Structure of Subdynamics in Non-equilibrium

Statistical Mechanics

by

C. C. Chiang and E. C. G. Sudarshan
1. Introduction

About a century ago, Boltzmann \(^{(1)}\) introduced probabilistic considerations into mechanics in an attempt to establish the connection between thermodynamic irreversibility and the laws of mechanics which are reversible, and deduced his famous irreversible kinetic equation which has been found to be adequate and useful for describing the behaviours of dilute gases. Boltzmann's work has however been the subject of serious criticism since then. The probabilistic argument used by Boltzmann is quite different from that used in quantum mechanics. The concept of probability in quantum mechanics is closely related to its description in terms of classical models and of measurement, but the dynamical law governing the probability amplitude which controls the distribution of the result of measurement is exact and reversible. In statistical mechanics, the notion of distribution function itself has a probabilistic character. To Boltzmann, in addition to this notion of probability implicit in the distribution function, there is another element of probability which is part of the dynamical law governing the distribution function. Why a law of nature for a large system should be a combination of an exact law with a probabilistic element but for a small system this probabilistic element does not manifest itself has never been clearly understood. In addition to obtaining a more general theory of irreversible processes with a larger range of application, attempts have been made either to modify this probabilistic argument in a conceptually more
acceptable way or to avoid it in the theory.

Among others, the work by the Brussels school\(^\text{(2)}\) had made important contributions to the subject of non-equilibrium statistical mechanics. They start from the exact Liouville equation and treat the statistical system as a many-body mechanical system. Indeed, by the use of an eigen function expansion (in terms of the free Liouville operator) they are able to obtain a generalized kinetic equation with a wide range of applicability. From a pragmatic point of view, this approach, in addition to its elegance, makes definite progress in non-equilibrium statistical mechanics. However, there are certain limitations in the current formulation of this theory which may be easily recognized from a study of some global properties of the mathematical structure of the solutions of the Liouville equation.

It is the purpose of this paper to clarify some of the basic mathematical and conceptual problems in their formulation of the theory.

First of all, although the problem of irreversibility and the problem of approach to equilibrium, might be closely related, they are nevertheless two different problems and have to be carefully separated. Irreversibility does not necessarily imply the approach to equilibrium, and vice versa. This point is quite often overlooked. In Section 2, we will first survey the general non-stationary (time-dependent) solution of the Schrodinger-like equation and to the Liouville equation. We will also rewrite the solution in the form given by Prigogine and collaborators. The problem
of approach to equilibrium will then be studied in Section 3. The fact that approach to equilibrium does not imply irreversibility will also be discussed there.

In the approach pursued by Prigogine and his collaborators, any probabilistic arguments of the Boltzmann type have been avoided. The mechanism by which irreversibility is introduced into the theory which starts from the reversible Liouville equation then becomes one of the central issues of this approach. In this context the concept of invariant subdynamics has been introduced by the Brussels school during the last few years and the origin of the irreversibility is then attributed to the existence of this invariant subdynamics. In Section 4, we will show that even though the subdynamics exists, it is still a reversible subdynamics. The conditions for the existence of subdynamics will also be discussed there. In Section 5, we will briefly discuss the extension of the method to the quantum mechanical Liouville-Von Neumann equation.

2. Non-stationary Solution of the Schrödinger-like Equation

In order to simplify the discussion and to make the statements as clear as possible, the discussion in connection with the Liouville equation will be restricted to classical mechanics in this section and in Sections 3 and 4.

Consider a system of N particles. A state of this system can be specified in phase space by the 3N canonical coordinates \( r_1, r_2, \ldots, r_N \) and the 3N canonical momenta \( p_1, p_2, \ldots, p_N \). In statistical mechanics we are interested in the macroscopic behaviour of the system. It is
obvious that there is a large number of states corresponding to a
given macroscopic condition, therefore it is most convenient to
use the notion of the statistical representative ensemble intro-
duced by Gibbs. An ensemble is completely specified by a (con-
tinuous) function \( \rho(p, r, t) = \rho(p_1^+, p_2^+, \ldots, p_N^+, r_1^+, r_2^+, \ldots, r_N^+, t) \) which
is so defined that

\[
\rho(p, r, t) \, d^{3N}p \, d^{3N}r
\]

is the relative number of representative points which, at time \( t \),
are contained in the infinitesimal volume element \( d^{3N}p \, d^{3N}r \) of phase
space centered at point \((p, r)\). We may normalize the distribution
function \( \rho \) in such a way that

\[
\int \rho(p, r, t) \, d^{3N}p \, d^{3N}r = 1. \tag{1}
\]

One can then compute a macroscopic quantity over the distribution
function of a suitable ensemble.

\[
\langle 0(t) \rangle = \int 0(p, r) \rho(p, r, t) \, d^{3N}p \, d^{3N}r. \tag{2}
\]

It is well-known that the distribution function \( \rho \) satisfies
the Liouville equation

\[
\frac{\partial \rho}{\partial t} = [H, \rho]. \tag{3}
\]
where the Poisson bracket is defined as

\[ [H, \rho] = \sum_{j=1}^{N} \left( \frac{\partial H}{\partial \tilde{x}_j} \frac{\partial }{\partial \tilde{p}_j} - \frac{\partial H}{\partial \tilde{p}_j} \frac{\partial }{\partial \tilde{x}_j} \right) \]

with \( H \) the total Hamiltonian of the system.

The question now is: How much information about the dynamical behaviour of the system can be abstracted from the solution of equation (3)? Let us multiply (3) by \( i = -1 \), and write

\[ i \frac{\partial \rho}{\partial t} = L\rho . \]

Here \( L \) is a linear operator, called the Liouville operator, given by

\[ L = -i \sum_{j=1}^{N} \left( \frac{\partial H}{\partial \tilde{p}_j} \frac{\partial }{\partial \tilde{x}_j} - \frac{\partial H}{\partial \tilde{x}_j} \frac{\partial }{\partial \tilde{p}_j} \right) \]

and it can be easily verified that \( L \) is a Hermitian linear operator.

Let us compare Eq. (5) with the Schroedinger equation

\[ i \frac{\partial \psi}{\partial t} = H\psi , \]

where \( H \) is the total Hamiltonian of the system under consideration.

The formal analogy between Eqs. (5) and (7) is obvious, and the mathematical method used to solve the Schroedinger equation can also be applied to the Liouville equation. Let us call all of the differential equations such as the Schroedinger or the Liouville equation (5), Schroedinger-like equations. In what follows we will first briefly dis-
cuss the general solution of this Schrödinger-like equation which has the form

\[ i \frac{\partial \phi}{\partial t} = K \phi \tag{8} \]

where \( K \) is a Hermitian linear operator. For \( K = L \) and \( \phi = \rho \), we have the Liouville equation and for \( K = H \) and \( \phi = \psi \), we have the Schrödinger equation.

As in quantum mechanics, let us assume that the operator \( K \) consists of two parts, the unperturbed (free) part \( K_0 \) may consist, for example, of a continuous part and discrete part. The existence of a discrete spectrum for \( K_0 \) which is not there for \( K \) is connected with decay and resonance problems in quantum mechanics. For our purpose, we will assume that \( K_0 \) has only a continuous spectrum for 0 to \( \infty \). To simplify the problem, we also assume that \( K \) has only a continuous spectrum from 0 to \( \infty \) and has no "bound states".

With the above assumptions on spectra, the task of finding the solution for Eq. (8) becomes much simpler. We are going to find the solution in the representation in which \( K_0 \) is diagonal. This can be done within the framework of the perturbation theory.

Denote the eigenfunction of \( K_0 \) with the eigenvalue \( k_n \), by \( \phi_n(t) \), we have

\[ i \frac{\partial \phi_n}{\partial t} = K_0 \phi_n = k_n \phi_n. \tag{9} \]

It is obvious that \( \phi_n(t) \) has the general time dependent form
\[ \phi_n(t) = e^{-ik_nt} \chi_n \]  

(10)

\( \chi_n \) depends on the other variables but not on \( t \). Assuming that \( \phi_n \)'s form a complete set of vectors, we may expand \( \phi \) in terms of \( \chi_j \)

\[ \phi(t) = \sum_j b_j(t) e^{-ik_jt} \chi_j. \]  

(11)

Strictly speaking, in the case of the Liouville equation, \( L \) is only Hermitian, not necessarily selfadjoint. The completeness of the eigenfunction expansion is, therefore, an assumption. Also, the space of allowed phase densities (which are integrable but not necessarily square integrable) is not a Hilbert space.

For a stationary solution, i.e. \( \phi(t) \) is an eigenfunction of \( K \), the eigenvalue \( k \) is conserved in the course of time, and \( b_j(t) \) has the simple form

\[ b_j(t) = e^{-ik_jt} B_j, \]  

(12)

and

\[ \phi(t) = e^{-ikt} \sum_j B_j \chi_j. \]  

(13)

\[ = e^{-ikt} F_k \]

\( F_k \) is an eigenfunction of \( K \) and satisfies the Lippmann-Schwinger equation (3) in time independent perturbation theory. We are interested in finding a nonstationary solution in which \( K \) is not diagonal and to which consequently no conserved label \( k \) can be assigned. More precisely, we want to find the explicit solution which at \( t=0 \) is a speci-
fied linear combination of the eigenstates of $K_0$,

$$
\phi(0) = \sum_{\ell} \eta_{\ell} x_{\ell}.
$$

(14)

Here the $\eta_{\ell}$ are parameters depending on the initial condition of the problem and do not depend on the variables of $x_{\ell}$'s.

The formal solution of (8) can be written in the form

$$
\phi(t) = e^{-iKt}\phi(0).
$$

(15)

With the help of (11) and (14), we can rewrite (15) in the following form

$$
\sum_{j} b_j(t) e^{-iK_jt} x_j = e^{-iKt}\sum_{\ell} \eta_{\ell} x_{\ell}.
$$

(16)

Multiplying both sides of (16) by $x_i e^{ik_i t}$ from left, we obtain

$$
b_i(t) = \sum_{\ell} x_i^\dagger e^{-iK_{\ell}t} \eta_{\ell} e^{iK_{\ell}t} = e^{-iK_{\ell}t} \sum_{\ell} e^{-iK_{\ell}t} |\ell\rangle \langle \ell |.
$$

(17)

We may write the solution $\phi(t)$ in a matrix form

$$
\begin{pmatrix}
\psi_0(t) \\
\psi_1(t)
\end{pmatrix}
= U(t)
\begin{pmatrix}
\psi_0(0) \\
\psi_1(0)
\end{pmatrix}
$$

(18)
with \( U_{ij}(t) = e^{iKt} <i|e^{-iKt}|j> = e^{iKt} T_{ij} \) \( \quad (19) \)

\[ V_i(t) = b_i(t) \chi_i \] \( \quad (20) \)

and \( b_i(0) = \eta_i. \) \( \quad (21) \)

The problem now is reduced to that of finding \( T_{ij}. \) It can be obtained by the construction of the resolvent for the operator \( K. \) The resolvent operator is defined by:

\[ R(Z) = (Z-K)^{-1} \] \( \quad (22) \)

where \( Z \) is a complex number. It is well known \(^{(4)} \) that the spectral theory of the operator \( K \) can be based on the considerations of its resolvent, and analytic functions of the operator \( K \) can be constructed in terms of the resolvent by a formula which is the analog of Cauchy's formula for analytic functions of a complex variable.

\[ f(K) = \frac{1}{2\pi i} \oint_C R(Z)f(Z)\,dz \] \( \quad (23) \)

Here the function \( f(Z) \) must be regular at all points of the spectrum of \( K \) and the integral is extended along a closed contour \( C \) (consisting of one or more simply-connected closed contours such that all values of \( K \) are encircled by \( C \) and all singularities of \( f(Z) \) lie outside).

Let us apply (22) to \( f(K) = e^{-iKt} \)

\[ e^{-iKt} = \frac{1}{2\pi i} \oint_C R(Z)e^{-iZt}\,dz. \] \( \quad (24) \)
$T_{ij}$'s are nothing but the matrix elements of (24) in the representation in which $K_0$ is diagonal.

The forms of $T_{ij}$'s for a special case in which only one of $\eta_{k_i}$'s is not equal to zero has been obtained by Heitler and Ma (5). The general form of $T_{ij}$'s have been given, e.g., by Zumino (6)

$$<i|e^{-iKt}|j> = <i|j>e^{-iKt} + \frac{1}{2\pi i} \oint \frac{e^{-izt}}{z-k_j} \frac{1}{z-k_i} <i|\Gamma(z)|j> \frac{1}{z-k_j} dz$$

(25)

where $\Gamma(z)$ satisfies the equation

$$\Gamma(z) = K_I + K_I \frac{1}{z-K_0}$$

$$\Gamma(z) = K_I + K_I \sum_{\ell \neq m} \frac{\ell < \ell |}{z-K_\ell} \Gamma(z),$$

(26)

with the formal solution

$$\Gamma(z) = K_I (1 - (z-K_0)^{-1} V)^{-1}.$$

(27)

Let us write (26) in the following form

$$\Gamma(z) = K_I + K_I \left[ \frac{\langle m | \langle \ell |}{z-K_m} + \sum_{\ell \neq m} \frac{\ell < \ell |}{z-K_\ell} \right] \Gamma(z),$$

(28)

$\langle m |$ is an arbitrary state with eigenvalue $\gamma_{\mu}$. (This is to be contrasted with the choice of $|m\rangle$ as the state with its eigenvalue zero, i.e. 0, by the Brussels school.) Substituting (26) into (25), we obtain

$$<m|e^{-iKt}|j> = \frac{1}{2\pi i} \oint \sum_{n=0}^{\infty} \frac{\psi(z)}{(z-K_m)^{n+1}} e^{-izt} dz$$

(29)

with
\[ \psi(z) = \langle m | \sum_{\nu=0}^{\infty} \frac{1}{Z-K_0} | m \rangle_{\text{irr}}. \] (30)

In eq. (30), \( \text{irr.} \) means that in the sum over intermediate states, the state \( |m\rangle \) is excluded. Similarly

\[ \langle i | e^{-ikt} | m \rangle = \frac{1}{2\pi i} \int e^{-izt} C_i(z) \sum_{n=0}^{\infty} \frac{(\psi(z))_n}{(Z-k_m)_n+1} dz \] (31)

\[ \langle m | e^{-ikt} | j \rangle = \frac{1}{2\pi i} \int e^{-izt} \sum_{n=0}^{\infty} \frac{(\psi(z))_n}{(Z-k_m)_n+1} D_j(z) dz \] (32)

\[ \langle i | e^{-ikt} | j \rangle = \frac{1}{2\pi i} \int e^{-izt} [R_{ij}(z) + C_i(z)\langle 0 | \Gamma(z) | 0 \rangle D_j(z)] dz \] (33)

with

\[ C_i(z) = \langle i | \sum_{n=1}^{\infty} \frac{1}{Z-K_0} K_{i}^n | m \rangle_{\text{irr}}. \] (34)

\[ D_j(z) = \langle m | \sum_{n=1}^{\infty} \frac{1}{Z-K_0} K_{i}^n | j \rangle_{\text{irr}}. \] (35)

\[ R_{ij}(z) = \langle i | \sum_{n=0}^{\infty} \frac{1}{Z-K_0} K_{i}^n \frac{1}{Z-K_0} | j \rangle_{\text{irr}}. \] (36)

\( C_i(z) \) and \( D_j(z) \) are respectively called creation and destruction operators by the Brussels school. (7)

In order to obtain the expression given by Brussels school, let us define

\[ \phi_i(t) = e^{-ik_i t} \phi_i(t) \] (37)

Then it is obvious that
\[ \phi_i(t) = \sum_j T_{ij}(t) \phi_j(0) \]
\[ = \sum_j T_{ij}(t) \eta_j x_j \] (38)

In (38), if we write out the explicit forms of $T_{ij}$'s given in (30), (31) and (32), then (38) has exactly the same expression given by Brussels school, when we replace $\phi_i(t)$ by $\rho_v(t)$ and $\eta_i x_i$ by $\rho_v(0)$, and take $|m\rangle = |0\rangle$.

3. Asymptotic Behaviour of the Non-Stationary Solution, Approach to Equilibrium, and Irreversibility

In quantum mechanics, the asymptotic behaviour of the non-stationary solution gives us the information about the scattering amplitude, while in statistical mechanics it is closely related to the problem of approach to equilibrium. More precisely, $U_{ij}(t)$ in the limit of $t \to \infty$ gives us the transition amplitude of the state $j$ at $t = 0$ to the state $i$ at $t \to \infty$ in the interaction representation in quantum mechanics. In statistical mechanics, $\rho^F_i(t) = \rho_i(t)$ is the Fourier coefficient of the total distribution function and is related to $U_{ij}$ by (18)

\[ \rho^F_i(t) = e^{ik_i t} \phi_i(t) = \sum_j U_{ij}(t) \eta_j x_j. \] (39)

The question of whether the distribution function $\rho$ would approach a constant as $t$ approaches infinity is the same as whether $U_{ij}(t)$'s would approach a constant matrix in this limit.
From (25) it is easy to see that $T_{ij}(t)$ has the following asymptotic form

$$\lim_{t \to 0} T_{ij}(t) = \langle i | j \rangle e^{-i k_1 t} + e^{-i k_1 t} \langle i | \Gamma^+(k_i) | j \rangle \frac{1}{k_i - k_j} +$$

$$+ \frac{1}{k_j - k_i} \langle i | \Gamma^+(k_j) | j \rangle e^{-i k_j t}. \quad (40)$$

But

$$\lim_{t \to \infty} \frac{e^{i t (k_j - k_i)}}{k_i - k_j} = i\pi \delta(k_i - k_j), \quad (41)$$

therefore

$$\lim_{t \to \infty} U_{ij}(t) = \lim_{t \to \infty} e^{i k_1 t} T_{ij}$$

$$= \langle i | j \rangle + \left[ \frac{1}{k_j - k_i} - i\pi \delta(k_j - k_i) \right] \langle i | \Gamma^+(k_i) | j \rangle. \quad (42)$$

But (42) can be rewritten in a more familiar form

$$\lim_{t \to \infty} U_{ij}(t) = \langle i | j^+ \rangle, \quad (43)$$

with $|j^+\rangle$ satisfying the Lippmann-Schwinger equation

$$|j^+\rangle = |j\rangle + \lim_{\epsilon \to 0} \frac{1}{k - k_0 + i \epsilon} K_1 |j^+\rangle. \quad (44)$$

In terms of the Møller wave operator $\Omega$, (42) can be rewritten as

$$|j^+\rangle = \Omega^(-)^* |j\rangle \quad (45)$$

where

$$\Omega^(-)^* = \lim_{t \to \infty} e^{i K_0} e^{-i k t} \quad (46)$$

The wave operator $\Omega$ has been studied extensively in the literature.
and we will not discuss it further here. (9)

In non-equilibrium statistical mechanics, one of the main problems is to see whether the distribution function approaches equilibrium. Here we have to make it clear what we mean by "approach to equilibrium". In a global sense, we may define the state of equilibrium as a state which is constant in time. Within this definition, we see that as long as the wave operator exists, the Fourier components of the distribution function should approach equilibrium. However, according to Maxwell and Boltzmann, the distribution function should approach a state which is not only constant in time but also belongs to a certain class of distribution functions, such as the Maxwell-Boltzmann family of distribution functions for dilute gases. It is obvious that the state of equilibrium in this restrictive sense can not always be reached, since the final distribution function depends both on the initial conditions and the structure of the total Liouville operator.

As mentioned before, the problem of the approach to equilibrium is not always carefully distinguished from irreversibility in the literature. (10) For example, let the distribution function which is a solution of the Liouville equation developed from \( t = 0 \) to \( t = t_1 \), at which time we invert the velocities (which is equivalent to the reversal of the time). At \( t = 2t_1 \) the distribution function will be the same as that at \( t = 0 \) provided the velocities are again inverted. This is to be expected, since the Liouville equation is a reversible equation. Now let the time evolve continuously. When \( t \to \infty \), the distribution function will approach a function which is constant in time and is
the same as if it develops from \( t = 0 \) directly to \( t = \infty \). Here we see that the distribution function always approaches its equilibrium value in the global sense. These kinds of solutions which always approach equilibrium are quite often mistakenly considered as irreversible solutions. (A simple elementary example can help to clarify the point that approach to equilibrium can not always be considered as irreversibility. Consider a ball released from a height \( h \) above the ground at \( t = 0 \). We know that it will fall down to the ground. Now consider the case that at \( t = t_1 \), the velocity of the ball is inverted. We also know that the ball will travel up to its original position and then fall down to the ground. In both cases the ball always falls down to the ground. However, no one would say that this is an irreversible phenomenon and the law describing this phenomenon is an irreversible law.) The non-stationary solution of the Liouville equation always approaches equilibrium in the global sense, as long as the Möller operator exists. It is however a reversible solution, unless an additional assumption is introduced into the theory. The treatment of the decay problem in quantum mechanics is an example of introducing additional assumptions to make a reversible solution describe an irreversible phenomenon. It is know that if the spectrum of the free Hamiltonian consists of a discrete spectrum and a continuous part, and the total Hamiltonian has only a continuous spectrum, then the time development of the transition probabilities from discrete states to continuous states will vanish as \( t \). The solution itself for any finite value of \( t \) is a reversible solution. The "irreversibility" is obtained by assuming that the initial states are always discrete
states. This assumption introduces an asymmetry equivalent to the choice of a time direction. Here we see that in the decay problem, the time direction is not a result derived from the theory, but depends on the bias in the choice of initial conditions. Similarly, in the non-equilibrium problem, the reversible solutions which always approach equilibrium might be used to describe irreversible phenomena with such initial conditions as are equivalent to the choice of a time direction.

4. Subdynamics

During the past several years, the concept of "subdynamics" has been introduced by the Brussels in an attempt to unravel the origin of irreversibility. In this section, we will demonstrate that the projection operator for subdynamics defined by the Brussels school is simply the eigenprojection operator for the eigenvalue zero, provided both the free and total Liouville operators have an "isolated" eigen value zero. The question about the irreversibility then becomes trivial in that the subdynamics defined in this subeigen-space is a reversible invariant subdynamics.

To start with, let us consider the resolvent R(z) of the perturbed operator K,

$$R(z) = \frac{1}{z-K}.$$  \hspace{1cm} (47)

It is well known that the singularities of the resolvent correspond to the eigenvalues of the operator K. We may define the projection
\[ P_k = \frac{1}{2\pi i} \oint_{C_k} R(z) \, dz \]  

(48)

where the contour \( C_k \) encircles the set of eigenvalues of \( K \) labeled by \( k \). All other eigenvalues lie outside the contour. \( P_k \) is called eigenprojector if \( C_k \) encircles only one eigenvalue. It is obvious that in general \( P_k \) is equal to the sum of the eigenprojectors for all the eigenvalues lying inside \( C_k \). It can be shown that the projection operator so defined satisfies the following relations  

(4)

\[ a) \quad P_k P_{k'} = \delta_{kk'} P_k \]  

(49)

\[ b) \quad \sum_k P_k = 1 \]  

(50)

\[ c) \quad P_k K = K P_k \]  

(51)

The first relation indicates the \( P_k \) is an orthogonal projection operator. The second relation is the statement of completeness of the projection operator. The last relation shows that \( P_k \)'s are invariants of motion, and therefore we can talk about the invariant subdynamics within the subspace projected out by a particular \( P_k \).

It is important to point out that is is possible to define the projection operator in terms of a contour integral of the resolvent of \( K \) if and only if the contour is well defined, i.e. the contour can be defined without passing through any singularities of the resolvent. (This is not always possible. For example, a projection operator to decompose a continuous spectrum can not be defined in
this fashion. It has to be defined quite differently, and the following formulas are not applicable.)

To obtain the expression for the projection operator given by the Brussels school, let us proceed to express \( P_k \) defined in (48) in terms of the resolvent \( R_O(Z) \) of the unperturbed operator \( K_O \). To do this, let us expand the resolvent \( R(Z) \) in terms of \( R_O(Z) \)

\[
R(Z) = R_O(Z) \left[ 1 + \sum_{n=1}^{\infty} (K_I R_O(Z))^n \right]
\]

\[
= \sum_{n=0}^{\infty} R_O^{(n)}(Z)
\]

with

\[
R_O^{(n)}(Z) = R_O(Z) \cdot (K_I R_O(Z))^n
\]

and

\[
R_O(Z) = \frac{1}{Z - K_O}
\]

Integrating (52) term by term, we have

\[
P_k = \sum_{n=0}^{\infty} P_k^{(n)}
\]

with

\[
P_k^{(n)} = \frac{1}{2\pi i} \oint_{C_K} R_O^{(n)}(Z) \, dz.
\]

We may write (52) in a somewhat different form

\[
R(Z) = R_O(Z) + R_O(Z) \Gamma(Z) R_O(Z)
\]

where \( \Gamma(Z) \), as defined in Section 2, satisfies the following relation

\[
\Gamma(Z) = K_I + K_I R_O \, \Gamma(Z)
\]

Let us insert the intermediate states in the right hand side of (58), and rewrite it in the form of (28) in Section 2, then we can display
the projection operator in the representation, where the unperturbed operator \( K_0 \) is diagonal, in the following form

\[
\langle m | P_k | m \rangle = \frac{1}{2\pi i} \oint_{C_k} \sum_{n=0}^{\infty} \frac{(\psi(Z))^n}{(Z-k_m)^{n+1}} \, dz,
\]

(59)

\[
\langle 1 | P_k | m \rangle = \frac{1}{2\pi i} \oint_{C_k} C_i(Z) \sum_{n=0}^{\infty} \frac{(\psi(Z))^n}{(Z-k_m)^{n+1}} \, dz,
\]

(60)

\[
\langle m | P_k | j \rangle = \frac{1}{2\pi i} \oint_{C_k} \sum_{n=0}^{\infty} \frac{(\psi(Z))^n}{(Z-k_m)^{n+1}} \, dz,
\]

(61)

\[
\langle i | P_k | j \rangle = \frac{1}{2\pi i} \oint_{C_k} [R_{ij}(Z) + C_i(Z) < 0 | \Gamma(Z) | 0 > D_j(Z)] \, dz,
\]

(62)

where \( \psi(Z) \), \( C_i(Z) \), \( D_j(Z) \) and \( R_{ij}(Z) \) are defined in Section 2. Here we present a matrix representation of the projection operator. This expression is quite general. We have not yet specified the set of eigenvalues \( k \) nor the specially chosen eigenvalue \( k_m \). The important point is that the contour \( C_k \) has to be well defined.

Now we are ready to discuss the subdynamics proposed by the Brussels school. Let us take \( |m\rangle \) to be \( |0\rangle \), i.e., \( k_m = 0 \), and separate the distribution function into two parts,

\[
\rho = \rho + \beta \]

(63)

is obtained by shrinking the integral contour of its components

\( i \)'s of (29), (31), (32), and (33) (there we replace \( i \)'s for \( i \)'s for the Liouville equation) to include only the pole at
\[ Z = +i\varepsilon \text{ with } \varepsilon \to 0, \text{ excluding all other singularities,} \]

\[ \bar{\rho}_k(t) = \frac{1}{2\pi i} \int_{C_0} dZ \sum_{n=0}^{\infty} \frac{1}{Z^{n+1}} e^{-izt} (\psi(Z))^n (\rho_0(0) + \sum_k D_{k'}(Z) \rho_{k'}(0)) \]

(64)

\[ \bar{\rho}_k(t) = \frac{1}{2\pi i} \int_{C_0} dZ \sum_{n=0}^{\infty} \frac{1}{Z^{n+1}} e^{-izt} c_k(Z) (\psi(Z))^n (\rho_0(0) + \sum_{k'} D(Z) \rho_{k'}(0)) \]

(65)

or in the matrix form

\[ \bar{\rho}_i(t) = \sum_j T_{ij}(t) \rho_j(0) \]

(66)

\( T_{ij} \) is obtained from \( T_{ij}(t) \) by shrinking the contour as mentioned above. It is assumed that \( \psi(Z), C_i(Z), D_j(Z) \) and \( R_{ij}(Z) \) are well behaved at \( Z = +i\varepsilon \), and therefore the term including \( R_{ij}(Z) \) does not appear in (65).

Compare (64) and (65) with (59) through (62), we see that the matrix elements of \( \bar{T}(0) \) is just the matrix elements of the projection operator given in (59), (60), (67) and (62) with \( C_k \) encircling the point \( +i\varepsilon \). In other words, \( \bar{T}(0) \), (which is denoted by \( \pi \) by the Brussels school) is the eigenprojection operator to project out the eigenspace with eigenvalue zero. Consequently \( \pi = \bar{T}(0) \) satisfies the following relations, as is to be expected

a) \( \pi^2 = \pi \)

\[ \bar{\rho}(t) = \pi \rho(t) \]

(67)

(68)

b) \( \pi L = L \pi \)

(69)

which implies that
\[ \pi T(t) = T(t) \pi = \overline{T(t)}, \]  
where \( \overline{T(t)} \) satisfies the following group property

\[ \overline{T(t_1)T(t_2)} = \overline{T(t_1 + t_2)}. \]  

Two remarks are in order. First, from the fact that 

\( \pi = \overline{T(0)} \) commutes with \( L \), the subdynamics is obviously reversible.

Consider the Liouville equation

\[ i \frac{\partial \rho}{\partial t} = L \rho. \]  

Operate \( i \) on (72) from the left on both sides

\[ i \frac{3 \pi \rho}{\partial t} = \pi \overline{L \rho}. \]  

With the help of (69), we have

\[ i \frac{\partial \rho}{\partial t} = L \rho. \]  

Eq. (74) is a reversible equation just like Eq. (72), and irreversibility can not be obtained without an additional assumption as explained in Section 3 (unless one takes the approach to equilibrium as the definition of irreversibility!) In this case, the existence of the invariant subdynamics has nothing to do with the task of obtaining the irreversibility.

The next remark is about the existence of the projection opera-
ator \( \pi \). In the derivation of the solutions for the Schrödinger-like equation given in Section 2, we have assumed that both \( K \) and \( K \) have pure continuous spectra from zero to infinity. In this case, as we have pointed out already, it is impossible to define a projection operator in terms of the integral of a contour of the resolvent, since we cannot draw a contour without crossing the cut of the resolvent. Therefore the projection operator

is not defined by any contour integral and consequently the corresponding subdynamics does not exist. Nevertheless, the theory of subdynamics can be saved if we make some proper device for computation. For example, for the classical Liouville equation, if we take the normalization volume to be finite, then we can have a discrete spectrum. In this case each discrete eigenvalue can be isolated and the corresponding projection operator can be defined in terms of the integral of a contour of the resolvent.

5. Von Neumann's Density Matrix

So far we have restricted our discussions to classical aspects of the Liouville equation. The general method of obtaining solutions for the Schrödinger-like equation can be easily extended to the quantum mechanical Liouville Von-Neumann equation. Consider a pure state \( \psi \) of a quantum mechanical system; one can expand \( \psi \) in terms of eigenstates \( U_n \) of some complete set of operators with coefficients \( \beta_n \)

\[
\psi = \sum_n \beta_n U_n. \tag{75}
\]

For a system in this state, an operator \( 0 \) represented by a matrix \( 0_{\beta n; \beta n} \)
has the expectation value

\[ <0> = \sum_{n' n} O_{n' n} \beta_{n'}^{*} \beta_{n}. \] (76)

It is possible that the system is in a non-pure state which is the incoherent superposition of a number of pure states \( \psi^{(i)} \) with statistical weight \( h^{i} \). In this case, to each pure state corresponds a mean value \( <0^{i}> \), and the mean value of 0 for the system is

\[ <0> = \sum_{i} h^{i} <0^{i}> = \sum_{n' n} O_{n' n} \sum_{i} h^{i} \beta_{n'}^{i} \beta_{n}^{i}. \] (77)

One defines the density matrix as

\[ \rho_{n' n} = \sum_{i} h^{i} \beta_{n'}^{i} \beta_{n}^{i}. \] (78)

So that (77) becomes

\[ <0> = \sum_{n' n} O_{n' n} \rho_{n' n} = \sum_{n} (0^{\rho})_{n' n} = Tr(0^{\rho}) \] (79)

One can also formally define the eigendensity matrix as

\[ \rho_{k} = \sum_{n i} h^{i} \beta_{n-k}^{i} \beta_{n}^{i}. \] (80)

The expectation value \( <0> \) can be written in terms of \( \rho_{k} \)'s instead of \( \rho_{n' n} \)'s

\[ <0> = \sum_{k} O_{k} \rho_{k} \] (81)
with

\[ 0_n^k = \Sigma_{n-k}^n 0_{n-k,n} \]  \hspace{1cm} (82)

By making use of the definition of the eigendensity matrix one can treat the Von Neumann equation as a Schrödinger-like equation and the solutions can be obtained by the method discussed in Sections 2 and 3.

The Von Neumann equation is defined as

\[ i \frac{\partial \psi}{\partial t} = H \rho = [H, \rho] \]  \hspace{1cm} (83)

which is a direct consequence of the Schrödinger equation

\[ i \frac{\partial \psi}{\partial t} = H \psi \]  \hspace{1cm} (84)

As a simple example, let us find the asymptotic solution of the Von Neumann equation for a separable potential model of a quantum system. (14)

Let \( H = H_o + H_t \), and choose a basis for the Hilbert space such that

\[ (H_o)_{\omega \omega'} = \delta (\omega - \omega') \hspace{1cm} \text{for} \ \omega \geq 1 \]

\[ = 0 \hspace{1cm} \text{for} \ \omega < 1 \]  \hspace{1cm} (85)

and

\[ (H_t)_{\omega \omega'} = \eta G(\omega) G(\omega') \]  \hspace{1cm} (86)

The eigenstate \( \psi^o_\lambda \) of \( H_o \) which satisfies the equation \( H_o \psi^o_\lambda = \lambda \psi^o_\lambda \)

\[ \]
i.e. \[ \int d\omega' \, H_0(\omega, \omega') \psi^0(\omega') = \lambda \, \psi^0(\omega) \]  \hspace{1cm} (87)

can be easily found and has the form

\[ \psi^0(\omega) = \delta(\lambda - \omega) \]  \hspace{1cm} (88)

This is not a normalizable solution and it was only to be expected since the eigenvalue belongs to the continuous spectrum. The corresponding Liouville operator for \( H_0 \) has the form

\[ L_0 = (\omega_1 - \omega_2) \delta(\omega_1 - \omega') \delta(\omega_2 - \omega') \]  \hspace{1cm} (89)

and the eigendensities of \( L_0 \) are

\[ \rho_k(\omega_1, \omega_2) = \delta(k - (\omega_1 - \omega_2)) \, f(\omega_1) \]  \hspace{1cm} (90)

with eigenvalue \( k = \omega_1 - \omega_2 \) where \( f(\omega_1) \) is an arbitrary function.

Indeed

\[
L_0 \, \rho_k(\omega_1, \omega_2) = \int d\omega_1' d\omega_2' \, (\omega_1 - \omega_2) \delta(\omega_1 - \omega') \delta(\omega_2 - \omega') \delta(k - (\omega_1' - \omega_2')) \, f(\omega_1') \\
= (\omega_1 - \omega_2) \delta(k - (\omega_1 - \omega_2)) \, f(\omega_1) \\
= k \, \rho_k(\omega_1, \omega_2) \]  \hspace{1cm} (91)

We can also obtain \( \rho_k(\omega_1, \omega_2) \) from \( \psi^0(\omega) \). From the definition of \( \rho_k \) given
in (80) and the expression of $\psi^o(\omega)$ given in (88), we have

\[ \rho_k(\omega_1, \omega_2) = \int \psi^*_{\lambda}(\omega_1) \psi_{\lambda-k}(\omega_2) f(\lambda) d\lambda \]

\[ = \delta(k-(\omega_1-\omega_2)) f(\omega_1) \]  \hspace{1cm} (92)

which is the same as (90) as expected.

Let us proceed to find the asymptotic outgoing eigendensity matrix which is an eigenstate of $L$. As for the free system, we may obtain $\rho_k(\omega, \omega')$ from the outgoing wave function $\psi^o(\omega)$ which is an eigenstate of $H$, or by solving the eigenvalue problem for the Liouville operator directly. The outgoing wave function can be easily found and has the form

\[ \psi^o_{\lambda}(\omega) = \delta(\lambda-\omega) + \frac{\eta G(\lambda) G(\omega)}{\beta^-(\lambda) (\lambda-\omega-i\varepsilon)} \]  \hspace{1cm} (93)

where

\[ \beta^\pm(\lambda) = 1 - \eta \int \frac{G^2(\lambda)}{\lambda - \chi \pm i\varepsilon} d\lambda \]  \hspace{1cm} (94)

With the help of the solution (93), we find

\[ \rho_k(\omega_1, \omega_2) = \int \psi^*_{\lambda}(\omega_1) \psi_{\lambda-k}(\omega_2) f(\lambda) d\lambda \]

\[ = f(\omega) \delta(k-(\omega_1-\omega_2)) + \frac{\eta}{\beta^-(k+\omega_2)} \left[ \frac{G(k+\omega_2)G(\omega_1)f(\omega_1)}{\beta^+(k+\omega_2)} - \frac{G(\omega_1-k)G(\omega_2)f(\omega_2)}{\beta^+(\omega_1-k)} \right] \]

\[ + \eta^2 G(\omega_1) G(\omega_2) \int_1^\infty \frac{G(\lambda-k) G(\lambda) f(\lambda) d\lambda}{\beta^+(\lambda-k) \beta^-(\lambda) (\lambda-k-\omega_2+i\varepsilon) (\lambda-\omega_2-i\varepsilon)} . \]
To obtain by solving the eigenvalue equation of the operator \( L \), let us first write down the corresponding Liouville operator \( L \) for \( H \),

\[
L = (\omega_1 - \omega_2) \delta (\omega_1 - \omega_1') \delta (\omega_2 - \omega_2') + \eta G(\omega_1) G(\omega_1') \delta (\omega_2 - \omega_2') - \eta G(\omega_2) G(\omega_2') \delta (\omega_1 - \omega_1') \tag{96}
\]

Let us also write

\[
\rho(\omega_1, \omega_2) = u(\omega_1) v(\omega_2). \tag{97}
\]

By substituting (96) and (97) into the eigenequation

\[
L \rho = k \rho \tag{98}
\]

we obtain

\[
(\omega_1 - k) u(\omega_1) v(\omega_2) + \eta G(\omega_1) v(\omega_2) \alpha
\]

\[
= \omega_2 u(\omega_1) v(\omega_2) + \eta G(\omega_2) u(\omega_1) \gamma \tag{99}
\]

with

\[
\alpha = \int G(\omega) u(\omega) d\omega \\
\gamma = \int G(\omega) v(\omega) d\omega \tag{100}
\]

Dividing both sides of (99) by \( u(\omega_1) v(\omega_2) \), and equating both sides...
to a constant $\lambda$-$k$, we have

$$(\omega_1 - \lambda)u(\omega_1) + \eta G(\omega_1) = 0$$  \hspace{1cm} (101)

$$(\omega_2 - (\lambda-k))v(\omega_2) + \eta G(\omega_2) = 0$$  \hspace{1cm} (102)

Here $\lambda$ is a new label since the eigenvector is not non-degenerate.

The general form for $\rho^\lambda_k(\omega_1, \omega_2)$ is

$$\rho^\lambda_k(\omega_1, \omega_2) = \left\{ \delta(\lambda - \omega_1) + \eta \frac{G(\lambda)G(\omega_1)}{(\lambda - \omega_1 + i\epsilon)\beta(\lambda + i\epsilon)} \right\} X$$

$$\{ \delta(\lambda - k - \omega_2) + \eta \frac{G(\lambda - k)G(\omega_2)}{(\lambda - k - \omega_2 + i\epsilon)\beta(\lambda - k + i\epsilon)} \}$$  \hspace{1cm} (103)

For each of the four sets, $++$, $+-$, $-+$, $--$, we have acceptable solutions. The $+$ corresponds to the outgoing solution of the eigen-density matrix $\rho^\lambda_k(\omega_1, \omega_2)$ which is nothing but $\psi_\lambda^* \psi_\lambda$ in (95).

Integrating (103) over $\lambda$ with the weight function we obtain

$$\rho_k(\omega_1, \omega_2) = \int \rho_k^\lambda(\omega_1, \omega_2) f(\lambda) d\lambda.$$  \hspace{1cm} (104)

Thus we get the same expression for $\rho_k(\omega_1, \omega_2)$ as was obtained in (95) which is to be expected. There is no irreversibility though we can easily ask for the limit of the density matrix as a function of time as $t \rightarrow \infty$. 


5. Conclusion

We have given a general mathematical analysis of the solution of the Liouville equation from which the scope of the applicability and the limitation of the theory proposed by the Brussels school can be visualized. In this approach the states of a statistical system are represented by distribution functions which supposedly form a Hilbert space in the functional space. In general, the dynamical mapping among the states can be furnished by unitary or non-unitary canonical transformations.

The solutions of the Liouville equation discussed in this paper corresponds to the former type of mappings which are reversible transformations. It is the main attempt of the Brussels school to find the origin of irreversibility from this reversible solution. The concept of invariant subdynamics was introduced for this purpose. However, as we have pointed out in Section 4, this invariant subdynamics is a reversible dynamics. This conclusion is elementary. The solution of a reversible equation is always reversible, unless some additional factors are introduced to destroy the symmetry. Boltzmann's Stossahlansatz was introduced just for this purpose. Of course there are other ways of destroying the symmetry. For example, one can introduce some additional parameters such as a relaxation time to destroy the correlations in each period of the relaxation. The deeper significance of the mechanism of destroying the correlations has to be the subject of further investigations.
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