BROWNIAN MOTION AND WEAK COUPLING IN CLASSICAL AND QUANTUM SYSTEMS

by

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B.S. Physics, Universidad Autonoma Metropolitana - Mexico (1982)

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ABSTRACT

The relaxation properties of a small system weakly coupled to a large system, which acts as a heat bath are studied. Both classical and quantum system are considered. The Brownian motion of a heavy particle immersed in a fluid of light particles, is treated separately. Our results are equations of motion for the reduced distribution function (classical) and for the reduced density matrix (quantum) of the small system. To lowest non-trivial order in the coupling parameter, we obtain generalized Fokker-Planck equations and generalized Master equations, respectively. The main assumption of this work is that the relaxation time of the bath must be shorter than the relaxation time of the system, in interaction with the bath.

These equations are derived, in general, using projection operator techniques; these projection operators are chosen such that: 1) correct thermal equilibrium of the small system is ensured; 2) streaming and dissipative contributions are separated; and 3) the fast variables are eliminated.

In the weak coupling case, two specific examples are treated in detail. We consider a harmonic oscillator linearly coupled to a heat bath, for the classical case, and demonstrate that there is a dynamic frequency shift as well as a statistical shift of the oscillator frequency. For the quantum case, we treat a two level system with linear coupling to the bath as well; the relevance of this problem to the study of quantum tunneling in condensed media is discussed. In the quantum Brownian motion study, we derive the Fokker-Planck equation for the reduced density matrix of the heavy particle using both Wigner function and density matrix approaches. The Langevin equation for the Brownian particle momentum is derived in the Wigner representation.

Unlike previous treatments, special initial states for the overall system-bath composite are not assumed; furthermore, higher order corrections to the equations can be obtained in a systematic fashion.

Thesis Supervisor: Dr. Irwin Oppenheim

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A mi esposa, Gabriela,

con todo mi amor.
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TABLE OF CONTENTS

Abstract ................................................................. 2
Dedication ................................................................. 3
Acknowledgements ...................................................... 4

CHAPTER I INTRODUCTION ........................................... 7

CHAPTER II WEAK COUPLING IN CLASSICAL AND
QUANTUM SYSTEMS .................................................. 14

II. A. WEAK COUPLING IN CLASSICAL SYSTEMS ............... 15
II. A. 1. Projection Operator and Exact Dynamic equations .... 15
II. A. 2. A Generalized Fokker-Planck Equation ................. 23
II. A. 3. Harmonic Oscillator with Linear Coupling ......... 31
II. B. WEAK COUPLING IN QUANTUM SYSTEMS ............. 38
II. B. 1. Projection Operator and Exact Dynamic equations .... 38
II. B. 2. A Generalized Master Equation ......................... 43
II. B. 3. Two Level System with Linear Coupling.
Application to Tunneling Processes in Condensed Media ........ 49

II. C. COMPARISON TO EARLIER WORK ......................... 64
II. D. REMARKS ............................................................ 72

CHAPTER III. BROWNIAN MOTION IN CLASSICAL AND
QUANTUM SYSTEMS .................................................. 75

III. A. REVIEW OF CLASSICAL BROWNIAN MOTION .......... 77
III. A. 1. Conditions for Brownian Motion .................... 77
III. A. 2. A Derivation of the Fokker-Planck Equation ....... 78
III. B. QUANTUM BROWNIAN MOTION.
WIGNER FUNCTION APPROACH ................................. 84
CHAPTER I

INTRODUCTION.

The theoretical description of the relaxation properties of weakly coupled systems has long been of central importance to the understanding of time dependent, irreversible phenomena\textsuperscript{1-35}. In problems as diverse as Brownian motion, kinetics of chemical reactions, fluctuations in hydrodynamics and spin relaxation to mention a few, reduced descriptions in terms of Master or Fokker-Planck equations for the system distribution function, or in terms of Langevin equations for the system dynamical variables, have been possible because of either weak coupling of some variables of the system to other variables within the system, or weak coupling of the system to an external bath. An essential feature for these reduced descriptions is the separation of time scales, namely the time dependence of the relevant variables is on a slow time scale compared to the time dependence of the other variables within the system or in the bath.

A first principles study of weakly coupled systems based on the dynamical laws of classical and quantum mechanics is important for several reasons. First of all, it justifies the phenomenological stochastic theories from which the equations mentioned before originated\textsuperscript{10-12}. Second, it enables a determination of the parameters that characterize the irreversible behavior, such as diffusion coefficients, in terms of microscopic variables. Once the limitations of those treatments have been understood, insight as to how to deal with more complicated problems is gained; of particular interest in this regard has been the extension of the description to cases where the clear cut separation of time scales does not hold.
Along the lines of first principles studies the modern treatment of weakly coupled systems was initiated with the seminal works by van Hove\textsuperscript{1}, Prigogine and collaborators\textsuperscript{2}, Montroll\textsuperscript{3} and Zwanzig\textsuperscript{4,5}. These treatments are based on splitting the system Hamiltonian, $H$, into two parts, $H_0$ and $\lambda V$ and discussing the decay of the system to equilibrium with respect to the Hamiltonian $H_0$ due to the perturbation $\lambda V$, using the weak coupling approximation. The results of these studies are master equations for the diagonal elements of the density matrix of the system. All these descriptions use the assumption that initially ($t = 0$), there are random phases in the system. Parallel to these efforts, the studies on spin relaxation by Wangsness and Bloch\textsuperscript{6} and Redfield\textsuperscript{7} must also be mentioned.

In this thesis our interest is in the properties of a small system of few degrees of freedom in weak interaction with a large, macroscopic system or heat bath. We will refer to the former as the "system" and the latter as the "bath", while the composite system plus bath is the "overall system". We develop a general scheme for obtaining an equation of motion for the reduced probability distribution (classical case) and for the reduced density matrix (quantum case) of the system. Our work builds on the previous studies on classical Brownian motion of Mazur and Oppenheim\textsuperscript{8} and van Kampen and Oppenheim\textsuperscript{9}.

Interest in the properties of these systems has arisen in fields of research as varied as vibrational relaxation in polyatomic molecules\textsuperscript{13,14}, atoms in the presence of a radiation field\textsuperscript{15,16}, and quantum tunneling in condensed media\textsuperscript{17-28}. A variety of techniques have been used to study these and related problems such as projection operators\textsuperscript{21,22}, cumulant expansions\textsuperscript{13,14,18-20}, Feynmann path integrals\textsuperscript{23-28}, and ad-hoc transformations for the particular models that we describe below\textsuperscript{29-35}. The results of these investigations have yielded master or generalized Fokker-Planck equations for the system distribution function or density matrix, or generalized Langevin equations for the dynamical variables of the system. The properties of interest are the mode of decay of the small system to equilibrium
and the form of its equilibrium distribution. In almost all cases, special forms for the
system, the bath and the coupling interaction between them have been chosen. The system,
understandably, has been considered to be a two level system or a harmonic oscillator; the
bath has been chosen as a collection of uncoupled harmonic oscillators; and the coupling
interaction a product of linear functions of the bath and system coordinates. As an extra
assumption, all these treatments require special initial states for the overall system; most
frequently it is assumed, similar to the initial random phases, that the system and bath are
initially uncorrelated, the latter being in canonical equilibrium by itself. Unfortunately, there
is no reason to believe that these initial conditions are appropriate for the treatment of these
systems; partial motivation for the present work is to avoid this assumption.

Since we are attempting a first principles derivation we must start from the
Liouville equation for the distribution function, or density matrix, \( \rho(t) \), for the overall
system: the reduced description of the system must be extracted from the Liouville equation
by eliminating in a suitable way the bath degrees of freedom.

Our treatment is based on the premise that due to the large number of degrees of
freedom of the bath the overall system relaxes to equilibrium. In the absence of the
interaction the isolated bath also relaxes to equilibrium but the isolated system does not.
Therefore, in the presence of the interaction, weak or strong, the equilibrium distribution
for the system is given by its \textit{reduced} form:

\[
W_e = \int dX_B \rho_e \quad \text{(classical)}
\]

\[
W_e = \text{Tr}_B \rho_e \quad \text{(quantum)}
\]

that is, integrating out the bath degrees of freedom from the overall equilibrium probability
distribution or density matrix, \( \rho_e \). As in all cases, relaxation to equilibrium is valid for
reduced quantities involving small number of degrees of freedom. The total distribution
function does not decay to equilibrium either for the overall system or for the isolated bath\textsuperscript{37}.

The technique, then, consists of defining a projection operator $\mathcal{P}$, that while integrating out the bath degrees of freedom, insures that the reduced distribution function of the system relaxes to the appropriate form given by Eqs(1) or (2). The main property of the projection operator is

$$\mathcal{P}\rho_e = \rho_e,$$  \hspace{1cm} (3)

i.e. the overall distribution function is projected onto itself. With standard projection operator transformations we obtain a reduced Liouville equation for the system\textsuperscript{4,48,52}; this equation consists of two parts. One accounts for the deterministic motion of the system and contains the Liouvillian of the isolated system plus corrections due to the interaction with the bath; we call this term streaming, systematic or Euler. The remaining terms must therefore be responsible for the dissipation and relaxation to equilibrium; we call this term dissipative. The distinction between these terms can be made since both terms vanish \textit{separately} in equilibrium, i.e. when $W_e$ as given by Eqs(1) and (2) is substituted in the equation. The above connotation is inspired by the more phenomenological transport equations\textsuperscript{10-12}, where the dissipative term is truly irreversible (in the sense of being non-time reversal invariant). In our case, of course, such a property is only achieved once approximations and appropriate assumptions have been introduced.

The approximations consist of a systematic expansion in powers of the coupling parameter of the interaction between the system and the bath; here, we discriminate between two cases: a) the interaction potential is weak and a strength parameter, $\lambda$, is associated with it; we refer to this case as "weak coupling" and it is studied in Chapter II; and b) the coupling parameter arises from the different magnitude of the dynamical variables; this case is denoted as "Brownian motion" and the small parameter is the ratio of the mass of the
fluid particles to the mass of the heavy particle, i.e. $\epsilon^2 = m/M$; this special case is treated in Chapter III.

We recognize essentially three characteristic time scales for the overall system: the relaxation time for the isolated bath (or in the presence of the Brownian particle fixed at some position in space), $\tau_B$; the characteristic or natural time for the isolated system, $\tau_S$; and the relaxation time for the system in weak interaction with the bath, $\tau_R$. The main assumption of this work is that the time $\tau_B$ is very short; for classical systems this is usually a reasonable assumption, but for quantum ones it can only be correct for not too low temperatures. The time $\tau_R$, proportional to $\lambda^{-2}$ or $\epsilon^{-2}$, is much longer than $\tau_B$; this is the essential separation of time scales necessary for this and other similar theories to provide a simple reduced description\textsuperscript{8,9}. An improvement of this treatment is that the time $\tau_S$ may be comparable to or appreciably longer than $\tau_B$.

A very important point that must be stressed since it distinguishes our formalism from virtually all previous treatments, is that we do not assume a specific form for the initial ($t = 0$) overall distribution function or density matrix. As we said before, there is no reason to believe that initial random phases or system and bath initially uncorrelated correspond to realistically initially prepared systems encountered in the problems to which these theories are supposed to describe. We show that under the assumption that $\tau_B$ is short, the initial form of the distribution function becomes irrelevant. Indeed, it is the form of the distribution function for times longer than a molecular time (say $\sim 10^{-12}$ sec), but shorter than $\lambda^{-2}\tau_B$, which is important for deriving the relaxation equations of interest. It is worth mentioning that most of the theories\textsuperscript{5,48-52} that address the problem in which $\tau_B$ is no longer small are possible because of special initial conditions such as the one outlined above; as we will briefly discuss our treatment casts doubt on these studies. This is certainly a point for further research.
Hence, for times $t \gg \tau_B$, the equation of motion for the reduced probability distribution or density matrix is a closed, linear time-local equation which can be systematically expanded to arbitrary order in $\lambda$ or $\varepsilon$. For the weak coupling case, Chapter II, to order $\lambda^2$ we obtain a generalized Fokker-Planck equation; for the quantum problem we call this equation a generalized Master equation to distinguish it from the classical case. They are generalized in the sense that there is no assumption on the system time scale, $\tau_S$, and in the quantum case also because the equation involves both diagonal and off-diagonal elements of the density matrix. For $\tau_S \gg \tau_B$ we recover the standard Fokker-Planck equations, with the additional result that the streaming term is not only the Liouvillian of the isolated system but must also contain $\lambda^2$ corrections due to the interaction with the bath.

Regarding the Brownian motion problem, to order $\varepsilon^2$ we obtain the corresponding classical and quantum Fokker-Planck equations; we present two derivations of the latter for the quantum case: one using the general projection operator utilized in Chapter II; and another one, using a different projection operator but with the same property given by Eq(3), in which we extend the technique for eliminating fast variables previously developed for the study of classical Brownian motion; this derivation is also reviewed in Chapter III. The latter technique is similar to the other, but from the outset, exploits the fact that the bath time dependence is faster than the system time dependence; in this respect it is more advantageous than the other technique; its disadvantage, only for the quantum case, is that it does not completely separate the streaming terms, although the difference is not serious for this particular case since those corrections only appear in higher orders of $\varepsilon$. To order $\varepsilon^2$ there is no difference.

It should be recognized that application of the present formalism to classical systems is clearer and faces less difficulties than when applied to quantum systems.
Besides the technical aspects*, the most important problem is the role of the temperature in quantum systems that among other complications implies an extra time scale. This is not surprising since at low temperatures pure quantum effects may become dominant and one should not expect that a simple relaxation theory, based predominantly on mechanistic concepts, applies. Our treatment applies when the time scale of the pure quantum effects is shorter than the relaxation time of the system. Nevertheless the precise difference between "low" and "high" temperatures depends on the problem at hand.

As a matter of organization, the thesis is divided into Chapters, denoted by roman numerals; the Chapters into Parts, denoted by capital letters; and the Parts into Sections, denoted by arabic numerals. Equations are numbered per Section and the Chapter number and Part letter are included when necessary; for instance, Eq(II.B.2.3) refers to equation 3 of Section 2 of Part B of Chapter II. As has been already mentioned, Chapter II deals with the weak coupling case and Chapter III deals with the Brownian motion problem. Three appendices complement the text: Appendices A and C are included to outline tedious calculations and in Appendix B we briefly review the Wigner equivalent formalism used in Chapter III.

* Technical aspects such as to whether the equation represents a quantum Markovian process or not, or as to how construct multitime correlation function are problems not only of our treatment but of all similar ones. For a discussion of these points, see Refs. 56 and 57.
CHAPTER II

WEAK COUPLING IN CLASSICAL AND QUANTUM SYSTEMS.

This Chapter deals with the weak coupling of a small system with a heat bath. As we explained in the Introduction this is the case in which the interaction potential, between the system and the bath, is weak and a parameter, $\lambda$, measures its strength. The Chapter is divided into four parts: Parts A and B deal with systems that obey classical and quantum mechanics respectively*; in Part C a brief comparison to earlier theories is made; and in Part D we highlight certain aspects of the theory and some comments regarding future research are also included. Parts A and B are divided in the same way: in Sections 1 we describe the overall system under consideration, the projection operator and its essential properties and derive exact equations for the projected distribution function (Part A) and for the projected density matrix (Part B). In Sections 2 the appropriate approximations and assumptions are introduced to obtain a generalized Fokker-Planck equation for the classical case and a generalized Master equation for the quantum case. Sections 3 are devoted to examples that serve to further clarify certain aspects of the theory, especially the time dependence: in Part A a harmonic oscillator weakly coupled to the bath by a potential linear in the system coordinates is considered, and in Part B we study a two level system with linear coupling as well and its relevance in the study of quantum tunneling in condensed media is discussed.

II. A. WEAK COUPLING IN CLASSICAL SYSTEMS.

II. A. 1. Projection operator and exact dynamic equations.

In this section we introduce a projection operator that ensures the correct equilibration and allows us to separate the Liouville equation into Euler (streaming) and dissipative parts.

We consider a classical overall system consisting of a system with a small number of degrees of freedom interacting with its environment. The latter, denoted the bath, has a large number of degrees of freedom. The Hamiltonian of the overall system, i.e. system plus bath, is

\[ H = H_S(R,P) + H_B(r^N_p^N) + \lambda \Phi(R,r^N) \]  \hspace{1cm} (1.1)

where,

\[ H_S = \frac{p^2}{2M} + V(R) \]  \hspace{1cm} (1.2)

is the Hamiltonian of the system, and \( P \) and \( R \) denote the small number of momenta and coordinates;

\[ H_B = \frac{p^2}{2m} + U(r^N) \]  \hspace{1cm} (1.3)

is the Hamiltonian of \( N \) bath particles interacting via the potential \( U(r^N) \); \( \Phi(R,r^N) \) is the interaction potential between the system and the bath, depending only on their position coordinates, and \( \lambda \) is the strength of this interaction. The phase point of the bath is denoted by \( X=(r^N,p^N) \).
In the absence of interaction between the system and bath \((\lambda = 0)\), the bath will relax towards equilibrium, due to its large number of degrees of freedom, with characteristic time \(\tau_B\); the system, however, will not relax to equilibrium due to its small number of degrees of freedom. The characteristic time of the system motion is \(\tau_S\). When the interaction is turned on \((\lambda \neq 0)\), the overall system will relax to equilibrium. If the interaction is sufficiently weak, the relaxation time, \(\tau_R\), will be much longer than \(\tau_B\). The relaxation for the overall system \((\lambda \neq 0)\) and for the isolated bath \((\lambda = 0)\) has to be understood in the sense that reduced quantities depending on a small number of degrees of freedom, will relax towards their equilibrium values\(^{37}\). Since the overall system is closed, the natural equilibrium distribution function should be the microcanonical one, with fixed energy, number of particles and volume; however, as long as we are interested only in reduced quantities we can as well use the distribution function in its canonical form with fixed temperature, number of particles and volume, where the temperature is that of the different subsystems of the overall system, and has to be consistent with the microcanonical energy. In equilibrium, of course, the temperature is the same throughout the whole system\(^{36}\).

Before proceeding with the analysis of the time-dependence of the distribution functions of the system, we present the equilibrium forms for these functions. The equilibrium distribution function for the overall system is

\[
\rho_e(P,R,X) = \frac{e^{-\beta H}}{\int dX dPdR e^{-\beta H}} ;
\]

(1.4)

the reduced equilibrium function for the system is
\[ W_d(P, R) \equiv \int dX \rho_d(P, R, X) = \frac{e^{-\beta H_S} \int dX e^{-\beta(H_B + \lambda \Phi)}}{\int dPdR e^{-\beta H_S} \int dX e^{-\beta(H_B + \lambda \Phi)}}. \]  

(1.5)

We define the quantity \( \omega(R, \lambda) \) by

\[
e^{-\beta \lambda \omega(R, \lambda)} \equiv \frac{\int dX e^{-\beta(H_B + \lambda \Phi)}}{\int dX e^{-\beta H_B}} = \int dX \rho_B e^{-\beta \lambda \Phi} \equiv \langle e^{-\beta \lambda \Phi} \rangle_B
\]

(1.6)

where \( \lambda \omega(R, \lambda) \) is the potential of mean force due to the interaction of the system with the bath and

\[
\rho_B = \frac{e^{-\beta H_B}}{\int dX e^{-\beta H_B}} \quad \text{(1.7)}
\]

is the equilibrium distribution function of the isolated bath. Eqs (1.4) and (1.5) can be rewritten as

\[
\rho_d(P, R, X) = \frac{\rho_B e^{-\beta(H_S + \lambda \Phi)}}{\int dPdR e^{-\beta(H_S + \lambda \omega)}} \quad \text{(1.8)}
\]

and

\[
W_d(P, R) = \frac{e^{-\beta(H_S + \lambda \omega)}}{\int dPdR e^{-\beta(H_S + \lambda \omega)}}. \quad \text{(1.9)}
\]

Finally, the conditional equilibrium function for the bath for fixed \( R \) and \( P \) is given by

\[
\tilde{\rho}^e(R, X) = \frac{\rho^e}{W_e} = \rho_B e^{-\beta \lambda \Phi} e^{\beta \lambda \omega}
\]

(1.10)
where
\[ \int dX \tilde{\rho}_e = 1 \] (1.11)

and
\[ \rho_e = \tilde{\rho}_e \mathcal{W}_e \] (1.12)

exactly.

The time evolution of the probability distribution function of the overall system is given by the Liouville equation,
\[ \frac{\partial}{\partial t} \rho(R,P,X;t) = L \rho(R,P,X;t) \] (1.13)

where L is the total Liouvillian given by
\[ L = L_S + L_B + \lambda L_1 = L_0 + \lambda L_1 \] (1.14)

The isolated system Liouvillian is
\[ L_S = -\frac{P}{M} \cdot \nabla_R + \nabla_R V(R) \cdot \nabla_P \] (1.15a)

the isolated bath Liouvillian is
\[ L_B = -\frac{p^N}{m} \cdot \nabla_r \cdot U(r^N) \cdot \nabla_P \] (1.15b)

and the interaction Liouvillian is
\[ L_1 = \nabla_r \Phi \cdot \nabla_P \] (1.15c)

The equation for the reduced probability distribution function of the system,
\[ W(R,P;t) \equiv \int dX \rho(X,R,P;t) \] (1.16)

is obtained by integrating Eq.(1.13) over X, i.e.
\[ \frac{\partial}{\partial t} W(R,P;t) = L_S W(R,P;t) + \lambda \int dX \ L_1 \rho(X,R,P;t) \] (1.17)

Our goal is then to use projection operator techniques, in such a way, that under suitable assumptions and approximations, Eq.(1.17) becomes an equation for \( W(t) \) only and
its RHS is separated into streaming and dissipative parts. The conditions that these terms should satisfy are:

i) In equilibrium, the Euler and dissipative terms must be zero independently; that is when $W(t) = W_e$, where $W_e$ is given by Eq(1.9). Since the correct equilibrium distribution function of the system is given by Eq(1.9), of which only the $\lambda^0$ corresponds to the canonical equilibrium of the system by itself, the systematic or Euler term must include not only the Liouvillian of the isolated system, but also terms that should account for the corrections due to the interaction with the bath; and

ii) When $t \to \infty$, the dissipative term should vanish and should drive $W(t)$ towards $W_e$. In other words, as $t \to \infty$, the stationary solution should be approached.

The first condition is actually a guide for the choice of the projection operator and will be shown to hold by construction. Now, for the dissipative term to deserve its name, as well as for the second condition to hold, certain assumptions are required as we shall see in the next section.

Presumably, one could construct several projection operators to achieve the separation of terms and to satisfy the above conditions. Since we will assume that the bath relaxation occurs on a fast time scale, and we want to obtain a useful expansion in powers of $\lambda$, the projection operator must also eliminate the fast modes of the bath. This will be made clear below and in the next Section.

The appropriate projection operator is defined by

$$P B = \tilde{\rho}_e \int dX B$$

(1.18)

where $B$ is an arbitrary dynamical variable and $\tilde{\rho}_e$ is the conditional probability distribution given by Eq(1.10). The operators $P$ and $Q = 1 - P$, are projection operators since $P^2 = P$.

We now introduce the quantities
\[ \dot{y}(t) = P \rho(t) = \tilde{\rho}_e W(P, R, t) \]  
(1.19)

and

\[ z(t) \equiv (1 - P) \rho(t) \equiv Q \rho(t) . \]  
(1.20)

With the choice Eq(1.18) for the projection operator we will see that \( z(t) \) not only vanishes in equilibrium but is also negligible, to lowest order in \( \lambda \), for times longer than the relaxation time of the bath, \( \tau_B \). While the first property is necessary to satisfy conditions i) and ii), the second one is essential for the proper treatment of the fast modes of the bath. Again, we defer further comments for the next Section.

The time derivatives of \( y(t) \) and \( z(t) \) obey the equations

\[ \dot{y}(t) = \tilde{\rho}_e \frac{\partial}{\partial t} W(t) \]

\[ = \tilde{\rho}_e \left( L_S W(t) + \lambda \int dX \nabla_R \Phi \tilde{\rho}_e \nabla_P W(t) + \lambda \nabla_P \int dX \nabla_R \Phi z(t) \right) \]

and

\[ \dot{z}(t) = QL y(t) + QL Q z(t) \]

(1.21b)

which follow from Eq(1.13) and the facts that

\[ PL_B = 0 \]

\[ PL_\beta = \tilde{\rho}_e L_S \int dX B \]

\[ PL_L B = \tilde{\rho}_e \int dX \nabla_R \Phi \cdot \nabla_P B \]

\[ \int dX y(t) = W(t) \]

\[ \int dX z(t) = 0 . \]

(1.22)

It follows from the definition of \( \tilde{\rho}_e \), Eq(1.10) that

\[ \nabla_R \int dX \tilde{\rho}_e = 0 = - \beta \int dX \tilde{\rho}_e (\lambda \nabla_R \Phi - \lambda \nabla_R \omega) \]

and, thus

\[ 20 \]
\[ \nabla_R \omega = \int dX \tilde{\rho}_e \nabla_R \Phi \]

The term \(QLy(t)\) in Eq(1.21b) becomes
\[
QLy(t) = W(t) \text{QL} \tilde{\rho}_e + Q\tilde{\rho}_e \text{L} W(t)
\]
\[
= W(t) \text{L} \tilde{\rho}_e + \lambda \tilde{\rho}_e \nabla_R (\Phi - \omega) \cdot \nabla_P W(t)
\]
\[
= \lambda \tilde{\rho}_e \nabla_R (\Phi - \omega) \left( \nabla_P + \beta \frac{P}{M} \right) W(t)
\] (1.24)

Thus, Eqs(1.21) become
\[
\frac{\partial}{\partial t} W(t) = \tilde{L}_S W(t) + \lambda \nabla_P \int dX \nabla_R \Phi z(t)
\] (1.25a)

and
\[
\dot{z}(t) = QLQz(t) + \lambda \tilde{\rho}_e \nabla_R (\Phi - \omega) \left( \nabla_P + \beta \frac{P}{M} \right) W(t)
\] (1.25b)

where
\[
\tilde{L}_S = L_S + \lambda \nabla_R \omega \cdot \nabla_P = -\frac{P}{M} \nabla_R + \nabla_R (\nabla + \lambda \omega) \cdot \nabla_P
\] (1.26)

is an effective Liouvillian corresponding to the Hamiltonian
\[
\tilde{H}_S = \frac{P^2}{2M} + V(R) + \lambda \omega(R,\lambda)
\] (1.27)

Eqs.(1.25) are exact. Note that \(\omega(R,\lambda)\) can be expanded as a power series in \(\lambda\) starting with a \(\lambda^0\) term. Since \(P\rho_e = \rho_e, z_e = 0\) and since \(\tilde{L}_S W_e = (\nabla_P + \beta P/M) W_e = 0\), the terms in Eqs(1.25) involving \(W\) and \(z\) are separately equal to zero at equilibrium.

Substitution of the formal solution to Eq(1.25b) into Eq(1.25a) yields
\[
\frac{\partial}{\partial t} W(t) = \tilde{L}_S W(t) + \lambda \nabla_P \int dX \nabla_R \Phi e^{QLQt} z(0) +
\]
\[
+ \lambda^2 \nabla_P \int_0^t d\tau \int dX \nabla_R \Phi e^{QLQ(t-\tau)} \tilde{\rho}_e \nabla_R (\Phi - \omega) \cdot \left( \nabla_P + \beta \frac{P}{M} \right) W(t - \tau)
\] (1.28)
The first term on the RHS of Eq(1.28) is a streaming or Euler term; the second term on the RHS is an initial value term; and the last term, involves a time-dependent correlation function. Again, Eq(1.28) is an exact equation and each term on the RHS is zero in equilibrium.

Since Eq(1.28) is exact, it is equivalent to Newton's laws for the overall system. It is in a suggestive form for reduction to a generalized Fokker-Planck equation when \( \lambda \) is small. This reduction, as well as the systematic expansion in powers of \( \lambda \), are possible because of the special properties of the projection operator, Eq(1.18), and the propagator \( e^{QLQt} Q \).

In the next Section we will explicitly show, from Eq(1.28), that starting from a non-equilibrium initial condition the initial value term becomes negligible for \( t > t_B \) and the last term is zero as \( t \to \infty \) when \( W(t) = W_e \). Because of these properties we identify the first and the last terms as the streaming and dissipative terms respectively, and in this sense, conditions i) and ii) are satisfied. The reversible or irreversible character of these terms, with respect to their time reversal symmetry, will also be discussed in the next Section.

Other choices of projection operators have been previously used but they have limited applicability since they do not satisfy the present conditions. We will return to this point in Part C of this Chapter.

In this section we analyze Eq(1.28) when $\lambda$ is small. We proceed to expand the initial value term and the last term of the RHS of Eq(1.28), in order to show that, under the assumption that the bath relaxes on the the time scale $\tau_B$, the initial condition term becomes negligible for $t > \tau_B$, and the dissipative term drives the system towards equilibrium as $t \to \infty$. Then, we obtain a generalized Fokker-Planck equation valid in the weak coupling limit$^1$ in which $\lambda$ is small, $t$ large, and $\lambda^2t$ of arbitrary size. In carrying out this procedure, we must be careful not to neglect any terms which contribute to the $\lambda^2t$ dependence of $W$. Extensions to higher orders in $\lambda$ are straightforward even though they are complicated algebraically.

We first turn our attention to the initial value term in Eq(1.28), which can be expanded to yield

$$\lambda \nabla_{f} \int dX \nabla_{R} \Phi \ e^{QLQ_{t}} Qz(0) = \lambda \nabla_{f} \int dX \nabla_{R} \Phi \ e^{L_{0}t} Qz(0) +$$

$$+ \lambda^{2} \nabla_{f} \int dX \nabla_{R} \Phi \int_{0}^{t} dt \ e^{L_{0}(t-t)} QL_{-1} Q \ e^{L_{0}t} Qz(0) + O(\lambda^{3}).$$

(2.1)

by iterating the identity

$$e^{(A+B)t} = e^{At} + \int_{0}^{t} dt \ e^{A(t-t)} B e^{(A+B)t},$$

(2.2)

and using the fact that $QL_{0}Q = L_{0}Q$. The propagator $e^{L_{0}t}$ has the property

$$\int dX C e^{L_{0}t} QBz(0) = 0$$

(2.3)

for $t > \tau_B$ where $B$ and $C$ are dynamical variables involving bath coordinates and/or momenta. This property follows from the assumption that the isolated bath relaxes to equilibrium on the time scale $\tau_B$. Although we believe that Eq(2.3) holds for any realistic
initial condition, we can, nevertheless consider a very general class of initial conditions in order to justify the neglect of Eq.(2.1).

Such a class can be written in the general form
\[ \rho(0) = \rho_{Bi}(0) \left( 1 + \lambda f(\Phi, S, \lambda) \right) W(0) \]  \tag{2.4}

where \( \rho_{Bi}(0) \) is the initial distribution function of the bath in the absence of the interaction, \( W(0) \) is the initial reduced probability distribution for the system and \( f(\Phi, S, \lambda) \) is a function depending on the interaction potential and system variables denoted by \( S \); it is assumed to have a convergent series expansion in powers of \( \lambda \) for \( \lambda < 1 \). The only property that \( \rho_{Bi}(0) \) must satisfy is that it has to be a well defined probability distribution (or density matrix in the quantal case); since,
\[ W(0) = \int dX \rho(0), \]  \tag{2.5}

and
\[ \int dX \rho_{Bi}(0) = 1, \]  \tag{2.6}

it follows that
\[ \int dX \rho_{Bi}(0) f(\Phi, S, \lambda) = 0. \]  \tag{2.6}

The assumption that the bath relaxes to equilibrium for times greater than its characteristic time \( \tau_B \) is understood as follows:
\[ \int dX B(X) e^{\frac{L_B t}{\rho_{Bi}(0)}} \rightarrow \int dX B(X) \rho_B , \]  \tag{2.7}

where \( \rho_B \) is the equilibrium distribution function of the bath by itself, Eq.(1.7), and \( B(X) \) is a function depending on few bath degrees of freedom (and usually also a function of system variables).

In analogous fashion a correlation of bath functions behaves as:

24
\[ \int dX \, B_1(X) \, e^{L_B t} \rho_{B_1}(0) B_2(X) \rightarrow \int dX \, B_1(X) \, \rho \, B_2(X, t) \quad t > \tau_B \] (2.8)

\[ \equiv \langle B_1(X, t) B_2(X) \rangle_B = \int dX \, B_1(X, t) \, \rho_B \int dX' \, B_2(X') \, \rho_B = \langle B_1(X, t) \rangle_B \langle B_2(X') \rangle_B, \]

where \( B_2(X, -t) = e^{L_B t} B_2(X) \); the first equality follows after an integration by parts and the last equality follows from the fact that the above function becomes uncorrelated for \( t >> \tau_B \).

Eq(2.3) then follows because of the factor of \( Q \).

We can now show explicitly that the initial value term not only vanishes as \( t \) tends to infinity, but also that it is negligible for the time scale of interest as long as \( \lambda \) is small. Since there is further dependence on \( \lambda \) in \( \tilde{\rho}_e \), we give its expansion in powers of \( \lambda \):

\[ \tilde{\rho}_e = \rho_B \left\{ 1 - \lambda \beta (H_1 - \langle H \rangle_B) + \frac{(\lambda \beta)^2}{2} (H_1^2 - \langle H_1 \rangle_B^2) - 2 H_1 \langle H \rangle_B + 2 \langle H \rangle_B^2 + O(\lambda \beta)^3 \right\} \] (2.9)

We start by looking at the first term of the RHS of Eq(1.28), explicitly proportional to \( \lambda \):

\[ \lambda \nabla_{\tilde{r}}' \int dX \, \nabla \cdot \Phi \, e^{L_\Phi t} Q(0) = \lambda \nabla_{\tilde{r}}' \int dX \, \nabla \cdot \Phi \, e^{L_\Phi t} \left( (\rho_{B_1}(0) - \tilde{\rho}_e) + \lambda \rho_{B_1}(0) f(\Phi, S, \lambda) \right) W(0) \]

\[ \rightarrow \lambda \nabla_{\tilde{r}}' \left( \langle \nabla \cdot \Phi \rangle_B + \lambda \langle \nabla \cdot \Phi \rangle_B f(\Phi, S, \lambda) \right) - \int dX \, \nabla \cdot \Phi \, e^{L_\Phi t} \tilde{\rho}_e e^{L_{\tilde{u}} t} W(0). \]

(2.10)

This term can be seen to vanish with the aid of Eqs(2.9) and (2.6). We also find that for \( t < \tau_B \) it is bounded, from above, by \( \lambda T_1 \), where \( T_1 \) is the maximum value of the absolute value of the term in parenthesis in the RHS of Eq(2.10). The second order term,

\[ \lambda^2 \nabla_{\tilde{r}}' \int dX \, \nabla \cdot \Phi \int_0^t d\tau \, e^{L_\Phi(\tau-t)} Q L_\Phi Q e^{L_\Phi t} Q(0) = \]

\[ = \lambda^2 \nabla_{\tilde{r}}' \int dX \, \nabla \cdot \Phi \int_0^t d\tau \, e^{L_\Phi(\tau-t)} Q(\nabla_n \nabla_n + \nabla_{\tilde{r}}' \nabla_{\tilde{r}}') e^{L_\Phi t} Q(\rho(0) - \tilde{\rho}_e W(0)), \] (2.11)
for $\tau > \tau_B$ vanishes because of the last factor of $Q$, and using Eq(2.8); now, for $t - \tau > \tau_B$ it is zero because of the first factor of $Q$, in analogy to Eq(2.10). For $t > 2\tau_B$ one of the inequalities holds and the whole term vanishes. Therefore, for $2\tau_B > t > \tau_B$ the second order term is bounded by $\lambda^2 \tau_B T_2$, and for $t < \tau_B$ by $\lambda^2 t T_2$, where $T_2$ is the maximum value of the absolute value of the integrand. For higher order terms we follow the same analysis, leading to the following conclusion:

The $n$-th term in the expansion is bounded by $\lambda^n t^{n-1} T_n$ for $t < \tau_B$; for $n \tau_B > t > \tau_B$ it is bounded by $\lambda^n \tau_B^{n-1} T_n$; and it is zero for $t > n \tau_B$. Hence, for $\lambda << 1$, the initial value term vanishes as $t \to \infty$; and since $\lambda \tau_B$ is negligible the whole term in Eq(1.28) can be neglected. (For a similar argument, see Mazur and Oppenheim^b).

The $\lambda$ dependence of the dissipative term i.e. the last term of Eq(1.28) arises from: the explicit factor of $\lambda^2$; the propagator $e^{QLQ_{\tau}}$; the distribution function $\rho e$; the potential of mean force $\omega$; and the distribution function $W(t - \tau)$. The propagator is handled in analogous fashion to the initial value term, yielding:

$$
\lambda^2 \nabla_P \int_0^t d\tau \int dX \nabla_R \Phi e^{QLQ_{\tau}} \rho e \nabla_R (\Phi - \omega) \cdot (\nabla_P + \beta \frac{P}{M}) W(t - \tau) =
$$

$$
= \lambda^2 \nabla_P \int_0^t d\tau \int dX \nabla_R \Phi e^{L_S + L_B \tau} \rho e \nabla_R (\Phi - \omega) \cdot (\nabla_P + \beta \frac{P}{M}) W(t - \tau) +
$$

$$
+ \lambda^3 \nabla_P \int_0^t d\tau_1 \int_0^{\tau_1} dX \nabla_R \Phi e^{L_S + L_B (\tau - \tau_1)} Q(L_1 - \nabla_R \omega \cdot \nabla_P) Q \times
$$

$$
\times e^{L_S + L_B \tau_1} \rho e \nabla_R (\Phi - \omega) \cdot (\nabla_P + \beta \frac{P}{M}) W(t - \tau) + O(\lambda^4)
$$

(2.12)

(Notice that in contrast to Eq(2.11) here we have expanded around $(L_S + L_B)$ instead of $(L_S + L_B)$). The behavior of each term in the above expansion is the same as with the initial value term, that is each integrand will vanish for times sufficiently long, depending on the
power of $\lambda$, and it is bounded in time. Because of the factor $\left(\nabla_p + \beta \frac{P}{M}\right)$ in Eq.(2.1) each term vanishes when $W(t)$ equals $W_e$ which is attained as $t \to \infty$. This result combined with the vanishing of the initial term indicate that the dissipative term is responsible for the relaxation to equilibrium, i.e. condition ii) of the previous Section is satisfied. These conclusions are of a formal nature and only physically correct if $\lambda$ is small. Notice that due to the short relaxation time of the bath the expansion in powers of $\lambda$ is useful.

In the weak coupling limit, only the first term of the RHS of Eq(2.12) will contribute. The $\lambda$ dependent terms in $\widetilde{\rho_e}$ and $\nabla_R \omega$ will contribute to $O(\lambda^3 t)$ and thus we can substitute

$$\widetilde{\rho_e} \nabla_R (\Phi - \omega) = \rho_B \nabla_R \Phi$$

(2.13)

where

$$\nabla_R \Phi = \nabla_R \Phi - \int dX \rho_B \nabla_R \Phi$$

(2.14)

Since $\tau_s$ and $\tau_B$ may be comparable, we cannot neglect the time displacement of $W(t - \tau)$ in this term. As we explained before, because of the properties of the propagator $e^{L_B t}$, the correlation function in this term is zero for times greater than $\tau_B$ and $W(t - \tau)$ can be written

$$W(t - \tau) = e^{-L_s \tau_s} W(t)$$

(2.15)

up to $O(\lambda^2)$ which follows from Eq(1.28).

Finally, we can now approximate Eq(1.28) by

$$\frac{\partial}{\partial t} W(t) = \tilde{L}_s W(t) + \lambda^2 \nabla_p \int_0^\infty dt \int dX \nabla_R \Phi \times$$

$$\times e^{(\tilde{L}_s + L_B) \tau} \rho_B \tilde{\nabla}_R \Phi \cdot (\nabla_p + \beta \frac{P}{M}) e^{-\tilde{L}_s \tau_s} W(t)$$

(2.16)

for $t > \tau_B$. Eq(2.16) is a generalized Fokker-Planck equation and it is correct through $O(\lambda^2 t)$. Indeed, it contains some parts of higher order terms due to the presence of the $\tilde{L}_s$ Liouvillians which, in principle, contain terms to all orders in $\lambda$. We have used the
propagators \( e^{-\tilde{S}t} \) in Eq(2.16) in order to obtain a closed equation for \( W(t) \) such that \( W_e \) is an exact solution to all orders in \( \lambda \). (The higher order corrections arising from Eq(2.12) must be treated as perturbations to Eq(2.16) if an appropriate transport equation is to be obtained; see e.g. Refs.9 and 46).

Again, the streaming and dissipative parts of Eq(2.16) are separately equal to zero when \( W(t) = W_e \). Because of the dissipative nature of the second term of the RHS of Eq(2.16), \( W(t) \rightarrow W_e \) as \( t \rightarrow \infty \). The relaxation of \( W(t) \) to \( W_e \) described by Eq(2.16) is correct to order \( \lambda^2 t \) but there are higher order terms \( (\lambda^3 t \) ) in the time dependence which have been omitted. We remark that these properties of Eq(2.16) are due to the choice of the projection operator in Eq(1.17).

Eq(2.16) can be written
\[
\frac{\partial}{\partial t} W(t) = \tilde{L}_S W(t) + \lambda^2 \nabla_p \int_0^\infty d\tau \left\langle \nabla_R \Phi \tilde{L}_S \nabla_R \Phi(-\tau) \right\rangle_B \times \\
\times \left( e^{\tilde{L}_S \tau} \nabla_p e^{-\tilde{L}_S \tau} \beta \frac{p(-\tau)}{M} \right) W(t)
\]  

(2.17)

here,
\[
\nabla_R \Phi(-\tau) \equiv \left( \nabla_R \Phi(R,r^N) \right)(-\tau)
\]

(2.18)

and the time dependence is given by
\[
\begin{align*}
\mathbb{N}(\tau) &\equiv e^{L_B^N} \mathbb{N}, \\
\mathbb{R}(\tau) &\equiv e^{\tilde{L}_S \tau} \mathbb{R} \quad \text{and} \quad \mathbb{P}(\tau) \equiv e^{\tilde{L}_S \tau} \mathbb{P}.
\end{align*}
\]

(2.19)

Before applying Eq(2.17) to a particular situation, we must retain \( \tilde{L}_S \) to an appropriate order in \( \lambda \).

The operator acting on \( W(t) \) in Eq(2.17) can be approximated in the following way:
\[
e^{-\tilde{L}_S \tau} W(R,P,t) = W(R(\tau),P(\tau),t) + O(\lambda^2)
\]
\[
\nabla_p e^{-\tilde{L}_S \tau} W(R,P,t) = \left( \nabla_p P(\tau) \cdot \nabla_{p(\tau)} + \nabla_p R(\tau) \cdot \nabla_{R(\tau)} \right) W(R(\tau),P(\tau),t) + O(\lambda^2)
\]

\[28\]
\[ e^{-\mathcal{L}_S^T \nabla_p} e^{-\mathcal{L}_S^T W(R,P,t)} = \left( e^{-\mathcal{L}_S^T \nabla_p P(\tau)} \right) \cdot \nabla_p W(R,P,t) + \left( e^{-\mathcal{L}_S^T \nabla_p R(\tau)} \right) \cdot \nabla_R W(R,P,t) + O(\lambda^2) \] (2.20)

The error introduced into Eq(2.17) by this approximation is of order \( \lambda^4 \).

Eq(2.17) can be written in a more recognizable way by substituting in it Eq(2.20):

\[ \frac{\partial}{\partial t} W(t) = \mathcal{L}_S W(t) + \lambda^2 \nabla_p \cdot D_3(R,P) W(t) \]

\[ + \lambda^2 \nabla_p \cdot \tilde{D}_1(R,P) \cdot \nabla_p W(t) + \lambda^2 \nabla_p \cdot \tilde{D}_2(R,P) \cdot \nabla_R W(t) \] (2.21)

where the "generalized friction" coefficients are given by

\[ \tilde{D}_1(R,P) = \int_0^\infty dt \left\langle \nabla_R \Phi \nabla_R \Phi(-\tau) \right\rangle_B e^{-\mathcal{L}_S^T \nabla_p P(\tau)} \] (2.22a)

\[ \tilde{D}_2(R,P) = \int_0^\infty dt \left\langle \nabla_R \Phi \nabla_R \Phi(-\tau) \right\rangle_B e^{-\mathcal{L}_S^T \nabla_p R(\tau)} \] (2.22b)

\[ D_3(R,P) = \frac{\beta}{M} \int_0^\infty dt \left\langle \nabla_R \Phi \nabla_R \Phi(-\tau) \right\rangle_B e^{-\mathcal{L}_S^T P} \] (2.22c)

Clearly \( \mathcal{L}_S \) is purely reversible since it changes sign under time reversal; however, without an explicit evaluation of the coefficients given by Eqs(2.22), we cannot assess the sign of the dissipative term under the above transformation. In general, we expect that, besides involving the irreversible part responsible for the relaxation to equilibrium, the dissipative term can also have a reversible component. The latter must be of a dynamical nature: its effect can only be detected while the system is relaxing to equilibrium, since the streaming part already accounts for the terms that give rise to the equilibrium form.

Furthermore, if the characteristic time of the system, \( \tau_3 \), is much longer than \( \tau_H \), the dynamic streaming terms are negligible and the dissipative term becomes purely irreversible. That is, Eq(2.17) can be approximated by

29
\[
\frac{\partial}{\partial t} W(t) = \mathcal{L}_S W(t) + \lambda^2 \int_0^\infty dt \left\langle \nabla_K \Phi e^{L_B \nabla_K \Phi} \right\rangle_B \cdot \nabla_p (\nabla_p + \beta \frac{P}{M}) W(t)
\]

(2.23)

which is the usual Fokker-Planck equation (the particular case of Brownian motion is analyzed in Chapter III). Notice, however, that in contrast to the phenomenological equation, the streaming part is given by the effective system Liouvillian. We cannot neglect those corrections without affecting the time evolution of \( W(t) \). This suggests that in applications, where the phenomenological equations are successful, what is actually "measured" is \( \mathcal{L}_S \) instead of \( L_S \).

In the next section, we solve Eq.(2.17) for a simple example which further clarifies important aspects of the time dependence inherent in this equation.

We conclude this section by emphasizing that besides the main property the projection operator must have in order to ensure the correct equilibration, i.e. \( P \rho_e = \rho_e \), it must also separate the equilibrium streaming contribution. Other projection operators could be defined as having the former property but not the latter, and still obtain correct equations to order \( \lambda^2 \). For the present (classical) case it does not seem to be many other choices since the auxiliary function, \( \tilde{\rho}_e \), used in the definition of the projection operator, is the conditional probability distribution of the bath for fixed coordinates and momenta of the system, which in turn is appropriate for the assumption that the bath equilibrates fast in comparison to the system. However, for systems that obey quantum mechanics, as we will see in the next Chapter where we study the problem of quantum Brownian motion, it is not necessarily the case.
II. A. 3. Harmonic oscillator with linear coupling.

In this section we analyze Eq(2.17), through second order in $\lambda$, for the simple case of a one-dimensional overall system in which the system is a harmonic oscillator linearly coupled to the bath. For convenience, we set $M = 1$ in the following. Here,

$$H_S = \frac{P^2}{2} + \frac{1}{2} \Omega^2 R^2$$

(3.1)

and

$$\Phi(R, r^N) = R \phi(r^N)$$

(3.2)

where $\phi(r^N)$ is an arbitrary function of the coordinates of the bath particles; without loss of generality we assume that

$$\langle \phi(r^N) \rangle_B = \int dX \rho_B \phi(r^N) = 0$$

(3.3)

We substitute Eqs(3.1) and (3.2) into Eq(3.17) and to second order in $\lambda$, we obtain

$$\frac{\partial}{\partial t} W(t) = -P \frac{\partial W(t)}{\partial R} + \Omega^2 R \frac{\partial W(t)}{\partial P} +$$

$$+ \lambda^2 \int_0^\infty d\tau \langle \phi(\tau) \phi \rangle_B \left[ \frac{\partial}{\partial P} \tilde{L}_S \tau \left( \beta P + \frac{\partial}{\partial P} \right) e^{-\tilde{L}_S \tau} W(t) \right]$$

(3.4)

where,

$$\tilde{L}_S = -P \frac{\partial}{\partial R} + \Omega^2 R \frac{\partial}{\partial P}$$

(3.5)

and

$$\Omega^2 = \Omega - \lambda \beta \langle \phi \rangle_B$$

(3.6)

Namely, we have included Euler terms up to second order in $\lambda$, and accordingly in $\tilde{L}_S$.

The term in brackets in Eq(3.4) can now be evaluated, yielding
\[ e^{-L_S \tau} (\beta P + \frac{\partial}{\partial P}) e^{-L_S \tau} W(t) = \cos \Omega_1 \tau (\beta P + \frac{\partial}{\partial P}) W(t) + \frac{1}{\Omega_1} \sin \Omega_1 \tau (\beta \Omega_1 R + \frac{\partial}{\partial R}) W(t) \]

(3.7)

Substituting Eq(3.7) into Eq(3.4) we obtain the desired equation,

\[
\frac{\partial}{\partial t} W(t) = -P \frac{\partial W(t)}{\partial R} + \Omega_1^2 \frac{\partial W(t)}{\partial P} + \\
+ \lambda \Gamma_1 \frac{\partial}{\partial P} (\beta P + \frac{\partial}{\partial P}) W(t) + \lambda \Gamma_2 \frac{\partial}{\partial P} (\beta \Omega_1 R + \frac{\partial}{\partial R}) W(t)
\]

(3.8)

where

\[
\Gamma_1 = \int_0^\infty d\tau \left< \phi(\tau) \phi \right>_B \cos \Omega_1 \tau
\]

(3.9)

and

\[
\Gamma_2 = \int_0^\infty d\tau \left< \phi(\tau) \phi \right>_B \frac{1}{\Omega_1} \sin \Omega_1 \tau
\]

(3.10)

As was mentioned in Section 2, if the bath correlation time \( \tau_B \rightarrow 0 \), or if \( \Omega_1^{-1} \gg \tau_B \) we recover the standard Fokker-Planck equation, since \( \Gamma_2 \rightarrow 0 \).

Notice that for this particular example, in accordance with the discussion of the previous section, the last term of Eq(3.8) involves a correction to the frequency in addition to the shift coming from the Euler term. This correction is of a dynamic nature; namely, the equilibrium distribution function will be independent of it. This point will be clarified later once the exact solution of Eq(3.8) is obtained.

In order to solve Eq(3.8), we will follow very closely the method outlined by Chandrasekhar.\(^6^8\)
We first write down the associated subsidiary system of Eq.(3.8) (i.e. the equations for the first moments of the distribution):

\[
\dot{\beta} = -\lambda \Gamma_1 \beta \beta - \Omega \ \beta \text{R} \\
\dot{\beta} = \beta \text{R} \tag{3.11}
\]

where

\[
\Omega = \Omega_1 (1 + \lambda \beta \Gamma_2) \tag{3.13}
\]

Now, we introduce as variables two first integrals of Eqs(3.11) and (3.12), that is

\[\xi = (R\mu_1 - \beta)e^{-\mu_2 t} \tag{3.14a}\]
\[\eta = (R\mu_2 - \beta)e^{-\mu_1 t} \tag{3.14b}\]

where

\[
\mu_1 = -\frac{\lambda^2 \Gamma_1 \beta}{2} + i \sqrt{\Omega - \left(\frac{\lambda^2 \Gamma_1 \beta}{2}\right)^2} \tag{3.15a}
\]

and

\[
\mu_2 = -\frac{\lambda^2 \Gamma_1 \beta}{2} - i \sqrt{\Omega - \left(\frac{\lambda^2 \Gamma_1 \beta}{2}\right)^2} \tag{3.15b}
\]

are the roots of the secular equation of the system Eqs(3.11) and (3.12),

\[\mu^2 + \lambda \beta \Gamma_1 \mu + \Omega = 0 \tag{3.16}\]

where we have assumed that \(\Omega\) is of order \(O(1)\), giving rise to complex roots.

In these variables, and by making the further transformation,

\[W(\xi, \eta; t) = e^{\lambda \Gamma_1 \beta t} \chi(\xi, \eta; t) \tag{3.17}\]

Eq(3.8) becomes,

\[
\frac{\partial \chi(t)}{\partial t} = \lambda \left(\Gamma_1 - \Gamma_2 \mu_1\right) e^{-2 \mu_2 t} \frac{\partial^2 \chi(t)}{\partial \xi^2} + \]

33
\[ + \lambda^2 \left( \Gamma_1 - \Gamma_2 \mu_2 \right) e^{-2\mu_1 t} \frac{\partial^2}{\partial \eta^2} \chi(t) + \]
\[ + \lambda^2 \left( 2\Gamma_1 - \Gamma_2 (\mu_1 + \mu_2) \right) e^{-(\mu_1 + \mu_2)t} \frac{\partial^2}{\partial \eta \partial \xi} \chi(t) \]

The solution of Eq(3.18) for the initial condition

\[ \chi(t=0) = \delta(\xi - \xi_0) \delta(\eta - \eta_0) \]

that is, corresponding to \( W(P,R; t=0) = \delta(P-P_0) \delta(R-R_0) \) where \( \xi_0 = R_0 \mu_1 - P_0 \) and \( \eta_0 = R_0 \mu_1 - P_0 \) is,

\[ \chi(\xi,\eta,t; \xi_0,\eta_0) = \frac{1}{\sqrt{2\pi\Delta^2}} \exp\left\{ -\frac{1}{\Delta} \left[ v(t)(\xi - \xi_0)^2 + u(t)(\eta - \eta_0)^2 - w(t)(\xi - \xi_0)(\eta - \eta_0) \right] \right\} \]

where

\[ v(t) = \lambda^2 \left( \Gamma_1 - \Gamma_2 \mu_2 \right) \left( \frac{1 - e^{-2\mu_1 t}}{2\mu_1} \right) \]

\[ u(t) = \lambda^2 \left( \Gamma_1 - \Gamma_2 \mu_1 \right) \left( \frac{1 - e^{-2\mu_2 t}}{2\mu_2} \right) \]

\[ w(t) = \lambda^2 \left( 2\Gamma_1 - \Gamma_2 (\mu_1 + \mu_2) \right) \left( \frac{1 - e^{-(\mu_1 + \mu_2)t}}{\mu_1 + \mu_2} \right) \]

and,
\[ \Delta = 4u(t)v(t) - w^2(t) \quad (3.21d) \]

Hence, the normalized solution \( W(t) \) in the variables \( P \) and \( R \), whose initial condition is \( W(0) = \delta(P-P_0) \delta(R-R_0) \) is,

\[
W(P,R,t;P_0,R_0) = \frac{(\mu_1-\mu_2)^2}{2\pi\Delta^2} \exp\left(\lambda^2 \beta \Gamma_1 t \right) \times
\]

\[
\times \chi((R\mu_1-P)e^{\mu_2 t},(R\mu_2-P)e^{\mu_1 t},(R_0\mu_1-P_0),(R_0\mu_1-P_0)) \quad (3.22)
\]

Although it is evident that \( W(t) \) is a Gaussian function in \( P \) and \( R \), its time dependence is somewhat complicated and not very illuminating. Nevertheless, we can look at the time evolution of its moments and to some limiting cases.

First of all we note that when \( t \to \infty \), we obtain the equilibrium distribution function \( W_e \) valid up to second order in \( \lambda \),

\[
W_e(P,R) = \frac{e^{-\beta\left(\frac{P^2}{2} + \frac{1}{2}\Omega_1 R^2\right)}}{\int dP \, dRe^{-\beta\left(\frac{P^2}{2} + \frac{1}{2}\Omega_1 R^2\right)}} \quad (3.23)
\]

with the property \( \mathcal{L}_S W_e = 0 \).

Note that at equilibrium the frequency of the oscillator is given only by \( \Omega_1 \) (see Eq(3.6)); that is, only the streaming shift contributes, as predicted.

In order to analyze the time dependence we calculate two of the second moments of the distribution, \( P^2(t) \) and \( R^2(t) \):

\[
P^2(t) = \int dP \, dR \, P^2 \, W(P,R,t) \quad (3.24a)
\]

\[
R^2(t) = \int dP \, dR \, R^2 \, W(P,R,t) \quad (3.24b)
\]
which give,

\[
\frac{P^2(t)}{t} = e^{-\lambda^2 \beta \Gamma_1 t} \left[ \frac{\Omega^2}{\omega} R_0 \sin \omega t + P_0 (\cos \omega t - \frac{\lambda^2 \beta \Gamma_1}{2\omega} \sin \omega t) \right]^2
\]

(3.25a)

\[
+ \frac{1}{\beta} \left[ 1 + e^{-\lambda^2 \beta \Gamma_1 t} \left\{ -1 + \frac{\lambda^2 \beta \Gamma_1}{2\omega} \sin 2\omega t + \frac{1}{\omega^2} \left( \frac{\lambda^2 \beta \Gamma_1}{2} \right)^2 \sin^2 \omega t \right\} \right]
\]

\[
\frac{R^2(t)}{t} = e^{-\lambda^2 \beta \Gamma_1 t} \left[ R_0 (\cos \omega t + \frac{\lambda^2 \beta \Gamma_1}{2\omega} \sin \omega t) + \frac{1}{\omega} P_0 \sin \omega t \right]^2
\]

(3.25b)

\[
+ \frac{1}{\beta \Omega_1^2} \left[ 1 + e^{-\lambda^2 \beta \Gamma_1 t} \left\{ -1 + \frac{\lambda^2 \beta \Gamma_1}{2\omega} \sin 2\omega t + \frac{1}{\omega^2} \left( \Omega - \Omega_1 + \frac{\lambda^2 \beta \Gamma_1}{2} \right)^2 \sin^2 \omega t \right\} \right]
\]

where

\[
\omega = \sqrt{\frac{Q^2}{\Omega} - \left( \frac{\lambda^2 \beta \Gamma_1}{2} \right)^2}
\]

(3.26)

From Eqs(3.25) and (3.26) we find that the time evolution is given by the expected exponential relaxation times an oscillatory term. The frequency of such oscillations, apart from the standard shift of the friction coefficient, is given by $\tilde{\Omega}$, that is, the frequency that involves both the streaming and the "dissipative" term, see Eq(3.13). This is the dynamical shift to the frequency to which we referred earlier. It is a dynamical
effect since its presence can only be detected while the system is relaxing towards equilibrium and does not affect the stationary state. We emphasize once more that this effect is due to the fact that the natural time scale of the system is comparable with the relaxation time of the bath.

In the weak coupling limit, Eq (3.25) become

\[
P^2(t) \equiv e^{-\lambda^2 \beta \Gamma_1 t} \left( P_{\Omega \cos \omega t} - \frac{1}{\Omega} R_{\Omega \sin \omega t} \right)^2 - \frac{1}{\beta} \left( 1 - e^{-\lambda^2 \beta \Gamma_1 t} \right) \tag{3.27a}
\]

\[
R^2(t) \equiv e^{-\lambda^2 \beta \Gamma_1 t} \left( R_{\Omega \cos \omega t} + \frac{1}{\Omega} P_{\Omega \sin \omega t} \right)^2 + \frac{1}{\beta \Omega} \left( 1 - e^{-\lambda^2 \beta \Gamma_1 t} \right) \tag{3.27b}
\]

with

\[
\omega \equiv \Omega + \frac{\lambda^2}{2} \left( \beta \Omega \Gamma_2 - \frac{\beta}{\Omega} \left< \phi^2 \right>_B \right) \tag{3.28}
\]

The frequency \( \omega \) contains a dynamic shift \( \sim \lambda^2 \beta \Omega \Gamma_2 / 2 \) and a statistical shift \( \sim -\lambda^2 \beta \left< \phi^2 \right>_B / 2 \Omega \), neither of which can be neglected on the \( \lambda^2 t \) time scale.
II. B. WEAK COUPLING IN QUANTUM SYSTEMS.

II. B. 1. Projection operator and exact dynamic equations.

In this section we define, by analogy with the classical case a projection operator that ensures a separation of the Liouville equation into streaming (systematic) and dissipative contributions. This section is devoted to exact results only. Approximations and assumptions are considered in the next section (see footnote of this page).

The overall system in consideration is described by the Hamiltonian

\[ H = H_S + H_B + \lambda H_I, \]  

(1.1)

where \( H_S \) is the Hamiltonian of the system with a small number of degrees of freedom; \( H_B \) is the Hamiltonian of the bath with a very large number of degrees of freedom; \( H_I \) represents the interaction between the system and the bath. \( \lambda \) is the strength of the interaction.

The Hamiltonians \( H_S \) and \( H_B \) act on different Hilbert spaces, i.e. the operators involved in \( H_S \) obey certain commutation relations, unspecified at this moment, and so do the operators of \( H_B \), but the operators of the former commute with those of the latter. Thus, the total Hilbert space is the direct product of the system and bath Hilbert spaces:

\[ \mathcal{H} = \mathcal{H}_S \otimes \mathcal{H}_B. \]  

(1.2)

Again, we base our analysis on the fact that due to its large number of degrees of freedom the bath will relax to equilibrium with a certain characteristic time \( \tau_B^* \); and that reduced quantities, e.g. the reduced density matrix of the system, will also relax to equilibrium due to the interaction with the bath.

* The identification of \( \tau_B \) as the relaxation time of the bath due to the interaction of its many degrees of freedom, as the analog of the corresponding classical quantity, is only correct if the temperature is not too low. This is discussed in the next section.
The total equilibrium density matrix for the overall system is given by

\[ \rho_e = \frac{\mathcal{E}^{-\beta H}}{\text{Tr}_S \text{Tr}_B \mathcal{E}^{-\beta H}} , \]

(1.3)

where Tr denotes the trace of the operator, and the subindexes S and B refer to system and bath Hilbert spaces. The temperature \( \beta^{-1} \) is determined by the energy of the overall closed system (see Section II.A.1).

The reduced equilibrium density matrix for the system is

\[ W_e = \text{Tr}_B \rho_e \]

(1.4)

and the bath equilibrium density matrix, in the absence of the interaction, is

\[ \rho_B = \frac{\mathcal{E}^{-\beta H_B}}{\text{Tr}_B \mathcal{E}^{-\beta H_B}} . \]

(1.5)

The time evolution of the overall density matrix is given by the quantum von Neumann-Liouville equation (we set \( \hbar = 1 \) for convenience)

\[ \frac{\partial}{\partial t} \rho(t) = -i \left[ H, \rho(t) \right] \equiv L \rho(t) \]

\[ = -i \left[ H_S + H_B + \lambda H_1 , \rho(t) \right] \equiv (L_S + L_B + \lambda L_1) \rho(t) \]

(1.6)

with obvious definitions.

We want to rewrite Eq(1.6) for the reduced density matrix of the system,

\[ W(t) = \text{Tr}_B \rho(t) \]

(1.7)

using the same projection operator technique as in the classical case, such that a separation of systematic and dissipative terms results.

From the analysis of Section II.A.1 we find that an essential property the projection operator should have in order to ensure the correct equilibration and achieve the desired separation of terms, is

\[ \mathcal{P} \rho_e = \rho_e \]

(1.8)
the total equilibrium density matrix must be projected onto itself. In the classical case the natural auxiliary function needed for Eq(1.8) to hold was the conditional probability distribution function of the bath for fixed coordinates and momenta of the system, Eq(2.10). In quantum mechanics the concept of a "conditional density matrix" is not useful since it is not uniquely defined\textsuperscript{56,57}.

Considering the projection operator as a mathematical tool to integrate out the bath degrees of freedom in a convenient way, we define our projection operator by\textsuperscript{55}
\[
\mathcal{P}A = \frac{1}{2} \left( \tilde{\rho} \text{Tr}_B A + (\text{Tr}_B A) \tilde{\rho}^+ \right)
\]  
(1.9)

where
\[
\tilde{\rho} \equiv \rho_e W_e^{-1} \quad \text{and} \quad \tilde{\rho}^+ \equiv W_e^{-1} \rho_e
\]  
(1.10)

and A is a dynamical operator in the total Hilbert space \(\mathcal{H}\). It is a projection operator, i.e. \(\mathcal{P}^2 = \mathcal{P}\), since
\[
\text{Tr}_B \tilde{\rho} = \text{Tr}_B \tilde{\rho}^+ = 1
\]  
(1.11)

By construction Eq(1.8) is satisfied.

The operators \(\tilde{\rho}\) and \(\tilde{\rho}^+\) have little physical significance. However, their expansion in powers of \(\lambda\) involves the equilibrium density matrix of the bath \(\rho_B\)(see next Section). Therefore, once the analysis based on \(\lambda\) being small is performed, the resulting formulae will involve averages of bath operators weighted by \(\rho_B\), analogous to the classical case.

Acting with the projection operator, Eq(1.9), on Eq(1.6), and taking the trace over the bath variables, we obtain
\[
\frac{\partial}{\partial t} W(t) = -i \left[ H_S, W(t) \right] - \frac{i}{2} \lambda \text{Tr}_B \left[ H_I, \tilde{\rho} W(t) + W(t) \tilde{\rho}^+ \right]
\]
\[\quad - i \lambda \text{Tr}_B \left[ H_I, z(t) \right], \quad (1.12)
\]

where
\[ z(t) = (1 - \mathcal{P}) \rho(t) = \mathcal{Q} \rho(t) \]

obeys, again from Eq(1.6),
\[ \frac{\partial}{\partial t} z(t) = -i \mathcal{Q} \left[ H, \tilde{\rho} \ W(t) + W(t) \ \tilde{\rho}^+ \right] - i \mathcal{Q} \left[ H, z(t) \right] ; \]

the following facts were used
\[ \mathcal{P}[H_B, A] = 0 , \]
\[ \mathcal{P}[H_S, A] = \frac{1}{2} (\tilde{\rho} [H_S, \text{Tr}_B A] + [H_S, \text{Tr}_B A] \tilde{\rho}^+) , \]
\[ \mathcal{P}[H_B A] = \frac{1}{2} (\tilde{\rho} \text{Tr}_B [H_B, A] + (\text{Tr}_B [H_B, A]) \tilde{\rho}^+) \]

and
\[ \text{Tr}_B z(t) = 0 . \]

We identify the first two terms on the RHS of Eq(1.12) as the streaming part, since at equilibrium they equal the equation satisfied by \( W_e \), as can be seen from Eqs(1.6), (1.7) and (1.10). The second term contains all the statistical, or equilibrium shifts, to the energy levels of the isolated system given by the first term.

The last term on the RHS of Eq(1.12) bears all the information concerning the relaxation and dissipation. At equilibrium it is zero because of Eq(1.8).

From Eq(1.3) and the definition of \( \tilde{\rho} \), Eq(1.10), it follows that
\[ [H_S + H_B, \tilde{\rho} W_e] = -\lambda [H_I, \tilde{\rho} W_e] \]

so that
\[ [H_S + H_B, \tilde{\rho}] = - (\tilde{\rho} [H_S, W_e] + \lambda [H_I, \tilde{\rho} W_e]) W_e^{-1} ; \]

on the other hand, by taking the trace over the bath, Eq(1.16) becomes
\[ [H_S, W_e] = -\lambda \text{Tr}_B [H_I, \tilde{\rho} W_e] \]

Substituting Eq(1.18) into Eq(1.17), we obtain
\[ [H_S + H_B, \tilde{\rho}] = -\lambda (-\tilde{\rho} \text{Tr}_B [H_I, \tilde{\rho} W_e] + [H_I, \tilde{\rho} W_e]) W_e^{-1} . \]
Thus, the first term of Eq(1.14) becomes
\[
\frac{1}{2} Q\left[H, \tilde{\rho} W(t) + W(t) \tilde{\rho}^+ \right] = \frac{1}{2} Q\left([H_S + H_B, \tilde{\rho}] W(t) + W(t)[H_S + H_B, \tilde{\rho}^+] \right) \\
+ \lambda [H, \tilde{\rho} W(t) + W(t) \tilde{\rho}^+] \\
= -\frac{\lambda}{2} Q\left((-\tilde{\rho} \text{Tr}_B[H_1, \tilde{\rho} W_e] + [H_1, \tilde{\rho} W_e]) W^{-1}_e W(t) \\
+ W(t) W^{-1}_e (- (\text{Tr}_B[H_1, W^{-1}_e \tilde{\rho}^+]) \tilde{\rho}^+ + [H_1, W^{-1}_e \tilde{\rho}^+] \\
- [H_k, \tilde{\rho} W(t) + W(t) \tilde{\rho}^+] \right) . \tag{1.20}
\]

Substitution of the formal solution to Eq(1.14), together with Eq(1.20), into Eq(1.12), yields
\[
\frac{\partial}{\partial t} W(t) = -i \left[ H_S, W(t) \right] - i \lambda \text{Tr}_B \left[ H, \tilde{\rho} W(t) + W(t) \tilde{\rho}^+ \right] \\
+ \frac{\lambda^2}{2} \text{Tr}_B[H_1, \int_0^t d\tau \ e^{Q_L Q^t} Q \times \left((-\tilde{\rho} \text{Tr}_B[H_1, \tilde{\rho} W_e] + [H_1, \tilde{\rho} W_e]) W^{-1}_e W(t - \tau) \\
+ W(t - \tau) W^{-1}_e (- (\text{Tr}_B[H_1, W^{-1}_e \tilde{\rho}^+]) \tilde{\rho}^+ + [H_1, W^{-1}_e \tilde{\rho}^+] \\
- [H_k, \tilde{\rho} W(t - \tau) + W(t - \tau) \tilde{\rho}^+] \right) \\
- i \lambda \text{Tr}_B[H_1, e^{Q_L Q^t} z(0)] \right] , \tag{1.21}
\]

where the propagator is given by
\[
e^{Q_L Q^t} Q_A = QA - i t Q[H, Q A] - \frac{t^2}{2} Q[H, Q[H, Q A]] + \ldots . \tag{1.22}
\]

Again, Eq(1.21) is exact and amenable to reduction to a generalized Master equation for \( \lambda \) small. This is made possible by the same reasons outlined for the classical case: a) since \( P \rho_e = \rho_e \) the Euler and dissipative terms are zero at equilibrium and b) within the context of the separation of time scales, and for \( \lambda \) small, the initial value term becomes negligible and the dissipative term drives the system towards equilibrium as \( t \to \infty \).
II. B. 2. A generalized Master equation.

We now turn our attention to the expansion of Eq(1.21) in powers of \( \lambda \). In the weak coupling limit we obtain a generalized Master equation for the matrix elements of the reduced density matrix for the system, \( W(t) \). The approach here developed parallels the procedure of Section II.A.1, although emphasis is made regarding the differences that arise due to the quantal nature of the present problem.

We start by discussing the main assumption of this work: the bath relaxes to equilibrium on the short time scale \( \tau_B \). In principle, this can be formulated by writing the quantum analogs of Eqs(II.A.2.7) and (II.A.2.8) and assuming an initial density matrix of the form given by Eq(II.A.2.4).

It must be acknowledged, however, that the time \( \tau_B \) is of a "mechanistic" nature: it is the natural time associated with the interaction potential \( U(r^N) \) of the \( N \) bath particles, e.g. the inverse of the Debye frequency for a bath of acoustical phonons. In order to assert that this is the relevant time scale of the bath requires that the temperature be not too low. That is, at low temperatures, quantum effects play an important role and we can no longer assume that the time evolution of correlations of the type involved in the initial value as well as in the higher order terms, occurs within \( \tau_B \). These effects should start being important at the crossover time scale \( \tau_Q \equiv \hbar/k_B T \), where \( \hbar \) is Planck's constant, \( k_B \) Boltzmann's constant and \( T \) the temperature. For low enough temperature the "thermal transient" \( \tau_Q \) can be greater than \( \tau_B \) and become the relevant time scale of the bath.*

On the other hand, we know in advance that the relaxation of the system, \( \tau_R \), will be proportional to \( \lambda^{-2} \). Therefore, for a given interaction strength, we will consider only temperatures such that \( \tau_R \gg \tau_Q \).

* This has been explicitly shown\(^{44,45} \) to be the case for the case of a quantum oscillator linearly interacting with a bath also composed of harmonic oscillators.
Hence, the short time scale of our problem will be given
\[ \tau_m \equiv \max(\tau_B, \tau_Q) \] (2.1)
and our formalism will be valid for
\[ \tau_R \gg \tau_m \] (2.2)

It is important, then, to keep in mind that for quantum processes the assumption of fast bath correlations has its natural limitations. After all, at very low temperature, the quantum effects are dominant and one should not expect a simple relaxation theory to include the whole description of the problem.

Having specified the short time scale of the process, we can now translate the results of Part A to the present case by changing distribution functions to density operators and integrals over the bath degrees of freedom to traces over the bath; the initial value term as well as the higher order terms can be shown to be negligible, because of the factors \( \lambda \tau_m \).

We note as before, that the \( \lambda \) dependence of the RHS of Eq.(1.21) arises from: the explicit factors of \( \lambda \); the operators \( \tilde{\rho} \) and \( \tilde{\rho}^\dagger \); the propagator \( e^{QLQ_t} \) and the reduced density matrix \( W(t - \tau) \).

Contrary to the classical case we cannot, generally, rewrite the whole Euler term as a commutator of an effective Hamiltonian and the reduced density matrix for the system, because the second term of the RHS on Eq.(1.21) cannot be written in terms of an effective potential analogous to the potential of mean force \( \omega(R, \lambda) \), Eq. (II.A.1.27), as in the classical case\(^\#\). We shall show this result with a particular counterexample in the next section, where we study the two level system interacting with a heat bath.

\(^\#\) Using the present formalism Romero-Rochin, Orsky and Oppenheim\(^47\), have derived the Redfield equations\(^7\) for spin relaxation and shown that for the so called secular terms, the streaming term can be written as an effective Liouvillian and the dissipative term can accordingly be modified.
This impediment prevents us from expanding the propagator and \( W(t - \tau) \) in terms of a quantum effective Liouvillian \( \mathcal{L}_S \) in order to obtain the quantum analogs of Eqs.(II.A.2.15) and (II.A.2.16). Therefore, we will expand the propagator \( e^{QLQ_t} \) and \( W(t - \tau) \) in terms of \( L_S = -i [H_S, \cdot] \) and consequently the dissipative term, proportional to \( \lambda^2 \), will drive the system towards the zeroth order term of the equilibrium density matrix of the system:

\[
W_S \equiv W_e^{(0)} = \frac{e^{-\beta H_S}}{\text{Tr}_S e^{-\beta H_S}}.
\]  

(2.3)

For the time evolution to be correct up to order \( \lambda^2 t \) we must consider Euler corrections up to second order in \( \lambda \).

Although this is a drawback of the present approach from the aesthetic point of view since the resulting equation will not have as its stationary solution \( W_e^{(0)} \) (nor \( W_e^{(2)} \)), it is not of any physical consequence since what matters is the solution to the equation in the weak coupling limit. We will come back to this point later on.

We now proceed with the expansion in powers of \( \lambda \) of the RHS of Eq.(1.21) up to second order (neglecting the initial condition term); due to the explicit factors of \( \lambda \) we must know \( \tilde{\rho} \) and \( \tilde{\rho}^+ \) explicitly up to first order. Higher order terms can be systematically obtained.

We start with the identity

\[
e^{-\beta H} = e^{-\beta H_0} - \lambda \int_0^\beta d\theta \ e^{-(\beta - \theta)H_0} H_1 e^{-\theta H}
\]

\[
= e^{-\beta H_0} - \lambda \int_0^\beta d\theta \ e^{-\theta H} H_1 e^{-(\beta - \theta)H_0}
\]

(2.4)

where

\[H_0 = H_S + H_B, \]

(2.5)
and the second equality follows from the Hermiticity of the operators involved. By further defining
\[ D(\beta, \lambda) = \int_{0}^{\beta} d\theta \ e^{-\beta H_{0}} H_{1} e^{\theta H} \]  
(2.6)

Eq(2.4) becomes
\[ e^{-\beta H} = e^{-\beta H_{0}} e^{-\frac{\lambda}{2} \left( D(\beta, \lambda) e^{-\beta H_{0}} + e^{-\beta H_{0}} D^{\dagger}(\beta, \lambda) \right)} . \]  
(2.7)

Iteration of Eq(2.4) in Eq(2.7) gives the expansion of \( e^{-\beta H} \) in powers of \( \lambda \).

Multiplying and dividing Eq(2.7) by \( Z_{S}Z_{B} \), where
\[ Z_{S} = \text{Tr}_{S} e^{-\beta H_{S}} \]  
(2.8)

and
\[ Z_{B} = \text{Tr}_{B} e^{-\beta H_{B}} \]  
(2.9)

yields
\[ e^{-\beta H} = Z_{S}Z_{B} \left( \rho_{0} - \frac{\lambda}{2} \left( D(\beta, \lambda) \rho_{0} + \rho_{0}D^{\dagger}(\beta, \lambda) \right) \right) . \]  
(2.10)

where
\[ \rho_{0} = \frac{e^{-\beta H_{0}}}{Z_{S}Z_{B}} = \rho_{B} W_{S} . \]  
(2.11)

Expanding \( D \) and \( D^{\dagger} \), in Eq(2.10), in powers of \( \lambda \) using Eq(2.4), we obtain the following results valid to first order
\[ \rho_{e} = \frac{e^{-\beta H}}{\text{Tr}_{S} \text{Tr}_{B} e^{-\beta H}} = \rho_{0} - \frac{\lambda}{2} \left( (D_{0}(\beta) - \beta \langle H_{SB} \rangle) \rho_{0} + \rho_{0}(D_{0}^{\dagger}(\beta) - \beta \langle H_{SB} \rangle) \right) + O(\lambda^{2}) \]  
(2.12)

and
\[ W_{e} = \text{Tr}_{B} \rho_{e} = W_{S} - \frac{\lambda}{2} \left( (\langle D_{0}(\beta) \rangle_{B} - \beta \langle H_{SB} \rangle) W_{S} + \right. \]

46
\[ + W_S \left( \left< D_0^+ (\beta) \right>_B - \beta \left< H_{\lambda} \right>_{SB} \right) + O(\lambda^2), \quad (2.13) \]

where
\[ D_0(\beta) = \int_0^\beta d\theta \ e^{-\theta H_0} H_1 e^{\theta H_0}, \quad (2.14a) \]
\[ \left< H_{\lambda} \right>_{SB} = Tr_S Tr_B \rho_0 H_1, \quad (2.14b) \]
\[ \left< D_0 (\beta) \right>_B = Tr_B \rho_B D_0 (\beta), \quad (2.14c) \]

and \( \rho_B \) and \( W_S \) are given by Eqs(1.5) and (2.3) respectively.

On the other hand, we have
\[ \rho_e = \frac{1}{2} \left( \sim \rho W_e + W_e \sim \right) \quad (2.15) \]

which expanded to first order in \( \lambda \) gives
\[ \rho_e = \rho_0 + \frac{\lambda}{2} \left( \sim \rho_0 W_e^{(1)} + W_e^{(1)} \sim + \sim \rho_1 W_e^{(0)} + W_e^{(0)} \sim + \right) + O(\lambda^2). \quad (2.16) \]

From the definition of \( \sim \rho \) and \( \sim \rho^+ \), Eq(1.10), we immediately identify
\[ \sim \rho_0 = \sim \rho^+_0 = \rho_B, \quad (2.17) \]

thus, comparing Eq(2.15) with Eq(2.11) and using Eq(2.12), the first corrections to \( \sim \rho \) and \( \sim \rho^+ \) are:
\[ \sim \rho_1 = - \left( D_0 - \left< D_0 \right>_B \right) \rho_B \quad (2.18a) \]
and
\[ \sim \rho^+_1 = - \rho_B \left( D_0^+ - \left< D_0^+ \right>_B \right) \quad (2.18b) \]

Eqs(2.17) and (2.18) suffice to express the Euler term up to second order in \( \lambda \). Moreover, with the aid of the above expansion it can be verified that, indeed, the streaming terms give the corrections to \( W_S \) in equilibrium.

The dissipative term is explicitly of order \( \lambda^2 \). Thus, we need to consider \( \sim \rho \), \( \sim \rho^+ \) and \( W_e \) to lowest order only; the propagator \( e^{-QLT} \) is handled with the same expansion.
used in the classical case (see e.g. Eq(II.A.2.12)); the time displacement of \( W(t - \tau) \) is approximated by
\[
W(t - \tau) = e^{i \frac{H_S}{\tau} \tau} W(t) e^{-i \frac{H_S}{\tau} \tau}
\]  
(2.19)
because, as before, \( \tau_S \) and \( \tau_m \) may be comparable. The higher orders terms can be shown not to contribute in the weak coupling limit, in a completely analogous fashion to Part A.

Substituting Eqs(2.16)-(2.18), the lowest order of the propagator and Eq(2.19) into Eq(1.21), we finally obtain
\[
\frac{\partial}{\partial t} W(t) = -i \left[ H_S, W(t) \right] - i \lambda \left[ \langle H_1 \rangle_B, W(t) \right] \\
+ i \frac{\lambda^2}{2} \text{Tr}_B \left[ H_1, \left( C_0 - \langle C_0 \rangle_B \right) \rho_B W(t) + W(t) \rho_B \left( C^+_0 - \langle C^+_0 \rangle_B \right) \right] \\
- \lambda^2 \int_0^\infty d\tau \text{Tr}_B \left[ H_1, \left( 1 - \mathcal{P}_0 \right) \left[ H_1(-\tau), W(t) \rho_B \right] \\
- \frac{1}{2} W(t) e^{\beta H_S} \left( 1 - \mathcal{P}_0 \right) \left[ H_1(-\tau), e^{-\beta H_S} \rho_B \right] \\
- \frac{1}{2} \left( 1 - \mathcal{P}_0 \right) \left[ H_1(-\tau), e^{-\beta H_S} \rho_B \right] e^{\beta H_S} W(t) \right]
\]  
(2.20)
where
\[
H_1(-\tau) \equiv e^{-i \frac{H_0}{\tau} \tau} H_1 e^{i \frac{H_0}{\tau} \tau}
\]  
(2.21)
and
\[
\mathcal{P}_0 A = \rho_B \text{Tr}_B A
\]  
(2.22)
We have extended the upper limit of the time integral, in Eq(2.20), to infinity because the integrand involves correlations of \( H_1 \) at different times, that by assumption decay on the short time scale \( \tau_m \).

It must be pointed out that Eq(2.20), and the higher order terms, are operators that act on the system Hilbert space. This implies that the properties ascribed to the integrands of the Eq(2.20) and the higher order terms, are understood to hold for their
matrix elements. That is, one obtains the short lived correlations after matrix elements of the system operators have been taken.

We emphasize once more that in the present case, the dissipative part of Eq(2.20), i.e. the last term, drives the system towards the lowest order of the reduced equilibrium density matrix, \( W_e^{(0)} \), only; but the Euler part in equilibrium requires the knowledge of \( W_e \) up to second order in \( \lambda \) in order to vanish. This "discrepancy" is resolved in the weak coupling limit: the Euler corrections will influence only the time evolution. This will be made clearer in the next section where we solve Eq(2.20) for a particular example; furthermore, we will also verify that the dynamic streaming corrections are negligible for the case that the natural time scale of the system is much longer than that of the bath, in analogy to the result in the classical case.

II. B. 3. Two Level System with linear coupling.

Application to tunneling processes in condensed media.

As in any perturbative scheme, for the present theory to be useful in solving realistic problems, a full knowledge of the zeroth order term, that is the exact solution to the Hamiltonian \( H_0 \) must be available.

A very simple model, but widely used, that falls into the category described above, is the two level system (TLS) linearly coupled to a heat bath:

\[
H = -\frac{\Delta_0}{2} \sigma_x + \frac{\epsilon}{2} \sigma_z + H_B + \lambda \sigma_x \phi(r^N) \tag{3.1}
\]

where \( \sigma_x, \sigma_z \) (and \( \sigma_y \)) are the standard Pauli matrices:

\[
\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \text{and} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{3.2}
\]
Most frequently, the environment is modeled by a "phonon heat bath" and the interaction is assumed linear in the bath coordinates; that is \( H_B \) and \( \phi \) are given by

\[
H_B = \sum_n \hbar \omega_n \left( b_n^+ b_n + \frac{1}{2} \right)
\]  

(3.3a)

and

\[
\phi(r^N) = \sum_n G_n \left( b_n^+ + b_n \right)
\]

(3.3b)

where \( b_n^+ \) and \( b_n \) are boson creation and annihilation operators. The details of the bath and the interaction are now embedded in the function \( G_n \), which has to be given. This so-called Spin-Boson Hamiltonian has been extensively studied as a model for tunneling in condensed media, in connection with a variety of problems such as dynamics of handed molecules, tunneling states of substitutional atoms in ionic crystals, and tunneling of magnetic flux in superconducting interference devices.

Let us briefly explain how such a Hamiltonian is obtained. In the problems mentioned above, as well as in many other problems in physical chemistry and solid state physics, the "generic" potential that describes those processes is the double well potential, as shown in the figure.
We are considering the general case (asymmetric or "biased") where there is an energy difference ($\hbar \varepsilon$) between the two local minima. For such potentials, the energy levels are split into pairs with a small energy separation called the tunneling splitting or tunneling frequency; the magnitude of this splitting is determined by the the relative magnitudes of the barrier height ($V_0$), the spatial separation of the two minima ($2R_0$) and their energy asymmetry ($\hbar \Delta$).

Now, for
\begin{equation}
V_0 >> \hbar \omega_{ex}
\end{equation}
\begin{equation}
\hbar \omega_{ex} >> \hbar \Delta
\end{equation}
and
\begin{equation}
\hbar \omega_{ex} >> k_B T > \hbar \Delta - \hbar \varepsilon
\end{equation}
that is, for barrier heights \((V_0)\) and excitation energy to the first pair of excited states
\(\hbar \omega_{ex}\) large compared with the splitting of the two lowest lying states \(\hbar \Delta\), Eqs(3.4) and (3.5), and for temperatures larger than the splitting but smaller than the excitation energy, Eq(3.6), the problem can effectively be reduced to the two lowest states: this is the so-called "truncation" approximation*. That is, the problem is reduced to a two level system.

To obtain the system part of the Hamiltonian, Eq(3.1), we proceed as follows: Let \(\hbar \Delta_0\) be the splitting when \(\hbar \varepsilon = 0\); denote the two states by \(|\downarrow\rangle\) and \(|\uparrow\rangle\), where \(|\uparrow\rangle\) is the symmetric ground state and \(|\downarrow\rangle\) is the antisymmetric excited state; the Hamiltonian of the system can be taken proportional to any of the Pauli matrices: we take \(\sigma_x\) following convention. Thus,
\[
\sigma_x |\uparrow\rangle = |\downarrow\rangle \quad \text{and} \quad \sigma_x |\downarrow\rangle = - |\uparrow\rangle .
\] (3.7)

By constructing linear combinations of \(|\downarrow\rangle\) and \(|\uparrow\rangle\) we can form states whose amplitudes are different from zero only in one of the wells; we denote such states as "left" and "right":
\[
|L\rangle = \frac{1}{2} (|\uparrow\rangle + |\downarrow\rangle )
\] (3.8a)
and
\[
|R\rangle = \frac{1}{2} (|\uparrow\rangle - |\downarrow\rangle )
\] (3.8b)
These states are eigenstates of \(\sigma_z\). When the asymmetry is different from zero these states differ in energy by \(\hbar \varepsilon\).

Therefore the Hamiltonian of the system can be written as: \((\hbar \equiv 1)\)
\[
H_S = - \frac{\Delta_0}{2} \sigma_x + \frac{\varepsilon}{2} \sigma_z ;
\] (3.9)
that is, in the representation \(|L\rangle\) and \(|R\rangle\)

* Parris and Silbey\(^{20}\) and Sethna\(^{23}\) have extended this approximation and considered the effect of more states; for the bath and the interaction they keep the forms given by Eqs(3.3).
\[ \sigma_x = |L\rangle\langle R| + |R\rangle\langle L| \]  
(3.10)

represents the tunneling between the two states ("kinetic energy"), and
\[ \sigma_z = |R\rangle\langle R| - |L\rangle\langle L| \]  
(3.11)

the occupation of the two localized states in the wells ("potential energy").

The interaction between the system and the heat bath is assumed to be dependent on the coordinates of the bath particles and the generalized coordinate \( R \) only, i.e. \( H_I = H_I(R^N, R) \). This interaction is supposed to weakly perturb both the bath and the system and the particular physical problem at hand should guide us as to which type of interaction should be considered. However, the fact of the matter is that once the truncation approximation has been made, the most general form that \( \Phi \) can have is\(^{18} \)
\[ H_I(R^N, R) = \tilde{f}(R_0) \cdot \vec{\phi}(r^N) \]  
(3.12)

where
\[ \tilde{f}(R_0) = (f_x(R_0)\sigma_x, f_y(R_0)\sigma_y, f_z(R_0)\sigma_z) \]  
(3.13a)

and
\[ \vec{\phi}(r^N) = (\phi_x(r^N), \phi_y(r^N), \phi_z(r^N)) \]  
(3.13b)

Now, for the temperatures allowed, the bath cannot knock the particle over the barrier (thermal activation) nor through it; consequently, only the term proportional to \( \sigma_z \) should be considered. (That is, the interaction only "tilts" the potential \( V(R) \)). Thus the interaction term becomes
\[ H_I = \lambda \sigma_z \vec{\phi}(r^N) \]  
(3.14)

where \( f_z(R_0) \) has been absorbed into the definition of \( \vec{\phi} \) and \( \lambda \) is the strength parameter.

(The same result can also be obtained, without attempting to be general, by assuming an interaction linear in the generalized coordinate \( R \):\n\[ H_I = \lambda R \phi(r^N) \]  ;

53
then in the TLS states the expectation values of $R$ are
\[ \langle R \mid R \mid R \rangle = R_0 \quad \text{and} \quad \langle L \mid R \mid L \rangle = -R_0 ; \]
thus Eq(3.14) follows.

The specific forms of $\phi$ and of $H_B$ will be left unspecified for the rest of this section, due to the generality of our scheme; their particular forms should be dictated by the specific problem to which the theory is applied. We point out, nevertheless, that the forms almost universally employed in other theoretical treatments, are given by Eqs(3.3), with a particular model for $G_n$, (the so called "ohmic" case); this model is very attractive since it allows for explicit analytic solutions. This is further discussed at the end of this section.

Having thus understood the origin of the Hamiltonian Eq(3.1), we can now study the equation for the reduced density matrix of the system, $W(t)$, derived in the previous section, Eq(2.19). We shall find its solution valid in the strict weak coupling limit.

Without any loss of generality we assume that
\[ \langle \phi(r) \rangle_B = \text{Tr}_B \rho_B \phi(r) = 0 . \tag{3.15} \]
Hence, Eq(2.19) yields
\[
\frac{\partial}{\partial t} W(t) = -i \left[ -\frac{\Delta_0}{2} \sigma_x + \frac{\varepsilon}{2} \sigma_z , W(t) \right] \\
+ i \frac{\lambda}{2} \text{Tr}_B \left[ \sigma_z \phi , \left( \left[ \sigma_z(-\tau) \phi(-\tau) , W(t) \rho_B \right] \\
- \frac{1}{2} W(t) e^{\beta H_S} \left[ \sigma_z(-\tau) \phi(-\tau) , e^{-\beta H_S} \rho_B \right] \\
- \frac{1}{2} \left[ \sigma_z(-\tau) \phi(-\tau) , e^{-\beta H_S} \rho_B \right] e^{\beta H_S} W(t) \right] \tag{3.16}
\]
where $H_S$ is given by Eq(3.9),
\[
\sigma_z(-\tau) = e^{-i H_S t} \sigma_z e^{i H_S t} . \tag{3.17}
\]
\[ \phi(r^N, -\tau) = e^{-i \hat{H}_B \tau} \phi(r^N) e^{i \hat{H}_B \tau} \]

(3.18)

and

\[ D_0 = \int \alpha^B e^{-\theta \hat{H}_S} \beta^2 e^{\theta \hat{H}_S} e^{-\theta \hat{H}_B} \beta^2 e^{\theta \hat{H}_B} \]

(3.19)

As we already indicated, Eq(3.16) is meaningful for its matrix elements only. Hence, the first step is to evaluate it in the eigenstates of \( \hat{H}_S \). The diagonalization of \( \hat{H}_S \) is easily achieved with the following results

\[ \hat{H}_S \left| \begin{array}{c} 1 \\ 1 \end{array} \right\rangle = \frac{1}{2} \sqrt{\epsilon + \Delta_0^2} \left| \begin{array}{c} 1 \\ 1 \end{array} \right\rangle \equiv E \left| \begin{array}{c} 1 \\ 1 \end{array} \right\rangle \]

(3.20)

\[ \hat{H}_S \left| \begin{array}{c} 2 \\ 2 \end{array} \right\rangle = -\frac{1}{2} \sqrt{\epsilon + \Delta_0^2} \left| \begin{array}{c} 2 \\ 2 \end{array} \right\rangle \equiv -E \left| \begin{array}{c} 2 \\ 2 \end{array} \right\rangle ; \]

\( E \) corresponds to the tunneling splitting \( \Delta \) in the figure, but we will use \( E \) to avoid confusion with \( \Delta_0 \). With the definitions

\[ \cos \alpha = \frac{\Delta_0}{\sqrt{\epsilon + \Delta_0^2}} \quad \text{and} \quad \sin \alpha = \frac{\epsilon}{\sqrt{\epsilon + \Delta_0^2}}, \]

(3.21)

the states \( \left| \begin{array}{c} 1 \\ 1 \end{array} \right\rangle \) and \( \left| \begin{array}{c} 2 \\ 2 \end{array} \right\rangle \) are related to the states \( \left| L \right\rangle \) and \( \left| R \right\rangle \) by

\[ \left| \begin{array}{c} 1 \\ 1 \end{array} \right\rangle = \frac{1}{\sqrt{2}} \left( \sqrt{1 + \sin \alpha} \left| \begin{array}{c} 1 \\ 1 \end{array} \right\rangle - \frac{\cos \alpha}{\sqrt{1 + \sin \alpha}} \left| \begin{array}{c} 1 \\ 1 \end{array} \right\rangle \right) \]

(3.22)

\[ \left| \begin{array}{c} 2 \\ 2 \end{array} \right\rangle = \frac{1}{\sqrt{2}} \left( \sqrt{1 + \sin \alpha} \left| \begin{array}{c} 1 \\ 1 \end{array} \right\rangle + \frac{\cos \alpha}{\sqrt{1 + \sin \alpha}} \left| \begin{array}{c} 1 \\ 1 \end{array} \right\rangle \right) ; \]

We pause briefly to use the present example to show that, in general, the correction to the systematic term, i.e. the second term on the RHS of Eq(3.16), cannot be written as a commutator of a system operator and the reduced density matrix. First, we note that we can write
\[ e^{-\beta H_S} \sigma_x e^{\beta H_S} = \sigma_x (\sin^2 \alpha + \cos^2 \alpha \cosh 2\theta E) \]

\[ + \sigma_x \sin \alpha \cos \alpha (-1 + \cosh 2\theta E) + i \sigma_y \cos \alpha \sinh 2\theta E \]

Substitution of this equation into the second term on the RHS of Eq (3.16) yields

\[ i \frac{\lambda}{2} \int_0^\beta d\theta (\text{Tr}_B \rho_B e^{-\beta H_B} \phi e^{\beta H_B} \phi) (\sin \alpha \cos \alpha (\cosh 2\theta E - 1) \left[ \sigma_x, \left[ \sigma_x, W(t) \right] \right] \]

\[ - i \cos \alpha \sinh 2\theta E \left[ \sigma_x, \left[ \sigma_y, W(t) \right] \right] \]

which cannot be written as a single commutator of a system operator with \( W(t) \). Therefore, the whole systematic term cannot be written as the commutator of an effective Hamiltonian with the reduced density matrix, in contrast to the classical case.

The evaluation of Eq (3.16), in the states Eqs (3.22), is straightforward, though tedious, yielding the following set of coupled equations for the matrix elements of \( W(t) \), where we use the notation \( W_{ij} = \langle i | W | j \rangle \):

\[ \frac{\partial}{\partial t} W_{11}(t) = - \lambda^2 W_{11}(t) \cos^2 \alpha \Re \int_{-\infty}^{\infty} d\tau C(\tau) e^{2iE\tau} \]

\[ + \lambda^2 W_{22}(t) \cos^2 \alpha \Re \int_{-\infty}^{\infty} d\tau C(\tau) e^{-2iE\tau} \]  

\[ + \lambda^2 (W_{12}(t) + W_{21}(t)) \cos \alpha \sin \alpha \Re \int_{-\infty}^{\infty} d\tau C(\tau) \]  

\[ (3.23a) \]

\[ \frac{\partial}{\partial t} W_{22}(t) = - \frac{\partial}{\partial t} W_{11}(t) \]  

\[ (3.23b) \]

(this equation guarantees conservation of probability)

\[ \frac{\partial}{\partial t} W_{12}(t) = - 2i E W_{12}(t) - i \lambda^2 \cos \alpha \sin \alpha \int_0^\beta d\theta C(-i\theta) \]

\[ + i \lambda^2 W_{11}(t) \cos \alpha \sin \alpha \int_0^\beta d\theta C(-i\theta) e^{2\theta E} \]
\[ + i \lambda^2 W_{22}(t) \cos \alpha \sin \alpha \int_{0}^{\beta} d\theta \ C(-i\theta) e^{-2\theta E} \]
\[ + i \lambda^2 (W_{12}(t) + W_{21}(t)) \cos^2 \alpha \int_{0}^{\beta} d\theta \ C(-i\theta) \sinh 2\theta E \]
\[ + \lambda^2 W_{11}(t) \cos \alpha \sin \alpha \int_{0}^{\infty} d\tau \ \{ C(\tau)e^{2\beta E} + C^{\dagger}(\tau) \} e^{-2i Et} \]
\[ - \lambda^2 W_{22}(t) \cos \alpha \sin \alpha \int_{0}^{\infty} d\tau \ \{ C^{\dagger}(\tau)e^{-2\beta E} + C(\tau) \} e^{-2i Et} \]
\[ - \frac{\lambda^2}{2} W_{12}(t) \int_{0}^{\infty} d\tau \ \{ C(\tau)(4\sin^2 \alpha + \cos^2 \alpha (1 + e^{-2\beta E}) e^{2i Et}) + C^{\dagger}(\tau)(4\sin^2 \alpha + \cos^2 \alpha (1 + e^{2\beta E}) e^{-2i Et}) \} \]
\[ + \frac{\lambda^2}{2} W_{21}(t) \int_{0}^{\infty} d\tau \ \{ C(\tau) \cos^2 \alpha (1 + e^{2\beta E}) e^{-2i Et} + C^{\dagger}(\tau) \cos^2 \alpha (1 + e^{-2\beta E}) e^{2i Et} \} \]

and
\[ \frac{\partial}{\partial t} W_{21}(t) = \frac{\partial}{\partial t} W_{12}(t) \]  

(3.23d)

where
\[ C(x) = \left\langle \phi(r', x) \phi(r) N \right\rangle_B \]  

(3.24)

As can be directly verified, the equilibrium solution

\[ W_{11} = \frac{e^{-\beta E}}{e^{-\beta E} + e^{\beta E}} \]  

(3.25a)

\[ W_{22} = \frac{e^{\beta E}}{e^{-\beta E} + e^{\beta E}} \]  

(3.25b)

and
\[ W_{12} = W_{21} = 0 \]  \hspace{1cm} (3.25c)

is not a solution to the set of equations Eqs(3.23) unless we neglect the terms proportional to \( C(-i \theta) \); that is, those arising from the correction to the Euler term. But we cannot disregard them without tampering with the time dependence of the matrix elements.

The relevance of the knowledge of the matrix elements of the density matrix lies in the evaluation of averages of measurable quantities; to illustrate this we will compute the time evolution of the expectation values of the Pauli matrices (e.g. \( \langle \sigma_z \rangle \) gives us information regarding the "position" of the particle in the potential).

The expectation value of the Pauli matrices is given by
\[ \left\langle \sigma_i(t) \right\rangle \equiv \text{Tr}_S W(t) \sigma_i \quad \text{for} \quad i = x, y, z \]  \hspace{1cm} (3.26)

which can be written as
\[ \left\langle \sigma_x(t) \right\rangle = (W_{22}(t) - W_{11}(t)) \cos \alpha + (W_{12}(t) + W_{21}(t)) \sin \alpha \]  \hspace{1cm} (3.27a)

\[ \left\langle \sigma_y(t) \right\rangle = i \left( W_{12}(t) - W_{21}(t) \right) \]  \hspace{1cm} (3.27b)

and
\[ \left\langle \sigma_z(t) \right\rangle = (W_{11}(t) - W_{22}(t)) \sin \alpha + (W_{12}(t) + W_{21}(t)) \cos \alpha. \]  \hspace{1cm} (3.27c)

Thus, using Eqs(3.23) we readily obtain the equations satisfied by \( \langle \sigma_i \rangle \):
\[ \frac{\partial}{\partial t} \left\langle \sigma_x(t) \right\rangle = -2E \sin \alpha \left\langle \sigma_y(t) \right\rangle + \lambda^2 \Gamma_1 \cos \alpha \tanh \beta E \]
\[ + \lambda^2 \left\langle \sigma_z(t) \right\rangle (\Gamma_1 - \Gamma_2) \sin \alpha \cos \alpha \]  \hspace{1cm} (3.28a)

\[ - \lambda^2 \left\langle \sigma_z(t) \right\rangle (\Gamma_1 \cos^2 \alpha + \Gamma_2 \sin^2 \alpha) \]

\[ \frac{\partial}{\partial t} \left\langle \sigma_y(t) \right\rangle = 2E \sin \alpha \left\langle \sigma_x(t) \right\rangle + 2\lambda^2 \sin \alpha \cos \alpha \int_0^\beta d\theta \; C(-i \theta)(1 - \cos 2\theta E) \]
\[ + S_1 \sinh \beta E \cosh \beta E + S_2 \sinh^2 \beta E \]
+ 2\langle \sigma_z (t) \rangle \cos \alpha \{ E - \lambda^2 (E_1 - S_1 \cosh^2 \beta E - S_2 \cosh \beta \sinh \beta E) \}
- \lambda^2 \langle \sigma_y (t) \rangle (\Gamma_1 \cos^2 \alpha + \Gamma_2 \sin^2 \alpha) \quad ,

\text{(3.28b)}

and

\frac{\partial}{\partial t} \langle \sigma_z (t) \rangle = -2E \cos \alpha \langle \sigma_y (t) \rangle \quad ;

\text{(3.28c)}

where

\Gamma_1 \equiv \int_{-\infty}^{\infty} d\tau \langle \{ \phi(\tau), \phi \} \rangle_B \cos 2E\tau

\text{(3.29)}

and

\Gamma_2 \equiv \int_{-\infty}^{\infty} d\tau \langle \{ \phi(\tau), \phi \} \rangle_B

\text{(3.30)}

are dissipative coefficients;

S_1 \equiv \int_{0}^{\infty} d\tau \langle \{ \phi(\tau), \phi \} \rangle_B \sin 2E\tau

\text{(3.31)}

and

S_2 \equiv \int_{0}^{\infty} d\tau \langle i [\phi(\tau), \phi] \rangle_B \cos 2E\tau

\text{(3.32)}

are dynamic shifts to the energy; and

E_1 \equiv \int_{0}^{\beta} d\theta \langle \phi(-i \theta), \phi \rangle_B \sin 2\theta E

\text{(3.33)}

is a statistical or equilibrium shift.

Although the exact solution to Eqs(3.28) can be obtained, we are interested in the result valid in the weak coupling limit only (\lambda^2 \to 0, t \to \infty but \lambda^2 t \text{ finite}). The details are given in Appendix A; here, we just quote the results for an arbitrary initial condition:

\langle \sigma_x (t) \rangle = \langle \sigma_x (0) \rangle \left( e^{-\lambda^2 \gamma_1 t} \cos^2 \alpha + e^{-\lambda^2 \gamma_2 t} \sin^2 \alpha \cos(2E + \lambda \Omega t) \right)

59
\[-\langle \sigma_y(0) \rangle e^{-\lambda^2 \gamma_2 t} \sin \alpha \sin(2E + \lambda^2 \Omega)t \]
\[+ \langle \sigma_z(0) \rangle \cos \alpha \sin \alpha \left( -e^{-\lambda^2 \gamma_1 t} + e^{-\lambda^2 \gamma_2 t} \cos(2E + \lambda^2 \Omega)t \right) \]
\[+ \cos \alpha \tanh \beta E \left( 1 - e^{-\lambda^2 \gamma_1 t} \right) \]
\[= \langle \sigma_x(0) \rangle e^{-\lambda^2 \gamma_2 t} \sin \alpha \sin(2E + \lambda^2 \Omega)t \]
\[+ \langle \sigma_y(0) \rangle e^{-\lambda^2 \gamma_2 t} \cos(2E + \lambda^2 \Omega)t \]
\[+ \langle \sigma_z(0) \rangle e^{-\lambda^2 \gamma_2 t} \cos \alpha \sin(2E + \lambda^2 \Omega)t \]
\[\text{(3.34a)}\]

and
\[\langle \sigma_z(t) \rangle = \langle \sigma_x(0) \rangle \cos \alpha \sin \alpha \left( e^{-\lambda^2 \gamma_2 t} \cos(2E + \lambda^2 \Omega)t - e^{-\lambda^2 \gamma_1 t} \right) \]
\[+ \langle \sigma_y(0) \rangle e^{-\lambda^2 \gamma_2 t} \cos \alpha \sin(2E + \lambda^2 \Omega)t \]
\[+ \langle \sigma_z(0) \rangle \left( e^{-\lambda^2 \gamma_1 t} \sin^2 \alpha + e^{-\lambda^2 \gamma_2 t} \cos^2 \alpha \cos(2E + \lambda^2 \Omega)t \right) \]
\[- \sin \alpha \tanh \beta E \left( 1 - e^{-\lambda^2 \gamma_1 t} \right) \]
\[\text{; (3.34c)}\]

where the relaxation rates are given by
\[\gamma_1 = \Gamma_1 \cos^2 \alpha \]
\[\text{(3.35a)}\]

and
\[\gamma_2 = \frac{1}{2} \Gamma_1 \cos^2 \alpha + \Gamma_2 \sin^2 \alpha \]
\[\text{; (3.35b)}\]

and the shift to the frequency by
\[\Omega = \frac{3}{4} \left( -E_1 + 2 \cos \alpha \left( S_1 \cosh^2 \beta E + S_2 \sinh \beta E \cosh \beta E \right) \right) - \frac{\gamma_1}{16 E} \]
\[\text{(3.36)}\]

This solution shows that
\[\langle \sigma_x \rangle = \cos \alpha \tanh \beta E \]
\[\langle \sigma_y \rangle = 0 \]
\[\text{(3.37)}\]
\[ \langle \sigma_z \rangle = -\sin \alpha \tanh \beta E \]

is both the stationary and the equilibrium solution (reached as \( t \to \infty \), having started from a non-equilibrium state), of the system given by the Hamiltonian \( H_S \), Eq(3.9). It corresponds to canonical equilibrium at temperature \( \beta^{-1} \). The time dependence of Eqs(3.34), however, includes the shifts to the energy levels due to the interaction.

This solution, Eqs(3.34), should only be appropriate for the cases where the time scales of the uncoupled system and bath, \( E^{-1} \), the inverse of the tunneling splitting, and \( \tau_B \) respectively, are either comparable or the former is larger than the latter, but both time scales smaller than the relaxation time, proportional to \( (\lambda^2 \Gamma_1)^{-1} \) and \( (\lambda^2 \Gamma_2)^{-1} \), i.e. the underdamped case. Or in other words, valid for relatively "large" tunneling splitting in comparison with the interaction energy, proportional to \( \lambda \). For the case \( E^{-1} \gg \tau_B \), we find, as expected, that the dynamic shifts become negligible while the equilibrium shift does not, as can be seen from Eqs(3.31)-(3.33).

Much of the recent interest in this tunneling problem, i.e. Eq(3.1)-(3.3), has been for the opposite case, namely, when the tunneling splitting is the small parameter, and \( \lambda \), the coupling parameter, is allowed to have arbitrary values (even larger than 1)\(^{19,21,26-28} \). However, as we mentioned before, most of the interesting results, e.g. transition from coherent to incoherent tunneling, localization in one of the wells, etc., appear only for the so called "ohmic" case. This is a particular choice of the function \( G_n \), appearing in Eq(3.3b), in the continuum approximation:

\[
\lambda \sum_n G_n^2 \to \lambda \int d\omega D(\omega) \ G^2(\omega) = \eta \int d\omega \ \omega \quad \text{for } \omega \leq \omega_c
\]

(3.38)

where \( D(\omega) \) is the density of phonon states; that is, the spectral density of the interaction is assumed to be linear in frequency up to a cutoff value, say proportional to the Debye frequency. Silbey and Harris\(^ {19} \) have pointed out that, besides leading to an infrared
divergence, such a form is not very realistic since it does not correspond to a three
dimensional phonon bath. For a detailed discussion of the present problem, in the ohmic
case, we suggest the work of Silbey and Harris\textsuperscript{19} and Aslangul et. al.\textsuperscript{21,22} within the
formalism of relaxation theories such as ours; and the review paper of Leggett et. al.\textsuperscript{28} in
the context of path integral formalisms. (See in particular Ref.\textsuperscript{122}, where it is
demonstrated that both techniques give identical results).

Using the present approach, provided of course we transform the Hamiltonian
Eq\textsuperscript{(3.1)} so as to be able to make the expansion in terms of $\Delta_0$ for an arbitrary value of $\lambda$,
we can recover all those results. This is achieved, first, by introducing the unitary
transformation\textsuperscript{19}
\begin{equation}
U = e^{i \lambda \sigma_x \sum_n \frac{G_n}{\omega_n} (b_n^+ - b_n)} ,
\end{equation}

the Hamiltonian Eqs\textsuperscript{(3.1)-(3.3)} thus becomes,
\begin{equation}
\tilde{H} = \frac{e}{2} \sigma_z + H_B - \frac{\Delta_0}{2} (B_+ \sigma_+ + B_- \sigma_-) ,
\end{equation}

where $H_B$ is given by Eq\textsuperscript{(3.3a)},
\begin{equation}
B_\pm = e^{i \lambda \sum_n \frac{G_n}{\omega_n} (b_n^+ - b_n)}
\end{equation}

and
\begin{equation}
\sigma_\pm = \frac{1}{2} (\sigma_x \pm i \sigma_y) .
\end{equation}
The treatment developed in the previous Section can immediately be applied to this
Hamiltonian using as a small parameter the tunneling frequency $\Delta_0$; i.e. the last term of
Eq\textsuperscript{(3.39)} becomes the interaction potential and $\lambda$ can have any value. We will not present
the results here since there are no important differences due to the simplicity of the TLS.
Our work differs in general from past treatments as we discuss in the next Section.

62
Although with Eqs(3.28) we cannot allow values of $\lambda > 1$, we can nevertheless understand, in a qualitative fashion, the meaning of "tunneling friction"\textsuperscript{25,26} responsible for the localization in one of the wells, by extending the validity of our equations for the overdamped case in which $E < \lambda^2 \Gamma \equiv \lambda^2 \Gamma_1 = \lambda^2 \Gamma_2$. (In this case both the dynamic and statistical shifts can be neglected and Eqs(3.28) become the Bloch equations\textsuperscript{6}). Considering for simplicity the "unbiased" case, $\varepsilon = 0$ and therefore $E = \Delta_0$, and assuming that the particle is initially completely localized in one of the wells, say the one on the right, i.e. $W(0) = |R < R|$, the time evolution of the position of the particle is found to be given by

$$\left\langle \sigma_x(t) \right\rangle \equiv \mathcal{E} \frac{\Delta_0^2}{\lambda^2 \Gamma}$$

(3.43)

The relaxation time, $\lambda^2 \Gamma / \Delta_0^2$, is enormously longer than the natural time of the uncoupled system, $\Delta_0^{-1}$, and the particle appears as if it would stay localized for a long time. This result was first obtained by Harris and Silbey\textsuperscript{18} as an explanation for the stabilization of optical isomers. The main objection to this result has been that the tunneling frequency that appears in Eq(3.43) should not be the bare frequency but rather a "renormalized" one; the derivation explained above, i.e. using Eqs(3.39)-(3.42), takes this into account.
II. C. COMPARISON TO EARLIER WORK.

The list of papers dealing with the description of the time evolution of a system of few degrees of freedom interacting with a reservoir is immense; the purpose of this discussion is not to review the different approaches used in the past, but rather to briefly compare our results with previous theories based on projection operator techniques similar to ours. We discuss in some detail the results of a particular choice of the projection operator.

Using a projection operator in order to integrate out the bath degrees of freedom* is, by now, a very common mathematical tool: one can always rewrite the Liouville equation as an equation for the projected distribution function or density matrix.

That is, starting with the Liouville equation
\[ \frac{\partial}{\partial t} \rho(t) = L \rho(t), \]

(1)

and using a projection operator, \( \mathcal{P}^2 = \mathcal{P} \), Eq(1) can be written as (see e.g. Section II.A.1)
\[ \frac{\partial}{\partial t} \mathcal{P} \rho(t) = \mathcal{P} L \mathcal{P} \rho(t) + \int_0^t dt' \mathcal{P} L e^{Q L Q \tau} Q L \mathcal{P} \rho(t) + \]
\[ + \mathcal{P} L e^{Q L Q \tau} (1 - \mathcal{P}) \rho(0), \]

(2)

where \( Q = (1 - \mathcal{P}) \). Eq(2) would be a closed equation for \( \mathcal{P} \rho(t) \) if the initial term were not present. In some applications, the projection operator and the initial density matrix of the overall system are chosen in such a way that the last term of Eq(2) vanishes identically, i.e. \( \mathcal{P} \rho(0) = \rho(0) \).

Some initial states commonly used are:

i) \( \rho(0) = \rho_B W(0) \).

(3)

* It has of course a wider use, e.g. to separate the diagonal from the off-diagonal matrix elements in the derivation of Master equations. See e.g. Zwanzig, Ref.4.
This is the so called "factorization assumption" in which the bath and the system are initially uncorrelated and the former is in equilibrium by itself. We shall analyze this case in more detail below.

\[
\rho(0) = \frac{e^{-\beta(H - \sum_i h_i S_i)}}{\int dX dP d\text{Re} e^{-\beta(H - \sum_i h_i S_i)}}
\]

(4)

In this generalized canonical form, \(h_i\) are external fields conjugate to the system variables \(S_i\). It is assumed that the system is adiabatically driven from \(t = -\infty\) towards this equilibrium and at \(t = 0\) the external fields are turned off. Grabert and collaborators\(^{49,51}\) have developed a quite formal treatment based on this type of initial condition.

iii) Another typical case is to force the system into a particular state while coupled to an equilibrium bath. This case has been used mainly in the study of two level systems\(^{55}\).

All these initial conditions are in fact of the general type, Eq(II.A.2.4), to which our formalism applies. It can also accommodate other realistically prepared states.

Among the initial conditions, Eq(3) is the most widely used\(^{4,22,49-51}\), especially in the quantum case. (It has been used not only in projection operator formalisms but in fact is the assumption behind many treatments, e.g the seminal works of van Hove\(^{1}\) and Redfield\(^{7}\).) Then, a natural choice for the projection operator is

\[
\mathcal{P}_0 A = \rho_B \text{Tr}_B A
\]

(5)

where \(A\) is a dynamical variable. Note that \(\mathcal{P}_0\) is the lowest order term of our projection operator, Eq(II.B.1.9).

Using Eq(5), Eq(2) becomes, after tracing over the bath variables

\[
\frac{\partial}{\partial t} W(t) = -i \left[ H_S, W(t) \right] - i \lambda \left[ \langle H_I \rangle_B, W(t) \right] - \lambda^2 \int_0^t d\tau \text{Tr}_B \left[ H_I, e^{Q_0^L Q_0^\tau} Q_0[H_I, \rho_B W(t - \tau)] \right]
\]

(6)
To obtain Eq(6), we used the lowest order of Eqs(II.B.1.15) and the definition Eq(II.B.2.13.c).

By assuming with no loss of generality
\[ \langle H \rangle_B = 0, \quad (7) \]

Eq(6) certainly looks appealing: the zeroth order term is the Liouvillian of the isolated system, whereas the whole effect of the interaction is buried in the last term. In the limit of weak interaction, the last term is approximated by taking the lowest order of the propagator. One then obtains
\[ \frac{\partial}{\partial t} \ W(t) = -i \ [H_S, W(t)] - \lambda^2 \int_0^1 d\tau \ Tr_B \ [H_I, e^{L_0 \tau} \ [H_I, \rho_B W(t - \tau)]] \quad (8) \]

where
\[ L_0 = L_S + L_B. \quad (9) \]

(The classical counterparts of Eqs(6) and (8) can be obtained using the classical forms of the Liouvillians and changing the traces over the bath by integrals over the phase space of the bath.)

The appeal of Eq(8) is reinforced by the fact that in the limit \( t \to \infty \), and substituting \( W(t) = W_e^{(0)} \), the diagonal matrix elements of Eq(8) vanish, in the basis in which \( H_S \) is diagonal;
\[ W_e^{(0)} = \frac{e^{-\beta H_S}}{Tr e^{-\beta H_S}}. \quad (10) \]

This property seemingly ensures that Eq(8) properly describes the time evolution of \( W(t) \) since the relaxation to equilibrium is assured. However, the off-diagonal matrix elements of the last term of Eq(8) do not vanish: it is argued that this is due to shifts to the energy levels of \( H_S \). In some particular cases such as the the harmonic oscillator and the "unbiased" TLS, i.e. Eq(II.B.3.1) with \( \epsilon = 0 \), linearly coupled to the bath, the off-diagonal elements also
vanish, but this is because the interaction is purely off-diagonal and because the eigenstates of $H_S$ are evenly separated in energy.

Although, in the light of the present work, the above conclusions are indeed correct only in the weak coupling limit, as we shall see below, we have several additional objections to this approach, that our formalism corrects:

The first criticism, of course, is the choice of the initial condition: first it is unrealistic and second, in real experiments a precise knowledge of the initial state of the overall system is usually unavailable. One can argue in their favor, that such an assumption can be relaxed, and consider initial density matrices of the type given by Eq(II.A.2.4); with the further assumption that the bath relaxation is short, the initial value term could be neglected in an analogous way to our case.

The separation of Eq(8) into streaming and dissipative terms would not be explicit however. Furthermore, the equation does not have as its stationary solution the equilibrium reduced density matrix $W_e$, Eq(II.B.1.4). This takes us to the other property: the thermal equilibration shown by Eq(8) in the limit $t \to \infty$, is somewhat "accidental", rather than an assured consequence.

This can be shown as follows: the overall equilibrium density matrix $\rho_e$, Eq(II.B.1.3), is a solution of the Liouville equation, Eq(1), that is,

$$ (L_S + L_B) \rho_e = -\lambda L_1 \rho_e \quad . $$ (11)

Expanding $\rho_e$ in powers of $\lambda$, we obtain the following set of equations:

$$ (L_S + L_B) \rho_e^{(0)} = 0 \quad , $$ (12.a)

$$ (L_S + L_B) \rho_e^{(1)} = -L_1 \rho_e^{(0)} \quad , $$ (12.b)

$$ (L_S + L_B) \rho_e^{(2)} = -L_1 \rho_e^{(1)} \quad , $$ (12.c)

and so on. Tracing over the bath variables, these become

$$ L_S W_e^{(0)} = 0 \quad , $$ (13.a)

67
\[ L_S W_e^{(1)} = - \text{Tr}_B L^{-1}_1 \rho_e^{(0)} \] (13.b)

\[ L_S W_e^{(2)} = - \text{Tr}_B L^{-1}_1 \rho_e^{(1)} \] (13.c)

and so on.

From Eq(II.B.2.15) we have
\[ \rho_e^{(1)} = \rho_B W_e^{(1)} + \frac{1}{2} (\bar{\rho}_1 W_e^{(0)} + W_e^{(0)} \bar{\rho}_1^\tau) \] (14)

then, from Eqs(12.b) and (13.b) it follows that
\[ (L_S + L_B) \frac{1}{2} Q_0 (\bar{\rho}_1 W_e^{(0)} + W_e^{(0)} \bar{\rho}_1^\tau) = - Q_0 L^{-1}_1 \rho_B W_e^{(0)} \] (15)

Due to the factor \( Q_0 \), we can solve Eq(14), obtaining
\[ \frac{1}{2} (\bar{\rho}_1 W_e^{(0)} + W_e^{(0)} \bar{\rho}_1^\tau) = -(L_S + L_B)^{-1} Q_0 L^{-1}_1 \rho_B W_e^{(0)} \]
\[ = \int_0^\infty dt \ e^{(L_S + L_B)\tau} Q_0 L^{-1}_1 \rho_B W_e^{(0)} \] (16)

Substitution of Eq(15), with Eq(13), into Eq(12.c) yields
\[ L_S W_e^{(2)} = - \text{Tr}_B L^{-1}_1 \rho_B W_e^{(1)} - \int_0^\infty dt \ Tr_B L^{-1}_1 e^{(L_S + L_B)\tau} Q_0 L^{-1}_1 \rho_B W_e^{(0)} \] (17)

The convergence of the integral representation Eq(16) is guaranteed in Eq(17) by the factor \( Q_0 \) and the assumption that the bath relaxes within \( \tau_B \), i.e. the integrand decays to zero as \( t \to \infty \).

Eq(17) is the origin of the equilibrium results of Eq(8). Note that the first term of Eq(17) is identically zero if \( \langle H_B \rangle_B = 0 \), and that its last term equals the last term of Eq(8) in the limit \( t \to \infty \) and substitution of \( W(t - \tau) \) by \( W_e^{(0)} \). The correct way to perform this evaluation consists in taking matrix elements of Eq(8), then Laplace transforming each equation, and substituting for the residues at \( z=0 \), where \( z \) is the Laplace variable, the matrix elements of \( W_e^{(0)} \). The results are equivalent.
By taking diagonal elements of Eq(17) in the basis in which $H_s$ is diagonal, we see that the LHS is zero. Since the first term is identically zero by assumption Eq(7), the last term is also zero; this explains the result that in such a case the two terms of the RHS of Eq(8) vanish separately in the limit above described. If $\langle H_I \rangle_B \neq 0$ this property still holds as long as $H_I$ is purely off-diagonal.

In general, regardless of whether $H_I$ is purely off-diagonal or not, Eq(17) indicates that the off-diagonal matrix elements of the RHS of Eq(8) cannot be zero in such a limit. What one obtains are precisely the equilibrium streaming corrections to second order in $\lambda$. In other words, the equilibrium results of Eq(8) are just part of a whole hierarchy of equations, Eqs(13), whose solution is the reduced density matrix of the system $W_e = \text{Tr}_B \rho_e$.

These points are important because the equations for the matrix elements of $W(t)$, as given by Eq(8), are in general coupled. Consequently, their solution will not show that the system relaxes to the canonical equilibrium of the isolated system, i.e. $W_e^{(0)}$.

We have analyzed in some depth the results of the projection operator $P_0$ because in many respects it is similar to the projection operator $P$ of the two previous Parts. This is not surprising because the starting point, Eq(2), is just an exact transformation of the Liouville equation: for the same initial condition, Eq(2) is the same regardless of the precise form of the projection operator. Once approximations and assumptions are introduced, the results of course can be different. For the two projection operators at hand, $P_0$, Eq(5) and $P$, Eqs(II.A.1.18) or (II.B.1.9), the former being the lowest order of the latter in a $\lambda$ expansion, it turns out that in the strict weak coupling limit (i.e. neglecting the initial value term, extending the upper limit of the time integral to infinity, approximating $W(t - \tau) = e^{-L_\tau}W(t)$ in the equations and keeping only terms with time dependence $\lambda^2 t$), the solution of Eq(8) agrees with the ones obtained from our equations Eq(II.A.2.17) and (II.B.2.19),

69
although in the $P_0$ case the separation of the statistical and dynamic corrections to the Euler term will not be achieved. Because our method takes this into account from the start, in the classical case we were able to write a closed equation for $W(t)$ having as its stationary solution $W_e$ valid up to second order in $\lambda$; in the quantum case, as we saw in Section II.B.2, in general this is not possible, although an understanding of how the terms of the equations should be handled is gained.

Serious differences can arise when the equations are pushed beyond their strict validity; for example, a frequently used approximation is to consider the operators acting on $W(t)$ in the convolution term of Eq(2), as a "memory kernel"*. In principle, if the initial value term vanishes identically, the memory term is indeed correct, although as we discussed above, the equation has very limited applicability since a complete knowledge of the memory kernel is equivalent to the solution of the Liouville equation. A typical approximation of the memory term consists of taking the lowest order of the propagator, and with a model for the interaction proceed with the evaluation of $W(t)$. From the present work we conclude that, strictly speaking, this treatment is inconsistent: the neglect of the higher order terms is not only possible because $\lambda$ is small but also because the integrand decays fast with respect to the time scale of interest. That is, if the kernel of the dissipation is not short lived, the expansion in powers of $\lambda$ is not completely valid. On the other hand, by depending on the whole past history of the process, the Markovian property is lost and the resulting probability distribution function becomes of very limited applicability; we will return to this point in Part III.D.

In some instances however, it might be important to consider the relaxation rates as being time dependent, for example in quantum problems at intermediate temperatures

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* In most of the literature the notation "generalized" Fokker-Planck or "generalized" Master equations refers to this approximation.
where the bath correlations can no longer be considered as decaying fast, or in classical systems where effects due to the slow hydrodynamical modes of the bath must be considered\textsuperscript{42,43}. A better approximation would be to "deconvolve"\textsuperscript{21} that term mentioned above, but leave the upper limit of the integral as $t$. The results obtained by implementing this approximation would be different depending on the projection operator used.
II. D. REMARKS.

The main purpose of this Chapter is to systematically derive the relaxation properties of a small system in weak interaction with a heat bath for classical and quantum systems. This is achieved by using the projection operator, Eq(II.A.1.18), for the classical case

$$\mathcal{P}_B = \bar{\rho}_e \int dX B \quad ;$$

and Eq(II.B.1.9) for the quantum case

$$\mathcal{P}_B = \frac{1}{2} (\bar{\rho} Tr_B B + (Tr_B B) \bar{\rho}^T) \quad .$$

In Eq(1), $\bar{\rho}_e$ is the equilibrium conditional distribution for the bath for fixed system coordinates and momenta. The analysis of Part A indicates that an important property of $\mathcal{P}$ is that it projects the overall equilibrium distribution function onto itself. This fact is used to extend the treatment when quantum mechanics is obeyed; $\bar{\rho}$, in Eq(2) is defined such that $\mathcal{P}\rho_e = \rho_e$. (See Eq(II.B.1.10)).

Exact equations for the reduced distribution function and the reduced density matrix are obtained where systematic and dissipative parts are separated. These equations can be approximated to any order in $\lambda$, the strength of the system-bath coupling, and to order $\lambda^2$ the results are a generalized Fokker-Planck equation and a generalized Master equation for the classical and quantum cases respectively. In the latter case, in contrast to the former, it is not possible in general to write the whole streaming term as an effective Hamiltonian. This problem is nevertheless fixed in the weak coupling limit. The range of validity of the equations mentioned above is determined by

$$\lambda^2 \ll 1$$

and
\[ \tau_B(\text{classical}) \text{ and } \tau_m(\text{quantum}) \ll \tau_R \]  \hspace{1cm} (4)

where \( \tau_R \) is the relaxation time of the system in interaction with the bath. No assumption is made regarding the time scale associated with \( H_S \), the Hamiltonian of the isolated system. However, when the latter is longer than the characteristic time of the bath, it is found that the dynamic streaming corrections arising from the dissipative term become negligible and a connection with the corresponding stochastic equations\(^{12}\) is established.

The general results are applied to particular problems. In the classical case we study a harmonic oscillator linearly coupled to the bath, and it is demonstrated that the system relaxes to equilibrium in an oscillating fashion with a frequency that is shifted from the frequency of the isolated oscillator by dynamic as well as statistical shifts; the dynamic shifts do not appear in the equilibrium distribution function whereas the statistical shifts do. For the quantum case we analyze the two level system linearly interacting with a bath and in the weak coupling limit, similar conclusions to the classical case regarding the time evolution of the system are reached; the relevance of this model in the study of tunneling in condensed media is also discussed.

In Part C we compare with previous treatments based on projection operators. Emphasis is placed on the fact that our theory does not depend on a specific initial state for the overall system but rather applies to most realistic initial conditions.

A future problem, both as an application and a test of the present theory, especially in its classical form, would be to reexamine the so-called Kramers problem or escape over a barrier\(^{38}\) for the case in which the natural time of the system is comparable to the bath relaxation time. Interest in this subject has been renewed\(^{39}\), although most of the treatments have been based on stochastic theory and with equations having a memory kernel. A variety of results have been obtained and the discussion continues unabated\(^{40}\). On the other hand, very recent computer simulations\(^{41}\) of the dissociation of isomers have
indicated that the relaxation rates depend on the coordinates of the system. Our treatment, in
general (see Eq II.A.2.21), indicates that this should be the case; due to the non-linearity
of the potential involved a numerical study should be the way to proceed.
CHAPTER III

BROWNIAN MOTION IN CLASSICAL AND QUANTUM SYSTEMS.

The study of Brownian motion deserves a separate treatment from the case of "weak coupling" developed in Chapter II in spite of the fact that the analysis is based again on the short time scale of correlations of bath quantities, and on the existence of a small parameter, namely the ratio of the mass of bath particles, $m$, to the mass, $M$, of the heavy particle. The main reasons being that the use of the above described small parameter depends on the magnitude of the dynamical variables as will be clear later on. For Brownian motion in fluid systems, the interaction potential depends on the relative distances of the Brownian particle and the bath particles and is usually assumed to be of short range. We shall use the translational invariance of the interaction potential in our treatment below.

The main purpose of this Chapter is the study of quantum Brownian motion: in Part B we derive the quantum Langevin and Fokker-Planck equations in the language of Wigner equivalents\textsuperscript{63-65} by means of the technique for eliminating fast variables\textsuperscript{66}; in Part C we use the projection operator technique developed in the previous Chapter, with the appropriate modifications required for Brownian motion. The projection operators used in these two parts are different, though they share the same property: the overall equilibrium density matrix and Wigner function are projected onto themselves; the difference in the corresponding equations for the reduced density matrix and the reduced Wigner function for the system is that the streaming terms are not completely separated in the latter case; since these terms only affect the higher order corrections, in both cases the Fokker-Planck equation is obtained. We review the classical case\textsuperscript{6,9} in Part A not only for reasons of
completeness, but also to emphasize the conditions of validity of Brownian motion that are also relevant for the quantum case, and to exhibit the technique of elimination of fast variables used in Part B. We conclude this Chapter, and the present work, in Part D with some relevant remarks.

In the past, there have been several derivations of Langevin$^{48,58}$ and Fokker-Planck$^{59-62}$ equations for a heavy particle immersed in a bath of light particles for quantum systems. Similar studies have been made for a particle weakly coupled to a bath of particles especially for harmonic oscillator systems$^{16,31-35,44}$.

The major differences between the treatments for classical and quantum systems arise from the facts that: (1) the equilibrium Wigner function, or the matrix elements of the equilibrium density matrix, for the quantum systems is an explicit function of the ratio of the mass of the Brownian particle and the masses of the bath particles; (2) at very low temperatures the magnitudes of the momenta of the Brownian particle and of the bath particles are determined by the zero point motion and we can no longer assert that the momentum of the former is much larger than the momenta of the latter. (This is reminiscent of the problem encountered in the weak coupling limit case for low temperatures). While the techniques that we utilize solve the difficulties arising from (1), they do not solve those arising from (2). The difficulties arising from (2) also occur in classical systems when the momentum of the Brownian particle, $P$, is of comparable magnitude to the momentum of a bath particle, $p$. There is no reason to expect that Langevin or Fokker-Planck equations are suitable descriptions of these systems. This is explicitly clarified in Part A.

The previous studies on quantum Brownian motion have led to a variety of different forms for the friction coefficients in the Langevin and Fokker-Planck equations. Our results agree with the explicit forms obtained by Dagonnier and Resibois$^{59}$ and by Hynes and Deutch$^{58}$.
III. A. REVIEW OF CLASSICAL BROWNIAN MOTION.

This Part is devoted to a review of the main ideas behind the derivation of the equations that govern classical Brownian motion, namely the Fokker-Planck or the Langevin equation. The former is derived using the technique for eliminating fast variables\(^9\).


Consider for simplicity the motion of a heavy particle of mass \(M\) and momentum \(P\), immersed in a fluid of light particles of mass \(m\), with typical momentum \(p\).

The Brownian motion of the heavy particle is characterized by the average linear damping, on a slow time scale, and by the rapid fluctuations of its velocity, both caused by the interaction with the rapidly moving particles of the fluid.

For the damping to be linear, the fluid should not be greatly disturbed by the motion of the heavy particle; therefore, the magnitude of the velocity of the latter must be smaller than the magnitude of the typical velocity of the fluid particles, i.e.

\[
| V | = \frac{| P |}{M} \ll | v | = \frac{| p |}{m}
\]

(1.1)

At the same time, owing to its mass, the change of momentum of the Brownian particle due to a collision with a single light particle should not be appreciable; this implies

\[
| P | \gg | p |
\]

(1.2)

Eqs(1.1) and (1.2) can be viewed as the conditions, on the magnitude of the momentum of the heavy particle, for Brownian motion to occur:

\[
| p | \ll | P | \ll \frac{M}{m} | p |
\]

(1.3)

On the other hand, as we are interested in situations in which

\[
P^2 \sim M k_B T \quad \text{and} \quad p^2 \sim m k_B T
\]

(1.4)
for a given temperature $T$ of the fluid, the magnitude of the heavy particle momentum is roughly of the order of $M^{1/2}$, while its change after a collision with a bath particle is of the order of 1. (i.e. assuming $|p|$ of the order of 1.)

When the above conditions are not met the heavy particle does not undergo Brownian motion and of course its description in terms of a Langevin or a Fokker-Planck equation is no longer valid.

It is therefore important to keep in mind that when a first principles derivation of the above mentioned equations governing Brownian motion is made in terms of an expansion in the reciprocal of the heavy particle mass, important conditions on the magnitude of the momentum of the Brownian particle are tacitly assumed. The same is true for the quantum mechanical version as we shall see in Parts B and C of this Chapter.

### III. A. 2. A derivation of the Fokker-Planck equation.

Most of the treatments that deal with the derivation of the Langevin or the Fokker-Planck equation start from the equations of motion, or the Liouville equation, for the heavy particle interacting with the bath of light particles. An expansion in the inverse of the mass of the heavy particle is performed, having previously prescribed initial conditions for both the Brownian particle and the bath. The asymptotic behavior that remains after the special initial transient has died out, is extracted from the solution.

Here, we present a derivation of the Fokker-Planck equation due to van Kampen and Oppenheim\(^9\) based on the method for eliminating fast variables which provides a direct derivation of the asymptotic state. The idea is to take advantage of the fact that for $M >> m$ there is a separation of time scales: the motion of the fluid is much faster than that of the
Brownian particle, and adjusts itself to the presence of the latter. That is, when one observes a Brownian particle the initial state of the bath is irrelevant.

It must be pointed out that all the above ab-initio derivations do not take into account the slow hydrodynamic modes of the bath.\textsuperscript{42,43}

We start by presenting the Hamiltonian of the system:

\[
H = \frac{p^2}{2M} + \sum_{n} \frac{p_n^2}{2m} + U(r^n) + \Phi(r^N, R) \quad \text{(2.1)}
\]

\[
= \frac{p^2}{2M} + H_0 \quad , \quad \text{(2.2)}
\]

where

\[
U(r^n) = \sum_{i < j} u(|r_i - r_j|) \quad \text{(2.3)}
\]

\[
\Phi(r^N, R) = \sum_{i=1}^{N} \phi(|r_i - R_l|) \quad \text{(2.4)}
\]

are short range, translation invariant potentials accounting for the interaction among the light particles and their interaction with the heavy particle. Note that $H_0$ is the Hamiltonian for the fluid in the presence of the Brownian particle at the fixed position $R$.

Following the discussion of the previous Section, we scale the momentum of the Brownian particle by setting

\[
P \equiv \sqrt{\frac{M}{m}} P^* \equiv \varepsilon^{-1} P^* \quad \text{(2.5)}
\]

where $\varepsilon$ will be our small parameter; because of Eqs(1.4), $P^*$ is of order $\varepsilon^0$.

The equations of motion for the system are ($m \equiv 1$)

\[
\dot{P}^* = -\varepsilon \nabla_R \Phi \equiv \varepsilon F(r^N, R)
\]

\[
\dot{R} = \varepsilon P^* \quad \text{(2.6)}
\]

\[
\dot{p}_n = -\nabla_{r_a} U - \nabla_{r_a} \Phi
\]

\[
\dot{r}_n = p_n
\]
Clearly, the variables \( R, P^* \) evolve on the slow time scale \( \epsilon t \) while the bath variables \( r^N, p^N \) are fast.

The distribution function for the system, \( \rho(R, P^*, r^N, p^N, t) \) obeys the Liouville equation

\[
\frac{\partial}{\partial t} \rho(t) = (L_0 + \epsilon L_1) \rho(t)
\]

\[
L_0 = -\sum_n p_{n^*} \cdot \nabla_{r_n} + \sum_n \nabla_{r_n} (U + \Phi) \cdot \nabla_{p_n}
\]

\[
L_1 = -P^* \cdot \nabla_R - F \cdot \nabla_{p^*}
\]

The method consists in extracting the slow component of Eq(2.7a) by eliminating the fast variables \( r^N, p^N \).

This elimination is achieved with the use of a projection operator \( P \), which projects on the null space* of the fast operator \( L_0 \):

\[
P A(R, P^*, X) \equiv \rho_0(X) \int dX' A(R, P^*, X')
\]

where \( A \) is any function of \( R, P^* \) and the phase point \( X \equiv (r^N, p^N). \rho_0(X) \), the only relevant null vector of \( L_0 \), is the equilibrium distribution of the fluid for fixed position \( R \) of the Brownian particle:

\[
\rho_0(X, R) = \frac{e^{-\beta H_0}}{\int dX' e^{-\beta H_0}}
\]

In particular we have

\[
P \rho(R, P^*, X, t) = \rho_0(X) \ W(R, P^*, t)
\]

where

---

* For the method to work it is only necessary to project on the left null space of \( L_0 \); in the present case the left null space is equal to the right null space due to the antihermiticity of \( L_0 \).
\[ W(R, P^*, t) = \int dX' \rho(R, P^*, X', t) \] (2.11)

is the marginal (reduced) probability distribution of \( R, P^* \).

With the definitions \( y = \mathcal{P} \rho, \ z = (1 - \mathcal{P}) \rho \equiv \mathcal{Q} \rho \) and the aid of the slow time variable \( s = \varepsilon t \), Eq(2.7a) can be decomposed into

\[ \frac{\partial}{\partial s} y = Ay + Bz \] (2.12a)

\[ \frac{\partial}{\partial s} z = \frac{1}{\varepsilon} Gz + Cy + Dz \] (2.12b)

where

\[ A = \mathcal{P} L_1 \mathcal{P} \quad B = \mathcal{P} L_1 \mathcal{Q} \quad C = \mathcal{Q} L_1 \mathcal{P} \quad D = \mathcal{Q} L_1 \mathcal{Q} \] (2.13a)

and

\[ G = \mathcal{Q} L_0 \mathcal{Q} \] (2.13b)

\( G \) is the operator \( L_0 \) restricted to the space orthogonal to the null space of \( L_0 \). In this orthogonal space its inverse exists.

From Eqs(12) we see that \( z \) is fast, while \( y \) varies on the slow time scale. We substitute in Eq(12) the expansion

\[ z = z^{(0)} + \varepsilon z^{(1)} + \varepsilon^2 z^{(2)} + \ldots \] (2.14)

and solve order by order.

From Eq(2.12b) we have

\[ G z^{(0)} = 0 \] (2.15a)

\[ \frac{\partial}{\partial s} z^{(0)} = G z^{(1)} + Cy \] (2.15b)

and so on. Eq(2.15a) implies that \( z^{(0)} = 0 \) since \( G \) acts on the space orthogonal to the null space of \( L_0 \).
Therefore, substituting the solution to Eq(2.15b) into Eq(2.12a) we obtain to first order in $\varepsilon$:

$$\frac{\partial}{\partial s} y = Ay - \varepsilon BG^{-1}Cy \quad .$$

(2.16)

Now, from Eqs (2.9) and (2.6) it follows that

$$\nabla_R \rho_0 = \beta F_0 \quad .$$

(2.17)

Moreover, one has

$$\langle F \rangle_0 \equiv \int dX \ F \rho_0 = 0 \quad \text{and} \quad \int dX \ G^{-1}F \rho_0 = 0 \quad (2.18)$$

due to spatial symmetry.

Hence, we obtain

$$Ay = -\rho_0 \ P^* \cdot \nabla_R \ W$$

(2.19)

and

$$-\varepsilon BG^{-1}Cy = -\varepsilon \rho_0 \langle F_i G^{-1}F_i \rangle_0 \nabla_{p^*_i} \left( \nabla_{p^*_j} + \beta p^*_j \right) W$$

(2.20)

where summation over repeated indices is understood.

The operator $G^{-1}$ can be written as

$$G^{-1} = -\int_0^\infty d\theta \ e^{L_0 \theta} Q \quad .$$

(2.21)

The zero eigenvalue of $L_0$ is removed by $Q$ and all others are purely imaginary; thus, the correlation appearing in Eq(2.20) becomes

$$\langle F_i G^{-1}F_i \rangle_0 = \delta_{ij} \langle F_i G^{-1}F_i \rangle_0 = -\delta_{ij} \int_0^\infty d\theta \ \langle F_i e^{-L_0 \theta} F_i \rangle_0 \ ;$$

(2.22)

the convergence of the integral representation is guaranteed by the fast decay of the correlation function. Note that the latter is the autocorrelation of the force that the fluid exerts on the Brownian particle fixed at the position $R$. 

82
With these results, Eq(2.12a) becomes the Fokker-Planck equation
\[
\frac{\partial}{\partial s} W = -\mathbf{P}^* \cdot \nabla R W - \epsilon \langle F_1 G^{-1} F_1 \rangle_0 \nabla_{\mathbf{p}^*} \left( \beta \mathbf{P}^* + \nabla_{\mathbf{p}^*} \right) W.
\] (2.23)

This equation is equivalent to the Langevin equation
\[
\frac{\partial}{\partial s} \mathbf{P}^* = \epsilon \beta \left< F_1 G^{-1} F_1 \right>_0 \mathbf{P}^* + \mathbf{E}_i(s)
\] (2.24)

where the random force \( \mathbf{E}_i \) obeys
\[
\mathbf{E}_i(s) = 0, \quad \mathbb{E}_i(s)\mathbb{E}_j(s') = -2\epsilon \left< F_1 G^{-1} F_1 \right>_0 \delta(s - s') \delta_{ij}.
\] (2.25)

Of course, Eqs(2.24) and (2.25) can also be obtained from the equations of motion, Eqs(2.6), using the adjoint projection operator to Eq(2.8). Mazur and Oppenheim have shown that the friction coefficient appearing in the Langevin equation, Eq(2.24), is identical to the friction coefficient which characterizes the drag on a macroscopic body moving with a prescribed velocity.

With the present method the higher order terms can be treated systematically, though they have to be treated perturbatively in order for the solution to be connected with a stochastic process. These higher order terms depend on \( \mathbf{P}^* \) and involve higher order derivatives with respect to \( \mathbf{P}^* \); therefore, we emphasize once more, if the momentum of the Brownian particle is not restricted in the way we explained before, (see Eqs(1.3)-(1.4)), the expansion in powers of \( \epsilon \) is no longer useful.
III. B. QUANTUM BROWNIAN MOTION.
WIGNER FUNCTION APPROACH.

The Wigner function formalism\textsuperscript{63-65} is used in this Part to obtain our results\textsuperscript{*}; see Appendix B for a review of the Wigner equivalent formulae used in this Part. In Section 1, we describe the system of interest and discuss the equilibrium properties of the Wigner function for the Brownian particle and some additional partial Wigner functions. In Section 2, the technique developed by van Kampen and Oppenheim\textsuperscript{9} for classical systems, described in Part A, is extended to obtain the Fokker-Planck equation for the reduced Wigner function of the Brownian particle. In Section 3 we modify the techniques used by Mazur and Oppenheim\textsuperscript{8} for classical systems to obtain the Langevin equation for the Brownian particle immersed in a quantum mechanical bath of light particles.

III. B.1. Equilibrium Considerations.

In this section we obtain the form of the equilibrium Wigner function as a power series in $\varepsilon \equiv (m/M)^{1/2} << 1$.

We consider a system of one heavy particle of mass $M$, position $\mathbf{R}$, and momentum $\mathbf{P}$ immersed in a bath of $N$ light particles of mass $m$, positions $\mathbf{r}^N$ and momenta $\mathbf{p}^N$ all in a box of volume $V$. The classical Hamiltonian of the system is

\[
H(X,R,P^*) = \frac{P^*^2}{2m} + \frac{P^N P^N}{2m} + U(r^N) + \Phi(r^N, R) = \frac{P^*^2}{2m} + H_0
\]  

(1.1)

\textsuperscript{*} This Part has appeared in its entirety in: 
where $H_0(X,R)$ is the Hamiltonian of the bath particles in the presence of a fixed Brownian particle. Here, $X = (r^N, p^N)$ is the phase point of the bath and $P^*$, the scaled momentum of the Brownian particle, is given by

$$P^* = \varepsilon P$$

and is assumed to have magnitude comparable to the momentum of a typical bath particle, i.e. of order $\varepsilon^0$. The bath particles interact with each other via the potential

$$U(r^N) = \sum_{i<j} u(|r_i - r_j|)$$

where $u$ is a short-range potential two-body interaction which depends on the scalar distance between the particles. The bath particles interact with the Brownian particle via the potential

$$\Phi(r^N, R) = \sum_{i=1}^{N} \phi(|r_i - R|)$$

where, again, $\phi$ is a short-range two-body interaction which depends on the scalar distance between the particles.

The unnormalized equilibrium Wigner function, $f^e$, for this system obeys the Bloch equation (see Appendix B)

$$\frac{\partial f^e}{\partial \beta} = O(\varepsilon)f^e,$$

where $f^e$ is a function of $X, R, P^*, \varepsilon$ and $\beta$. The operator $O(\varepsilon)$ can be written in the form

$$O(\varepsilon) = \frac{\hbar^2}{8m} \nabla_{r^N}^2 - \frac{\mathbf{P}^N \cdot \mathbf{P}^N}{2m} - c(U + \Phi) - \frac{P^* \cdot P^*}{2m} + \varepsilon^2 \frac{\hbar^2}{8m} \nabla_R^2 - [c(C-1) - sS] \Phi$$

$$\equiv O_0 - \frac{P^* \cdot P^*}{2m} + \varepsilon O_1(\varepsilon)$$

where $O_0$ is the operator corresponding to $H_0$ and contains the terms preceding $-P^*^2/2m$ and $\varepsilon O_1(\varepsilon)$ contains the terms after $-P^*^2/2m$ and tends to zero as $\varepsilon \to 0$. Here,

$$c = \cos \left[ \frac{\hbar}{2} \nabla_{r^N} \cdot \nabla_{p^N} \right], \quad s = \sin \left[ \frac{\hbar}{2} \nabla_{r^N} \cdot \nabla_{p^N} \right],$$
\[ C = \cos \left( \frac{f}{2} \nabla_R \cdot \nabla_{P^*} \right), \quad S = \sin \left( \frac{f}{2} \nabla_R \cdot \nabla_{P^*} \right), \quad \text{(1.7)} \]

and the spatial derivatives act only on the potentials following these operators.

We now define the quantity \( g(X, R, P^*, \epsilon, \beta) \) by

\[ f'_\epsilon = e^{\frac{\beta P^*^2}{2m}} \epsilon \nabla_{P^*} \nabla_{P^*} g \quad \text{(1.8)} \]

and find that \( g \) obeys the equation

\[ \frac{\partial g}{\partial \beta} = O_0 g + \left( e^{\frac{\beta P^*^2}{2m}} \epsilon \nabla_{P^*} \nabla_{P^*} \right) g \quad \text{(1.9)} \]

It is easy to find \( g \) as a power series in \( \epsilon \) from Eq(1.9). For \( \epsilon = 0 \), we obtain

\[ g_0(\beta) = e^{O_0 \beta} g(\beta=0) \quad \text{(1.10)} \]

where \( g_0 = g(X, R, \epsilon=0, \beta) \) which is the unnormalized Wigner function for the system with the Hamiltonian \( H_0 \). Note that \( g_0 \) is an even function of the momenta of the bath particles and can be written \( g_0(X', \beta) \) where \( X' = (\rho^N, p^N) \) and \( \rho_i = r_i - R \).

The operator \( O_1(\epsilon) \) consists of terms which are products of even functions of \( \rho \) times even functions of \( P^* \) plus terms which are products of odd functions of \( \rho \) times odd functions of \( P^* \). Thus, the power series expansion of \( g - g_0 \) will consist of a sum of terms which are tensors of even rank, \( T^{(2n)}(X') \), dotted into tensors of even rank, \( T^{(2n)}(P^*) \), times even powers of \( \epsilon \) plus tensors of odd rank, \( T^{(2n+1)}(X') \), dotted into tensors of odd rank, \( T^{(2n+1)}(P^*) \), times odd powers of \( \epsilon \). The tensors \( T^{(2n)}(X') \) are even in \( \rho \) and the tensors of odd rank \( T^{(2n+1)}(X') \) are odd in \( \rho \).

The normalized equilibrium Wigner function can be written as:

\[ f_\epsilon = \frac{e^{-\frac{\beta P^*^2}{2m}} g(X', P^*, \epsilon, \beta)}{Z(\epsilon, \beta)} \quad \text{(1.11)} \]

where
\[ Z(\varepsilon, \beta) = \int e^{-\beta P^*^2/2m} g dR dP^* dX \]

\[ = V \int e^{-\beta P^*^2/2m} g dP^* dX \]

(1.12)

The odd tensors \( T^{(2n+1)}(X') \) do not contribute to \( Z \) and therefore its expansion is only in even powers of \( \varepsilon \).

The normalized reduced equilibrium Wigner function for the position and momentum of the Brownian particle, \( W_e \), is given by

\[ W_e(R, P^*, \varepsilon, \beta) \equiv \int \phi_e dX = \frac{\int g dX'}{\int e^{-\beta P^*^2/2m} g dP^* dX} \]

(1.13)

Because of the properties of \( g \), \( W_e \) is independent of \( R \) and consists of terms which are even in \( P^* \) and even in \( \varepsilon \).

Finally, the quantity \( \tilde{f}_e \) is defined by

\[ \tilde{f}_e(X', P^*, \varepsilon, \beta) = \frac{f_e}{W_e} \]

\[ = \frac{g(X', P^*, \varepsilon, \beta)}{\int g dX'} \]

(1.14)

This function, per se, has little physical significance. However, \( \tilde{f}_e(X', P^*, \varepsilon=0, \beta) \equiv \tilde{f}_{0e} \) is the equilibrium Wigner function for the system described by the Hamiltonian \( H_0 \). Furthermore, \( \tilde{f}_e W_e = f_e \) is the equilibrium Wigner function for the system described by the Hamiltonian \( H \). In the classical limit \( \tilde{f}_e \) becomes the conditional distribution function for the bath for fixed momentum of the Brownian particle. In our analysis, \( \tilde{f}_e \) will appear as an intermediate function but in the final expressions, it appears either as \( \tilde{f}_{0e} \) or \( \tilde{f}_e W_e \).
Explicit expansions in powers of $\varepsilon$ for $f_{\varepsilon}$, $W_{\varepsilon}$ and $\bar{f}_{\varepsilon}$ follow from the expansion of $g$ in powers of $\varepsilon$. The results are

$$
g(\varepsilon,\beta) = g_0(\beta) + \varepsilon \frac{\hbar}{2} \int_0^\beta d\tau e^{-O(\beta-\tau)} (-\frac{\tau}{m})[sg_0(\tau)\nabla_R \Phi \cdot P^* + \frac{d}{8} \int_0^\beta d\tau e^{-O(\beta-\tau)} \left[ \frac{1}{m} \nabla_R g_0(\tau) + (cg_0(\tau)\nabla_R \nabla_R \Phi) : (-\frac{\tau}{m} + \frac{\tau^2}{m^2}) \right] + \frac{\hbar}{2} \int_0^\beta d\tau e^{-O(\beta-\tau)} s\nabla_R \Phi \cdot (-\frac{1}{m} A(X',\tau) \cdot P^* + A(X',\tau)) + O(\varepsilon^3) \right) \right) + O(\varepsilon^3)
$$

where

$$A(X',\tau) = \frac{1}{2} \int_0^\tau d\theta e^{-O(\tau-\theta)} (-\frac{\theta}{m})[sg_0 \nabla_R \Phi] \frac{1}{2} \int_0^\tau d\theta e^{-O(\tau-\theta)} (-\frac{\theta}{m})[sg_0 \nabla_R \Phi].$$

Eq(1.15) can be written schematically as

$$g(\varepsilon,\beta) = g_0(\beta) + \varepsilon \frac{\hbar}{2} A(X',\beta) \cdot P^* + \frac{\hbar^2}{8} \int_0^\beta d\tau e^{-O(\beta-\tau)} \left[ (B(X',\beta) + D(X',\beta)) : P^* P^* \right] + O(\varepsilon^3),$$

where $A$ is odd in $p$ and $B$ and $D$ are even in $p$.

It follows from Eqs(1.17) and (1.12) that

$$Z(\varepsilon,\beta) = Z_0 + \varepsilon \frac{2}{\beta} \left( V \int dP^* e^{-\beta P^*^2/2m} \right) \left[ \int B dX' + \frac{3m}{\beta} \int D dX' \right] \frac{1}{2},$$

where,

$$Z_0 = V \int dP^* e^{-\beta P^*^2/2m} \int g_0 dX'.$$

It follows from Eqs(1.11), (1.17) and (1.18) that

$$f_{\varepsilon}(\varepsilon,\beta) = f_{0\varepsilon}(\beta) + \varepsilon \frac{\hbar}{2} A \cdot P^* \frac{W_{0\varepsilon}}{\beta} + \int g_0 dX'$$
\[ + \frac{\epsilon}{4 \pi^2} \left[ W_0 \epsilon - f_0 \int B dX' \right. \\
+ W_0 D : P^* P^* - f_0 \int D_{xx} dX' \left. \right] + O(\epsilon^3), \tag{1.20} \]

where
\[ f_0 \equiv \frac{e^{-\beta P^*/2m}}{\int dP^* \int g_0 dX'} = \frac{W_0 g_0}{\int g_0 dX'} \tag{1.21} \]

and
\[ W_0 = \frac{e^{-\beta P^*/2m}}{\int dP^* \int g_0 dX'} \tag{1.22} \]

It follows from Eqs (1.13) and (1.20) that
\[ W_0(\epsilon, \beta) = W_0 \left(1 + \frac{\epsilon}{4 \pi^2} \int D_{xx} dX' \left( P^* P^* - \frac{3m}{\beta} \right) + O(\epsilon^4) \right). \tag{1.23} \]

Finally, it follows from Eqs (1.14), (1.20) and (1.23) that
\[ \tilde{\epsilon} = \tilde{f}_0 + \frac{\epsilon \hat{\epsilon} A \cdot P^*}{\int g_0 dX'} + \frac{\epsilon}{4 \pi^2} \left[ B - \tilde{f}_0 \int B dX' + D : P^* P^* - \tilde{f}_0 \int D_{xx} dX' P^* \right] \]
\[ + O(\epsilon^3), \tag{1.24} \]

where
\[ \tilde{f}_{0e} = \frac{f_{0e}}{W_{0e}} = \frac{g_0}{\int g_0 dX'} . \]  

(1.25)

Note that \( \tilde{f}_{0e} \) is the normalized equilibrium Wigner function for the system with Hamiltonian \( H_0 \). To all orders Eq(1.24) can be written as

\[ \tilde{f}_d(\epsilon, \beta) = \tilde{f}_{0d}(\beta) + \epsilon \left[ J(\epsilon, \beta) - \tilde{f}_{0e} \int J(\epsilon, \beta) \, dX' \right] , \]

(1.26)

where \( J(\epsilon, \beta) \) is a power series expansion in \( \epsilon \) with the same tensorial properties discussed above for \( g \).

In the next section, we shall need the properties of Eq(1.26) and the fact that \( W_e \) is independent of \( R \) to all orders and has an expansion in powers of \( \epsilon^2 \).

---

III. B. 2. The quantum Fokker-Planck equation.

In this section, the techniques developed by van Kampen and Oppenheim\(^9\) will be utilized to obtain the equation for the time dependence of the reduced Wigner function, \( W(R, P^*, t) \). In the appropriate limit, this equation becomes a Fokker-Planck equation.

We start with the Liouville equation for the total Wigner function, \( f(X, R, P^*, t) \), which is (see Appendix B)

\[ \frac{\partial f(t)}{\partial t} = L(\epsilon) \, f(t) \]

(2.1)

where

\[ L(\epsilon) = L_0 + \epsilon L_1(\epsilon) , \]

(2.2)

\[ L_0 = -\frac{p}{m} \cdot \nabla_f \, \frac{2}{\hbar^2} \, s(U + \Phi) \]

(2.3)

and
\[ e L_1(\epsilon) = -\epsilon \frac{P^*}{m} \cdot \nabla_R + \frac{2}{\hbar} \left[ \text{Sc} + (C-1)s \right] \Phi. \]  

(2.4)

Note that \( L_0 \) is the Liouville operator corresponding to the Hamiltonian \( H_0 \) for the system in which the Brownian particle acts as a fixed field of force for the bath particles.

We introduce the projection operator, \( \mathcal{P} \), where

\[ \mathcal{P}B = \int B \mathcal{D}X, \quad \int j \mathcal{D}X = 1. \]  

(2.4)

We define \( y(t) \) and \( z(t) \) by

\[ y(t) = \mathcal{P}f(t) = j W(R,P^*,t), \]

\[ z(t) = Qf(t) = (1 - \mathcal{P})f(t) = (\tilde{f}(t) - j) W(R,P^*,t). \]  

(2.5)

Here

\[ W(R,P^*,t) = \int f(t) \mathcal{D}X \]  

(2.6)

is the reduced Wigner function for the Brownian particle and

\[ \tilde{f}(X,R,P^*,t) = \tilde{f}(t) = \frac{f(t)}{W(t)} \]  

(2.7)

is the Wigner analogue of the classical conditional distribution function for the bath and has the property

\[ \int \tilde{f}(t) \mathcal{D}X = 1. \]  

(2.8)

In equilibrium, \( f(t) = f_e, \quad \tilde{f}(t) = \tilde{f}_e \) (see Eq(1.14)) and \( W(t) = W_e \).

Since \( \mathcal{P}L_0 = 0 \), the equations for \( y \) and \( z \) are

\[ \dot{y}(t) = \mathcal{P}f(t) = \mathcal{P}e L_1 y(t) + \mathcal{P}e L_1 z(t), \]

\[ \dot{z}(t) = Qf(t) = QL_0 Q z(t) + Qe L_1 Qz(t) + QL_0 y(t) + Qe L_1 y(t). \]  

(2.9)

We use the properties

\[ \mathcal{P}e L_1 B = j \left[ -\epsilon \frac{P^*}{m} \cdot \nabla_R \int B \mathcal{D}X + \frac{2}{\hbar} S \int B \Phi \mathcal{D}X \right]. \]
\[ \int z(t) \, dX = 0 \]  \hspace{1cm} (2.10)

to rewrite the y equation as:
\[ \dot{W}(t) = -\frac{p^*}{m} \nabla_R \dot{W}(t) + \frac{2}{\hbar} \mathcal{S} \left[ \int \dot{J}(\Phi) dX \, \dot{W}(t) \right] + \frac{2}{\hbar} \mathcal{S} \left[ \int z(t) \Phi dX \right]. \]  \hspace{1cm} (2.11)

Note that \( \dot{W}(t) \) is at least proportional to \( \varepsilon \) and the pertinent time scale for the Brownian particle is \( \tau \equiv \varepsilon t. \)

We now rewrite Eqs (2.9) using this time scale:
\[ \dot{W}(\tau) = -\frac{p^*}{m} \nabla_R W(\tau) + \frac{2}{\varepsilon \hbar} \mathcal{S} \left[ \int dX \, \dot{J}(\Phi) W(\tau) \right] + \frac{2}{\varepsilon \hbar} \mathcal{S} \left[ \int dX \, z(\tau) \Phi \right], \]  \hspace{1cm} (2.12)
\[ \dot{z}(\tau) = \frac{Q_{L0} \gamma}{\varepsilon} z(\tau) + Q_{L1}(\varepsilon) Qz(\tau) + \frac{Q_{L0} \gamma}{\varepsilon} + Q_{L1}(\varepsilon) y(\tau). \]

Our technique involves the expansion of the fast variable \( z \), its time derivative, and the time derivative of \( W \) in powers of \( \varepsilon \), i.e.
\[ z(\tau) = z^{(0)}(\tau) + \varepsilon z^{(1)}(\tau) + \varepsilon^2 z^{(2)}(\tau) + \ldots, \]
\[ \dot{z}(\tau) = \dot{z}^{(0)}(\tau) + \varepsilon \dot{z}^{(1)}(\tau) + \ldots, \]  \hspace{1cm} (2.13)
\[ \dot{W}(\tau) = \dot{W}^{(0)}(\tau) + \varepsilon \dot{W}^{(1)}(\tau) + \ldots. \]

We cannot proceed further without specifying the function \( J \).

The properties that \( J \) must have are the following:

(1) \( Q_{L0} \gamma(\tau) = (L_{0j}) W(\tau) \sim O(\varepsilon). \)

(2) On the short time scale \( t \) governed by the Liouville operator \( L_0 \), \( z^{(0)} \) must go to zero.

(3) The projection operator \( Q \) must remove the pertinent zero eigenvalue of the operator \( L_0 \).

(4) On the long time scale \( \tau \), \( z^{(1)} \), \( z^{(2)} \), etc. must approach 0 as \( \tau \to \infty \).

The only \( J \) that satisfies these conditions is \( J = \tilde{f}_e \).
We use the fact that
\[ L(\epsilon)\tilde{f}_e = 0 = L(\epsilon)[\tilde{f}_e W_\epsilon] = [L_0 \tilde{f}_e] W_\epsilon + \epsilon L_1(\epsilon)[\tilde{f}_e W_\epsilon] \]  (2.14)

to write
\[ L_0 \tilde{f}_e = -\frac{1}{W_\epsilon} \epsilon L_1(\epsilon)[\tilde{f}_e W_\epsilon] . \]  (2.15)

Therefore, \( \tilde{f}_e \) satisfies condition (1). Since
\[ z(\tau) = [\tilde{f}(\tau) - \tilde{f}_e] W(\tau) , \]  (2.16)
z clearly approaches zero, to all orders, as \( \tau \to \infty \), and condition (4) is satisfied.

We use the fact that \( L_0 \) drives \( \tilde{f}(\tau) \) to \( \tilde{f}_0e \) on the short time scale to write
\[ z(t) = [\tilde{f}_0e - \tilde{f}_e] W(t) \]  (2.17)
for \( t \sim \tau_b \) where \( \tau_b \) is a characteristic relaxation time for the bath and is assumed to be much shorter than the relaxation time for the Brownian particle. It is at this point that we must insist that the temperature of the system not be so low that the zero-point motion of the particles be important. Since \( \tilde{f}_e \) can be written in the form of Eq(1.26), it is clear that condition (2) is satisfied.

Finally, we find that
\[ L_0(1 - \mathcal{P})B = L_0 \left[ B - \tilde{f}_e \int dX \ B \right] \]  (2.18)
\[ = L_0 \left[ B - \tilde{f}_0e \int dX \ B - \epsilon \left[ J - \tilde{f}_0e \int dX J \int dX \ B \right] \right], \]

where we have used Eq(1.26). The zero eigenvalue of \( L_0 \) is eliminated by the projection operator and condition (3) is satisfied.

We use the fact
\[ S \left[ \int dX \ \tilde{f}_e \Phi \ W \right] = 0 \]  (2.19)

93
to all orders, because of the symmetry properties of \( \tilde{f}_e \) described in section 2. This, in turn indicates that the present projection operator does not separate the equilibrium streaming corrections; they are included in the higher order terms of the last term of Eq(2.11) and are therefore fast. (That the streaming corrections are higher order is explicitly shown in Appendix B). With Eqs(2.15) and (2.19) we can rewrite Eqs(2.12) as

\[
\dot{W}(\tau) = -\frac{P^*}{m} \cdot \nabla_R W(\tau) + \frac{2}{\epsilon \tilde{f}_1} S \left[ \int dX \, z(\tau) \Phi \right],
\]

\[
\dot{z}(\tau) = \frac{Q_0 L_0 \, Q_0}{\epsilon} z(\tau) + Q \, L_1(\epsilon)z(\tau) +
\]

\[
+ Q \left[ L_1(\epsilon) \left[ \tilde{f}_e \, W(\tau) \right] - \frac{W(\tau)}{W_e} L_1(\epsilon) \left[ \tilde{f}_e \, W_e \right] \right],
\]

(2.20)

where

\[
Q_0 \, B \equiv (1 - P_0) \, B \equiv B - \tilde{f}_{0e} \int B \, dX
\]

(2.21)

Eqs(2.20) are correct to all orders in \( \epsilon \).

We now set the coefficients of equal powers of \( \epsilon \) equal to each other in the \( \dot{z} \) equation. The coefficients of \( \epsilon^{-1} \) are

\[
Q_0 \, L_0 \, Q_0 \, z^{(0)}(\tau) = 0.
\]

(2.22)

Since the only pertinent eigenfunction of \( L_0 \) with zero eigenvalue, \( \tilde{f}_{0e} \), is removed by \( Q_0 \), Eq(2.22) implies that \( z_0 = 0 \). Setting the coefficients of \( \epsilon^0 \) equal yields:

\[
z^{(1)}(\tau) = -G_0^{-1} \left[ Q \left[ L_1(\epsilon) \left[ \tilde{f}_e \, W(\tau) \right] - \frac{W(\tau)}{W_e} L_1(\epsilon) \left[ \tilde{f}_e \, W_e \right] \right] \right]^{(0)}
\]

\[
= -G_0^{-1} \left( c \nabla_R \Phi \tilde{f}_{0e} \cdot \left[ \nabla_{p*} + \frac{\beta P^*}{m} \right] W(\tau) \right),
\]

(2.23)

where

\[
G_0 \equiv Q_0 \, L_0 \, Q_0,
\]

(2.24)
and is clearly invertible since the zero eigenvalue has been removed. Higher order terms in \( \varepsilon \) are easily obtained after some algebra.

Substitution of Eq(2.23) into the equation for \( \dot{W} \), Eq(2.20), yields

\[
\dot{W}(\tau) = -\frac{\mathbf{P}^*}{m} \cdot \nabla_R W(\tau)
\]

\[
- \varepsilon \int dX \nabla_R \Phi \mathbf{G}_0^{-1}(c \nabla_R \Phi \tilde{f}_{0e}) : \nabla_{\mathbf{P}^*} \left( \nabla_{\mathbf{P}^*} + \frac{\beta \mathbf{P}^*}{m} \right) W(\tau) + O(\varepsilon^2)
\]

\[
= -\frac{\mathbf{P}^*}{m} \cdot \nabla_R W(\tau) + \varepsilon \int_0^\infty d\theta \int dX \left( e^{-L_0 \theta} \nabla_\alpha \Phi \right)
\]

\[
\times (c \nabla_R \Phi \tilde{f}_{0e}) : \nabla_{\mathbf{P}^*} \left( \nabla_{\mathbf{P}^*} + \frac{\beta \mathbf{P}^*}{m} \right) W(\tau) + O(\varepsilon^2),
\]

(2.25)

where \( \nabla_\alpha \) is the derivative with respect to the \( \alpha \) component of \( \mathbf{R} \). We have used the symmetry properties of \( \tilde{f}_{0e} \), and have written \( \mathbf{G}_0^{-1} \) as

\[
\mathbf{G}_0^{-1} = \int_0^\infty d\theta \; e^{Q_0 L_0 Q_0}.
\]

(2.26)

Thus,

\[
\dot{W}(\tau) = -\frac{\mathbf{P}^*}{m} \cdot \nabla_R W(\tau) + \varepsilon \Gamma \nabla_{\mathbf{P}^*} \cdot \left( \nabla_{\mathbf{P}^*} + \frac{\beta \mathbf{P}^*}{m} \right) W(\tau) + O(\varepsilon^2),
\]

(2.27)

which to order \( \varepsilon \) is the Fokker-Planck equation. The dissipative coefficient \( \Gamma \) is

\[
\Gamma = \int_0^\infty d\theta \int dX \left( e^{-L_0 \theta} F_\alpha \right) (c F_\alpha \tilde{f}_{0e})
\]

(2.28)

which can be written as

\[
\Gamma = \int_0^\infty d\theta \int dX \tilde{f}_{0e} \frac{1}{2} \left[ \left( e^{-L_0 \theta} F_\alpha \right) F_\alpha + F_\alpha \left( e^{-L_0 \theta} F_\alpha \right) \right]_W,
\]

(2.29)

where \( F_\alpha = -\nabla_\alpha \Phi \), and the subscript \( W \) denotes the Wigner equivalent of the anti commutator of \( e^{-L_0 \theta} F \) and \( F \). The equilibrium solution to this Fokker-Planck equation is
\[ W_{0e} = \frac{e^{-\beta P^* / 2m}}{V \int dP^* e^{-\beta P^* / 2m}}. \]

(2.30)

In order to obtain the higher order terms for \( W_e \) we must proceed to higher order in \( \varepsilon \). It is clear from the form of Eqs(2.20) that \( z_e = 0 \) and \( W = W_e \) are the equilibrium solutions to the exact equations.

We emphasize the fact that to obtain consistent solutions to higher orders in \( \varepsilon \) we must use the projection operator in which \( j = \tilde{f}_e \). In the higher order terms, the expansion of \( \tilde{f}_e \) in powers of \( \varepsilon \) is used, i.e.

\[ \tilde{f}_e = \tilde{f}_{0e} + \tilde{f}_{e}^{(1)} + \ldots. \]

(2.31)

Useful forms for these higher order terms can be obtained from Eq(2.15) in the form

\[ \tilde{f}^{-1}_e = \frac{1}{W_{0e}} \int_{0}^{\infty} d\theta \ e^{Q_0 L_0 Q_0 \theta L_{1}^{(0)} \left( \tilde{f}_{0e} W_{0e} \right)}. \]

(2.32)

e etc. Thus

\[ \int dX \tilde{f}^{-1}_e B = \frac{1}{W_{0e}} \int_{0}^{\infty} d\theta \int dX \left[ e^{Q_0 L_0 Q_0 \theta \left( -\frac{P^*}{m} \cdot \nabla_{R} \tilde{f}_{0e} + (c \nabla_{R} \varphi) \frac{\beta}{m} \right)} \right] B \]

\[ = \frac{P^*}{m} \int_{0}^{\infty} d\theta \int dX \tilde{f}_{0e} \left[ (\nabla_{R} - \beta c \nabla_{R} \varphi) \right] e^{-Q_0 L_0 Q_0 \theta} B. \]

(2.33)

The integrand decays to zero rapidly for \( \theta \geq \tau_b \).
III. B. 3. The quantum Langevin equation.

We now proceed to derive the equation of motion for the Brownian particle following a modification of the techniques introduced by Mazur and Oppenheim for classical systems\(^8\). As in the classical system we expect that the equation of motion will be the Langevin equation, to lowest order, as long as the magnitude of the momentum of the heavy particle is bounded by \(\epsilon^0 \ll |p| \ll \epsilon^{-2}\). Accordingly we will assume that \(P^*\) defined by Eq(1.2) is roughly of order \(\epsilon^0\). The basic assumption, as in Section 3, is that the bath variables in the presence of a fixed Brownian particle decay on a fast time scale.

We first derive an exact equation for the time derivative of \(P^*\) using the adjoint of the projection operator defined in Eq(2.4) with \(j = \tilde{r}_\epsilon\). Thus,

\[
\mathcal{P}^* B = \int dX \tilde{r}_\epsilon B .
\]  

(3.1)

We define the quantity

\[
\epsilon K(t) = -e^{-(1 - \mathcal{P}^*)L} t \left(1 - \mathcal{P}^*\right)L P^*
\]

\[= e^{-(1 - \mathcal{P}^*)L} t P^* = \epsilon e^{-(1 - \mathcal{P}^*)L} t F ,
\]

(3.2)

where

\[F = -\nabla_R \Phi ,
\]

(3.3)

\(L\) is the Liouville operator given in Eqs(2.2) and (2.3), and we have used the fact that \(\mathcal{P}^* F = 0\) because of the symmetry properties of \(\tilde{r}_\epsilon\).

By using the operator identity

\[e^{-(1 - \mathcal{P}^*)L} t = e^{-L t} + \int_0^t d\tau e^{-L (t - \tau)} \mathcal{P}^* L e^{-(1 - \mathcal{P}^*)L} \tau
\]

(3.4)
24 : 1
we can write the exact equation:

\[ \hat{P}^*(t) = \epsilon K(t) - \epsilon \int_{0}^{t} d\tau \, e^{-L(t-\tau)} P^+ L K(\tau), \quad (3.5) \]

where we have used the fact that

\[ B(t) = e^{-L t} B(0), \]

where \( B = B(X,R,P^*) \). The quantity \( K(t) \) has the properties

\[ P^+ K(t) = 0, \quad P^+[K(t)G(R,P^*)]_W = 0, \quad (3.6) \]

where \( G \) is an arbitrary function of \( R \) and \( P^* \). Thus \( K(t) \) is orthogonal to all the slow variables of the system and has a time dependence governed by the bath time scales. Note that all the dynamical variables that occur in this treatment are the Wigner equivalents of the classical dynamical variables.

The projection operator \( P^+ \) has the property

\[ P^+ L B \equiv \int dX \, \tilde{f}_e \left[ L_0 + \epsilon L_1 \right] B \]

\[ = \int dX \, \left[ (-L_0 \tilde{f}_e) B + \tilde{f}_e \epsilon L_1 B \right] \]

\[ = \epsilon \int dX \, \left[ \frac{1}{\omega_e} (L_1 \tilde{f}_e W_e) B + \tilde{f}_e L_1 B \right], \quad (3.7) \]

where we have integrated by parts and used Eq(2.15). Eq(3.7) still has implicit \( \epsilon \) dependence because of the forms of \( L_1, \tilde{f}_e \) and \( W_e \). Eq(3.7) can be written more explicitly in the form

\[ P^+ L B \equiv \frac{2}{\hbar} \int dX \, B \frac{1}{\omega_e} \left[ \frac{1}{S} \left( C - 1 \right) s \right] \Phi \tilde{f}_e W_e \]
\[ + \frac{2}{\hbar} \int dX \tilde{f}_e [S c + (C - 1)s] \Phi B , \]  

(3.8)

where we have used the fact that \( \int \tilde{f}_e B dX \) is independent of \( R \), though it does depend on \( P^* \), as long as \( B = B(X, P^*) \).

We now expand \( K(\tau) \) in the form

\[ K(\tau) = e^{-L_0 \tau} F + \int_0^\tau d\tau_1 e^{-L_0 (\tau - \tau_1)} \left[ P^L \right] e^{-L_0 \tau_1} F \]

\[ + \int_0^\tau d\tau_2 e^{-L_0 (\tau_2 - \tau_1)} \left[ P^L \right] e^{-L_0 (\tau_1 - \tau_2)} \left[ P^L \right] e^{-L_0 \tau_2} F \]

\[ + \ldots \]  

(3.9)

to make part of the \( \epsilon \) dependence explicit. Note that there is an explicit factor of \( \epsilon \) appearing for each operator of the form \( P^L \epsilon L_1 \) due to Eq(3.8).

Substitution of Eq(3.9) into Eq(3.5) yields

\[ P^*(t) = eK(t) - \epsilon \int_0^t d\tau e^{-L (t - \tau)} P^L e^{-L_0 \tau_1} F \]

\[ + \epsilon^2 \int_0^t d\tau \int_0^\tau d\tau_1 e^{-L (t - \tau)} P^L e^{-L_0 (\tau - \tau_1)} L_1 e^{-L_0 \tau_1} F \]

\[ + \epsilon^2 \int_0^t d\tau \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 e^{-L (t - \tau)} P^L e^{-L_0 (\tau - \tau_1)} L_1 e^{-L_0 (\tau_1 - \tau_2)} \times \]

\[ \times (P^L \epsilon L_1) e^{-L_0 \tau_2} F + \ldots , \]  

(3.10)
where we have used the fact that $\mathcal{P}^+ L \mathcal{P}^+ = 0$. Note that the second term on the RHS of Eq(3.10) is at least of order $\epsilon^2$, the third term at least of order $\epsilon^3$ and the fourth term at least of order $\epsilon^4$.

The implicit $\epsilon$ dependence of these terms can be found from the properties of $L_1$, the expansion of $\tilde{f}_e$ in powers of $\epsilon$, Eq(1.24), the symmetry properties of these terms, and the expansion of $W_\epsilon$ in powers of $\epsilon$, Eq(1.23). We find that the second term on the RHS of Eq(3.10) is of order $\epsilon^2 + \epsilon^4 \tilde{f}_1^2$, the third term of order $\epsilon^4 \tilde{f}_1$ and the fourth term at least of order $\epsilon^4$. Thus, the dissipative terms in Eq(3.10) can be expanded in powers of $\epsilon^2$.

In order for this expansion to be useful, we must show that there are no adiabatic terms, i.e. it is important that $\mathcal{P}^+ L K(\tau)$ goes to zero on a fast time scale. We will demonstrate that $\mathcal{P}^+ L K(\tau) = 0$ for $\tau \geq \tau_b$ where $\tau_b$ is the bath relaxation time. We use the assumption that correlation functions of the form $\langle A e^{-L_0 \tau} B \rangle_0$ factorize on the bath time scale, i.e.

$$\langle A e^{-L_0 \tau} B \rangle_0 \rightarrow \langle A \rangle_0 \langle B \rangle_0 \quad \text{for} \quad \tau > \tau_b$$

(3.11)

where the subscript 0 implies an average over $\tilde{f}_{0e}$,

$$\langle B \rangle_0 \equiv \int dX \, \tilde{f}_{0e} B = \mathcal{P}^+_0 B .$$

(3.12)

The term $\mathcal{P}^+ e^{-L_0 \tau} F$ is zero for $\tau > \tau_b$ since $\langle F \rangle_0 = 0$. The term

$$\mathcal{P}^+ L e^{-L_0 (\tau - \tau_1)} L_1 e^{-L_0 \tau_1} F = \mathcal{P}^+ L e^{-L_0 (\tau - \tau_1)} \left( \frac{\mathbf{P}^*}{m} \cdot \nabla_R \right) e^{-L_0 \tau_1} F$$

(3.13)

decays to zero for $\tau_1 > \tau_b$ for the same reason; for $\tau - \tau_1 > \tau_b$, Eq(3.13) becomes
\( \mathcal{P}^+ \mathcal{P}^+_0 e^{-L_0(\tau - \tau_1)(- (P^*/m) \cdot \nabla_R)} e^{-L_0 \tau_1 F} \) which is zero. Thus Eq(3.13) becomes zero
for \( \tau_1 > \tau_b \) or \( \tau - \tau_1 > \tau_b \) or \( \tau > 2 \tau_b \). The term
\[
\mathcal{P}^+ L \mathcal{P}_1 e^{-L_0(\tau - \tau_1)} \mathcal{P}^+_1 e^{-L_0(\tau_1 - \tau_2)(\mathcal{P}^+ L - e L_1)} e^{-L_0 \tau_2 F} = 
\]
\[
= \mathcal{P}^+ L \mathcal{P}_1 e^{-L_0(\tau - \tau_1)} \mathcal{P}^+_1 L \mathcal{P}^+ L e^{-L_0 \tau_2 F}
\]
\[
- \varepsilon \mathcal{P}^+ L \mathcal{P}_1 e^{-L_0(\tau - \tau_1)} \left( - \frac{P^*}{m} \nabla_R + c \nabla_R \Phi \cdot \nabla_p \right) \times 
\]
\[
x e^{-L_0(\tau_1 - \tau_2)} \frac{P^*}{m} \nabla_R e^{-L_0 \tau_2 F}. \tag{3.14}
\]
This term is zero for \( \tau_2 > \tau_b \) or \( \tau - \tau_1 > \tau_b \). For \( \tau_1 - \tau_2 > \tau_b \) it becomes
\[
\mathcal{P}^+ L \mathcal{P}_1 e^{-L_0(\tau - \tau_1)} \mathcal{P}^+_1 L \mathcal{P}^+ L e^{-L_0 \tau_2 F} + \varepsilon \mathcal{P}^+ L \mathcal{P}_1 e^{-L_0(\tau - \tau_1)} \mathcal{P}^+_0 \frac{P^*}{m} \nabla_R e^{-L_0 \tau_2 F} 
\]
\[
= \mathcal{P}^+ L \mathcal{P}_1 e^{-L_0(\tau - \tau_1)} \left[ \mathcal{P}^+_0 \frac{P^*}{m} \nabla_R e^{-L_0 \tau_2 F} \right], \tag{3.15}
\]
to lowest order in \( \varepsilon \), the term in brackets in Eq(3.15) becomes
\[
\varepsilon \int dX \left[ \frac{1}{W_{0e}} (c \nabla_R \Phi f_{0e}) \cdot \nabla_p + \frac{P^*}{m} \nabla_R \right] e^{-L_0 \tau_2 F}, 
\]
where we have used Eq(3.8). This becomes
\[
\varepsilon \int dX \frac{1}{W_{0e}} e^{L_0 \tau_2} L_1^{(0)} \left( \tilde{f}_{0e} W_{0e} \right) F, 
\]
by integrating by parts. This term, when integrated over \( \tau_2 \), for \( \tau_1 > \tau_b \) becomes \( \int_{f_{0e}}^{(1)} F \ dX = 0 \). Thus, Eq(3.14) is zero for \( \tau_2 > \tau_b, \tau_1 > \tau_b \) or \( \tau - \tau_1 > \tau_b \) or for \( \tau > 3 \tau_b \).

All the terms in the expansion \( \mathcal{P}^+ L K(\tau) \) can be analyzed in this way and the conclusion is that their time dependences are essentially identical to those in the classical case.

Thus, we can write Eq(3.10) in the form
\[
\dot{P}^*(t) = \varepsilon K(t) - \varepsilon^2 \int_0^t d\tau e^{-L(t - \tau)} \frac{P^*}{m} \cdot c \nabla f_{0e} \ e^{-L_0 \tau} F + O(\varepsilon^4). \tag{3.16}
\]
The integrand in Eq(3.16) decays to zero on the bath time scale.
Eq (3.16) finally can be written in the form

$$
\dot{\mathbf{P}}^\ast (t) = \varepsilon \mathbf{K}(t) - \varepsilon \gamma \mathbf{P}^\ast + O(\varepsilon^3),
$$

(3.17)

where we have used the facts that $\dot{\mathbf{P}}^\ast \sim \varepsilon$ and that the time integral can be extended to infinity for times greater than $\tau_b$ because of the fast decay of the correlation function. Here, the friction coefficient $\gamma$ is given by

$$
\gamma = \frac{\beta}{3m} \int_0^\infty d\tau \int dX \left[ cF \frac{r_{1o}}{e} \right] e^{-L_0 \tau F}
$$

$$
= \frac{\beta}{3m} \int_0^\infty d\tau \int dX \frac{r_{1o}}{e} cF \cdot e^{-L_0 \tau F}
$$

$$
= \frac{\beta}{3m} \int_0^\infty d\tau \int dX \frac{1}{2} \left[ F \cdot e^{-L_0 \tau F} + \left( e^{-L_0 \tau F} \right) F \right] w,
$$

(3.18)

which is the same result obtained from the Fokker-Planck equation (Eqs (2.27) and (2.29)).

Eq (3.17) is the Langevin equation as long as $\mathbf{K}(t)$ has the appropriate properties of a fluctuating force, namely:

(a) Its average over the bath must be zero, i.e.

$$
\mathbf{P}^\dagger \mathbf{K}(t) = 0.
$$

(3.19)

This follows from its definition.

(b) Correlation functions of the Wigner equivalents of its products must decay quickly in time. The analysis to demonstrate this is similar to the one carried out above. On the Brownian particle time scale, $\varepsilon^2 \tau$, these correlation functions can be represented by delta functions in time.

(c) The properties of $\mathbf{K}(t)$ can be represented by a Gaussian stochastic process of zero mean and with

$$
\mathbf{P}^\dagger [\mathbf{K}(t)\mathbf{K}(0) + \mathbf{K}(0)\mathbf{K}(t)]_w \sim I \delta(t).
$$

(3.20)
The Gaussian property is difficult to demonstrate because of the complications inherent in the determination of the appropriate Wigner equivalents\(^{56-58}\).

With properties (a) and (b) above, we can solve the Langevin equation to yield the results:

\[
P^+ P^*(t) = e^{-\epsilon \gamma t} P^*(0),
\]

(3.21)

\[
P^+ P^*(t)P^*(0) = e^{-\epsilon \gamma t} P^*(0)P^*(0),
\]

(3.22)

and

\[
\langle \left[ P^*(t)P^*(0) + P^*(0)P^*(t) \right] \rangle_w = \int dX dR dP^* f_\epsilon \left[ P^*(t)P^*(0) + P^*(0)P^*(t) \right]_w
\]

\[
= e^{-\epsilon \gamma t} (3m k_B T) I.
\]

(3.23)

This result corresponds to approximating \( W_e \) by \( W_0 \). The higher order corrections can be systematically obtained using our techniques. The results obtained in Eq(3.23) are identical to those obtained by Hynes and Deutch\(^ {58}\).

The advantages of the technique presented here is that the extension to higher orders in \( \epsilon \) is straightforward and that averages over the distribution function of the bath can be obtained. Thus, we can demonstrate the validity of the fluctuation-dissipation theorem\(^ {67}\) [see Eqs(3.21)-(3.23)].

A more direct method for obtaining the Langevin equation, Eq(3.17), is to start with the fluctuating force

\[
K_q(t) = e^{-\epsilon t} \langle 1 - (1 - P^+) L \rangle t F
\]

and to proceed in essentially the same manner as above. Here \( P^+ B \equiv \int f_\epsilon B dX \) and Eqs(3.21) and (3.22) contain \( P^+ B \) instead of \( P^+ \). In order to obtain Eq(3.18) we must make use of Eq(2.32).

The results that we have obtained are valid under the conditions that

103
$\varepsilon = (m/M)^{1/2} \ll 1$ and that $\varepsilon^0 \ll |P| \ll \varepsilon^{-2}$. While the bath can be fully quantum mechanical, the Brownian particle is assumed to be at worst semiclassical. At very low temperatures, the conditions on the magnitude of the momentum will not be met, and the separation in time scales assumed in this treatment will not be valid.
III. C. QUANTUM BROWNIAN MOTION

DENSITY MATRIX APPROACH.

In this Part we present an alternative derivation of the Fokker-Planck equation, Eq(III.A.2.25). The derivation is based on the same ideas as in the previous Part, but here we work directly with quantum mechanical operators rather than with Wigner equivalents.

The projection operator utilized in this section is the same one obtained in Chapter II, though its expansion is based not on the strength of the interaction potential, but rather on the magnitude of matrix elements of commutators of system operators. We will call system operators those referring to the Brownian particle.

Although this method deals with the density matrix language and Heisenberg operators, some useful results for this Part are obtained, in Appendix B, using Wigner equivalents.

Section 1 deals with the usual definitions of the system and projection operator. In Section 2 the expansion in powers of $\varepsilon$ is presented; the difference with the $\lambda$ expansion of the weak coupling case is made evident. In Section 3 the Fokker-Planck equation is obtained.

III. C. 1 Projection operator and exact dynamics.

The system under consideration is the same as in Section III.B.1 The following expressions denote Heisenberg operators unless otherwise specified or where the context is not obvious. We set $\hbar = 1$ for convenience. The Hamiltonian of the total system is then

$$ H = \frac{p^2}{2M} + H_B + \Phi(r^N, R) $$

(1.1)

where
\[ H_B = \frac{\mathbf{p}^N}{2m} \mathbf{p}^N + \sum_{i<j}^N u \langle \mathbf{r}_i - \mathbf{r}_j \rangle \]  

is the Hamiltonian of the N bath particles, and

\[ \Phi(\mathbf{r}_i, \mathbf{R}) = \sum_{i=1}^N \phi \langle \mathbf{r}_i - \mathbf{R} \rangle \]  

is the interaction potential of the Brownian particle with the bath particles. We are assuming, as before, that the above potentials have short range. The above operators obey canonical commutation relations:

\[ [p_{\alpha}, r_{\beta}] = \frac{i}{\hbar} \delta_{\alpha\beta} \quad \text{and} \quad [p_{\alpha i}, r_{\beta j}] = \frac{i}{\hbar} \delta_{ij} \delta_{\alpha\beta} \]  

where \( \alpha, \beta = x, y, z \) denote the cartesian components of the vector operators; and \( ij = 1, \ldots, N \) label the bath particles.

Using the projection operator

\[ \mathcal{P} A = \frac{1}{2} \left( \rho (\text{Tr}_B A) + (\text{Tr}_B A) \rho^+ \right) \]  

with the usual definitions

\[ \rho = \rho_e W_e^{-1}, \quad \rho^+ = W_e^1 \rho_e \]  

\[ \rho_e = \frac{e^{-\beta H}}{\text{Tr} S \text{Tr} B e^{-\beta H}} \quad \text{and} \quad W_e = \text{Tr}_B \rho_e \]  

and following the algebraic manipulations of Section II.B.1, the reduced Liouville equation for the system density matrix, \( W(t) = \text{Tr}_B \rho(t) \), is

\[ \frac{\partial}{\partial t} W(t) = - i \left[ \frac{\mathbf{p}^2}{2M}, W(t) \right] - i \text{Tr}_B \left[ \Phi, \frac{1}{2} \left( \rho W(t) + W(t) \rho^+ \right) \right] 
\]

\[ + \frac{1}{2} \text{Tr}_B \left[ \Phi, \int_0^t d\tau \mathcal{Q} \mathcal{L}^\tau \mathcal{Q} \times \right. 
\]

\[ \left. \times \left( (\rho \text{Tr}_B[\Phi, \rho W_e] + [\Phi, \rho W_e]) W_e^{-1} W(t - \tau) \right) \right] \]
\[+ W(t - \tau)W_c^{-1}( - \text{Tr}_B[\Phi, W\tilde{\rho}^\dagger]\tilde{\rho}^\dagger + [\Phi, W\tilde{\rho}^\dagger])
- [\Phi, \tilde{\rho} W(t - \tau) + W(t - \tau)\rho^\dagger])\]
\[-i \text{Tr}_B[\Phi, e^{Q_1L_1Q} \rho(0)]\]  \hfill (1.8)

where
\[L = -i[H, ]\]  \hfill (1.9)

Again, Eq(1.8) is just the Liouville (or Heisenberg) equation, but written in a suitable form to implement approximations. As mentioned earlier, the strength of the interaction potential is not the small parameter; therefore, in contrast to the case of weak coupling we cannot proceed in a straightforward fashion with the expansion. For Brownian motion the appropriate small parameter is the ratio of the mass of the bath particles to the mass of the Brownian particle \(\varepsilon \equiv (m/M)^{1/2}\), as explained in Part A of this Chapter. For the classical problem this means that the magnitude of the momentum of the classical Brownian particle should be of order \(\varepsilon^{-1}\), whereas the magnitude of the momentum of the bath particles is of order 1. Clearly, a requirement of this sort cannot be imposed on the quantum momentum operators themselves; rather, the requirement must be made on their expectation values for a certain class of states.

To be precise, let \(|k\rangle\) denote the complete set of eigenstates of the momentum operator \(P\),
\[P|k\rangle = k|k\rangle\]  \hfill (1.10)

thus, Brownian motion will be possible for \(|k| \sim \varepsilon^{-1}\). Now, due to collisions the change in the Brownian particle momentum will be of the order of the bath particles momenta; namely of order 1.

Therefore, we will be interested only in matrix elements of system operators \(<k_1|S|k_2\rangle\), e.g. the reduced density matrix, between states of the momentum operator that satisfy the following requirement:
\[ |k_1| - |k_2| \sim \varepsilon^{-1} \quad \text{but} \quad |k_1 - k_2| \sim 1 \quad . \tag{1.11} \]

III. C. 2. Expansion in powers of \( \varepsilon \) and Equilibrium considerations.

Before performing the expansion in powers of \( \varepsilon \) we first analyze the magnitude of the matrix elements of different commutators that appear in Eq(1.8) using as criterion Eq(1.11). We will find that each commutator contributes with at least a factor of \( \varepsilon \); using this property and the expansions of the different operators involved we will reduce the equation to a more manageable form. In the next section we will explicitly take matrix elements of the equation here obtained. We take this seemingly complicated detour due to the difficulty in assessing the order in \( \varepsilon \) of the different terms as it will be clear below.

To achieve the first step we analyze the matrix elements of: (a) the commutator of \( \frac{P^2}{2M} \) with a system operator; and (b) the trace over the bath of the commutator of \( \Phi \) with an arbitrary operator in the overall Hilbert space. For (a) we get

\[ \langle k_1 | \left[ \frac{P^2}{2M}, S \right] | k_2 \rangle = \langle k_1 | S | k_2 \rangle \frac{1}{2M} (k_1 - k_2) \cdot (k_1 + k_2) \quad . \tag{2.1} \]

Since \( |(k_1 - k_2)| \sim O(1) \), \( |(k_1 + k_2)| \sim O(\varepsilon^{-1}) \) with \( 1/M = \varepsilon^2/m \), the whole term is of order \( \varepsilon \). It will prove convenient to define

\[ k_1 = k - \frac{\Delta}{2} \quad \text{and} \quad k_2 = k + \frac{\Delta}{2} \quad , \tag{2.2} \]

such that \( |k| \sim O(\varepsilon^{-1}) \) and \( |\Delta| \sim O(1) \). Furthermore we define \( k^* = \varepsilon k \), so that \( k^* \sim O(1) \).

Hence, Eq(2.1) becomes

\[ \langle k - \frac{\Delta}{2} | \left[ \frac{P^2}{2M}, S \right] | k + \frac{\Delta}{2} \rangle = \varepsilon \frac{1}{m} k^* \cdot \Delta \langle k - \frac{\Delta}{2} | S | k + \frac{\Delta}{2} \rangle \quad , \tag{2.3} \]

which is explicitly of order \( \varepsilon \). Thus, the appropriate matrix element of the first term on the RHS of Eq(1.8) is of order \( \varepsilon \).
We now consider the other relevant commutator:

\[
\langle k - \frac{\Delta}{2} | \text{Tr}_B \left[ \Phi, A \right] | \frac{\Delta}{2} + k \rangle = \langle k - \frac{\Delta}{2} | \text{Tr}_B \left( \Phi A - A \Phi \right) | \frac{\Delta}{2} + k \rangle
\]

\[
= \frac{V}{(2\pi)^3} \int dk_j \text{Tr}_B \left( \langle k - \frac{\Delta}{2} | \Phi | k_j \rangle \langle k_j | A | \frac{\Delta}{2} + k \rangle - \langle k - \frac{\Delta}{2} | A | k_j \rangle \langle k_j | \Phi | \frac{\Delta}{2} + k \rangle \right)
\]  

(2.4)

where \( A \) is any operator in the overall Hilbert space; to obtain the second equality we introduced a complete set of states of the Brownian particle momentum. By introducing a complete set of states of the Brownian particle position,

\[
| R \rangle | R' \rangle = R | R' \rangle,
\]

(2.5)

where \( R' \) is the eigenvalue of the operator \( R \), we get for the RHS of Eq(2.4)

\[
= \frac{1}{(2\pi)} \int dR' \int dk_j \text{Tr}_B \left( e^{-i \langle k - \frac{\Delta}{2}; R' \rangle} e^{i k_j R'} \langle k_j | A | \frac{\Delta}{2} + k \rangle \right.

- \left. e^{i k_j R'} e^{i \langle k + \frac{\Delta}{2}; R' \rangle} \langle k - \frac{\Delta}{2} | A | k_j \rangle \right) \sum_m \phi(| r_m - R' \rangle \langle r_m | ,
\]

(2.6)

where we have used \( \langle R' | k_j \rangle = V \frac{1}{2} e^{i k_j R} \), the free particle wavefunction. Note that now \( \phi(| r_m - R' \rangle \langle r_m | \) is only an operator in the bath Hilbert space; i.e. \( R' \) is a c-number operator in this space. For the trace over the bath we can choose, in this case, the complete set of states of the bath particles position, \( | r^N \rangle = | r_1 \rangle \otimes | r_2 \rangle \otimes \ldots \otimes | r_N \rangle \). Thus, Eq(2.6) becomes

\[
= \frac{1}{(2\pi)} \int dR' \int dk_j \int dr^N \left( e^{-i \langle k - \frac{\Delta}{2}; R' \rangle} e^{i k_j R'} \langle k_j r^N | A | r^N \frac{\Delta}{2} + k \rangle \right.

- \left. e^{-i k_j R'} e^{i \langle k + \frac{\Delta}{2}; R' \rangle} \langle k - \frac{\Delta}{2}, r^N | A | r^N, k_j \rangle \right) \sum_m \phi(| r_m - R' \rangle \langle r_m | ,
\]

(2.7)

where \( \phi \) is now only a function and no longer an operator. Expressing \( \phi \) in terms of its Fourier transform,
\[ \phi(\mid r_m - R')\mid = \frac{1}{(2\pi)^3} \int dq_m e^{-i q_m \cdot (r_m - R')} \phi(q_m), \quad (2.8) \]

and using the identity
\[ e^{i q \cdot R'} e^{i k \cdot R'} = e^{q \cdot \nabla_k} e^{i k \cdot R'}, \quad (2.9) \]

the RHS of Eq(2.6) finally becomes
\[ = \frac{1}{(2\pi)^3} \sum_m \int dq_m \int dr^N \phi(q_m) e^{-i q_m r_m} \times \]
\[ \times \left( e^{q_m \cdot \nabla_k} - \frac{\Delta}{2} - e^{q_m \cdot \nabla_k} + \frac{\Delta}{2} \right) \langle k - \frac{\Delta}{2}, r^N \mid S \mid r^N, \frac{\Delta}{2} + k \rangle. \quad (2.10) \]

The term in parenthesis can be written in the following way:
\[ -2 e^{q_m \cdot \nabla_k} \sinh \left( \frac{1}{2} q_m \cdot \nabla_k \right); \quad (2.11) \]

hence, the commutator Eq(2.4) has an expansion in odd powers of \( \epsilon \); it is at least order \( \epsilon \).

The reduction of the equation for \( W(t) \), Eq(1.8), is therefore accomplished by expanding the operators involved in this equation in terms of the above commutators, since each of them will contribute, at least, a factor of \( \epsilon \). These operators are essentially the projection operator, the equilibrium density matrices, Eq(1.7), and the propagator appearing in Eq(1.8).

For the projection operator and the equilibrium density matrices we make use of the identity:
\[ e^{-\beta(A + B)} = e^{-\beta A} e^{-\beta B} \left( 1 + \int_0^\beta d\tau e^{\tau B} \left[ B, e^{\tau A} \right] e^{-\tau(A + B)} \right) \quad (2.12) \]

Then, by setting \( A = P^2/2M \) and \( B = H_B + \Phi \), we obtain
\[ e^{-\beta \left( \frac{P^2}{2M} + H_B + \Phi \right)} = e^{-\frac{P^2}{2M} \beta} e^{-\beta (H_B + \Phi)} \left( 1 + \int_0^\beta d\tau e^{\tau (H_B + \Phi)} \left[ \Phi, e^{\frac{\tau P^2}{2M}} \right] \times \]

\[ \right) \]
\[
\times e^{-\frac{\beta}{2M} \frac{P^2}{2M}} e^{-\tau (H_B + \Phi) + \ldots} \\
= (1 - \int_0^\beta d\tau e^{-\tau (H_B + \Phi)} e^{-\frac{\beta}{2M} \frac{P^2}{2M}} \left[ \Phi e^{\frac{\beta}{2M} \frac{P^2}{2M}} \right] \times \\
\times e^{\tau (H_B + \Phi) + \ldots} e^{-\beta (H_B + \Phi)} e^{-\frac{\beta}{2M} \frac{P^2}{2M}}),
\]

where the higher order terms can be obtained by iteration of Eq(2.12). The second equality follows from the Hermiticity of all the operators involved. We now notice that due to the translation invariance of \(H_B\) and \(\Phi\),

\[
\text{Tr}_B e^{-\beta (H_B + \Phi)} = Z_0 I_S,
\]

where \(I_S\) is the unit operator in the system, or Brownian particle Hilbert space, and \(Z_0\) is the partition function of the bath in the presence of the Brownian particle fixed at some position in space. To show that Eq(2.14) holds, take matrix elements of this equation between states of the momentum of the massive particle:

\[
\langle k_1 \mid \text{Tr}_B e^{-\beta (H_B + \Phi)} \mid k_2 \rangle = \frac{1}{V} \int dR' \ e^{-i k_1 \cdot R' - i k_2 \cdot R'} \text{Tr}_B e^{-\beta (H_B + \sum_i \Phi(|r_i - R'|))}.
\]

By defining bath operators \(\rho_i = r_i - R'\), where \(R'\) is a c-number operator in the bath Hilbert space, and noting that the commutation relations \([\rho_i, \rho_j] = \delta_{ij}\) are obeyed, we find that the trace is independent of \(R'\):

\[
Z_0 \equiv \text{Tr}_B e^{-\beta (H_B + \sum_i \Phi(|r_i - R'|))} = \int d\rho \ \rho^N \ e^{-\beta (H_B + \sum_i \Phi(|\rho_i|))} \rho^N.
\]

Hence, Eq(2.14) follows.

By taking traces over the bath and the system of Eq(2.13) we get the following results, valid to lowest order in the commutator \([\Phi, e^{\frac{\beta}{2M} \frac{P^2}{2M}}]\):

The total partition function
\[ Z = \text{Tr}_S \text{Tr}_B \ e^{-\beta \left( \frac{P^2}{2M} + H_B + \Phi \right)} = Z_S Z_0 + \ldots , \quad (2.15) \]

where \( Z_S \) is the partition function of the Brownian particle in the absence of the interaction,

\[ Z_S = \text{Tr}_S \ e^{-\beta \frac{P^2}{2M}} . \quad (2.16) \]

The total equilibrium density matrix

\[ \rho_e = \frac{e^{-\beta \left( \frac{P^2}{2M} + H_B + \Phi \right)}}{\text{Tr}_S \text{Tr}_B \ e^{-\beta \left( \frac{P^2}{2M} + H_B + \Phi \right)}} = \frac{1}{2} \left[ W_{e0} \rho_0 + \tilde{\rho}_0 W_{e0} \right] + \ldots , \quad (2.17) \]

where \( W_{e0} \) is the lowest order contribution to the reduced density matrix for the Brownian particle

\[ W_e = \text{Tr}_B \rho_e = \frac{e^{-\beta \frac{P^2}{2M}}}{Z_S} + \ldots = W_{e0} + \ldots , \quad (2.18) \]

and \( \tilde{\rho}_0 \) is the lowest order correction to the operator appearing in the projection operator, Eq.(1.6),

\[ \tilde{\rho} = \tilde{\rho}_0 + \ldots = \frac{e^{-\beta (H_B + \sum_i \phi( |r_i - R| ) )}}{Z_0} + \ldots \]

\[ \tilde{\rho}^+ = \tilde{\rho}_0 + \ldots = \frac{e^{-\beta (H_B + \sum_i \phi( |r_i - R| ) )}}{Z_0} + \ldots . \quad (2.19) \]

Accordingly the projection operator becomes

\[ \mathcal{P} A = \mathcal{P}_0 A + \ldots = \frac{1}{2} \left\{ \tilde{\rho}_0, \text{Tr}_B A \right\} + \ldots . \quad (2.20) \]

where \( \{ , \} \) denotes the anticommutator.

We have not written the higher order terms in the above formulae since we will not need them in the present derivation. It is straightforward to calculate them, though one must be careful with the fact that \( \tilde{\rho}_0 \) is an operator in both bath and particle Hilbert spaces.
Since the dissipative term in Eq.(1.8) already involves two commutators we will need to consider the propagator to lowest order only. First, approximate \( L \) by \( L_0 \), where \( L_0 = -i \{ H_B + \Phi, \_ \} \); then approximate \( Q \) by \( Q_0 \) and note that due to Eqs(2.4) and (2.11) \( L_0 P_0 \) and \( P_0 L_0 \) are at least of order \( \varepsilon \). Hence, to lowest order, the propagator can be approximated as
\[
e^{QLQ^t} Q_A = e^{-i \{ H_B + \Phi, \} t} Q_0 A = e^{-i (H_B + \Phi)t} Q_0 A e^{i (H_B + \Phi)t}.
\]

(2.21)

III. C. 3. The quantum Fokker-Planck equation.

With the results obtained in the previous Section, we are now able to write the equation for the reduced density matrix, Eq(1.8), valid up to second order in commutators of system operators. Our goal is to obtain an equation valid up to second order in \( \varepsilon \). The neglect of the initial value as well as the higher order terms can be achieved in a fashion completely analogous to the weak coupling case discussed in the previous Chapter. In Appendix B we use the Wigner equivalent technique to show that the correction to the Euler terms, i.e. the second term on the RHS of Eq(1.8), is at least of order \( \varepsilon^3 \), and therefore does not contribute to the equation valid up to second order in \( \varepsilon \); we also show that this term is identically zero in equilibrium. Hence, using Eqs(2.18), (2.19) and (2.21), Eq(1.8) becomes:
\[
\frac{\partial}{\partial t} W(t) = -i \left[ \frac{P^2}{2M}, W(t) \right] \\
+ \frac{i}{2} \text{Tr}_B[\Phi, \int_0^t e^{-i (H_B + \Phi)\tau} \times \\
\times \left( [\Phi, \tilde{\rho}_0 W_{e_0}^{-1} W(t - \tau) + W(t - \tau) W_{e_0}^{-1} [\Phi, W_{e_0} \tilde{\rho}_0] \right)
\]

(3.1)
\[- \left[ \Phi, \tilde{\rho}_0 \left( W(t - \tau) + W(t - \tau) \tilde{\rho}_0 \right) \right] e^{i (H_B + \Phi)\tau} \].

Since the dissipative term is at least of order $\varepsilon^2$, we can commute the propagator with $W(t - \tau)$ and $W_\varepsilon \tilde{\rho}_0$; then, we obtain

$$\Phi(-\tau) = e^{-i (H_B + \Phi)\tau} \Phi e^{i (H_B + \Phi)\tau}, \quad (3.2)$$

which corresponds to the operator $\Phi$ reversibly propagated to $-\tau$ in the subspace of the bath in the presence of the Brownian particle fixed at some position in space.

With Eq.(3.2), Eq.(3.1) can be further simplified, yielding

$$\frac{\partial}{\partial t} W(t) = -i \left[ \frac{P^2}{2M}, W(t) \right]$$

$$- \frac{1}{2} \int_0^t \int_0^t \text{Tr}_B \left[ \Phi, \tilde{\rho}_0 \left( e^{-\frac{P^2}{2M}} \Phi(-\tau) e^{\frac{P^2}{2M}} W(t-\tau) - W(t-\tau) \Phi(-\tau) \right) \right] e^{\frac{\beta P^2}{2M} \Phi(-\tau) e^{-\frac{\beta P^2}{2M}} \tilde{\rho}_0]}. \quad (3.3)$$

We emphasize once more that Eq.(3.3) is not the lowest order contribution, but is in a form appropriate for taking the relevant matrix elements which yield the true corrections of order $\varepsilon$ and $\varepsilon^2$.

The next step is the evaluation of Eq.(3.3) between the states $|k - \Delta/2 \rangle$ and $|k + \Delta/2 \rangle$. We leave the details of the calculation to the Appendix C. The final result is the formidable expression
\[
\frac{\partial}{\partial t} \langle k \frac{\Delta}{2} | W(t) | \frac{\Delta}{2} + k \rangle = -i \frac{e}{m} k^{*} \cdot \Delta \langle k \frac{\Delta}{2} | W(t) | \frac{\Delta}{2} + k \rangle
\]
\[
+ \frac{1}{2} \int_0^t d\tau \text{Tr}_B \tilde{\rho}_0 \int dq^N e^{-i q^N \cdot r^N} \times
\]
\[
\times \left\{ \left( \Phi(q^N, -\tau) \Phi - (\Phi(-\tau) \Phi)(q^N) \right) e^{Q_1 V_k}
+ \left( \Phi \Phi(q^N, -\tau) - (\Phi \Phi(-\tau))(q^N) \right) e^{-Q_1 V_k}
+ \Phi(q^N, -\tau) \Phi \left( e^{\frac{\beta}{2M} \frac{(k^* \Delta)}{2}} e^{Q_2 V_{k, \Delta/2}} - e^{\frac{\beta}{2M} (k \cdot \Delta)} \right)
+ \Phi \Phi(q^N, -\tau) \left( e^{\frac{\beta}{2M} \frac{(k \cdot \Delta)}{2}} e^{Q_2 V_{k, \Delta/2}} - e^{\frac{\beta}{2M} (k \cdot \Delta)} \right) \right\}
\times \langle k \frac{\Delta}{2} | W(t - \tau) \frac{\Delta}{2} + k \rangle
\]
\[
- \frac{1}{2} \int_0^t d\tau \text{Tr}_B \tilde{\rho}_0 \int dq_1^N e^{-i q_1^N \cdot r^N} \int dq_2^N e^{-i q_2^N \cdot r^N} \times
\]
\[
\times \left\{ \tilde{\Phi}(q_2, -\tau) \tilde{\Phi}(q_1) e^{Q_1 V_k} \left( e^{\frac{\beta}{2M} \frac{(k^* \Delta)}{2}} e^{Q_2 V_{k, \Delta/2}} - e^{\frac{\beta}{2M} (k \cdot \Delta)} \right)
+ \tilde{\Phi}(q_1) \tilde{\Phi}(q_2, -\tau) e^{-Q_1 V_k} \left( e^{\frac{\beta}{2M} \frac{(k \cdot \Delta)}{2}} e^{Q_2 V_{k, \Delta/2}} - e^{\frac{\beta}{2M} (k \cdot \Delta)} \right) \right\}
\times \langle k \frac{\Delta}{2} | W(t - \tau) \frac{\Delta}{2} + k \rangle .
\]

(3.4)

In the last two terms the gradient with respect to \( k \), in the exponentials of \( Q_1 \), act also on the density matrix element.

First, note that \( \tilde{\rho}_0 \) and \( \Phi \) are pure bath operators. Those with the tilde denote the Fourier transforms with arguments \( q \). These Fourier transforms are of a formal nature since we are dealing with operators, but due to the trace over the bath this is possible. Of
course we can evaluate the traces explicitly and obtain the same results; we have chosen to express them in this way to ease the notation.

We have defined

$$Q = \sum_{i=1}^{N} q_i$$

In order to handle these factors we expand each exponential in its Taylor series; each factor of $Q^n$, where $n$ is the order of the term in the series, is evaluated in the following way

$$\int dq^{N} \sum_{i=1}^{N} q_i \sum_{i=1}^{N} e^{-i q_i \cdot r_i^{N}} g(q^{N}) = \int dq^{N} \sum_{i=1}^{N} q_i \sum_{i=1}^{N} e^{-i q_i \cdot r_i^{N}} \tilde{g}(q^{N})$$

$$= i \sum_{i=1}^{N} \nabla_{r_i} \int dq^{N} e^{-i q_i \cdot r_i^{N}} \tilde{g}(q^{N}) = i \sum_{i=1}^{N} \nabla_{r_i} \tilde{g}(r_i^{N}) = i \nabla \tilde{g}$$

(3.5)

We can now proceed and obtain the contributions up to order $\epsilon^2$. The factors of $\epsilon$ arise from

$$\frac{1}{M} = \epsilon^{2} \frac{1}{m} , \quad k = \epsilon^{-1} k^{*} \quad \text{and} \quad \nabla_{k} = \epsilon \nabla_{k^{*}} ;$$

hence, we have the following results for the dissipative term of Eq(3.4):

a) order $\epsilon^0$: take all the exponentials equal to one. By inspection it can be seen that all terms cancel.

b) order $\epsilon^1$: take, one at the time, the first order of the series of the exponentials that involve factors of $Q$'s. Each term vanishes, after taking the trace over the bath, due to spherical symmetry. See Eq(3.5).

c) order $\epsilon^2$: first we note that by taking the exponentials of $Q_1$ in the two terms in the lower time integral equal to one, these cancel the last two terms in the upper time integral. Therefore, the contributions arise from: 1) the second orders of the series exponentials of the first two terms in the upper time integral; 2) the second orders of the series exponential
of $Q_1$ and the zeroth order of the exponential of $Q_2$; and 3) the first orders of the exponents of $Q_1$ and $Q_2$. Using Eq.(3.5) the dissipative term becomes,

$$-rac{1}{4} \varepsilon \int_0^t d\tau \text{Tr}_B \rho_0 \times$$

$$\times \left\{ \left( \nabla^2 \Phi(-\tau) \right) \Phi - \nabla^2 \left( \Phi(-\tau) \Phi \right) + \Phi \left( \nabla^2 \Phi(-\tau) \right) - \nabla^2 \left( \Phi \Phi(-\tau) \right) \right\} \nabla_{k^*} \nabla_{k^*} \left| k^* - \frac{\Delta}{2} \right| W(t - \tau) \left| \frac{\Delta}{2} + k \right>$$

$$+ \left( \nabla^2 \Phi \right) \Phi(-\tau) + \Phi(-\tau) \left( \nabla^2 \Phi \right) \right\} \nabla_{k^*} \beta \frac{k^*}{m} k^* \left| k^* - \frac{\Delta}{2} \right| W(t - \tau) \left| \frac{\Delta}{2} + k \right>$$

$$- \left( 2 \nabla \Phi(-\tau) \nabla \Phi + 2 \nabla \Phi \nabla \Phi(-\tau) \right) \right\} \nabla_{k^*} \beta \frac{k^*}{m} k^* \left| k^* - \frac{\Delta}{2} \right| W(t - \tau) \left| \frac{\Delta}{2} + k \right>$$

(3.6)

With further simplification of Eq.(3.6), and writing the force $F = -\nabla \Phi$, the terms under the trace over the bath can be written as

$$- \text{Tr}_B \rho_0 \frac{1}{2} \left\{ e^{-i \left( H_B + \Phi \right) \tau} F e^{i \left( H_B + \Phi \right) \tau}, F \right\} ;$$

(3.7)

this symmetrized correlation, by assumption, decays to zero in the short time scale; i.e. vanishes for $t > \tau_b$, where $\tau_b$ is the relaxation time of such bath correlations.

Therefore, for $t > \tau_b$ we can implement the "weak coupling" limit approximation in Eq.(3.4); that is, $W(t - \tau) = W(t)$ and extend the upper limit of the time integral to infinity. The final result is the quantum Fokker-Planck equation:

$$\frac{\partial}{\partial t} \left( k^* - \frac{\Delta}{2} \right) W(t) \left| \frac{\Delta}{2} + k \right> = i \varepsilon \frac{1}{m} k^* \cdot \Delta \left( k^* - \frac{\Delta}{2} \right) W(t) \left| \frac{\Delta}{2} + k \right>$$

$$+ \varepsilon^2 \Gamma \nabla_{k^*} \left( \nabla_{k^*} + \beta \frac{k^*}{m} \right) \left( k^* - \frac{\Delta}{2} \right) W(t) \left| \frac{\Delta}{2} + k \right>$$

(3.8)

The dissipative coefficient $\Gamma$ is exactly the same as that obtained in the previous section, Eq.(III.B.2.29),

$$\Gamma = \int_0^\infty dt \int dX \tilde{r}_0 e^{\frac{1}{2}} \left( \left[ e^{-i \left( H_B + \Phi \right) \tau} F e^{i \left( H_B + \Phi \right) \tau}, F \right] \right)_W$$

(3.9)
One can then verify, by taking the Fourier transform of Eq(3.8), that the Fokker-Planck equation obtained in this section is identical to the one obtained in Section III.B.3, where we worked exclusively in terms of Wigner equivalents. This result is expected: it follows from the fact that although the corresponding projection operators are different, they have the same essential property, namely, that the overall equilibrium density matrix, or total Wigner function, is projected onto itself. Of course, the agreement also depends on being able to expand consistently in the same parameter and to the same order.

An important point that must be stressed is the validity of the equation regarding matrix elements: it is correct only for $k \sim \epsilon^{-1}$ and $\Delta \sim 1$; this is similar to the classical case where the validity is assured only if the magnitude of the momentum of the Brownian particle is of order $\epsilon^{-1}$. On the other hand, in order to have complete knowledge of a quantum operator one must know all of its matrix elements (especially in this case since the density matrix is useful for calculating different expectation values), and our equation is restricted to the class of states mentioned above. This problem can be resolved by imposing the requirement that initially all those matrix elements outside the range of validity are negligible, and therefore will remain so. This assumption is supported not only by the physical picture of Brownian motion, but also by the fact that the equation itself for the relevant matrix elements is closed: there is no coupling between different matrix elements.
III. D. REMARKS.

In this Chapter we have presented a systematic first principles derivation of the equations that govern Brownian motion for classical and quantum systems. Our analysis is based on three main conditions: (1) the existence of a small coupling parameter $\varepsilon^2$, i.e. the ratio of the bath particles masses, $m$, to the heavy particle mass, $M$; (2) a separation of time scales, namely a short correlation time of bath variables; and (3) the restrictions on the magnitude of the Brownian particle momentum, $P \sim \varepsilon^{-1}$ and $\varepsilon^0 \ll P \ll \varepsilon^{-2}$ (for the quantum problem this translates into the type of matrix elements that should be considered). The last condition differentiates the present treatment from the one of Chapter II.

The quantum Fokker-Planck and Langevin equations are not valid for low enough temperatures: there is a slow time scale of purely quantum nature of the order of $\hbar/k_B T$; when this time is of the order or larger than the relaxation time, the Fokker-Planck and Langevin equations do not describe the process appropriately. After all, when the de Broglie wavelength of the heavy particle becomes comparable to the mean free path Brownian motion no longer occurs$^{58-60}$.

Restricting the range of temperatures, a short time scale can be associated with the bath. In this case we are able to extend the method for eliminating fast variables$^9$, utilized in the classical case (Part A), to study quantum Brownian motion in a systematic fashion using the Wigner equivalent representation (Part B).

In Part C we rederive the Fokker-Planck equation obtained in Part B with the aid of the projection operator defined in Chapter II and dealing directly with Heisenberg operators. The analysis is not as clear as in Part B due to the difficulties in assessing the order in $\varepsilon$ of the terms of the expansion. The use of Wigner equivalents seems to be a better and easier way of handling this problem. (See also the last paragraph of Section
III.B.3). The only disadvantage of the latter method is that the streaming terms are not completely separated, therefore care should be taken when one considers higher order terms.

The results that we have obtained for the Fokker-Planck equation in lowest order are in agreement with those obtained by Dagonnier and Resibois\textsuperscript{59,60}. Some of the results given in Section III.B.3 for the Langevin equation are in agreement with those obtained by Hynes and Deutch\textsuperscript{58}.

As a last comment, and as a problem for further research, we emphasize the dependence of the validity of this treatment, and therefore the microscopic foundation of the Fokker-Planck and Langevin equations, on the first two conditions outlined at the beginning of this Part: the separation of time scales and the fact that $\varepsilon << 1$ (the same comments apply to the weak coupling case studied in the previous Chapter). This point should not be overlooked for the following reason: the power of the standard Langevin and Fokker-Planck equations, as well as their equivalence, in describing the whole stochastic process rests on the process being Markovian\textsuperscript{12}. Because the relaxation time of the bath is small we are able to obtain time-local equations and a connection to a Markovian process can be made\textsuperscript{*}. It has long been recognized that there are many interesting effects with which these type of equations cannot properly deal since there is not a clear separation of time scales; for instance the long time tails in Brownian motion due to the slow hydrodynamic modes of the fluid\textsuperscript{42,43} and the long correlation times of quantum variables at low temperatures\textsuperscript{44,45}.

In the literature we find many attempts, some based on projection operators\textsuperscript{5,48,53} as we explained in Part II.C, some phenomenological based on stochastic theory\textsuperscript{39}, and

\textsuperscript{*} Although there are other technicalities to work out, especially for quantum systems\textsuperscript{53,54}, the important point is that the initial time is not singled out; this means that any time that we observe the system, its behavior is properly described by the same equation.
some based on very specific microscopic models\textsuperscript{33,70}, to extend or "generalize" the Fokker-Planck and Langevin equations to the case when the decay of the bath correlations no longer occurs in a short time scale giving rise to a so called memory term; the first problem that one faces is that these processes are no longer Markovian, and from the theory of stochastic processes\textsuperscript{12} we know that these "generalized" Fokker-Planck or Langevin equations do not provide a full description of the process, i.e. from its solution the whole hierarchy of probability distributions cannot be obtained, but only the one-time distribution function depending on the particular chosen initial time; moreover, the Langevin and the Fokker-Planck equations are no longer equivalent as before. In some cases, however, Markovian equations can be obtained by considering a larger set of variables (see e.g. Ref.\textsuperscript{39}).

On the other hand, as pointed out before, all the microscopic derivations of these equations appeal to particular initial states for the overall system. It is interesting to note from our treatment that if the relaxation time of the bath is not small enough, not only the initial condition term must be kept, but the expansion in powers of $\varepsilon$, or $\lambda$, breaks down. This indicates that in order to accommodate "non-Markovian" effects one should consider higher order terms: the result will not be, in general, a Langevin or Fokker-Planck equation with a memory term. It is therefore clear that much theoretical work remains to be done.
APPENDIX A
Solution of Eqs(II.B.3.29).

In this Appendix we sketch how the solution to Eqs(II.B.3.29), for an arbitrary initial condition, is obtained in the weak coupling limit.

Eqs(II.B.3.29) is a set of coupled inhomogeneous linear differential equations in the variable \( t \). This set can be written in the form

\[
\begin{align*}
\dot{X} + A_{11}X + A_{12}Y + A_{13}Z &= D_1 \\
\dot{Y} + A_{21}X + A_{22}Y + A_{23}Z &= D_2 \\
\dot{Z} + A_{32}Y &= 0
\end{align*}
\] (1.1 - 1.3)

where \( X \equiv <\sigma_x> \), \( Y \equiv <\sigma_y> \), \( Z \equiv <\sigma_z> \) and the matrix of the coefficients, \( A_{ij} \), as well as the inhomogeneous terms, \( D_i \), can be read off Eqs(II.B.3.29).

In order to find the homogeneous solution for an initial \((t = 0)\) set of values \( X_0, Y_0 \) and \( Z_0 \) we propose a solution of the form

\[
\vec{X}_h = \vec{C} e^{\vec{Z} t}.
\] (2)

Therefore, the secular equation,

\[
\det \begin{vmatrix} A_{ij} + z\delta_{ij} \end{vmatrix} = 0 ,
\] (3)

is a cubic equation for \( z \), whose three roots are given by

\[
\begin{align*}
z_1 &= (P_1 + P_2) - \frac{2}{3} A_{11} \\
z_2 &= -\frac{1}{2} (P_1 + P_2) - \frac{2}{3} A_{11} + i \frac{\sqrt{3}}{2} (P_1 - P_2) \\
z_3 &= -\frac{1}{2} (P_1 + P_2) - \frac{2}{3} A_{11} - i \frac{\sqrt{3}}{2} (P_1 - P_2)
\end{align*}
\] (4.1 - 4.3)

where

\[
\begin{align*}
P_1 &= \left[ r + (q^3 + r^2)^{1/2} \right]^{1/3} \\
P_2 &= \left[ r - (q^3 + r^2)^{1/2} \right]^{1/3}
\end{align*}
\] (5.1 - 5.2)
and
\[ r = \frac{1}{6} [(A_{11}A_{22} - A_{12}A_{21} - A_{32}A_{23})(A_{11} + A_{22}) - 3A_{32}(A_{21}A_{13} - A_{23}A_{11})] \]
\[ - \frac{1}{27} (A_{11} + A_{22})^3 \]  \hspace{1cm} (6.a)
\[ q = \frac{1}{3} (A_{11}A_{22} - A_{12}A_{21} - A_{32}A_{23}) - \frac{1}{9} (A_{11} + A_{22})^2 \]  \hspace{1cm} (6.b)

Since we are considering the case \( E \sim O(1) \), i.e. \( E > \lambda^2 \Gamma_1, \lambda^2 \Gamma_2, \lambda^2 S_1, \lambda^2 S_2 \) and \( \lambda^2 E_1 \), we have that \( q^3 + r^2 > 0 \) and therefore two roots are complex and one is real; furthermore, the real root as well as the real parts of the complex roots are negative thus assuring the relaxation towards equilibrium as \( t \to \infty \).

With the above roots and the initial condition, it is a problem of linear algebra to find the complete homogeneous solution which will be of a tremendous complexity. In the limit \( \lambda^2 \to 0 \), \( t \to \infty \) but \( \lambda^2 t \) arbitrary the solution simplifies considerably. It is clear that \( \lambda^2 t \) appears only in the exponentials \( e^{z_i t} \) of our ansatz Eq(2); hence, the coefficients can be approximated to order \( \lambda \). This is easily achieved by starting with the ansatz for \( Z(t) \):
\[ Z(t) = C_{31} e^{z_{1t}} + C_{32} e^{z_{2t}} + C_{33} e^{z_{3t}} \]  \hspace{1cm} (7)

\( X(t) \) and \( Y(t) \) are then expressed in terms of the unknown coefficients \( C_{3i} \) using Eqs(1). The resulting equations are evaluated at \( t = 0 \), and we obtain to zeroth order in \( \lambda \):
\[ C_{31} = -X_0 \cos \alpha \sin \alpha + Z_0 \sin^2 \alpha \]  \hspace{1cm} (8.a)
\[ C_{32} = -\frac{1}{2} X_0 \cos \alpha \sin \alpha + \frac{1}{2} Z_0 \cos^2 \alpha + \frac{i}{2} Y_0 \cos \alpha \]  \hspace{1cm} (8.b)
\[ C_{33} = -\frac{1}{2} X_0 \cos \alpha \sin \alpha + \frac{1}{2} Z_0 \cos^2 \alpha - \frac{i}{2} Y_0 \cos \alpha \]  \hspace{1cm} (8.c)

The roots \( z_i \) are then evaluated to second order in \( \lambda \) with the following results:
\[ z_1 = -\lambda^2 \Gamma_1 \cos^2 \alpha \]  \hspace{1cm} (9.a)
\[ z_2 = -(\frac{1}{2} \lambda^2 \Gamma_1 \cos^2 \alpha + \lambda^2 \Gamma_2 \sin^2 \alpha) + i (2E + \lambda^2 \Omega) \]  \hspace{1cm} (9.b)
\[ z_3 = -(\frac{1}{2} \lambda^2 \Gamma_1 \cos^2 \alpha + \lambda^2 \Gamma_2 \sin^2 \alpha) - i (2E + \lambda^2 \Omega) \]  \hspace{1cm} (9.c)

123
With Eqs(8) and (9) the homogeneous solution follows (see Eqs(II.B.3.34)).

The particular solution is calculated using

$$\tilde{X}_p = \int_0^t \mathrm{d}\tau \ G(\tau) \cdot \tilde{D}$$

(10)

where $\tilde{D} = (D_1, D_2, 0)$ and the matrix $G(\tau)$ is the Green's function given by

$$G_{ij}(t) = L^{-1} \left[ (A + z I)^{-1} \right]_{ij};$$

(11)

$L^{-1}$ represents the inverse Laplace transform.

Evaluation of Eq(10) is straightforward, though quite lengthy, and again approximating the coefficients to zeroth order in $\lambda$, it yields

$$X_p(t) = \cos \alpha \ tanh \beta E \left( 1 - e^{z_1 t} \right)$$

(12.a)

$$Y_p(t) = 0$$

(12.b)

$$Z_p(t) = - \sin \alpha \ tanh \beta E \left( 1 - e^{z_1 t} \right)$$

(12.c)

Eqs(II.B.3.34) follow.
APPENDIX B

Wigner equivalents formulae. Calculation of the correction to the systematic terms for the quantum Fokker-Planck equation.

Here we present the definition of the Wigner equivalent of a quantum operator and useful formulae. The proof of the latter can be found in Refs. 63 - 65.

Let \( A(R,P) \) be a quantum operator depending on the coordinate and momentum operators \( R \) and \( P \). Wigner\(^63\) defines a function \( A_W(r,p) \) as the Fourier transform of the off-diagonal matrix elements of the operator \( A(R,P) \)

\[
A_W(r,p) = \int dz \, e^{i \frac{r \cdot z}{\hbar}} \langle r - \frac{z}{2} \mid A(R,P) \mid r + \frac{z}{2} \rangle
\]

\[
= \int dk \, e^{i \frac{r \cdot k}{\hbar}} \langle p - \frac{k}{2} \mid A(R,P) \mid p + \frac{k}{2} \rangle . \tag{1}
\]

It is readily verified that

\[
\frac{1}{3} \int dp \, A_W(r,p) = \langle r \mid A(R,P) \mid r \rangle \tag{3}
\]

\[
\frac{1}{3} \int dr \, A_W(r,p) = \langle p \mid A(R,P) \mid p \rangle \tag{4}
\]

\( A_W(r,p) \) is called the Wigner equivalent of \( A(R,P) \).

From Eqs (1) - (4) we see that if \( \rho \) is the density matrix, assuming that the Hamiltonian of the system depends only on \( P \) and \( R \), we have

\[
\text{Tr} \, \rho A = \frac{1}{3} \int dr \, dpp \rho_W(r,p) A_W(r,p) \tag{5}
\]

the Wigner "distribution" function is then conveniently defined as

\[
f(r,p) = \frac{1}{3} \rho_W(r,p) \tag{6}
\]

Three very useful formulae are
a) if $A = A(P)$, i.e. only a function of $P$, then $A_W(p) = A(p);

b) if $A = A(R)$, i.e. only a function of $R$, then $A_W(r) = A(r);

c) the Wigner equivalent of a product of two operators is given by

$$\langle A(R,P)B(R,P) \rangle_W = A_W(r,p)e^{\frac{\hbar}{2i}\Lambda}B_W(r,p)e^{-\frac{\hbar}{2i}\Lambda}A_W(r,p) \quad (7)$$

where

$$\Lambda = \nabla_r - \nabla_p \quad , \quad (8)$$

and the arrows indicate the direction in which the gradients operate.

With the above results we can immediately derive the Wigner equivalents of the

Liouville and Bloch equations:

The Liouville equation is

$$\frac{\partial}{\partial t} \rho = -\frac{i}{\hbar} [H,\rho] \quad ; \quad (9)$$

taking Wigner equivalents in both sides we obtain

$$\frac{\partial}{\partial t} f = -\frac{i}{\hbar} (H_W e^{2i\Lambda} f - \frac{\hbar}{2} H_W)$$

$$= -\frac{2}{\hbar} H_W \sin(\frac{\hbar}{2} \Lambda) f \quad . \quad (10)$$

The Bloch equation for the unnormalized density matrix in canonical equilibrium,

$$\rho'_e = e^{-\beta H}$$, is

$$\frac{\partial}{\partial t} \rho'_e = -\frac{1}{2} (H \rho'_e + \rho'_e H) \quad ; \quad (11)$$

taking Wigner equivalents, we get

$$\frac{\partial}{\partial t} f'_e = -\frac{1}{2} (H_W e^{2i\Lambda} f'_e + f'_e e^{2i\Lambda} H_W)$$

$$= -H_W \cos(\frac{\hbar}{2} \Lambda) f'_e \quad . \quad (12)$$
For a Hamiltonian as given by Eq(III.B.1.1), Eqs(III.B.1.5) - (III.B.1.6) and Eqs(III.B.2.1) - (III.B.2.4) follow from Eqs(11) and (12) respectively.

We now proceed to show that the second term on the RHS of Eq(III.C.1.8), i.e. the correction to the Euler term is at least order ε³, and that at equilibrium the whole term vanishes. This term is

\[ \frac{i}{\hbar} \text{Tr}_B \left[ \Phi, \frac{1}{2} \left( \hat{\rho} W(t) + W(t) \hat{\rho} \right) \right] ; \]

(13)

taking Wigner equivalents we get

\[ \int d\mathbf{r}^N d\mathbf{p}^N \Phi_w(r, R) \sin \left( \frac{\hbar}{2} \mathbf{\nabla}_R \cdot \mathbf{\nabla}_P \right) \Re \left\{ \hat{\rho}_w e^{\frac{\hbar}{2i} \Lambda_s W_W(t)} \right\} \]

(14)

where

\[ \Lambda_s \equiv \varepsilon \left( \mathbf{\nabla}_{P^*} \cdot \mathbf{\nabla}_R - \mathbf{\nabla}_R \cdot \mathbf{\nabla}_{P^*} \right) . \]

(15)

Furthermore

\[ \hat{\rho}_w = f_e e^{-\frac{\hbar}{2i} \mathbf{\nabla}_R \cdot \mathbf{\nabla}_{P^*}} W_e^{-1} \]

(16)

where \( f_e \) is given by Eq(III.B.1.20), \( W_e \) by Eq(III.B.1.23) and we have taken into account that the latter only depends on \( P^* \). Incidentally, we can see from Eq(16) that the projection operator used in Part III.B is the first term in the Taylor series of the exponentials involved in the projection operator used in Part III.C.

Writing the exponentials in terms of sines and cosines, taking into account that \( \Phi_w \) is only a function of the coordinates and using the symmetry properties of \( f_e \) described in Section III.B.1, Eq(14) becomes

\[ \frac{2}{\hbar} \int d\mathbf{r}^N d\mathbf{p}^N \Phi_w(r, R) \sin \left( \frac{\hbar}{2} \mathbf{\nabla}_R \cdot \mathbf{\nabla}_{P^*} \right) \times \]

\[ \times \left\{ (f_e c(\varepsilon \frac{\hbar}{2} \mathbf{\nabla}_R \cdot \mathbf{\nabla}_{P^*}) W_e^{-1} \right\} s(\varepsilon \frac{\hbar}{2} \mathbf{\nabla}_R \cdot \mathbf{\nabla}_{P^*}) s(\varepsilon \frac{\hbar}{2} \mathbf{\nabla}_{P^*} \cdot \mathbf{\nabla}_R) \]

(17)
+ \left( f_{\phi} s\left( \frac{\hbar}{2} \nabla_{R'} \nabla_{P^*} \right) W_{e^{-1}} \right) c\left( \frac{\hbar}{2} \nabla_{R'} \nabla_{P^*} \right) s\left( \frac{\hbar}{2} \nabla_{P^*} \nabla_{R} \right) W_{W(t)} \right),

where \( c \) stands for \( \cos \) and \( s \) for \( \sin \).

Again, due to the symmetry properties of \( f_{\phi} \), Eq(17) is a series expansion in odd powers of \( \varepsilon \). Furthermore we see explicitly from Eq(17) that the lowest order is \( \varepsilon^3 \).

Moreover, we found in Part III.B that at equilibrium, \( W_{W(t)} = W_{e} \) is a function of \( P^* \) only, see Eq(III.B.1.23); from Eq(17) we see that, at equilibrium, the correction to the Euler term vanishes to all orders in \( \varepsilon \); qed.
APPENDIX C

Derivation of Eq(III.C.3.4).

To obtain Eq(III.C.3.4) we evaluate Eq(III.C.3.3) between the states \( |k - \Delta/2 \rangle \) and \( |k + \Delta/2 \rangle \). The first term on the RHS of Eq(III.C.3.4) is trivially obtained. For the second term on the RHS we will explicitly explain how to evaluate one of the terms; the others are obtained in a similar fashion.

Let us consider the term
\[
I \equiv \text{Tr}_B \Phi \tilde{\rho}_0 W(t - \tau) \Phi(-\tau) .
\] (1)

Taking matrix elements between the states mentioned above and introducing complete sets of states of the momentum \( P \), we get
\[
\langle k - \frac{\Delta}{2} | I | k + \frac{\Delta}{2} \rangle = \int dk_1 \int dk_2 \text{Tr}_B \langle k - \frac{\Delta}{2} | \Phi \tilde{\rho}_0 | k_1 \rangle \times
\]
\[
\times \langle k_1 | W(t - \tau) | k_2 \rangle \langle k_2 | \Phi(-\tau) | k + \frac{\Delta}{2} \rangle. \tag{2}
\]

Since \( \Phi \) and \( \tilde{\rho}_0 \) depend on the Brownian particle operator \( R \), we introduce complete sets of eigenstates of the operator \( R \):
\[
\langle k - \frac{\Delta}{2} | I | k + \frac{\Delta}{2} \rangle = \int dk_1 \int dk_2 \frac{1}{\sqrt{2}} \int dR_1 \int dR_2 \text{Tr}_B \langle k - \frac{\Delta}{2} | R_1 \rangle \Phi(R_1) \tilde{\rho}_0(R_1) \times
\]
\[
\times \langle R_1 | k_1 \rangle \langle k_1 | W(t - \tau) | k_2 \rangle \langle k_2 | R_2 \rangle \Phi(R_2, -\tau) \langle R_2 | k + \frac{\Delta}{2} \rangle
\]
\[
= \int dk_1 \int dk_2 \langle k_1 | W(t - \tau) | k_2 \rangle \int dR_1 \int dR_2 e^{i \frac{(k_1 - k + \Delta/2) R_1}{2}} e^{i \frac{(k + \Delta/2 - k_2) R_2}{2}} \times
\]
\[
\times \text{Tr}_B \tilde{\rho}_0(R_1) \Phi(R_2, -\tau) \Phi(R_1) . \tag{3}
\]

Note that \( R_1 \) and \( R_2 \) are c-number operators in the bath Hilbert space. The trace may be evaluated using the eigenstates of the coordinates \( r^N \). Recalling that the \( R \) and \( r_i \) dependence of \( \Phi \) and \( \tilde{\rho}_0 \) is through factors \( (r_i - R) \) and \( (r_i - r_j) \), we make the change of variables \( \rho_i = r_i - R \) for \( i = 1, \ldots, N \), and the trace in Eq(3) becomes.

129
\[ \text{Tr}_B \rho_0 \Phi(R_2 - R_1 - \tau) \Phi \quad ; \quad (4) \]
i.e. the \( R \) dependence is on the first operator \( \Phi \) only, through \((r_i - (R_2 - R_1))\); \( \tilde{\rho}_0 \) and the last factor of \( \Phi \) no longer depend on \( R \). We can now write the \( \Phi(r_i - (R_2 - R_1)) \) in terms of its Fourier transform (as we mentioned in the text this may be done by taking appropriate matrix elements in the bath Hilbert space; the final result will be the same):

\[ \tilde{\Phi}(q^N, -\tau) = \int dq^N e^{-i q \cdot r^N} e^{i Q \cdot (R_2 - R_1)} \Phi(r_i - (R_2 - R_1), -\tau) \quad . \quad (5) \]

In this equation there is an implicit dependence on \( p^N \), of course. We have defined

\[ Q = \sum_j q_j \quad . \quad (6) \]

Substitution of Eq(5) into Eq(3) yields for the RHS

\[ \int dk_1 \int dk_2 \int dR_1 \int dR_2 \int dq^N \text{Tr}_B \rho_0 \tilde{\Phi}(q^N, -\tau) \Phi^{-i q \cdot r^N} \times \]

\[ e^{i Q \cdot (R_2 - R_1)} e^{i (k_n - k + \Delta/2) \cdot R_1} e^{i (k_0 - k_m) \cdot R_2} \langle k_i | W(t - \tau) | k_2 \rangle \quad . \quad (7) \]

Using the following identities

\[ e^{-i Q \cdot R_2} \frac{e^{i (k_0 - k + \Delta/2) \cdot R_2}}{e^{i (k_0 + \Delta/2) \cdot R_2}} = e^{-Q \cdot \nabla_{k_2}} \left( e^{i (k_0 + \Delta/2) \cdot R_2} \right) \quad . \quad (8.a) \]

\[ e^{-i Q \cdot R_1} \frac{e^{i (k_n - k + \Delta/2) \cdot R_1}}{e^{i (k_n - k + \Delta/2) \cdot R_1}} = e^{-Q \cdot \nabla_{k_1}} \left( e^{i (k_n - k + \Delta/2) \cdot R_1} \right) \quad , \quad (8.b) \]

then, after integrating \( k_1 \) and \( k_2 \) by parts the integrals over \( R_1 \) and \( R_2 \) can be performed yielding \( \delta(k_1 - (k - \Delta/2)) \delta(k_2 - (k + \Delta/2)) \); noting that

\[ e^{-Q \cdot \nabla_{k_{+ \Delta/2}}} = e^{Q \cdot \nabla_{k}} \quad . \quad (9) \]

Eq(2) finally becomes

\[ \langle k - \frac{\Delta}{2} \mid I \mid k + \frac{\Delta}{2} \rangle = \text{Tr}_B \int dq^N \tilde{\rho}_0 \tilde{\Phi}(q^N, -\tau) \Phi^{-i q \cdot r^N} \times \]

\[ e^{Q \cdot \nabla_k} \langle k - \frac{\Delta}{2} \mid W(t - \tau) \mid k + \frac{\Delta}{2} \rangle \quad ; \quad (10) \]
Eq(10) is the first term inside the curly brackets on the RHS of Eq(III.C.3.4). The other terms can be obtained analogously.
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