A Unifying Approach to Quantum Statistical Mechanics: a Quantum Description of Macroscopic Irreversibility

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Preface [*draft*]

The term *Statistical Mechanics* was coined by Gibbs, who at the same time created the concept of *ensemble* [1]. Gibbs simply assumed, on physical grounds, that macroscopic quantities are obtained as averages over a myriad of microstates (*ensemble*), in a way compatible with macroscopic constraints. The methods was justified by its physically satisfactory results. Boltzmann tried to justified the ensemble theory, introducing the so called *ergodic hypothesis*: what we observe macroscopically is a time average of a physical quantity over a 'long' period of time. This time average is identical with the statistical average over an ensemble. This statement is based on the strong assumption that the orbit of a system comes arbitrarily close to any point in phase space, during a time equivalent to the one used to calculate the time average. Boltzmann also pursued a different route introducing his transport equation (Boltzmann equation), in his formulation of the kinetic theory of gases. Boltzmann equation, to the author's knowledge, is one of the first *Master Equation* ever written in Physics. Differently from dynamical equations of mechanics, master equations are intrinsically irreversible, and remarkably, they allow us to calculate typical relaxation times. In writing his equation, Boltzmann assumed that velocities of colliding molecules are uncorrelated and independent of position. This hypothesis is known with the name of *molecular chaos* (*Stosszahlansatz*), and it allowed Boltzmann to demonstrate his famous *H-theorem*, in an attempt to derive the Second Law of thermodynamics from kinetic theory[2]. Objections to Boltzmann's approach pointed to the fact that one cannot deduce irreversibility from time-symmetric dynamic equations. Boltzmann then advanced a probabilistic interpretation of his results, arguing that they can be understood in terms of most probable distributions for systems with macroscopically large number of particles. On the other hand, the Boltzmann equation has been largely successful in describing transport properties of matter, even in semi-classical situations. In spite of the original opposition, the derivation of the kinetic theory from classical dynamics can be considered satisfactory.

After the introduction of Quantum Mechanics, Pauli followed the Boltzmann tradition to pursue the same program from the quantum mechanical point of view [3]. This procedure led him to formulate the basis of quantum master equations, in an attempt to establish the quantum analog of the *H-theorem*. Irreversibility is introduced through the *random phase hypothesis*, which is the quantum counterpart of Boltzmann molecular chaos assumption [4]. In the present book, we follow this approach, with the understanding of being more comprehensive and satisfactory in deriving equilibrium statistical mechanics. On physical grounds, this method allows, in principle, for calculation of relaxation times, being closer to experimental setups than other proposals (as for example, the ergodic hypothesis).

Our formulation of quantum statistical mechanics is based entirely on the Density Operator formalism, which includes both, quantum and thermal fluctuations[1]. The Density Operator describes the general state of a quantum system, for equilibrium or nonequilibrium phenomena, and embodies the probabilistic nature of quantum systems at finite temperature. We will show, with this formalism at hand, that a satisfactory derivation of Statistical Mechanics is fulfilled. Important requirements that a meaningful theory should implement are:

i) when a physical system is prepared in an arbitrary initial state, the Density Operator should described its relaxation to equilibrium;

ii) the method should provide a quantitative estimation of relaxation times;

iii) at asymptotically long times (greater than typical relaxation times), the Density Operator should define the *equilibrium ensembles* which allow for calculation of thermodynamic properties;

iv) at equilibrium, the limit of low temperatures and high densities should reduce the formalism to ordinary Quantum Mechanics;

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[1] That explains the word "unifying" in the book title.

v) in contrast, the limit of high temperatures and low densities should recover results from classical statistical mechanics.

The above program will be developed in the various chapters of the present book. The presentation is divided in two parts. The basic concepts are discussed in *Part I:Foundations*, particularly important, the relaxation to equilibrium and the meaning of equilibrium itself. Afterwards, the equilibrium ensembles are defined and applied to a number of elementary systems. Interrelations among the ensembles are presented, along with connections with macroscopic thermodynamics. *Part I* also includes quantum statistics and treats ideal quantum gases. Special attention is given to the Bose-Einstein condensation. In *Part II:Applications*, we study interacting quantum systems, including interesting phenomena such as superfluidity and superconductivity.

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Bibliography

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BIBLIOGRAPHY — MANUSCRIPT

Part I

Foundations

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Chapter 1

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Classical or Quantum Probabilities. Or both?

The description of nature through quantum theory is intrinsically probabilistic, and statistical methods are developed in order to get information of physical observables. This distinctive feature has its roots in the probabilistic interpretation of the *wave function*, in conjunction with the Uncertainty Principle. As discussed in standard textbooks, quantum probabilities embody the dual nature of matter, reproducing phenomena such as interference and diffraction. This statistical representation, even for a one particle system, requires an *ensemble* of similarly prepared systems, in order to generate a set of well defined probabilities for all quantities. The ensemble is a conceptual set of an 'infinite' number of replicas of the same system that do not coexist in space or time.

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When all systems of the ensemble are represented by the same *wave function* or *state vector* $|\psi\rangle$, we say that we have prepared a *pure state.* In Statistical Mechanics, $|\psi\rangle$ represents a possible *microstate* of the system. Physical predictions of an observable quantity $\mathbf{A}$ are given in terms of averages or mean values of the type:

$$\langle \mathbf{A} \rangle = \langle \psi \,| \mathbf{A} |\, \psi \rangle \,, \tag{1.1}$$

where the bracket is calculated following well established quantum rules. In turn, statistical fluctuations of quantum origin are obtained through:

$$\left\langle \mathbf{A}^2 \right\rangle - \langle \mathbf{A} \rangle^2 = \left\langle \psi \left| (\mathbf{A} - \langle \mathbf{A} \rangle)^2 \right| \psi \right\rangle \ , \tag{1.2}$$

where we have assumed that the state ψ is normalized, *i.e.* $<\psi|\psi>= 1$. The time evolution of this microstate is dictated by the Schrödinger equation, as long as no measurement is made on the system. We will not pursue here a thorough discussion on the fundamental concepts of Quantum Mechanics, and will assume that the reader has the proper background to follow this set of lectures [1, 2]. According to Quantum Mechanics, a pure state is the maximal information we can have of a quantum system, and represents an exception rather than the rule. In most situations, we do not know the wave function with certainty. A typical example is given by a system of coordinate $\mathbf{x}$ which is coupled to another system of coordinate $\mathbf{y}$ (the latter may be a thermal bath that keeps the system at a constant temperature). In general, we cannot assign a wave function to our system $\mathbf{x}$, which is a part of the whole system $(\mathbf{x}, \mathbf{y})$. In this case, we say that the system $\mathbf{x}$ is in a *mixed state* and we have to look for a more general mathematical object to describe this situation. This lack of information closely resembles the classical statistical problem. In fact, in many instances this case is denominated as *incoherent mixture*, to mean the lack of quantum coherence and the absence of interference effects. As will be discussed later on, quantum and thermal fluctuations compete in this scenario as function of temperature. Quantum coherence is realized at low temperatures, and asymptotically at zero temperature the system is driven exclusively by quantum fluctuations. As long as the temperature is increased, the system develops thermal fluctuations, which eventually dominate the statistics, leading to decoherence of quantum effects (classical statistics). The description of the general ensemble, encompassing all cases, is attained quite naturally employing the so called *state operator* $\boldsymbol{\rho}$ (or *density operator)*, which is a generalization of the wave function concept. The operator $\boldsymbol{\rho}$ is the relevant quantity to construct quantum statistical mechanics. The name *density* is reminiscent of the classical function $\rho(q,p)$ that yields the density of points in phase space to perform classical statistics. A single point in phase space represents one of the systems of the ensemble. An important task to be accomplished is to relate the quantum density operator $\boldsymbol{\rho}$ with the classical function $\rho(q,p)$. In the next section, we develop the basis of the mathematical formalism.

A

1.1 Ensembles and Density Operator

We begin by defining the different ensembles we encounter to describe a physical system [3].

Definition 1 ***Pure Ensemble***. *It is a collection or set of identical physical systems, such that all members of the ensemble (systems) are characterized by the same state vector or ket* $|\psi\rangle$. *This is the usual case we encounter in standard quantum mechanics textbooks, when the state of a system is represented by a single wave function. This ensemble represents a microstate.*

Calculation of averages and standard deviations for the ensemble are given by equations (1.1) and (1.2). This pure state $|\psi\rangle$ may be an eigenstate of a particular physical observable, or may be a linear superposition of eigenstates of an arbitrary operator.

Definition 2 ***Mixed ensemble***. *The wave function is not known with certainty, and we have several possibilities that we write as* $\left\{\left|\psi^{(1)}\right\rangle, \left|\psi^{(2)}\right\rangle ... \left|\psi^{(i)}\right\rangle ...\right\}$. *This collection may be finite or infinite. A fraction of the members of the ensemble, with relative population* w_i, *is assigned to the ket* $\left|\psi^{(i)}\right\rangle$. *Normalization requires that*

$$\sum_i w_i = 1. \tag{1.3}$$

The weights $\{w_i\}$ *are positive (or zero) real numbers. We say that this ensemble represents a macrostate of the system.*

The states vectors $\left\{\left|\psi^{(1)}\right\rangle, \left|\psi^{(2)}\right\rangle ... \left|\psi^{(i)}\right\rangle ...\right\}$ are normalized but not necessarily orthogonal, and the number of such states may be greater than the dimension of the linear space. The numbers $\{w_i\}$ cannot be interpreted as ordinary probabilities, since the quantum states $\left\{\left|\psi^{(1)}\right\rangle, \left|\psi^{(2)}\right\rangle ... \left|\psi^{(i)}\right\rangle ...\right\}$ are not 'mutually exclusive'. This has to be understood in the sense that the overlap between two states of the collection does not vanish in general, *i.e.*

$$\left\langle\psi^{(i)}|\psi^{(j)}\right\rangle \neq 0 \tag{1.4}$$

in the general case. Now, we have to prescribe the calculation of averages for the mixed ensemble. Let $\mathbf{A}$ be a physical observable. We denote by [...] the average for the ensemble, to distinguish from $\langle ... \rangle$ used for the pure quantum case.

Definition 3 *Average or Mean Value for the mixed ensemble.*

$$[\mathbf{A}] \equiv \sum_i w_i \left\langle\psi^{(i)}\left|\mathbf{A}\right|\psi^{(i)}\right\rangle \ . \tag{1.5}$$

In the above definition, we see that the ordinary quantum average $\left\langle\psi^{(i)}\left|\mathbf{A}\right|\psi^{(i)}\right\rangle$ for the state $\psi^{(i)}$ is weighed by its relative population w_i, so the average $[\mathbf{A}]$ has a mixed quantum and statistical nature. We rewrite the definition (1.5) using a general basis of states $\{|n\rangle\}$, which is orthonormal and complete:

$$\begin{aligned}[\mathbf{A}] &= \sum_i w_i \sum_{n,n'} < \psi^{(i)}|n > < n|\mathbf{A}|n' > < n'|\psi^{(i)} > \\ &= \sum_{n,n'} \left(\sum_i w_i < n'|\psi^{(i)} >< \psi^{(i)}|n > \right) < n|\mathbf{A}|n' > \ . \qquad (1.6)\end{aligned}$$

The expression above suggests the following definition:

Definition 4 *State Operator or Density Operator,* $\boldsymbol{\rho}$

$$\boldsymbol{\rho} \equiv \sum_i w_i \ |\psi^{(i)} >< \psi^{(i)}| \ . \qquad (1.7)$$

Its matrix elements are given by:

$$\langle n' |\boldsymbol{\rho}| n\rangle = \sum_i w_i < n'|\psi^{(i)} >< \psi^{(i)}|n > \ ,$$

and the mean value can be written as a trace:

$$[\mathbf{A}] = \sum_{n,n'} \langle n' |\boldsymbol{\rho}| n\rangle \langle n |\mathbf{A}| n'\rangle = \mathrm{Tr}\left(\boldsymbol{\rho}\mathbf{A}\right) \ . \qquad (1.8)$$

From the definition, we get some immediate properties:

i) $\boldsymbol{\rho}$ is an Hermitian operator:

$$\boldsymbol{\rho}^\dagger = \sum_i w_i^* \ \left(|\psi^{(i)} >< \psi^{(i)}| \ \right)^\dagger = \sum_i w_i \ |\psi^{(i)} >< \psi^{(i)}| \ = \boldsymbol{\rho} \ ,$$

because the $\{w_i\}$ are real numbers. The eigenvalues of $\boldsymbol{\rho}$ are then real. We will show that they are all positive;

ii) the density operator is normalized in the sense:

$$\begin{aligned}\text{Tr}\,\boldsymbol{\rho} &= \sum_n \sum_i w_i < n\,|\psi^{(i)} >< \psi^{(i)}|\,n >= \sum_i w_i \sum_n < \psi^{(i)}|\,n >< n\,|\psi^{(i)} >= \\ &= \sum_i w_i < \psi^{(i)}|\psi^{(i)} >= \sum_i w_i = 1 \ , \qquad (1.9)\end{aligned}$$

since the states $\psi^{(i)}$ are normalized. This condition reduces to the fact that the unit operator **1** has mean value equal to 1;

iii) consider an observable **A**. The operator $\mathbf{A}^\dagger\mathbf{A}$ is said to be positive definite (non negative). That means that its average is positive or zero:

$$\left[\mathbf{A}^\dagger\mathbf{A}\right] = \sum_i w_i \left\langle \psi^{(i)}\,|\mathbf{A}^\dagger\mathbf{A}|\,\psi^{(i)} \right\rangle = \sum_i w_i \left\langle \varphi^{(i)}|\varphi^{(i)} \right\rangle \ ,$$

where $|\varphi^{(i)} >= \mathbf{A}|\psi^{(i)} >$. Since the metric is positive, we have $\left\langle \varphi^{(i)}|\varphi^{(i)} \right\rangle \geqq 0$, resulting $\left[\mathbf{A}^\dagger\mathbf{A}\right] \geqq 0$. Since **A** is an observable, it is Hermitian, $\mathbf{A}^\dagger = \mathbf{A}$, with real eigenvalues. Consider the basis that leaves **A** in diagonal form, $A_{mn} = A_n\delta_{mn}$ and calculate $\left[\mathbf{A}^\dagger\mathbf{A}\right]$:

$$0 \leqq \left[\mathbf{A}^\dagger\mathbf{A}\right] = \text{Tr}\left(\boldsymbol{\rho}\mathbf{A}\mathbf{A}\right) = \sum_{k,m,n} \rho_{nm} A_{mk} A_{kn} = \sum_n \rho_{nn} A_n^2 \ ,$$

and since **A** is arbitrary, we obtain that $\rho_{nn} \geqq 0$. Result: any diagonal element of $\boldsymbol{\rho}$, for an arbitrary representation, is non negative. In particular, if we choose the representation where the operator $\boldsymbol{\rho}$ is diagonal, $\rho_{mn} = \rho_n\delta_{mn}$, we obtain that the eigenvalues are non negative, $\rho_n \geqq 0$, with $\sum_n \rho_n = 1$;

iv) using the same representation, we obtain

$$\mathrm{Tr}\left(\boldsymbol{\rho}^2\right) = \sum_n \rho_n^2 \leqq \left(\sum_n \rho_n\right)^2 = (\mathrm{Tr}\ \boldsymbol{\rho})^2 = 1\ ,$$

that is $\mathrm{Tr}\left(\boldsymbol{\rho}^2\right) \leqq 1$, and since the trace is invariant, this result is valid in any representation;

v) the pure ensemble can be considered as a limit case of the mixed ensemble, when only one of the weighs is different from zero, *i.e.*

$$w_i = \begin{cases} 1,\ \text{for } i = j, \\ 0, \text{for } i \neq j\ . \end{cases}$$

and $\boldsymbol{\rho} = |\psi^{(j)} >< \psi^{(j)}|$. In the following, we will review some properties of the pure ensemble. ■

A

1.2 Pure versus mixed ensembles

For pure states, the density operator has the simple form:

$$\boldsymbol{\rho} = |\psi >< \psi|\ ,$$

from where we get the properties:

a) idempotence of $\boldsymbol{\rho}$,

$$\boldsymbol{\rho}^2 = (|\psi >< \psi|)\,(|\psi >< \psi|\ ) = |\psi >< \psi|\psi >< \psi| = |\psi >< \psi|\ = \boldsymbol{\rho}\ ,$$

since $< \psi|\psi >= 1$. This relation can be factorized:

$$\boldsymbol{\rho}\left(\boldsymbol{\rho} - \mathbf{1}\right) = 0 \ . \tag{1.10}$$

b) the equation (1.10) is also satisfied by its eigenvalues:

$$\rho_n \left(\rho_n - 1\right) = 0 \ ,$$

with solutions $\rho_n = 0, 1$. Due to normalization, $\sum_n \rho_n = 1$, it follows that only one of the eigenvalues is 1, and all the other are zero. In the diagonal form, the density matrix is written as

$$\boldsymbol{\rho} \doteq \begin{pmatrix} 0 & 0 & . & . & . & 0 & 0 \\ 0 & ... & & & & ... & 0 \\ . & & 0 & & & & . \\ . & & & 1 & & & . \\ . & & & & 0 & & . \\ 0 & ... & & & & ... & 0 \\ 0 & 0 & . & . & . & 0 & 0 \end{pmatrix} \ .$$

c) due to the idempotent property, we get

$$\mathrm{Tr}\left(\boldsymbol{\rho}^2\right) = \mathrm{Tr}\left(\boldsymbol{\rho}\right) = 1 \ . \tag{1.11}$$

Relation (1.11) can be considered as a necessary and sufficient condition for an ensemble to be pure.