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A Systematic Derivation of Exact Generalized Brownian Motion Theory

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We present here a simple unified derivation of the exact Fokker–Planck equation obtained earlier by Zwanzig and the exact Langevin and transport equations derived by Mori. The derivation, based on the use of a Hilbert space formulation of the dynamics, leads to substantial generalizations of these results in a straightforward manner. We obtain nonlinear Langevin equations for classical systems and discuss the extension of the theory to driven transport and to quantum dynamics based either on the use of density matrices or Γ-space densities as suggested by Wigner. Remaining limitations of the theory are pointed out.

KEY WORDS: Generalized Brownian motion; projection operator; Langevin equation; Fokker–Planck equation; nonlinear transport equations; time-dependent external field; Wigner phase space density.

1. INTRODUCTION

We shall be concerned here with the derivation on the basis of microscopic first principles of an exact generalized Brownian motion theory. There are

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already a large number of articles published on this topic, which has seen rapid development over the last fifteen years, and recently the emphasis has shifted from basic theoretical work to application. Here we shall, however, reexamine the very foundation of the theory. The justification for so doing is twofold: (i) We would like to present what we feel is a particularly simple derivation of the exact generalized Brownian motion theory which unifies and clarifies the many important original contributions to this field; (ii) on the basis of this derivation we would like to point out a number of straightforward but important extensions of the theory while at the same time focusing attention on the remaining limitations of the theory.

Brownian motion theory in its many forms has a long and distinguished history. In its traditional form the theory dealt with the motion of a physically separable subsystem such as a colloidal particle in contact with a medium which supplies a stochastic force. The theory was phenomenological. That is, no attempt was made to base the stochastic theory on the exact equations of motion of the total system. Excellent reviews of this approach to Brownian motion are available.[1,2] In the early 1950's. Green[3] argued forcefully that the traditional theory of Brownian motion should be eztended to the study of a much larger class of time-dependent phenomena in statistical mechanics. The main idea was to replace the Brownian particle by some sufficiently large set of gross variables and then use the traditional methods of stochastic theory to derive transport laws satisfied by these gross variables. Although the phenomenological stochastic theory approach to generalized Brownian motion has by no means been abandoned,[4] much interest has now been drawn to the possibility that the phenomenological character can be dropped and the theory be based entirely on microscopic first principles. Significant progress in this direction has been made on the basis of projection operator techniques suggested by Zwanzig[5] in 1960 and used by him to derive an exact generalized Fokker–Planck equation.[6] Mori[7] obtained a linear generalized Langevin equation in 1965 using similar projection operator methods and Kawasaki,[8] in the process of constructing a mode–mode coupling theory of critical dynamics, noted that Mori's equation by a straightforward extension could be applied also to nonlinear phenomena.

In recent years the basic ideas of the generalized Brownian motion theory have been applied to the study of equilibrium time-correlation functions,[9] kinetic theory,[10–12] transport coefficients,[13–16] quantum optics,[17,18] and other problems, and time-dependent projection operators have been used.[19,20] Despite this proliferation of applications of the basic ideas, the contributions are fragmented due to the use of seemingly dissimilar derivations and the status of the generalized Brownian motion theory is hard to glean from the literature. It is for this reason that we would like to present here a particularly simple but still general derivation of the generalized

Brownian motion theory. This derivation results in a complete unification of the master equation or Fokker–Planck equation approach and the Langevin-transport equation approach to nonequilibrium dynamics. Apart from the very important pedagogical advantage, it also allows us to point out a number of straightforward extensions of the theory together with the remaining limitations of the basic methods used.

In Section 2 we introduce the classical form of the Hilbert space representation of dynamics upon which our derivations are based. The derivation of the Langevin and transport equations in the case of a closed classical system is illustrated in detail in Section 3.1. for both the linear and the nonlinear cases. Section 3.2. extends the results to yield the generalized Fokker–Planck equation and Section 3.3 shows how time-dependent external driving forces can be incorporated in the derivations. We then examine how the quantum effects will enter the theory. In Section 4.1 we use the traditional density matrix formulation as a basis and in Section 4.2 we point out the advantages of a Γ-space formulation of quantum dynamics as an alternative basis for the derivations.

2. STATE VECTOR FORMULATION OF CLASSICAL DYNAMICS

The exact microscopic derivation of a generalized Brownian motion theory will start from the Liouville equation,

$$(\partial/\partial t)f(t;\Gamma) = -iLf(t;\Gamma) \tag{1}$$

where Γ is a multidimensional coordinate summarizing all the positions and momenta of a point particle system, $f(t;\Gamma)$ is a probability density in Γ-space, and L is the Liouville operator,

$$LB(\Gamma) = -i\{B(\Gamma), H(\Gamma)\}_{\text{PB}} \tag{2}$$

[$\{\ ,\ \}_{\text{PB}}$ is the Poisson bracket and $H(\Gamma)$ is the Hamiltonian], or the derivation will start from the equation of motion of the time-dependent property functions

$$(\partial/\partial t)A(t;\Gamma) = iLA(t;\Gamma) \tag{3}$$

Applying projection operators in a Hilbert space of probability densities to the Liouville equation, one obtains generalized Fokker–Planck and master equations,[5,6] while projection operators in a Hilbert space of property functions applied to Eq. (3) yield Langevin and transport equations.[7] In fact, the two starting points are equivalent and either one of them is sufficient by itself as a starting point for the derivation of a generalized Brownian motion theory.

Previous derivations can be unified and considerable conceptual advantages can be gained by exploiting further the Hilbert space formulation of classical dynamics implicit in earlier work. Note that in statistical mechanics the information we seek takes the form of an average value of some relevant property $A(\Gamma)$,

$$\langle A \rangle_t = \int d\Gamma f(0; \Gamma) A(t; \Gamma) \tag{4}$$

The information available at the start of the experiment at $t = 0$ determines the probability density $f(0;\Gamma)$ and the time dependence is here taken to be carried by the time-dependent property functions satisfying the equation of motion (3). However, the same information can be obtained by solving the Liouville equation and using the relation

$$\langle A \rangle_t = \int d\Gamma f(t; \Gamma) A(\Gamma) \tag{5}$$

Thus the time dependence can be carried by either the property function or the probability density.

It should now be noted that the familiar relations (4) and (5) have the form of scalar products in a Hilbert space of functions of Γ. In order to exploit this observation, we construct a Hilbert space which contains all necessary property functions and probability densities so that (1) and (3) become linear first-order differential equations in this space and (4) and (5) can be written as

$$\langle A \rangle_t = (A(t), f(0)) = (A, f(t)) \tag{6}$$

We shall assume that the scalar product can be defined by

$$(A, B) = \int d\Gamma A(\Gamma) B^*(\Gamma) \tag{7}$$

where the asterisk indicates complex conjugation. Since $f(t; \Gamma)$ is real, (6) will then be equivalent to (4) and (5).

It will not be our purpose here to examine in any detail the mathematical justification for the construction of such a Hilbert space of classical dynamics. That it is possible to do so is suggested already in the classic work by Koopman[21] and von Neumann.[22] The crucial point is that now both the properties and the probability density are vectors in the same Hilbert space and the information is extracted by taking a scalar product between a property vector and a state vector as in (6). This will allow us to derive the basic equations of the exact generalized Brownian motion theory in a particularly simple and general way by using standard manipulations of Hilbert space

operators well known from quantum mechanics. As a first example, we note that Hamilton's equation (3) has the formal solution

$$A(t; \Gamma) = e^{iLt}A(\Gamma) \tag{8}$$

which when inserted in (4) yields (5) after shifting the operator e^{iLt} from one side to the other in the scalar product and noting that L will normally be a Hermitian operator. By this simple manipulation one easily gets from (3) to the Liouville equation (1).

It is important to note that the dynamical Hilbert space is not unique. The scalar product (7) may be generalized to

$$(A, B) = \int d\Gamma\, A(\Gamma)B^*(\Gamma)w(\Gamma) \tag{9}$$

where $w(\Gamma)$ is a real-valued and nonnegative weighting function. The corresponding Hilbert space will be denoted $\mathscr{H}(w|\Gamma)$. It is not hard to see that $w(\Gamma)$ controls the resolution of the Hilbert space. Suppose, for example, that there is a volume in Γ-space $w(\Gamma)$ vanishes. Then we find that functions which differ only in this volume will not be resolved by $\mathscr{H}(w|\Gamma)$. Clearly the dynamical problem we wish to solve will introduce certain requirements upon the resolution and thus limit the range of functions $w(\Gamma)$ that could be used. Moreover, one normally would find it convenient to choose $w(\Gamma)$ to be a stationary function in the unit metric,

$$i\Gamma w(\Gamma) = 0 \tag{10}$$

since this will mean that L is Hermitian in $\mathscr{H}(w|\Gamma)$ if it is in $\mathscr{H}(1|\Gamma)$.

The unit metric, $w(\Gamma) = 1$, would perhaps appear most natural to work with. The state vector can then be identified as the conventional probability density and $\mathscr{H}(1|\Gamma)$ will generally be a multidimensional L_2-space. However, it is often very convenient to adapt the metric to the equilibrium state of the statistical ensemble with which one is working. Thus we shall make use of the canonical equilibrium metric defined by

$$w(\Gamma) = e^{-\beta H(\Gamma)} \Big/ \int d\Gamma\, e^{-\beta H(\Gamma)} = \rho(\beta; \Gamma) \tag{11}$$

For a finite system $w(\Gamma)$ will vanish only if $H(\Gamma)$ is infinitely large. However, if the initial energy is finite, such states will not be visited since energy is conserved, so the physically relevant states should be well resolved.

3. DYNAMICS IN A REDUCED DESCRIPTION

3.1. Langevin and Transport Equations

Not only does the above Hilbert space framework expose the statistical content in a simple fashion, but it is also a very convenient starting point

for the reduction of the description of the system to some small subset of chosen variables. Let us first assume that we are only interested in the time-dependent averages of the functions $\{A_j(\Gamma)\}_{j=1}^{M}$ corresponding to some set of properties of the system. Recalling relation (6), we note that these averages are given by the projection of the time-dependent state vector on the respective property vectors. If we then let P be a projection operator corresponding to the subspace of $\mathscr{H}(w|\Gamma)$ spanned by the set of vectors $\{A_j(\Gamma)\}_{j=1}^{M}$, it follows that

$$\langle A_j \rangle_t = (A_j(\Gamma), f_w(t;\Gamma)) = (A_j(\Gamma), Pf_w(t;\Gamma)) \tag{12}$$

Thus we see that all of the relevant information is contained in a reduced state vector $Pf_w(t;\Gamma)$ belonging to a space, $P\mathscr{H}(w|\Gamma) = \mathscr{H}_A(w|\Gamma)$, of much smaller dimensionality.

The hope raised by the relation (12) is that perhaps we can limit our dynamical problem to the subspace $\mathscr{H}_A$. To verify this, we shall first seek an equation of motion for $Pf_w(t;\Gamma)$ which makes no reference to the remaining part of the complete state vector $(1-P)f_w(t;\Gamma)$ containing orthogonal information. Applying the projection operators P and $(1-P)$ to the Liouville equation (1), we obtain[5]

$$\frac{\partial}{\partial t} Pf_w(t;\Gamma) = -PiLPf_w(t;\Gamma) - PiL(1-P)f_w(t;\Gamma) \tag{13a}$$

$$\frac{\partial}{\partial t}(1-P)f_w(t;\Gamma) = -(1-P)iL(1-P)f_w(t;\Gamma) - (1-P)iLPf_w(t;\Gamma) \tag{13b}$$

Formally solving the second equation, noting that it is inhomogeneous and of first order, we get

$$(1-P)f_w(t;\Gamma) = e^{-it(1-P)L}(1-P)f_w(0;\Gamma) - \int_0^t ds\, e^{-is(1-P)L}(1-P)iLPf_w(t-s;\Gamma) \tag{14}$$

This result substituted into (13a) yields

$$\frac{\partial}{\partial t} Pf_w(t;\Gamma) = -PiLPf\omega(t;\Gamma) + \int_0^t ds\, PiLe^{-is(1-P)L}(1-P)iLPf_w(t-s;\Gamma) - PiLe^{-it(1-P)L}(1-P)f_w(0;\Gamma) \tag{15}$$

The rate of change of the vector $Pf_w(t;\Gamma)$ representing relevant information has now been separated into three parts. The first part,

$-PiLPf_w(t;\Gamma)$, is directly related to $Pf_w(t;\Gamma)$ itself, and it is the Markovian part of the rate of change.

The second part, $\int_0^t ds\, PiLe^{-is(1-P)L}(1-P)iLPf_w(t-s;\Gamma)$, represents the effects of relevant information which has leaked from the chosen subspace $\mathscr{H}_A$ to its orthogonal complement $\bar{\mathscr{H}}_A$. More specifically, $(1-P)iLP_w(t-s;\Gamma)$ is the flow of information from $\mathscr{H}_A$ to $\bar{\mathscr{H}}_A$ at earlier time $t-s$. The operator $e^{-is(1-P)L}$ propagates this information forward in time while keeping it orthogonal. The operator PiL on the left measures the effect of such orthogonal information upon the time development of $Pf_w(t;\Gamma)$, and, finally, the integration sums such effects over the time at which the orthogonal information left $\mathscr{H}_A$. This term represents memory effects and will, therefore, be called non-Markovian.

The third part, $-PiLe^{-it(1-P)L}(1-P)f_w(0;\Gamma)$, represents the effects of that part of the instantaneous orthogonal information that was orthogonal also at $t=0$ and never left $\mathscr{H}_A$.

Note now that if the third term vanishes, as it will if there is no orthogonal information at $t=0$,

$$(1-P)f_w(0;\Gamma)=0 \tag{16}$$

then (15) becomes an equation of motion for the reduced state vector closed in the corresponding subspace $\mathscr{H}_A$, just as desired.

We shall now go on to show that corresponding linear transport equations can be obtained from (15) by a simple manipulation. We start from the following relation for the rate of change of the average:

$$\begin{aligned}\frac{\partial}{\partial t}\langle A_j\rangle_t &= \left(A_j, \frac{\partial}{\partial t}Pf_w(t)\right)\\ &= -(A_j, PiLPf_w(t))\\ &\quad + \int_0^t ds\,(A_j, PiLe^{-is(1-P)L}(1-P)iLPf_w(t-s))\\ &\quad - (A_j, PiLe^{-it(1-P)L}(1-P)f_w(0))\end{aligned} \tag{17}$$

Noting that P, $(1-P)$, and L are Hermitian operators and i is anti-Hermitian, we shift the operators from right to left in the scalar product and obtain

$$\begin{aligned}(\partial/\partial t)\langle A_j\rangle_t &= (PiLA_j, f_w(t)) + \int_0^t ds\,(PiLe^{is(1-P)L}\\ &\quad \times (1-P)iLA_j, f_w(t-s)) + (e^{it(1-P)L}(1-P)iLA_j, f_w(0))\end{aligned} \tag{18}$$

Next we use the fact that any vector in $\mathscr{H}_A$ can be expanded as a linear combination of the vectors $\{A_j(\Gamma)\}_{j=1}^M$ to write

$$PiLA_j(\Gamma) = \sum_{l=1}^{M} c_{j,l}A_l(\Gamma) \tag{19}$$

$$PiLe^{is(1-P)L}(1 - P)iLA_j(\Gamma) = \sum_{l=1}^{M} d_{j,l}(s)A_l(\Gamma) \tag{20}$$

If we assume that the chosen properties are linearly independent, then the coefficients in the above expansions are unique and are given by

$$c = (PiL\mathbf{A}, \tilde{\mathbf{A}})(\mathbf{A}, \tilde{\mathbf{A}})^{-1} \tag{21}$$

$$d(s) = (PiLe^{is(1-P)L}(1 - P)iL\mathbf{A}, \tilde{\mathbf{A}})(\mathbf{A}, \tilde{\mathbf{A}})^{-1} \tag{22}$$

Here we have used matrix notation such that a vector is a column matrix and the tilde above a matrix indicates transpose. Although, in principle, it is always possible to pick the chosen variables so that they are linearly independent, it may not always be convenient to do so. We wish to emphasize that given correct expansions (19) and (20), the theory is valid also for linearly dependent variables. An expansion method which works also for linearly dependent variables may, for example, be based on the well-known Gram–Schmidt orthogonalization procedure.

Using these expansions, we can rewrite (18) in vector notation as follows:

$$(\partial/\partial t)\langle\mathbf{A}\rangle_t = c\langle\mathbf{A}\rangle_t + \int_0^t ds\, d(s)\langle\mathbf{A}\rangle_{t-s} + \langle\mathbf{F}(t)\rangle_0 \tag{23}$$

In the last term we have set

$$\mathbf{F}(t; \Gamma) = e^{it(1-P)L}(1 - P)iL\mathbf{A}(\Gamma) \tag{24}$$

We observe that if $\langle\mathbf{F}(t)\rangle_0$ vanishes, as it would if (16) is satisfied, then (23) becomes a linear, generally non-Markovian, transport equation

$$(\partial/\partial t)\langle\mathbf{A}\rangle_t = c\langle\mathbf{A}\rangle_t + \int_0^t ds\, d(s)\langle\mathbf{A}\rangle_{t-s} \tag{25}$$

The corresponding Langevin equation describes the time development of a single experiment. Thus it can be obtained from Eq. (23) by taking the limit as $f_w(0; \Gamma)$ approaches a δ-function describing the initial conditions for a single system. Noting that in this limit there is no dispersion in the ensemble, we get

$$(\partial/\partial t)\mathbf{A}(t; \Gamma) = c\mathbf{A}(t; \Gamma) + \int_0^t ds\, d(s)\mathbf{A}(t - s; \Gamma) + \mathbf{F}(t; \Gamma) \tag{26}$$

The linear Langevin and transport equations (25) and (26) were first obtained by Mori[7] for the case when w is the canonical equilibrium density. His derivation made use of projection operators in Hilbert space, but otherwise bears little resemblance to the present derivation. As pointed out by Mori, the fluctuating force $\mathbf{F}(t; \Gamma)$, representing the effect of orthogonal information in a single experiment, is related to the memory kernel $d(t)$ by a fluctuation-dissipation theorem which for linearly independent variables reads

$$d(t) = -(\mathbf{F}(t + s), \tilde{\mathbf{F}}(s))(\mathbf{A}, \tilde{\mathbf{A}})^{-1} \tag{27}$$

This is easily verified if we note that

$$\begin{aligned}(\mathbf{F}(t + s), \tilde{\mathbf{F}}(s)) &= (e^{i(t+s)(1-P)L}(1 - P)iL\mathbf{A}, e^{is(1-P)L}(1 - P)iL\tilde{\mathbf{A}}) \\ &= -(PiLe^{it(1-P)L}(1 - P)iL\mathbf{A}, \tilde{\mathbf{A}})\end{aligned} \tag{28}$$

and compare to (22).

It should now be clear that whether the relation (26) deserves the name Langevin equation or not depends on the statistical ensemble with which it is associated. A sufficient condition is that the initial state vector describing this ensemble contains no orthogonal information so that (16) holds. It then follows that the average of the fluctuating force vanishes, and the linear transport equation (25) is satisfied. This condition imposes a rather severe limitation on the validity of the linear Langevin and transport equations. However, we shall see that the study of equilibrium time correlations and small deviations from equilibrium allow the use of the linear theory.

The equilibrium time-correlation matrix $\theta(t)$ is defined by

$$\theta_{j,l}(t) = \int d\Gamma\, A_j(t; \Gamma)A_l^*(\Gamma)\rho(\beta; \Gamma) \tag{29}$$

where $\rho(\beta; \Gamma)$ is the canonical equilibrium density. But this can be written as a scalar product in the Hilbert space with $w(\Gamma) = \rho(\beta; \Gamma)$,

$$\theta_{j,l}(t) = (A_j(t), A_l) = \langle A_j \rangle_t \tag{30}$$

where the initial state vector is just $A_l(\Gamma)$, which satisfies (16). Thus we find immediately that the time-correlation matrix satisfies

$$(\partial/\partial t)\theta(t) = c\theta(t) + \int_0^t ds\, d(s)\theta(t - s) \tag{31}$$

In a more general case we may suppose that the initial information is provided in the form of the initial values for the averages of the chosen properties, $\{\langle A_j \rangle_0\}_{j=1}^M$. There is a whole range of initial state vectors that are

consistent with these averages but it is customary to chose the one that minimizes the information defined in $\mathscr{H}(1|\Gamma)$ by

$$I(0) = \int d\Gamma f_1(0;\Gamma) \ln f_1(0;\Gamma) \tag{32}$$

Given that the average energy is also known, the initial state vector will then be of the form

$$f_1(0;\Gamma) = C \exp[-\beta H(\Gamma) + \boldsymbol{\gamma}\cdot\mathbf{A}(\Gamma)] \tag{33}$$

where the coefficients β and $\boldsymbol{\gamma}$ are determined by the known averages. In $\mathscr{H}(\rho(\beta)|\Gamma)$ the corresponding initial state vector would be

$$f_\beta(0;\Gamma) = C' \exp[\boldsymbol{\gamma}\cdot\mathbf{A}(\Gamma)] \tag{34}$$

which, generally speaking, does not belong to $\mathscr{H}_A(\rho(\beta)|\Gamma)$. However, if the deviations of the initial averages $\{\langle A_j\rangle_0\}_{j=1}^M$ from their equilibrium values are small, one may approximate $f_\beta(0;\Gamma)$ by $C'(1 + \boldsymbol{\gamma}\cdot\mathbf{A}(\Gamma))$. Choosing our variables so that $1 \subset \mathscr{H}_A$ or $1 \subset \mathscr{H}_A$, we easily verify that $\langle \mathbf{F}(t)\rangle_0$ vanishes to first order in $\boldsymbol{\gamma}$, and thus the linear theory is valid in the limit of small deviations from equilibrium.

Although the linear Langevin equations of Mori have been found quite useful, the limitation pointed out above excludes from consideration the general case when initial deviations from equilibrium cannot safely be assumed small. Moreover, it should be noted that even when it is applicable, the linear theory may turn out to be impractical if a significant part of the dynamics is contained in the form of memory effects. An example of current interest is critical dynamics, where the deviations from equilibrium become large due to the closeness to a second-order phase transition.

We shall now proceed to show that the derivation of the linear Langevin equation can easily be extended to give Langevin equations of any desired degree of nonlinearity. This is done simply by replacing the projection operator P above by one that corresponds to an enlarged subspace of $\mathscr{H}(w|\Gamma)$. Thus we define $\mathscr{H}_{A^n}$ as the subspace spanned by all products of the properties $\{A_j(\Gamma)\}_{j=1}^M$ up to and including those of order n, $A_{j_1}(\Gamma)A_{j_2}(\Gamma)\cdots A_{j_n}(\Gamma)$, and the corresponding projection operator will be denoted P_n. The reduced state vector $P_n f_w(t;\Gamma)$ now contains complete information about moments of order n or smaller,

$$\langle A_{j_1}\cdots A_{j_m}\rangle_t = (A_{j_1}\cdots A_{j_m}, P_n f_w(t)), \qquad m \leqslant n \tag{35}$$

but no more information.

The equation of motion for $P_n f_w(t;\Gamma)$ is obtained from (15) by just adding the subscript n everywhere P occurs, and the same can be done to the

equation (18) for the time-dependent moments. However, the expansions (19) and (20) now take the following form:

$$P_n iLA_j(\Gamma) = \sum_{l_1=1}^{M} c_{j,l_1} A_{l_1}(\Gamma) + \cdots + \sum_{l_1=1}^{M} \cdots \sum_{l_n=1}^{M} c_{j,l_1\cdots l_n} A_{l_1}(\Gamma) \cdots A_{l_n}(\Gamma) \tag{36}$$

$$P_n iL e^{is(1-P_n)L}(1 - P_n) iLA_j(\Gamma) = \sum_{l_1=1}^{M} d_{j,l_1}(s) A_{l_1}(\Gamma) + \cdots + \sum_{l_1=1}^{M} \cdots \sum_{l_n=1}^{M} d_{j,l_1\cdots l_n}(s) A_{l_1}(\Gamma) \cdots A_{l_n}(\Gamma) \tag{37}$$

Such expansions do exist but the coefficients are not uniquely determined since all of the ordered product vectors are not linearly independent. The vector is, for example, unchanged by a permutation of order. Thus the set of product vectors satisfying $l_1 \leqslant l_2 \leqslant \cdots \leqslant l_m$, $m \leqslant n$, suffices to expand $\mathscr{H}_{A^n}$, but even in this reduced set we may find linear dependence.

Substituted into the generalized form of (18), the above expansions yield

$$\frac{\partial}{\partial t}\langle A_j\rangle_t = \sum_{l_1=1}^{M} c_{j,l_1}\langle A_{l_1}\rangle_t + \cdots + \sum_{l_1=1}^{M} \cdots \sum_{l_n=1}^{M} c_{j,l_1\cdots l_n} \times \langle A_{l_1} \cdots A_{l_n}\rangle_t + \int_0^t ds \left\{ \sum_{l_1=1}^{M} d_{j,l_1}(s)\langle A_{l_1}\rangle_{t-s} + \cdots + \sum_{l_1=1}^{M} \cdots \sum_{l_n=1}^{M} d_{j,l_1\cdots l_n}(s)\langle A_{l_1} \cdots A_{l_n}\rangle_{t-s} \right\} + \langle F_j^{(n)}(t)\rangle_0 \tag{38}$$

where

$$F_j^{(n)}(t; \Gamma) = e^{it(1-P_n)L}(1 - P_n) iLA_j(\Gamma) \tag{39}$$

If $\langle F_j^{(n)}(t)\rangle_0$ vanishes for all j, then (38) can be turned into a Langevin equation by considering again a subensemble of only one system. We obtain

$$\frac{\partial}{\partial t} A_j(t; \Gamma) = \sum_{l_1=1}^{M} c_{j,l_1} A_{l_1}(t; \Gamma) + \cdots + \sum_{l_1=1}^{M} \cdots \sum_{l_n=1}^{M} c_{j,l_1\cdots l_n} \times A_{l_1}(t; \Gamma) \cdots A_{l_n}(t; \Gamma) + \int_0^t ds \left\{ \sum_{l_1=1}^{M} d_{j,l_1}(s) A_{l_1}(t; \Gamma) + \cdots + \sum_{l_1=1}^{M} \cdots \sum_{l_n=1}^{M} d_{j,l_1\cdots l_n}(s) A_{l_1}(t - s; \Gamma) \cdots A_{l_n}(t - s; \Gamma) \right\} + F_j^{(n)}(t; \Gamma) \tag{40}$$

For the minimum information initial state (34) we note that

$$\langle F_j^{(n)}(t)\rangle_0 = O(|\gamma|^{n+1}) \tag{41}$$

and thus effects up to order n in $|\gamma|$ are accounted for in the nth-order nonlinear Langevin equation. The fully nonlinear equation obtained from (40) by setting n equal to infinity is an exact Langevin equation for the initial state vector (34) as well as any other initial ensemble which contains no information about properties orthogonal to the subspace $\mathscr{H}_A^{\infty}$.

It should be pointed out in this context that if we maximize the linear part of the memory effects occurring in the nonlinear Langevin equation and assume the linear variables $\{A_j(\Gamma)\}_{j=1}^{M}$ to be independent, then the fluctuation–dissipation theorem (27) holds exactly also in the nonlinear case. That is, the linear memory is directly related to the time correlation of the fluctuating forces. The nonlinear memory is clearly also related to the time correlation of the fluctuating forces since they depend on the same orthogonalized propagator, but the relation is less direct than in the linear case.

We find then a much greater range of validity for the nonlinear Langevin equations in comparison with the linear equations. However, we must point out one added difficulty with the nonlinear formulation. Due to the dispersion in the statistical ensemble we have in general

$$\langle A_{l_1} \cdots A_{l_m} \rangle_t \neq \langle A_{l_1} \rangle_t \cdots \langle A_{l_m} \rangle_t \tag{42}$$

and (38) is not closed in the first moments even if $\langle F_j^{(n)}(t) \rangle_0$ vanishes. Neglecting the dispersion and using (42) as an equality, (38) turns into a bare transport equation but this may not be a good approximation, in which case the simple relation between Langevin and transport equations is lost. Particularly in the case of critical dynamics there is a need to fluctuation-renormalize the bare nonlinear transport equations. A general scheme of this sort has been proposed and discussed elsewhere.[23]

3.2. Microscopic Fokker–Planck Equations

We have seen above how to derive, by exact projection operator methods in Hilbert space, microscopic analogs of the Langevin and transport equations of traditional Brownian motion theory. The third aspect of this theory concerns the time development of the probability density of the chosen variables as determined by the Fokker–Planck equation. In an important early application of the projection operator methods Zwanzig[6] showed how under certain conditions exact microscopic Fokker–Planck equations, generally of non-Markovian character, could be obtained, and he suggested simplifying approximations. We shall now use the results of preceding sections to point out how the Fokker–Planck equation fits into the general theory and to outline a straightforward derivation which somewhat generalizes the class of equations obtained by Zwanzig.

Let us suppose that we define a new set of coordinates which collectively form the vector coordinate $\mathbf{a}$ by the relation $\mathbf{A}(\Gamma) = \mathbf{a}$. That is, the new

coordinates are just the values of the properties we have chosen to study. Then all the information about these properties can be collected into a probability density $g(t; \mathbf{a})$, a function in $\mathbf{a}$-space satisfying

$$\langle A_{l_1} \cdots A_{l_m} \rangle_t = \int d\mathbf{a}\, a_{l_1} \cdots a_{l_m} g(t; \mathbf{a}) \tag{43}$$

Thus this function contains all of the information in the reduced state vector $P_\infty f_w(t; \Gamma)$.

The equation of motion of $g(t; \mathbf{a})$, which we shall now seek, is called a Fokker–Planck equation for the time-dependent properties. We note first that $g(t; \mathbf{a})$ can be obtained from $P_\infty f_w(t; \Gamma)$ by application of the coordinate transformation. One easily verifies that the desired transformation can be written as follows:

$$g(t; \mathbf{a}) = \int d\Gamma\, \delta(\mathbf{A}(\Gamma) - \mathbf{a}) w(\Gamma) P_\infty f_w(t; \Gamma) \tag{44}$$

where

$$\delta(\mathbf{A}(\Gamma) - \mathbf{a}) = \prod_{j=1}^{M} \delta(A_j(\Gamma) - a_j) \tag{45}$$

We now apply this transformation to the equation of motion of $P_\infty f_w(t; \Gamma)$ as given by (15) with P replaced by P_∞. The details of the calculation are available elsewhere[24] so we merely note that the result is the following equation of motion for $g(t; \mathbf{a})$:

$$\begin{aligned}
&\frac{\partial}{\partial t} g(t; \mathbf{a}) \\
&\quad = -\sum_{l=1}^{M} \frac{\partial}{\partial \alpha_l} [v_l(\mathbf{a}) g(t; \mathbf{a})] \\
&\qquad + \int_0^t ds \int d\mathbf{a}' \sum_{k=1}^{M} \sum_{l=1}^{M} \frac{\partial}{\partial a_k} K_{k,l}(\mathbf{a}, \mathbf{a}'; s) S(w|\mathbf{a}) \frac{\partial}{\partial a_l'} g(t - s; \mathbf{a}') \\
&\qquad \times S^{-1}(w|\mathbf{a}') - S(w|\mathbf{a}) Y(t; \mathbf{a})
\end{aligned} \tag{46}$$

Here $\mathbf{v}(\mathbf{a})$ is a generalized streaming velocity defined by

$$v_l(\mathbf{A}(\Gamma)) = P_\infty i L A_l(L) \tag{47}$$

We note that the microscopic Fokker–Planck equation is generally nonlocal in both space and time with a kernel $K(\mathbf{a}, \mathbf{a}'; t)$ defined by

$$\begin{aligned}
&K_{k,l}(\mathbf{a}, \mathbf{a}'; t) \\
&\quad = S^{-1}(w|\mathbf{a}) \int d\Gamma\, w(\Gamma)\, \delta(\mathbf{A}(\Gamma) - \mathbf{a}) \\
&\qquad \times (iLA_k(\Gamma)) e^{-it(1 - P_\infty)L} (1 - P_\infty)(iLA_l(\Gamma))\, \delta(\mathbf{A}(\Gamma) - \mathbf{a}')
\end{aligned} \tag{48}$$

Finally, unless the initial ensemble $f_w(0;\Gamma)$ contains only information concerning the chosen variables, there will be an inhomogeneous force in the Fokker–Planck equation given by the last term on the right in (46), where

$$Y(t;\mathbf{a}) = S^{-1}(w|\mathbf{a}) \int d\Gamma\, \omega(\Gamma)\, \delta(\mathbf{A}(\Gamma) - \mathbf{a}) \times P_\infty iL e^{-it(1-P_\infty)L}(1 - P_\infty) f_w(0;\Gamma) \tag{49}$$

The function $S(w|\mathbf{a})$ appearing in these relations is the structure function

$$S(w|\mathbf{a}) = \int d\Gamma\, w(\Gamma)\, \delta(\mathbf{A}(\Gamma) - \mathbf{a}) \tag{50}$$

which accounts for the change in measure as one transforms from Γ-space to $\mathbf{a}$-space.

The original derivation of Zwanzig corresponds to the special case when the unit metric $w(\Gamma) = 1$ is used in Γ-space and the initial ensemble density is

$$f(0;\Gamma) = \delta(\mathbf{A}(\Gamma) - \mathbf{a}_0)\, S^{-1}(1|\mathbf{a}_0) \tag{51}$$

so that $g(0;\mathbf{a})$ is a δ-function and there is no orthogonal information initially. Thus the inhomogeneous force will vanish in this case.

A word of caution concerning the use of δ-functions is called for. Although they are of great use in various branches of physics, it is well known that δ-functions are functions only in a generalized sense, and they are usually used merely to represent a well-defined limit process. Thus it should be noted that the δ-functions appearing above must be properly interpreted as limit functions in the Hilbert space of the dynamics. It may sometimes be necessary to give explicit consideration to the limit process represented by the δ-function. In the derivations presented here, no use of the δ-functions has been made in the basic formulation of the theory, and their role in the variable transformation performed above to obtain the Fokker–Planck equation is straightforward. In this regard we feel our derivation above is an improvement upon a recent derivation by Mori and Fujisaka[13] of an exact Fokker–Planck equation for the special case of equilibrium metric, $w(\Gamma) = \rho(\beta;\Gamma)$.

3.3. Driven Transport in Classical Dynamics

It is our purpose here to point out that the projection operator techniques applied above to obtain microscopic Langevin and Fokker–Planck equations in the case of closed classical dynamics can be extended with minor complications to apply also to driven dynamics. Since the general outline of the

derivations remains unchanged, we shall be brief, focusing on the more important differences and their consequences. A more detailed development is available elsewhere.[24]

In the case of driven transport, the Hamiltonian consists of two terms,

$$H(t; \Gamma) = H_0(\Gamma) + H_1(t; \Gamma) \tag{52}$$

where the last term accounts for some time-dependent external force applied to the system. Similarly, the Liouville operator in the dynamical Hilbert space of the system splits into two parts,

$$L(t) = L_0 + L_1(t) \tag{53}$$

where the latter part, due to the external driving force, is defined by

$$L_1(t)A(\Gamma) = -i\{A(\Gamma), H_1(t; \Gamma)\}_{\text{PB}} \tag{54}$$

for any Γ-space function $A(\Gamma)$.

Hamilton's equations hold, and they yield

$$(\partial/\partial t)A(t; \Gamma) = [iL(t)A(L')]_{\Gamma' = \Gamma(t;\Gamma)} = T(0|t)iL(t)A(\Gamma) \tag{55}$$

for the equation of motion of a property of the system. The first complication arises from the fact that in the presence of the driving force it will be more difficult to find stationary weighting functions other than $w(\Gamma) = 1$. As a consequence, the adjoint of the Liouville operator will be

$$L^\dagger(t) = L(t) + (L(t)w(\Gamma))/w(\Gamma) \tag{56}$$

and will be different from $L(t)$ when the second term does not vanish. Thus we may have to work with a non-Hermitian Liouville operator.

Another complication arises due to the time dependence of $L(t)$ in solving (55), but in the formal theory the result can be written as

$$A(t; \Gamma) = T(0|t)A(\Gamma) = \left\{\overrightarrow{\exp}\left[\int_0^t ds\, iL(s)\right]\right\}A(\Gamma) \tag{57}$$

where the propagator $T(0|t)$ has now become the time-ordered operator

$$T(0|t) = 1 + \int_0^t ds\, iL(s) + \cdots + \int_0^t ds_1 \cdots \int_0^{s_{n-1}} ds_n\, iL(s_n)$$

$$\cdots iL(s_1) + \cdots = \overrightarrow{\exp}\left[\int_0^t ds\, iL(s)\right] \tag{58}$$

The corresponding solution to the driven Liouville equation is

$$f_w(t; \Gamma) = T^\dagger(0|t)f_w(0; \Gamma) = \left\{\overleftarrow{\exp}\left[-\int_0^t ds\, iL^\dagger(s)\right]\right\}f_w(0; \Gamma) \tag{59}$$

where the reversed direction of the arrow indicates a reversed direction of time ordering, as can be verified by taking the Hermitian conjugate of (58). We note that the formal solutions have not only become more complicated in terms of notation, but the straightforward procedure of solving linear equations by diagonalization of the Liouville operator is no longer applicable.

The equation of motion of the reduced state vector $Pf_w(t;\Gamma)$ is found to be, after some simple calculation,

$$\begin{aligned}(\partial/\partial t)Pf_w(t;\Gamma) &= -PiL^\dagger(t)Pf_w(t;\Gamma) + \int_0^t ds\, PiL^\dagger(t) \\ &\times \left\{\overleftarrow{\exp}\left[-\int_s^t ds_1\,(1-P)iL^\dagger(s_1)\right]\right\}(1-P)iL^\dagger(s)Pf_w(s;\Gamma) \\ &-PiL^\dagger(t)\left\{\overleftarrow{\exp}\left[-\int_0^t ds\,(1-P)iL^\dagger(s)\right]\right\}(1-P)f_w(0;\Gamma) \qquad (60)\end{aligned}$$

and the equations of motion of the first moments can be obtained as before by shifting operators from right to left in the scalar product. We find

$$\begin{aligned}(\partial/\partial t)\langle A_k\rangle_t &= \langle PiL(t)A_k\rangle_t + \int_0^t ds \left\langle PiL(s)\right. \\ &\times \left\{\overrightarrow{\exp}\left[\int_s^t ds_1\,(1-P)iL(s_1)\right]\right\}\left.(1-PiL(t)A_k\right\rangle_s + \langle F_k(t)\rangle_0 \qquad (61)\end{aligned}$$

where the fluctuating force is defined by

$$F_k(t;\Gamma) = \left\{\overrightarrow{\exp}\left[\int_0^t ds\,(1-P)iL(s)\right]\right\}(1-P)iL(t)A_k(\Gamma) \qquad (62)$$

Equation (61) yields driven Langevin equations, and linear and bare nonlinear transport equations by expanding the first two terms on the right in the variables $\{A_k(\Gamma)\}_{k=1}^M$ and their products and then considering $f(0;\Gamma)$ to be the δ-function describing a single system or the full statistical ensemble. Likewise, Eq. (60) can be transformed into a driven Fokker–Planck equation by the same method as described above.[24]

Clearly, our microscopic transport theory will generally be somewhat complicated by the time-dependent driving forces, but it does exist and, given some straightforward modifications, it can be obtained by the projection operator methods described in detail above for closed classical systems.

4. GENERALIZED BROWNIAN MOTION THEORY BASED ON QUANTUM MECHANICS

4.1. The Matrix Formulation

We shall show here that the state vector formulation and the projection operator methods used above for classical dynamics can be applied also to quantum dynamics, while fundamental quantum effects impose further limitations on the results that can be obtained. Since the Hilbert space methods would be exactly the same as those used above, we shall not here repeat the individual steps in the derivation, but merely point out and discuss the problems posed by the quantum effects.

We must first take note of the rather obvious fact that it is not the usual Hilbert space of wave functions that we will use to obtain the quantum version of the generalized Brownian motion theory. In order to represent the state of the system as well as the properties of the system by vectors in the same Hilbert space, the most obvious solution is to use the well-known density matrix for the state and similarly well-known Heisenberg matrices for the properties. The unit metric would then be defined by the scalar product

$$(A, B) = Tr(AB^{\dagger}) = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} A_{ij} B_{ij}^{*} \tag{63}$$

The explicit form of the matrices is, of course, dependent upon the complete set of wave functions one chooses to work with, but the trace and therefore also the scalar product are independent of basis set used in its evaluation. Thus the Hilbert space structure itself is basis independent. The quantum Liouville equation describing the time dependence of the density matrix is

$$(\partial/\partial t)\rho(t) = -(i/\hbar)[H, \rho(t)] = -iL\rho(t) \tag{64}$$

and this relation also defines the quantum Liouville operator L in the unit metric.

Again it is possible to generalize the metric used by altering the form of the scalar product. As is clear from the work of Kubo[25] and Mori,[7] it is convenient to work with an equilibrium metric defined by the scalar product

$$(A, B) = Tr\left(\rho_{\beta}\beta^{-1} \int_0^{\beta} d\lambda\, e^{\lambda H} A e^{-\lambda H} B^{\dagger}\right) \tag{65}$$

where ρ_{β} is $Ce^{-\beta H}$, the canonical density matrix. It turns out that this form of metric will allow small deviations from equilibrium to be treated by a linear transport equation also in the quantum case. This can easily be verified by repeating the steps taken in Section 3.1, keeping in mind that quantum operators do not commute in general.

The projection operator methods can be used just as before to derive the reduced Liouville equations which play such an important role in the derivations here. The first problem posed by the quantum effects concerns the definition of a quantum Langevin equation. If we take the Langevin equation to be concerned with c-numbers, then we suggest that the exact value $A_\kappa(t; \Gamma)$ in the classical equation should be replaced by the pure state expectation value $(A_\kappa, \rho(t))$ in quantum mechanics, where $\rho(t)$ then must be an idempotent density matrix as would be constructed from a single wave function. This is the closest we can come to the dynamics in a single experiment but we note that due to the intrinsic quantum dispersion even the Langevin equation is now satisfied only in a statistical sense.

The linear Langevin and transport equations can be obtained by exactly the same steps as in the classical case. However, when we go to the nonlinear theory we now find that not only the transport equation, but also the Langevin equation must be obtained by fluctuation renormalization. The point is that we cannot in the quantum formulation rid ourselves of dispersion even in the case of a single experiment. Thus the straightforward projection operator techniques do not suffice to obtain an exact generalized Brownian motion theory of nonlinear form. This serves to emphasize the crucial role played by the coupling between first moments and statistical fluctuations in nonlinear transport theories.

The quantum dispersion or, equivalently, the fact that in quantum theory the properties of the system correspond to operators which generally do not commute also prevents us from extending the classical derivation of the generalized Fokker–Planck equation to yield an analogous equation in quantum theory. Unless all the chosen variables commute, there is no quantum analog of the classical δ-function $\delta(A(\Gamma) - a)$. There is simply no density matrix in the quantum Hilbert space which assigns dispersionless values to all the chosen properties.

It has been proposed by Sewell,[26] on the basis of coarse-graining and a limitation to macroscopic observables, that the chosen variables can be assumed to commute. This will suppress the quantum effects in several important respects, and Sewell made use of this fact in a derivation of a quantum version of Zwanzig's Fokker–Planck equation. We would like to point out that the restriction to commuting variables severely limits the theory. Most observables, by far, do not commute. Note that if the total energy is among the chosen variables, then only constants of the motion could be included in order to satisfy the commutation requirement. Furthermore, the fact that all chosen variables commute leads to the absence of any Markovian terms in the dynamics as noted by Sewell. This is highly undesirable since the remaining non-Markovian terms, which are much more difficult to deal with, then contain all of the dynamics. On the contrary, we feel that the variables

to be included in the chosen set should normally be chosen so as to maximize the Markovian effects and have the non-Markovian terms susceptible to simple approximation. Thus we conclude that the quantum effects pointed out above are important and must be directly confronted.

4.2. An Extension Based on the Wigner–Moyal Transformation of Quantum Mechanics

We have seen above that quantum mechanics can be given a Hilbert space structure similar to the classical one by a slight extension of the well-known density matrix formulation. Although the projection operators can be applied as before, we found that the change from classical to quantum mechanics brought a number of new complications into the theory. Some of these complications represent fundamental quantum effects and will persist. However, we will now show that the relationship between the classical and quantum theories of generalized Brownian motion can be significantly simplified by the use of a transformation of quantum mechanics into the classical Γ-space.

Wigner[27] first pointed out that for certain specific purposes any pure quantum wave function $\psi_i(r_1,\cdots,r_n;t)$ can be transformed to a Γ-space density $f_i(t;\Gamma)$,

$$f_i(t;\Gamma) = (\hbar\pi)^{-n}\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty} dy_1\cdots dy_n\,\psi_i^*(r_1+y_1,\ldots,r_n+y_n;t) \times \psi_i(r_1-y_1,\ldots,r_n-y_n;t)e^{2i(p_1y_1+\cdots+p_ny_n)/\hbar} \tag{66}$$

which was shown to satisfy a quantum mechanical Liouville equation,

$$(\partial/\partial t)f_i(t;\Gamma) = -i\mathscr{L}f_i(t;\Gamma) \tag{67}$$

Under the assumption that the potential $V(r_1,\ldots,r_n)$ is analytic in all the spatial coordinates, he showed that the quantum Liouville operator possessed a series expansion in $\hbar^2$ given by

$$i\mathscr{L} = \sum_{k=0}^{\infty} i\hbar^{2k}\mathscr{L}_k \tag{68}$$

$$i\mathscr{L}_0 = \sum_{l=1}^{n}\left(\frac{p_l}{m_l}\right)\frac{\partial}{\partial r_l} - \sum_{l=1}^{n}\frac{\partial V}{\partial r_l}\frac{\partial}{\partial p_l} \tag{69}$$

$$i\mathscr{L}_k = -\left(\frac{1}{2i}\right)^{2k}\sum^{k}\frac{1}{\lambda_1!\cdots\lambda_n!}\frac{\partial^{2k+1}}{\partial p_1^{\lambda_1}\cdots\partial p_n^{\lambda_n}} \times \frac{\partial^{2k+1}}{\partial r_1^{\lambda_1}\cdots\partial r_n^{\lambda_n}}V, \qquad k=1,2,\ldots \tag{70}$$

where $\sum^k$ indicates a summation over all sets of positive integers $\lambda_1,\ldots,\lambda_n$ satisfying

$$\lambda_1 + \lambda_2 + \cdots + \lambda_n = 2k + 1 \tag{71}$$

Wigner also noted that the corresponding Γ-space density for a mixed quantum state with probability w_i of finding the system in the pure state ψ_i could be obtained by simple summation

$$f(t;\Gamma) = \sum_i w_i f_i(t;\Gamma) \tag{72}$$

and since the Liouville equation (67) is linear, it holds also for densities corresponding to mixed quantum states. Moyal[28] later obtained Wigner's Γ-space densities by a derivation which clarified their content. In particular, Moyal found that $f(t;\Gamma)$, as defined by Wigner, could be used to calculate all quantum mechanical expectation values (caret denotes quantum operator)

$$\sum_i w_i \langle\psi_i|\hat{G}|\psi_i\rangle = \int d\Gamma\, f(t;\Gamma) G(\Gamma) \tag{73}$$

provided only that the quantum mechanical operator $\hat{G}$ was chosen according to the Weyl correspondence

$$\hat{G} = (2\pi)^{-2n} \int \cdots \int dx_1 \cdots dy_n \times g(x_1,\ldots,y_n) \exp\left[i \sum_{l=1}^{n} (x_l \hat{r}_l + y_l \hat{p}_l) \right] \tag{74}$$

$$g(x_1,\ldots,y_n) = \int \cdots \int dr_1 \cdots dp_n\, G(\Gamma) \exp\left[-i \sum_{l=1}^{n} (x_l r_l + y_l p_l) \right] \tag{75}$$

It should be noted that the Weyl correspondence transforms the classical variable $\varphi(r)p^m$ according to

$$\varphi(r)p^m \to \sum_{k=0}^{m} \binom{m}{k} (\hat{p})^k \varphi(r) (\hat{p})^{m-k} \tag{76}$$

which can be immediately generalized to obtain an explicit expression for all quantum operators if only the corresponding classical variable is analytic in the momenta.

If we recall now that quantum mechanics demands that all physical properties correspond to Hermitian operators in the space of quantum states but does not distinguish among the many possible ways of constructing such operators from the corresponding classical Γ-space function, we see that the Weyl correspondence imposed above is quite a natural way of satisfying the Hermitivity requirement and is really no limitation at all. Thus we have here a formulation of quantum dynamics in Γ-space upon which we can base a theory of generalized Brownian motion in exactly the same way as illustrated

for classical systems in previous sections. Rather than repeating the formal derivations, we shall here focus on the advantages gained as compared to the matrix representation discussed in the first part of this section and on the remaining quantum effects.

Obviously, there are practical reasons to prefer a Hilbert space of Γ-space functions. Although a Hilbert space of matrices corresponding to quantum observables is a useful theoretical construct, the practical problems of calculating scalar products and expanding in terms of a chosen set of basis matrices are likely to be considerable and more difficult than the corresponding problems in a Hilbert space of Γ-functions. Moreover, it is certainly an advantage to include both the classical and the quantum theory in the same Hilbert space so that the asymptotic relationship of the two theories can be studied simply by taking the limit as $\hbar$ becomes small. Clearly, the series expansion (68) of the quantum Liouville operator is particularly convenient for the estimation of the magnitude of quantum dynamical corrections in terms of $\hbar^2$ for various potentials. Note, for example, that linear or harmonic potentials lead to no dynamical quantum corrections at all. For other potentials perturbation methods based on the smallness of $\hbar^2$ may be applied.

It should be pointed out that there are also static quantum corrections which reside in the initial form of the density, $f(0; \Gamma)$. We note that if $f(t; \Gamma)$ is to represent a single experiment or an ensemble of experiments, then it must always satisfy the Heisenberg uncertainty relations, which impose a minimum dispersion on the density. This is automatically taken care of if we construct $f(0; \Gamma)$ from a pure or mixed quantum state according to the prescription given by Wigner. The resulting density will be real, but, in general, not positive definite. Thus it is not a probability density in the classical sense, although it can be used to calculate all expectation values of the properties of the system.

Clearly, we can consider $f(t; \Gamma)$ as the state vector in the unit metric and in analogy with the discussion of classical systems transform to a Hilbert space of another appropriate metric. The equation of motion for the reduced state vector and the corresponding linear transport equation and bare nonlinear transport equations follow as before, while the exact nonlinear transport equations must be obtained by a fluctuation renormalization of the bare equations. The problem encountered in obtaining an exact quantum mechanical Langevin equation within the matrix representation is present here also. Even the density $f(\Gamma)$ corresponding to a pure quantum state contains dispersion.

With respect to the Fokker–Planck equation the situation is significantly improved since the reduced density $P_\infty f(t; \Gamma)$ obviously can be mapped into a density $g(t; \mathbf{a})$ by the generalized coordinate transformation proposed by Zwanzig. Although we shall not undertake to do so here, it should be possible

to generalize the derivation so as to obtain the corresponding equation of motion for the quantum mechanical density $g(t; \mathbf{a})$. We would, of course, have to keep in mind that $g(t; \mathbf{a})$ is not a probability density in the classical sense since it may take on negative values and, moreover, only a limited class of functions $g(0; \mathbf{a})$ can properly represent an experimental ensemble.

One may perhaps be tempted to neglect the restrictions on $f(t; \Gamma)$ to define and obtain Langevin equations exactly as in the classical case by considering dispersionless initial conditions

$$f(0; \Gamma) = \delta(\Gamma - \Gamma_0) \tag{77}$$

However, even so we would not be able to obtain nonlinear Langevin equations since the quantum dynamics does not preserve the δ-function property. That is, choosing initial conditions as in (77), $f(t; \Gamma)$ at a later time is not generally a δ-function. This is a reflection of the fact that the quantum operator $i\mathscr{L}$ does *not* have the distributive property satisfied by the classical Liouville operator. Thus the quantum dynamics of Γ-space densities cannot be broken up into a sum over independently developing trajectories as in the classical theory, but involve the fluctuations in a more fundamental way which can be described as an interaction among the classical trajectories. This will clearly require nonlinear Langevin equations to be obtained by fluctuation renormalization even in the case when the quantum restrictions are neglected and δ-function initial conditions assumed.

5. CONCLUDING COMMENTS

The unified derivation of the generalized Brownian motion theory presented here can be summarized in a flow chart as in Fig. 1. The original results of Zwanzig and Mori now fit together into a single structure, exposing their complementarity and common root. It is, of course, possible to apply projection operators directly to Hamilton's or Heisenberg's equations of motion for the time-dependent property vectors and thus obtain Langevin and transport equations.[29] But the Liouville equation is a better starting point because it is always concerned with a single state vector and it yields, as we have shown here, all of the results, including the master and Fokker–Planck equations, very easily. The key point of this derivation which has not been fully exploited before is the unity and simplification achieved by bringing both the state of the system and its properties into the same Hilbert space from which the desired information is extracted by taking a scalar product between the state and property vectors.

On the basis of this general derivation we have discussed a number of important extensions and limitations of the generalized Brownian motion theory which to a varying degree have not been clearly stated or properly

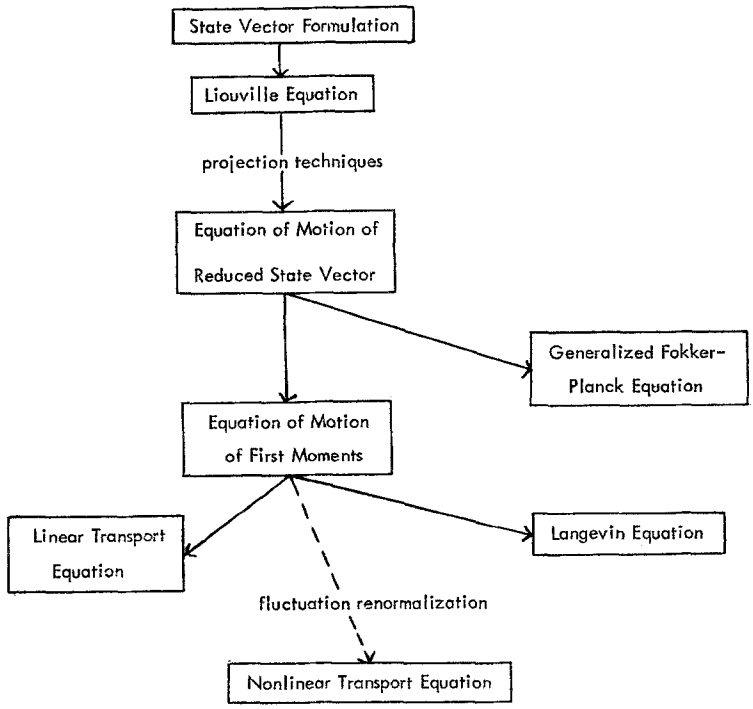

Fig. 1. Diagram illustrating the unified nature of the derivations.

emphasized before. Probably the most important point is the limitations of the basically linear projection operator techniques in the derivation of the very important nonlinear form of the theory. Only the classical Langevin and Fokker–Planck equations can be obtained straightforwardly in the nonlinear formulation. The transport equations, and in the quantum case even the Langevin equation describing single experiment dynamics, must be obtained by decoupling the dynamics of the first moments from that of the statistical fluctuations with the help of a fluctuation renormalization procedure. We have discussed such procedures in a previous article.[23]

In the case of the quantum Fokker–Planck equation there is a problem due to the fact that the chosen properties will generally not commute. For this reason the classical derivation does not have a direct analog in the matrix formulation of quantum mechanics. However, we have noted that there is in this respect distinct advantages in using the Wigner–Moyal Γ-space formulation of quantum mechanics as a starting point for the derivation. Note that in the case of a traditional Brownian motion problem, where the chosen properties completely describe a physically separable subsystem, the the reduced Liouville equation itself has the form of a Fokker–Planck

equation if a Γ-space formulation is used. This point has been exploited already by McKenna and Frisch,[30] who used the Husimi transform in a derivation of a quantum mechanical Fokker–Planck equation for a Brownian particle moving in a fluid.[31]

We have also shown here that the derivations can be extended in a straightforward manner to the case when time-dependent external forces are present, with only minor complications. The reduced Liouville equation for the case of driven transport was obtained before by Muriel and Dresden.[32] The point to note here is that there is in general no stationary equilibrium metric. Thus we may want to stay with the unit metric or work with a non-Hermitian Liouville operator in a nonstationary metric.

What we have presented here is an exact but formal generalization of traditional Brownian motion theory obtained by straightforward application of projection techniques in Hilbert space. This part of the theory is clear and unambiguous and very useful both conceptually and practically. Unfortunately, the simple exact methods used above do not suffice to obtain the nonlinear theory except for the classical Langevin equations. Other methods, most likely to be in the form of approximations, are needed to complete the theory. The conceptual advantages of starting from microscopic first principles are great but it must be recognized that the formal theory will only provide quantitative predictions after we have solved a whole range of problems that have merely been hinted at here. The explicit evaluation of the transport coefficients in the theory, particularly those that display memory effects, may well be an exceedingly difficult mathematical problem that will force us back to intuitive and empirical approximation schemes.

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REFERENCES

1. S. Chandrasekhar, *Rev. Mod. Phys.* **15**:1 (1943).
2. M. C. Wang and G. E. Uhlenbeck, *Rev. Mod. Phys.* **17**:323 (1945).
3. M. S. Green, *J. Chem. Phys.* **20**:1281 (1952); **22**:398 (1954).
4. M. Lax, *Rev. Mod. Phys.* **32**:25 (1960); **38**:359 (1966); **38**:541 (1966).
5. R. Zwanzig, *J. Chem. Phys.* **33**:1338 (1960); *Lectures in Theoretical Physics*, ed. by W. E. Brittin, B. W. Downs, and J. Downs (Interscience, New York, 1961), Vol. III, pp. 106–141.
6. R. Zwanzig, *Phys. Rev.* **124**:983 (1961).
7. H. Mori, *Progr. Theor. Phys.* **33**:423 (1965); **34**:399 (1965).
8. K. Kawasaki, *Phys. Rev.* **150**:291 (1966); *Ann. Phys.* **61**:1 (1970).

9. B. J. Berne and G. D. Harp, *Advan. Chem. Phys.* **XVII**:63 (1970).
10. A. Z. Akcasu and J. J. Duderstadt, *Phys. Rev.* **188**:479 (1969).
11. D. Forster and P. C. Martin, *Phys. Rev. A* **8**:1575 (1970).
12. H. Mori, *Progr. Theor. Phys.* **49**:1516 (1973).
13. H. Mori and H. Fujisaka, *Progr. Theor. Phys.* **49**:764 (1973).
14. T. Keyes and I. Oppenheim, *Phys. Rev. A* **8**:973 (1973).
15. R. Kapral and M. Winberg, *Phys. Rev. A* **8**:1008 (1973); **9**:1676 (1974).
16. D. Bedeaux and P. Mazur, *Physica* **73**:431 (1974).
17. H. Haken, *Z. Phys.* **219**:411 (1969).
18. F. Haake, *Z. Phys.* **223**:364 (1969).
19. K. Kawasaki and J. D. Gunton, *Phys. Rev. A* **8**:2048 (1973).
20. C. R. Willis and R. H. Picard, *Phys. Rev. A* **9**:1343 (1974).
21. B. O. Koopman, *Proc. Natl. Acad. Sci.* **17**:315 (1931).
22. J. von Neumann, *Ann. Math*, **33**:587 (1932).
23. K. S. J. Nordholm and R. Zwanzig, *J. Stat. Phys.* **11**:143 (1974).
24. K. S. J. Nordholm, Nonlinearities and Fluctuations in Microscopic Transport Theory, Diss. Univ. of Maryland, May 1972.
25. R. Kubo, *J. Phys. Soc. Japan* **12**:570 (1957); R. Kubo, M. Yokota, and S. Nakajima, *J. Phys. Soc. Japan* **12**:1203 (1957).
26. G. L. Sewell, *Physica* **31**:1520 (1965); **34**:493 (1967).
27. E. Wigner, *Phys. Rev.* **40**: 749 (1932).
28. J. E. Moyal, *Proc. Camb. Phil. Soc.* **45**:99 (1949).
29. K. Kawasaki, *J. Phys. A* **6**:1289 (1973).
30. J. McKenna and H. L. Frisch, *Phys. Rev.* **145**:93 (1966).
31. J. L. Lebowitz and E. Rubin, *Phys. Rev.* **131**:2381 (1963); J. L. Lebowitz and P. Resibois, *Phys. Rev.* **139**:A1101 (1965).
32. A. Muriel and M. Dresden, *Physica* **43**:449 (1969).