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The quantum roots of irreversibility

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Abstract

Irreversible phenomena are considered unapproachable by quantum mechanics: any attempt to explain non-equilibrium processes is likely to contradict one or more aspects of that theory.

In this paper, to single out these contradictions, we try a quantum mechanical analysis of the dynamics of the ideal gas (an elementary model of irreversible phenomena briefly reviewed here). It turns out that to endow quantum mechanics with the power to explain non-equilibrium phenomena, besides adding the laws of motion that it lacks, an amendment to that theory is required: the rejection of the absolute character usually ascribed both to the Pauli and the indistinguishability principles.

1 Introduction

The ideal gas is here understood as a finite set of identical particles that randomly enter and leave an enumerable set of possible states so that, at a given instant t , the state j is occupied by $\mathbf{r}_j(t)$ particles ($j = 1, 2, \dots$). In the usual approach, the \mathbf{r}_j 's are treated as random variables whose behavior is likened to the placement of balls in cells. SM¹ provides a variety of methods to derive the equilibrium PDF's of these variables; however, they were not devised to explain the transient processes the gas undergo while moving from an arbitrary initial state towards the final state of rest.

In a different approach [1], the population dynamics in each state is treated as a Markovian birth and death process in which the birth and death rates are given in terms of the creation and annihilation operators of QM. While the PDF's of the occupation numbers \mathbf{r}_j 's there obtained, exactly reproduce those given by SM in the equilibrium, in non-equilibrium

¹PDF, SM, QM and GF are acronyms here used to designate *probability distribution function*, *Statistical Mechanics*, *Quantum Mechanics* and *generating function*, respectively.

states they were shown to violate both the Pauli and the indistinguishability principles.

After presenting a summary of paper [1] in section 2 (where the ideal gas is redefined, so to be endowed with kinetic faculties), the present paper discusses, in section 3, the conflicts that arise when this gas is confronted with QM.

2 The dynamics of the ideal gas

To represent the motion of a gas we assume that during a short interval of time, not all, but only a small number of particles change their positions, most of them remaining in the same state they were in the beginning of the interval. We therefore state

Hypothesis 2.1 (Continuity) The smaller the time interval considered, the smaller the number of particles changing their states.

Besides, as attested by SM, the values of both the equilibrium expectation and variance of the $\mathbf{r}_j(t)$'s are negligible when compared with the extremely large numbers of particles and states in the gas. This leads to

Hypothesis 2.2 (Independence) The removal of any state from the gas (together with the particles it contains), will not modify the flow processes that take place in the remaining states. In other words, the flow of particles in a given state is independent of the flow that occurs in any other state.

With these assumptions, the investigation of the laws of motion of the ideal gas is therefore reduced to find the laws that rule the arrival and departure rates, to and from, a single quantum state. To describe this flow we denote by $A_j(\Delta t)$ and $D_j(\Delta t)$, respectively, the number of particles entering and leaving the state j during the time interval Δt , and consider their power series,

$$\begin{aligned} A_j(\Delta t) &= A_j(0) + \dot{A}_j \Delta t + \dots \\ D_j(\Delta t) &= D_j(0) + \dot{D}_j \Delta t + \dots \end{aligned}$$

where $\dot{A}_j(t)$ and $\dot{D}_j(t)$ are identified, respectively, with the arrivals and departure rates of that state. According to hypothesis 2.1, we have $A_j(0) = D_j(0) = 0$. Therefore the first-order equilibrium condition of the flow becomes,

$$\dot{A}_j(t) = \dot{D}_j(t). \quad (1)$$

Denoting by $\mathbf{P}_{\mathbf{r}_j}(t)$, the probability of finding \mathbf{r}_j particles in the state j at the instant t , it can be easily verified that both the hypotheses 2.1 and 2.2 are subsummed in

Axiom 2.1 (Law of motion) The flow of particles in a quantum state is a Markovian birth and death process.

The master equation for $\mathbf{P}_{\mathbf{r}_j}(t)$ of a Markovian birth-and-death process is given by the difference-differential equation [2],

$$\frac{\partial \mathbf{P}_{\mathbf{r}_j}(t)}{\partial t} = -(\lambda_{\mathbf{r}_j} + \mu_{\mathbf{r}_j}) \mathbf{P}_{\mathbf{r}_j}(t) + \lambda_{\mathbf{r}_j-1} \mathbf{P}_{\mathbf{r}_j-1}(t) + \mu_{\mathbf{r}_j+1} \mathbf{P}_{\mathbf{r}_j+1}(t), \quad (2)$$

where $\lambda_{\mathbf{r}_j}$ and $\mu_{\mathbf{r}_j}$ are, respectively, the arrivals and departures rates of particles. To complete de description of the movements of the gas, we have to search for the laws that determine these rates.

2.1 Arrhenius rates

In this section the arrivals and departures rates for the ideal gases of *Bose*, *Fermi* and *Boltzmann* particles are derived.

Let ϵ_j designate the energy of the quantum state j of an ideal gas. The average number of particles occupying that state is given by the well-known formula²,

$$\bar{\mathbf{r}}_j = \frac{1}{e^{(\epsilon_j - \eta)/kT} - \beta}, \quad (3)$$

where $\beta = 1$ for *Bose*, $\beta = -1$ for *Fermi* and $\beta = 0$ for *Boltzmann* particles. It is more suggestive to rewrite equation (3) in the form,

$$\lambda(1 + \beta \bar{\mathbf{r}}_j) = \mu \bar{\mathbf{r}}_j, \quad (4)$$

where

$$\lambda = \xi e^{-\epsilon_j/kT} \quad \text{and} \quad \mu = \xi e^{-\eta/kT}, \quad (5)$$

and ξ is an unknown frequency rate³. The factors λ and μ can be identified with the *Arrhenius rates* of chemical kinetics [3]. By assuming an equivalence between equations (1) and (4), we identify, in the left side, the arrivals rate at the state j and, in the right side, the corresponding departures rate. Accordingly, we split (4) in two independent rates⁴,

$$\lambda_{\mathbf{r}_j} = \lambda(1 + \beta \mathbf{r}_j) \quad \text{and} \quad \mu_{\mathbf{r}_j} = \mu \mathbf{r}_j. \quad (6)$$

It can be seen that these rates are proportional respectively to aa^+ and a^+a , where a^+ and a are, respectively, the second-quantization creation and annihilation operators [4].

²In this paper, k designates the Boltzmann's constant, h , the Planck's constant T , the absolute temperature, η , the chemical potential of the gas, N , the number of particles in the gas and V , the volume it occupies.

³For photons ξ is expressed in terms of the *Einstein's* coefficients.

⁴It is remarkable that these rates are time-invariant.

2.2 The master equation

Let us denote by $\Pi_j(z, t) = \sum_{\mathbf{r}_j} \mathbf{P}_{\mathbf{r}_j}(t) z^{\mathbf{r}_j}$, the GF of the PDF $\mathbf{P}_{\mathbf{r}_j}(t)$. After substituting the *laws of change* (6) in (2), we arrive at [1],

$$\lambda(z-1)\Pi_j = \frac{\partial \Pi_j}{\partial t} - (z-1)(\beta z - \mu) \frac{\partial \Pi_j}{\partial z}, \quad (7)$$

whose solutions are,

$$\Pi_j(z, t) = \begin{cases} \left(\frac{\mu-\lambda}{\mu-\lambda z} \right) \cdot f \left(\frac{\lambda-\lambda z}{\mu-\lambda z} e^{-(\mu-\lambda)t} \right) & \text{(Bose),} \\ \left(\frac{z+\frac{\mu}{\lambda}}{1+\frac{\mu}{\lambda}} \right) \cdot g \left(\frac{z-1}{z+\frac{\mu}{\lambda}} e^{-(\lambda+\mu)t} \right) & \text{(Fermi),} \\ e^{\frac{\lambda}{\mu}(z-1)} \cdot h((z-1) e^{-\mu t}) & \text{(Boltzmann),} \end{cases} \quad (8)$$

where f, g and h are arbitrary functions whose forms are determined by the initial configuration $\Pi_j(z, 0)$ of the gas.

Equations (8) have the common general form, $\Pi_j(z, t) = \varphi_j(z) \cdot \mathfrak{S}_j(z, t)$, where $\varphi_j(z)$ is the GF of the average occupancy numbers $\bar{\mathbf{r}}_j$ of the state j in the equilibrium, and $\mathfrak{S}_j(z, t)$, is the GF of the transient population $\mathbf{y}_j(t)$ in that state, at time t . According to the convolution theorem, the total population at time t is $\mathbf{r}_j(t) = \bar{\mathbf{r}}_j + \mathbf{y}_j(t)$.

2.3 Radiation and change

By referring to equation (2) as the *equation of motion* of the particles in a quantum state, and to (6), as the *laws of force* which determine that motion, we are implying an analogy with *Newton's* mechanics and a re-statement of his first law in a wording that makes it closer to QM⁵,

Wording 2.1 Every *particle* continues in its state of rest (*occupying one of a set of stationary states*) (...) unless it is compelled to change that state by forces impressed upon it.

In his famous paper on the quantum theory of radiation, Einstein recognized, in the argument of the exponential function in the equilibrium equation (3), the *Bohr's* frequency rule, $\epsilon_j - \eta = h\nu$. After almost a century, Bohr's frequency rule remains the *only* form of energy conversion known by QM. Although this fact passed unnoticed (or rated as irrelevant) through this period, it implies that the occupancy number of any state cannot change *unless* there is the absorption or the emission of at least one photon. As a consequence, the whole gas can undergo no change, unless its particles interact with radiation. Thus, the “forces” referred to in

⁵We emphasize the use by *Newton* of the word “unless”, which ascribes to the “forces” the *only* cause of change.

wording 2.1 of *Newton's* first law, are shown to have their origins in the way matter and radiation interact. We then arrive at a stricter restatement of 2.1:

Wording 2.2 Every *particle* continues in its state of rest (*occupying one of a set of stationary states*) unless it is compelled to change that state by *interacting with radiation*.

Law 2.2 holds for every microscopic transformation occurring in the gas in which a particle undergoes a change of state, *whatever* its nature (elastic⁶ or inelastic collision, chemical reaction, etc.). It discloses the “entropy law” as the result of the unceasing random interaction between matter and radiation, so that no cogent explanation of irreversible phenomena can be obtained unless the interaction matter-radiation is considered. Summarizing informally,

*Radiation is the nature's way to induce matter to dissipate its available energy*⁷.

3 Discussion

Quantum theory (...) tells us that what was formerly considered as the most obvious and fundamental property of the corpuscles, (...) their being identifiable individuals, has only a limited significance. Only when the corpuscle is moving with sufficient speed in a region not too crowded with corpuscles of the same kind does its identity remain (nearly) unambiguous. Otherwise it becomes blurred.

E. Schrödinger, *Nature and the Greeks*, p. 16 [5].

Equation (7) can be seen as a mere alternative mathematical representation of the random placement of balls in cells. As shown in the previous sections of this paper, the gas game, whose *laws of change* derive directly from the first-principles of QM, defines a model for the *dynamics of the ideal gas*. As opposed to the usual combinatorial approaches of SM, in which the particles are required to “possess” certain properties, it requires no different treatments to deal with distinguishable, indistinguishable or “exclusivistic” balls, for these behaviors arise as natural consequences of the *laws of change* that rule the placement of balls in cells.

⁶In an elastic collision there is a momentum reversal which implies the change of state of the colliding particles (and consequently to an emission or absorption of photon) but not necessarily to an energy change.

⁷As much as propaganda is the business' way to persuade people to dissipate their savings (see topic §14).

As any other explanation of non-equilibrium phenomena is likely to, some of the conclusions derived from the model of the gas here introduced, are in conflict with the axioms of QM. In the following we discuss the reinterpretations of, and amendments to QM, to attenuate some of the arisen conflicts.

- §1. While SM does not explain irreversible phenomena, the explanation of equilibrium it provides is considered essentially correct. Hence, before we use our model of the *dynamics of the ideal gas* as a guide to analyze the issues that obstruct QM to enter the non-equilibrium realm, we must verify if the description of the equilibrium given by the former is in agreement with that given by the latter.

In fact, since $\lim_{t \rightarrow \infty} \frac{\partial \Pi}{\partial t} = 0$, then $\Pi_\infty(z) = \lim_{t \rightarrow \infty} \Pi(z, t)$ is the solution of the asymptotic equation,

$$\frac{d\Pi}{dz} = \left(\frac{\lambda}{\mu - \beta z} \right) \Pi, \quad (9)$$

which exactly reproduces the well known formula of SM. Hence, when the system it describes is in equilibrium, equation (7) is in complete agreement with QM.

- §2. It is therefore expected that conflicts are likely to arise when $\partial \Pi / \partial t \neq 0$. In fact, equation (7) departs from QM, *not only* because it becomes time-asymmetric, *but also* because its solutions violate both the *Pauli* and indistinguishability principles, as confirmed by the following evidences:

- (a) As opposed to $\Pi_\infty(z)$, the general solutions of (7) depend on the initial configurations of the system, a requirement to which the quantum mechanical description is not subject.
- (b) It is in the equilibrium (but *only* in the equilibrium!) that the PDF of the occupancy numbers is given by the asymptotic form (9). In non-equilibrium, the PDF departs from it — in particular, the initial PDF is an *arbitrary* function. As opposed to the explanation given by QM, we cannot say that the particles *are* indistinguishable or exclusive, but instead that they *become* indistinguishable or exclusive.
- (c) For *Fermi* particles, the non-equilibrium solution of equation (7) admits *any* non negative value of the occupancy number \mathbf{r}_j . It is therefore *not a mathematical necessity* that in non-equilibrium this number be restricted to the values 0 or 1, as has been tacitly assumed for these particles.

- §3. If we insist in ascribing to indistinguishability and exclusivity an absolute character that is invariant under every transformation the gas can undergo, then the dynamics of the ideal gas described by (7) becomes, as noted in §2, doubly incompatible with QM. If we, instead, acknowledge axiom 2.1 together with the laws of change (6), then indistinguishability and exclusivity

arise as natural consequences of the master equation (7), however not as conditions of necessity, but of equilibrium. With this subtle modification that has no impact on QM when the system it deals with is in equilibrium, we reduce the incompatibility between the dynamics of the ideal gas and QM, exclusively to the time-asymmetry of (7).

- §4. A complete compatibilization of QM with the gas dynamics model can be obtained if — while preserving the Schrödinger’s spatial equation untouched (that is required to determine the stationary quantum states of the gas) — his time equation is replaced by the master equation (7).
- §5. The inference drawn in §3 suggests the following amendments to QM:
 - (a) To reject those statements (together with their consequences) that ascribe to indistinguishability and exclusivity an absolute and invariant character, thereby removing them from their status of principles and,
 - (b) to raise, in their places, the elementary actions of creation and annihilation to the rank of invariant principles.

This amendment obviously holds also for the symmetric and anti-symmetric structure of wave functions: they should be acknowledged not as conditions of necessity but of equilibrium.

- §6. Since the rates (6) can be derived from the first-principles, as proposed in §5b, they emerge as the *universal laws of change*, *i.e.*, the unceasing elementary processes that randomly remove and insert particles in quantum states.
- §7. As explained in section 2.3, the laws of change and the absorption and emission of photons are indissoluble from each other: they arise as different manifestations of the same principle. If matter were somehow prevented from interacting with radiation, then change would be impossible; in summary,

wherever there is a change of state, there is an interaction with radiation, and vice-versa.

- §8. As shown in §2b and §2c, it is the PDF, itself, that departs from its stationary form. Hence, departures from equilibrium should not be confused with mere fluctuations around the stationary PDF, for fluctuations are inherent to equilibrium: compared to non-equilibrium states, they are negligible.
- §9. A closer analysis of games of chance shows that shuffling is the *agent* of a process in which dice, coins, game cards, balls or particles are its *patients*. This opposition between *agent* and *patient* is absent in the usual formulation of SM, where a behavior that is imparted by an *agent’s* faculty (to induce particles to behave as indistinguishable) to its *patient*, has been arbitrarily ascribed to the latter, as one of their *properties*.
- §10. Indistinguishability cannot be treated as a *property* of a particle: it does not fit the idea of something that always existed together with the particle, at least not with the meaning usually assigned to it when we speak of mass

or electric charge. The mathematics of indistinguishability is, instead, that of an *equivalence relation* of algebra. In fact, while it can be assigned a meaning to the statement

$$\text{“if } A \equiv B \text{ and } B \equiv C, \text{ then } A \equiv C\text{”}$$

(where the symbol ‘ \equiv ’ holds for ‘*is indistinguishable from*’), no meaning can be assigned to statements such as “an isolated particle is indistinguishable” or “such particle has indistinguishability”.

Note: Indistinguishability can be treated as an *equivalence relation* exclusively in the case of elementary particles (see §13).

- §11. As opposed to the meaningless examples given in §10, it is meaningful to say that “such particle has spin”. *Bose* and *Fermi* particles behave differently when subject to shuffling, not because they are indistinguishable or exclusive, but (as far as is known) because their behavior under shuffling is thus conditioned by a corresponding property, the spin.
- §12. Indistinguishability is also a statistical phenomenon. In fact, it is possible to obtain the same *statistical* result by randomly placing balls of whatever nature (billiard balls, for instance) in cells, provided the shuffling is made by some device that properly reproduces the *laws of change* that “indistinguishabilize” the balls.
- §13. Artificial processes of indistinguishabilization involving macroscopic bodies cannot be confused with the natural processes that involve elementary particles. Quantum particles seem to be shuffled — by means of a mysterious property (see §11) — that is independent of any *device*. Besides, even when the PDF of the occupancy numbers in the case of macroscopic bodies (such as the billiard balls of §12) fit the geometric distribution that characterizes indistinguishability, these bodies, as opposed to elementary particles, can be distinguished by the values of any of its degrees of freedom that do not influence the mechanisms of the shuffling device.
- §14. It is remarkable that *indistinguishabilization* can also occur in non-quantum mechanical systems (see §12). The most noteworthy examples, that might be of paramount importance for Economic Theory, are given by the trading processes involving money⁸ in which wealth is shuffled. This phenomenon might be one of the causes of the unfair income distribution among humans. Economic Theory should pay much more attention to the inquire on the mechanisms of distribution formation, than to the equilibrium distribution itself.
- §15. As shown in this paper, the *dynamics of the ideal gas* implies the existence of a transient process of indistinguishabilization. Since QM does not provide a cogent explanation of transient phenomena, we try an explanation of the origins of indistinguishabilization process in terms of the following conjectures:

⁸This character of money was recognized and used by *Sir James Jeans* in the concluding portion of his book *Physics and Philosophy* to explain the indistinguishability of electrons [6].

- (a) A microscopic particle is completely characterized by the set of values $X = \{x_1, x_2, \dots, x_n\}$, of its n degrees of freedom that, jointly define its global quantum state. This set is the only identifying character a particle has. Therefore, we assume that the necessary condition for two particles to *become* indistinguishable is that they display exactly the same set of values of X . Since, from photons to (small-size) molecules, n is a small integer, there is a non negligible probability that two particles become indistinguishable.
- (b) Each degree of freedom of a particle is compelled by the laws of change (that thus endow it with a natural tendency) to abandon an excited state towards its ground state. As the outcome of this process — to which the uncertainty relations impart a decisive influence⁹ — the particles occupying a given state lose all distinctive characters they had, thus *becoming* indistinguishable.
- (c) One of the most distinguishing character that singles out one particle from another is the set of coordinates that locates it in space. In a gas, as the temperature decreases and its density increases, so that,

$$\sqrt{3mkT} \sqrt[3]{\frac{V}{N}} \rightarrow \frac{h}{2\pi}, \quad (10)$$

then, according to Schrödinger [7],

one has, I think, to say that the particles become entirely blurred, the particle aspect breaks down, and one is no longer allowed to speak of a granulated structure of matter.

When all degrees of freedom of two different particles decay to the minimum allowed, location remains their only distinguishing characters, at least until the Heisenberg's uncertainty relation turns it *blurred*.

- (d) That indistinguishabilization is a non-reversible process should not be surprising for it is impossible to restore the individualities of two particles that have lost, in that process, their identities.
- (e) By acknowledging indistinguishability not as a condition of necessity, but of equilibrium, it seems that we can interpret (without the slightest modification of its mathematics) that the method of the Most Probable Distribution of statistical mechanics establishes, not the maximum entropy for a constant internal energy, but instead the minimum available (Helmholtz's free) energy for a given, prescribed entropy.

In summary,

The particles of a gas are neither indistinguishable nor exclusive; they become increasingly so as the system approaches its equilibrium.

⁹see §15c. A different explanation of this issue is presented in [1].

4 Conclusion

Most of the requirements that, in the view of Huang, a “satisfactory” derivation of SM should fulfill [8], are satisfied by the alternative approach to the gas dynamics discussed in this paper, namely by providing

1. a non-*ad hoc* assumption of 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 (7) expressed, however, not in terms of wave functions, but of the PDF’s of occupancy numbers.

By confronting the behavior of the gas here defined, with the principles of QM, it was possible to identify, in the absolute character ascribed to *Pauli’s* exclusion and indistinguishability principles, one of the possible barriers that keep QM away from a first-principles explanation of irreversible phenomena.

If the amendments to QM, proposed in §5 and their generalizations turn out to be justified, then, besides the interpretation of these principles, many of the current explanations of the persisting puzzles that arose during the development of thermodynamics, kinetic theory and SM, such as the *Boltzmann’s* principle, the direction of thermodynamic processes, the opposition between order and chaos, the derivation of the rates of change of irreversible processes, the *Gibbs* correction, etc., should be revised.

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References

- [1] Mammana C Z 1997 *The Transient Distinguishability of Identical Particles*, Phys Ess, **10**(4) pp 608–14.
- [2] Feller W 1968 *An Introduction to Probability Theory and its Applications*, vol **I**, John Wiley & Sons.
- [3] Moore W J 1972 *Physical Chemistry*, Prentice-Hall.
- [4] Landau L & Lifchitz E 1966 *Mécanique Quantique*, MIR.
- [5] Schrödinger E 1996 *Nature and the Greeks & Science and Humanism*, Cambridge Univ. Press.
- [6] Jeans J 1943 *Physics and Philosophy*, Cambridge Univ. Press & Macmillan Company.
- [7] Schrödinger E 1989 *Statistical Thermodynamics*, DOVER.
- [8] Huang K 1963 *Statistical Mechanics*, John Wiley & Sons, Inc.