the inadequacy of Newtonian mechanics to describe the equilibrium state and its formation, it is legitimate to insist in a classical analysis of this motion, seeking, if not the for trajectories of the particles, at least for finding the conditions that impede Newtonian mechanics explain the formation of the thermodynamic equilibrium in gases.

It has been hitherto accepted that, according to Heisenberg uncertainty principle, the determination of the trajectories of real particles (atoms and molecules) in real gases has no physical meaning, and that the entropy of the gas — defined by the *Boltzmann principle* as the logarithm of the volume of the phase space — in opposition to the Liouville's theorem — is not preserved when the gas undergoes thermodynamic fluctuations in the equilibrium, not to say when it undergoes large scale thermodynamic transformations.

In Chapter 2 it was shown that the entropy of a discrete fluid of material particles is an exclusive function of the magnitude θ. Hence, one of the mechanical characteristic magnitudes of the gas, as imposed by the dimensionless requisite, has the dimension of *action*, there introduced together with Planck's constant, h.

Let us then review the notion of action that justifies the definition of entropy in classical mechanics, as suggested by Boltzmann and formulated by Planck [38].

A.5 The action in classical mechanics

In classical mechanics the *action* $\mathscr{A}$ occurs in two applications, where it is defined either by the line, or by a multiple integral. The line integral,

$$\Delta\mathscr{A}_A^B = \frac{1}{2}\int_A^B p\cdot dq, \tag{A2}$$

can be interpreted as the *evolution* that a mechanical system undergoes in traversing the trajectory between the points A and B of the Euclidean space. The interpretation of this integral is analogous to that of the *work* exerted by the force, $f = dp/dt$ in that trajectory, defined by the integral,

$$\Delta\mathscr{W}_A^B = \int_A^B \frac{dp}{dt}\cdot dq.$$

The other application of the action in classical mechanics is found in the definition (A1) of the *volume of the phase space*, inside which a degree of freedom of a mechanical system evolves, given by the double integral,

$$\Delta\mathscr{A} = \int_{p_A}^{p^B}\int_{q_A}^{q_B} dp\cdot dq, \tag{A3}$$

A.5.1 Ambiguity in the interpretation of action

Let us consider the differential expression of the energy E written in form,

$$dE = \frac{dp \cdot dq}{dt}, \tag{A4}$$

that has two distinct *ambiguous* meanings, either as the work of a force f, or as the kinetic energy $p^2/2m$,

$$\frac{dp \cdot dq}{dt} = \begin{cases} f \cdot dq, & \text{where} \quad f = \frac{dp}{dq}, \\ d\frac{p^2}{2m}, & \text{where} \quad p = m\frac{dq}{dt}. \end{cases} \tag{A5}$$

> *Ambiguity in expressions* (A5) *can only be eliminated in the scope of special relativity, where action, usually assumed to be a scalar, is redefined as a complex magnitude. The preliminary arguments that justify the relativistic redefinition of the phase space were introduced in Chapter 3.*

The main occurrence of the action in classical mechanics is in the formulation of Hamilton's *Principle of Least Action*, where it plays the role of a *condition*, rather than that of (a curious and perplexing [39]) *property* of the motion. As a condition, the numeric values it acquires are irrelevant; what matters in this application is that the time integral of the Lagrangian of motion is maximum or minimum.

With the revelation of the universal Planck's constant, however, the numerical value of action acquires crucial importance in the role it plays in the laws that rule the motion of atoms, molecules and subatomic particles, requiring redefine the mechanical action as a *dimensionless variable* by assuming the existence of a universal (Planck) constant, thereby endowing entropy with the additive property.

A.6 The entropy in classical mechanics

Let us consider the variation of the action

$$(\Delta\mathscr{A}_\ell)_A^B = \int_{p_\ell^A}^{p_\ell^B} \int_{q_\ell^A}^{q_\ell^B} dp_\ell \cdot dq_\ell,$$

developed by a particle with degrees of freedom $\{p_\ell, q_\ell\}$, as it moves from A to B in the free space.

Assuming that the motions of the F degrees of freedom of the system of particles are *mutually independent*, then the volume $\Delta\Omega$ of the *phase space* developed by a system of F particles, is defined by the multiple integral,

$$\Delta\Omega = \prod_{\ell=1}^{F} \int_{A_\ell}^{B_\ell} \mathrm{d}p_\ell \cdot \mathrm{d}q_\ell = \prod_{\ell=1}^{F} \int_{A_\ell}^{B_\ell} \mathrm{d}\alpha_\ell. \tag{A6}$$

The infinitesimal volume of the phase space, where the degrees of freedom p_ℓ, q_ℓ vary, can be rewritten in the form,

$$dp_\ell dq_\ell \Rightarrow d\alpha_\ell.$$

Rearranging its terms, we can rewrite (A6) in the form

$$d\Omega = \int_{A_\ell}^{B_\ell} \prod_{\ell=1}^{F} dp_\ell dq_\ell = \int_{A_\ell}^{B_\ell} \prod_{\ell=1}^{F} d\alpha_\ell. \tag{A7}$$

For a mechanical system of F mutually independent degrees of freedom composed of $N \geq F$ point-particles, taking into account the differentiation of a product,

$$d(uvw\cdots) = (uvw\cdots)\left(\frac{du}{u} + \frac{dv}{v} + \frac{dw}{w} + \cdots\right),$$

we can rewrite (A6) in the logarithmic form,

$$\mathrm{d}\sigma = \mathrm{d}\ln\Omega = \sum_{\ell=1}^{F} \mathrm{d}\ln(\alpha_\ell),$$

that defines the quantity σ. Let us recall Liouville's theorem:

> *A system of particles moving under the influence of forces defined by functions that depend exclusively on its coordinates, or also on the time, we can write:*
>
> $$S = k\sigma = k\ln\Omega = k\sum_{\ell=1}^{F} \ln(\alpha_\ell), \tag{A8}$$
>
> *were k is the Boltzmann constant, is an invariant quantity of motion.*

A.6.1 Classical entropy is non-additive

It is important to warn the reader that the entropy "'defined' in classical mechanics does not satisfy the dimensionlessness requisite (See Section 2.1.1).

While electromagnetic radiation can be ignored in the analysis of the motion of large (macroscopic) bodies, from Perrin's granules to planets, it must be taken into account when the bodies are microscopic, such as atoms or molecules.

Equation (A8) can be adopted as the *formal definition* of the *entropy* of the system considered. This definition is in agreement with Definition I of Newton's *Principia*, that discards, at the outset, any influence of thermal radiation on the motion of the parts of the discrete fluid.

> *Being the logarithm a transcendental function, to give it a physical meaning, we must assume that its argument is a dimensionless number. The way out this difficulty has been obtained in classical thermodynamics by adopting the definition of the relative entropy, defined by the variation it undergoes when the thermodynamic system evolves from a reference state 1 to an arbitrary state 2,*
>
> $$S_2 - S_1 = k \ln \frac{\Omega_2}{\Omega_1}, \tag{A9}$$
>
> *so that* Ω_2/Ω_1 *becomes dimensionless.*
>
> *However, since according to Liouville theorem,* $\Omega_1 = \Omega_2$*, classical entropy is always zero.*
>
> *The impossibility to form a dimensionless number with the quantities* Ω_1 *and* Ω_2 *in classical mechanics, impedes one to write,*
>
> $$\ln \frac{\Omega_2}{\Omega_1} = \ln \Omega_2 - \ln \Omega_1,$$
>
> *and thereby, interpret entropy as an additive quantity, as required by thermodynamics. This requirement is fulfilled only with the introduction of Planck constant.*
>
> *That the volume* Ω *of the phase space is not an invariant quantity under the influence of heat radiation can be easily verified by substituting the action* α_ℓ *by the dimensionless quantity* $\theta_\ell = h/\alpha_\ell$ *(where h is Planck's constant), in equation* (A8)*, to obtain the Sackur-Tetrode absolute entropy per degree of freedom of the monatomic gas, that depends both on the thermodynamic state (temperature, volume, etc.) of the perfect vapor, and on the quantum states (their population) of the clusters, conjointly.*

Although inadequate to properly represent the thermodynamic entropy, the above derivation reveals some of its functional properties, providing a justification of its definition in terms of the logarithm $\ln \Omega$ of the volume Ω of the phase space, and of the addition of Planck constant, $\ln\left(\frac{\Omega}{h^F}\right)$, to satisfy the dimensionlessness requisite.

A more adequate definition of entropy could be obtained by following the above steps, after assuming, at the outset, that the dimensionless volume of the phase space, given by expressions (8.1) and (8.2), is a complex quantity, as shown in Section 8.1.

A.7 The thermodynamic phase space

As previously shown, the equilibrium condition § 40 is in contradiction with the principle § 41 of Newtonian mechanics. Besides, according to Newton's Definition I of his *Principia*, the equation (A8), that defines the entropy of a classical system of particles, holds only if the influence of electromagnetic radiation on the motion of the particles can be ignored. Such hypothesis can be assumed in the equilibrium condition, for, in spite of the unceasing action of radiation on the motion of the particles of the fluid, it does not perceptibly affect the values of the macroscopic (thermodynamic) variables that characterize the system.

> *It is impossible to give thermodynamic meaning to a discrete fluid unless it is assumed that its particles interact with radiation.*

Hence, equilibrium can be understood as the *asymptotic behavior* of the particles of the gas, as time approaches infinity[5].

A.8 The statistical approach

With the confirmation that a classical model of the gas is unattainable, some authors capitulated and proposed a different research program, known as *statistical mechanics*, expressed by the following proposition:

§ 43 (Principle of the Molecular Chaos)
*To find the characteristic Probability Distribution Functions (*PDF*) of two random variables, namely, the degrees of freedom (positions and velocities) of the particles of the gas in its thermodynamic equilibrium.*

Without explaining how, statistical mechanics assumes that heat imparts to the chemical substances the *disordered* motions of their *atoms* and *molecules*, whatever the word *disorder* might mean[A.1].

A.9 Equilibrium as an asymptotic behavior

Examples of mathematical expressions in which an approximated formula to calculate the value of a function $f(n)$ for large values of the integer variable n led to the field of *Asymptotic Analysis*. A classical example is the *de Moivre-Stirling* formula,

$$n! \approx \sqrt{2\pi n}\left(n^n e^{-n}\right). \tag{A10}$$

---

[5] In experimental thermodynamics the asymptotic behavior can be observed when the *relaxation time* is reached.

that arises in statistical mechanics where it is required to calculate the derivatives of an originally combinatorial function of the integer quantity $n!$.

To evaluate the equilibrium state of a discrete fluid we can seek for inspiration in the principle of asymptotic analysis, by advancing the following conjecture:

> *If the asymptotic equivalents of the (unknown) laws of movement of the particles of a discrete fluid can be found, then it might be possible to characterize its equilibrium state in terms of thermodynamic variables and criteria.*

Maxwell and Boltzmann realized that, if the particles of a gas are regarded as the *moving pieces* of a *game of chance*, such as in the throwing of dice, the flipping of coins, or the shuffling of cards, then it would be possible to apply *asymptotic analysis*, then established in *Probability Theory* by the *de Moivre-Laplace* theorem[6], to the study of the movement of its particles in the equilibrium.

Hence, it is assumed that the equilibrium state of the discrete fluid is the result of each trial of this game, i.e., each equilibrium state is described by the outcome of a trial that starts at any instant of time and ends after the relaxation time has elapsed.

> *Relaxation processes in real gases might either be almost instantaneous in explosive chemical reactions, or last for hours, as can be observed in the metamorphosis of atmospheric clouds.*

To apply this theorem to the motion of particles in a discrete fluid, the following principle was stated:

> *For the molecules of gas in a closed box, in the absence of external force, all positions in the box and all directions of velocity are* equally probable. [4].

Several applications of the principle of molecular chaos to approach the equilibrium of a discrete fluid were proposed. It is worthwhile mentioning the *Statistical Mechanics* of gases, the *Kinetic Theory of Gases* and the *Theory of Brownian Movement*.

> *Statistical Mechanics.* This theory is based on the *Boltzmann Principle*, that postulates the equivalence between the *phase space* of Hamiltonian mechanics and *sample space* of Probability Theory. This approach allows redefine *entropy* in terms of molecular chaos.
>
> *Kinetic Theory of Gases.* The purpose of this approach can be stated in terms of the attempts to answer to the following question:

---

[6] The *de Moivre-Laplace* theorem is a special case of the *Central Limit Theorem*, proved in 1901 by Lyapunov.

> *What is the distribution of velocities and, thereby, of the kinetic energy of the particles of a discrete fluid in its equilibrium state?*

Having recourse to the *de Moivre-Laplace* theorem of Probability Theory, Maxwell and Boltzmann were able to solve the equilibrium distribution of velocities and energies for the particular case of the *Perfect Gas*.

> *The present approach supersedes the Boltzmann Transport Equation.*

A.9.1 The sample space (combinatorial) approach

Two new approaches to derive the thermodynamic properties of gases from quantum theory, were later proposed. After the revelation by Bose that photons in equilibrium behave as a combinatorial system of indistinguishable particles, Einstein proposed the extension of this character to the particles of a gas, and after the formulation by Pauli of his exclusion rule, Fermi explained the behavior of electrons in equilibrium in a metal as a gas of particles constrained by Pauli's exclusion principle.

Both these derivations were based on identifying the phase space of the gases with the *sample space*, that led Planck, inspired by a suggestion given by Boltzmann, to adopt the logarithm of the volume of the phase space as the mechanical redefinition of entropy [38].

The combinatorial analysis of the two types of particles superseded the *Principle of Molecular Chaos* in favor of the Boltzmann principle in the calculation of the thermodynamic properties of these gases. With the theorems of the many-body quantum systems, that predict the existence of two kinds of wave functions, symmetric and anti-symmetric, the successful derivation of the Bose-Einstein and Fermi-Dirac statistics has sustained the orthodox sample space approach to statistical mechanics.

The recent history of physics leads us to conclude that the empirical sources of quantum theory, as well as the phenomena it intends to explain, pervades classical mechanics, probability theory, thermodynamics, chemistry, electromagnetic theory, and special relativity. Each one of these theories addresses a certain domain of phenomena, expressed in its own language, with its own vocabulary, grammar and epistemology.

The translation of the different notions established by those competing theories into the language of a single unified target theory requires the conciliation of their original meanings.

A.10 The Brownian movement

Let us recall another important simplification of the motion of particles of a gas in equilibrium: Krönig's description of the motion of its particles:

§ 44 (The Krönig Gas)
The molecules of the gas (do not oscillate about definite positions of equilibrium, but that they)[7] *move with constant velocity in right lines until they strike against other molecules, or against some surface which is to them impermeable.*

Statement § 44, which provides a kinetic theoretical description of the *Brownian movement*, can be restated in terms of a directed graph, where the edges F correspond to the inertial motion in straight lines and the vertexes C, to the elastic collisions against either another particle or the internal surface of the container. We can then frame our analysis on the following abstraction,

> *The trajectory of a particle moving in a gas can be depicted as a polygonal line, represented by the symbol*[8]*,*
>
> $$\ldots FCFCFCFC\ldots \tag{A11}$$

A.10.1 Action change during the free path traversing

The momentum p_s of a particle traversing the side s of length Δz_s of the polygonal line is constant. Assuming that the particles of the gas are identical, the action developed by this particle during this motion is given by,

$$\alpha_s = p_s \cdot \Delta z_s = \frac{m}{2}\frac{(\Delta z_s)^2}{\Delta t_s},$$

where Δt_s is the time between two consecutive collisions.

> *Random Variable.* In the theory of the Brownian motion the quantity α_s is treated as a *random variable*, $\mathbf{A}_{\mathscr{K}}$. Hence, the values acquired by the variable α_s during the motion of the particle between two consecutive collisions, represent the *outcomes of experiments of a random process*, *where each collision is a trial.* Hence, according to the *Law of Large Numbers* of probability theory we have,
>
> $$\langle \mathbf{A}_{\mathscr{K}} \rangle = \lim_{n\to\infty} \frac{1}{n} \sum_{s=1}^{n} \frac{m}{2}\frac{(\Delta z_s)^2}{\Delta t_s} = \frac{m}{2}\frac{\langle \Delta z_s^2 \rangle}{\langle \Delta t_s \rangle}, \tag{A12}$$

---

[7] As shown in § 11, being an exclusive function of temperature, vibration can be ignored here

[8] The symbol $\{FC\}^+$ of formal Language Theory can be used instead of the notation $FCFCFCFC\ldots$.

> Equation (A12) allows the empirical estimation of the *expectation* of the random variable $\mathbf{A}_{\mathscr{K}}$.

Note that the condition $n \to \infty$ that defines the convergence process in (A12) can be replaced by a large value of Δt, that is determined, for practical purposes, by the value known as the *relaxation time*.

> *The waiting time for a collision can be assumed to have a Poisson distribution. It is interesting to inquire if this hypothesis allows derive straightforwardly such distribution with the amplitude parameter θ. Such derivation will justify in Appendix C to assume that the action of the ladder operators on the many-body system can be properly represented by a Markovian birth and death stochastic processes.*

Perrin's Experiments. Since the values of the Δt_s are difficult to be measured, an approximation to them was obtained by Perrin in a series of n measurements of the lengths $\Delta z_s, \quad s = 1, 2, \ldots, n$, of the sides of the polygonal line, performed at equal intervals of time τ.

In these experiments it was confirmed that the quantity $\Delta q^2/\tau$ (where Δq is the distance traversed by the corpuscle between two consecutive observations made at equally spaced time intervals τ) is — as previewed by Einstein in his *Theory of the Brownian Movement* — an invariant magnitude characteristic of the state of equilibrium [20].

We can then conclude that, for identical corpuscles, the average action $\langle \alpha_{\mathscr{K}} \rangle$ developed by the particles traversing their free paths, is an *invariant property* of a gas in equilibrium.

A.10.2 Traversing a conservative trajectory

In a second moment, we consider the polygonal line in which the motion across the edge F is, according to Krönig's conjecture § 44, inertial, hence, conservative. The quantity Δt_s now represents the time between two consecutive elastic collisions. Since the trajectory of a particle in its motion is interrupted by elastic collisions, we can still work with the same formula (A12) to obtain a more realistic value of the average action $\langle \alpha_{\mathscr{K}} \rangle$ developed by the particle in the edges F of the polygonal line.

From Maxwell-Boltzmann kinetic theory, the average value of the variation of momentum of a particle (treated as a random an independent variable), during its translation between two consecutive collisions, is given by the expression $\langle \Delta p \rangle = \sqrt{2\pi mkT}$, and the average *inter-collisions length* $\langle \Delta q \rangle$ can be approximated by *the average inter-particle distance*, $\sqrt[3]{V/N}$, whence we can write,

$$\langle \Delta p \cdot \Delta q \rangle = \sqrt{2\pi mkT}\sqrt[3]{\frac{V}{N}}. \tag{A13}$$

The average *activity* (defined as the kinetic action developed during a finite interval) $\alpha_{\mathscr{K}} = \langle \Delta p \cdot \Delta q \rangle$ of the Krönig gas is revealed to be a function of the temperature T, a non-classical magnitude. Hence, the thermodynamic properties of this gas cannot be derived from purely classical hypotheses. Expression (A13) is also found in the Sackur-Tetrode entropy of the monatomic gas, whose connection with the Brownian Movement approach will be discussed in Sections 2 and 5.

Since the particles of the gas are identical, we can assume that the probability distribution function of the random variable $\alpha_{\mathscr{K}}$ is the same for all the particles and assume that the same holds for all inter-collisions trajectories of each particle. From the standpoint of probability theory, it can be said that

> *To the random variable $\alpha_{\mathscr{K}}$ there corresponds the sample space of a game of chance, where each collision can be interpreted as a trial whose outcome is the action developed by the particles between two consecutive inter-collision displacement.*
>
> *The volume of the Ω_K of a gas composed of N Krönig particles is given by the multiple integral,*
>
> $$\Omega_K = \int \prod_{\ell=1}^{N} dp_\ell dq_\ell.$$

Appendix B

On Uncertainty and Indistinguishability

Introduction

The thermodynamic consequences of indistinguishability of identical molecules were considered by Maxwell in the analysis of diffusion processes; by Gibbs in the calculation of the entropy of a mixture of a gas with itself; by Tetrode in the derivation of the entropy of the monatomic gas; by Bridgman in the mixture of two imaginary gases whose molecules are infinitesimally different; by Bose, who revealed it as a character of the photons in equilibrium radiation; and by Einstein in his derivation of condensation in a gas of Bose particles.

B.1 Heisenberg's justification

In his *description of the determination of the position of a free particle*, Heisenberg refers to "*the light illuminating it*[1]".

In the procedure to localize the particle, it is *illuminated*, a phenomenon that can be identified as the *agent that causes the change* on the position of the particle, for it is known that light is endowed with the momentum degree of freedom, thereby causing a change on the state of motion of the particle. Instead of interpreting the effect of illumination as an uncertainty imparted by the procedure, as prescribed by the uncertainty principle, we can explain it in terms of the change caused by the incidence of a photon on the population of the quantum state of the many-body system where to the particle is moved.

This reinterpretation leads us to conclude that there is an *epistemological*

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[1] §2 a), p. 20-1 [40]

precedence of a quantum elementary process, namely the interaction between the particle and radiation, over its consequence, namely, the progressive statistical indistinguishability of identical particles of the perfect vapor [7].

Condensation is here described as the result of a large number of the transient elementary processes of absorptions and emissions that take place during the interaction of the vapor with radiation.

B.2 Einstein versus Einstein

In 1905 Einstein identified that high frequency radiation behave as it were composed of discrete particles. Almost two decades later, de Broglie suggested that material particles might exhibit, as photons do, undulatory behavior. It became then natural at that time to hint: "*that which works for photons, works for material particles as well*". When Bose discovered that radiation can be regarded as a system of indistinguishable particles, it should not be surprising that Einstein's conspicuous intuition led him to conclude that *if photons are indistinguishable, as Bose said, then material particles might behave similarly*, thereby conducting him to develop the presently known theory of Bose-Einstein condensation.

This assumption, introduced *ad hoc* by Einstein, was later shown, in the scope of the many-body approach to the gas, to be a character of the wave function of such systems, expressed in terms of the symmetry (indistinguishability and Pauli's exclusion) principles. This understanding still persists in the current tenets of many-body theory, in spite of the serious objections raised against it at the time of its introduction [41]. An alternative hypothesis about the physical origins of the symmetry principles, which eliminates these objections, and allows explain condensation kinetics, is reviewed in the Appendix C.

Some physicists, notably Ehrenfest and Schrödinger promptly raised objections against the way Einstein treated material particles as indistinguishable. It is opportune to reproduce Schrödinger's criticism here:

> *The essential point in the new theory of the gas, developed recently by A. Einstein, consists in the need to invoke a completely new statistics to describe the movements of the molecules of the gas, the Bose statistics. This new statistics should not be considered as <u>something primary, requiring no explanation</u>. Furthermore it seems to hide the hypothesis of a certain dependence or <u>interaction among molecules</u> of the gas that is difficult to analyse here*[2].

In response to these objections, Einstein wrote,

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[2] Second-hand citation (pp 199-200 [42]).

> *Mr. Ehrenfest and some other colleagues objected that in Bose's Theory of Radiation and in mine analogous theory for the ideal gas, the quanta and the molecules, respectively, are not treated statistically as mutual independent entities without any explicit warning about it in our works. This critic is completely justified.* (...) *The counting of these "complexions" of different probabilities would not result in the correct value for entropy in the case of an effective independence among molecules. The formula (for entropy) expresses, therefore, indirectly, a certain hypothesis about reciprocal influence among molecules, influence of a completely mysterious nature up to now, that results in precisely the same statistical probability that we have been defining as "complexions"*[3].

However, as astonishingly as it seems, almost a decade *before* Bose's finding, Einstein derived Planck's radiation formula — and thereby the same Bose-Einstein statistics characteristic of indistinguishable particles — based, not on a supposedly "ontological" character of the ensemble of particles, but, instead, on the condition of *equilibrium* between matter and radiation, thereby opposing two irreconcilable interpretations, which were confronted neither by Einstein himself, nor by anybody else at that time.

The whole of experimental data about black-body radiation, from Kirchhoff onwards favours the hypothesis that Planck's radiation law (hence, indistinguishability) is not a necessary, but an equilibrium condition.

In the subsequent development of Bose-Einstein and Fermi-Dirac statistics, however, Schrödinger's forecast of the existence of "*interactive*" processes was bypassed in the most radical way, by acknowledging indistinguishability as a fundamental principle, i.e., *as something primary, requiring no further explanation*. The symmetrical and anti-symmetrical character of wave functions of a system of identical particles and the subsequent definitions of the creation and annihilation operators, together with their mathematical properties, were thereby derived as mere consequences of those principles.

Such confrontation, which recovers the opposition between *being* and *becoming* of pre-Socratic philosophers, deserves some considerations as follows.

B.3 Loss of identity

In the classical mechanics of a system of identical particles, the *identity* of each particle is specified by its position and momentum. These degrees of freedom have been unconditionally accepted to be *persistent* characters of a particle, i.e., something that, although variable, always existed together with it.

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[3] idem, p. 191.

Hence, as a consequence of a chemical reaction, reactant molecules loose their *identities*, and the molecules of its products receive new ones. In summary, chemistry reveals that classical degrees of freedom are *non-persistent* characters of molecules.

That which can be treated in chemistry as the *loss of identity*, has been treated by the uncertainty principle as an ontological character of the particles belonging to a system of identical particles, which impedes a given particle to be distinguished from any other in the system. One might say that *God decided that not even Himself can distinguish two ontologically indistinguishable particles.*

As opposed to the interpretation given by the uncertainty principle, we can assume that particles are not ontologically indistinguishable, but they become so inside a cluster, for instance, as a consequence of a chemical reaction that adds a radicle to that cluster.

Though the explanation of the loss of identity of molecules due to chemical reaction is in agreement with the finding § 23, as discussed in Section 6.3, it is in conflict with the interpretation currently given to the relations (5.4)-(5.5) by the uncertainty principle. As showed in Section 5.8, the classical degrees of freedom, position and momentum are constrained by Planck's constant in (5.13), and replaced, respectively in (5.14), by a new description, expressed in terms of quantum operators *coupled* indistinctly by the Hamiltonian of the system in Schrödinger's partial differential equation.

In its creation in (transference to) the cluster $\mathbb{Q}(\psi_\ell)$, position and momentum become coupled (*conjugated*, in the jargon of quantum theory formalism) to the other radicles inside the same cluster.

Once these corpuscular attributes are lost, according to Section 5.8, the system formed by the conjugated radicles become described by a single wave function.

B.4 Automorphism and equilibrium

Eadem mutata resurgo.
Epitaph to Jakob Bernoulli I

It is well known from thermodynamics that no meaning can be assigned to the entropy of a gas, unless every transient internal dynamic process has been consummated. In the Boltzmann principle approach to equilibrium, entropy is described by the *average* values of the occupancy numbers of the quantum states of the gas, as prescribed by its wave function. While large scale variations of these numbers are still occurring, one cannot speak of average values, and therefore no meaning can be assigned to Boltzmann entropy. Correspondingly, the wave function of a many body system, that ultimately specifies the population of its quantum states, cannot be adopted to describe this system if it has been removed from equilibrium.

To decide upon these two opposing understandings, viz. equilibrium versus necessary conditions, we need to recognize that the wave function of a system of particles, as much as it happens with entropy, is defined *only in the equilibrium state*. Since indistinguishability has been interpreted as imposed by the symmetric or anti-symmetric character of the wave functions, we must reconsider the scope of these functions, specially of a system of Bose particles, to become in agreement with the equilibrium character of Planck's radiation law.

Recall that wave functions are the way Schrödinger equation specifies those stationary states previewed by Bohr in his first postulate. In Schrödinger's equation, however, stationary states are not postulated, but are, instead, consequences of its definition as an *automorphism*, $\hat{H}\psi = E\psi$.

From its algebraic definition, an automorphism can be adopted as a rigorous definition of equilibrium. In fact, as much as Jakob Bernoulli's epitaph, that properly describes the logarithmic spiral curve which, after transformed (undergoing its *characteristic* rotation and homothety), results in itself, any system defined by an automorphism, after undergoing its *characteristic transformation*, continues in the same state it was before the change. Each quantum system has its own *characteristic* transformation, expressed in terms of its *Hamiltonian operator*, of which the equilibrium state gives physical meaning to its mathematical eigen-states[4].

We are then suggested to assume that "*to be* indistinguishable" is not an intrinsic character of the particles of a gas, but, instead, the result of a certain general faculty of which the gas is endowed, namely, that of *becoming*, under certain circumstances, susceptible to radiation. It is the persistent interaction between the gas and radiation that leads the particles to *become* indistinguishable in its final state of equilibrium.

Let us recall the meaning to the automorphism equation given by Dirac in his statement,[5]:

> *If the dynamical system is in an eigenstate of a real dynamic variable ξ, belonging to the eigenvalue ξ', then a* measurement *of ξ will certainly give as result the eigenvalue ξ' to which this eigenstate belongs.*

By recognizing that an automorphism defines a condition of equilibrium, one can give a new meaning to the same equation, by maintaining the same premise. We can rewrite the statement above in the following terms:

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[4] If the system is already in the equilibrium state, after undergoing its characteristic Hamiltonian transformation, it remains there.

[5] Equation (10) of Section 9 of Chapter II of Dirac's *Principles of Quantum Mechanics*

> *If the dynamical system is in an eigenstate of a real dynamic variable ξ, then the eigenvalue ξ', corresponds to the state of equilibrium of the dynamical system.*

While a variety of algorithms to derive the eigenvectors of an operator and their corresponding eigenvalues can be conceived by mathematicians, physicists must ask: *what is the "algorithm" followed by a natural system to move it towards the equilibrium state*? From fluctuation phenomena revealed by thermodynamics we conclude that the quantum state occupancy numbers are *random numbers*, so that their values vary according to the *persistent stochastic iteration of the same invariable agents* throughout the relaxation time, until the eigenstate (equilibrium value) is achieved, i.e., until each state contains the equilibrium *random number* of particles given by the automorphism. An appropriate description of this kinetic process is obtained by the Markovian birth-and-death stochastic process, as reviewed in Appendix C.

B.5 The uncertainty principle and indistinguishability

Let us recall Landau's analysis of the *gedanken* experiment designed to localize two electrons in space [29]. Although conceived to *justify* the indistinguishability principle in many-body theory, by considering special relativity, as I have shown [7], that this experiment provides, instead, a sensible argument to understand indistinguishability as the result of a *finite process* during which two observed particles, originally *distinguishable*, *become* indistinguishable as a consequence of the certain *force-like agents* on their motion, i.e., it asserts the epistemological precedence of the taut constraint (5.4) over the indistinguishability principle. If the word *principle* is understood as synonymous for axiom, i.e., as *something primary, requiring no explanation*, then indistinguishability should not be taken as a principle in itself, but instead, as a corollary of the symmetric and anti-symmetric characters of wave functions, which hold only in equilibrium.

If each of the two inelastic collisions of the experiment just discussed give rise to indeterminacy, we are naturally led to believe that the same effect occurs as a consequence of a single inelastic collision between two systems of particles. With this assumption, we can think of an *objective indeterminacy*, as intrinsic to inelastic collisions, that eliminates the need of a *measurement process* as an explanatory element of the theory. It then allows one to conclude:

> *That the inelastic collision of two identical particles is a transient, non-reversible process is evident, for it is impossible to restore the individuali-*

> *ties of two particles that, as a consequence of this process, have lost their identities.*

If we read either Heisenberg's considerations about the localization of an electron in space [40], or § 61 in Landau's [29], we conclude that there is an intermediate irreversible phenomenon, namely, the interaction of a photon with an electron. This process, described by the transitions (5.14), destroys the degrees of freedom of the electrons, thus erasing its identifying characters (position and momentum).

Recall that, as stated in § 23, Dalton's and Avogadro's laws revealed that classical degrees of freedom are *non essential*, but *accidental* attributes of molecules: they are created or annihilated during a chemical reaction. Besides, according to quantum theory, the values of the degrees of freedom of the products that arise are unpredictable random variables.

B.6 Further comments on the uncertainty principle

As Kragh reports,

> *"Dirac (...) did not see any point in all the talk about complementarity. It did not result in new equations and could not be used to for the calculations that Dirac tended to identify with physics."* [10].

A similar critics, made by L. Landau, applies to the uncertainty principle, that is devoid of the faculties to produce equations to be used for calculations:

> *"In that it rejects the ordinary ideas of classical mechanics, the uncertainty principle might be said to be negative in content. Of course, this principle in itself does not suffice as a basis on which to construct a new mechanics of particles. Such a theory must naturally be founded on some positive assertions (...)"* [29].

Hence, the meaning of the quantity θ is not necessarily given by the interpretations proposed by Heisenberg in his uncertainty principle. As in natural languages, they can be treated as homograph words[6].

B.6.1 Critics of the uncertainty principle

It is generally accepted that all the mentioned interpretations formulated during the OQTE, namely, the description of the photo-electric effect by Einstein, the

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[6] Homograph words are spelled the same with different meanings, in our case it is the operator Δ that describes different effects it causes on the entities on which it acts.

derivation of the entropy of a monatomic gas by Sackur and Tetrode based on Sommerfeld's conjecture § 18, or the formulation of Bohr's postulates, are endowed both with explanatory power, and with empirical substance. As we have seen above, the meaning of mechanical action stated in § 19 can be derived from the definition of the volume of the phase space of a system of particles.

It is expected that any posterior interpretation of the relations (5.4)-(5.5), would supersede its predecessors, enlightening their meaning, extending their explanatory power, and giving more rigor and precision to the derivation of the formulas they provide. However, if reinterpreted according to the uncertainty principle, the opposite happens: all the previous explanations given, cogently or not so, to all those phenomena are refuted, and replaced by ... nothing.

The uncertainty principle therefore does not convey to the relations (5.4)-(5.5) a realistic meaning; instead, it is an equivocal connotation that might lead to confusion. It can be used, however, as a speculative diagnostic of a symptom, a warning about the imminence of the occurrence of an elementary processes of quantum exchange, which will cause, on the radicles and clusters involved, a radical change of their structures. It might be possibly helpful in the explanation of the yet enigmatic transformations (5.14), thus suggesting some heuristic idea about the conditions that trigger a chemical reaction.

Due to its incapacity to explain, specially in the most critical and representative situation that characterizes the uncertainty principle, namely, a chemical reaction, when an interaction of matter with radiation is consummated, we remove that principle, together with the notion of "measurement" from the formulation of the present theory.

If we restore the interpretations proposed during the OQTE, then chemical reactions can be understood according to its meaning already established by chemistry, namely, as a transient phenomenon during which the classical degrees of freedom of the reactants collapse, giving rise to the quantum description of the products characterized by other degrees of freedom, with unpredictable values. These products, in their turn, are described in quantum mechanics as many-body quantum systems (atoms and molecules) whose internal state is characterized, not by classical degrees of freedom but, instead, by the quantum numbers determined by their wave functions.

Appendix C

The Kinetics of the Perfect Vapor

Summary

This Chapter presents a summary of the results obtained by the author [7] in the treatment of a gas whose state is given by the population of particles in its enumerable set of quantum states. These numbers are treated as random variables, whose PDFs are the solutions of the general difference-differential equation of Markovian birth-and-death stochastic processes, whose *laws of change* are deduced from the reciprocal theorem of many-body theory, where from the indistinguishability and Pauli's exclusion principles have been hitherto derived.

These solutions describe the transient evolution of the gas towards the thermodynamic equilibrium, that reproduce the results already obtained for the equilibrium state of the gases of Bose and Fermi particles, that can be extended to a gas of Boltzmann particles.

Besides predicting the time asymmetry previewed by second law, it reveals that the indistinguishability of identical particles and Pauli's exclusion rule are not conditions of necessity, but of equilibrium. Hence, the particles of a gas removed from equilibrium are not said to be indistinguishable, but rather to *become statistically indistinguishable* in the state of equilibrium.

Introduction

It is known that for high temperatures and low densities the gases of Bose particles (the black-body radiation) behave as a perfect gas, characteristic of its $\mathfrak{G}$-phase. For lower temperatures and higher densities (smaller frequencies), the quantum phenomena become increasingly relevant. The purpose of this Chapter is to study the influence of the $\mathfrak{L}$-phase on the formation of thermodynamic equilibrium. We will then focus on the time evolution of the random occupation numbers,

$$\mathfrak{R}(t) = \{\mathbf{r}_0(t), \mathbf{r}_1(t), \mathbf{r}_2(t), \cdots, \mathbf{r}_\ell(t), \cdots\}$$

of the corresponding enumerable set of wave functions,

$$\Psi = \{\psi_0, \psi_1, \psi_2, \cdots, \psi_\ell, \ldots\}$$

that characterize the clusters $\ell = 0, 1, \cdots$ that comppose the $\mathfrak{L}$-phase of the gases of Boltzmann, Bose and Fermi particles, as described by the Second Quantization formalism.

Recall that, according to the Axiom 4 of quantum theory that, amended by this approach, the average values,

$$\bar{\mathbf{r}}_\ell = \lim_{t \to \infty} \mathbf{r}_\ell(t), \ \ell = 0, 1, 2, \cdots$$

are given by the eigen-values of the dynamic variables under the persistent action of the ladder operators. Here the time variable t is the same where the Markovian processes are defined.

> The current interpretation of Axiom 4 evokes a whimsical comment of Szent Györgyi when he joined the Institute for Advanced Study in Princeton about the behavior of more than two electrons[1]:
>
> *"I did this in the hope that by rubbing elbows with those great atomic physicists and mathematicians I would learn something about living matters. But as soon as I revealed that in any living system there are more than two electrons, the physicists would not speak to me. With all their computers they could not say what the third electron might do. So that little electron knows something that the wise men of Princeton don't, and this can only be something very simple."*

While talented humans can devise algorithms to calculate *with all their computers* the eigen-values and eigen-vectors specified in Axiom **4**, photons can not. Since the a and $\mathsf{a}^\dagger$ act independently in nature, we can neither assume that a is the inverse of $\mathsf{a}^\dagger$, for it is not, nor are we allowed to conclude that photons are endowed with the algorithmic faculties to calculate those eigen-stuff.

What is required here is to prove that the eigen (equilibrium) state of a dynamical variable is attained by the recurrent action of the conditional probabilities of the elementary quantum state transitions, described by the ladder operators, that

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[1] Cited by von Bertalanffy [43].

are mutually time independent. This process is neither deterministic, nor asymptotic in the sense of regular convergence, but instead, stochastic[2]. This approach supersedes the *Principle of Molecular Chaos* § 43 adopted in statistical mechanics:

> *To derive the probability distribution functions of the occupancy numbers of the quantum states that characterize the $\mathfrak{L}$-phase of the perfect vapor, from the laws of change described by the conditional probabilities laws of creation and annihilation.*

Hence, it is reasonable to assume that the evolution of these transitions in time must be described as conceived in probability theory,

> *A "conceptually (...) analogue of the processes of classical mechanics, where the future development is completely determined by the present state and is independent of the way in which the present state has developed."*[3].

Such analogue is the Markovian birth-and-death processes, whose *laws of change* — that correspond to the *laws of force* of Newtonian mechanics — are given by the creation and annihilation operators.

The difference of the present approach from the current tenets of statistical mechanics is subtle. While in the former, time is intrinsic to the Markov equation, in the latter it is assumed to derive from Schrödinger's time equation. The main consequences of this difference are that (a) the former previews time asymmetry, while the latter does not, and (b) in the former, indistinguishability and Pauli's exclusion principles are interpreted as conditions of equilibrium imparted to the system of particles by the way they are shuffled, while in the latter these principles assume that the behavior of these particles are due to their ontological nature.

We have then to face the following dilemma:

§ 45 *Whether we assign to the creation–annihilation operators a secondary and passive role in quantum theory, as a mere mathematical curiosity designed to help us in our resignation to accept the bizarre behavior of these particles, or we recognize in them a primary active role in the shuffling process, as the elementary chaos that cause that behavior. In the words of the philosophers of Ancient Greece, they are to be seen as the* unchanging principles of change, *that gives physical meaning to the* clinamen *(swerve) of Atomistic doctrine* [44].

A brief review of the alternative derivation of Maxwell-Boltzmann, Fermi-Dirac, and Bose-Einstein statistics from these operators proposed by the author [7] is described in Appendix C.

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[2] Or, if preferred, a Monte-Carlo algorithm.

[3] p. 420, [30]

C.1 On being and becoming

Far away from saying that the object precedes the point of view,
we would say that it is the point of view that creates the object.

F. Saussure, *Cours de Linguistique Générale (1916).*

Being unconcerned with the accidental circumstances of an actual experiment, the sample space approach to random phenomena considers neither the *initial configuration* of its moving parts (balls, dice, coins, cards or particles), nor the changes they undergo *during* the trial. These considerations suggest that the replacement of the kinetic theoretical methods by those of statistics of sample space, resulted in what might be a misleading epistemological shift that can be described by Saussure's aphorism reproduced in the heading of this Section: by focusing on the outcomes of the irreversible processes instead of on the processes themselves, one might be subtly persuaded to interpret *indistinguishability* and *exclusivity* as essential characters of the particles, instead of a mere effect of shuffling on their outcomes.

While Saussure's approach to Linguistics is a conscious epistemological decision, the choice of the sample space approach to the statistical mechanics of gases is a convenient, although misleading, simplification.

In fact, any attempt to derive the properties of a phenomenon that depends on the process of shuffling from the statistical analysis of its outcomes, might be illusive, as evidenced by the following abstract example.

C.1.1 Sample space mirages

Let us consider the random placement of **r** balls in **n** cells[4].

> *Suppose that the balls are made of ice, each one with the same mass* **m** *and frozen into a different mold, so that they can be numbered, thereby being distinguishable by any observer. Let us suppose also that* $\mathbf{n} = 26$*, and that each cell is labeled with one letter of the alphabet, so that any point in the sample space of such experiment can be uniquely identified with a word of length* **r***: the first letter denotes the cell in which ball 1 was placed, the second, the cell containing ball 2, and so on*[5]*. Let us also suppose, as it happens with the particles in a gas, that the shuffling is non observable and performed below the fusion temperature of water. Hence, any observer can*

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[4] This is an imaginary shuffling process. It should not be taken as a model for the molecular chaos in a gas.

[5] Think of the sequential placement of balls in the cells as the sequence of the keys (cells) you stroke (put the ball) in a keyboard to produce a word.

> *read, in the outcome of each trial, a word of* **r** *letters. He then concludes that the ice balls are distinguishable.*
>
> *Let us suppose now another shuffling performed at a higher temperature and lengthy enough to allow the balls to melt during the relaxation process. As the time goes on, the shuffling process will, as it were, act no longer on solid balls, but instead on melted balls. The balls, originally distinguishable,* become *indistinguishable. In fact, looking at the outcome of the shuffling, the observer will be unable to read, in the configuration he sees, a word of length* **r**, i.e., *he cannot identify the balls in the cells. Instead, the only information he can draw from his observation — by weighting each cell to know the mass of water it contains — is given by the occupancy numbers,* i.e., *the number of balls he finds in each cell. Misled by the "external aspects" of the experiments (their* phenotypes*), instead of recognizing that the balls* became *indistinguishable during the shuffling process, he concludes incorrectly that, since they* are *indistinguishable at the moment of the observation, they* have always been *so.*
>
> *A privileged observer of this game (knowing its* genotypes*) knows, as opposed, that he cannot blame the balls for their indistinguishability, for it is the shuffling process itself that imparts to the balls such bizarre behavior. Instead, he knows that shuffling engenders a sort of* "indistinguishabilization" *process, so that the ice balls, originally distinguishable,* become *indistinguishable.*

The paradox raised in confronting Einstein's (1917) "*kinetic*" against Bose's "*combinatorial*" derivation of Planck's radiation law disappears when examined in terms of the elementary processes that, as in the example above, lead a system of Bose particles to its final state of equilibrium.

Hence, indistinguishability need not be understood as a ontological permanent characteristic of a system of identical particles. It can, instead, be seen as the consequence of the way its particles are shuffled, i.e., as the way they interact with radiation. In fact, when the gas is removed from equilibrium by a finite thermodynamic transformation[6], Einstein's equilibrium equation no longer holds, i.e., the symmetry of its wave function is necessarily broken[7].

As a corollary of Einstein's *kinetic* derivation of Planck's radiation formula, we can state:

§ 46 (Indistinguishability and equilibrium)
Indistinguishability is not a condition of necessity, but of equilibrium.

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[6] A thermodynamic transformation is understood as a large scale departure from equilibrium that removes the system far away from the statistical fluctuation domain.

[7] Einstein's equilibrium equation can be obtained as the asymptotic form of the kinetic equation of gases [7].

The same holds for Pauli's exclusion principle.

C.2 Transient processes in the perfect vapor

Differently from the ideal gas, the perfect vapor is a two phase system. While the behavior of the $\mathfrak{G}$-phase has been satisfactorily described in kinetic theory[8], the description of the $\mathfrak{L}$-phase requires a quantum approach. Hence, to give a kinetic approach to *condensation phenomena* we shall extend the theoretical definition of a *many-body quantum system* to fit the elementary processes of quantum exchange that conduct the particles of the perfect vapor to its thermodynamic equilibrium.

Recall that a many-body quantum system is composed by a number $n > 1$ of particles *entangled* with each other by their Hamiltonian, that merge them into a single wave function. According to the current tenets, every wave function is subject to the symmetric and anti-symmetric constraints, known as the indistinguishability and Pauli exclusion principles. Such definition imposes indistinguishability and exclusivity at the outset.

Nevertheless, quantum axioms allow predict the existence of state transition phenomena, assigning conditional probabilities to their occurrence. As shown in Appendix B, once transition probabilities are assigned to the occupancy numbers, the values of such numbers cannot be prescribed; they must, instead, be treated as *random variables*, thereby allowed to acquire arbitrary values not necessarily equal to the value $\bar{\mathbf{r}}_\ell$, imparted by the symmetric or anti-symmetric constraints.

The way out this contradiction is merely a matter of choice between the two interpretations of the indistinguishability and Pauli exclusion principles expressed in § 45, whether we assume with the current tenets that these rules reveal the ontological character of every many-body system of identical particles, or that they merely describe the condition of *thermodynamic equilibrium*.

In the following it will be shown that, by assuming that the ladder operators describe the agents that cause the changes the occupancy numbers of quantum states undergo, it is possible to obtain the time evolution of the quantum states that starts from an arbitrary initial PDF until it attains the PDF characteristic of thermodynamic equilibrium.

The $\mathbf{r}_\ell$'s are random variables whose behavior can be likened to the placement of balls (particles) in cells (quantum states).

The replacement of the ideal gas by the perfect vapor to represent real gases, that recognizes the existence of a random number of components, as opposed to

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[8] While some authors assume that the translation of a molecule in a fixed volume is quantized, its supposedly discrete energy levels have not yet been measured by spectroscopy. In the domain (5.9) of the phase space, the particles do not interact with radiation and therefore, cannot be supposed to exhibit quantum behavior.

the misleading mirage just discussed, leads to a far reaching approach to its "laws of motion", that are described, not in terms of the *trajectories* of its particles, but in terms of the time evolution of the PDF of the *occupancy random numbers* of the quantum states of the many-body system in question.

C.3 The kinetics of the perfect vapor

To represent the motion of the gas it is more realistic to assume that during a short interval of time, not all, but only a small number of particles change their positions (whether in the $\mathfrak{G}$-phase, or in the $\mathfrak{L}$-phase), most of them remaining in the same phase they were in the beginning of the interval. We are therefore justified to state the *continuity hypothesis*[9]:

§ 47 (Continuity)
The smaller the time interval considered, the smaller the number of particles changing their states.

It is known from statistical mechanics that the values of both the expectation and the variance of the random variables $\mathbf{r}_\ell(t)$ in the equilibrium, are negligible when compared with the extremely large numbers of particles and quantum states in the perfect vapor. Hence, we are allowed to state the *independence hypothesis*[10]:

§ 48 (Independence)
The removal of any cluster (together with the radicles it contains) from the perfect vapor, will not modify the flow processes that take place in the remaining clusters. In other words, the flow of radicles in a given cluster is independent of the flow that occurs in any other cluster[11].

With these assumptions, the investigation of the laws of motion of the perfect vapor is therefore reduced to find the laws that rule the arrival and departure rates, to and from, a single cluster.

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[9] Since this hypothesis does not refer to equilibrium, it is superfluous to statistical mechanics.

[10] Statement § 48 is here treated as a *proposition*, in spite of being tacitly stated as true in the method of *most probable distribution* of statistical mechanics, where from its preamble derives. It is not possible to decide, at this point, whether it describes the general behavior of molecules, or merely represents a complement to the definition of ideal gases, as expressed in (C3).

[11] In fact, this flow depends exclusively on the population of the state and on the properties of radiation.

To describe this flow let us denote by $A_\ell(\Delta t)$ and $D_\ell(\Delta t)$, respectively, the number of particles arriving to, and departing from, the state ψ_ℓ during the time interval Δt. Let us consider their time power series expansion,

$$\begin{aligned} A_\ell(\Delta t) &= A_\ell(0) + \dot{A}_\ell \Delta t + \ldots \\ D_\ell(\Delta t) &= D_\ell(0) + \dot{D}_\ell \Delta t + \ldots \end{aligned}$$

where $\dot{A}_\ell(t)$ and $\dot{D}_\ell(t)$ are, respectively, the arrivals and departure rates of state ψ_ℓ. According to hypothesis § 47, we have $A_\ell(0) = D_\ell(0) = 0$. Therefore the first-order equilibrium condition of the flow is given by,

$$\dot{A}_\ell(t) = \dot{D}_\ell(t). \tag{C1}$$

It can be easily verified that both the hypotheses § 47 and § 48 are subsumed in the following axiom that determines the *law of motion* of the PDF of the occupancy number of a given state:

> *The flow of particles in a quantum state is a Markovian birth-and-death process.*

Recall that the master equation for $\mathbf{P}_{\mathbf{r}_\ell}(t)$ of a Markovian birth-and-death process is given by the difference-differential equation [30],

$$\frac{\partial \mathbf{P}_{\mathbf{r}_\ell}(t)}{\partial t} = \lambda_{\mathbf{r}_\ell - 1} \mathbf{P}_{\mathbf{r}_\ell - 1}(t) - (\lambda_{\mathbf{r}_\ell} + \mu_{\mathbf{r}_\ell}) \mathbf{P}_{\mathbf{r}_\ell}(t) + \mu_{\mathbf{r}_\ell + 1} \mathbf{P}_{\mathbf{r}_\ell + 1}(t), \tag{C2}$$

where $\lambda_{\mathbf{r}_\ell}$ and $\mu_{\mathbf{r}_\ell}$ are, respectively, the arrival and departure rates that describe the laws that rule the shuffling processes. To complete the description of the motion of the gas, the knowledge of the laws that determine these rates are required.

> *In this approach, Planck's constant acknowledged as an imaginary entity, $\imath\hbar$, thus assigning a correspondingly different meaning to* time*, derived from the Minkowski space-time description of special relativity. The time partial operator $\frac{\partial}{\partial t}$ is then detached from Schrödinger's equation, and superseded by the Markov difference-differential equation, treated independently from Schrödinger's amplitude equation, that, according to* § B.4*, is understood as descriptor of the thermodynamic equilibrium condition.*

The values of the arrival and departure rates for the gases of Fermi, Bose, and Newtonian particles are given by [7],

$$\lambda_{\mathbf{r}_\ell} = \lambda\,(1 + \beta \mathbf{r}_\ell) \quad \text{and} \quad \mu_{\mathbf{r}_\ell} = \mu \mathbf{r}_\ell. \tag{C3}$$

where $\lambda = \xi e^{-\varepsilon_\ell/kT}$, $\mu = \xi e^{-\eta/kT}$, and ξ is an unknown frequency rate. From the creation-annihilation operators of second quantization, we have $\beta = 1$ for Bose, $\beta = -1$ for Fermi particles. The value $\beta = 0$ results in the Maxwell-Boltzmann PDF.

Let us denote by $\Pi_\ell(z,t) = \sum_{\mathbf{r}_\ell} \mathbf{P}_{\mathbf{r}_\ell}(t) z^{\mathbf{r}_\ell}$, the generating function (GF) of $\mathbf{P}_{\mathbf{r}_\ell}(t)$. After substituting the *laws of change* (C3) in (C2), we arrive at,

$$\lambda(z-1)\Pi_\ell = \frac{\partial \Pi_\ell}{\partial t} - (z-1)(\beta z - \mu)\frac{\partial \Pi_\ell}{\partial z}, \qquad \text{(C4)}$$

whose solutions can be written in the general form,

$$\Pi_\ell(z,t) = \varphi_\ell(z) \cdot \Phi_\ell(z,t),$$

where $\varphi_\ell(z)$ is the GF of the average occupancy numbers $\bar{\mathbf{r}}_\ell$ of the state ℓ in the equilibrium, and $\Phi_\ell(z,t)$, is the GF of the transient population $\mathbf{y}_\ell(t)$ in that state, at time t. According to the convolution theorem, the population of state ℓ at time t is $\mathbf{r}_\ell(t) = \bar{\mathbf{r}}_\ell + \mathbf{y}_\ell(t)$.

C.4 Probabilistic dynamics of particles

A parallel between the equation (C2) and Newton's second law can help elucidate the nature of the former. The Newtonian differential equation $\dot{p} = f$ remains indeterminate until a *law of force* $f(r)$ that is independent of the postulates and axioms of mechanics, is provided. The mathematically indeterminate role played by the law of force in Newtonian mechanics, is played by the correspondingly indeterminate *laws of change* (the arrivals and departures rates) in quantum mechanics. Both lead to the laws of evolution: the former giving the trajectory of the particle, the latter, the time evolution of the PDF of the occupancy numbers of the states of the quantum state. Both require the specification of initial conditions.

C.5 Further Comments on Indistinguishability

Equation (C2) is abstract enough to be in the foundations of a *General Theory of Change*, that can be applied to non-thermodynamic phenomena. Equation (C4) is a confirmation that indistinguishability can be legitimately interpreted as a statistical phenomenon that can be represented by the random placement of balls of whatever nature (billiard balls, for instance) in cells, provided the *shuffling* is performed according to appropriate *laws of change* that "indistinguishabilize" the balls. Indistinguishabilization can therefore be seen as a random process whose effect is to induce a particular partition on an set. As a mere consequence of the *shuffling* in a birth and death process, indistinguishability is therefore expected to be found not only in quantum phenomena but also in the population dynamics of systems of elements whose nature might be quite unlike the physical elementary particles dealt with in quantum physics and statistical mechanics.

It is worthwhile to note that most of the requirements that, in the view of *Huang*, a "satisfactory" derivation of statistical mechanics should fulfill [14], are satisfied by the present approach to the gas dynamics described in Section C.3:

1. *a non-ad hoc assumption of the molecular chaos by reducing it to a first-principles representation, given in terms of natural laws of change;*
2. *a detailed description, at least for the case of ideal gases, of the approach to equilibrium;*
3. *a master equation* (C2) *expressed, not in terms of wave function, but of the* PDFs *of occupancy numbers of the states of the ideal gases.*

Appendix D

Thermodynamic Properties of Steam

Summary

This Appendix confronts the pVT data of steam against the equation of state of the perfect vapor, and its departure from the ideal gas law. The remarkable symmetry observed in the graphisc here presented deserves further inquire.

Introduction

While the indeterminacy of the function $f(\theta)$ endows the perfect vapor with generality, its universality cannot be claimed until an extensive confrontation with experiment is fulfilled, an endeavor that is beyond the scope of this paper.

Since z and θ are both dimensionless quantities, the plot of the pVT data of any substance in the $\theta \times z$ plane is meaningful for both a thermodynamic and a quantum reading. The closer these data are to a single curve[1], the better the substance can be represented by equation (3.4), where $f(\theta)$ represents the departure of the perfect vapor from the Clapeyron equation.

D.1 The departure of steam from the ideal gas

To form a rough idea of the functional form of $f(\theta)$, the graphic of $\theta \times z$ of the steam pVT data[2] is exhibited in fig. D.1.

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[1] The quotient obtained by dividing the area occupied by the pVT data, by the total area determined by the selected intervals of z and θ, gives a rough measure of how close the substance is to

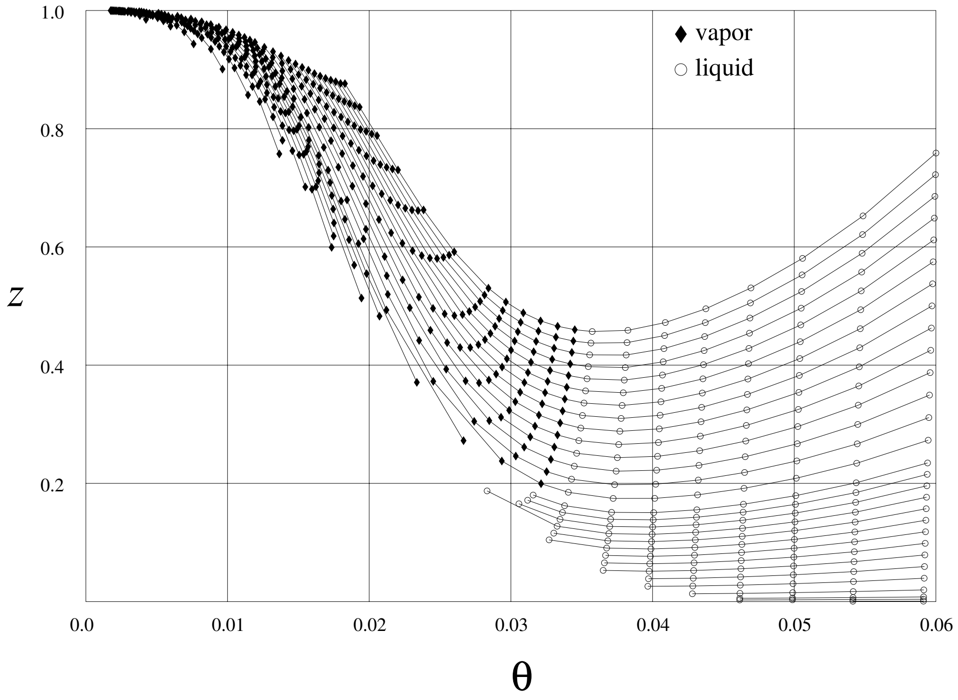

Figure D.1: pVT data for steam in the $\theta \times z$ plane.

While the isobaric curves of steam do not meet in a single curve, they form a family of isomorphic shapes, regularly displaced in the vertical direction, I was suggested to believe that the departure of the steam pVT data from the ideal gas law is due to the composition of at least two phenomena: on one hand, the displacements explained by the perfect vapor, and on the other hand, the contribution of an independent phenomenon that causes the departure of the isobaric curves from the perfect vapor.

Considerations about the causes of the formation of the entropy of steam led me to assume that steam is described by the superposition of the Clapeyron-Clausius entropy variation during a phase transition to the perfect vapor behavior,

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the perfect vapor.

[2] Figures D.1 and D.2 were introduced here for illustration purposes only. The data there exhibited were obtained from an old steam table I had at hand [45], when I programmed and used the algorithms to obtain the value of the parameter p_ℓ, required to produce fig. D.2. Since its determination was based on a low accuracy visual trial and error procedure, higher accuracy in the approximation (D1) would be of little value.

supposedly described by the clustering of water molecules[3]. I therefore propose the following conjecture:

> *The departure of the isobaric curves from the perfect vapor are due to nucleation processes, and that nucleation and clustering are independent processes.*

D.2 The departure of steam from the perfect vapor

To form a clearer idea of the functional form of $f(\theta)$, it would be necessary to eliminate the influence of the unknown cause of the departure of the steam from the perfect vapor.

It is here conjectured that such departure is due to the nucleation phenomenon, by assuming that the vapor pressure p of a substance is given by the equation,

$$\frac{p}{p_\ell} = e^{-\frac{\Delta H}{RT}},$$

where ΔH is the variation of the enthalpy of the system during a vaporization/condensation process, and p_ℓ is a constant pressure, characteristic of the liquid state.

For small values of $\Delta H/RT$, we can write $\exp(-\Delta H/RT) \approx 1 - \Delta H/RT$ to express the energy equation,

$$\frac{p}{p_\ell}RT + \Delta H \approx RT = \frac{p}{p_\ell}RT + \Delta U + p\Delta V \approx RT.$$

Since in a change of state $p\Delta V = V - V_\ell$ where V is the volume of gas and V_ℓ of the liquid, we can write $p\Delta V \approx pV$, thus obtaining,

$$pV + \frac{p}{p_\ell}RT + \Delta U \approx RT, \tag{D1}$$

Comparing the quantities $RT - pV$ obtained from equations (3.4) and (D1), we conclude that they represent different departures from the Clapeyron equation, due to distinct phenomena. By assuming that the behavior of steam is the result of their combined action, we obtain its equation of state in the following form,

$$z + f(\theta) + \frac{p}{p_\ell} \approx 1. \tag{D2}$$

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[3] This hypothesis is justified by its consequences.

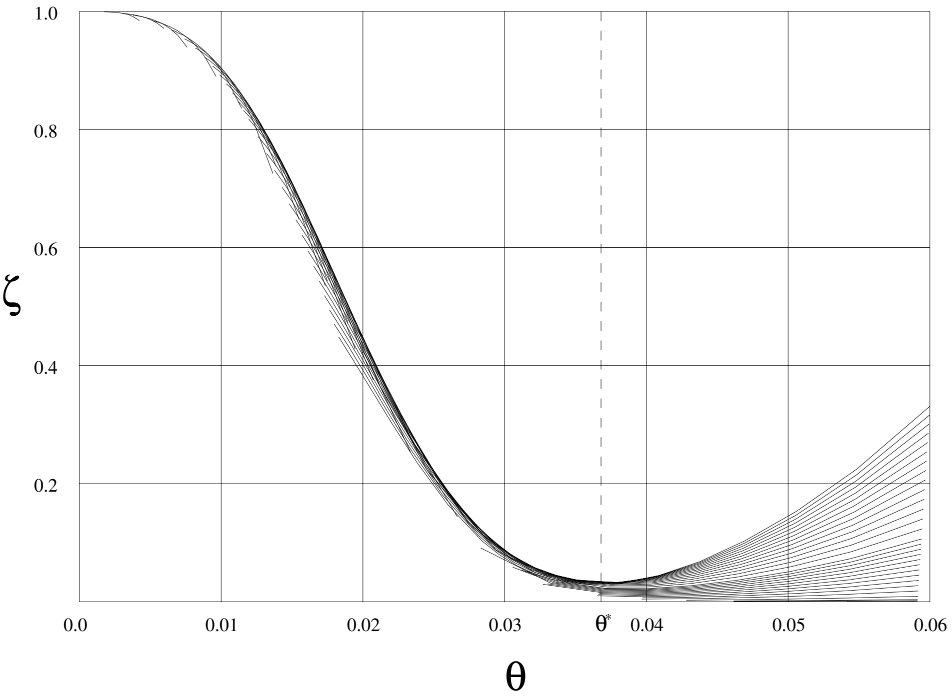

Figure D.2: pVT data for steam in the $\theta \times \zeta$ plane.

Fig. D.2 represents the steam data in the $\theta \times \zeta$ plane[4], where,

$$\zeta = z - p/p_\ell. \tag{D3}$$

Without the influence of nucleation on the properties of steam, the pressure dispersion becomes largely attenuated, so that *all* isobaric curves inside the vapor region become confined in a remarkably narrow belt upper-bounded by a single, sharp limiting curve.

The determination of the values of θ^*, z^*, and p_ℓ, that requires further knowledge about steam, were merely guessed for the construction of fig. D.2. Hence, this graphic cannot be considered as conclusive, but as merely suggestive of the potential of the present approach.

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[4] The value of $p_l \approx 2341$ bar in equation (D2) was obtained by a low-accuracy visual trial and error method, that made the consideration L/RT superfluous for a reliable estimation of p_ℓ.

D.3 Remarkable symmetries in steam

Some aspects of the upper-bound curve in this graphic are noteworthy. The experimental data closely adheres to a single curve in the whole vapor region. As opposed to the small deviations observed under it, this curve is extraordinarily sharp.

Let us denote the maximum and minimum of the curve, respectively, by A and B, whose coordinates in the $\theta \times \zeta$ plane are $A = [0, 1]$, and $B = [\theta^*, \zeta^*]$. These two points delimit the vapor region[5]. It can be clearly seen that around the mid-point of the segment AB the curve exhibits a remarkable half-turn symmetry. It can be seen that, the greater the value of θ in the vapor region, the more degenerate is the gas and the closer it is to its liquid state. It is interesting to confront these symmetries against those that arise in the quasi-particles representation of collective phenomena.

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[5] It can be seen that the value of θ at B separates the vapor from the liquid phase of water.

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