The Liouville Equation : A rapid review

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This paper presents our findings after having reviewed some aspects of Classical Liouville theorem and we have noted some mathematical theorems about its initial value problem. Furthermore, we have implied on the formal framework of Stochastic Liouville equation (SLE).

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INTRODUCTION

This short essay has two purposes: (I) A rapid review of classical and stochastic quantum Liouville equation and proof of that and some use of Liouville equation in statistical mechanics and (II) to present a short solution for a simple solvable model. The Liouville equation is valid for both equilibrium and non-equilibrium systems. It is imperative to the proof of fluctuation theorem from which the second law of thermodynamics can be derived and also it is the key component of derivation of Green Kubo relation for linear transport coefficients such as shear viscosity, thermal conductivity or electrical conductivity.

The dynamics of such composite systems is governed by a quantum-classical Liouville equation for either the density matrix or dynamical variables which are operators in the Hilbert space of the quantum subsystem and functions of classical phase space variables of the classical environment. For more applications in quantum mechanics refer [2].

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I. DESCRIPTION OF CLASSICAL LIOUVILLE EQUATION AND ITS PROOF

The Liouville equation is a cardinal equation of statistical mechanics. This equation depicts the development of phase space distribution function for the conservative Hamiltonian system and also supplies a complete description of the system both at equilibrium and away from equilibrium. On the other hand Liouville equation is a persistent for the flux and meditate the phase space of micro-canonical ensemble of a N-particle system (NVE). Let \( \rho(q^{(N)}, p^{(N)}, t) \) refer the phase space density. If we contemplate a volume element \( dp^{(N)} dq^{(N)} \), then \( \rho(q^{(N)}, p^{(N)}, t) dp^{(N)} dq^{(N)} \) acquire the number of distinctive points in volume element.

It is a typical form of equation of motion of \( \rho(q^{(N)}, p^{(N)}, t) \).

The number of system in the ensemble preserved the abidance equation for development of phase space density assumed as:

\[
\frac{\partial \rho}{\partial t} = -\nabla \cdot \mathbf{J} \tag{1}
\]

\[
\frac{\partial \rho}{\partial t} = -\sum_{i=1}^{N} \sum_{\alpha=1}^{3} \left[ \frac{\partial}{\partial q_{i\alpha}} (\rho \dot{q}_{i\alpha}) + \frac{\partial}{\partial p_{i\alpha}} (\rho \dot{p}_{i\alpha}) \right] \tag{2}
\]

implementing chain rule one obtains

\[
\frac{\partial \rho}{\partial t} = -\sum_{i=1}^{N} \sum_{\alpha=1}^{3} \left( \frac{\partial}{\partial q_{i\alpha}} \rho_{i\alpha} + \frac{\partial}{\partial p_{i\alpha}} \rho_{i\alpha} \right) - \rho \sum_{i=1}^{N} \sum_{\alpha=1}^{3} \left( \frac{\partial \dot{q}_{i\alpha}}{\partial q_{i\alpha}} + \frac{\partial \dot{p}_{i\alpha}}{\partial p_{i\alpha}} \right) \tag{2}
\]

In a Hamiltonian conservative system, the energy is kept up as a function of time and the time derivatives are measured by Hamiltonian equations of motion of classical mechanics. They are assumed by a set of coupled first order partial differential equations,

\[
\dot{q}_{i\alpha} = \frac{\partial H}{\partial p_{i\alpha}} \tag{3}
\]

\[
\dot{p}_{i\alpha} = -\frac{\partial H}{\partial q_{i\alpha}} \tag{4}
\]

\[
\dot{q}_{i\alpha} = 1, 2, ..., N \]

\[
\alpha = 1, 2, 3
\]

where \( q_{i\alpha} \) is the \( \alpha - th \) component of the situation, \( q_i \) of the \( i - th \) particle.

If we use Hamilton’s equation of motion we acquire:

\[
\frac{\partial q_{i\alpha}}{\partial \dot{q}_{i\alpha}} = \frac{\partial^2 H}{\partial q_{i\alpha} \partial p_{i\alpha}} \tag{5}
\]

\[
\frac{\partial p_{i\alpha}}{\partial \dot{p}_{i\alpha}} = -\frac{\partial^2 H}{\partial p_{i\alpha} \partial q_{i\alpha}} \tag{6}
\]
thus the last term in equation (4) is indistinguishably zero leaving us with

\[
\frac{\partial \rho}{\partial t} = - \sum_{i,\alpha} \left[ \frac{\partial \rho}{\partial q_{i\alpha}} \dot{q}_{i\alpha} + \frac{\partial \rho}{\partial p_{i\alpha}} \dot{p}_{i\alpha} \right]
\]

\[
\frac{\partial \rho}{\partial t} = - \sum_{i,\alpha} \left[ \frac{\partial \rho}{\partial q_{i\alpha}} \frac{\partial H}{\partial \rho_{i\alpha}} + \frac{\partial \rho}{\partial p_{i\alpha}} \frac{\partial H}{\partial q_{i\alpha}} \right]
\]

(7)

The last equation is the classical Liouville equation. Some of scientists can use the classical Liouville equation symbolically:

\[
\frac{\partial \rho}{\partial t} = [H, \rho]
\]

(8)

Proof: consider an arbitrary "volume" \(\omega\) in the relevant region of the phase space and let the "surface" enclosing this volume be denoted by \(\sigma\). Then the rate at which the number of representative points in this volume increases with time is written as:

\[
\frac{\partial}{\partial t} \int_\omega \rho d\omega
\]

(9)

Where \(d\omega \equiv (d^3N q d^3N p)\). On the other hand, the net rate at which the representative points "flow" out of \(\omega\) (across the bounding surface \(\sigma\)) is given by:

\[
\int_\sigma \rho (v \cdot \hat{n}) d\sigma
\]

(10)

Here, \(v\) is the velocity vector of the representative points in the region of the (outward) unit vector normal to this element. By the divergence theorem (10) can be written as:

\[
\int_\omega \text{div}(\rho v) d\omega
\]

(11)

of course the operation of divergence here means the following:

\[
\text{div}(\rho v) \equiv \sum_{i=1}^{3N} \{ \frac{\partial}{\partial q_i} (\rho \dot{q}_i) + \frac{\partial}{\partial p_i} (\rho \dot{p}_i) \}
\]

(12)

In view of the fact that there are no "surfaces" or "sinks" in the phase space and hence the total number of representative points remains conserved\(^1\), we have, by (9) and (11),

\[
\frac{\partial}{\partial t} \int_\omega \rho d\omega = - \int_\omega \text{div}(\rho v) d\omega
\]

(13)

That is:

\[
\int_\omega \left\{ \frac{\partial \rho}{\partial t} + \text{div}(\rho v) \right\} d\omega = 0
\]

(14)

\(^1\) This means that in the ensemble under consideration neither have any new members being admitted nor have any old ones being expelled.
Now, the necessary and sufficient condition that integral (14) vanishes for all arbitrary volumes $\omega$ is that the integrand itself vanishes everywhere in the relevant region of the phase space. Thus we must have:

$$\frac{\partial \rho}{\partial t} + \text{div}(\rho v) = 0$$

(15)

Which is the *equation of continuity* for the swarm of the representative points. Combining (12) and (15), we obtain:

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left( \frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) + \rho \sum_{i=1}^{3N} \left( \frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right) = 0$$

(16)

The last group of terms vanishes identically because, by the equation of motion, we have for all $i$,

$$\frac{\partial \dot{q}_i}{\partial q_i} = \frac{\partial^2 H(q_i, p_i)}{\partial q_i \partial p_i} = \frac{\partial^2 H(q_i, p_i)}{\partial p_i \partial q_i} = -\frac{\partial \dot{p}_i}{\partial p_i}$$

(17)

Further, since $\rho \equiv \rho(q_i, p_i, t)$, the remaining terms in (16) may be combined to form the *total* time derivative of $\rho$, with the result that:

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + [\rho, H] = 0$$

(18)

Equation (18)$^2$ embodies the so-called *Liouville theorem* (1838). According to this theorem, the "local" density of the representative points, as viewed by an observer moving with a representative point, stays constant in time.

Now we can understand:

$$L = i[H, \cdot]$$

(19)

where $i[H, \cdot]$ is a Liouville operator, symbolized by $L$ and defined as:

$$iL = \sum_{i=1}^{N} \left( \frac{\partial H}{\partial p_i} \frac{\partial}{\partial q_i} - \frac{\partial H}{\partial q_i} \frac{\partial}{\partial p_i} \right)$$

(20)

so we write:

$$\frac{\partial \rho}{\partial t} = [H, \rho]$$

$$\frac{\partial \rho}{\partial t} = -iL\rho$$

(21)

this has formal solution,

$$\rho(t) = \exp(-iLt)\rho(0)$$

(22)

the classical Liouville equation is a highly non-trivial equation, where the momenta and coordinates of all the $N$-particles of the system are in principle coupled with each other.

---

$^2$ We recall that the *poisson bracket* $[\rho, H]$ stands for the sum:

$$\sum_{i=1}^{3N} \left( \frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} \right)$$
II. PHYSICAL INTERPRETATION

The quantity \( \rho(q^{(N)}, p^{(N)}, t) dp^{(N)} dq^{(N)} \) is the probability that at a time \( t \) the physical system is in a microscopic state corresponded by a phase point lying in the trivial 6\( N \)-dimensional phase space element \( dp^{(N)} dq^{(N)} \). Hence the total number of systems in the ensemble is assumed by the integral over phase space of distribution, \( \int \rho(p^{(N)}, q^{(N)}) dp^{(N)} dq^{(N)} \).

The Liouville equation is the 6\( N \)-dimensional analogue of equation of persistence of an incompressible fluid. It explains the fact that phase point of ensemble are neither created nor destroyed. Thus we can interpret it as a conservation theorem similar to charge conservation role in Electrodynamics.

III. LIOUVILLE THEOREMS

The initial value problem for the Liouville equation was first studied by Petrina and Gerasimenko \[3\] and then by Jiang \[4\], with its initial data in \( L^1 \) and \( L^2 \), respectively. It has been shown by using the operator semigroup theory that this problem has a unique solution if its initial data belong to some subset of \( L^1 \) or \( L^2 \).

A: CAUCHY PROBLEM FOR THE LIOUVILLE EQUATION

The Liouville equation is an evolution:

\[
\frac{d}{dt} f_N(t) = -H_N^\Lambda f_N(t)
\]

(23)

Where \( H_N^\Lambda \) is the infinitesimal operator of the group \( S_N^\Lambda (-t) \). Let us consider the liouville equation (23) as an abstract evolution equation in the Banach space \( L_N(\Lambda) \) with initial conditions

\[ f_N(0) = f_N^0. \]

THEOREM 1.A. The Cauchy problem for the Liouville equation (23) has a unique solution in the space \( L_N(\Lambda) \) of summable functions. It is given by the formula

\[ f_N(t) = S_N^\Lambda (-t)f_N^0. \]

(24)

For initial conditions \( f_N^0 \in L^0_N(\Lambda) \) this solution is a strong one and for arbitrary \( f_N^0 \in L_N(\Lambda) \) it is a generalized solution.

PROOF. According to the well known result of functional analysis \[103\] the Cauchy problem for equation

\[
(S_N^\Lambda(t)f_N)(x_1, \ldots, x_N) = f_N(X_1(t,x), \ldots, X_N(t,x)), (x_1, \ldots, x_N) \in \Gamma^N \setminus W^0_N
\]

\[ 0, (q_1, \ldots, q_N) \in W_N. \]

has the unique solution in \( L_N(\Lambda) \) which is given by (24). We shall demonstrate that in the formula (24) defines a generalized solution. For this purpose we consider the functional

\[
(\varphi, f_N(t)) = \int dx_1 \ldots dx_N \varphi(x_1, \ldots, x_N) f_N(t, x_1, \ldots, x_N)
\]
Where $\varphi$ is a continuously differentiable function with a compact support that vanishes like functions from $L^1_0(A)$ in some neighborhood of forbidden configurations and $\partial A$. Since $\varphi$ is bounded and $f_N(t)$ is summable, the functional $((\varphi, f_N(t)))$ exists. Using (24) and the fact that $S_N^N(-t)$ is isometric we transform $(\varphi, f_N(t))$ to the form

$$(\varphi, f_N(t)) = (S_N^N(t)\varphi, f_N^0) = \int dx_1...dx_N(S_N^N(t)\varphi)(x_1, ..., x_N)f_N^0(x_1, ..., x_N).$$

As in Theorem 1.A we can show that the function $(S_N^N(t)\varphi)(x_1, ..., x_N)$ is differentiable with respect to $t$, and expression

$$\left|\frac{1}{\Delta t}(S_N^N(t+\Delta t)\varphi - S_N^N(t)\varphi) - \sum_{i=1}^N p_i \cdot \frac{\partial}{\partial q_i} S_N^N(t)\varphi\right| \rightarrow 0$$

as $\Delta t \rightarrow 0$ uniformly with respect to $(x_1, ..., x_N)$ belonging to compact sets. The functional $(\sum_{i=1}^N p_i \cdot \frac{\partial}{\partial q_i}(S_N^N(t)\varphi), f_N^0)$, since the function $\sum_{i=1}^N p_i \cdot \frac{\partial}{\partial q_i}(S_N^N(t)\varphi)(x)$ is bounded. Therefore we can differentiate with respect to $t$ under the integral sign in the functional $(S_N^N(t)\varphi, f_N^0)$. As a result we get

$$\frac{d}{dt}(\varphi, f_N(t)) = (\sum_{i=1}^N p_i \cdot \frac{\partial}{\partial q_i}(S_N^N(t)\varphi), f_N^0) = (S_N^N(t)\sum_{i=1}^N p_i \cdot \frac{\partial}{\partial q_i} \varphi, f_N^0) = (\sum_{i=1}^N p_i \cdot \frac{\partial}{\partial q_i} \varphi, f_N(t))$$

and these equalities mean that the function $f_N(t) = S_N^N(-t)f_N^0$ is a generalized (weak) solution of the Cauchy problem for the Liouville equation (23).

Theorem (1.A) holds also for a system of particles in $\mathbb{R}^n$. We only have to replace $S_N^N(-t)$ and $H_N^N$ by their counterparts $S^N(-t)$ and $H^N$ in $L_N$.

Let us construct the Liouville equation starting from the Hamiltonian dynamics of a system of elastic balls. As well known [104], the class of pure states of Hamiltonian system of particles can be described by the distribution function

$$D_{N,A}(t, x_1, ..., x_N) = \sum_{\{i_1, ..., i_N\}} \prod_{k=1}^N \delta(x_{ik} - X_k(t, x^0))$$ (25)

Where $X(t, x^0)$ is the phase point that is occupied by a system of $N$ particle at time moment $t$ if at the initial time moment $t = 0$ the system was at phase point $x^0 \in \mathbb{R}^{nN} \times (L^N \setminus W_N)$. Here the summation with respect to $\{i_1, ..., i_N\}$ is carried out over all the permutations of the indices $i_k \in (1, ..., N)$. All possible states of the system considered can be described by the distribution function on the phase space $\Gamma^N(A)$:

$$D_{N,A}(t, x_1, ..., x_N) = \int_{\Gamma^N(A)} dx_1^0...dx_N^0 D_N^0(x_1^0, ..., x_N^0) \sum_{\{i_1, ..., i_N\}} \prod_{k=1}^N \delta(x_{ik} - X_k(t, x^0))$$ (26)

Which is superposition of the pure states (25) of the system with a definite weight $D_N^0(x_1^0, ..., x_N^0)$. The last quantity is a known function of the distribution of particle coordinates and momenta that is specified at the initial time moment $t = 0$. Consequently an initial state of a system of $N$ elastic balls is, in general, described by the function

$$D_{N,A}(0, x_1, ..., x_N) = \int_{\Gamma^N(A)} dx_1^0...dx_N^0 D_N^0(x_1^0, ..., x_N^0) \sum_{\{i_1, ..., i_N\}} \prod_{k=1}^N \delta(x_{ik} - x_k^0)$$ (27)
Which is equal to
\[ D_{N,\Lambda}(0, x_1, ..., x_N) = N!D^0_N(x_1, ..., x_N). \]

We note that the distribution function \( D_{N,\Lambda}(t) \) has the following properties:
\[
\begin{align*}
D_{N,\Lambda}(t, x_1, ..., x_N) &= D_{N,\Lambda}(t, x_1, ..., q_i, p_i; ..., x_N), \\
|q_i - q_j| &= d, i \neq j \in (1, ..., N), \\
D_{N,\Lambda}(0, x_1, ..., x_N) &= D_{N,\Lambda}(t, x_1, ..., x_N), q_i \in \partial \Lambda, \\
D_{N,\Lambda}(t, x_1, ..., x_N) &= 0, (q_i, ..., q_N) \in W_N.
\end{align*}
\]

If we change the variables \( x^0 \rightarrow X(-t, x) \) in the integrand of (26), then after calculating the integrals we get the relation
\[
D_{N,\Lambda}(t, x_1, ..., x_N) = D_{N,\Lambda}(0, X_1(-t, x),..., X_N(-t, x)).
\]

From this formula and definition (2.3) of the evolution operator is follows that the state at an arbitrary time moment is connected with the initial state by the following formula:
\[
D_{N,\Lambda}(t, x_1, ..., x_N) = (S^N_N(-t)D_{N,\Lambda}(0))(x_1, ..., x_N).
\]

In order to construct an equation that determines the evolution of a state of a system of elastic balls we differentiate the right hand side of (30) with respect to time for \( D_{N,\Lambda}(0) \in L^0_N(\Lambda) \).

From Theorem 1.A it follows that
\[
\frac{\partial}{\partial t}D_{N,\Lambda}(t, x_1, ..., x_N) = -\sum_{i=1}^N P_i \cdot \frac{\partial}{\partial q_i}D_{N,\Lambda}(t, x_1, ..., x_N)
\]

With the corresponding boundary condition in Poissonbracket and condition (28). The relation (31) is obtained as consequence of (29). From now on we shall treat (31) as an equation for an unknown function \( D_{N,\Lambda}(t, x_1, ..., x_N) \), which is the Liouville equation. We have to add to it initial and boundary condition (28), which are satisfied by \( D_{N,\Lambda}(t, x_1, ..., x_N) \).

**B: ON THE LIOUVILLE THEOREM**

Headword to study our problem by using the operator semigroup theory, equation (8) can be rewritten as
\[
\frac{d\rho}{dt} + A\rho = 0
\]

Where \( A \triangleq -[H,.] \). A can be in regarded to as either a distributional differential operator in \( L^2(\mathbb{R})^{2k} \) or a mapping of \( L^2(\mathbb{R})^{2k} \) into itself.

**THEOREM 1.B**. Operator \( A \) is the infinitesimal generator of a contractive operator semigroup.

In order to prove Theorem 1.B, we’ll first show the following lemmas.
LEMMA 1.B. A is an increasingly-generated operator, i.e., $\Re(Au,u) \geq 0$ for $\forall u \in D(A)$, where $(.,.)$ denotes the internal product in $L^2(R^{2N})$.

PROOF. By equation (8), we know that the for $\forall u, \nu \in D(A)$,

$$(Au, u) = -\int \nabla \sum_{i=1}^{N} \left( \frac{\partial H}{\partial q_i} \frac{\partial \nu}{\partial p_i} - \frac{\partial \nu}{\partial q_i} \frac{\partial H}{\partial p_i} \right) dq dp.$$

By integrating partially and using the Hamiltonian equation, the above integral can also be written as:

$$(Au, u) = \int \nu \sum_{i=1}^{N} \left( \frac{\partial H}{\partial q_i} \frac{\partial u}{\partial p_i} - \frac{\partial u}{\partial q_i} \frac{\partial H}{\partial p_i} \right) dq dp = -(Au, \nu)$$

In particular,

$$(Au, u) = -(Au, u)$$

Or equivalently, $\Re(Au, u) = 0$, for $\forall u \in D(u)$.

LEMMA 2.B. $A$ is a closed operator with dense domain in $L^2(R^{2N})$.

LEMMA 3.B. $\lambda I + A$ is mapping of $L^2(R^{2N})$ on to itself, i.e., the range $R(\lambda I + A)$ of the mapping $\lambda I + A$ is $L^2(R^{2N})$, for any given $\lambda > 0$, where $I$ is identity mapping.

For $\forall \chi \in D(A)$. Then $-A$ is the infinitesimal generator of $S(t)$.

Similarly, we can also show that THEOREM 2.B. operator $-A$ is the infinitesimal generator of a contractive operator semigroup.

According to the operator semigroup theory, by Theorem 1.B, we define

THEOREM 3.B. If $u_0 \in D(A)$ then the initial value problem $\left(\frac{d}{dt} + Au = 0, u|_{t=0} = u_0\right)$ has a unique solution $u = S(t)u_0 \in C^1([0, +\infty); L^2(R^{2N})) \cap C^0([0, +\infty); D(A))$ where $S(t)$ is defined by Eqs. $[S(t) = \lim_{\lambda \to +\infty} S_\lambda(t); (S_\lambda(t) = \exp^{A\lambda t}; (A\lambda \chi = [\lambda^2(\lambda I + A)(1^2 - 1) - \lambda I]|\chi); \forall \chi \in L^2(R^{2N}) and, as \lambda \to +\infty; (A\lambda \chi \to -A\chi)]$

THEOREM 4.B. If $u_0 \in D(A^k)$, $k$ is a positive integer, then the solution $u$ of Eqs. $\left(\frac{d}{dt} + Au = 0, u|_{t=0} = u_0\right)$ belongs to $\cap_{j=0}^{k} C^{k-j}(0, +\infty); D(A^j)$ where, $D(A^0) \triangleq L^2(R^{2N})$. For study their proofs refer [4].

The total time derivative of the phase space density is denoted by $\frac{dp}{dt}$. Then:

$$\frac{dp}{dt} = \frac{\partial p}{\partial t} + \sum_{i=1}^{N} \left( \frac{\partial p}{\partial q_i} \frac{\partial q}{\partial t} + \frac{\partial p}{\partial p_i} \frac{\partial p}{\partial t} \right) = 0$$ (32)

Where $\frac{dp}{dt} = 0$, thus we provide the Liouville Theorem in classical Liouville equation: In conservative system the distribution function is constant along any trajectory in phase space.
The Petrina and Gerasimenko survey contains more and sound physical description in related to the operational approach to the solution of Liouville equation and non-linear ones (Bogolyubov). The Jiang argument constructed a weak group based on the non-differential operator version of the Liouville equation and the result as we can guess from the elementary group theory is a semi group represents a formal solution. As Petrina and Gerasimenko discussed, this formal solution can be rewritten as a familiar Dyson series in terms of the normal generators of a complete group. However, since \( L^1(\mathbb{R}^{2k}) \) and \( L^2(\mathbb{R}^{2k}) \) have not any mutual inclusion relation, the two existence results are different and the \( L^2 \) existence theorem is not a theoretical scrutiny of the \( L^1 \) one.

**C: SOLUTION OF BOGOLYUBOV EQUATION**

The Bogolyubov equations for a system of elastic balls are the evolution equations

\[
\frac{d}{dt} F(t) = -HF(t) + d^2 A F(t) \tag{33}
\]

Where \(-H + d^2 A\) is the infinitesimal operator of the group \( U(t) \). Let us consider the Bogolyubov equation (34) as abstract evolution equations in the Banach space \( L \) with the initial conditions

\[ F(0) = F^0 \]

It can be show that [3] [104], [103] that Cauchy problem (34) for the Bogolyubov equations has in the space \( L \) of sequence of summable functions a unique solution that is given by the formula

\[
F(t) = U(t)F^0 = \exp(\int dx)S(-t)\exp(\int dx)F^0. \tag{34}
\]

In components (35) can be written as follows:

\[
F_s(t, x_1, \ldots, x_s) = \sum_{n=0}^{\infty} \sum_{k=0}^{n} \frac{(-1)^k}{k!(n-k)!} \int dx_{s+1} \ldots dx_{s+n} S^{s+n-k}(-t, x_1, \ldots, x_{s+n-k}) \times F_{s+n}^0(x_1, \ldots, x_{s+n}) \tag{35}
\]

Each term on the right hand side of (36) is well defined, since the integrand is defined almost everywhere outside \( M^0_{s+n} \), and the series converges in the metric of space \( L_s \) for \( t \in ]-\infty, +\infty[ \).

**THEOREM 1.C.** The Cauchy problem for the Bogolyubov equations (34) has the unique solution in \( L \) that is given by (35). For initial conditions \( F^0 \in L^0 \) this solution is a strong solution and for arbitrary \( F^0 \in L \) it is a generalized (weak) solution.

For study its proof refer [3].

We note that the evolution equation

\[
\frac{d}{dt} \varphi(t) = H\varphi(t) + d^2 A^*\varphi(t)
\]
Are called the dual Bogolyubov equations \[104,105\]. Obviously Theorem 1.C holds also for the Bogolyubov equations that describe a system of particles moving in \(\Lambda\):

\[
\frac{d}{dt} F_\Lambda(t) = -H F_\Lambda(t) + d^2 A F_\Lambda(t) \tag{36}
\]

Where \(-H + d^2 A\) is the infinitesimal operator of the group \(U_\Lambda(t)\) in \(U(t) = \exp(\int dx S(-t) \exp(-\int dx))\). The solution of Cauchy problem for equations (37) is defined by

\[
F_\Lambda(t) = U_\Lambda(t) F^0_\Lambda = \exp(\int_\Lambda dx S_\Lambda(-t) \exp(-\int_\Lambda dx) F^0_\Lambda. \tag{37}
\]

We note that the rigorous derivation of the Bogolyubov equations (34)((37)) for a system of elastic balls, as an evolution equation in the space \(L(L(\Lambda))\) of sequences of summable functions with the infinitesimal operator \(-H + d^2 A\) of the group \(U(t)\). Another method of justifying Bogolyubov equations consists in constructing these equations starting from Liouville equations (23).

**IV. THE STOCHASTIC LIOUVILLE EQUATION**

The transport equation is the stochastic Liouville equation (SLE).\[5-9\]

It was shown,\[10\], that the SLE can be re-expressed as presenting a formal trapping problem in a manner analogous to that employed in the theory of mutual annihilation of exciton’s developed by one of the present authors.\[11\]

The exact solution is particularly appropriate as a starting point for the study of the scattering function relevant to experiments involving probe particles such as neutrons. The particular feature that their solution,\[10\], possesses is the ability to address the degree of transport coherence of the moving particle which produces the scattering line shape.

Before we explain section V we want to deal with spins which are in random motion.

**A: THE DENSITY MATRIX** \(p(\Omega)\)

The simplest example of such a type of motion is that of spins which jump back and forth among a number of sites with different chemical or magnetic environment. They label the sites with the numbers \(\nu = 1, 2, ..., n\) and define the distribution vector \(p_\nu(t)\) as the vector of the probabilities of finding spins in the sites \(\nu\) at the time \(t\). Another example is the case of translational motion.

The position of a spin is then characterized by the spatial coordinate \(\vec{r}\) and the distribution function is \(p(\vec{r}, t)\). The case of rotatory motion of molecules is very common. The orientation of the molecules is then defined by the Eulerian angles, \(\Omega\). All these cases in one formalism and choose \(\Omega\) as notation of the random coordinate. Thus the function \(p(\Omega, t)\) will denote the probability density of finding spins in the environment characterized by a particular \(\Omega\).

The spins can satisfactorily be described in terms of elementary magnets \(\vec{m}\), which can differ in direction but not in magnitude \(|m|\).
The state of the whole spin system is then given by the combined probability density \( P(\Omega, \vec{m}) \), which we take to be normalized:

\[
\int \int P(\Omega, \vec{m}) d\Omega d\vec{m} = 1
\]  

(38)

From this function we can extract the following quantities; the molecular distribution function:

\[
p(\Omega) = \int P(\Omega, \vec{m}) d\vec{m}
\]  

(39)

The distribution function of the magnetization:

\[
f(\vec{m}) = \int P(\Omega, \vec{m}) d\Omega
\]  

(40)

The average magnetic moment:

\[
\langle \vec{m} \rangle_0 = \int \int \vec{m} P(\Omega, \vec{m}) d\Omega d\vec{m}
\]  

(41)

The macroscopic magnetization of the sample:

\[
\vec{M}_0 = N \langle \vec{m} \rangle_0
\]  

(42)

Where \( N \) is the total number of spins per unit volume; and finally the quantities:

\[
\langle \vec{m}(\Omega) \rangle = \int \vec{m} P(\Omega, \vec{m}) d\vec{m}
\]  

(43)

and

\[
\vec{M}(\Omega) = N \langle \vec{m}(\Omega) \rangle
\]  

(44)

Which may be called the \( \Omega \) – dependent magnetization density. These last two quantities have the following physical meaning. Suppose that we could measure separately the total magnetization of the molecules which have their orientations between \( \Omega \) and \( \Omega + d\Omega \). Their measurement would then yield \( \vec{M}(\Omega)d\Omega \). or suppose that we could measure the total magnetization of the sample, but with an \( \Omega \) – dependent weight \( w(\Omega) \). We would then measure \( \int w(\Omega) \vec{M}(\Omega)d\Omega \). We can define \( \langle \vec{m}(\Omega) \rangle \) in a slightly different way by writing:

\[
P(\Omega, \vec{m}) = p(\Omega)q(\Omega, \vec{m})
\]  

(45)

Where \( q(\Omega, \vec{m}) \) is the normalized probability density of finding the magnetic moment at the value \( \vec{m} \), provided that we know that the molecule is in \( \Omega \). We then have:

\[
\langle \vec{m}(\Omega) \rangle = p(\Omega) \int \vec{m}q(\Omega, \vec{m}) d\vec{m}
\]  

(46)

This notation emphasizes that \( \langle \vec{m}(\Omega) \rangle \) is the average magnetic moment of the molecules with orientation \( \Omega \), multiplied by the probability of finding the molecules in \( \Omega \). Thus
\( \langle \vec{m}(\Omega) \rangle \) contains information on the internal magnetic state of the molecules and on the molecular distribution in \( \Omega - space \). It is important to appreciate this point when the theory is applied to systems where \( p(\Omega) \) is not a uniform function, as is the case with chemical exchange between unequally populated sites, or with partially oriented molecules. It is not necessary to say, in the case of jumps the parameter \( \Omega \) is replaced by an index \( \nu \) and the integrations over \( \Omega \) became summations.

We want consider molecular spin systems which are not adequately represented by a single magnetic moment \( \vec{m} \). The state of the spins has then to be described quantum mechanically by the wave function \( \psi \) or the density matrix \( \rho \). As for the density matrix, we should distinguish between \( \rho \) of each separate spin system whose matrix elements \( \rho_{nm} \) are the products \( a_n a_m^* \) of the coefficient in the expansion of \( \psi \) and its ensemble average, which we denote by \( \rho^{-3/2} \). If the spin system consists of a single spin \( I = \frac{1}{2} \), there is a one to one correspondence between \( \vec{m} \) and \( \rho \), and between \( \langle \vec{m} \rangle \) and \( \rho^{-3/2} \). However, if the spin system has more than two levels, this comparison cannot always be made. Nevertheless it is often convenient to visualize the behavior of complicated spin systems through a model of magnetization. They utilized\[12\] this analogy and assume a combined probability density \( P(\rho, \Omega) \)[13], from which we drive the distribution function of the density matrices:

\[
f(\rho) = \int P(\Omega, \rho) d\Omega \quad (47)
\]

The function \( f \) and \( P \) are defined in the space of all the possible density matrices \( \rho \). This space is restricted to \( \rho s \) with matrix elements which are products of \( a_n \) and \( a_m^* \), taken from normalized sets of coefficients \( a_n \). These are the matrices which satisfy the conditions of so-called pure states. Not that the space of \( \vec{m} \) was also restricted to vectors with a constant modulus \( |m| \).

The determination of the functions \( P(\Omega, \rho) \) and \( f(\rho) \) is very difficult. We come to the main subject of introduction. Somewhat inexact, call the \( \Omega - dependent \) spin density matrix

\[
\tilde{\rho}(\Omega) = \int \rho P(\Omega, \rho) d\rho \quad (48)
\]

Which is the analogy of \( \langle \vec{m}(\Omega) \rangle \). It may be used to compute the ensemble average of the expectation value of any physical quantity \( Q(\Omega) \). Which also depends on \( \Omega \),

\[
\langle Q \rangle = \int tr[\rho Q(\Omega)] P(\Omega, \rho) d\Omega d\rho = \int tr[\tilde{\rho}(\Omega) Q(\Omega)] d\Omega \quad (49)
\]

In most experiment performed on the spin system we measure a property \( Q \) which is independent of \( \Omega \). It is then sufficient to know \( \tilde{\rho}_0 \) in order to calculate:

\[
\langle Q \rangle = tr Q \tilde{\rho}_0; \tilde{\rho}_0 = \int \tilde{\rho}(\Omega) d\rho \quad (50)
\]

By analogy with equation (47) we can also write:

\[
\tilde{\rho}(\Omega) = p(\Omega) \int \rho q(\Omega, \rho) d\rho = p(\Omega) \tilde{\rho}_\Omega \quad (51)
\]

Which emphasizes that \( \tilde{\rho}(\Omega) \) is the product of local ensemble average \( \tilde{\rho}_\Omega \) and the probability of finding molecules in \( \Omega \).
B: THE DENSITY MATRIX $\rho(t)$ AND SLE

Let us now assume that the interaction of the spins are describe by an $\Omega$-dependent Hamiltonian $H(\Omega)$, i.e. a Hamiltonian which is different for spins belonging to molecules with different points. How then, does $P(\Omega, \rho, t)$ develop in time if the molecules are moving randomly in $\Omega$-space?

One starts to look at one particular spin system in the ensemble. Since this system belongs to a molecule which moves rapidly from one $\Omega$ to the other, a time-dependent Hamiltonian $H(t)$ is observed by the spins. $H(t)$ is now written as the sum of a constant $H_0$ and a time-dependent local Hamiltonian $H'(t)$ with vanishing time average.

The density matrix of spin system in question changes according to this Hamiltonian:

$$\frac{d}{dt}\rho(t) = \frac{i}{\hbar}[\rho(t), H_0] + \frac{i}{\hbar}[\rho(t), H'(t)]$$  \hspace{1cm} (52)

This equation is first solved by following a perturbation treatment, and then the ensemble average is taken. This yields the master equation. An essential point in the averaging procedure is that the correlation $\rho(t)$ and $H(t)$ is neglected. This is only permissible if the correlation times $\tau$ of the matrix elements of $H'(t)$ are so short that:

$$|H'(t)|\tau \ll \hbar$$  \hspace{1cm} (53)

It is important to stress the difference between the density matrices $\rho(t)$ and $\bar{\rho}(\Omega)$. $\rho(t)$ is a pure state [12] and $\bar{\rho}(\Omega)$ is an ensemble average. Equation (53) is a stochastic equation which defines the stochastic process $\rho(t)$ in terms of the stochastic process $H(t)$. More precisely by writing:

$$\frac{d}{dt}\rho(t) = \frac{i}{\hbar}[\rho(t), H_0 + H'\{\Omega(t)\}]$$  \hspace{1cm} (54)

We see that process $\rho(t)$ actually depends on the stochastic process $\Omega(t)$. In most problems dealt whit in magnetic resonance theory some model is assumed for the description of stochastic process $\Omega(t)$. In nearly all cases this is a stationary Markovian process. It is then assumed that the probability density $p(\Omega, t)$ satisfies the equation:

$$\frac{\partial}{\partial t}p(\Omega, t) = \Gamma p(\Omega, t)$$  \hspace{1cm} (55)

Where $\Gamma$ is a time-independent Markovian operator, operating on functions of $\Omega$. More generally, $\Omega(t)$ is the projection of a Markovian process, i.e. $\Omega$ should be supplemented with additional variables to form a complete set of random variables which make a Markovian process. In order to retain a simple notation we assume that $\Omega$ itself is a Markovian process. Equation (56) fits well in formalism of section (IV.A) but it can be less directly applied to further development (53). Thus we follow Kubo's development [13] and write formally for the rate equation of $P(\Omega, \rho, t)$

$$\frac{\partial}{\partial t}P(\Omega, \rho, t) = \left\{-\frac{\partial}{\partial \rho}\frac{i}{\hbar}[\rho, H(\Omega)] + \Gamma\right\} P(\Omega, \rho, t)$$  \hspace{1cm} (56)

This can be regarded as a composite Markovian process. It is a coarse-grained description of complete Liouville equation of the density of states of combined system of lattice
and spins utilizing the stochastic property $\Gamma$. Thus we may call it a stochastic Liouville equation\cite{13,18}.

We first multiply equation (57) by $\rho$ and integrate over $\rho$. This yields, with equation (49),

$$
\frac{\partial}{\partial t}\bar{\rho}(\Omega, t) = \frac{i}{\hbar}[\bar{\rho}(\Omega, t), H(\Omega)] + \Gamma \bar{\rho}(\Omega, t) \tag{57}
$$

This is the equation which we shall refer to as the SLE.

In this derivation of SLE an important approximation has been made. It is assumed that the molecules execute their random motions regardless of the state in which the spins find themselves. Thus the reaction of spin system to its surroundings is ignored. In other words we neglected the energy exchange between the lattice and the spins. However, as Kubo stated\cite{13}, this is permissible for instance when the temperature of the bath is sufficiently high compared with the possible energy exchange. Many examples in NMR or Mossbauer effects belong to this category because the reaction to the molecular motion of the bath is extremely small. Thus equation (58) has a wide range of application in line shape problems in magnetic resonance\cite{18}.

In the case of jumps the operator $\Gamma$ is a matrix and the SLE takes the form:

$$
\frac{d}{dt}\bar{\rho}_\nu = \frac{i}{\hbar}[\bar{\rho}_\nu, H_\nu] + \sum_\mu \Gamma_{\nu\mu}\rho_\mu \tag{58}
$$

Where $\Gamma_{\nu\mu}$ are reciprocals of mean residence times.

\section*{V. SLE AND METHOD OF SOLUTION}

The stochastic Liouville equation in its simplest form is given by:

$$
\dot{\rho}_{mn} = -i[H, \rho]_{mn} - \alpha(1 - \delta_{mn})\rho_{mn} \tag{59}
$$

and describes the time evolution of density matrix $\rho$ of the moving particle in the representation of site states $m, n$. The system in which the particle moves is a crystal, i.e., possesses translational periodicity. The intersite interaction is $H$. The last in (60) describes the randomizing process whereby the off-diagonal elements of $\rho$ decay, $\alpha$ being the rate at which this process occurs. Alternatively, $\alpha$ may be looked upon as the average rate of scattering among the band states of the particle. In the limit of no scattering, (60) describes coherent motion whereas, in the opposite limit it describes hopping or incoherent motion. The indices $m, n$ are vectors in the appropriate number of dimensions. A different form of the SLE is:

$$
\dot{\rho}_{mn} = -i[H, \rho] - \alpha(1 - \delta_{mn})\rho_{mn} + 2\delta_{mn} \sum_r (\gamma_{mr}\rho_{rr} - \gamma_{rm}\rho_{mm}) \tag{60}
$$

and describes in addition to the processes included in (60), a transport channel wherein the particle hops from sites $r$ to sites $m$ at rates $2\gamma_{mr}$.

The SLE(60) can be looked upon as presenting a formal trapping problem in a 2d-dimensional space where is $d$ the dimensionality of the system under analysis. We should use $\eta$ to denote the homogeneous solution of (60), i.e., its solution in the last term:

$$
\eta_{mn}(t) = \sum_{m'n'}(\psi_{m'-m, n'-n}(t)\rho_{m'n'}(0)) \tag{61}
$$
The quantities $\psi$ are the density-matrix propagators, i.e., the solution of (60) for $\alpha = 0$ for the initial conditions $\rho_{mn}(0) = \delta_{m0}\delta_{n0}$. If we recast (60) as:

$$\dot{\rho}_{mn} + \alpha \rho_{mn} = -i[H, \rho]_{mn} + \alpha \delta_{mn}\rho_{mn}$$

(62)

We see that $\alpha$ produces two perturbations on (62): that caused by $(\alpha \rho_{mn})$ on the left side and that caused by $\alpha \delta_{mn}\rho_{mn}$ on the right side.

In the context of the dynamics of a hypothetical walker whose unperturbed motion is given by (62), these two terms represent, respectively, an overall decay akin to the radiative decay of a moving exciton, which takes place only when $m = n$, i.e., in a special trap-influenced region in the $m,n$ space.

The first of the two terms introduces a simple multiplicative factor into the solutions (62), but the second requires an analysis through the defect technique.

Equation (63) takes the form:

$$\tilde{\rho}_{mn}(\epsilon) = \tilde{\eta}_{mn}(\epsilon + \alpha) + \alpha \sum_{m'}(\tilde{\psi}_{m-m',n-n'}(\epsilon + \alpha)\tilde{\rho}_{m'm'}(\epsilon))$$

(63)

in the Laplace domain where $\epsilon$ is the Laplace variable and tildes denote Laplace transforms. The case $m = n$ gives:

$$\tilde{\rho}_{mm}(\epsilon) = \tilde{\eta}_{mm}(\epsilon + \alpha) + \alpha \sum_{m'}(\tilde{\psi}_{m-m',m-m'}(\epsilon + \alpha)\tilde{\rho}_{m'm'}(\epsilon))$$

(64)

which involves only diagonal elements of the density matrix in the representation of $m,n$.

We solve (65) through the use of discrete Fourier transforms. These are defined through relations such as:

$$\rho^k = \sum_m \rho_{mm} \exp(ikm)$$

(65)

where $k$ is generally a vector and $km$ a dot produce.

The result is:

$$\tilde{\rho}^k(\epsilon) = \frac{\tilde{\eta}^k(\epsilon + \alpha)}{1 - \alpha \tilde{\psi}^k(\epsilon + \alpha)}$$

(66)

It is straightforward to substitute (67) into (64).

One then finds that the solution of the SLE (60) is given by (62) with the replacement:

$$\tilde{\psi}_{m-m',n-n'}(\epsilon) \rightarrow \tilde{\psi}_{m-m',n-n'}(\epsilon + \alpha) + \frac{\alpha}{N} \sum_{r,s,k} \frac{\exp(ik(s-r))}{1 - \alpha \tilde{\psi}^k(\epsilon + \alpha)} \tilde{\psi}_{m-r,n-r}(\epsilon + \alpha)\tilde{\psi}_{s-m',s-n'}(\epsilon + \alpha)$$

(67)

This result is exact and explicit. It is explicit in the sense that once one knows the $\psi$’s, i.e., the propagators of (60) or (63) in the absent of $\alpha$, one can write down the solutions of (60) by following the prescription of (68) and the right-hand side of (62), for arbitrary initial conditions.

The practical usefulness of (68) depends on the simplicity, or lack thereof, of the quadrature problem involved in the inversions of the transforms.
VI. CLASSICAL LIOUVILLE THEORY AND THE MICROSCOPIC INTERPRETATION OF BLACK HOLE ENTROPY

It has been computed that the entropy of a Schwarzschild black hole could be derived by finding a classical central charge of the Virasoro algebra of a Liouville theory and using the Cardy formula. This is done by performing a dimensional reduction of the Einstein-Hilbert action with the Ansatz of spherical symmetry and writing the metric in conformally flat form. Near horizon approximation the field equation for the conformal factor decouples becoming a Liouville equation. This computation is independent from a specific quantum theory of gravity model [20]. In order to understand the role of 2-D conformal symmetry in counting the black hole microstates let us recall some standard features of 2-D conformal symmetry. By introducing complex coordinates the flat metric can be written in the form $ds^2 = dzd\bar{z}$. The infinitesimal generators of such transformations $G_n = z^{n+1}z$ close a Lie algebra $[G_n, G_m] = (n - m)G_{n+m}$.

In 2D CFT the stress energy tensor has only two components, i.e., one analytic and the other anti-analytic:

\[
T = T_{zz} \\
\bar{T} = \bar{T}_{\bar{z}\bar{z}}
\]

\[\partial_z \bar{T} = 0 \]
\[\partial_{\bar{z}} T = 0\] (69)

We can therefore expand for example $T$ in Laurent series:

\[
T(z) = \sum_{-\infty}^{\infty} L_n z^{-n-2}.
\] (70)

In the quantum case the $L_n$ become operators and relatively to the commutator form a Virasoro algebra:

\[
[L_n, L_m] = (n - m)L_{n+m} + \frac{c}{12}(m^3 - m)\delta_{m,-n}.
\] (71)

This is a central extension of the algebra ($[G_n, G_m] = (n - m)G_{n+m}$). The central extension in the commutator algebra arises because of the normal ordering of the creation operators. It is a standard result for quantum CFT in 2-D that the asymptotic density of states for given $L_0$ is completely determined by the Virasoro algebra by means of the Cardy formula [21]

\[
\rho(L_0) = \exp(2\pi \sqrt{cL_0/6}).
\] (72)

The entropy can therefore be calculated by using the logarithm of the Cardy formula $S = \ln \rho$.

A central extension of the conformal algebra ($[G_n, G_m] = (n - m)G_{n+m}$) can already arise at classical level in the Poisson algebra of the charges, as for example in the Liouville theory [22].

VII. APPROXIMATE SOLUTION OF THE CLASSICAL LIOUVILLE USING GAUSSIAN PHASE PACKET DYNAMICS

Their approach [23] to classical Liouville equation draws on the formal equivalence of this equation to the time dependent Schrödinger equation [24]. Gaussian wave packets, first
popularized by Heller\cite{25, 26}, for integrating the time dependent Schrödinger equation, have also been applied to the calculation of spectrosopic correlation functions using the von Neumann (quantum Liouville) equation\cite{27–30}. 

Mukamel and co-workers observed that the equation of motion for a Gaussian approximation to the density matrix can be adapted to classical mechanics by replacing the quantum Liouville operator and phase space density distribution\cite{31}. The classical density distribution of each particle is represented by a single Gaussian phase packet. The many-body density distribution is expressed in a Hartree approximation as a product of distributions for each particle\cite{32, 33}.

Equation of motion for the density distribution are derived for both constant energy and constant temperature dynamics and exact results are obtained for the time evolution in the free particle and harmonic potentials. We demonstrate the general applicability of the Gaussian phase packet dynamics method through two application. The first involves the calculation of equilibrium thermodynamic averages for a Lennard-Jones cluster and fluid using Gaussian phase packets.

VIII. QUANTUM-CLASSICAL LIOUVILLE DYNAMICS OF PROTON AND DEUTERON TRANSFER RATES IN A SOLVATED HYDROGEN-BONDED COMPLEX

They studied\cite{34} an intermolecular proton transfer reaction in a bulk polar solvent of the form $AH - B \rightleftharpoons A^- - H^+B$. The model under study, which was constructed by Azzouz and Borgis\cite{35}, describes a hydrogen-bonded phenol ($A$) trimethylamine ($B$) complex dissolved in methyl chloride. The proton transfer rate constant and kinetic isotope effect ($KIE$) have been computed for this model using a wide variety of techniques\cite{36–43}. The specific forms of the interaction potentials, parameter values used, and the remaining details of the model can be found in\cite{36, 44} and\cite{45}. In a previous work, they calculated the proton transfer rate constant for this model with the $AB$ distance constrained at $R_{AB} = 2.7\AA$.

A: QUANTUM-CLASSICAL RATE THEORY

The rate constant calculations are based on an expression for the time dependent rate coefficient of the proton transfer reaction $A \rightleftharpoons B$

$$k_{AB}(t) = \frac{1}{n_{eq}^A} \sum_\alpha \sum_{\alpha \geq \alpha} (2 - \delta_{\alpha \alpha}) \int dX \times Re[N_B^{\alpha \alpha}(X, t)W_A^{\alpha \alpha}(X, \frac{i\hbar\beta}{2})]$$ (73)

which is written in terms of a partial Wigner representation of the bath degrees of freedom and a representation of the protonic degrees of freedom in adiabatic states\cite{46}. Here the bath phase space variables (coordinates and momenta, respectively) are denoted by $X = (R, P)$, $n_{eq}^A$ is the equilibrium density of species $A$ and $\beta = \frac{1}{k_BT}$ is the inverse temperature.

In this partial Wigner transform representation\cite{47}, the Hamiltonian $\hat{H}$ of the system is $\hat{H}_W = \frac{P^2}{2M} + \hat{h}(R)$, where $\hat{h}(R)$ is the protonic Hamiltonian in the field of fixed bath particles with mass $M$. The adiabatic basis states $\{|\alpha; R\rangle\}$ are the solutions of the eigenvalue problem $\hat{h}(R)|\alpha; R\rangle = E_\alpha(R)|\alpha; R\rangle$, where $\{E_\alpha\}$ are the adiabatic energies. In this expression for the rate coefficient, $N_B^{\alpha \alpha}(X, t)$ is the time evolved species $B$ (product) operator, while
$W^{\alpha}(X, \frac{\text{d}H}{\text{d}t})$ is the spectral density function that contains all information on the quantum equilibrium structure. The solvent polarization reaction coordinate \[48, 49\].

IX. STATISTICAL MECHANICS OF NON-HAMILTONIAN SYSTEMS

The dynamics of Hamiltonian systems is characterized by conservation of phase space volume under time evolution \[50\], and this conservation of phase volume is a cornerstone of conventional statistical mechanics \[51, 52\]. Invariance of phase space volume under Hamiltonian time evolution is the content of Liouville's theorem for divergenceless flows \[50, 53\]. At a deeper level, conservation of phase space volume is understood to be a consequence of the existence of an invariant symplectic form in the phase space of Hamiltonian systems, and application of geometric methods and concepts from the theory of differentiable manifolds \[54–58\] is essential for a fundamental description of classical Hamiltonian systems \[50, 54, 59, 61\]. Non-Hamiltonian dynamics, characterized by nonzero phase space compressibility \[53, 62–71\], is relevant when we consider the statistical mechanics of thermostatted systems \[72, 73\]. Such systems arise in the simulation of ensembles other than microcanonical \[76\], and in the treatment of nonequilibrium steady states \[72, 73, 75, 77\].

Various homogeneous thermostating mechanisms have been introduced to remove heat supplied by nonequilibrium mechanical and thermal perturbations. Phase space volume is no longer necessarily conserved, and for nonequilibrium steady states the phase space probability distribution is found to collapse onto a fractal set of dimensionality lower than in the equilibrium case \[72, 73, 75, 78, 79\]. This phenomenon indicates a lack of smoothness of the invariant measure in phase space in nonequilibrium steady states \[73, 80, 81\]. The dynamical evolution of the phase space distribution function for Hamiltonian systems is described by the Liouville equation \[50, 51\]. The Hamiltonian equation is often considered be a special case of a so-called generalized Liouville equation (henceforth GLE) appropriate for systems with compressible dynamics \[53, 62, 71, 82\], although the equation for the time-evolution of the Jacobian determinant in a general compressible flow given in Liouville's original paper \[53\] is, in fact, equivalent to the GLE \[66, 68, 70\]. A number of authors \[62, 71\] have treated the statistical mechanics of non-Hamiltonian systems in terms of the GLE, and all have derived the result that the rate of change of the Gibbs entropy for non-Hamiltonian systems is the ensemble average of the divergence of the dynamical vector field (phase space compressibility). Steeb \[67, 74, 82\] applied the theory of Lie derivatives and differential forms to derive the GLE for both time-independent and time-dependent vector fields. Some explicit solutions to the Liouville equation were given, and the existence of singular solutions for systems with limit cycles (attracting periodic orbits) was noted \[67\]. The important paper by Ramshaw \[71\] gave a covariant formulation of the Liouville equation and of the entropy. It was noted that invariant measures (volume elements) associated with zero entropy production rate in non-Hamiltonian systems must be smooth stationary solutions of the GLE. Some limitations of the description of nonequilibrium steady states in terms of the GLE were discussed by Holian et al. \[83\].

Tuckerman et al. \[84\] (hereafter, TEA) have recently applied geometric methods from the theory of differentiable manifolds \[55–58\], in particular the concepts of Riemannian geometry \[57\], to the classical statistical mechanics of non-Hamiltonian systems \[85, 87\]. TEA have argued that, through introduction of so-called metric factors, it is always possible to define a smooth invariant phase space measure in non-Hamiltonian systems, even for nonequilibrium stationary states \[85, 86\]. Moreover, the Gibbs entropy of the associated phase space distri-
bution function is found to be constant in time, just as for Hamiltonian systems. TEA also claim that previous formulations of the GLE (for example, papers[72, 73]) are in some way incorrect, incomplete, or at least coordinate-dependent[83, 87]. These claims have proved controversial[84, 88–95].

By definition, a coordinate-free formulation in the language of differential forms[54–58] removes any question[87] concerning the coordinate dependence of any results obtained. The apparatus of differential forms is the appropriate machinery for treating the transformations of variables and volume elements arising in the dynamics of both Hamiltonian and non-Hamiltonian systems. For any region of phase space, the fraction of the ensemble inside the region is obtained by integration of the density n-form over the region. The density n-form can be written as the product of a volume form[55, 56] (comoving volume element) and a phase space distribution function. The GLE, which describes the evolution of the phase space distribution function, then follows from the transport equation[67].

To determine the fraction of the ensemble in a given region, we simply need to count ensemble members. As we do not need a volume form to count ensemble members inside a prescribed region of phase space, the density n-form $\rho$ is defined without reference to any particular volume form. Any result expressed in terms of $\rho$ alone is therefore manifestly independent of the choice of volume form on the phase space manifold. This covariance with respect to the choice of volume form is the essential advantage of a description of the ensemble density in terms of the n-form $\rho$.

When considering the phase space structure and dynamics of Hamiltonian and non-Hamiltonian systems, the notion of distance associated with the familiar properties of Riemannian manifolds[55] is irrelevant. Volume forms provide exactly the construct needed, namely, a definition of volume without distance. Moreover, the Lie derivative of the volume form provides a definition of divergence without metric connection. The existence of an invariant volume form is important for simulation of equilibrium properties via non-Hamiltonian dynamics; if the dynamics preserves a given volume form (invariant measure) then, provided the system is ergodic, and that all relevant constraints are taken into account[87], phase space averages with respect to the invariant measure can be evaluated by computing long-time averages over a single trajectory. For all the equilibrium non-Hamiltonian systems discussed to date, a smooth stationary invariant measure can be found[87]. Nevertheless, any system with net attracting or repelling periodic orbits cannot possess a smooth invariant measure[90], so that, contrary to the assumption made in[86], smooth invariant measures for arbitrary non-Hamiltonian systems do not exist. True invariant measures, which are in general singular (not absolutely continuous with respect to the usual volume element), can be defined in terms of infinite-time averages of the density n-form $\rho_t$[81].

If the metric tensor is stationary, then compatibility of the Riemannian structure with the dynamics requires the associated metric factor $\sqrt{g}$ to be a time-independent solution of the GLE. In this case, the metric factor defines an invariant (Riemannian) volume form in the usual fashion[55]. On the other hand, if the metric tensor is allowed to be time-dependent[87, 97, 98], then compatibility requires the associated metric factor to be a non-stationary solution of the Liouville equation. The entropy defined with respect to the associated time-dependent Riemannian volume form is then constant[87]; for nonequilibrium steady states, the underlying metric factor will become ever more nearly singular (fractal) at long times, so that this result is only of formal significance[99].
X: SMALL-TIME PARAMETER METHOD IN LIOUVILLE EQUATION

Considering the formal asymptotic solution of Cauchy problem \( \frac{\partial}{\partial t} f(q,p,t) = Lf(q,p,t) \) \( f(q,p,t)|_{t=0} = f_0(q,p) \) by the method of the small time space in\(^{100}\) and defined by mapping \( \tau = 1 - \exp(-st), s > 0 \) Gennady Rudykh, Alexander Sinitsyn and Eugene Dulov, transformed the initial infinite time interval \( R^+ \) onto a small finite one \( J \equiv \{ \tau : 0 \leq \tau < 1 \} \).

This technique is quite general and was applied to Liouville equation by G. Rudykh and A. Sinitsyn \(^{101}\) at the earlier 80’s of the 20th century.

The small-time transformation is also well known to the applied mathematicians because it suits for numerical integration over the semi-infinite intervals. The obvious benefit for such kind of transform lies in power series expansion over a time scale. Using finite interval \([0, 1]\) one can pay the attention to the series coefficients and their convergence properties.

In our particular case a transformed Cauchy problem becomes:

\[
(1 - \tau) \frac{\partial}{\partial \tau} f(q,p,\tau) = \frac{1}{s} Lf(q,p,\tau) \\
f(q,p,\tau)|_{\tau=0} = f_0(q,p)
\]

A solution of the Cauchy problem (75) in the small-time space was studied in the form of asymptotic expansion:

\[
f(q,p,\tau) = \sum_{k=0}^{\infty} f_k(q,p) \cdot \tau^k.
\]

Substituting (76) into (75) and equating the coefficients for \( \tau \), one obtains\(^{102}\)

\[
f_k(q,p) = \frac{k-1}{k} f_{k-1}(q,p) + \frac{1}{sk} ([H(q,p), f_{k-1}(q,p)] - \sum_{i=1}^{n} \frac{\partial}{\partial p_i} (Q^*_i(q,p) \cdot f_{k-1}(q,p))) (76)
\]

Hence

\[
f_k(q,p) = \frac{1}{sk} L \left[ \prod_{r=1}^{k-1} (1 + \frac{1}{sr} L) \right] f_0(q,p)
\]

\( k = 2, 3, ... \)

With

\[
\prod_{r=1}^{k-1} (1 + \frac{1}{sk} L) = a_{k-1} + \frac{1}{s} a_{k-2} L + ... + \frac{1}{s^{k-1}} a_0 L^{k-1}
\]

(78)

Where \( a_0 = \frac{1}{(k-1)!}, a_{k-1} = 1 \).

APPENDIX

In this short section we present a concise proof for the theorem 2.A

2.A: The family \( S_{N,0}^N(t), t \in ]-\infty, +\infty[ \), constitutes a strongly continuous one-operator group
of isometric operators in $L_N(\Lambda)$ whose infinitesimal operator $H^N_\Lambda$ is given on $L^0_N(\Lambda)$ by the Poisson bracket with the Hamiltonian of system of non-interacting particles with boundary conditions.

**PROOF.** Group properties of the family $S^N_\Lambda(t)$ follow from the group property of a phase trajectory $X(t, \chi)$. For $f_N \in L^0_N(\Lambda)$ we show that:

$$\lim_{\Delta t \to 0} \| S^N_\Lambda(t + \Delta t) f_N - S^N_\Lambda(t) f_N \| = 0. \quad (79)$$

Indeed, for $f_N \in L^0_N(\Lambda)$ since $S^N_\Lambda(t)$ is isometric we have

$$\| S^N_\Lambda(t + \Delta t) f_N - S^N_\Lambda(t) f_N \| = \| S^N_\Lambda(\Delta t) f_N - f_N \| = \int dx | f_N(X(\Delta t, \chi)) - f_N(\chi) |.$$ 

Since for sufficiently small $\Delta t$ and $f_N(X(\Delta t, \chi))$ is non-zero outside some neighborhood of forbidden configurations and the boundary $\partial \Lambda$ of the domain $\Lambda$, where there are no particle collisions, we have $f_N(X(\Delta t, \chi)) \to f_N(\chi)$ uniformly with respect to $\chi$ as $\Delta t \to 0$. Thus we can carry out the $\lim \Delta t \to 0$ under the integral, hence the validity of (79) is proved. Since $L^0_N(\Lambda)$ is dense everywhere in $L_N(\Lambda)$, from (79) and the boundedness of the group $S^N_\Lambda(t)$ there follows the strong continuity of the group $S^N_\Lambda(t)$ in $L_N(\Lambda)$.

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