

On Second Quantization Methods Applied to Classical Statistical Mechanics

A. MATOS NETO* and J.D.M. VIANNA

Departamento de Física, Universidade de Brasília, 70910, Brasília, DF, Brasil

Recebido em 26 de julho de 1984

Abstract A method of expressing statistical classical results in terms of mathematical entities usually associated to quantum field theoretical treatment of many particle systems (Fock space, commutators, field operators, state vector) is discussed. It is developed a linear response theory using the "second quantized" Liouville equation introduced by sch8nberg. The relationship of this method to that of Prigogine *et al.* is briefly analyzed. The chain of equations and the spectral representations for the new classical Green's functions are presented. Generalized operators defined on Fock space are discussed. It is shown that the correlation functions can be obtained from Green's functions defined with generalized operators.

It is known that statistical mechanics treats two areas of difficulties of apparently different nature, namely equilibrium and non-equilibrium systems. On the one hand, equilibrium statistical mechanics is well established: given the hamiltonian for a many-body system the partition function and thermodynamic functions can be calculated by definite rules. On the other hand, non-equilibrium statistical mechanics, which deals with time-dependent (then more difficult) problems and with this fundamental question of irreversibility, is not so well established. Several authors have studied this subject (an account for this historical development can be found in ref. 1) Prigogine and coworkers¹⁻⁵ developed a framework which makes it possible to treat with the same tools the short - or long-time dissipative evolution of ionized gases from the highest temperature regions, where they are purely classi-

This paper is dedicated to Professor M. Schönberg, in the occasion of his 70th anniversary.

*On leave from Instituto de Física, Universidade Federal da Bahia; partially supported.

cal, down to absolute zero. Zubarev⁶⁻⁸ introduced the local-equilibrium operators for classical and quantum systems. Callen and Welton⁹ introduced the use of spectral representations for the time-correlation functions and for retarded Green functions in statistical mechanics of irreversible processes. Bogolyubov and Sadovnikov¹⁰ extended the quantum statistical Green-function's approach to classical systems and studied transport processes. Aronson¹¹ developed a perturbation method for the classical time-dependent pair-correlation functions. Klimontovich¹² gave a method to introduce collective variables to describe a many-particles system; he introduced as independent variables the number of particles in different points of coordinate-momentum phase space. Kubo¹³ developed the theory of transport coefficients. Balescu^{14,16} showed the usefulness of causal and anti-causal Green's functions in the initial-value solution of the Liouville equation and in the study of transport coefficients. Matsubara¹⁷ used temperature-dependent, time-independent Green's functions. Herzog¹⁸⁻¹⁹ defined classical retarded many-time thermodynamic Green's function in order to formulate a non-linear response theory. Prigogine et al.¹⁵ developed a microscopic theory of irreversible processes.

It is also known that the classical statistical mechanics can be developed as the limiting case of quantum statistical mechanics when quantum corrections can be neglected. However, classical statistical mechanics is of interest in itself⁵ and is perfectly adequate for a number of problems, e.g. the study of ionized gases¹⁶. Even more, the methods of classical and quantum statistics have much in common in what concerns the fundamental formulation of the problem, and they show very similar difficulties when one attempts to justify them.

Recently some physicists and mathematicians have given attention²⁰⁻²⁷ to the problem of expressing the quantum mechanical mean values as classical averages over phase-space distribution functions. In this connection we raise the problem of expressing statistical classical results with the mathematical structure of the quantum theory for many particles systems (Fock space, field operators, commutators and anti-commutators, etc.). In fact, some time ago Schönberg²⁸⁻³⁰ proposed the employment of methods similar to those of second quantization for the Liouville equation of classical statistical mechanics. He defined

field operators $\psi(\vec{x}, \vec{p})$ on phase space and introduced a "second quantized" Liouville equation. Such a new formulation - with the associated picture - would be expected, in general, to reveal new aspects of the physical and mathematical construction of statistical mechanics, and to suggest new hints to the future progress of the statistical theory. Furthermore, in this formulation various field-theory techniques can be used (e.g., perturbation theory, operator methods, variational procedure) for practical application to a specified class of problems in equilibrium and non-equilibrium theories.

The purpose of the present paper is to develop the methods due to Schönberg into a consistent formulation of linear response theory.

We shall see from our results that the generalized operators are natural objects to obtain time-correlation functions within the linear response theory.

Our work has been divided into five parts. Part 1 presents the formulation of the statistical classical mechanics using second-quantization methods. Although the results obtained in this part are not new, they are put in such a form that they can be readily applied to the new situation of linear response, what we do in part 3. In part 2 the generalized operators are discussed. In part 4 we proceed to an application, in order not to interrupt the main line of argumentation in the preceding parts. Part 5 contains some conclusive remarks.

1. LIOUVILLE EQUATION AND SECOND QUANTIZATION²⁸

Let us consider the Liouville equation for classical statistical mechanics

$$\begin{aligned} \frac{\partial}{\partial t} f_n &= (H_n, f_n)_n = \left(\sum_{\ell=1}^n \frac{\vec{p}_\ell^2}{2m} + \frac{1}{2} \sum_{\ell \neq \ell'} V(\vec{x}_\ell - \vec{x}_{\ell'}) \right), f_n)_n \\ &= -i K_n f_n \end{aligned} \quad (1)$$

where

$$(F, G)_n = \sum_{\ell=1}^n \left\{ \frac{\partial F}{\partial \vec{x}_\ell} \frac{\partial G}{\partial \vec{p}_\ell} - \frac{\partial F}{\partial \vec{p}_\ell} \frac{\partial G}{\partial \vec{x}_\ell} \right\}$$

\vec{p}_ℓ denoting the momentum of the particle whose position vector is \vec{x}_ℓ , and $f_n(\vec{x}_1, \dots, \vec{x}_n, \vec{p}_1, \dots, \vec{p}_n)$ being the probability density in the phase space of the n-particles' system.

The basic operators of the second quantization method introduced by Schönberg²⁸ are the hermitian conjugated $\psi(\tau)$ and $\psi^\dagger(\tau)$, $\tau \equiv (\vec{x}, \vec{p})$, defined on phase space and characterized by the commutation rules

$$[\psi(\tau), \psi^\dagger(\tau')]_{\pm} = \delta(\tau - \tau') \quad (2)$$

$$[\psi(\tau), \psi(\tau')]_{\pm} = [\psi^\dagger(\tau), \psi^\dagger(\tau')]_{\pm} = 0$$

where

$$\delta(\tau - \tau') = \delta(\vec{x} - \vec{x}') \delta(\vec{p} - \vec{p}')$$

$$[A, B]_{\pm} = AB \pm BA$$

Signs + and - correspond to two different forms of the second quantization. In ordinary second quantization they refer to bosons (-) and fermions (+). The choice of sign in the rules (2) determines the statistics of the particles, considered here indistinguishable. The theory considers the operator

$$K = \int \psi^\dagger(\tau) \left(\frac{\vec{p}^2}{2m} \right) \psi(\tau) d\tau + \frac{i}{2} \iint \psi^\dagger(\tau) \psi^\dagger(\tau') (V(\vec{x} - \vec{x}'), \psi(\tau') \psi(\tau))_2 d\tau d\tau'$$

$$= K_{\text{kin}} + K_{\text{pot}}$$

and the functional χ defined by

$$i \frac{\partial}{\partial t} \chi = K \chi \quad (3)$$

There is an operator N_{op} for the number of particles,

$$N_{\text{op}} = \int \psi^\dagger(\tau) \psi(\tau) d\tau$$

for which the eigenvalues 0, 1, 2, 3, ... (∞) are assigned.

The general solution of (3) is given by a series which has the form

$$\chi(t) = \Theta_0(t) \chi_0 + \sum_{n=1}^{\infty} \frac{1}{\sqrt{n!}} \int \Theta_n(t; \tau_1 \dots \tau_n) \chi_n(\tau_1 \dots \tau_n) d\tau_1 \dots d\tau_n \quad (4)$$

χ_0 being the eigenfunctional of N_{op} corresponding to the eigenvalue 0, with a suitable normalization, i.e.

$$N_{op} \chi_0 = 0 ; \int \chi_0^\dagger \chi_0 d\mu \equiv (\chi_0, \chi_0) = 1 ;$$

$\chi_n(\tau_1 \dots \tau_n)$ are also eigenfunctionals of N_{op}

$$N_{op} \chi_n(\tau_1 \dots \tau_n) = n \chi_n(\tau_1 \dots \tau_n) \quad (5)$$

($n =$ a positive integer),

and are defined by $\chi_n(\tau_1 \dots \tau_n) = \psi^\dagger(\tau_1) \dots \psi^\dagger(\tau_n) \chi_0$. So each term in the expansion (4) is an eigenfunctional of N_{op} , the eigenvalue being the corresponding value of n . $\Theta_n(t; \tau_1 \dots \tau_n)$ are functions of the variables τ_i and t , given by

$$\Theta_n(t; \tau_1 \dots \tau_n) = \frac{1}{\sqrt{n!}} (\chi(\tau_1 \dots \tau_n), \chi(t))$$

Whenever χ satisfies the condition

$$N_{op} \chi = n \chi \quad (6)$$

there is only one term left in the right hand side of eq. (4), i.e.

$$\chi(t) = \frac{1}{\sqrt{n!}} \int \Theta_n(t; \tau_1 \dots \tau_n) \chi_n(\tau_1 \dots \tau_n) d\tau_1 \dots d\tau_n \quad (7)$$

In general $\chi(t)$ does not satisfy conditions of the type (6), and the number of particles will not be determined, so that the solution of eq. (3) describes *grand* ensembles. The rules to the physical interpretation of the formalism based on χ are analogous to those of quantum theory, but they lead to the same results given by classical statistical mechanics whenever the number of particles is determined.

In fact, in the case of a solution $\chi(t)$ to eq. (3) Θ_n satisfies²⁸ the equation

$$\frac{\partial}{\partial t} \Theta_n = (H_n, \Theta_n)_n = -iK_n \Theta_n \quad (8)$$

Hence, if we put

$$f_n(0, \tau_1 \dots \tau_n) = |\Theta_n(0, \tau_1 \dots \tau_n)|^2 \quad (9)$$

the solution for the Liouville equation (1) for f_n follows from that for Θ_n (i.e., eq. (8)), since the square of the absolute value of any solution of the Liouville equation is another of its solutions. Thus, the functions

$$|\Theta_n(t; \tau_1 \dots \tau_n)|^2 d\tau_1 \dots d\tau_n \quad (10)$$

give the probability of finding, at a given time t , only n particles at the points τ_ℓ of the phase space R in the interval $(\tau_1, \tau_2, \dots, \tau_n)$, $(\tau_1 + d\tau_1, \dots, \tau_n + d\tau_n)$. Therefore, $\chi_n(r, \dots, \tau_n)$ describes the n -particle state, for which the particles are at points τ_ℓ of R , and $\chi(t)$ is a non-stationary grand ensemble. Θ_n is either symmetrical or antisymmetrical, according to the sign chosen in the commutation rules (2), and we are thus led to a kind of wave function in classical statistical mechanics. Equation (8) may be considered as the classical wave equation, the hermitean operator K_n playing the role of the hamiltonian operator.

These last considerations show that both the wave functions Θ_n in the phase space and the wave functional χ can be used as appropriate tools of statistical mechanics. In fact, the O -description and the χ -description of statistical mechanics can be regarded as two pictures of the equation

$$i \frac{\partial}{\partial t} |\Phi(t)\rangle = K |\Phi(t)\rangle \quad (11)$$

defined on an abstract vectorial space \mathcal{H} . (This space is the Hilbert space introduced by Koopman³¹, and we shall call it the Hilbert - X space to indicate that O_n is defined on phase space).

The above considerations allow us to introduce the following set of interpretation rules in the Hilbert - K space²⁸:

i) The states of a statistical ensemble are described by vectors $|\Phi(t)\rangle \in \mathbb{H}$, satisfying eq. (11);

ii) Physical quantities are represented by linear hermitean operators A , defined by their action on the vectors $|\Phi(t)\rangle$. The possible numerical values of a physical quantity represented by an operator A are the eigenvalues a ;

iii) The probability of finding the values $\{a'_\lambda\}$ of a set of commuting operators $\{A_\lambda\}$ is given by

$$P(a'_\lambda) = \langle \Phi(t) | \Pi_{a'_\lambda} | \Phi(t) \rangle$$

where $\Pi_{a'_\lambda}$ is the projection operator²⁸ on the linear manifold of the eigenvectors of A_λ corresponding to the eigenvalues a'_λ .

The description of statistical mechanics in terms of the vectorial space \mathbb{H} above summarized can be considered a generalization of the framework introduced by Prigogine and coworkers¹⁻⁵ once that

i) The dynamical variables of a system are operators defined on \mathbb{H} . This allows a generalization of the concept of classical observables, by introducing new physical quantities as, for instance, the Liouville operator K and another generalized operators (see section 2);

ii) With the use of Fock space $IF = \sum_{n=0}^{\infty} IF^{(n)}$, where $IF^{(n)}$ is the space of n -particle systems, we can introduce in a natural way the concept of *grand ensabtes*;

iii) The use of symmetric or antisymmetric Fock space allows us to introduce the indistinguishability of particles within the context of classical mechanics.

1.1 - Classical Pictures

As In quantum mechanics we can introduce three pictures for the state vector $|\Psi\rangle$ and the operators of the theory.

The first considers time-independent operators and a time-dependent wave functional. In this case we have $|\Phi(t)\rangle = U(t, t_0) |\Phi(t_0)\rangle$, with $U(t_0, t_0) = 1$ and $U(t, t_0) = e^{-iK(t-t_0)}$, if K does not depend on time explicitly. Since K is a hermitean operator, $U(t, t_0)$ is an unitary operator. We may refer to this picture as the Classical Schrödinger Picture (CSP).

Another representation, which we shall call the Classical Heisenberg Picture (CHP) is obtained from CSP by the transformation

$$|\Phi_H(t)\rangle = e^{iKt} |\Phi(t)\rangle \quad (12)$$

$$A_H(t) = e^{iKt} A_S e^{-iKt} \quad (13)$$

where the indexes refer to CSP. For this picture we have

$$\frac{\partial}{\partial t} |\Phi_H(t)\rangle = 0 \quad (14)$$

$$i \frac{\partial}{\partial t} A_H(t) = [A_H(t), K]_- \quad (15)$$

Equation (15) can be solved by an iterative method to give

$$A_H(t) = A_H(0) + \sum_{n=1}^{\infty} \frac{(it)^n}{n!} [K, [K, \dots [K, A_H(0)] \dots]]_- \quad (16)$$

A third type, the Classical Interaction Picture (CIP) can also be defined. Assume that the Liouville operator can be divided into two parts, say, K_0 and K_1 . The appropriate division for a given problem must be clear from the physical situation. In this approach the state vector and operators are defined by

$$|\Phi_I(t)\rangle = e^{iK_0 t} |\Phi_S(t)\rangle \quad (17)$$

$$A_I(t) = e^{iK_0 t} A_S e^{-iK_0 t} \quad (18)$$

It follows that

$$i \frac{\partial}{\partial t} |\Phi_I(t)\rangle = K_I(t) |\Phi_I(t)\rangle$$

$$K_I(t) = e^{iK_0 t} K_1 e^{-iK_0 t} \quad (19)$$

and

$$i \frac{\partial}{\partial t} A_I(t) = [A_I(t), K_0]_- \quad (20)$$

As for the CSP case, it is defined an evolution time operator $U_I(t, t_0)$ such that

$$i \frac{\partial}{\partial t} U_I(t, t_0) = K_I(t) U_I(t, t_0) \quad (21)$$

and it can be obtained that

$$U_I(t, t_0) = 1 + \sum_{n=1}^{\infty} \frac{(-i)^n}{n!} \int_{t_0}^t dt_1 \dots \int_{t_0}^{t_1} dt_n T(K_I(t_1)K_I(t_2)\dots K_I(t_n)) \quad (22)$$

where T is the Wick chronological ordering operator³² defined by

$$T(K_I(t_1) \dots K_I(t_n)) = \sum_{\sigma} \Theta(t_{\sigma_1} - t_{\sigma_2}) \dots \Theta(t_{\sigma_{n-1}} - t_{\sigma_n}) K_I(t_{\sigma_1}) \dots K_I(t_{\sigma_n})$$

where

$$\Theta(t-t') = \begin{cases} 1 & \text{if } t > t' \\ 0 & \text{if } t < t' \end{cases}$$

and

σ is element of the permutation group of n objects

2. GENERALIZED OPERATORS

For each additive physical quantity $F(\tau_1 \dots \tau_n)$ defined on phase space and depending symmetrical and essentially on N particles, there is a correspondent operator F defined on \mathbf{IF} and given in χ -formalism by²⁸

$$F = \frac{1}{N!} \int \psi^\dagger(\tau_1) \dots \psi^\dagger(\tau_N) F(\tau_1 \dots \tau_N) \psi(\tau_N) \dots \psi(\tau_1) d\tau_1 \dots d\tau_N \quad (23)$$

It follows that the average value of the quantity $F(\tau_1 \dots \tau_N)$ is

$$\overline{F(\tau_1 \dots \tau_N)} = (\chi(t), F\chi(t))$$

However, in this formalism we may introduce more general operators than $F(\tau_1 \dots \tau_n)$. One of them is the Liouville operator

$$K = i \int \psi^\dagger(\tau) \left(\frac{\vec{p}^2}{2m}, \psi(\tau) \right)_1 d\tau + \frac{i}{2} \iint \psi^\dagger(\tau) \psi^\dagger(\tau') (V(\vec{x}, \vec{x}'), \psi(\tau) \psi(\tau'))_2 d\tau d\tau' \quad (24)$$

which reduces to

$$K_n = i(H(\tau_1 \dots \tau_n), \cdot)_n \quad (25)$$

in the sub-space $\mathbf{IF}(n)$

Relations (24) and (25) allows one to define other generalized operators. In fact we can associate to each physical quantity $A(\tau_1 \dots \tau_n)$ an operator

$$\Gamma(A) = \frac{i}{N!} \int \psi^\dagger(\tau_1) \dots \psi^\dagger(\tau_N) A(\tau_1 \dots \tau_N) \psi(\tau_N) \dots \psi(\tau_1) d\tau_1 \dots d\tau_n \quad (26)$$

In the χ -formalism; the factor i is employed to assure the hermiticity of $\Gamma(A)$. It seems natural to assume that these more general operators may also correspond to physical quantities, although no such correspondence has yet been established. In particular, we will show that they are the natural objects with which we can develop a linear response theory, in the present formulation of classical statistical mechanics.

It is interesting to notice that if A is a constant of motion, that is

$$[A, K]_- = 0$$

then $\Gamma(A)$ is also a constant of motion.

As examples of generalized operators we have

$$\Gamma\left(\sum_{\ell=1}^n \vec{p}_\ell\right) = i \int \psi^\dagger(\tau) (\vec{p},)_1 \psi(\tau) d\tau$$

$$\Gamma\left(\sum_{\ell} (\vec{x}_\ell \wedge \vec{p}_\ell)\right) = i \int \psi^\dagger(\tau) (\vec{x} \wedge \vec{p},)_1 \psi(\tau) d\tau$$

which are represented by

$$\Gamma_n\left(\sum_{\ell} \vec{p}_\ell\right) = -i \sum_{\ell=1}^n \left(\frac{\partial}{\partial \vec{x}_\ell}\right)$$

and

$$\Gamma_n\left(\sum_{\ell} (\vec{x}_\ell \wedge \vec{p}_\ell)\right) = -i \sum_{\ell=1}^n \left(\vec{x}_\ell \wedge \frac{\partial}{\partial \vec{p}_\ell} + \vec{p}_\ell \wedge \frac{\partial}{\partial \vec{p}_\ell}\right)$$

respectively, in the sub-space $\mathbb{F}^{(n)}$.

From the above results, it follows that $\Gamma(A)$ is essentially the infinitesimal contact transformation determined by $A(\tau_1 \dots \tau_n)$.

3. A LINEAR RESPONSE THEORY

Let us consider a many-particle classical system with interactions, and its time-independent Hamiltonian operator H given by (23). Suppose then that the system is disturbed at $t = t_0$ by turning on an additional time-dependent Hamiltonian $H^{ex}(t)$. Hence the total Hamiltonian is

$$H^T(t) = H + H^{ex}(t)$$

with the condition

$$H^T(t) \xrightarrow[t \rightarrow t' \leq t_0]{} H$$

Correspondently, since the Liouville operator is essentially the infinitesimal contact transformation determined by H we have

$$K^T(t) = K + K^{ex}(t) \tag{27}$$

for the Liouville operator, with the condition that

$$K^T(t) \xrightarrow[t \rightarrow t' \leq t_0]{} K \tag{28}$$

i.e., we suppose that before $t = t_0$ the system is in a macroscopic equilibrium state. So, in the formalism of the Hilbert K space it is described by a convenient stationary state of K ; we denote this state by $|\Phi\rangle$, that is

$$K |\Phi\rangle = 0$$

We can find out how the physical quantities are modified by the introduction of the perturbation $K^{ex}(t)$. In fact, if we consider a quantity $A(\tau_1 \dots \tau_n)$ represented by the operator A , its average value is given by

$$\overline{A(\tau_1 \dots \tau_n, t)} = \langle \Phi_T(t) | A_T(t) | \Phi_T(t) \rangle \tag{29}$$

In CIP, with $|\Phi_T(t)\rangle$ normalized.

Now, we observe that for the Liouville operator (27), the operator in CIP coincide with the CHP operators defined by K , the Liouville operator for a non-perturbed system. Then, from eq. (29) we have

$$\overline{A(\tau_1 \dots \tau_n; t)} = \langle \Phi_I(t) | A_H^0(t) | \Phi_I(t) \rangle \quad (30)$$

where the superscript 0 in $A_H^0(t)$ denotes that this operator is in CHP formalism defined by K.

Considering that

$$|\Phi_I(t)\rangle = U_I(t, t_0) |\Phi_I(t_0)\rangle \quad (31)$$

we have

$$\overline{A(\tau_1 \dots \tau_n, t)} = \langle \Phi_I(t_0) | U_I^\dagger(t, t_0) A_H^0(t) U_I(t_1, t_0) | \Phi_I(t_0) \rangle \quad (32)$$

with

$$U_I(t, t_0) = \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \int_{t_0}^t dt_1 \dots \int_{t_0}^t dt_n T(K_I^{\text{ex}}(t) \dots K_I^{\text{ex}}(t_n)) \quad (33)$$

$$K_I^{\text{ex}}(t) = e^{iKt} K^{\text{ex}}(t) e^{-iKt}$$

Furthermore, we have

$$|\Phi_I(t_0)\rangle = |\Phi\rangle$$

and if we denote

$$A_H(t) \equiv U_I^\dagger(t, t_0) A_H^0(t) U_I(t, t_0)$$

then we have, from eq. (32)

$$\overline{A(\tau_1 \dots \tau_n; t)} = \langle \Phi | A_H(t) | \Phi \rangle \quad (34)$$

where, using eq. (33)

$$A_H(t) = A_H^0(t) + \sum_{n=1}^{\infty} (i)^n \int_{t_0}^t dt_1 \dots \int_{t_0}^{t_{n-1}} dt_n \left[K_I(t_n) \left[\dots \left[K_I(t_1), A_H^0(t) \right] \dots \right] \right] \quad (35)$$

or simply

$$A_H(t) = A_H^0(t) + \sum_{n=1}^{\infty} (i)^n \int_{t_0}^t dt_1 \dots \int_{t_0}^{t_{n-1}} dt_n \left[K_H^{\text{ex}}(t_n), \dots \left[K_H^{\text{ex}}(t_1), A_H^0(t) \right] \dots \right] \quad (36)$$

because the operators in the CIP defined by $K^T(t)$ coincide with the operators in the CHP defined by K ,

Then, with the notion of switching on the interaction adiabatically, we have, from eq. (36),

$$A_H(t) - A_H^0(t) = \Delta A(t) = \sum_n \Delta_n A(t) \quad (37)$$

with

$$\Delta_n A(t) = (-i)^n \int_{-\infty}^{\infty} dt_1 \dots \int_{-\infty}^{\infty} dt_n \Theta(t-t_1) \dots \Theta(t_{n-1} - t_n) \left[\dots \left[A_H(t), K_H^{\text{ex}}(t_1) \right] \dots \right], K_H^{\text{ex}}(t_n) \exp(-\varepsilon(|t_1| + \dots + |t_n|))$$

where we have used the Heaviside function and the property of commutators

$$[A, B] = - [B, A]$$

If we define the $(n+1)$ - time Green operator as

$$G_{n+1}(A(t), B(t_1), \dots, B(t_n)) = i^n \Theta(t-t_1) \dots \Theta(t_{n-1} - t_n) [\dots [A(t), B(t_1)] \dots B(t_n)]$$

where

$$A(t) = e^{iKt} A_s e^{-iKt}$$

and

$$B(t_i) = e^{iKt_i} B_s e^{-iKt_i}$$

we can write

$$\Delta_n A(t) = (-i)^n \int_{-\infty}^{\infty} dt_1 \dots \int_{-\infty}^{\infty} dt_n e^{-\varepsilon(|t_1| + \dots + |t_n|)} G_{n+1}(A_H^0(t), K_H^{\text{ex}}(t_1) \dots K_H^{\text{ex}}(t_n))$$

being the average value of $A(\tau_1 \dots \tau_n; t)$ given by

$$\overline{A(\tau_1 \dots \tau_n; t)} = \langle \Phi | A_H^0(t) | \Phi \rangle + \sum_{n=1}^{\infty} \langle \Phi | \Delta_n A(t) | \Phi \rangle$$

But the average value of the $(n+1)$ -time Green operator, if $|\Phi\rangle$ is a stationary state, is correspondently the $(n+1)$ -time Green function G_{n+1} , that is

$$G_{n+1}(A_H^0(t), K_H^{\text{ex}}(t) \dots K_H^{\text{ex}}(t_n)) = \langle \Phi | G_{n+1}(A_H(t), K_H^{\text{ex}}(t_1) \dots K_H^{\text{ex}}(t_n)) | \Phi \rangle$$

In the case of a weak external perturbation it is sufficient to consider only the first term in (37), $\Delta_1 A(t)$; in this case we only have to care of the calculation of the 2-time retarded Green function.

3.1 - Retarded and Advanced Green Functions

As we saw above, the formulation of Classical Statistical Mechanics in terms of the Hilbert-K space allows us to define $(n+1)$ -time Green's functions analogous to those of Statistical Quantum Theory, i.e., by using commutators and operators associated to classical functions. In particular we can define 2-time advanced (a) and retarded (r) Green's

$$G_r(t, t') \equiv \langle\langle A(t); B(t') \rangle\rangle_r = -i\theta(t-t') \langle \Phi | [A(t), B(t')]_- | \Phi \rangle$$

$$G_a(t, t') \equiv \langle\langle A(t); B(t') \rangle\rangle_a = i\theta(t'-t) \langle \Phi | [A(t), B(t')]_- | \Phi \rangle$$

where $A(t)$ and $B(t)$ are operators in the CHP and $|\Phi\rangle$ is a suitable stationary state of the Liouville operator.

We notice that the Green functions $G_a(t, t')$ and $G_r(t, t')$ depend on t and t' only through $(t-t')$. Let us consider the advanced function $G_a(t, t')$, for instance:

$$\begin{aligned} \langle\langle A(t); B(t') \rangle\rangle_a &= i\theta(t'-t) \langle \Phi | A(t)B(t') - B(t')A(t) | \Phi \rangle \\ &= i\theta(t'-t) \{ \langle \Phi | A(0) e^{-iK(t-t')} B(0) | \Phi \rangle - \langle \Phi | B(0) e^{iK(t-t')} A(0) | \Phi \rangle \} \\ &= i\theta(t'-t) \{ \langle \Phi | e^{-iK(t-t')} e^{iK(t-t')} A(0) e^{-iK(t-t')} B(0) | \Phi \rangle \} \end{aligned}$$

$$\begin{aligned}
& - \langle \Phi | B(0) e^{iK(t-t')} A(0) e^{-iK(t-t')} e^{iK(t-t')} | \Phi \rangle \\
& = i\theta(t'-t) \{ \langle \Phi | [A(t-t'), B(0)]_- | \Phi \rangle \equiv \langle\langle A(t-t'); B(0) \rangle\rangle_a
\end{aligned}$$

because $|\Phi\rangle$ is a stationary state (so, $K|\Phi\rangle = 0$).

The equations of motion for the Green functions follow from the fact that, for the CHP

$$i \frac{dA}{dt} = - [K, A]_-$$

then

$$\begin{aligned}
i \frac{dG}{dt} &= i \frac{d}{dt} \langle\langle A; B \rangle\rangle_{a,r} = \frac{d\theta(t-t')}{dt} \langle \Phi | [A(t), B(t')]_- | \Phi \rangle \\
&+ \langle\langle i \frac{dA(t)}{dt}; B(t') \rangle\rangle_{a,r} \\
&= \delta(t-t') \langle \Phi | [A(t), B(t')]_- | \Phi \rangle + \langle\langle [A(t), K]_-, B(t') \rangle\rangle_{a,r} \quad (38)
\end{aligned}$$

This equation is the same for both G_r and G_a Green functions, since $\frac{d}{dt} \theta(-t) = -\frac{d}{dt} \theta(t)$. We can see that the double-time Green functions on the right hand side of eq. (38) are, generally speaking, of a higher order than the initial one. We can then write an equation of motion for this new Green's function, thus establishing an infinite chain of equations.

As in statistical quantum mechanics³³ we can introduce time-correlation functions

$$\begin{aligned}
h(A, B) &= \langle \Phi | A(t) B(t') | \Phi \rangle \\
h(B, A) &= \langle \Phi | B(t') A(t) | \Phi \rangle
\end{aligned} \quad (39)$$

and study their Fourier transform \mathcal{F}

$$f[h(A, B)] \equiv h(A, B; \omega) = \int_{-\infty}^{\infty} h(A, B; t-t') e^{i\omega(t-t')} dt-t'$$

$$f[h(B, A)] \equiv h(B, A; \omega) = \int_{-\infty}^{\infty} h(B, A; t-t') e^{i\omega(t-t')} dt-t'$$

It follows that the Fourier transform of the retarded Green function is

$$\begin{aligned}
\langle\langle A|B\rangle\rangle_w^r &= \int_{-\infty}^{\infty} \langle\langle A(t);B(t')\rangle\rangle^r e^{i\omega(t-t')} d(t-t') \\
&= -\frac{i}{2\pi} \int_{-\infty}^{\infty} \Theta(t-t') \{h(A,B;\omega') - h(B,A;\omega')\} e^{i(\omega-\omega')(t-t')} d\omega' d(t-t')
\end{aligned}
\tag{40}$$

Using the integral representations of $\Theta(t-t')$ and $\delta(t-t')$, i.e.,³³

$$\begin{aligned}
\Theta(t-t') &= \frac{i}{2\pi} \int_{-\infty}^{\infty} \frac{e^{-ix(t-t')}}{x+i\epsilon} dx, \quad \epsilon \rightarrow 0 \\
\delta(t-t') &= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-ix(t-t')} dx
\end{aligned}$$

eq. (40) can be written as

$$\langle\langle A|B\rangle\rangle_w^r = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{h(A,B;\omega') - h(B,A;\omega')}{\omega - \omega' + i\epsilon} d\omega' \quad ; \quad (\omega \text{ real})$$

and, correspondently

$$\langle\langle A|B\rangle\rangle_w^\alpha = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{h(A,B;\omega') - h(B,A;\omega')}{\omega - \omega' - i\epsilon} d\omega' \quad ; \quad (\omega \text{ real})$$

If a cut is made along the real axis ω , the function⁸

$$\langle\langle A|B\rangle\rangle_w = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{h(A,B;\omega') - h(B,A;\omega')}{\omega - \omega'} d\omega' \quad ; \quad (\omega \text{ complex})
\tag{41}$$

can be considered as an analytical function consisting of two branches, one defined on the upper, and the other in the lower half-plane of complex values of ω , such that

$$\langle\langle A|B\rangle\rangle_w = \begin{cases} \langle\langle A|B\rangle\rangle_w^r, & \text{for } \text{Im}(\omega) > 0 \\ \langle\langle A|B\rangle\rangle_w^\alpha, & \text{for } \text{Im}(\omega) < 0 \end{cases}$$

We can get information about the correlation functions from the singularities of eq. (41) on the ω -real axis; in effect, we have

$$\langle\langle A|B\rangle\rangle_{\omega+i\epsilon} - \langle\langle A|B\rangle\rangle_{\omega-i\epsilon} = -i(h(A,B;\omega) - h(B,A;\omega))
\tag{42}$$

To conclude this section we obtain the equation of motion for $\langle\langle A|B\rangle\rangle_w$. From (38) we have

$$\begin{aligned}
 & i \int_{-\infty}^{\infty} e^{i\omega(t-t')} \frac{d}{dt} \langle\langle A(t); B(t')\rangle\rangle^{r,a} d(t-t') \\
 &= \int_{-\infty}^{\infty} \delta(t-t') e^{i\omega(t-t')} \langle\Phi| [A(t), B(t')]_- \Phi\rangle d(t-t') \\
 &+ \int_{-\infty}^{\infty} e^{i\omega(t-t')} \langle\langle [A(t), K]_- ; B(t')\rangle\rangle^{r,a} d(t-t') \quad (43)
 \end{aligned}$$

But

$$\begin{aligned}
 & i e^{i\omega(t-t')} \frac{d}{dt} \langle\langle A(t); B(t')\rangle\rangle^{r,a} = \omega e^{i\omega(t-t')} \langle\langle A(t); B(t')\rangle\rangle^{r,a} \\
 &+ i \frac{d}{dt} e^{i\omega(t-t')} \langle\langle A(t); B(t')\rangle\rangle
 \end{aligned}$$

Then with the boundary condition

$$\lim_{|t-t'| \rightarrow \infty} \langle\langle A(t); B(t')\rangle\rangle^{r,a} = 0$$

we obtain from the relation (43)

$$\omega \langle\langle A|B\rangle\rangle_w = \langle\Phi| [A, B]_- |\Phi\rangle_w + \langle\langle [A, K]_- |B\rangle\rangle_w \quad (44)$$

which is the equation of motion for $\langle\langle A|B\rangle\rangle_w$.

4. APPLICATIONS

In the preceding section the operators A and B were any two hermitean operators in Hilbert - K space. Now let us consider A as given by (23) and $B \equiv \Gamma(B)$ defined by (26). In this case we have, from (39)

$$\hbar(\Gamma(B), A(t-t')) = \langle\Phi| \Gamma(B) A(t-t') |\Phi\rangle \quad (45)$$

Consider now a n -particles system. Hence we can restrict ourselves to a sub-space $IF^{(n)}$ of the space $IF = \sum_{i=0}^m IF^{(i)}$, and we obtain for the basis set $\{|\tau_1 \dots \tau_n\rangle\}$

$$\begin{aligned}
h(\Gamma(B), A(t-t')) &= \\
&= \int d\tau_1 \dots d\tau_n \Phi^*(\tau_1 \dots \tau_n) \Gamma(B) A(\tau_1 \dots \tau_n, t-t') \Phi(\tau_1 \dots \tau_n) \\
&= \int (d\tau) \Phi^*(\tau_1 \dots \tau_n) \Gamma(B) A(\tau_1 \dots \tau_n, t-t') \cdot \Phi(\tau_1 \dots \tau_n) \\
&+ \int (d\tau) \Phi^*(\tau_1 \dots \tau_n) A(\tau_1 \dots \tau_n, t-t') \Gamma(B) \Phi(\tau_1 \dots \tau_n) \\
&= \int (d\tau) \Phi^*(\tau_1 \dots \tau_n) \Gamma(B) A(\tau_1 \dots \tau_n, t-t') \cdot \Phi(\tau_1 \dots \tau_n) + h(A(t-t'), \Gamma(B))
\end{aligned}$$

or

$$\begin{aligned}
h(\Gamma(B), A(t-t')) - h(A(t-t'), \Gamma(B)) &= \\
&= \int (d\tau) \Phi^*(\tau_1 \dots \tau_n) \Gamma(B) A(\tau_1 \dots \tau_n; t-t') \cdot \Phi(\tau_1 \dots \tau_n) \quad (46)
\end{aligned}$$

where the point indicates that $\Gamma(B)$ acts only upon $A(\tau_1 \dots \tau_n; t-t')$.

Applying the Fourier transform operator f to eq. (46) and using eq. (42) we obtain

$$\begin{aligned}
\langle\langle A | \Gamma(B) \rangle\rangle_{w+i\varepsilon} - \langle\langle A | \Gamma(B) \rangle\rangle_{w-i\varepsilon} &= \\
if \left\{ \int (d\tau) \Phi^*(\tau_1 \dots \tau_n) \Gamma_n(B) A(\tau_1 \dots \tau_n) - \tau \cdot \Phi(\tau_1 \dots \tau_n) \right\} & \quad (47)
\end{aligned}$$

But for our system the stationary state $\Phi(\tau_1 \dots \tau_n)$ is

$$\Phi(\tau_1 \dots \tau_n) = \exp \left[\frac{F - H}{2kT} \right] \quad \begin{array}{l} T = \text{Temperature} \\ k = \text{Boltzman constant} \end{array}$$

where F is the Helmholtz free energy and H is the hamiltonian of the system, and then we get after some integrations by parts

$$\begin{aligned}
\langle\langle A | \Gamma(B) \rangle\rangle_{w+i\varepsilon} - \langle\langle A | \Gamma(B) \rangle\rangle_{w-i\varepsilon} &= \\
= if \left\{ - \frac{1}{kT} \int (d\tau) \Phi^*(\tau_1 \dots \tau_n) B(\tau_1 \dots \tau_n) \cdot K_n A(\tau_1 \dots \tau_n; t-t') \Phi(\tau_1 \dots \tau_n) \right\} & \quad (48)
\end{aligned}$$

And, once that

$$iK_n A(\tau_1 \dots \tau_n; t-t') = - \frac{\partial}{\partial (t-t')} A(\tau_1 \dots \tau_n; t-t')$$

It follows from eq. (48) that

$$\begin{aligned} \langle\langle A | \Gamma(B) \rangle\rangle_{w+i\varepsilon} - \langle\langle A | \Gamma(B) \rangle\rangle_{w-i\varepsilon} &= \\ &= f \left\{ \frac{1}{kT} \frac{\partial}{\partial (t-t')} \int (d\tau) \Phi^*(\tau_1 \dots \tau_n) B(\tau_1 \dots \tau_n) \right. \\ &\quad \left. A(\tau_1 \dots \tau_n; t-t') \Phi(\tau_1 \dots \tau_n) \right\} \end{aligned}$$

or else

$$\begin{aligned} \langle\langle A | \Gamma(B) \rangle\rangle_{w+i\varepsilon} - \langle\langle A | \Gamma(B) \rangle\rangle_{w-i\varepsilon} &= \frac{1}{kT} f \left\{ \frac{\partial}{\partial (t-t')} h(B, A(t-t')) \right\} \\ &= - \frac{iw}{kT} h(B, A; w) \end{aligned} \quad (49)$$

where we have used the condition⁸

$$\lim_{|t-t'| \rightarrow \infty} \langle \Phi | A_+(t) B(t') | \Phi \rangle = \langle \Phi | A(0) | \Phi \rangle \langle \Phi | B(0) | \Phi \rangle$$

Equation (49) shows that in the present formulation of classical statistical mechanics we can obtain the time-correlation function for two physical quantities A and B, from the Green function defined in terms of the operator B and the generalized operator $\Gamma(B)$ associated to B.

In order to clarify how the general methods hitherto developed should be applied, we consider a very simple example: we will determine the correlation function $h(x, x; w)$ for a system whose Hamiltonian is $H = \frac{p^2}{2} + V(x)$, where $V(x)$ is a position-dependent potential. Because of the result expressed by (49) it is necessary to obtain the Green function $\langle\langle x | \Gamma(x) \rangle\rangle_w$. From relation (44) we have

$$w \langle\langle x | \Gamma(x) \rangle\rangle_w = \langle \Phi | [x, \Gamma(x)]_- | \Phi \rangle + \langle\langle [x, K]_- | \Gamma(x) \rangle\rangle_w$$

Then, using that $[x, K]_- = ip$ and $[x, \Gamma(x)]_- = 0$, we have

$$w \langle\langle x | \Gamma(x) \rangle\rangle_w = i \langle\langle p | \Gamma(x) \rangle\rangle_w \quad (50)$$

To calculate $\bar{\mu} \ll p | \Gamma(x) \gg_w$ we must consider the equation

$$\omega \ll p | \Gamma(x) \gg_w = \langle \Phi | [p, \Gamma(x)]_- | \Phi \rangle + \ll [p, K]_- | \Gamma(x) \gg_w \quad (51)$$

But we have

$$[p, \Gamma(x)]_- = -i, \quad [p, K]_- = -i \nabla V(x) \equiv -iV'$$

and then

$$\omega \ll p | \Gamma(x) \gg_w = -i (1 + \ll V' | \Gamma(x) \gg_w) \quad (52)$$

One may continue on writing equations of motion for $\ll V' | \Gamma(x) \gg_w$ and other Green functions which appear subsequently, thus establishing an infinite series of coupled equations of motions. To determine a solution to this it is natural to seek for some approximate means of interrupting and uncoupling it at an earlier stage. In order to proceed to this we suppose that

$$i \ll V'' p | \Gamma(x) \gg_w \approx \langle \Phi | V''(x) | \Phi \rangle \ll x | \Gamma(x) \gg_w \quad (53)$$

and then, once that

$$\omega \ll V' | \Gamma(x) \gg_w = i \ll V'' p | \Gamma(x) \gg_w$$

we have

$$\omega^2 \ll x | \Gamma(x) \gg_w = 1 + \langle \Phi | V''(x) | \Phi \rangle \ll x | \Gamma(x) \gg_w$$

or else

$$\ll x | \Gamma(x) \gg_w = \frac{1}{\omega^2 - \Omega_\epsilon^2} = \frac{1}{2\Omega_\epsilon} \left[\frac{1}{\omega - \Omega_\epsilon} - \frac{1}{\omega + \Omega_\epsilon} \right] \quad (54)$$

where $\Omega_\epsilon^2 = \langle \Phi | V''(x) | \Phi \rangle$ is the effective angular frequency. Introducing the result (54) into eq. (49) we obtain

$$\hbar(x, x; \omega) = -\frac{kT\pi}{\Omega_\epsilon^2 \omega} (\delta(\omega + \Omega_\epsilon) - \delta(\omega - \Omega_\epsilon))$$

and correspondently

$$\begin{aligned} \hbar(x(t), x(t')) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} \hbar(x, x; \omega) e^{-i\omega(t-t')} d\omega \\ &= \frac{kT}{\Omega_\epsilon^2} \cos \Omega_\epsilon(t-t') \end{aligned} \quad (55)$$

If $t' = t$ we obtain

$$h(x, x) = \frac{kT}{\Omega_\epsilon^2}$$

or, by the definition of the function h ,

$$\frac{\Omega_\epsilon^2 \langle x^2 \rangle}{2} = \frac{kT}{2}$$

which is a result known of the equipartition of energy theorem. It is clear that the potential $V(x)$, in the approximation we used (eq. (53)), is replaced by an effective potential given by $V(x) = \frac{\Omega_\epsilon^2 x^2}{2}$.

5. CONCLUSIONS

We have presented a linear response theory and defined Green's functions by using the formulation of classical statistical mechanics with second quantization methods. It is introduced in this formulation the field operators $\psi(\tau)$, $\tau \equiv (\vec{x}, \vec{p})$, defined on phase space, and the Liouville equation is written as

$$i \frac{\partial}{\partial t} |\Phi(t)\rangle = K |\Phi(t)\rangle$$

where $|\Phi(t)\rangle$ is an element of the Hilbert- K space and K is given by

$$K = i \int \psi^\dagger(\tau) \left(\frac{\vec{p}^2}{2m}, \psi(\tau) \right)_1 d\tau + \frac{i}{2} \iint \psi^\dagger(\tau) \psi^\dagger(\tau) (V(x-x'), \psi(\tau') \psi(\tau))_2 d\tau d\tau'$$

The retarded and advanced Green's functions are introduced by the relations

$$\langle\langle A(t); B(t') \rangle\rangle_r = -i\theta(t-t') \langle [A(t), B(t')]_- \rangle$$

$$\langle\langle A(t); B(t') \rangle\rangle_a = i\theta(t'-t) \langle [A(t), B(t')]_- \rangle$$

where the notation $\langle \rangle$ denotes average value of the contents and $[,]_-$ indicates a commutator. $A(t)$ and $B(t)$ are hermitean operators constructed from the classical functions $A(q, p)$ and $B(q, p)$ respectively. In this sense our definitions are different from those of Bogolyubov and Sadovnikov¹⁰, for they had used Poisson brackets and functions of the dynamical state of the system.

We have determined the chain of equations and the spectral representations for the "new" classical Green's functions. We have shown that the correlation functions can be obtained from the Green's func-

tions defined with generalized operators. In fact, except for the Liouville operator, these generalized operators do not still play an effective role in this formulation of classical statistical mechanics. In the present paper we have shown that it is possible to associate, to each classical observable A , a generalized operator $\Gamma(A)$ acting on Hilbert-K space; by this means we can determine the correlation functions $h(A, A; w)$ and $h(B, A; w)$, being B another observable of the system. The example illustrates the application of the methods here developed. One of the advantages of this formulation lies in the fact that the linear response theory for classical systems is presented in terms of mathematical entities usually associated to quantum systems (e.g., state vectors, commutators, hermitean operators, etc). Thus the method makes it possible to describe, in a simpler and unified way, a number of cases of processes that happen to classical and quantum systems.

We should still note that since the method considered here allows the use of field operators $\psi(\tau, t)$, it is in principle possible to define causal Green's functions in terms of those operators and to develop a diagrammatic approach to calculate these functions. This approach and some of its special problems will be further discussed in a forthcoming paper.

REFERENCES

1. I. Prigogine, *Non-Equilibrium Statistical Mechanics* (Interscience Publishers, Inc, New York, 1962).
2. I. Prigogine and R. Balescu, *Physica* 25, 281, 302 (1959).
3. I. Prigogine and F. Henin, *J. Math. Phys.* 1, 349 (1961).
4. I. Prigogine and R. Balescu, *Physica* 26, 145 (1960).
5. F. Henin, P. Resibois and F. Andrews, *J. Math. Phys.* 2, 68 (1961).
6. D.N. Zubarev, *Sov. Phys. Doklady* 6, 776 (1962).
7. D.N. Zubarev, *Sov. Phys. Doklady* 10, 526, 850 (1966).
8. D.N. Zubarev, *Nonequilibrium Statistical Thermodynamics* (Consultants Bureau Plenum Publish Corp., New York, 1974).
9. H.B. Callen and T.A. Welton, *Phys. Rev.* 83, 34 (1951).
10. N.N. Bogoliubov, Jr. and B. I. Sadovnikov, *Sov. Phys. JETP* 16, 482 (1963).
11. R. Aronson, *J. Math. Phys.* 4, 589 (1966).

12. Yu. L. Klimontovich, Sov. Phys. JETP 6, 753 (1958).
13. R. Kubo, J. Phys. Soc. Japan 12, 570 (1957).
14. R. Balescu, Physica 27, 693 (1961).
15. I. Prigogine *et al*, Proc. Natl. Acad. Sci USA 74,4152 (1977).
16. R. Balescu, *Statistical Mechanics of Charged Particles* (Interscience Publishers, Inc, New York, 1963).
17. T. Matsubara, Prog. Theor. Phys.14, 351 (1955).
18. J.C. Herzel, J. Math. Phys. 8, 1650 (1967).
19. J.C. Herzel, J. Math. Phys.11, 741 (1970).
20. C.L. Mehta, J. Math. Phys. 5, 66 (1966).
21. C.L. Mehta and E.C.G. Sudarshan, Phys. Rev. 138, B274 (1965)..
22. J.C.T. Pool, J. Math. Phys. 7, 66 (1966).
23. G.S. Agarwal and E. Wolf, Phys. Rev. D2, 2161, 2187, 2206 (1970).
24. M.D. Srinivas and E. Wolf, Phys. Rev. D11, 1477 (1975).
25. R.F. O'Connell and E. Wigner, Phys. Lett. 83A, 145 (1981).
26. R.F. O'Connell and E. Wigner, Phys. Lett. 85A, 121 (1981).
27. W. Guz, Int. J. Theor. Phys. 23, 157 (1984).
28. M. Schönberg, II N. Cimento 9, 1139 (1952).
29. M. Schönberg, II N. Cimento 10, 419 (1953).
30. M. Schönberg, II N. Cimento 10, 697 (1953).
31. B.O. Koopman, Proe. Natl. Acad. USA 17, 315 (1931).
32. G.C. Wick, Phys. Rev. 80, 268 (1950).
33. D.N. Zubarev, Sov. Phys. Uspekhi 3, 320 (1960).

Resumo

Discute-se um método para expressar resultados estatísticos clássicos em termos de entes usualmente associados à abordagem teórica de sistemas de muitas partículas com tratamento da teoria quântica de campos (espaço de Fock, comutadores, operadores de campo, vetor de estado). A seguir desenvolve-se uma teoria de-resposta linear, utilizando a equação de Liouville em segunda-quantização introduzida por Schönberg. Faz-se uma breve análise da relação entre este método e o de Prigogine *et al*. Apresenta-se a cadeia de equações e as representações espectrais para as novas funções de Green clássicas obtidas no método; mostra-se que destas funções de Green definidas com operadores generalizados pode-se obter funções de correlação. Discute-se operadores generalizados definidos no espaço de Fock.