TOWARD A NEW FOUNDATION OF STATISTICAL MECHANICS.

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Abstract

Our main goal is to propose a new point of view concerning the introduction of time-irreversibility in statistical mechanics. It is based on the existence of a transition function defined in terms of path integral and verifying a time-irreversible equation. Since we deal with dynamic processes we show first how they enter in the description of equilibrium states. In order to do that we select the closed paths, we define a mean value for the position fluctuations on the paths and we associate to them a time characterizing the equilibrium. For large isolated systems at equilibrium or for systems in contact with a thermostat our results are identical with those obtained with the Gibbs ensemble methods. For a model frequently used in the microscopic approaches of the brownian motion we show that no new basic assumption is required to predict a transition from a quantum state to a classical one exhibiting a time-irreversible behavior at a macroscopic level. This demonstration is not general but sufficient to show that very well accepted approximations can lead to time-irreversible behaviors for a large class of systems. We emphasize the difference between our work and the system+reservoir approaches and we show that equilibrium states and irreversible processes can be described on the same footing representing a progress in the question of time-irreversibility in statistical physics. The transition function can be also used for describing a small system for which there is no thermodynamics. By adding to the transition function a second one characterizing the reverse motion we may describe pure mechanical systems for which there is no friction. In a simple case we replace the two real valued transition functions by a complex function verifying a Schrödinger like equation. From this we see how to break the time-reversibility of this equation and how to investigate the connection quantum mechanics-thermodynamics from a very fundamental point of view.

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I. INTRODUCTION

From classical textbooks in statistical mechanics (see for instance (1)) we know that thermodynamics is primarily concerned with the general relationships between certain macroscopic properties of a system in equilibrium while statistical mechanics goes beyond these formal interrelationships and tries to connect the observed values of a thermodynamic quantity with the molecular properties of the system. Thus statistical mechanics adds something very useful to thermodynamics but it neither explains thermodynamics nor replaces it. The major part of this paper is connected with the relation between statistical mechanics and thermodynamics.

The part of statistical mechanics or thermodynamics that we can considered as firmly founded concerns the description of equilibrium states and the possible transformations between such states. This requires first to have a definition of equilibrium states. For Callen ((2) p.13), in all systems there is a tendency to evolve toward states in which the properties are determined by intrinsic factors and not by previously applied external influences, such terminal states are, by definition, time independent and they are called equilibrium states. Thus the existence of an infinitely long time is associated with these states; below another definition of the equilibrium will be introduced. One goal of statistical mechanical consists to predict the properties of an equilibrium state when systems are composed of a very huge number of particles; only in the so-called thermodynamic limit we may expect a comparison between thermodynamics and statistical physics (2). Since Gibbs (see for instance (1), (4)) we do not try to follow the precise changes of a particular system and we replace a time average by an average on an ensemble of systems having a similar structure of the system of actual interest. This is generally considered as an axiom but it exists some attempts trying to demonstrate the equivalence of the two averages, this is the main goal of the ergodic theory. A second axiom concerns the form of the distribution function on the ensemble. Hereafter the Gibbs ensemble method will be not used.

From a thermodynamic point of view the possible passage from an equilibrium state $A$ to another one, $B$, is determined by the change in entropy; in any a real transformation $A \rightarrow B$ the entropy must grow and for Planck and Einstein the law of evolution of a system is the law of entropy evolution (2). As noted by Planck ((5) p.88)) in nature no process is entirely free from friction or heat conduction, all the processes which actually take place in nature
exhibits an increase of entropy and then the transformation $B \rightarrow A$ is impossible. Despite of this we may imagine reversible transformations for which the two states have the same entropy. In reversible transformations a system can move from one state to another one or vice versa. Reversible processes form only a limiting case of considerable importance for theoretical demonstration. A quasi-equilibrium process is defined as a dense succession of equilibrium reversible states, it represents an ordered succession of equilibrium states whereas a real process is a temporal succession of equilibrium and non-equilibrium states. Equilibrium states and quasi-static transformations are first introduced in textbooks then the existence of irreversibility is added. It was natural to follow this route both in statistical mechanics and in thermodynamics because it corresponds to an order of growing complexity. However since the pioneer work of Boltzmann and the introduction of the H-theorem the question of irreversibility is all the time present in statistical mechanics (see for instance [7]). Hereafter we mainly retain the crucial problem how to go from a microscopic description based on the existence of a hamiltonian leading to time-reversible processes to macroscopic observations that are time-irreversible. Instead of this traditional route to irreversibility we suggest a totally different point of view based on the following hypothesis: since irreversibility is a fundamental aspect of thermodynamics that is a very general branch of Science, we expect that it must also exists at a microscopic level a class of irreversible processes and it is on these processes that we can based the statistical mechanics because from them the question of irreversibility must be more easy to apprehend. This point of view has several consequences: i) since irreversibility is observed via dynamic processes we have essentially to consider dynamic processes, ii) since we have to describe equilibrium states we have to show how to describe such states from a dynamic point of view and iii) the Schrödinger equation that is time reversible in the Wigner sense cannot be used as a possible starting point in our approach.

The paper is organized as follows. In Section 2 we introduce a transition function describing the time evolution of an isolated system in the quantum domain. This function is a dynamic quantity verifying a time-irreversible equation that is exactly equivalent to a Smoluchovski equation in a simple case. Our main task will be to show that all processes reversible as well as irreversible can be described from this transition function or from mathematical transformations of it. To have a convincing approach we have selected four problems that will be solved in the following Sections. In Section 3 we show how a dynamic approach
can be used to describe an equilibrium state of a very large and isolated system. This will be done by introducing i) closed paths, ii) position fluctuations on these paths and iii) a non-traditional definition of the equilibrium leading to the introduction of a characteristic time-interval and a path-temperature. When this path-temperature is identified with the thermal one we obtain the results derived from the Gibbs ensemble method but in addition new questions can be investigated as for instance the relation entropy and action or the existence of entropy for short time-interval. In Section 4 we describe the properties of a system in contact with a thermostat fixing its temperature. In Section 5 we show on a simple example that a simple quantitative change of the results previously obtained is sufficient the describe a typical irreversible behavior at a macroscopic level. This is illustrated by considering a model frequently used to derive the brownian motion from a microscopic level. In Section 7 we show how to extend our approach in order to describe and a reversible behavior corresponding to a pure mechanical system and a Schrödinger like equation will be derived in a simple case. Reciprocally this allows us to understand how we have broken the time-reversibility of the Schrödinger equation. The conclusions of this work appear in the last Section.

Our approach is restricted to systems in absence of gravity and radiations and theoretical questions as for instance the existence of a thermodynamic limit will be not discussed at this stage.

II. THE BASIC INGREDIENTS

In the presentation of statistical mechanics some authors introduce first the classical statistical mechanics and then its quantum version (see for instance (4)), for others (1) the first step is a quantum description and the classical one is the result of the limit $h \to 0$, in which $h$ is the Planck constant. Hereafter we begin with the quantum description that offers a fundamental introduction of the particles undiscernability and is able to explain why $h$ survives even in the so-called classical statistical mechanics.

In this Section we want to characterize a N-body mono component system enclosed in a volume $V$ via a transition function that will be our basic tool to describe as well as equilibrium states or irreversible behaviors.
A. Introduction of the transition function

Our first step concerns the description of the particles undiscernability. This effect has been discussed in standard statistical mechanics (1) as well as in the path integral formalism (2). The representation of this effect depends on the ratio $\frac{d}{\Lambda}$ in which $d$ is the mean distance on which we may observe significant variations in the potential energies and $\Lambda$ is the thermal de B"{o}glie wavelength given by $\Lambda^2 = \frac{\hbar^2}{2\pi mk_BT}$ in which $m$ is the mass of particles and $k_BT$ is the order of magnitude of the kinetic thermal energy. If $d^2 << \Lambda^2$ a detailed description of undiscernability must be considered however this is restricted to very particular cases, as for instance, helium at very low temperature. In more general situations we have $d^2 >> \Lambda^2$ and the effect of undiscernability is reduced to the introduction of a factor $\frac{1}{N!}$. Hereafter we assume that after redefining a length similar to $\Lambda$ we will be in this last case.

The basic tool on which we suggest to base the statistical mechanics is the time-dependent path integral

$$\phi(x^N(0), t_0; x^N, t) = \frac{1}{N!} \int \mathcal{D}x^N(t) \exp\left(-\frac{1}{\hbar} \int_{t_0}^t H(s)ds\right)$$

(1)

defined for $t \geq t_0$; $x^N(0)$ represents the set of the positions $x^i(0)$ occupied by the $N$ particles at the time $t_0$ and $x^N$ is a similar quantity but associated with the time $t$, $\mathcal{D}x^N(t)$ is the path integral measure and $H(s)$ is given by

$$H(s) = \sum_{i=1}^{N} \left[ \frac{1}{2} m \left( \frac{dx^i(s)}{ds} \right)^2 + v_1(x^i(s), s) + \sum_{j=1,j\neq i}^{N} v_2(x^i(s), x^j(s)) \right]$$

(2)

where $v_1(x^i(s), s)$ is the external potential acting on the particle $i$ located at the point $x^i(s)$ at the time $s$ and $v_2(x^i(s), x^j(s))$ is the pair potential between two particles $i$ and $j$ at time $s$. We may define the total potential on the particle $i$ located at the point $x^i$ as

$$u(x^i(s), s) = v_1(x^i(s), s) + \sum_{j=1,j\neq i}^{N} v_2(x^i(s), x^j(s))$$

(3)

The function $\phi(x^N(0), t_0; x^N, t)$ is a positive real valued function representing the sum of all the paths joining the points $x^N(0)$ and $x^N$ when the time is running from $t_0$ to $t$. From a physical point of view it seems natural of weighting each path by the euclidean action, thus the importance of a path depends on the total energy spent on it. The significant contribution to $\phi(x^N(0), t_0; x^N, t)$ is given by the paths for which the euclidean action is comparable to the Planck constant.
B. Properties of the transition function

Associated with the path integral formalism there it exists very well known results that are explicitly given for instance in (8), (9), (10). Here we focus on those useful hereafter.

To treat the path integral in (1) we introduce a time discretization, the discrete time step \( \delta t \) is given by \( \delta t = \frac{t - t_0}{n} \) where \( n \) is very large and we denote by \( \delta x \) the difference of position corresponding to \( \delta t \). The path integral measure is given by

\[
Dx^N(t) = \frac{1}{C} \prod_{i=1}^{N} \prod_{j=1}^{n-1} dx^i_j
\]

in which \( C \) is a normalization constant and \( dx^i_j \) represents the position of the particle \( i \) at the time \( t_0 + j\delta t \), we have \( x(0) = x(0) \) and \( x_{n-1}^i = x(t - \delta t) \).

The paths we consider are fractal (11) and those giving an important contribution to (1) in the limit \( \delta t \to 0 \) are those for which we have \( \frac{1}{n} m \delta x^2 \approx \delta t \) that we can also put in a kind of Heisenberg uncertainty relation adapted to the path integral formalism \( m \frac{\partial}{\partial t} \delta x \approx h \). On the paths the energy is not given but can fluctuate and in the limit \( \delta t \to 0 \) the relevant paths are those for which the action associated with \( \delta t \) corresponds to \( \frac{1}{2} m \left( \frac{\partial}{\partial t} \right)^2 \delta t \approx h \). Thus when the classical Hamiltonian (2) is put in the path integral formalism we measure the fluctuation of the action relative to \( h \), we have a sort of Heisenberg uncertainties relations and the particles undiscernability is introduced by the factor \( \frac{1}{N!} \) from these elements we can say that we have a quantum description of the system.

From the function \( \phi(x^N(0), t_0; x^N, t) \) we may define a semi-group since

\[
\phi(x^N(0), t_0; x^N, t) = \int \phi(x^N(0), t_0; x^N(1), t_1)\phi(x^N(1), t_1; x^N, t)dx^N(1)
\]

whatever \( t_1 \) provided \( t_0 \leq t_1 \leq t \). In the limit \( t \to t_0 \) we have

\[
\lim_{t \to t_0}\phi(x^N(0), t_0; x^N, t) = \delta(x^N - x^N(0)) = \prod_i \delta(x^i - x^i(0))
\]

From \( \phi(x^N(0), t_0; x^N, t) \) we define

\[
\phi(x^N, t) = \int \phi_0(x^N(0))\phi(x^N(0), t_0; x^N, t)dx^N(0)
\]

in which \( \phi_0(x^N(0)) \) is a given function and due to (6) we have \( \phi(x^N, t = t_0) = \phi_0(x^N(0)) \).

The equations (5), (6) and (7) show that \( \phi(x^N(0), t_0; x^N, t) \) plays the role of a transition function in the space-time.
C. Time evolution of the transition function

In order to investigate the time evolution of the transition function we follow a route similar to the one used in (8) to relate the path integral formalism to the Schrödinger equation. The technical details will be not repeated here. For an infinitely small increasing of time \( \epsilon \) we have using (5)

\[
\phi(x^N(0), t_0; x^N, t + \epsilon) = \int \phi(x^N(0), t_0; x^N(1), t)\phi(x^N(1), t; x^N, t + \epsilon)dx^N(1) \tag{8}
\]

In the part \( \phi(x^N(1), t; x^N, t + \epsilon) \) of this expression the dominating term is the kinetic energy proportional to \( \frac{1}{\epsilon} \) and the potential energy can be expanded linearly in term of \( \epsilon \), due to this we have to deal with gaussian quadratures. In the part \( \phi(x^N(0), t_0; x^N(1), t) \) we may expand \( x^N(1) \) around \( x^N \). Many terms can be eliminated with the gaussian quadrature and finally selecting all the terms of order \( \epsilon \) we are left with

\[
\frac{\partial \phi(x^N(0), t_0; x^N, t)}{\partial t} = \frac{\hbar}{2m} \sum_{i=1}^{N} \frac{\partial^2 \phi(x^N(0), t_0; x^N, t)}{\partial (x^i)^2} - \frac{1}{\hbar} \sum_{i=1}^{N} u(x^i(t), t)\phi(x^N(0), t_0; x^N, t) \tag{9}
\]

Introducing the function \( \phi(x^N, t) \) defined by (7) we obtain

\[
\frac{\partial \phi(x^N, t)}{\partial t} = \frac{\hbar}{2m} \sum_{i=1}^{N} \frac{\partial^2 \phi(x^N, t)}{\partial (x^i)^2} - \frac{1}{\hbar} \sum_{i=1}^{N} u(x^i(t), t)\phi(x^N, t) \tag{10}
\]

assuming that the transition function is regular in order to be able of permuting derivative and quadrature. This equation is time-irreversible since it is of diffusive type, here the diffusion can be associated with the existence of a path integration that selects the paths verifying a form of uncertainty relations. By integration over the volume it is clear that \( \phi(x^N, t) \) is not normalized and \( \phi(x^N, t) \) is not a probability. If there is no interaction between particles and in the case of an time-independent external potential following an idea of van Kampen (12) extensively used in (13) to describe chemical reactions we can show that an exact mathematical transformation of (10) leads to define a probability verifying a quantum Smoluchowski equation.

In a previous work (14) the equation (10) has been established from a semi-empirical point of view inspired by the chess-model (8); the space time was considered as initially discrete but a continuous limit was sufficient for the cases investigated. In this route we have first (10) and the path integral form of the transition function (1) is obtained via the Feynman-Kac formula. Here a more fundamental point of view is adopted: the space time is continuous but
a discretization appears from the process of quantification associated with the path integral. Note that the time that appears in equations is the ordinary time but not the imaginary time invoked in the relation between quantum physics and thermodynamics; this point will be discussed in Section 6.

D. A selection of problems

We suggest to found the statistical mechanics on the transition function $\phi(x^N(0), t_0; x^N, t)$ that is a time-dependent quantity verifying time-irreversible equations (9) and (10). We assume that all the relevant quantities can be expressed starting from (11) or from mathematical transformations of (11). On the paths the energy is not given but can fluctuate in agreement with a form of the Heisenberg uncertainty relations. We do not claim that $\phi(x^N(0), t_0; x^N, t)$ is the only possible choice for a new foundation of statistical mechanics simply we say that we have a tool at our disposal and we will try to analyze some consequences of this choice. Other choices are certainly possible but, as we shall see below, $\phi(x^N(0), t_0; x^N, t)$ leads to well known results already established in the literature for systems at equilibrium.

Until now there is no explicit relation between (11) and statistical mechanics. To progress in this route we have to solve problems proving the interest of our approach, among them we have selected the following:

1) From $\phi(x^N(0), t_0; x^N, t)$ that is a time dependent quantity we must be able to recover traditional results of thermodynamic equilibrium. This is equivalent to say how to describe an equilibrium state from a dynamic point of view

2) From a transition function we must be able to describe the equilibrium state of a system coupled with a large one fixing some parameters and playing the role of a thermostat. This leads to introduce a canonical description of systems

3) From the transition function of an isolated quantum system we must be able to describe the transition from a quantum regime to a classical one exhibiting an irreversible behavior at a macroscopic level

4) We must be able to extend our approach to describe pure mechanical systems that exhibit a time-reversible behavior

To answering these problems i)we will show that we are able to describe the statistical mechanics of a large variety of systems in very different conditions and ii) and we will see that
the question reversibility/irreversibility is not so hard as it appears in standard statistical mechanics.

III. DYNAMICAL DESCRIPTION OF A THERMODYNAMIC EQUILIBRIUM STATE

In this Section we derive standard results concerning equilibrium states, we give an answer to the first problem mentioned in 2D. In traditional statistical mechanics it is assumed that we have to wait an infinitely long time interval to reach a stationary equilibrium state and there is no explicit time in the calculation of an equilibrium quantity. Here since any quantity must be calculated from the transition function \( \Pi \) that is time-dependent we have to associated a dynamic process with an equilibrium state. In the transition function we first select the closed paths and we analyze the position fluctuations on these paths as a function of time. Secondly, a time associated with an equilibrium state is introduced via a dynamic definition of equilibrium. A connection with standard thermodynamics is established and the results of classical statistical mechanics are reobtained.

In equilibrium situation the total potential on the particle \( i \) located at point \( x^i \) is not an explicit function of time and the transition function associated with two times \( t \) and \( t_0 \) will only depend on \( (t - t_0) = \tau \) and we can take \( t_0 = 0 \). Explicit calculations are performed on a one-dimensional system, a generalization to three dimensions is straightforward.

A. Closed paths and position fluctuations

To describe equilibrium states we can select different classes of paths corresponding to different topologies. To each class corresponds a given degree of sophistication in the system description. Let first consider closed paths, they depend on the source point of the paths and for example on a given time-interval. If two points are considered we have to introduce the closed paths defined previously, one for each source point, but also the paths joining the two points and describing the correlations between the two points. This last description is more sophisticated than the previous one but it certainly requires more parameters than just a time interval. Hereafter we decide to stay with closed paths corresponding to the simplest
description. This choice is also inspired by what is done in traditional quantum statistical physics where the properties of thermal equilibrium are related to the trace of the density matrix, a more sophisticated description used the non-diagonal terms of the density matrix.

Let consider closed paths around the point \(x^i(0)\) and the associated transition function \(\phi(x^N(0), 0; x^N(0), \tau)\). We can use this function to calculate the quadratic deviation from the original position defined by

\[
< [x^i(t') - x^i(0)]^2 >_{path} = \frac{\int dx^N(0) [x^i(t') - x^i(0)]^2 \phi(x^N(0), 0; x^N(0), \tau)}{\int dx^N(0) \phi(x^N(0), 0; x^N(0), \tau)}
\]

Since the transition function is a positive real valued function its integration over \(dx^N\) is also positive and the ratio

\[
\frac{\phi(x^N(0), 0; x^N(0), \tau)}{\int dx^N(0) \phi(x^N(0), 0; x^N(0), \tau)}
\]

is a positive quantity, smaller or equal to one and normalized it be used as a density of probability on the space \(x^N(0)\) and the corresponding averages we will call averages over paths. For \(0 < t' < \tau\) and \(u(x^i) = 0\) we have \([x^i(t') - x^i(0)]^2 >_{path} = \frac{\hbar t'(\tau - t')}{m} \) that exhibits a maximum for \(t' = \frac{\tau}{2}\) leading to

\[
max < [x^i(t') - x^i(0)]^2 >_{path} = \frac{\hbar \tau}{2m} = \lambda^2
\]

Thus any free particle \(i\) can move in a sphere of radius \(\lambda = \sqrt{\frac{\hbar \tau}{2m}}\). This radius is unchanged if the variation of the total potential \(u(x^i)\) is negligible in this sphere.

**B. Characteristic time for equilibrium states**

The existence of a characteristic time associated with closed paths has been discussed first in (14). Let consider a function depending explicitly on \(\tau\) as for instance the one characterizing the energy fluctuations on the closed paths

\[
S(\tau) = \frac{1}{N!} \int dx^N(0) \int Dx^N(t) \exp\left(-\frac{1}{\hbar} \int_0^\tau (H(s) - U) ds\right) = \exp \frac{\tau U}{\hbar} \int dx^N(0) \phi(x^N(0), 0; x^N(0), \tau)
\]

where \(U\) is a given number corresponding to the internal energy needed to create the system. The first equality in (14) shows that the value of \(S(\tau)\) is determined by the paths having an energy different from \(U\) but such as \(\int_0^\tau (H(s) - U) ds \approx \hbar\). The last equality in (14) shows that \(S(\tau)\) results from an integration of the transition function over the source points \(x^N(0)\).
and a multiplication by $\exp\frac{\delta t}{h}$. In $S(\tau)$ we assume that $\tau$ is a function of $U$. To determine $\tau$ we consider the derivative $\left[\frac{\partial \ln S(\tau)}{\partial U}\right]_{N,V}$. We have

$$\left[\frac{\partial \ln S(\tau)}{\partial U}\right]_{N,V} = \frac{\tau}{h} + \left[\frac{\partial \tau}{\partial U}\right]_{N,V} \left[\frac{U}{h} - \left[\frac{\partial \ln \int dx^N(0)\phi(x^N(0),0;\tau^N,0)}{\partial \tau}\right]_{N,V}\right]$$

(15)

In order to use (9) in the calculation of the partial derivative of $\phi(x^N(0),0;\tau^N,0,\tau - \delta t)$ we rewrite this function according to

$$\phi(x^N(0),0;\tau^N,0,\tau - \delta t) = \int dx'^N\phi(x^N(0),0;x'^N,\delta t)\phi(x'^N,\delta t;x^N(0),\tau - \delta t)$$

(16)

and the derivative is given by

$$\frac{\partial \phi(x^N(0),0;\tau^N,0,\tau - \delta t)}{\partial \tau} = \int dx'^N\phi(x^N(0),0;x'^N,\delta t)\frac{\partial \phi(x'^N,\delta t;x^N(0),\tau - \delta t)}{\partial \tau}$$

or using (9)

$$\frac{\partial \phi(x^N(0),0;\tau^N,0,\tau - \delta t)}{\partial \tau} = \int dx'^N\phi(x^N(0),0;x'^N,\delta t)\left[\frac{h}{2m} \sum_{i=1}^{N} \frac{\partial^2 \phi(x'^N,\delta t;x^N,\tau - \delta t)}{\partial (x^i)^2} - \frac{1}{h} \sum_{i=1}^{N} u(x^i(\tau - \delta t))\right]$$

(18)

In the limit $\delta t \to 0$ the part associated with the interaction potential gives the following contribution to (17)

$$\frac{<U_p>_{path}}{h} = \frac{1}{h} \lim_{\delta t \to 0} \frac{\int dx^N(0)\int dx'^N\phi(x^N(0),0;x'^N,\delta t)\sum_{i=1}^{N} u(x^i(\tau - \delta t))}{\int \int dx^N(0)\phi(x^N(0),0;\tau^N,0,\tau)}$$

(19)

that we can interpret as the mean value of the potential energy calculated over the closed paths. The calculation of the remaining term in (18) requires to calculate the second derivative of $\phi(x'^N,\delta t;x^N,\tau - \delta t)$. This can be readily performed and it is convenient to write $x'^i = x^i + \delta x^i$. We have

$$\lim_{\delta t \to 0} \frac{\int dx^N(0)\int dx'^N\phi(x^N(0),0;\Pi_{i=1}^{N}(x^i + \delta x^i),\delta t)\sum_{i=1}^{N} \frac{1}{h} \left(\frac{m}{2}\frac{\delta x^i}{\delta t} - \frac{h}{2m}\right)\phi(\Pi_{i=1}^{N}(x^i + \delta x^i),\delta t;x^N,\tau - \delta t)}{\int \int dx^N(0)\phi(x^N(0),0;\tau^N,0,\tau)}$$

(20)

The average over closed paths of $\left(\frac{m}{2}\frac{\delta x^i}{\delta t} - \frac{h}{2m}\right)$ has been already calculated in (11). Although the first term $\frac{m}{2}\frac{\delta x^i}{\delta t}$ is the kinetic energy, it has been shown that its average over the paths generates two terms; the first produces a diverging term canceling $\frac{h}{2m}$ and the second gives rise to a finite negative quantity which is $-\frac{h}{2m}$. We define (20) as $- <U_k>_{path}$ and

$$<U_k>_{path} = \frac{Nh}{2m}.$$ Finally we can rewrite (17) according to

$$\left[\frac{\partial \ln S(\tau)}{\partial U}\right]_{N,V} = \frac{\tau}{h} + \frac{1}{h} \left[\frac{\partial \tau}{\partial U}\right]_{N,V} \left[\frac{U}{h} - \left( <U_k>_{path} + <U_p>_{path}\right)\right]$$

(21)
The sum $< U >_{path} = < Uk >_{path} + < Up >_{path}$ is a finite quantity associated with the paths. A natural equilibrium condition consists to choose $\tau$ in order to have

$$[U - < U >_{path}] = 0 \quad (22)$$

it means that after a time interval $\tau$ the total energy calculated on all the closed paths is equal to the internal energy needed to create the system. Thus $\tau$ is a characteristic of the equilibrium state in no way it represents the relaxation time that we may observe when a system not at equilibrium relaxes toward its equilibrium state. Now (15) is reduced to

$$\left[ \frac{\partial \ln S(\tau)}{\partial U} \right]_{N,V} = \frac{\tau}{h} = \frac{1}{k_B T_{path}} \quad (23)$$

in which we have introduced a temperature over the paths $T_{path}$ and since $\tau > 0$ we can conclude that $T_{path} > 0$.

**C. Relation with thermodynamics**

We can check that $\ln S(\tau)$ is identical to $\frac{S}{k_B}$ in which $S$ is the usual entropy defined in term of path integral provided we identify $T_{path}$ with the usual temperature $T$. Thus our result is identical to the one obtained from the Gibbs ensemble since the path integral formalism developed in (2) is just a mathematical transformation from the one derived with Gibbs ensemble method. Note that (23) corresponds to the usual definition of the temperature in thermodynamics. In our approach we have expressed $S$ as a function of $U, N$ and $V$ as usually in standard thermodynamics and we have created an entropy representation of thermodynamics (2) and from (14) we may calculate all the properties associated with the thermodynamic equilibrium. Thus to characterize the equilibrium state of a system the fundamental quantity is

$$\ln S(\tau) = \frac{\tau U}{h} + \ln \int dx^N(0) \phi(x^N(0),0;x^N(0),\tau) \quad (24)$$

More generally the previous result suggests that to describe an equilibrium situation we have to execute the following prescription: i) we focus on closed paths, ii) we associate to the paths a characteristic time and iii) we perform an integration over the path source point. The approach we have developed suggests several comments.
1. Relation entropy/action

From our definition (14) or (24) the entropy is based on a counting of paths in space time but not on the counting of microstates as suggested by Boltzmann with its relation
\[ S = k_B \ln W \]
in which \( W \) is the number of states consistent with some external constraints. Since our result is identical to the classical one we may conclude that the two ways of counting lead to identical results. However our dynamical point of view reveals also a relation between entropy and action that we cannot imagine in Gibbs ensemble method since it relates an equilibrium quantity (the entropy) to a dynamical one (the action). In (15) we have shown that for a transformation at constant volume we have
\[
\frac{\delta A_{\text{path}}}{\hbar} = -\frac{\delta S}{k_B}
\]
in which \( A_{\text{path}} \) is the average on the closed paths of the euclidean action. The search of such relation has a long history (14). The relation (25) has been derived in the case of Schwartschild black holes. In that case the entropy is calculated without any reference to a counting of microstates but via an functional integration of the euclidean action of the gravitational field and a characteristic time \( \beta h \) has been introduced (16). This may suggest than a definition of entropy more general than the one of Boltzmann might exist (17).

2. Entropy and short time

We may ask what is the meaning of \( \ln S(t') \) for \( 0 < t' < \tau \). The path integral is well defined from a mathematical point of view but if we write the time-energy uncertainty relation we can easily verified that during the time interval \( t' \) the quantum energy fluctuations are larger than the thermal ones represented by \( k_B T \) and we may conclude that during this time interval there is no thermodynamics. The non-existence of entropy for very short period of time has been already underlined by Landau (18) here we give a quantitative version to the Landau remark.
3. **Equilibrium states and dynamics**

It is interesting to mention that the relation between equilibrium and dynamics has been already investigated in the literature showing that an equilibrium state represented by a density matrix may reveal a dynamics. This has been done starting from an algebraic formulation of quantum theory (19), using a theorem due to Tomita and Takesaki (20) and the idea that the KMS condition (21) is the correct definition of thermal equilibrium for infinite dimensional quantum system. It has been established (22) that the density matrix implies the time evolution generated by the Hamiltonian provided the time is measured in units $\beta\hbar$ (24). This result is restricted to a reversible mechanics and the origin of the time rescaling is not explained. From our approach two equilibrium states are separated by $\tau = \beta\hbar$ and when only focusing on equilibrium states it seems natural to consider $\tau$ as the unit of time (23), this point will be illustrated below. Nowadays it seems difficult to go more deeply in a comparison between our approach and the one issue of the Tomita-Takesaki theorem. This theorem has been used by of Connes and Rovelli (24) to establish a thermodynamics origin of time in presence of gravity; in their work they proposed a definition of the equilibrium similar to the one introduced here.

**D. The classical limit**

The quadratic distance $\lambda$ defined in (13) is now $\lambda^2 = \frac{\hbar}{m} \tau = \pi \Lambda^2$ showing that $\lambda$ and $\Lambda$ represent basically the same quantity. During the time interval $\tau$ the fluctuations in the positions of a free particle are restricted to a volume of radius $\lambda \approx \Lambda$. The approximation introduced to get a simple expression for the particles undiscernibility effect (see subsection 2.A)) means now that the variations of $u(x^i)$ are negligible on a sphere of radius $\lambda$. Thus, with this approximation, we have

$$\left(\frac{1}{\hbar}\right) \int_0^\tau u(x^i(s))ds \approx \beta u(x^i(0))$$

and we have essentially to focus on the kinetic energy in a closed paths. To do that we may divide the time interval $\tau$ in two equal time intervals and we change $x^i(1)$ in $v^i$ according to
\[ x^i(1) = x^i(0) + \frac{v^i}{2} \tau \] we get

\[
\int dx^N(0) \phi(x^N(0),0;x^N(0),\tau) = \frac{1}{N!} \left( \frac{m}{\hbar} \right)^N \int dx^N(0) \exp(-\beta \sum_{i=1}^{N} u(x^i(0))) \int \prod_{i=1}^{N} dv^i \exp(-\beta \frac{m}{2}(v^i)^2)
\]

which is exactly the classical partition function for a one-dimensional system.

We may also derive the classical limit directly from the equilibrium condition (22). First, using the explicit value of \( \tau \) we have

\[
\langle U_k \rangle_{\text{path}} = \frac{\hbar}{2\tau} = \frac{Nk_B T}{2}
\]

the traditional value of the kinetic energy for a one-dimensional system. Second, from (19) we may introduce the fact that the potential \( u(x^n) \) does not vary on the time interval \( \tau \) and certainly on \( \delta t \ll \tau \) and we can approximate \( u(x^n) \) by \( u(x^i(0)) \) we get

\[
\langle U_p \rangle_{\text{path}} = \int dx^N(0) \sum_{i=1}^{N} u(x^i(0)) \phi(x^N(0),0;x^N(0),\tau)
\]

in which (16) has been used. In \( \phi(x^N(0),0;x^N(0),\tau) \) we may isolate the potential part which is calculated for the origin position and using (27) the result is

\[
\langle U_p \rangle_{\text{path}} = \int dx^N(0) \sum_{i=1}^{N} u(x^i(0)) \exp(-\beta \sum_{j=1}^{N} u(x^j(0)) \int dx^N(0) \exp(-\beta \sum_{j=1}^{N} u(x^j(0)))
\]

which is the usual form of the mean value of potential energy in classical limit. In addition with the result relative to the kinetic energy, the equilibrium condition (22) in the classical limit leads to the usual form of the internal energy.

**IV. SYSTEM IN EQUILIBRIUM WITH A THERMOSTAT**

In the previous Section we considered a very large system for which the thermodynamic properties are well defined. Now we analyze the properties of a system \( S \) enclosed in a box of volume \( V \) outside of which there is a very large system \( T \) having a volume \( V >> V \). This corresponds to the introduction of the canonical representation in standard statistical mechanics. Our work consists now to write (1) for two systems in contact.

The hamiltonian \( H(s) \) becomes \( H(s) = H_S(s) + H_T(s) + I(s) \) in which \( H_S(s) \) and \( H_T(s) \) are associated with the isolated systems and \( I(s) \) to their interaction. The position of a particle \( \alpha \) of \( T \) will be referred by \( y^\alpha \), their total number is \( M \) and their mass is \( m_\alpha \). The interaction energy \( I(s) \) can be written \( I(s) = \sum_{i=1}^{N} \sum_{\alpha=1}^{M} I(y^\alpha(s), x^i(s)), \) where \( I(y^\alpha(s), x^i(s)) \) the coupling pair potential. As usually we assume that \( I(s) \) is due to a short distance potential.
consequently $I(s)$ is proportional to the number $M_S$ of particles of $\mathcal{T}$ located near the surface of $S$ and to the number $N_{nn}$ of nearest neighbors of these particles but pertaining to $S$. The order of magnitude of $I(s)$ is $M_S N_{nn} \bar{I}(\alpha, i)$ where $\bar{I}(\alpha, i)$ is the mean value of the coupling pair potential.

Instead of $\phi(x^N(0), t_0; x^N, t)$ we consider now a quantity $\phi(x^N(0), y^M(0), t_0; x^N, y^M, t)$ integrated over the initial position $y^N(0)$, it corresponds to

$$\frac{1}{N_T \frac{1}{N}! \frac{1}{M}!} \int \mathcal{D}x^N(t) \int \mathcal{D}y^M(0) \int \mathcal{D}y^M(t) \exp\left(-\frac{1}{\hbar} \int_{t_0}^{t} H(s) ds\right) \exp\left(-\frac{1}{\hbar} \int_{t_0}^{t} (H_T(s) + I(s)) ds\right)$$

In which

$$N_T = \frac{1}{M!} \int dy^M(0) \int \mathcal{D}y^M(t) \exp\left(-\frac{1}{\hbar} \int_{t_0}^{t} (H_T(s) ds\right)$$

is a pure thermostat property. In order to go further, as usually, we assume that the thermostat is at equilibrium. The presence of $S$ behaves as an external potential for $\mathcal{T}$ but since $M_S << M$ the properties of $\mathcal{T}$ can be calculated independently of $I(s)$ i.e. from $N_T$ whatever the state of $S$. Following the procedure introduced in the previous Section to the equilibrium of $\mathcal{T}$ we associate to $\mathcal{T}$: i) a well defined temperature $T$, ii) a characteristic time $\tau = \frac{\hbar}{k_B T}$ and iii) $\lambda^2 = \frac{\hbar m}{k_B T}$. To describe the equilibrium states of $\mathcal{T}$ we follow the prescription given in 3.1. In the time interval $t - t_0$ we consider the set of time $t_j = t_0 + j \delta t$ where $j$ varies from 0 to $j_{max} = \frac{t - t_0}{\tau} - 1$ which is assumed to be an integer. On each time interval $t_j, t_{j+1}$ we focus on the closed paths involving the particles of the thermostat. Let consider

$$\frac{1}{N_T \frac{1}{N}! \frac{1}{M}!} \int \mathcal{D}x^N(t) \int dy^M(0) \int \mathcal{D}y^M(t) \exp\left(-\frac{1}{\hbar} \sum_{j=0}^{j_{max}} \int_{t_j}^{t_{j+1}} (H_S(s) + H_T(s) + I(s)) ds\right)$$

Excepted in very particular cases (see next Section) an exact analytical calculation of this expression cannot be performed and in general case approximations must be used. In each time interval in $I(s)$ we may replace $I(y^\alpha(s), x^i(s))$ by $I(y^\alpha(t_j), x^i(s)))$ since the particles of $\mathcal{T}$ stay in a domain of size $\lambda$ on which it is assumed that the variations of the potential energy is negligible. In addition since $I(s)$ corresponds to a short range potential we have

$I(y^\alpha(t_j), x^i(s)) \approx I(y^\alpha(t_j), x^i(s))$ leading to

$$\frac{1}{\hbar} \int_{t_j}^{t_{j+1}} I(s) ds \approx \tau \sum_{i=1}^{N} \sum_{\alpha=1}^{M} I(y^\alpha(t_j), x^i(t_j))$$
Second, since $I(s) << HT(s)$ we can perform an expansion around $HT(s)$ this leads leading to consider quantities such as

$$I(x^i(t_j)) = \frac{\int dy^M(0) \int dy^M(t) I(y^\alpha(t_j), x^i(t_j)) \exp\left(\frac{1}{\hbar} \sum_{l=0}^{\max} \int_{t_l}^{t_l+\tau} (HT(s)ds)\right)}{\int dy^M(0) \int dy^M(t) \exp\left(-\frac{1}{\hbar} \sum_{l=0}^{\max} \int_{t_l}^{t_l+\tau} (HT(s)ds)\right)} \tag{34}$$

that represent an average over the closed paths of the interaction potential between the particles $\alpha$ and $i$. Using the approximation $1 + \beta I(x^i(t_j)) \approx \exp \beta I(x^i(t_j))$ and canceling the pure thermostat contribution with $N_T$ the expression (30) can be rewritten as

$$\frac{1}{N!} \int D x^N(t) \exp \left(-\frac{1}{\hbar} \sum_{j=0}^{\max} \left[ \int_{t_j}^{t_j+\tau} H_S(s)ds - \beta \sum_{i=1}^N I(x^i(t_j)) \right] \right) \tag{35}$$

Let consider the case for which the external potential is time independent, then the hamiltonian $H(s)$ is time independent and in the previous result we can take $t_j = 0$. The presence of the thermostat forces us to focus on a time interval $\tau$ characterising the thermostat equilibrium. The expression (35) becomes

$$\frac{1}{N!} \int D x^N(t) \exp \left[ -\frac{1}{\hbar} \int_{t_0}^{t_0+\tau} \left( \sum_{i=1}^N \frac{1}{2} m \left( \frac{dx^i(s)}{ds} \right)^2 + u(x^i(s)) \right) ds - \beta \sum_{i=1}^N I(x^i(0)) \right] \tag{36}$$

This is our exact result in which the paths for the particles of $S$ are not restricted to closed paths. If we add the extra hypothesis that between $t = 0$ and $t = \tau$ the change on $u(x^i(s))$ is negligible then we have $u(x^i(s)) \approx u(x^i(0))$ and we are left with the calculation of the kinetic energy that we can perform by introducing the velocity as in the previous Section and after integration over $x^N(0)$ we obtain

$$\frac{1}{N!} \int dx^N(0) \prod_{i=1}^N dv^i \exp \left( -\beta \sum_{j=1}^N \frac{1}{2} m(v^j)^2 + u(x^j(0)) + I(x^j(0)) \right) \tag{37}$$

If the system $S$ is large in such a way that $N >> M_S N_{nn}$ we can neglect the contribution of $I(x^j(0))$ in comparison with the one of $u(x^j(0))$ and the traditional form of the partition function is reobtained and we solve the second problem mentioned in subsection 2D.

The derivation of (37) may seem a little bit tedious but it is of great importance, since as we shall see in the next Section, the derivation of a macroscopic time-irreversible behavior does not requires new fundamental assumption.

In the approach presented above we focused on the relation between thermodynamic equilibrium and statistical thermodynamics. However from the transition function we may also describe the evolution of systems for which there is no thermodynamics. For instance we
may consider an irreversible chemical reaction in vacuum or a nuclear fission process. This last process has been first investigated by Kramers (25) using a stochastic approach; in (13) we have shown that the stochastic approach can be found from physics first principles.

V. TIME-IRREVERSIBLE BEHAVIORS

In Section 2C we have seen that the transition function verifies (9) which is a time irreversible equation representing the natural evolution of a quantum system. In the next Section we will see how to force a system to stay in a pure mechanical regime. In this Section an answer to the third problem mentioned in subsection 2.5 will be given. In absence of general results concerning the time-irreversible behavior of a system our main goal we will be to show that for a very simple model frequently invoked in relation with the brownian motion a time-irreversible behavior can be predicted without the help of new basic assumption.

A. A simple system

In what follows the system $S$ will be reduced to one particle that we will call the Particle to be short, it obeys to the hamiltonian (2) in which the interaction potential is reduced to an external potential. Instead of the thermostat $T$ investigated in the previous section, we consider now that the Particle is embedded in a large bath $B$ having $M$ particles. In that case the interaction energy bath/Particle cannot be neglected in the Particle dynamics. In contrast the bath properties can be calculated in absence of the Particle. As in the previous Section we associate with the bath a characteristic time $\tau$ a temperature $T$ and a distance $\lambda$. System and bath are enclosed in a volume $V$ and the initial position of the Particle will be used to define the center of the spatial coordinates. Many technical details concerning this model are given in (26).

Now we write the total hamiltonian as $H(s) = H_S(s) + H_B(s) + I(s)$ and a particular forms will be chosen for $B$ and $I$. The bath is represented by $M$ particles oscillating around their initial positions, they behave as $M$ independent identical oscillators of frequency $\omega$ and of mass $m_B$. The hamiltonian associated with the bath is

$$H_B(t) = \sum_i \left[ \frac{1}{2} m_B \left( \frac{dr_i(t)}{dt} \right)^2 + \frac{1}{2} m_B \omega^2 r_i^2(t) \right]$$

(38)
in which \( r_i \) means for \( i \) its deviation from its initial equilibrium position. For the interaction between bath and Particle we use the bilinear hamiltonian frequently retained in the literature (26)

\[
I(t) = \sum_{i=1}^{M} C_i r_i(t) x(t)
\]

in which \( C_i \) is related to the second spatial derivative of the interaction potential between the Particle located at the center of the box at the initial time and the equilibrium position of the \( i \) bath particle; \( C_i \) depends on \( i \) and for a short range Particle-bath interaction potential the sum in (39) is restricted to the first neighbors of the Particle. This potential requires the introduction of a renormalization constant that has been largely discussed in the literature (26) and it will be not considered here. The transition function that we have to consider is

\[
q(x_0, r^M(0), t_0; x, r^M, t) = \frac{1}{M!} \int D x(t) \exp \left( -\frac{1}{\hbar} \int_{t_0}^{t} H_S(s) ds \right) \int D r^M(t) \exp \left( -\frac{1}{\hbar} \int_{t_0}^{t} (H_B(s) + I(s)) ds \right)
\]

In (40), \( r^M(t) \) represents the set of the deviations from the initial positions as defined above, \( r^M(t) = [r_1(t), ..., r_i(t), ..., r_M(t)] \). Due to the quadratic form of \( (H_B(s) + I(s)) \) the functional integral on the variables \( r^M(t) \) can be calculated exactly using a mathematical trick introduced in (8). We write \( r_i(t) = r_i(t)_\text{opt} + \delta r_i(t) \) in which \( r_i(t)_\text{opt} \) corresponds to the optimization of the euclidean action associated with \( (H_B(s) + I(s)) \). Here the optimization is a mathematical procedure leading to a differential equation which is not the equation of motion, in contrast with what is done in pure quantum mechanics where the optimization of the lagrangian action is performed. We can write

\[
\int D r^M(t) \exp \left( -\frac{1}{\hbar} \int_{t_0}^{t} (H_B(s) + I(s)) ds \right) = C_{\text{opt}} \exp \left( -\frac{1}{\hbar} \int_{t_0}^{t} (H_B(s) + I(s)) ds \right)_{\text{opt}}
\]

in which the subscript \( \text{opt} \) means that we have to calculate the trajectories on the optimum paths and \( C_{\text{opt}} \) is a quantity independent of the particle positions, it results from the integration on the variable \( \delta r_i(t) \). For two arbitrary times \( t \) and \( t_1 > t \) for which the sets of positions correspond to \( (x, r^M) \) and \( (x_1, r_1^M) \) respectively, we define

\[
\delta A[x, r^M, t; x_1, r_1^M, t_1] = \int_{t}^{t_1} (H_B(s) + I(s)) ds |_{\text{opt}}
\]
Using the hamiltonians (38) and (39) we can get the explicit form of $\delta A[x, r^M, t; x_1, r_1^M, t_1]$. Now we can write

$$q(x_0, r^N(0), t_0; x, r^N, t) = C_\delta \int Dx(t) \exp -\frac{1}{\hbar} [A[x_0, t_0; x, t] + \delta A[x_0, r^N(0), t_0; x, r^N, t]]$$

(43)

and the transition function for the small system $\bar{q}(x_0, t_0; x, t)$ can be written

$$\bar{q}(x_0, t_0; x, t) = C_\delta \int Dx(t) \exp -\frac{1}{\hbar} \bar{A}[x_0, t_0; x, t] < \exp -\frac{1}{\hbar} \delta A[x_0, r^N(0), t_0; x, r^N, t] >_{bath}$$

(44)

in which $C_\delta$ is a normalization constant and $< ... >_{bath}$ means that we have to take a procedure in order to eliminate the bath particle positions. This procedure depends on the physics under consideration.

We assume that the bath is in thermal equilibrium in the field created by the Particle for any value of $t$. To describe the bath equilibrium we follow the prescription given in Section 3C: we focus on closed paths explored during a time interval $\tau$. The time interval $(t - t_0)$ is sliced in equal intervals of thickness $\tau$ and we assume that $\tau$ is vanishingly small in comparison with $(t - t_0)$, this corresponds to a well common assumption, the Smoluchowski or Fokker-Planck equations do not describe short ranged processes. Finally we assume that $\omega \tau << 1$ a physical reasonable approximation taking into account that $\tau \approx 10^{-14} sec$. With such conditions we may show that $< \exp -\frac{1}{\hbar} \delta A[x_0, r^N(0), t_0; x, r^N, t] >_{bath}$ contains two parts one produced a renormalization of the interaction potential and the second one is given by

$$\frac{-1}{\hbar} \sum_{i=1}^{M} C_i^2 \int_{t_0}^{t} \left( \frac{dx}{ds} \right)^2 ds$$

(45)

This term has to be added to the kinetic part of $H_S$ this is equivalent to replace the mass of the Particle by an effective mass given by

$$m_{eff} = m + \frac{\sum_{i=1}^{M} C_i^2 \tau^2}{2m_B \omega^2}$$

(46)

If the interaction is short ranged we have $\sum_{i=1}^{M} C_i^2 \approx N_{nn} C$ in which $N_{nn}$ is the number of nearest neighbors at the initial time and $C$ the common value of the coupling constant. We may also introduce a characteristic length for the vibration $l$ to which we associate a mean value for the vibrational energy $E_{vib} = \frac{1}{2} m_B \omega^2 l^2$. The interaction energy can be estimated to $E_{int} = Cl \lambda$. The effective mass can be rewritten as

$$m_{eff} = m[1 + N_{nn} \frac{m_B}{m} \frac{E_{int}}{E_{vib} E_{kin}}]$$

(47)
in which $E_{\text{kin}} = \frac{1}{2}k_BT$. As expected $m_{\text{eff}} \to m$ if the bath is reduced to a dilute gas ($N_{nn} \to 0$). In opposite $m_{\text{eff}}$ is very different from $m$ if $N_{nn}m_Bm_{\text{eff}}\frac{E_{\text{ev}}^2}{E_{\text{kin}}^2} \gg 1$. More generally form (47) we may observe a smooth transition from the original quantum system to a classical one and a Smoluchovski equation will be associated to the system evolution (??).

B. More sophisticated model and other approaches

In the previous subsection we have used our formalism to predict one kind of irreversible behavior that does not require the introduction of any new basic assumptions in comparison with those needed for describing a thermal equilibrium state. Analytical results have been obtained resulting from simple assumptions. Some extensions can be easily introduced for instance $S$ can be formed by a given number of interacting particles instead of only one, the different time scales can be modified or a more sophisticated bath particle interaction can be considered. In a recent paper (27) we have investigated an example in which the Particle is not in equilibrium with its surrounding then a memory effect is introduced in the transition function and the dynamics of the Particle cannot be separated from the one of bath particles. Simple approximations show that we keep the irreversible behavior of the system as expected.

In the model investigated the source of irreversibility is due to the presence of a bath as in the case of brownian particles. There is a large literature devoted to the coupling between a small system and a bath in view to derive a Langevin or a Fokker-Planck type equation for brownian particles (see for instance (28),(29), (30), (31)). In these approaches the ensemble system+reservoir is at the equilibrium and described from a density matrix, the small system considered as an isolated system obeys to a Schrödinger equation and the irreversibility arises from the energy transfer from the small system to its large environment. Here the transition function (11) gives a quantum description of a N-body system and a time-irreversibility behavior exists even for small quantum systems in absence of bath. Consequently we are able to describe the irreversible evolution of a small system and also the smooth transition from a time-irreversible quantum regime to a time-irreversible classical regime. The mathematical apparatus used here is different and simpler that the one
used in system+reservoir approaches.
It is not obvious that the formalism developed here will be also efficient to describe a time-irreversibility having another origin but at least it is sufficient for describing the time-irreversibility of an important class of models.

VI. PURE QUANTUM MECHANICAL REGIME

In the previous Sections we focused on the connection between statistical mechanics and thermodynamics. Since with thermodynamics we describe processes that are in reality time-irreversible we try to find time irreversible processes at a microscopic level and to found the statistical mechanics on them in order to avoid the classical difficulty to conciliate a time reversibility at a microscopic level with a time irreversibility at a macroscopic level. However, besides thermodynamics a hamiltonian mechanics has been developed in which any friction process is absent and for which any evolution is time-reversible \(^{(32)}\). The highest level of this mechanics has been reached through the quantum mechanics. Now we would like to investigate the relation between pure mechanical systems and those investigated in this work.

Instead of \(\phi(x,t)\) defined in \((7)\) and verifying the differential equation \((10)\) with the condition \(\phi(x,t_0) = \phi_0(x)\) we may define a function \(\hat{\phi}(x,t)\) according to

\[
\hat{\phi}(x,t) = \int q(x,t;x_1,t_1)\phi_1(x_1)dx_1
\]

in which \(q(x,t;x_1,t_1)\) is the transition function that enters in the definition of \(\phi(x,t)\). Using \((6)\) we have have \(\hat{\phi}(x,t_1) = \hat{\phi}_1(x_1)\). The time dependence of \(\hat{\phi}(x,t)\) can be obtained in the same way as for \(\phi(x,t)\) and we get

\[
-\frac{\partial \hat{\phi}(x,t)}{\partial t} = \frac{h}{2m} \frac{\partial^2 \hat{\phi}(x,t)}{\partial x^2} - \frac{1}{h} u(x,t) \hat{\phi}(x,t)
\]

in which \(u(x,t)\) is an external potential. The use of \((10)\) or \((49)\) is a question of convenience depending on the information we have on the system. A new physical situation appears if we want to solve simultaneously \((10)\) and \((49)\) with fixed initial and final conditions. The first problem is to show that with this entry-exit process we have to deal with a well-identified mathematical object. The proof of this has been given by Nagasawa in \((33)\) and the mathematical details will be not reproduced here a deeper presentation has been given in
(44). From \(\phi(x, t), \hat{\phi}(x, t)\) and the initial and final conditions a Markov process can be defined in its the Schrödinger representation (33). It is possible to show that the product \(\mu(x, t) = \phi(x, t)\hat{\phi}(x, t)\) is a density of probability verifying the following equation of continuity

\[
\frac{\partial \mu(x, t)}{\partial t} - \nabla_x \left[ a(t, x) - \hat{a}(t, x) \right] \mu(x, t) = 0
\]

(50)

with \(a(t, x) = \frac{\hbar}{m} \nabla_x \ln \phi(t, x)\) and \(\hat{a}(t, x) = \frac{\hbar}{m} \nabla_x \ln \hat{\phi}(t, x)\). The equation (50) with the expressions of \(a(t, x)\) and \(\hat{a}(t, x)\) has been first derived by Kolmogorov (33).

From the pair of non-negative functions \(\phi(x, t)\) and \(\hat{\phi}(x, t)\) we may form two new quantities \(R(t, x)\) and \(S(t, x)\) defined by

\[
R(t, x) = \frac{1}{2} \ln \phi(t, x) \hat{\phi}(t, x)
\]

\[
S(t, x) = \frac{1}{2} \ln \frac{\phi(t, x)}{\hat{\phi}(t, x)}
\]

(51)

From \(R(t, x)\) and \(S(t, x)\) we may define two complex valued functions

\[
\psi(x, t) = \exp \left[ R(t, x) - iS(t, x) \right]
\]

\[
\hat{\psi}(x, t) = \exp \left[ R(t, x) + iS(t, x) \right]
\]

(52)

It is clear that \(\hat{\psi}(x, t)\) is the complex conjugate of \(\psi(x, t)\) and that we have \(\psi(x, t)\hat{\psi}(x, t) = \phi(x, t)\hat{\phi}(x, t)\) accordingly \(\psi(x, t)\hat{\psi}(x, t)\) corresponds to the density of probability \(\mu(x, t)\) and this leads immediately to the Born interpretation of \(\psi(x, t)\hat{\psi}(x, t)\) (33). Now it is easy to verify that \(\psi(x, t)\) verified a Schrödinger like equation (33)

\[
i\hbar \partial \psi(x, t)/\partial t + \frac{\hbar^2}{2m} \Delta_x \psi(x, t) - V(x, t)\psi(x) = 0
\]

(53)

and the potential \(V(x, t)\) is related to \(u(x, t)\) by the relation

\[
V(x, t) - u(x, t) + 2\hbar [\partial S(t, x)/\partial t + \frac{\hbar}{2m} (\nabla_x S(t, x))^2] = 0
\]

(54)

Thus, by adding to the transition function (1) describing the forward motion a transition function describing the reverse motion we may define a complex valued function verifying a Schrödinger like equation provided the potentials introduced in the various equations are related according to (54). On an example we may show that this change of potential is meaningful. Let start from the Schrödinger equation and consider the wave function corresponding to a gaussian free wave packet. It is given by (34)

\[
\psi(x, t) = C \int dk \exp \left[ \frac{-ik^2 t}{2m\hbar} + \frac{ikx}{\hbar} - \frac{k^2 (\delta)^2}{2\hbar^2} \right]
\]

(55)
It corresponds to a particle roughly localized in a sphere of radius \( \delta \) at \( t = 0 \). The quadrature in (55) can be performed explicitly and from it we may obtain the functions \( R(t, x) \) and \( S(t, x) \) and finally \( \phi(t, x) \) which is given by

\[
\phi(x, t) = \frac{\tilde{C}}{(1 + \tau^2)\tau} \exp \left[ -\frac{x^2}{2\delta^2(1 + \tau^2)} - \frac{x^2\tau}{2\delta^2(1 + \tau^2)} + \frac{1}{2} \arctan \tau \right] \tag{56}
\]

in which \( \tilde{C} = \left( \frac{1}{\delta \pi^2} \right)^{\frac{1}{4}} \) and \( \tau = \frac{\hbar t}{m\delta^2} \). For \( \tau \to 0 \) we have \( \phi(x, t) = \tilde{C} \exp -\frac{x^2}{2\delta^2} \) showing that the paths contributing to \( \phi(x, t) \) are those localized in a region \( x \sim \delta \). For long time \( \tau >> 1 \) we have \( \phi(t, x) = \tilde{C} \exp -\frac{mx^2}{2\hbar t} \) and in that case the important paths are those for which we have a diffusion process \( x^2 \sim \frac{\hbar t}{m} \) that is independent of the initial localization as expected. Using (54) we may determine the potential \( u(x, t) \) that we need to put in real space in order to get the free wave packet for which \( V(t, x) = 0 \). We have

\[
u(x, t) = \pi^{-\frac{1}{4}} \frac{\hbar^2}{m\delta^2(1 + \tau^2)} \left[ -1 + \frac{x^2}{\delta^2(1 + \tau^2)} \right] \tag{57} \]

For \( t = 0 \) the potential is attractive when \( \frac{x}{\delta} \in [-1, +1] \) and repulsive elsewhere, this is equivalent to introduce in space a slit of thickness \( \delta \). The potential \( u(t, x) \) disappears for large values of \( t \). Thus to perform the selection in the wave vectors giving rise to a gaussian free wave packet a particular slit has to be introduced in real space.

VII. CONCLUSIONS

In this work our main goal was not to challenge the usual methods of calculation in statistical mechanics but to show that the problem of time-irreversibility may be formulated in a new point of view. Here statistical mechanics is thought as the domain of science that allows us to calculate the thermodynamic properties from a description at a microscopic level. Since all real processes transforming an equilibrium state into another one are time-irreversible in reality we suggest to take into account the time irreversibility as a basic fact existing at a microscopic level at least for some properties. In following this way we expect that the time-irreversibility problem will be more easy to apprehend than in traditional approaches. In order to do that we introduce a transition function that is a time-dependent transformation of the hamiltonian via the path integral formalism. The transition function is a weighted sum over paths and the weight of a path corresponds to the total energy spent on
it. The energy over a path is no more fixed but can fluctuate in accordance with Heisenberg uncertainty relations that are at the origin of a diffusive motion and consequently the time evolution of the transition function verifies a time-irreversible equation. We consider this transition function as the corner stone on which the statistical mechanics can be founded. Due to the introduction of a time irreversibility we are forced to associate with each quantity a dynamic process. Our first task has been to show that the results obtained via the Gibbs ensemble method can be exactly rederived from a dynamic point of view. In order to do that we focused on the closed paths as representing the simplest description of an equilibrium state. A time interval is associated with the paths and an average over paths is introduced, in general the averages defined in this way differ from the standard averages as illustrated in the case of the kinetic energy. The equilibrium is defined in such a way that the introduced time is such that the mean value of the energy calculated over the paths is equal to the internal energy needed to create the system. This time interval is not a relaxation time but a characteristic of the equilibrium state. A second quantity associated with closed paths is the mean deviation of the particle from its origin position. A temperature is then associated with the paths and the Gibbs ensemble results are reobtained provided that the temperature associated with the paths is identified with the usual thermal temperature. The results of the so-called classical statistical mechanics are derived in two ways, one is based on the equilibrium condition. A prescription is given to calculate equilibrium states. The dynamic point of view allows us to establish a relation between entropy and action and to discuss the meaning of entropy for short time-intervals, we shortly compare what we have done with another approach in which a relation between equilibrium states and dynamics has been emphasized. In a second step we have calculated the properties of a system in contact with a thermostat. This derivation is useful to illustrate the fact that the description of a macroscopic time-irreversible does not require the introduction of new basic assumptions. To be illustrative the transition from a quantum to a classical regime has be described with a simple model largely invoked in the microscopic theories of the brownian motion for which the bath induces the time-irreversibility. In contrast with the system+reservoirs approaches in our case the small system exhibits a time-irreversible behavior and consequently we are able to describe the smooth transition between a quantum regime and a classical one. This model does not represent the most general case in which a time-irreversible behavior is observed and we cannot say that our approach should be also efficient for describing other
kind of irreversibility but nevertheless it allows us to treat a large class of situations. At this point it is fundamental to note that we have described on the same footing equilibrium states or time-irreversible evolutions in no way we have to deal with the problem to conciliate a reversible microscopic behavior with a macroscopic time-irreversible evolution.

Of course the use of a transition function is not restricted to the description of thermodynamic processes. This has been illustrated on two different aspects. First we can investigate the behavior of small systems for which there is no thermodynamics, an illustrative example corresponds to the description of an irreversible chemical reaction in vacuum. Secondly we can generate a time-reversible behavior in order to describe pure mechanical systems without any friction process. Our approach has been implemented by the existence of a second transition function describing the reverse motion. Instead of dealing with two real non-negative transition functions we can combine them into a complex valued function verifying a Schrödinger equation. This requires to have a potential associated with each representation. On a simple example we have shown that the change of potential is meaningful.

It was possible to start our work from the Schrödinger equation, to split it in two transition functions and to decide to keep only the one related to the forward motion in order to break the time-reversibility of this equation. From this point of view it is clear that the imaginary time introduced to link quantum mechanics and thermodynamics is just a mathematical trick that does not explain why the wave function is necessarily a complex valued function while in statistical physics it is sufficient to consider a real valued function having a physical meaning by itself and from which a density of probability can be defined. In this work we decided to ignore the Schrödinger equation from the very beginning preferring to follow a route that seems more constructive and more direct. This choice also results from Feynman remarks (8 p. 295) suggesting that it probably exists a way to derive the path integral approach in statistical physics directly from the path integral description for the time dependent motion without using the total apparatus associated with the Schrödinger equation. Many approximations used in this paper are not essential but they have been introduced to get analytical results from which a discussion is easy and all of them could be removed in a
future work.

1. T.L. Hill, in "Statistical Thermodynamics in Statistical Mechanics", Mc Graw-Hill, New York, 1956
2. H.B. Callen, in "Thermodynamics and an introduction to thermostatics", John Wiley, 1985
3. D. Ruelle, in "Statistical Mechanics: Rigorous Results", World Scientific, Singapore, 1969
4. R. C. Tolman in "The Principles of Statistical Mechanics", Dover Books on Physics, New York
5. A. Einstein in Biographical Notes, Schilpp P.A. Open course publishing company, La Salle Illinois, 1982
6. M. Planck, in "Treatise on thermodynamics", Dover publications N.Y, 1945
7. H.D. Zeh in "The Physical Basis of the Direction of Time", Springer-Verlag, Berlin, second edition, 1992
8. R.P. Feynman and A.R. Hibbs in "Quantum mechanics and path integrals", Mc Graw Hill, New York, 1965
9. L.S. Schulmann in "Techniques and applications of paths integrals", Wiley, 1996
10. H. Kleinert in "Path integrals in quantum mechanics, statistics and polymer physics", World Scientific Singapore, 1995
11. J.P. Badiali, 1999, Phys. Rev. E, 60, 2533
12. N.G. van Kampen, 1977, J. Stat. Phys., 17, 71
13. J.P. Badiali, 2011, J. Electroanal. Chem., 660, 332
14. J.P. Badiali, 2006, J. Phys. A Math. Gen., 39, 7175
15. J.P. Badiali, 2007, J. Phys. A Math. Gen., 38, 2835
16. G.W. Gibbons and S.W. Hawking, 1977, Phys. Rev. D, 15, 2572
17. R.M. Wald, 1999, Class. Quantum Grav., 16, 177
18. L. D. Landau and E.M. Lifshitz in "Statistical physics", Pergamon Press, Oxford, 1977
19. G.G. Emch in "Algebraic Methods in Statistical Mechanics and Quantum Field Theory", Wiley-Interscience, 197)
20. M. Takesaki, in "Tomita’s theory of modular Hilbert algebra and its applications", Berlin Springer, 1970
21. S.A. Fulling and S.N.M. Ruijsemaars, 1987, Phys. Reports, 152, 135
22 R. Haag, N.M. Hugenholtz and M. Winnink, 1967, Comm. math. Phys., 5, 215

23 J.P. Badiali, ArXiv cond-mat.stat.mech 0902.093lvl

24 A. Connes and C. Rovelli, 1994, Class. Quantum . Grav., 11, 2899

25 H.A. Kramers, 1940, Physica (UtrechtVII), 4, 284

26 J.P. Badiali, 2012, J. Electroanal. Chem., 676, 40

27 J.P. Badiali J. Condens. Matter Physics (in press)

28 A.O. Caldeira, A.J. Leggett, 1983, Physica, 121A, 587

29 H. Grabert, P. Schramm and G.L. Ingold, 1987, Phys. Report 168, 115

30 U. Weiss, in "Quantum dissipative Systems", second ed., World Scientific, Singapore, 1999.

31 S. Datta, 1990, J. Phys. Condens. Matter, 2, 8023

32 V.I. Arnold in "Mathematical Methods in Classical Mechanics", Springer Verlag, New York 1989

33 M. Nagasawa, in "Stochastic Processes in Quantum Physics", Monographs in Mathematics, 94, Birkhauser Verlag, Basel, 2000

34 C. Cohen-Tannougji, B. Diu and F. Laloe in "Mécanique Quantique" Herremann, Paris, 1977