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To my parents, for raising me in equilibrium.

To my wife, for introducing me to non-equilibrium.

Contents

Chapter 1

Introduction

1.1 Outline

The aim of this thesis is to introduce the concept of projection operators in classical statistical mechanics in a rigorous fashion and to compare four specific versions to each other. Approximation procedures and derivations of phenomenological equations are explicitly excluded, as the former doesn't elucidate the general structure of the theory and the latter lacks of an exact mathematical justification.

We therefore give a brief treatment of the fundamental concepts of statistical mechanics in the subsequent sections, which are necessary to understand the technique of projection operators. Four different, well-established manifestations of the projection operator formalism are then presented in separate chapters, and the thesis will be concluded by a comparison of them.

The author's own contribution (apart from a concise presentation of the subject) consists of an extended treatment (together with a proof) of an example of *Xing* (2009) in sec. 2.3.2 and a comparison of *Zwanzig* (1973) with Mori's formalism (*Mori* (1965)) for the choice of Hamiltonian systems in a heat bath of harmonic oscillators in sec. 2.4. In ch. 4, the author has generalised part of the work of *Kim and Oppenheim* (1972) as *Albers* (1971) did with the work of *Mazur and Oppenheim* (1970), and the proof in sec. 4.3.1 of the equivalence of the subsequently derived generalised Langevin equation with the aforementioned work of Zwanzig was also done by the author himself. Although the relation between Mori's and the δ-formalism to Grabert's formalism (sec. 5.3) are due to Grabert (see f.e. *Grabert* (1982)), the explicit and concise treatment with the addition of Mazur and Oppenheim's formalism is a new contribution

to the literature (to the best of the author's knowledge).

1.2 Fundamental Concepts

This section briefly summarises fundamental concepts of statistical mechanics, which are important for the comprehension of the thesis. It is based on the classic texts *Khinchin* (1949), *Evans and Morriss* (1990) and *Penrose* (1979), though any graduate textbook should explain the concepts in detail.

1.2.1 Statistical Mechanics

Statistical mechanics is a branch of physics, which tries to explain the macroscopic properties and behaviour of large systems by deriving them from simple, limited and microscopic descriptions of the elementary constituents. Its underlying mathematical model is the theory of probability and its results are thus inherently of statistical character. As many macroscopic systems appear to be irreversible, the statistical mechanical methods to treat them contain a coarse-graining procedure (f.e. the idea of molecular chaos or the Markov approximation).

1.2.2 Phase Space

We are interested in physical systems of n *microscopic* degrees of freedom, which are governed by a Hamilton function $\mathscr{H}(\Gamma)$. Γ as the dependent variable is a short form for the n-generalised coordinates $q_1, q_2, \ldots, q_n$ and the n-generalised momenta $p_1, p_2, \ldots, p_n$.

The equations of motions are derived from the Hamilton function by

$$\frac{dq_i}{dt} = \frac{\partial \mathscr{H}(\Gamma)}{\partial p_i}, \tag{1.2.1a}$$

$$\frac{dp_i}{dt} = -\frac{\partial \mathscr{H}(\Gamma)}{\partial q_i} \tag{1.2.1b}$$

and can in principle be integrated to yield every q_i and p_i dependent of initial states $q_i(0)$ and $p_i(0)$. However, apart from special cases (see f.e. sec. 1.4), this procedure is not feasible for typical systems consisting of 10^{23} degrees of freedom.

The generalised coordinates and momenta can be regarded as points $(q_1, q_2, \ldots, q_n, p_1, p_2, \ldots, p_n)$ in a $2n$-dimensional space (the phase space Φ), and the time evolution of the system traces a trajectory through it.

1.2.3 Ensembles

If one wants to measure a macroscopic property of the system using time averages, the experiment has to be repeated many times, because the dynamical state of the microscopic degrees of freedom is not accessible and thus different for each measurement process. The outcomes of many measurements for the same macroscopically prepared experiment will then approach a probability distribution associated with the physical setup. However, from a theoretical point of view, obtaining results with the aid of time averages fails due to the aforementioned largeness of the system. Therefore, the idea of ensembles was introduced by Gibbs.

Instead of performing an experiment many times, one can consider an experiment using a vast amount of different copies of the same system at the same time. This collection of copies of the system under equal macroscopic constraints is called ensemble. For each copy a point in phase space can be associated, and furthermore, an ensemble density $\rho(\Gamma, t)$ can be introduced, which describes the distribution of the ensemble systems in phase space at time t. If one integrates the ensemble density over a given region $\mathcal{M}$ of phase space, the probability of the system being in exactly this region arises, i.e.

$$P(\mathcal{M}, t) := \int_{\mathcal{M}} d\Gamma \ \rho(\Gamma, t). \tag{1.2.2}$$

As the system has to be somewhere in phase space with probability 1, eq. (1.2.2) immediately gives the normalisation

$$\int_{\Phi} d\Gamma \ \rho(\Gamma, t) = 1. \tag{1.2.3}$$

It is then possible to define the expectation value of an arbitrary dynamical variable $B(\Gamma(t))$ at time t in the usual way as

$$\langle B(\Gamma(t)) \rangle := \int_{\Phi} d\Gamma \ B(\Gamma(0)) \rho(\Gamma, t). \tag{1.2.4}$$

From now own, we will drop the notation for the region from the definite integrals, if it is an integration over the whole phase space Φ.

This idea of an ensemble average simplifies the calculation of averages of phase space functions, but shifts the problem to the choice of the ensemble or rather the probability density function $\rho(\Gamma, t)$. This situation was solved for equilibrium systems with the *microcanonical, canonical and grandcanonical* ensemble. On the other hand, non-equilibrium systems don't have a priori a specific ensemble density and great care has to be taken in the selection of it.

However, an important result reduces the set of possible ensemble densities: the Liouville equation.

Liouville equation

The Liouville equation

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \dot{\Gamma} \cdot \frac{\partial \rho}{\partial \Gamma} \tag{1.2.5}$$

has to be satisfied. Eq. (1.2.5) is general for phase spaces and can be proved without the notion of a Hamilton function (see f.e. *Evans and Morriss* (1990)). Nevertheless, as this thesis is only concerned with systems that can be described by a Hamilton function, the Liouville equation simplifies to

$$\frac{d\rho}{dt} = 0, \tag{1.2.6}$$

or

$$\frac{\partial \rho}{\partial t} = -\dot{\Gamma} \cdot \frac{\partial \rho}{\partial \Gamma}. \tag{1.2.7}$$

Eq. (1.2.6) is *the* fundamental equation of statistical mechanics and expresses the conservation of the ensemble density in time.

With the introduction of the Liouville-operator

$$i\mathcal{L}B(\Gamma, t) := \{B(\Gamma, t), \mathscr{H}\} = \dot{\Gamma} \cdot \frac{\partial B(\Gamma, t)}{\partial \Gamma}, \tag{1.2.8}$$

where $B(\Gamma, t)$ is an arbitrary real-valued function and $\{\cdot, \cdot\}$ denotes the Poisson bracket, eq. (1.2.7) can be written as

$$\frac{\partial \rho}{\partial t} = -i\mathcal{L}\rho. \tag{1.2.9}$$

If the Hamilton function doesn't include external fields which explicitly vary in time, eq. (1.2.9) can be formally solved by

$$\rho(\Gamma, t) = e^{-i\mathcal{L}t}\rho(\Gamma, 0), \tag{1.2.10}$$

where $\rho(\Gamma, 0)$ is the ensemble density at time 0 (or more commonly called the *initial distribution function*). Thus, the time evolution of the ensemble density can be derived from the initial distribution with the aid of the so-called ρ-Liouville propagator $e^{-i\mathcal{L}t}$.

1.2.4 State Space

Having defined the concept of phase space for microscopic states, we are now interested in a description for the macroscopic state. Therefore, one can introduce an m dimensional (macroscopic) state space (also called a-space in the literature), in which each macroscopic state of the

system (described by the macroscopic variables a_i) is represented by a point $a = (a_1, a_2, \ldots, a_m)$. Typical macroscopic variables are energy, pressure, magnetisation or the electric charge, but also the position or momentum of a massive Brownian particle.

As we are interested in deriving equations of motion for these macroscopic variables, a connection between the phase space and the state space description has to be made.

1.2.5 Connection between phase space and state space

This can be accomplished through phase functions $A_i(\Gamma) : \Phi \to \mathbb{R}$. A macroscopic variable a_i is then represented in phase space through the phase function $A_i(\Gamma)$ by $a_i = A_i(\Gamma)$. In general, one macroscopic state a in state space is associated with many microscopic states Γ in phase space. Accordingly, a hypersurface with $a = \text{const} = \mathrm{A}(\Gamma)$ in phase space corresponds to the point a in state space.

1.2.6 Choice of initial ensemble density

In sec. 1.2.3, we noted that the ensemble density function $\rho(\Gamma, t)$ for systems in non-equilibrium has to be chosen with care. Again, this is a non-trivial problem as there is no problem inherent choice for an ensemble density in non-equilibrium statistical mechanics. One simplification can be achieved by noting that there is no necessity for the whole ensemble density $\rho(\Gamma, t)$, but only for $\rho(\Gamma, 0)$, the initial ensemble density. This can be shown by evaluating the time evolution of an arbitrary phase space function $B(\Gamma)$, which is given by

$$\dot{B}(\Gamma) = \dot{\Gamma} \cdot \frac{\partial}{\partial \Gamma} B = i\mathcal{L}B(\Gamma). \tag{1.2.11}$$

The Liouville operator in eq. (1.2.11) is defined as before, and likewise the formal solution of this differential equation is given by

$$B(t) = e^{i\mathcal{L}t} B(0), \tag{1.2.12}$$

where for simplicity of notation, we wrote $B(t)$ for $B(\Gamma(t))$ and likewise for $B(0)$. The term $e^{i\mathcal{L}t}$ is called the p-Liouville propagator and is the adjoint of the ρ-Liouville propagator. Quite generally,

$$\int d\Gamma \ \rho(\Gamma, 0) i\mathcal{L}B(\Gamma) = -\int d\Gamma \ B(\Gamma) i\mathcal{L}\rho(\Gamma, 0), \tag{1.2.13}$$

so that the Liouville operator $\mathcal{L}$ is self-adjoint and $i\mathcal{L}$ anti-self-adjoint (a proof of this as well as of the next equation can be found f.e. in *Evans and Morriss* (1990)). Using these results, it

is possible to prove

$$\langle B(t)\rangle = \int d\Gamma\ \rho(\Gamma,0)B(t) = \int d\Gamma\ B(\Gamma)\rho(\Gamma,t), \tag{1.2.14}$$

i.e. either the phase function B or (exclusively) the ensemble density ρ is taken at time $t' = t$, where as the other function gets evaluated at time $t' = 0$.

This reduces the problem of finding an ensemble density $\rho(\Gamma, t)$ for all times t to finding an initial ensemble density $\rho(\Gamma, 0)$. In the literature, there are in principle two different approaches to the choice of the initial ensemble density: the experimental preparation and the maximum entropy principle (MaxENT). Both approaches require, that the mean values of the macroscopic variables as well as the constants of motion are known at time $t = 0$. As their results are the same, we will only discuss the experimental preparation.

Experimental preparation

The experimental preparation approach assumes an experimental setup, in which constant external fields h_i are applied to the system at time $t = -\infty$ and couple to the macroscopic variables through the phase functions A_i. The Hamilton function thus is $\mathscr{H}_{prep} = \mathscr{H} - \sum_i h_i A_i$. We assume that the system reaches equilibrium and then turn off the fields at time $t = 0$. As the system is at equilibrium, its initial ensemble density is

$$\rho(\Gamma, 0) = Z^{-1} e^{-\beta(\mathscr{H} - \sum_i h_i A_i)}, \tag{1.2.15}$$

where Z is the normalisation

$$Z = \int d\Gamma\ e^{-\beta(\mathscr{H} - \sum_i h_i A_i)}. \tag{1.2.16}$$

The elegance of this preparation procedure of a non-equilibrium ensemble density is due to its description as a real experiment. However, this also limits the physical cases we can inquire about, as the fields h_i have to be physically realisable. F.e. the preparation of spins of relevant variables through magnetic fields could be impossible without disturbing the spins of the irrelevant variables.

1.2.7 Macroscopic equations

In this thesis, we will be mainly concerned with the treatment of microscopic equations, which can be approximated to yield stochastic macroscopic equations. We will mainly concentrate on a specific subset of equations which resemble the Langevin (LE) or Fokker-Planck equation (FPE),

but are (apart from their exact nature) more general. Although neither the LE nor the FPE will be used, their definition is given in order to justify the later use of the term "generalised Langevin equation" or "generalised Fokker-Planck equation". For detailed derivations and treatments, see f.e. *Gardiner* (2009) or *van Kampen* (1992).

Definition 1. *The equation*

$$d\mathbf{x}(t) = \mathbf{A}[\mathbf{x}(t), t]dt + \mathbf{B}[\mathbf{x}(t), t]d\mathbf{W}(t), \tag{1.2.17}$$

where $\mathbf{x}(t)$ *is a stochastic process,* $\mathbf{A}[\mathbf{x}(t), t]$ *the drift and* $\mathbf{B}[\mathbf{x}(t), t]$ *the diffusion vector and* $\mathbf{W}(t)$ *a Wiener process, is called* ***Langevin equation****.*

In general, eq. (1.2.17) is a stochastic differential equation (SDE), which has to be treated according to a stochastic calculus. We mention

$$\left\langle \int_{t_0}^{t_1} \mathbf{B}[\mathbf{x}(t), t]d\mathbf{W}(t) \right\rangle = 0 \tag{1.2.18}$$

in Itō calculus. With the naive identification $d\mathbf{W}(t) = F(t)dt$, where $F(t)$ is called stochastic or random force, we require that its average vanishes, i.e. $\langle F(t) \rangle = 0$. The precise relationship between this expectation value interpreted as an ensemble average over initial conditions and its counterpart as an Itō noise expectation value in a Markov approximation of the corresponding generalised Langevin equation will not be discussed in this thesis. We will use the terms "Langevin equation" and "stochastic differential equation" interchangeably.

Definition 2. *Given a probability density* $p(x, t)$ *of a stochastic process* $X(t)$*, the* ***Fokker-Planck equation*** *(corresponding to an Itō LE) is defined as*

$$\frac{\partial p}{\partial t} = -\sum_i \partial_i \{A_i[\mathbf{x}(t), t]p\} + \frac{1}{2}\sum_{i,j} \partial_i \partial_j \{[B[\mathbf{x}(t), t]B^\intercal[\mathbf{x}(t), t]]_{ij}\, p\}, \tag{1.2.19}$$

where $A[\mathbf{x}(t), t]$ *is a drift and* $B[\mathbf{x}(t), t]$ *a diffusion vector.*

1.3 Projection Operators

One way of deriving macroscopic equations from microscopic ones is to use the method of projection operators. The physical system under consideration has to be split up in so called *relevant* and *irrelevant* variables. Relevant variables are all macroscopic variables we are interested in. In case of Brownian motion, the position and momentum of the massive Brownian particle or the probability density of them would be considered. For hydrodynamics, we would

choose the energy-, particle- and momentum-density etc. The choice of relevant variables for a given system is arbitrary and usually gets justified through experience (i.e. knowledge of phenomena, experiments, etc.). Having chosen those variables declares all other variables as irrelevant.

In the next step, a projection operator $\mathcal{P}$ has to be defined, which projects an arbitrary microscopic or macroscopic variable onto the relevant variables. Vice versa, the projection operator $(1 - \mathcal{P})$ projects on the irrelevant variables. In this way, the equations of motion for the relevant variables are decomposed in the sum of a relevant and an irrelevant part, and one tries to calculate or approximate the irrelevant part to get self-contained equations.

As a trivial example, one may be interested in the macroscopic probability density $p(x, v, t)$ of a massive Brownian particle with position x and velocity v in a heat bath of light particles j ($j \in \mathbb{N}$) with positions x_j and velocity v_j. The system may be described by the ensemble density $\rho(\Gamma, t)$. With the aid of a projection operator $\mathcal{P}$, we split the ensemble density according to

$$\rho(\Gamma, t) = \mathcal{P}\rho(\Gamma, t) + (1 - \mathcal{P})\rho(\Gamma, t). \tag{1.3.1}$$

As we are interested in $p(x, v, t)$ (i.e. this is our relevant "variable"), we define our projection operator acting on an arbitrary variable $X(\Gamma)$ by

$$\mathcal{P}X(\Gamma) := \int dx_1 \dots dx_N dv_1 \dots dv_N \; X(\Gamma)\rho(\Gamma, t). \tag{1.3.2}$$

Hence, the macroscopic probability density is given by

$$p(x, v, t) = \mathcal{P}\rho(\Gamma, t). \tag{1.3.3}$$

In general, equations like eq. (1.3.3) are still very hard to solve. In the past 50 years, physicists have therefore concentrated on deriving master-, generalised Langevin- or Fokker-Planck equations, in which the part stemming from irrelevant variables could be simplified through approximations. With the rise of computational power, the need for approximations is reduced, because the irrelevant parts can be calculated more directly.

1.4 Zwanzig's Generalised Langevin Equation

Zwanzig (1973) introduced a specific, but quite general formalism, with which he was able to derive an exact equation of motion by formally solving the equations of motion of a heat bath.

Although his derivation was even more general, we will apply it to Hamiltonian systems only. The Hamilton function had the formal structure

$$\mathscr{H}(X,Y) = \mathscr{H}_s(X) + \mathscr{H}_b(X,Y) = \mathscr{H}_S(X) + \frac{1}{2}\left[Y - a(X)\right]^\intercal \cdot K \cdot \left[Y - a(X)\right] \tag{1.4.1}$$

where X and Y are the system and heat bath coordinates, $\mathscr{H}_s(X)$ is the system and $\mathscr{H}_b(X,Y)$ the bath Hamiltonian, $a(X)$ an arbitrary function of the system variables and K a symmetric non-singular matrix. The equations of motion read

$$\frac{dX}{dt} = A \cdot \nabla_X(\mathscr{H}_s + \mathscr{H}_b), \tag{1.4.2a}$$

$$\frac{dY}{dt} = B \cdot \nabla_Y \mathscr{H}_b \tag{1.4.2b}$$

with A being the symplectic matrix

$$A = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}, \tag{1.4.3}$$

and B being also a constant anti-symmetric matrix.

The equation of motion for the system coordinates X after solving and reinserting the equation of motion for the heat bath coordinates is then

$$\frac{dX(t)}{dt} = V(X(t)) + \int_0^t dt'\ A \cdot W(X(t)) \cdot L(t') \cdot W^\intercal(X(t-t')) \cdot \dot{X}_{t-t'} + A \cdot W(X(t)) \cdot F(t), \tag{1.4.4}$$

where

$$V(X) = A \cdot \nabla_X \mathscr{H}_s(X), \tag{1.4.5a}$$

$$W(X) = \nabla_X a^\intercal(X), \tag{1.4.5b}$$

$$F(t) = -K \cdot e^{tB \cdot K} \cdot \left[Y(0) - a(X(0))\right], \tag{1.4.5c}$$

and L will be given below.

By choosing an equilibrium canonical ensemble for the heat bath of the form

$$\rho(X,Y) = \frac{1}{Z}\delta(X - X_0)e^{-\frac{\mathscr{H}_b}{kT}}, \tag{1.4.6}$$

where Z is the partition function such that $\int dX dY\ \rho(X,Y) = 1$, Zwanzig was able to derive the mean and auto-correlation of the noise as

$$\langle F(t) \rangle = 0, \tag{1.4.7a}$$

$$\langle F(t) F^\intercal(t') \rangle = kTL(t - t'), \tag{1.4.7b}$$

$$L(t) = K \cdot e^{tB \cdot K} \tag{1.4.7c}$$

where $L(t)$ is the friction coefficient and the average was taken over the ensemble as given in eq. (1.4.6). Equations of the form of eq. (1.4.4) are called generalised Langevin equations, because they resemble Langevin equations (see sec. 1.2.7), but are not necessarily of Markovian nature, i.e. they contain an integral term which integrates over the past history of the motion.

The specific form of the Zwanzig-GLEs eq. (1.4.4) for the macroscopic variables $\{x, v\}$ and the Hamilton function $\mathscr{H} = \frac{v^2}{2} + U(x) + \sum_i \left(\frac{p_i^2}{2} + \frac{k_i}{2} \left(q_i - f_i(x) \right)^2 \right)$ can be derived directly and gives

$$\frac{dx}{dt} = v(t), \tag{1.4.8a}$$

$$\begin{aligned} \frac{dv}{dt} = & -\frac{\partial U(x)}{\partial x} \\ & - \int_0^t ds \ \sum_j k_j \frac{\partial f_j(x(t-s))}{\partial x} \frac{\partial f_j(x(t))}{\partial x} \cos\left(\sqrt{k_j} s \right) v(t-s) \\ & + \sum_j \sqrt{k_j} \frac{\partial f_j(x(t))}{\partial x} p_j(0) \sin\left(\sqrt{k_j} t \right) \\ & + \sum_j k_j \frac{\partial f_j(x(t))}{\partial x} \left(q_j(0) - f_j(x(0)) \right) \cos\left(\sqrt{k_j} t \right). \end{aligned} \tag{1.4.8b}$$

Chapter 2

Mori-Projector

2.1 Introduction

Historically, Mori's generalised Langevin equations (GLE) were the first derived by the method of projection operators. They were introduced in *Mori* (1965) and were the starting point for other treatments of GLEs. Mori's formalism is mainly used in contexts where GLEs with a linear relation of the macroscopic variable are of interest. In recent years, the formalism also got attention from a mathematical point of view in optimal prediction theory (see f.e. *Chorin et al.* (2002)).

Following the work of *Zwanzig* (2001), we will derive the GLEs for an arbitrary vector A of macroscopic variables A_i. After the derivation, an example of Brownian motion, as given by *Zwanzig* (2001), will be considered in sec. 2.3.1 and following the comments in *Xing* (2009) enhanced by us. Finally, we will show explicitly in sec. 2.4, that Mori's equations are equivalent to Zwanzig's generalised Langevin equations in case of Zwanzig's heat bath model.

2.2 Derivation

Mori's formalism is based on non-equilibrium systems near the equilibrium. The initial ensemble density for this kind of systems can be given by an approximation of eq. (1.2.15), i.e.

$$\rho(\Gamma,0)=\frac{1}{Z}e^{-\beta(\mathscr{H}-\sum_i h_i\Delta A_i)}\approx\rho_{eq}(\Gamma)\left(1+\sum_i h_i\Delta A_i(\Gamma)+O(h^2)\right), \tag{2.2.1}$$

where $\rho_{eq}(\Gamma)$ denotes the canonical equilibrium ensemble density, and the variables $\Delta A_i(\Gamma)$ are the relevant variables. From here on, we will use the shorter notation B for every arbitrary variable $B(\Gamma)$ (which is a phase function at time $t = 0$), and we will write $B(t)$ to denote the same variable at time t (in the same way as in eq. (1.2.12)). We assume that the equilibrium average of the relevant variables always vanishes (i.e. we take "interesting" variables A_i and get the relevant variables through $\Delta A_i := A_i - \langle A_i \rangle_{eq}$). Their corresponding multipliers h_i are then known through the known averages at time $t = 0$,

$$\langle \Delta A_i \rangle = \sum_j \langle \Delta A_i \Delta A_j \rangle_{eq} h_j + O(h^2). \tag{2.2.2}$$

The projection operator $\mathcal{P}_M$, which was used by Mori to derive a generalised Langevin equation, is based on a scalar product. Therefore, we are not dealing with a phase space but a Hilbert space. Mori chose a Hilbert space $L^2(\Phi, \mu)$ with Φ being the phase space and μ being the measure defined by $d\mu(\Gamma) := \rho_{eq}(\Gamma) d\Gamma$. The scalar product of two elements B, C of the Hilbert space is defined by

$$(B, C) := \int_\Phi BC \rho_{eq}(\Gamma) d\Gamma. \tag{2.2.3}$$

and is identical to the equilibrium average, i.e.

$$(B, C) = \langle BC \rangle_{eq}. \tag{2.2.4}$$

Mori introduced the projection operator $\mathcal{P}_M$ acting on an arbitrary variable B through

$$\mathcal{P}_M B := (B, \Delta A) \cdot (\Delta A, \Delta A)^{-1} \cdot \Delta A, \tag{2.2.5}$$

where ΔA is a column vector of the macroscopic variables with m components, $(B, \Delta A)$ is a vector with the components $(B, \Delta A_i)$ $(1 \leq i \leq m)$ and $(\Delta A, \Delta A)^{-1}$ is an $m \times m$ normalisation matrix which is the inverse of the $m \times m$ matrix with the entries $(\Delta A, \Delta A)_{ij} = (\Delta A_i, \Delta A_j)$. $\mathcal{P}_M$ satisfies

$$\mathcal{P}_M \Delta A = \Delta A, \tag{2.2.6a}$$

$$\mathcal{P}_M \mathcal{P}_M B = \mathcal{P}_M B, \tag{2.2.6b}$$

$$(B, \mathcal{P}_M C) = (\mathcal{P}_M B, C), \tag{2.2.6c}$$

where ΔA is macroscopic variable and B, C are arbitrary elements of the Hilbert space. Property eq. (2.2.6a) follows directly from the definition eq. (2.2.5). Property eq. (2.2.6b), the

idempotence, can be seen as follows: The projection operator in eq. (2.2.5) can be explicitly written with components as

$$\mathcal{P}_M B = \sum_{j,k} (B, \Delta A_j) \left[(\Delta A, \Delta A)^{-1} \right]_{jk} \Delta A_k. \tag{2.2.7}$$

Thus, for $\mathcal{P}_M \mathcal{P}_M B$ follows

$$\begin{aligned}
\mathcal{P}_M \mathcal{P}_M B &= \sum_{l,m} (\mathcal{P}_M B, \Delta A_l) \left[(\Delta A, \Delta A)^{-1} \right]_{lm} \Delta A_m \\
&= \sum_{l,m} \sum_{j,k} (B, \Delta A_j) \left[(\Delta A, \Delta A)^{-1} \right]_{jk} \underbrace{(\Delta A_k, \Delta A_l)}_{(\Delta A, \Delta A)_{kl}} \left[(\Delta A, \Delta A)^{-1} \right]_{lm} \Delta A_m \\
&= \sum_{m} \sum_{j,k} (B, \Delta A_j) \left[(\Delta A, \Delta A)^{-1} \right]_{jk} \Delta A_m \underbrace{\sum_{l} (\Delta A, \Delta A)_{kl} \left[(\Delta A, \Delta A)^{-1} \right]_{lm}}_{=\delta_{km}} \\
&= \sum_{j,k} (B, \Delta A_j) \left[(\Delta A, \Delta A)^{-1} \right]_{jk} \Delta A_k \\
&= \mathcal{P}_M B.
\end{aligned} \tag{2.2.8}$$

The third property eq. (2.2.6c) follows from $(\Delta A, \Delta A)$ being a symmetric matrix.

$$\begin{aligned}
(B, \mathcal{P}_M C) &= (B, \sum_{j,k} (C, \Delta A_j) \left[(\Delta A, \Delta A)^{-1} \right]_{jk} \Delta A_k) \\
&= \sum_{j,k} (C, \Delta A_j) \left[(\Delta A, \Delta A)^{-1} \right]_{jk} (B, \Delta A_k) \\
&= \sum_{j,k} (B, \Delta A_k) \left[(\Delta A, \Delta A)^{-1} \right]_{kj} (C, \Delta A_j) \\
&= (\mathcal{P}_M B, C).
\end{aligned} \tag{2.2.9}$$

The operator $\mathcal{P}_M$ therefore satisfies the condition of idempotence and is thus a projection operator in the mathematical sense. It is the projection on the subspace of the relevant variables ΔA, i.e. the space spanned by the macroscopic variables ΔA_i.

Next, the Liouville operator will be separated into a relevant and irrelevant part

$$i\mathcal{L} = i\mathcal{P}_M \mathcal{L} + i(1 - \mathcal{P}_M)\mathcal{L}. \tag{2.2.10}$$

This allows to expand the propagator with the Dyson decomposition, i.e.

$$e^{i\mathcal{L}t} = e^{i(1-\mathcal{P}_M)\mathcal{L}t} + \int_0^t ds\ e^{i\mathcal{L}(t-s)} i\mathcal{P}_M \mathcal{L} e^{i(1-\mathcal{P}_M)\mathcal{L}s}, \tag{2.2.11}$$

and when operated on the quantity $i(1 - \mathcal{P}_M)\mathcal{L}\Delta A$, the generalised Langevin equation

$$\frac{\partial}{\partial t} \Delta A(t) = i\Omega \cdot \Delta A(t) - \int_0^t ds\ K(s) \cdot \Delta A(t - s) + F(t) \tag{2.2.12}$$

results with the following definitions

$$F(t) := e^{i(1-\mathcal{P}_M)\mathcal{L}t} i(1-\mathcal{P}_M)\mathcal{L}\Delta A, \tag{2.2.13a}$$

$$K(t) := -(i\mathcal{L}F(t), \Delta A)\cdot(\Delta A, \Delta A)^{-1}, \tag{2.2.13b}$$

$$i\Omega := (i\mathcal{L}\Delta A, \Delta A)\cdot(\Delta A, \Delta A)^{-1}. \tag{2.2.13c}$$

It still has to be shown that the average of $F(t)$ vanishes. With eq. (2.2.1), we get

$$\langle F(t)\rangle = \int d\Gamma\ F(t)\rho_{eq}(\Gamma)\left(1+\sum_i h_i\Delta A_i + O(h^2)\right). \tag{2.2.14}$$

We will firstly concern us with the first term in eq. (2.2.14), the equilibrium average of $F(t)$. As the equilibrium average of the generalised Langevin equation eq. (2.2.12) is

$$\frac{\partial}{\partial t}\langle\Delta A(t)\rangle_{eq} = i\Omega\cdot\langle\Delta A(t)\rangle_{eq} - \int_0^t ds\ K(s)\cdot\langle\Delta A(t-s)\rangle_{eq} + \langle F(t)\rangle_{eq}, \tag{2.2.15}$$

and $\langle\Delta A(t)\rangle_{eq} = \int d\Gamma\ \Delta A(t)\rho_{eq}(\Gamma,0) = \int d\Gamma\ \Delta A\rho_{eq}(\Gamma,t) = \langle\Delta A\rangle_{eq} = 0$, the equilibrium average of $F(t)$ has to vanish. The second term in eq. (2.2.14) is the sum of scalar products $h_i(F(t),\Delta A)$ and vanishes therefore too, because $F(t)$ and ΔA are orthogonal by construction (remember that $(F(t),\Delta A) = ((1-\mathcal{P}_M)F(t),\mathcal{P}_M\Delta A) = (\mathcal{P}_M(1-\mathcal{P}_M)F(t),\Delta A) = 0$). Hence, $\langle F(t)\rangle$ is of order h^2 and can be neglected for systems close to equilibrium.

An interesting feature can be extracted from the memory kernel eq. (2.2.13b), by exploiting the anti-Hermiticity of the Liouville operator $i\mathcal{L}$ and by inserting an additional, but redundant factor $(1-\mathcal{P}_M)$. We rewrite eq. (2.2.13b) as follows:

$$\begin{aligned} K(t) &= -(i\mathcal{L}F(t),\Delta A)\cdot(\Delta A,\Delta A)^{-1} \\ &= (F(t), i\mathcal{L}\Delta A)\cdot(\Delta A,\Delta A)^{-1} \\ &= ((1-\mathcal{P}_M)F(t), i\mathcal{L}\Delta A)\cdot(\Delta A,\Delta A)^{-1} \\ &= (F(t), \underbrace{(1-\mathcal{P}_M)i\mathcal{L}\Delta A}_{=F(0)})\cdot(\Delta A,\Delta A)^{-1}. \end{aligned} \tag{2.2.16}$$

Eq. (2.2.16) is a generalised fluctuation-dissipation theorem, i.e. rewritten in averages, it is

$$\langle F(0)F(t)\rangle_{eq} = K(t)\cdot\langle\Delta A\Delta A\rangle_{eq}. \tag{2.2.17}$$

2.3 Examples

This subsection will examine a particular example to compare the generalised Langevin equations of Mori with those of Zwanzig. The elaboration in sec. 2.3.1 is due to *Zwanzig* (1980)

and *Zwanzig* (2001), whereas the calculations in sec. 2.3.2 were hinted at in *Xing* (2009), but explicitly calculated by us.

2.3.1 Linear macroscopic variables

The Mori GLEs for the macroscopic (relevant) variables $\{x, v\}$ of the total system with Hamiltonian

$$\mathscr{H} = \frac{v^2}{2} + \frac{x^2}{2} + b\frac{x^4}{4} + \sum_j \left\{ \frac{p_j^2}{2} + \frac{1}{2}\omega_j^2 \left(q_j - \frac{\gamma_j}{\omega_j^2} x \right)^2 \right\} \tag{2.3.1}$$

should be calculated and compared to the Zwanzig GLEs. The Zwanzig GLEs are known from eq. (1.4.8) with the special choice of $f_i(x) = \frac{\gamma_i}{\omega_i^2} x$ and are therefore

$$\frac{dx(t)}{dt} = v(t), \tag{2.3.2a}$$

$$\frac{dv(t)}{dt} = -x(t) - bx(t)^3 - \int_0^t ds\ K_Z(s) v(t-s) + F_Z(t) \tag{2.3.2b}$$

with

$$K_Z(t) = \sum_j \frac{\gamma_j^2}{\omega_j^2} \cos(\omega_j t), \tag{2.3.3a}$$

$$F_Z(t) = \sum_j \gamma_j p_j(0) \frac{\sin(\omega_j t)}{\omega_j} + \sum_j \gamma_j \left(q_j(0) - \frac{\gamma_j}{\omega_j^2} x(0) \right) \cos(\omega_j t). \tag{2.3.3b}$$

In the Mori formalism, the choice of $\{x, v\}$ as the macroscopic variables yields the explicit projection operator

$$\mathcal{P}_M B = \langle Bx \rangle_{eq} \langle xx \rangle_{eq}^{-1} x + \langle Bv \rangle_{eq} \langle vv \rangle_{eq}^{-1} v. \tag{2.3.4}$$

The equilibrium second moments in eq. (2.3.4) are

$$\left\langle x^2 \right\rangle_{eq} = \frac{kT}{\omega_0^2}, \tag{2.3.5a}$$

$$\left\langle v^2 \right\rangle_{eq} = kT, \tag{2.3.5b}$$

which defines ω_0. As we are only interested in the dynamics for very small values of b, ω_0^2 can be expanded to second order by first noting that

$$e^{-\frac{b\beta}{4}x^4} \approx 1 - \frac{b\beta}{4} x^4 \tag{2.3.6}$$

as well as using the fact that $b \ll \beta$ due to the smallness of the Boltzmann constant k. Therefore, we can approximate $\langle x^2 \rangle$ with

$$\begin{aligned}
\langle x^2 \rangle_{eq} &= \frac{1}{Z} \int dx\ e^{-\beta\left(\frac{x^2}{2} + b\frac{x^4}{4}\right)} x^2 \\
&\approx \frac{1}{Z} \int dx\ e^{-\beta\frac{x^2}{2}} \left(1 - \frac{b\beta}{4} x^4\right) x^2 \\
&\approx \frac{1}{Z} \left(\int dx\ e^{-\beta\frac{x^2}{2}} x^2 - \frac{b\beta}{4} \int dx\ e^{-\beta\frac{x^2}{2}} x^6 \right) \\
&\approx \frac{1}{Z} \frac{\sqrt{2\pi}}{\beta^{3/2}} \left(1 - \frac{15}{4} b \frac{1}{\beta}\right),
\end{aligned} \tag{2.3.7}$$

where we have omitted the noncontributing integrations over the other variables. The normalisation Z can be calculated in the same way to give

$$Z \approx \frac{\sqrt{2\pi}}{\beta^{1/2}} \left(1 - \frac{3}{4} b \frac{1}{\beta}\right). \tag{2.3.8}$$

Hence,

$$\omega_0^2 = \frac{kT}{\langle x^2 \rangle} \approx \frac{1}{1 - \frac{12b}{4\beta - 3b}} \approx 1 + \frac{12b}{4\beta - 3b} \approx 1 + \frac{12b}{4\beta} = 1 + 3bkT + O(b^2). \tag{2.3.9}$$

Mori's procedure leads to the exact linear Langevin equations

$$\frac{dx(t)}{dt} = v(t) \tag{2.3.10a}$$

$$\frac{dv(t)}{dt} = -\omega_0^2 x(t) - \int_0^t ds\ K_M(s) v(t-s) + F_M(t), \tag{2.3.10b}$$

in which the random force is given by

$$F_M(t) = e^{it(1-\mathcal{P}_M)\mathcal{L}} i(1 - \mathcal{P}_M)\mathcal{L} v, \tag{2.3.11}$$

and the memory function is

$$\langle F_M(0) F_M(t) \rangle_{eq} = kT K_M(t). \tag{2.3.12}$$

In order to compare the exact terms of the random force and the memory function eq. (2.3.3) with the results of Mori's procedure, the operator expression for F_M in eq. (2.3.11) has to be evaluated. For this, the Liouville operator $i\mathcal{L}$ is separated into a linear part $i\mathcal{L}_0$ and a perturbation $i\mathcal{L}_1$,

$$i\mathcal{L} = i\mathcal{L}_0 + i\mathcal{L}_1, \tag{2.3.13a}$$

$$i\mathcal{L}_1 = -bx^3 \frac{\partial}{\partial v}. \tag{2.3.13b}$$

It is now possible to separate the orthogonal projection $(1-\mathcal{P}_M)\mathcal{L}v$ in eq. (2.3.11) in two parts,

$$i(1-\mathcal{P}_M)\mathcal{L}v = \sum_j \gamma_j \left(q_j - \frac{\gamma_j}{\omega_j^2} x \right) + \left[(\omega_0^2 - 1)x - bx^3 \right]. \tag{2.3.14}$$

The factor $(\omega_0^2 - 1)x$ results from the evaluation of $b\left\langle x^4 \right\rangle \cdot \left\langle xx \right\rangle^{-1} x$ with the following useful relations

$$\begin{aligned} (i\mathcal{L}v, x^n) &= -\left\langle x^{n+1} \right\rangle_{eq} - b\left\langle x^{n+3} \right\rangle_{eq} + \sum_j \gamma_j \left\langle x^n \left(\frac{\gamma_j}{\omega_j^2} x - q_j \right) \right\rangle_{eq} \\ &= -\left\langle x^{n+1} \right\rangle_{eq} - b\left\langle x^{n+3} \right\rangle_{eq}, \end{aligned} \tag{2.3.15}$$

and

$$\begin{aligned} (i\mathcal{L}v, x^n) &= -\frac{1}{Z}\int d\Gamma\ x^n \frac{\partial \mathscr{H}}{\partial x} e^{-\beta\mathscr{H}} = \frac{kT}{Z}\int d\Gamma\ x^n \frac{\partial}{\partial x} e^{-\beta\mathscr{H}} = \\ &= -\frac{kT}{Z} n \int d\Gamma\ x^{n-1} e^{-\beta\mathscr{H}} = -nkT\left\langle x^{n-1} \right\rangle_{eq}. \end{aligned} \tag{2.3.16}$$

Equating eqs. (2.3.15) and (2.3.16) results in the general equation

$$nkT\left\langle x^{n-1} \right\rangle_{eq} = \left\langle x^{n+1} \right\rangle_{eq} + b\left\langle x^{n+3} \right\rangle_{eq}. \tag{2.3.17}$$

Setting $n = 1$ gives the aforementioned result.

Using eq. (2.3.9), eq. (2.3.14) is to the first order in b

$$i(1-\mathcal{P}_M)\mathcal{L}v = \sum_j \gamma_j \left(q_j - \frac{\gamma_j}{\omega_j^2} x \right) + \left[b(3kTx - x^3) + O(b^2) \right]. \tag{2.3.18}$$

Due to the separation of the Liouville operator into two parts, the propagator appearing in eq. (2.3.11) can be (recursively) expanded by using the Dyson decomposition, yielding

$$e^{it(1-\mathcal{P}_M)\mathcal{L}} = e^{it(1-\mathcal{P}_M)\mathcal{L}_0} + \int_0^t ds\ e^{i(t-s)(1-\mathcal{P}_M)\mathcal{L}_0} i(1-\mathcal{P}_M)\mathcal{L}_1 e^{is(1-\mathcal{P}_M)\mathcal{L}_0} + \cdots. \tag{2.3.19}$$

Thus, Eq. (2.3.11) can now be written as

$$\begin{aligned} F_M(t) =& e^{it(1-\mathcal{P}_M)\mathcal{L}_0} \sum \gamma_j \left(q_j - \frac{\gamma_j}{\omega_j^2} x \right) + e^{it(1-\mathcal{P}_M)\mathcal{L}_0} \left[(\omega_0^2 - 1)x - bx^3 \right] \\ &+ \int_0^t ds\ e^{i(t-s)(1-\mathcal{P}_M)\mathcal{L}_0} i(1-\mathcal{P}_M)\mathcal{L}_1 e^{is(1-\mathcal{P}_M)\mathcal{L}_0} \sum_j \gamma_j \left(q_j - \frac{\gamma_j}{\omega_j^2} x \right). \end{aligned} \tag{2.3.20}$$

The first term, from now on called $F_0(t)$, can be evaluated by noticing that $i\mathcal{L}_0$ operated any linear combination of the variables $\{x, v, q_j, p_j\}$ yields another linear combination and the

orthogonal projection $(1 - \mathcal{P}_M)$ doesn't alter it. By choosing the ansatz

$$F_0(t) = \rho(t)x + \sigma(t)v + \sum_j \mu_j(t)q_j + \sum_j \nu_j(t)p_j, \tag{2.3.21}$$

we will try to solve the differential equation

$$\frac{\partial}{\partial t}F_0(t) = i(1 - \mathcal{P}_M)\mathcal{L}_0 F_0(t), \tag{2.3.22}$$

which was obtained by deriving $F_0(t)$ with respect to t. By substituting our ansatz eq. (2.3.21) on both sides of eq. (2.3.22), we can determine the following differential equations by equating the coefficients, i.e.

$$\dot{\sigma}(t) = 0, \tag{2.3.23a}$$

$$\dot{\rho}(t) = -\sigma(t)\sum_j \frac{\gamma_j^2}{\omega_j^2} + \sum_j \nu_j(t)\gamma_j, \tag{2.3.23b}$$

$$\dot{\nu_j}(t) = \mu_j(t), \tag{2.3.23c}$$

$$\dot{\mu_j}(t) = \sigma(t)\gamma_j - \omega_j^2\nu_j(t), \tag{2.3.23d}$$

with the initial values

$$\sigma(0) = \nu_j(0) = 0, \tag{2.3.24a}$$

$$\mu_j(0) = \gamma_j, \tag{2.3.24b}$$

$$\rho(0) = -\sum_j \frac{\gamma_j^2}{\omega_j^2}. \tag{2.3.24c}$$

The differential equations for μ_j and ρ_j in eqs. (2.3.23) can be solved directly and yield

$$\mu_j(t) = \cos(\omega_j t)\,\gamma_j, \tag{2.3.25a}$$

$$\nu_j(t) = \frac{\sin(\omega_j t)}{\omega_j}\gamma_j. \tag{2.3.25b}$$

Supplemented in the differential equation for $\rho(t)$ and further solving it, we get

$$\rho(t) = -\sum_j \frac{\gamma_j^2}{\omega_j^2}\cos(\omega_j t), \tag{2.3.26}$$

which can be used to get an expression for $F_0(t)$, namely

$$F_0(t) = \sum_j \gamma_j p_j \frac{\sin(\omega_j t)}{\omega_j} + \sum_j \gamma_j \left(q_j - \frac{\gamma_j}{\omega_j^2}x\right)\cos(\omega_j t) = F_Z(t). \tag{2.3.27}$$

The third term in eq. (2.3.20) can be written as

$$\int_0^t ds\ e^{i(t-s)(1-\mathcal{P}_M)\mathcal{L}_0} i(1-\mathcal{P}_M)\mathcal{L}_1 F_0(s) \tag{2.3.28}$$

and vanishes, because $F_0(s)$ is independent of v. The second term in eq. (2.3.20) is

$$F_1(t) = be^{it(1-\mathcal{P}_M)\mathcal{L}_0}(3kTx - x^3) + O(b^2) \tag{2.3.29}$$

and can be simplified by noticing that in the related differential equation

$$\frac{\partial}{\partial t}F_1 = i(1-\mathcal{P}_M)\mathcal{L}_0 F_1 \tag{2.3.30}$$

the projection $i\mathcal{P}_M\mathcal{L}_0 F_1$ vanishes. Therefore,

$$F_1(t) = be^{it\mathcal{L}_0}(3kTx - x^3) + O(b^2), \tag{2.3.31}$$

and the total random force term is given by

$$F_M(t) = F_Z(t) + be^{it\mathcal{L}_0}(3kTx - x^3) + O(b^2). \tag{2.3.32}$$

Due to the FDT eq. (2.2.17), this also gives us the memory kernel

$$K_M(t) = K_Z(t) + \frac{b^2}{kT}\left\langle (3kTx - x^3)e^{it\mathcal{L}_0}(3kTx - x^3)\right\rangle_{eq} + O(b^2). \tag{2.3.33}$$

We conclude that Mori's GLEs for the choice of the relevant variables x, v, though exact, appear differently than Zwanzig's GLEs. That they are in fact equal can't be easily seen due to the structure of the random force and memory kernel term. Only at $t = 0$, the equivalence is obvious.

2.3.2 Nonlinear macroscopic variables

The Mori procedure of the last section will be repeated, but this time, x^3 will be included in the choice of macroscopic variables. This is a reasonable choice as it was shown in eq. (2.3.29) that a correction term of x^3 occurs in the random force as well as in the memory kernel. Without knowledge of the exact form of $F_M(t)$, the intuitive choice would be x^2, but because of

$$(i\mathcal{L}v, x^{2n}) = \frac{1}{Z}\int d\Gamma\ \left(-x - bx^3 - \sum_i \gamma_i\left(\frac{\gamma_i}{\omega_i^2}x - q_i\right)\right)\cdot x^{2n}e^{-\beta\mathscr{H}} = 0, \tag{2.3.34}$$

all even powers of x don't contribute to the GLE of v. The integral in eq. (2.3.34) can be easily evaluated by taking advantage of symmetry properties of the functions in the product, f.e. x^{2n+1}

is an odd function whereas $e^{-\beta\mathscr{H}}$ is an even function. Another also very helpful property is time-reversal symmetry and parity, with which many scalar products can be evaluated without solving the integral directly. A well written account of symmetry considerations in the context of Mori's formalism can be found in *Berne* (1976).

Therefore, we will first evaluate Mori's procedure for $\Delta A = (x, v, x^3)$ and afterwards, the contributions of x^5,x^7,... will be considered. The new structure of the Mori projection operator $\mathcal{P}_M$ has to be established. The factors in eq. (2.2.5) have to be calculated. The normalisation matrix in the new variables is

$$(\Delta A, \Delta A)^{-1} = \begin{pmatrix} \frac{\langle x^6\rangle_{eq}}{d} & 0 & -\frac{\langle x^4\rangle_{eq}}{d} \\ 0 & \langle v^2\rangle_{eq}^{-1} & 0 \\ -\frac{\langle x^4\rangle_{eq}}{d} & 0 & \frac{\langle x^2\rangle_{eq}}{d} \end{pmatrix}, \tag{2.3.35}$$

where $d := \langle x^2\rangle_{eq}\langle x^6\rangle_{eq} - \langle x^4\rangle_{eq}^2$. Thus, the Mori projection operator can be written as

$$\begin{aligned} \mathcal{P}_M B = \; & (B, x^3)\cdot\langle x^4\rangle_{eq}^{-1}\cdot x + (B, v)\cdot\langle v^2\rangle_{eq}^{-1}\cdot v \\ & + \left[(B, x)\cdot\langle x^4\rangle_{eq}^{-1} - (B, x^3)\cdot\langle x^2\rangle_{eq}\langle x^4\rangle_{eq}^{-2}\right]\cdot x^3 \end{aligned} \tag{2.3.36}$$

With the matrix of scalar products

$$(i\mathcal{L}\Delta A, \Delta A) = \begin{pmatrix} 0 & kT & 0 \\ -\langle x^2\rangle_{eq} - b\langle x^4\rangle_{eq} & 0 & -\langle x^4\rangle_{eq} - b\langle x^6\rangle_{eq} \\ 0 & 3kT\langle x^2\rangle_{eq} & 0 \end{pmatrix}, \tag{2.3.37}$$

we get for the frequency term

$$i\Omega = (i\mathcal{L}\Delta A, \Delta A)\cdot(\Delta A, \Delta A)^{-1} = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & -b \\ 0 & \frac{3kT}{\omega_0^2} & 0 \end{pmatrix} \tag{2.3.38}$$

and therefore for the linear term of the Mori GLE

$$i\Omega\cdot\Delta A(t) = \begin{pmatrix} v(t) \\ -x(t) - bx^3(t) \\ \frac{3kT}{\omega_0^2}v(t) \end{pmatrix}. \tag{2.3.39}$$

Next, the random force term $F(t)$ has to be calculated. We do so component-by-component and have a look at the first (i.e. the random force term in the equation for $\frac{dx}{dt}$) component of

$F(t)$. As $i\mathcal{L}x = v$, $i(1-\mathcal{P}_M)\mathcal{L}v = 0$, and the equation for $\frac{dx}{dt}$ contains neither a random force nor a memory term. The second component of $F(t)$ contains the same $i\mathcal{L}v$ terms as in the linear case, but because x^3 is included in the set of macroscopic variables, the bx^3 term gets projected onto itself and we therefore get

$$i(1-\mathcal{P}_M)\mathcal{L}v = \sum_j \gamma_j \left(q_j - \frac{\gamma_j}{\omega_j^2} x \right), \tag{2.3.40}$$

which further results in exactly $F_Z(t)$. The third component is straightforward $e^{i(1-\mathcal{P}_M)\mathcal{L}t}\big(3x^2 v - 3\left\langle x^2 \right\rangle_{eq} v\big)$ and will not be further evaluated. To summarise, the random force term is given by

$$F(t) = \begin{pmatrix} 0 \\ F_Z(t) \\ e^{i(1-\mathcal{P}_M)\mathcal{L}t}\left(3x^2 v - 3\left\langle x^2 \right\rangle_{eq} v\right) \end{pmatrix}, \tag{2.3.41}$$

and we can conclude, that the random force term $F_Z(t)$ in the GLE for v is the same as in Zwanzig's GLE eq. (2.3.2b), and due to the FDT, the same holds for the memory kernel. Therefore, Zwanzig's and Mori's GLEs for x and v are equivalent for a Hamiltonian system as defined in eq. (2.3.1) in the vicinity of the equilibrium (small h in eq. (2.2.1)). However, we haven't been able to show the equality of Mori's equation for x^3 with the usual phase space identity $\frac{dx^3}{dt} = 3x^2(t)\frac{dx}{dt}$, though it should be possible due to the exactness of the procedure.

Additional powers of x

With the successful addition of x^3 to the macroscopic variables, one could be tempted to add higher (odd) powers of x for further simplifications of the random force term and the memory kernel in the equation for v. However, we will prove the following theorem (note the different order of macroscopic variables in the vector A):

Theorem 1. *Let $\mathscr{H}$ be defined as above and let ΔA be a $(N \times 1)$ dimensional vector with $N \geq 4$ defined by $\Delta A = (v, x, x^3, x^5, x^7, ...)^\intercal$ in which the order or specific occurrence of odd powers n $(n \geq 4)$ of x doesn't matter. Then the first component of the linear term $i\Omega \cdot A$ of the Mori GLE is identically equal to $-x - bx^3$.*

If one is thus interested in the equations of motion for x and v only, it is only necessary to compute the Mori GLE for $\Delta A = (v, x, x^3)^\intercal$.

Proof. We have to show that $(i\Omega)_{1j}$ vanishes for $j \geq 4$, i.e.

$$(i\Omega)_{1j} = \left[(i\mathcal{L}\Delta A, \Delta A) \cdot (\Delta A, \Delta A)^{-1}\right]_{1j} = 0 \quad \text{for j} \geq 4. \tag{2.3.42}$$

In its most general form, we will write for $(i\mathcal{L}\Delta A, \Delta A)$

$$(i\mathcal{L}\Delta A, \Delta A) = \begin{pmatrix} (i\mathcal{L}v, v) & (i\mathcal{L}v, x) & (i\mathcal{L}v, x^3) & (i\mathcal{L}v, x^5) & \cdots \\ (i\mathcal{L}x, v) & (i\mathcal{L}x, x) & (i\mathcal{L}x, x^3) & (i\mathcal{L}x, x^5) & \cdots \\ (i\mathcal{L}x^3, v) & (i\mathcal{L}x^3, x) & (i\mathcal{L}x^3, x^3) & (i\mathcal{L}x^3, x^5) & \cdots \\ (i\mathcal{L}x^5, v) & (i\mathcal{L}x^5, x) & (i\mathcal{L}x^5, x^3) & (i\mathcal{L}x^5, x^5) & \cdots \\ & & \cdots & & \end{pmatrix}. \tag{2.3.43}$$

As we are only interested in the first row, we notice that

$$i\mathcal{L}v = -x - bx^3 + \sum_j \gamma_j \left(q_j - \frac{\gamma_j}{\omega_j^2} x\right) \tag{2.3.44}$$

and therefore

$$(i\mathcal{L}v, v) = 0, \qquad (i\mathcal{L}v, x^n) = -\left\langle x^{2n}\right\rangle_{eq} - b\left\langle x^{2(n+1)}\right\rangle_{eq} \qquad (n = 1, 2, ...). \tag{2.3.45}$$

Thus the first row of $(i\mathcal{L}\Delta A, \Delta A)$ is

$$(i\mathcal{L}\Delta A, \Delta A)_1 = \left(0, -\left\langle x^2\right\rangle_{eq} - b\left\langle x^4\right\rangle_{eq}, -\left\langle x^4\right\rangle_{eq} - b\left\langle x^6\right\rangle_{eq}, \ldots\right). \tag{2.3.46}$$

The inverse of the normalisation matrix $(\Delta A, \Delta A)^{-1}$ is in general

$$(\Delta A, \Delta A) = \begin{pmatrix} \left\langle v^2\right\rangle_{eq} & 0 & 0 & 0 & \cdots \\ 0 & \left\langle x^2\right\rangle_{eq} & \left\langle x^4\right\rangle_{eq} & \left\langle x^6\right\rangle_{eq} & \cdots \\ 0 & \left\langle x^4\right\rangle_{eq} & \left\langle x^6\right\rangle_{eq} & \left\langle x^8\right\rangle_{eq} & \cdots \\ 0 & \left\langle x^6\right\rangle_{eq} & \left\langle x^8\right\rangle_{eq} & \left\langle x^{10}\right\rangle_{eq} & \cdots \\ & & \cdots & & \end{pmatrix}. \tag{2.3.47}$$

Eq. (2.3.42) describes the scalar product of the first row of $(i\mathcal{L}\Delta A, \Delta A)$ with the j$^{\text{th}}$ column vector of the normalisation matrix. For expressing the j$^{\text{th}}$ column vector of the normalisation matrix, we will use the cofactor description, i.e. let $C = (\Delta A, \Delta A)$, then the cofactor matrix is defined by $C \cdot C^{\#} = C^{\#} \cdot C = \det(\mathrm{C}) \cdot \mathbb{1}$ (hence $\frac{1}{\det(\mathrm{C})} C^{\#} = C^{-1} = (\Delta A, \Delta A)^{-1}$), and the j$^{\text{th}}$ column vector of $C^{\#}$ is thus given by

$$\mathbf{a_j^{\#}} := \sum_i (-1)^{i+j} \det(\mathrm{C_{ji}}) \mathbf{e_i} \tag{2.3.48}$$

where C_{ji} denotes the Matrix C with removed row j and removed column i. Therefore,

$$(i\mathcal{L}\Delta A, \Delta A)_1 \cdot \mathbf{a_j^{\#}} = \sum_i^N (-1)^{i+5} \mathrm{det}(\mathrm{C_{ji}}) \left(1 - \delta_{\mathrm{i1}}\right) \left(\left\langle \mathrm{x}^{2(\mathrm{i}-1)} \right\rangle_{\mathrm{eq}} + \mathrm{b} \left\langle \mathrm{x}^{2\mathrm{i}} \right\rangle_{\mathrm{eq}} \right), \tag{2.3.49}$$

where δ_{ij} is the Kronecker delta. By examining $\mathrm{det}(\mathrm{C_{ji}})$ we note, that for the relevant terms, the simple Laplace expansion in the first row is always possible with the factor $\left\langle v^2 \right\rangle_{eq}$ in front of the reduced determinant. The additional factor $\left\langle x^{2(i-1)} \right\rangle_{eq} + b \left\langle x^{2i} \right\rangle_{eq}$ can be integrated into the determinant, which results f.e. for the summand with C_{42} in

$$\left\langle v^2 \right\rangle \begin{vmatrix} \left\langle x^2 \right\rangle_{eq} + b \left\langle x^4 \right\rangle_{eq} & 0 & 0 & \cdots \\ 0 & \left\langle x^4 \right\rangle_{eq} & \left\langle x^6 \right\rangle_{eq} & \cdots \\ 0 & \left\langle x^6 \right\rangle_{eq} & \left\langle x^8 \right\rangle_{eq} & \cdots \\ 0 & \left\langle x^{10} \right\rangle_{eq} & \left\langle x^{12} \right\rangle_{eq} & \cdots \\ \vdots & \vdots & \vdots & \vdots \end{vmatrix}. \tag{2.3.50}$$

As one notices easily, changing the determinant in eq. (2.3.50) to

$$\left\langle v^2 \right\rangle_{eq} \begin{vmatrix} \left\langle x^2 \right\rangle_{eq} + b \left\langle x^4 \right\rangle_{eq} & 0 & 0 & \cdots \\ \left\langle x^2 \right\rangle_{eq} & \left\langle x^4 \right\rangle_{eq} & \left\langle x^6 \right\rangle_{eq} & \cdots \\ \left\langle x^4 \right\rangle_{eq} & \left\langle x^6 \right\rangle_{eq} & \left\langle x^8 \right\rangle_{eq} & \cdots \\ \left\langle x^8 \right\rangle_{eq} & \left\langle x^{10} \right\rangle_{eq} & \left\langle x^{12} \right\rangle_{eq} & \cdots \\ \vdots & \vdots & \vdots & \vdots \end{vmatrix} \tag{2.3.51}$$

doesn't change its value. Likewise, the summand with C_{43} can be expressed as

$$\left\langle v^2 \right\rangle_{eq} \begin{vmatrix} 0 & \left\langle x^4 \right\rangle_{eq} + b \left\langle x^6 \right\rangle_{eq} & 0 & \cdots \\ \left\langle x^2 \right\rangle_{eq} & \left\langle x^4 \right\rangle_{eq} & \left\langle x^6 \right\rangle_{eq} & \cdots \\ \left\langle x^4 \right\rangle_{eq} & \left\langle x^6 \right\rangle_{eq} & \left\langle x^8 \right\rangle_{eq} & \cdots \\ \left\langle x^8 \right\rangle_{eq} & \left\langle x^{10} \right\rangle_{eq} & \left\langle x^{12} \right\rangle_{eq} & \cdots \\ \vdots & \vdots & \vdots & \vdots \end{vmatrix}. \tag{2.3.52}$$

The same can be done for every C_{ji} with $(i \geq 2, j \geq 4)$. By applying the basic rule of

summation of determinants, it is thus possible to express the sum in eq. (2.3.49) as

$$
\begin{aligned}
(i\mathcal{L}\Delta A, \Delta A)_1 \cdot a_j^{\#} = \langle v^2 \rangle_{eq} &\begin{vmatrix} \langle x^2 \rangle_{eq} + b \langle x^4 \rangle_{eq} & \langle x^4 \rangle_{eq} + b \langle x^6 \rangle_{eq} & \langle x^6 \rangle_{eq} + b \langle x^8 \rangle_{eq} & \cdots \\ \langle x^2 \rangle_{eq} & \langle x^4 \rangle_{eq} & \langle x^6 \rangle_{eq} & \cdots \\ \langle x^4 \rangle_{eq} & \langle x^6 \rangle_{eq} & \langle x^8 \rangle_{eq} & \cdots \\ \vdots & \vdots & \vdots & \vdots \end{vmatrix} \\
= \langle v^2 \rangle_{eq} &\begin{vmatrix} \langle x^2 \rangle_{eq} & \langle x^4 \rangle_{eq} & \langle x^6 \rangle_{eq} & \cdots \\ \langle x^2 \rangle_{eq} & \langle x^4 \rangle_{eq} & \langle x^6 \rangle_{eq} & \cdots \\ \langle x^4 \rangle_{eq} & \langle x^6 \rangle_{eq} & \langle x^8 \rangle_{eq} & \cdots \\ \vdots & \vdots & \vdots & \vdots \end{vmatrix} \\
+ b^N \langle v^2 \rangle_{eq} &\begin{vmatrix} \langle x^4 \rangle_{eq} & \langle x^6 \rangle_{eq} & \langle x^8 \rangle_{eq} & \cdots \\ \langle x^2 \rangle_{eq} & \langle x^4 \rangle_{eq} & \langle x^6 \rangle_{eq} & \cdots \\ \langle x^4 \rangle_{eq} & \langle x^6 \rangle_{eq} & \langle x^8 \rangle_{eq} & \cdots \\ \vdots & \vdots & \vdots & \vdots \end{vmatrix},
\end{aligned}
\tag{2.3.53}
$$

and as both determinants contain linearly dependent rows, they are identically zero, which concludes the proof.

□

2.4 Equivalence of Mori-formalism and Zwanzig GLE

In this section, we will prove the general equivalence of Mori's procedure and Zwanzig's GLE near equilibrium for Zwanzig's Hamilton function

$$
\mathscr{H} = \frac{v^2}{2} + U(x) + \sum_i \left(\frac{p_i^2}{2} + \frac{k_i}{2} \left(q_i - f_i(x) \right)^2 \right). \tag{2.4.1}
$$

Two peculiarities may be noticed in the preceding examples.

1. The random force term eq. (2.3.29) contains $3kTx - x^3$, which is (except for the factor β^3) the fourth Hermite polynomial defined by the weight function $e^{-\beta \frac{x^2}{2}}$.

2. The resulting GLE for v has no one-to-one correspondence to the choice of the macrovariables. In particular, the choice of $\{x + bx^3, v\}$ results also in Zwanzig's GLE for v, which

Order	Generalised Hermite Polynomial
0	1
1	βx
2	$-\beta + \beta^2 x$
3	$-\beta^3 \left(3kTx - x^3\right)$

Table 2.1: Generalised Hermite Polynomials for weight function $e^{-\beta \frac{x^2}{2}}$

can be shown by following exactly the procedure of the example given in sec. 2.3.2.

The last peculiarity is also connected to Hermite polynomials and gives thus also rise to investigate them in the context of the Mori formalism. We therefore define the generalised Hermite polynomials as follows.

Definition 3. *The n^{th} ($n \in \mathbb{N}$) generalised Hermite polynomial in the microscopic variable x is the polynomial generated by the Rodrigues' formula*

$$He_n(x) := e^{\beta \mathscr{H}_s(x,v)} (-1)^n \left(\frac{\partial^n}{\partial x^n} e^{-\beta \mathscr{H}_s(x,v)} \right) \tag{2.4.2}$$

Generalised Hermite polynomials for the other variables of the Hamilton function eq. (2.4.1) are defined likewise, but they will be omitted here for the sake of simplicity. We can form an orthogonal basis of the Hilbert space by taking many variable Hermite polynomials (defined by the tensor product of the Hermite polynomials of the different microscopic variables), and we notice that they arise naturally as they are orthogonal with respect to the weight function $e^{-\beta \mathscr{H}}$, i.e. the same we are already using in our inner products.

Hence if we choose the proper generalised Hermite polynomial as a macroscopic variable, we can dramatically simplify the calculations of the random force and memory term, as they contain orthogonal projections of quantities containing the Liouville operator, which – nolens volens – has to contain a generalised Hermite polynomial itself. The following theorem and proof should elucidate the former statement.

Theorem 2. *Near equilibrium, Mori's procedure and Zwanzig's formalism yield the same generalised Langevin equation for the macroscopic variables x and v given the Zwanzig Hamiltonian eq. (2.4.1) and are thus in this sense equivalent.*

Order	Generalised Hermite Polynomial
0	1
1	$\beta\left(x+bx^3\right)$
2	$-\beta^2\left(kT+3kTbx^2+\left(x+bx^3\right)^2\right)$
3	$x\beta\left(6b-3\left(1+bx^2\right)\left(1+3bx^2\right)\beta+x^2\left(1+bx^2\right)^3\beta^2\right)$

Table 2.2: Generalised Hermite Polynomials for weight function $e^{-\beta\left(\frac{x^2}{2}+b\frac{x^4}{4}\right)}$

Proof. Mori's GLE for x is always

$$\frac{dx(t)}{dt}=v, \tag{2.4.3}$$

as the memory kernel and random force term vanishes due to $i(1-\mathcal{P}_M)\mathcal{L}v=0$ (see sec. 2.3.2).

Let us denote Mori's GLE for v as

$$\frac{dv(t)}{dt}=i\Omega_v-\int_0^t d\tau\ K(t)v(t-\tau)+F(t). \tag{2.4.4}$$

For the calculation of $F(t)$,$K(t)$ and $i\Omega$ in the GLE for the macroscopic variable v, the quantity $i\mathcal{L}v$ is essential. It can be evaluated as

$$i\mathcal{L}v=-\frac{dU(x)}{dx}+\sum_i k_i\left(\frac{\partial f_i(x)}{\partial x}\right)(q_i-f_i(x))=-\frac{\partial\mathscr{H}}{\partial x}=-\left(\frac{\partial\mathscr{H}_s}{\partial x}+\frac{\partial\mathscr{H}_b}{\partial x}\right). \tag{2.4.5}$$

But $\frac{\partial\mathscr{H}_s}{\partial x}=\frac{dU(x)}{dx}$ is exactly the generalised Hermite polynomial $\frac{1}{\beta}He_1(x)$ as defined in eq. (2.4.2). Thus, by selecting $\frac{dU(x)}{dx}$ as a macroscopic variable, we can simplify all terms involving inner products of $i\mathcal{L}v$ and $\frac{dU(x)}{dx}(=:U'(x))$. As $U(x)$ doesn't depend on v, the first term in the GLE is

$$i\Omega_v=(i\mathcal{L}v,U'(x))\cdot(U'(x),U'(x))^{-1}\cdot U'(x)=-U'(x), \tag{2.4.6}$$

because the derivative of the coupling vanishes in the inner product. The random force term $F(t)=e^{i(1-\mathcal{P}_M)\mathcal{L}t}(1-\mathcal{P}_M)i\mathcal{L}v$ cannot include $He_1(x)$ due to the orthogonal projection and as expected, after evaluating $i(1-\mathcal{P}_M)\mathcal{L}v$, we find

$$F(t)=e^{i(1-\mathcal{P}_M)\mathcal{L}t}\sum_i k_i\left(\frac{\partial f_i(x)}{\partial x}\right)(q_i-f_i(x)). \tag{2.4.7}$$

This looks similar to the first term in eq. (2.3.20), but the complete Liouville operator $i\mathcal{L}$ is still present in the propagator. Nevertheless, it can be shown with exactly the same procedure

as in sec. 4.3.1 that $F(t) = F_Z(t)$ and therefore $K(t) = K_Z(t)$. Thus, the two equations are equivalent. □

In the proof, Mori's equation for $U(x)$ was omitted, as we haven't been able to show the equivalence for this equation with Zwanzig's.

Chapter 3

δ-Projector

3.1 Introduction

Mori's generalised Langevin equations are inherently linear in the relevant variables and only valid for systems close to equilibrium. Hence, new types of projection operators where proposed to circumvent these problems. Notable are the works of *Mori and Fujisaka* (1973) and especially *Nordholm and Zwanzig* (1975), *Grabert et al.* (1980), *Zwanzig* (1980), *Grabert* (1982) and *Zwanzig* (2001), who more or less solved it, by introducing Dirac delta functions with A_i in the arguments as the macrovariables. As will be shown in the subsequent sections, this elegant procedure allows not only to include the information of the dynamics of macrovariables in one equation, but also allows the derivation of a generalised Fokker-Planck and a generalised Langevin equation at the same time, while staying exact.

In the derivation, we will follow the derivations of *Grabert et al.* (1980), *Grabert* (1982) and *Zwanzig* (2001).

3.2 Derivation

The δ-projector is essentially derived in the same way as the Mori projector, but the main difference lies in the relevant variables. Whereas Mori used the macrovariables ΔA_i to define his projector, we now take a variable $G_a(\Gamma)$, namely $G_a(\Gamma) := \delta(A(\Gamma) - a)$ as the relevant variable and derive the GLE for it. Here, A still describes the macrovariables (but this time, the equilibrium average doesn't have to vanish), and a is a parameter for the macroscopic value

of the function $A(\Gamma)$. By choosing a specific a, $G_a(\Gamma)$ becomes only then non-zero, when the phase point Γ lies on a compatible hypersurface with $A(\Gamma) = a$. This point of view can also be used to split the ensemble density $\rho(\Gamma, 0)$ in a macroscopic probability density function $p(a, 0)$, which is related to the probability of the system in a macroscopic state with the macroscopic values a at time 0, and a conditional probability density $w(\Gamma, A(\Gamma), 0) := w(\Gamma|A(\Gamma), 0)$ (i.e. a PDF for Γ given a macroscopic state) according to

$$\begin{aligned}\rho(\Gamma, 0) &= p(A(\Gamma), 0)w(\Gamma, A(\Gamma), 0) \\ &= \int da\ p(a, 0)w(\Gamma, a, 0)\delta(A(\Gamma) - a),\end{aligned} \tag{3.2.1}$$

where

$$p(a, t) := \int d\Gamma\ \delta(A(\Gamma) - a)\rho(\Gamma, t), \tag{3.2.2}$$

and especially at time $t = 0$

$$p(a, 0) := \int d\Gamma\ \delta(A(\Gamma) - a)\rho(\Gamma, 0). \tag{3.2.3}$$

In case of equilibrium, eq. (3.2.2) becomes

$$p_{eq}(a) = \int d\Gamma\ \delta(A(\Gamma) - a)\rho_{eq}(\Gamma). \tag{3.2.4}$$

In particular, we will confine the following discussion to the choice of

$$w(\Gamma) := w(\Gamma, A(\Gamma), 0) = \frac{\rho_{eq}(\Gamma)}{p_{eq}(A(\Gamma))}, \tag{3.2.5}$$

where subscript "*eq*" indicates the respective equilibrium probability density. As both $A(\Gamma)$ and a are vectors, the delta function $\delta(A(\Gamma) - a)$ is itself an abbreviation for the product of the delta functions $\delta(A_i(\Gamma) - a_i)$. When the function $A(\Gamma)$ becomes time-dependent (i.e. $A(\Gamma, t)$), we will write $G_a(\Gamma, t)$ for the relevant variable.

The resulting equation for $G_a(\Gamma)$ allows to express the GLE for any power of A, because a simple multiplication by a^n and further integration over the state space yields the corresponding GLE, i.e.

$$A^n(t) = \int da\ a^n G_a(\Gamma, t). \tag{3.2.6}$$

The relevant variables $G_a(\Gamma)$ also have the following properties:

$$G_a(\Gamma)G_{a'}(\Gamma) = \delta(a - a')G_a(\Gamma), \tag{3.2.7a}$$

$$\int d\Gamma\ w(\Gamma)G_a(\Gamma) = 1. \tag{3.2.7b}$$

The mean value of the relevant variables $G_a(\Gamma, t)$ is by definition (see eq.(3.2.2)) equal to the macroscopic probability density function $p(a, t)$, i.e. $\langle G_a(\Gamma, t)\rangle = p(a, t)$. Note that one can change to the Schrödinger picture in eq. (3.2.2) to obtain

$$p(a,t) = \int d\Gamma\ G_a(\Gamma, t)\rho(\Gamma, 0), \tag{3.2.8}$$

For each real-valued function in state space $f(a)$, there exists a corresponding (real-valued) function $F(\Gamma)$, which is connected to $f(a)$ according to

$$F(\Gamma) = \int da\ f(a)G_a(\Gamma) = f(A(\Gamma)). \tag{3.2.9}$$

Likewise, the time evolution of $F(\Gamma)$ can be written as

$$F(\Gamma, t) = \int da\ f(a)G_a(\Gamma, t) \tag{3.2.10}$$

Eq. (3.2.9) could be interpreted as a linear combination of the functions $G_a(\Gamma)$.

As in Mori's formalism, a Hilbert space $L^2(\Phi, \mu)$ is introduced, with Φ being the phase space and μ being the measure defined by $d\mu(\Gamma) := w(\Gamma)d\Gamma$. The scalar product is given by

$$(X, Y) := \int d\Gamma\ w(\Gamma)X(\Gamma)Y(\Gamma). \tag{3.2.11}$$

As can be seen from eqs. (3.2.7a), (3.2.7b), and (3.2.9), the $G_a(\Gamma)$ form an orthonormal basis of the subspace of all functions $F(\Gamma) \in L^2(\Phi, \mu)$, i.e.

$$(G_a(\Gamma), G_{a'}(\Gamma)) = \int d\Gamma\ w(\Gamma)G_a(\Gamma)G_{a'}(\Gamma) = \delta(a - a'). \tag{3.2.12}$$

Hence, it is possible to introduce a projection operator $\mathcal{P}$, which projects an arbitrary function $X(\Gamma)$ onto this subspace by virtue of

$$\mathcal{P}X(\Gamma) := \int da\ (G_a(\Gamma), X)G_a(\Gamma) \tag{3.2.13}$$

The projector $\mathcal{P}$ is time-independent, idempotent, orthogonal (i.e. self-adjoint) and projects (as required) on $G_a(\Gamma)$. In equations, that is

$$\mathcal{P}^2 = \mathcal{P}, \tag{3.2.14a}$$

$$(X, \mathcal{P}Y) = (\mathcal{P}X, Y) \quad \text{and} \tag{3.2.14b}$$

$$\mathcal{P}G_a(\Gamma) = G_a(\Gamma). \tag{3.2.14c}$$

The idempotence eq. (3.2.14a) can be shown for an arbitrary function $X(\Gamma)$ with

$$\begin{aligned}\mathcal{P}^2X(\Gamma) &= \int da'\ (G_{a'}(\Gamma), \mathcal{P}X(\Gamma))G_{a'}(\Gamma)\\ &= \int da'da\ \underbrace{(G_{a'}(\Gamma), G_a(\Gamma))}_{\delta(a-a')}(G_a(\Gamma), X(\Gamma))G_{a'}(\Gamma)\\ &= \int da\ (G_a(\Gamma), X(\Gamma))G_{a'}(\Gamma)\\ &= \mathcal{P}X(\Gamma).\end{aligned} \tag{3.2.15}$$

The proof of $\mathcal{P}$ being self-adjoint is straightforward:

$$\begin{aligned}(X, \mathcal{P}Y) &= \int d\Gamma\ w(\Gamma)X \int da'\ (Y, G_{a'})G_{a'}\\ &= \int da'\ (Y, G_{a'}) \underbrace{\int d\Gamma\ w(\Gamma)XG_{a'}}_{(X, G_{a'})}\\ &= \int d\Gamma\ w(\Gamma)Y \int da'\ (X, G_{a'})G_{a'}\\ &= (\mathcal{P}X, Y).\end{aligned} \tag{3.2.16}$$

Finally, eq. (3.2.14c) is proved by

$$\begin{aligned}\mathcal{P}G_a(\Gamma) &= \int da'\ \underbrace{(G_a, G_{a'})}_{\delta(a-a')}G_{a'}\\ &= G_a(\Gamma).\end{aligned} \tag{3.2.17}$$

3.2.1 Time evolution of $G_a(\Gamma, t)$

It remains to split up the time evolution of $G_a(\Gamma, t)$ into a systematic and a random part. Therefore, we use the decomposition of the Liouville propagator

$$e^{i\mathcal{L}t} = e^{i\mathcal{L}t}\mathcal{P} + \int_0^t du\ e^{i\mathcal{L}u}\mathcal{P}i\mathcal{L}(1-\mathcal{P})e^{i\mathcal{L}(1-\mathcal{P})(t-u)} + (1-\mathcal{P})e^{i\mathcal{L}(1-\mathcal{P})t}, \tag{3.2.18}$$

which can be proved by differentiation. By inserting eq. (3.2.18) into the time evolution equation

$$\frac{\partial}{\partial t}G_a(\Gamma, t) = e^{i\mathcal{L}t}i\mathcal{L}G_a(\Gamma), \tag{3.2.19}$$

one obtains the decomposed dynamics

$$\begin{aligned}\frac{\partial}{\partial t}G_a(\Gamma, t) = \ & e^{i\mathcal{L}t}\mathcal{P}\dot{G}_a(\Gamma) + i\int_0^t du\ e^{i\mathcal{L}u}\mathcal{P}\mathcal{L}(1-\mathcal{P})e^{i\mathcal{L}(1-\mathcal{P})(t-u)}\dot{G}_a(\Gamma)\\ & + (1-\mathcal{P})e^{i\mathcal{L}(1-\mathcal{P})t}\dot{G}_a(\Gamma).\end{aligned} \tag{3.2.20}$$

The structure of eq. (3.2.20) can be further simplified by introducing various substitutions which point to the physical interpretations of the terms. First, the term of the "random force" is defined by

$$F_a(t) := (1-\mathcal{P})e^{i\mathcal{L}(1-\mathcal{P})t}\dot{G}_a(\Gamma). \tag{3.2.21}$$

The time derivative of $G(\Gamma)$ may be casted into the form of a flux, i.e.

$$\dot{G}_a(\Gamma) = i\mathcal{L}G_a(\Gamma) = -\sum_j \frac{\partial}{\partial a_j} G_a(\Gamma)\dot{A}_j. \tag{3.2.22}$$

We have used the chain rule of differentiation to arrive at this form:

$$i\mathcal{L}\delta(A_j(\Gamma)-a_j) = \frac{\partial\delta(A_j(\Gamma)-a_j)}{\partial A_j}\cdot i\mathcal{L}A_j = -\frac{\partial\delta(A_j(\Gamma)-a_j)}{\partial a_j}\cdot i\mathcal{L}A_j. \tag{3.2.23}$$

Then, $F_a(t)$ may be rewritten as

$$F_a(t) = -\sum_j \frac{\partial}{\partial a_j} R_j(a,t), \tag{3.2.24}$$

where $R_j(a,t)$ is defined by

$$R_j(a,t) := (1-\mathcal{P})e^{i\mathcal{L}(1-\mathcal{P})t}G_a(\Gamma)\dot{A}_j. \tag{3.2.25}$$

The first term on the RHS in eq. (3.2.20) can be rewritten as

$$\begin{aligned} e^{i\mathcal{L}t}\mathcal{P}\dot{G}_a(\Gamma) &= e^{i\mathcal{L}t}\int da'\ (i\mathcal{L}G_a, G_a)G_{a'} \\ &= -\sum_j e^{i\mathcal{L}t}\int da'\ (\frac{\partial}{\partial a_j}G_a\dot{A}_j, G_{a'})G_{a'} \\ &= -\sum_j \int da'\ \frac{\partial}{\partial a_j}\underbrace{(\dot{A}_j, G_{a'})}_{=:v_j(a')}\delta(a-a')G_{a'}(\Gamma,t) \\ &= -\sum_j \frac{\partial}{\partial a_j}v_j(a)G_a(\Gamma,t), \end{aligned} \tag{3.2.26}$$

where $v_j(a)$ is called the drift vector. For the second term, we can simplify by

$$\mathcal{P}i\mathcal{L}(1-\mathcal{P})e^{i\mathcal{L}(1-\mathcal{P})(t-u)}\dot{G}_a(\Gamma) = \mathcal{P}i\mathcal{L}F_a(t-u), \tag{3.2.27}$$

and further

$$\begin{aligned} (G_{a'}(\Gamma), i\mathcal{L}F_a(t-u)) &= -(i\mathcal{L}G_{a'}(\Gamma), F_a(t-u)) \\ &= -\sum_{j,k}\frac{\partial}{\partial a_j}\frac{\partial}{\partial a'_k}\Big(G_{a'}(\Gamma), \dot{A}_k R_j(a,t-u)\Big) \\ &= -\sum_{j,k}\frac{\partial}{\partial a_j}\frac{\partial}{\partial a'_k}D_{jk}(a,a',t-u), \end{aligned} \tag{3.2.28}$$

where the diffusion kernels are defined by

$$D_{jk}(a,a',t-u) := \Big(R_j(a,t-u), \dot{A}_k G_{a'}(\Gamma)\Big) \tag{3.2.29}$$

By using these results and by partial integration with respect to a', eq. (3.2.20) can be rewritten as

$$\begin{aligned}\frac{\partial}{\partial t}G_a(\Gamma) = &-\sum_j \frac{\partial}{\partial a_j} v_j(a) G_a(\Gamma,t) \\ &+ \int_0^t du \ \sum_{j,k} \frac{\partial}{\partial a_j} \int da' \ D_{jk}(a,a',t-u) \frac{\partial}{\partial a'_k} G_{a'}(\Gamma,u) \\ &+ F_a(t).\end{aligned} \tag{3.2.30}$$

Eq. (3.2.30) concludes the decomposition and is an exact equation, which allows to derive either the generalised Fokker-Planck equation or the generalised Langevin Equation. The former results from averaging eq.(3.2.30) over an initial microscopic probability density function $\rho(\Gamma,0)$ of the aforementioned form, i.e.

$$\rho(\Gamma,0) = \int da \ p(a,0) w(\Gamma) \delta(A(\Gamma)-a), \tag{3.2.31}$$

whereas the latter can be generated by using the property eq. (3.2.6), i.e. we multiply eq. (3.2.30) by a and integrate over a. Hence, the GLE reads

$$\begin{aligned}\frac{\partial}{\partial t}A(t) = &\sum_j \int da \ v_j(a) G_a(\Gamma,t) \\ &+ \int da \ a \int_0^t du \ \sum_{j,k} \frac{\partial}{\partial a_j} \int da' \ D_{jk}(a,a',t-u) \frac{\partial}{\partial a'_k} G_{a'}(\Gamma,u) \\ &+ \int da \ a F_a(t).\end{aligned} \tag{3.2.32}$$

Additionally, it is possible to rewrite the diffusion kernels in eq. (3.2.29) by using the facts

$$\begin{aligned}R_j(a,0) &= (1-\mathcal{P}) G_a(\Gamma) \dot{A}_j \\ &= G_a(\Gamma)\dot{A}_j - G_a(G_a,\dot{A}_j),\end{aligned} \tag{3.2.33}$$

and

$$(G_a,(1-\mathcal{P})X) = (\mathcal{P}G_a,(1-\mathcal{P})X) = ((1-\mathcal{P})\mathcal{P}G_a,X) = 0. \tag{3.2.34}$$

Therefore,

$$D_{jk}(a,a',t-u) = (R_j(a,t-u),R_k(a',0)), \tag{3.2.35}$$

which is a generalised fluctuation-dissipation theorem.

Chapter 4

Mazur-Oppenheim Projector

4.1 Introduction

The work of *Mazur and Oppenheim* (1970) was the first rigorous derivation of the phenomenological Langevin equation of Brownian Motion from microscopic dynamics. The model was comprised of a Brownian particle (the system) suspended in a fluid of light particles (the bath). With the introduction of a projection operator $\mathcal{P}$ (henceforth the MO-projector), it was possible to derive an exact equation of motion from the Liouville-equation. By going to the Brownian limit and making assumptions about the time development of correlations of the bath variables, Mazur and Oppenheim arrived at the phenomenological Langevin equation of a free Brownian particle.

While the original work restricted itself to describe the momentum of the Brownian particle, the model was later extended to well behaved functions $\phi(\mathbf{R}, \mathbf{P})$ of the position and momentum of the B-particle (*Albers*, 1971). *Deutch* (1971) finally provided the general model for n B-particles. The lack of external potentials for the B-particle was overcome by *Kim and Oppenheim* (1972), although this work is only valid for the model of the original paper by Mazur and Oppenheim, i.e. the momentum of the Brownian particle. However, the generalisation to functions of the space and momentum of the B-particle is straightforward as will be shown in the derivation. About 25 years later, *Shea* (1997) again generalised the formalism to couplings to non-equilibrium baths.

The MO-projector was used f.e. in *Deutch and Silbey* (1971) to describe a Brownian particle in a harmonic lattice. *Kim and Oppenheim* (1971) used it to derive the phenomenological

Langevin equation of a rigid rotor, and *Mohanty et al.* (1982) did the same for a harmonic oscillator. Interesting recent developments are due to Plyukhin et al. (see f.e. *Plyukhin and Schofield* (2003), *Plyukhin and Schofield* (2004) and *Plyukhin* (2011)).

It should be noted that this model paved the way for an analysis of the B-particle in the Mori-Zwanzig formalism by Hynes et al. (see f.e. *Hynes et al.* (1975a) and *Hynes et al.* (1975b)).

4.2 Derivation

4.2.1 Generalised Langevin Equation

In our derivation, we will follow the works of *Mazur and Oppenheim* (1970), *Albers* (1971) and *Kim and Oppenheim* (1972). The Hamiltonian for the total system is given by

$$\mathscr{H} = \mathscr{H}_0 + \mathscr{H}_B, \tag{4.2.1}$$

where $\mathscr{H}_B$ is the Hamiltonian of the Brownian particle and consists essentially of the kinetic energy and an external potential which acts only on the Brownian particle but not on the bath particles,

$$\mathscr{H}_B = \frac{\mathbf{P}^2}{2M} + W(\mathbf{R}). \tag{4.2.2}$$

$\mathscr{H}_0$ is the bath Hamiltonian consisting of the kinetic energy of all bath particles, an interaction potential between bath particles $U(\mathbf{r}^N)$ and the interaction potential $V(\mathbf{r}^N, \mathbf{R})$ between bath particles and the fixed Brownian particle, i.e.

$$\mathscr{H}_0 = \frac{\mathbf{p}^N \cdot \mathbf{p}^N}{2m} + U(\mathbf{r}^N) + V(\mathbf{r}^N, \mathbf{R}). \tag{4.2.3}$$

Regarding V an assumption is made, which states that V has to be the sum of pair interactions

$$V = \sum_{i=1}^{N} v(|\mathbf{r_i} - \mathbf{R}|). \tag{4.2.4}$$

The Liouville operator $i\mathcal{L}$ gets split up in the usual way as

$$i\mathcal{L} = i\mathcal{L}_0 + i\mathcal{L}_B, \tag{4.2.5}$$

with

$$i\mathcal{L}_0 = \sum_{i=1}^{N} \left[\frac{\mathbf{p}_i}{m} \cdot \nabla_{\mathbf{r_i}} - \nabla_{\mathbf{r_i}}(U+V) \cdot \nabla_{\mathbf{p_i}} \right], \tag{4.2.6}$$

$$i\mathcal{L}_B = \left(\frac{\mathbf{P}}{M}\right) \cdot \nabla_{\mathbf{R}} + \mathbf{F} \cdot \nabla_{\mathbf{P}} + \mathbf{K} \cdot \nabla_{\mathbf{P}}, \tag{4.2.7}$$

where

$$\mathbf{F} := -\nabla_{\mathbf{R}} V \tag{4.2.8}$$

and

$$\mathbf{K} := -\nabla_{\mathbf{R}} W(\mathbf{R}). \tag{4.2.9}$$

Mazur and Oppenheim define the projection operator $\mathcal{P}$ acting on an arbitrary variable B as the expectation value over the bath + interaction equilibrium distribution, i.e.

$$\mathcal{P}B := \langle B \rangle := \int d\mathbf{r}^N d\mathbf{p}^N \ \rho_0 B, \tag{4.2.10}$$

where the density function is given by

$$\rho_0(\Gamma) = \frac{e^{-\beta \mathscr{H}_0}}{\int d\mathbf{r}^N d\mathbf{p}^N \ e^{-\beta \mathscr{H}_0}}. \tag{4.2.11}$$

By following the usual expansion with Duhamel's formula (or Dyson decomposition)

$$e^{i(1-\mathcal{P})\mathcal{L}t} = e^{i\mathcal{L}t} - \int_0^t d\tau \ e^{i\mathcal{L}(t-\tau)} i\mathcal{P}\mathcal{L} e^{i(1-\mathcal{P})\mathcal{L}\tau} \tag{4.2.12}$$

and letting it act on $(1-\mathcal{P})i\mathcal{L}\phi(0)$ where $\phi(0) = \phi(\mathbf{R}, \mathbf{P})$ ($\phi(t) := e^{i\mathcal{L}t}\phi(0)$) is an arbitrary function, we get

$$e^{i(1-\mathcal{P})\mathcal{L}t}(1-\mathcal{P})i\mathcal{L}\phi(0) = e^{i\mathcal{L}t}(1-\mathcal{P})i\mathcal{L}\phi(0) - \int_0^t d\tau \ e^{i\mathcal{L}(t-\tau)} i\mathcal{P}\mathcal{L} e^{i(1-\mathcal{P})\mathcal{L}t}(1-\mathcal{P})i\mathcal{L}\phi. \tag{4.2.13}$$

By first evaluating the first term on the right hand side of eq. (4.2.13), we can simplify it to

$$\begin{aligned} e^{i\mathcal{L}t}(1-\mathcal{P})i\mathcal{L}\phi(0) &= \underbrace{e^{i\mathcal{L}t} i\mathcal{L}\phi(0)}_{\frac{\partial}{\partial t} e^{i\mathcal{L}t}\phi(0) =: \dot{\phi}(t)} - e^{i\mathcal{L}t}\mathcal{P} i\mathcal{L}\phi(0) \\ &= \dot{\phi}(t) - e^{i\mathcal{L}t}\mathcal{P} i\mathcal{L}_B \phi(0) \\ &= \dot{\phi}(t) - e^{i\mathcal{L}t}\left(\left(\frac{\mathbf{P}}{M}\right) \cdot \nabla_{\mathbf{R}}\phi(0) + \mathbf{K} \cdot \nabla_{\mathbf{P}}\phi(0)\right). \end{aligned} \tag{4.2.14}$$

Here, we have used the facts that

$$\mathcal{P} i\mathcal{L}_0 \phi(0) = 0, \tag{4.2.15}$$

because $\phi(0)$ doesn't depend upon $\mathbf{r}^N$ or $\mathbf{p}^N$, and

$$\mathcal{P}i\mathcal{L}_B\phi(0) = \frac{\mathbf{P}}{M}\cdot\nabla_{\mathbf{R}}\phi(0) + \mathbf{K}\cdot\nabla_{\mathbf{P}}\phi(0). \tag{4.2.16}$$

Eq. (4.2.16) can be proved by

$$\begin{aligned}\mathcal{P}i\mathcal{L}_B\phi(0) = \langle i\mathcal{L}_B\phi(0)\rangle &= \frac{1}{Z}\int dr^N dp^N\ \rho_0 i\mathcal{L}_B\phi(0) = \\ &= \nabla_{\mathbf{P}}\phi(\mathbf{R},\mathbf{P})\cdot\frac{1}{Z}\int dr^N dp^N\ \rho_0 F + \left\langle\left(\frac{\mathbf{P}}{M}\right)\cdot\nabla_{\mathbf{R}}\phi(0) + \mathbf{K}\cdot\nabla_{\mathbf{P}}\phi(0)\right\rangle \\ &= -\nabla_{\mathbf{P}}\phi(\mathbf{R},\mathbf{P})\cdot\frac{1}{Z}\int dr^N dp^N\ e^{-\beta H_0}\nabla_{\mathbf{R}}H_0 + \left\langle\left(\frac{\mathbf{P}}{M}\right)\cdot\nabla_{\mathbf{R}}\phi(0) + \mathbf{K}\cdot\nabla_{\mathbf{P}}\phi(0)\right\rangle \\ &= \left\langle\left(\frac{\mathbf{P}}{M}\right)\cdot\nabla_{\mathbf{R}}\phi(0) + \mathbf{K}\cdot\nabla_{\mathbf{P}}\phi(0)\right\rangle = \left(\frac{\mathbf{P}}{M}\right)\cdot\nabla_{\mathbf{R}}\phi(0) + \mathbf{K}\cdot\nabla_{\mathbf{P}}\phi(0).\end{aligned} \tag{4.2.17}$$

In order to evaluate eq. (4.2.13) further, we introduce the definition of the projected dynamics force $F^\dagger(t)$ (which corresponds to the stochastic random force in the phenomenological theory)

$$\begin{aligned}F^\dagger(t) &:= e^{i(1-\mathcal{P})\mathcal{L}t}i(1-\mathcal{P})\mathcal{L}\phi(0) \\ &= e^{i(1-\mathcal{P})\mathcal{L}t}\mathbf{F}\cdot\nabla_P\phi(0).\end{aligned} \tag{4.2.18}$$

The second line of eq. (4.2.18) was derived by using eqs. (4.2.7),(4.2.15) and (4.2.16). Therefore, eq. (4.2.13) can be rewritten as

$$\dot{\phi}(t) = F^\dagger(t) + e^{i\mathcal{L}t}\left(\frac{\mathbf{P}}{M}\right)\cdot\nabla_{\mathbf{R}}\phi + e^{i\mathcal{L}t}\mathbf{K}\cdot\nabla_{\mathbf{P}}\phi(0) + \int_0^t d\tau\ e^{i\mathcal{L}(t-\tau)}\left\langle i\mathcal{L}_B F^\dagger(\tau)\right\rangle, \tag{4.2.19}$$

where we have used eq. (4.2.15) and eq. (4.2.16). We will simplify the expectation value under the integral sign in eq. (4.2.19). Firstly, we note that because of the idempotence of $\mathcal{P}$

$$\left\langle F^\dagger(t)\right\rangle = \left\langle(1-\mathcal{P})F^\dagger(t)\right\rangle = \mathcal{P}(1-\mathcal{P})F^\dagger(t) = 0. \tag{4.2.20}$$

Hence,

$$\begin{aligned}\nabla_{\mathbf{R}}\left\langle F^\dagger(t)\right\rangle &= 0 \\ &= \nabla_{\mathbf{R}}\mathcal{P}e^{i(1-\mathcal{P})\mathcal{L}t}i(1-\mathcal{P})\mathcal{L}\phi(0) \\ &= \nabla_{\mathbf{R}}\int dr^N dp^N\ e^{-\beta\mathscr{H}_0}F^\dagger(t) = \int dr^N dp^N\ \nabla_{\mathbf{R}}e^{-\beta\mathscr{H}_0}F^\dagger(t) \\ &= \int dr^N dp^N\ \beta\mathbf{F}e^{-\beta\mathscr{H}_0}F^\dagger(t) + \int dr^N dp^N\ e^{-\beta\mathscr{H}_0}\nabla_{\mathbf{R}}F^\dagger(t) \\ &= \left\langle\nabla_{\mathbf{R}}F^\dagger(t)\right\rangle + \beta\left\langle\mathbf{F}F^\dagger(t)\right\rangle.\end{aligned} \tag{4.2.21}$$

By using eq. (4.2.21), the expectation value simplifies to

$$\left\langle i\mathcal{L}_B F^\dagger(t)\right\rangle = \left(\nabla_{\mathbf{P}} - \beta\frac{\mathbf{P}}{M}\right)\cdot\left\langle \mathbf{F}F^\dagger(t)\right\rangle, \tag{4.2.22}$$

and the exact generalised Langevin equation for any arbitrary function of the system variables $\phi(\mathbf{R},\mathbf{P})$ is

$$\begin{aligned}\dot{\phi}(t) = F^\dagger(t) &+ e^{i\mathcal{L}t}\left(\frac{\mathbf{P}}{M}\right)\cdot\nabla_{\mathbf{R}}\phi(0) + e^{i\mathcal{L}t}\mathbf{K}\cdot\nabla_{\mathbf{P}}\phi(0)\\ &+\int_0^t d\tau\; e^{i\mathcal{L}(t-\tau)}\left(\nabla_{\mathbf{P}} - \beta\frac{\mathbf{P}}{M}\right)\cdot\left\langle\mathbf{F}F^\dagger(\tau)\right\rangle.\end{aligned} \tag{4.2.23}$$

4.3 Equivalence of the Mazur-Oppenheim and Zwanzig GLE

4.3.1 Equivalence

Having defined Zwanzig's GLE in eq. (1.4.4), we will prove the following theorem.

Theorem 3. *For the special case of no coupling between the momenta of the system and the heat bath, i.e.* $\mathscr{H}_b(X,Y) = \sum_i^N\left(\frac{p_i^2}{2} + \frac{k_i}{2}\left(q_i - f_i(x)\right)^2\right)$ *and a physical system Hamiltonian* $\mathscr{H}_s(X) = \frac{v^2}{2} + U(x)$*, the GLE derived by the Mazur-Oppenheim projector coincides with Zwanzig's GLE.*

Proof. The MO-GLEs for $\{x, v\}$ are given by

$$\frac{dx}{dt} = v(t), \tag{4.3.1a}$$

$$\frac{dv}{dt} = K(t) + \int_0^t d\tau\; e^{i\mathcal{L}(t-\tau)}\left(\partial_v - \beta v\right)\left\langle FF^\dagger(\tau)\right\rangle + F^\dagger(t). \tag{4.3.1b}$$

The eqs. (4.3.1) are equivalent to Zwanzig's GLEs eqs. (1.4.8b), if the stochastic force term $F^\dagger(t)$ is the same in MO's and Zwanzig's equations and if $\partial_v\left\langle FF^\dagger(\tau)\right\rangle = 0$. By definition,

$$\begin{aligned}F = -\frac{\partial}{\partial x}V(q,x) &= -\sum_i\frac{k_i}{2}\frac{\partial}{\partial x}\left(q_i - f_i(x)\right)^2\\ &= \sum_i k_i\left(q_i - f_i(x)\right)\frac{\partial f_i(x)}{\partial x},\end{aligned} \tag{4.3.2}$$

and F is therefore not dependent on v or p_i. Using this result, we know that

$$\partial_v\left\langle FF^\dagger(\tau)\right\rangle = \partial_v\left\langle Fe^{i(1-\mathcal{P})\mathcal{L}t}F\right\rangle = \left\langle F\partial_v e^{i(1-\mathcal{P})\mathcal{L}t}F\right\rangle, \tag{4.3.3}$$

and we therefore only have to inspect the term $\partial_v e^{i(1-\mathcal{P})\mathcal{L}t}F$. We will split the Liouville operator $i\mathcal{L}$ in a part $i\mathcal{L}_L$ linear in x and q and a nonlinear part $i\mathcal{L}_N$, i.e.

$$i\mathcal{L}_L := \frac{\partial\mathscr{H}}{\partial v}\frac{\partial}{\partial x} - \left(\frac{\partial\mathscr{H}}{\partial x}\right)_L \frac{\partial}{\partial v} + \sum_i \left(\frac{\partial\mathscr{H}}{\partial p_i}\frac{\partial}{\partial q_i} - \left(\frac{\partial\mathscr{H}}{\partial q_i}\right)_L \frac{\partial}{\partial p_i}\right), \tag{4.3.4a}$$

$$i\mathcal{L}_N := -\left(\frac{\partial\mathscr{H}}{\partial x}\right)_N \frac{\partial}{\partial v} - \sum_i \left(\frac{\partial\mathscr{H}}{\partial q_i}\right)_N \frac{\partial}{\partial p_i}, \tag{4.3.4b}$$

where subscript L or N indicates the linear or nonlinear terms. In case of the partial derivatives with respect to q_i, we can give them explicitly by

$$\left(\frac{\partial\mathscr{H}}{\partial q_i}\right)_L = k_i q_i, \tag{4.3.5a}$$

$$\left(\frac{\partial\mathscr{H}}{\partial q_i}\right)_N = -k_i f_i(x). \tag{4.3.5b}$$

We now expand $e^{i(1-\mathcal{P})\mathcal{L}t}F$ by using the Dyson decomposition in order to get

$$e^{i(1-\mathcal{P})\mathcal{L}t}F = e^{i(1-\mathcal{P})\mathcal{L}_L t}F + \int_0^t d\tau\; e^{i(1-\mathcal{P})\mathcal{L}(t-\tau)} i(1-\mathcal{P})\mathcal{L}_N e^{i(1-\mathcal{P})\mathcal{L}_L \tau}F. \tag{4.3.6}$$

As the term $e^{i(1-\mathcal{P})\mathcal{L}_L t}F$ is also repeated under the integral sign, we will first analyse that term. The derivative with respect to the time t results in a first order differential equation

$$\frac{\partial F_L(t)}{\partial t} = i(1-\mathcal{P})\mathcal{L}_L F_L(t) \tag{4.3.7}$$

with $F_L(t) := e^{i(1-\mathcal{P})\mathcal{L}_L t}F$. We use the ansatz

$$F_L(t) = \rho(t)x + \sigma(t)v + \sum_j \mu_j(t)q_j + \sum_j \nu_j(t)p_j + \sum_j \phi_j(t)f_j(x) \tag{4.3.8}$$

in the differential equation (4.3.7) to get the two equations

$$\frac{\partial F_L(t)}{\partial t} = \dot\rho(t)x + \dot\sigma(t)v + \sum_j \dot\mu_j(t)q_j + \sum_j \dot\nu_j(t)p_j + \sum_j \dot\phi_j(t)f_j(x) \tag{4.3.9}$$

and

$$(1-\mathcal{P})i\mathcal{L}_L F_L(t) = \sum_j \mu_j(t)p_j - \sum_j k_j q_j \nu_j(t) + \sum_j k_j \nu_j(t) f_j(x). \tag{4.3.10}$$

Equating the coefficients in eqs. (4.3.9) and (4.3.10), we deduce the coupled ODEs

$$\dot\rho(t) = 0, \tag{4.3.11a}$$

$$\dot\sigma(t) = 0, \tag{4.3.11b}$$

$$\dot\mu_j(t) = -k_j\nu_j(t), \tag{4.3.11c}$$

$$\dot\nu_j(t) = \mu_j(t), \tag{4.3.11d}$$

$$\dot\phi_j(t) = k_j\nu_j(t) = -\dot\mu_j(t), \tag{4.3.11e}$$

with the initial conditions (following from eq. (4.3.2))

$$\rho(0) = 0, \tag{4.3.12a}$$

$$\sigma(0) = 0, \tag{4.3.12b}$$

$$\mu_j(0) = k_j \frac{\partial f_j(x)}{\partial x}, \tag{4.3.12c}$$

$$\nu_j(0) = 0, \tag{4.3.12d}$$

$$\phi_j(0) = -k_j \frac{\partial f_j(x)}{\partial x}. \tag{4.3.12e}$$

By solving eqs. (4.3.11), we finally arrive at a solution for $F_L(t)$, namely

$$F_L(t) = \sum_j k_j \frac{\partial f_j(x)}{\partial x} \left(q_j - f_j(x)\right) \cos\left(\sqrt{k_j}t\right) + \sum_j \sqrt{k_j} \frac{\partial f_j(x)}{\partial x} p_j \sin\left(\sqrt{k_j}t\right). \tag{4.3.13}$$

As eq. (4.3.13) doesn't depend upon v, the partial derivative with respect to v vanishes in eq. (4.3.3). We now turn to the integral term in eq. (4.3.6) and analyse $i(1-\mathcal{P})\mathcal{L}_N F_L(s)$. As

$$i\mathcal{L}_N F_L(s) = -\sum_j k_j^{3/2} f_j(x) \frac{\partial f_j(x)}{\partial x} \sin\left(\sqrt{k_j}t\right) \tag{4.3.14}$$

is independent of $\{q_i, p_i\}$, the orthogonal projection $i(1-\mathcal{P})\mathcal{L}_N F_L(s)$ vanishes, and so does the integral.

The results so far are

$$e^{i(1-\mathcal{P})\mathcal{L}t} F = F_L(t) \tag{4.3.15}$$

and

$$\partial_v \left\langle F F^\dagger(\tau) \right\rangle = 0. \tag{4.3.16}$$

The MO-GLEs read therefore

$$\frac{dx}{dt} = v(t), \tag{4.3.17a}$$

$$\frac{dv}{dt} = -\frac{\partial U(x)}{\partial x} - \beta \int_0^t d\tau \ \left(e^{i\mathcal{L}(t-\tau)} \left\langle F F_L(\tau) \right\rangle\right) v(t-\tau) + F_L(t). \tag{4.3.17b}$$

$\langle F F_L(\tau) \rangle$ can be evaluated to give the memory kernel or FDT

$$K(\tau) := \beta \left\langle F F_L(\tau) \right\rangle = \sum_j k_j \left(\frac{\partial f_j(x(0))}{\partial x}\right) \left(\frac{\partial f_j(x(\tau))}{\partial x}\right) \cos\left(\sqrt{k_j}\tau\right) \tag{4.3.18}$$

This concludes our proof as these equations are equivalent to Zwanzig's GLEs derived in sec. 1.4. □

Chapter 5

Grabert-Projector

5.1 Introduction

Historically, the Grabert projector was introduced in *Grabert* (1977) and belongs to the family of projection operators derived by *Robertson* (1966) and *Kawasaki and Gunton* (1973). It was further developed in *Grabert* (1978), in which the focus was upon systems with a generalised canonical density matrix, and a final summary was given in *Grabert* (1982).

The Grabert projector differs from the different kinds of Mori-Zwanzig approaches in using a relevant probability density function to describe macrovariables and thus stays in the phase space description (as opposed to the Hilbert space description in the Mori-Zwanzig case). The projection operator is time-dependent and the decomposition of dynamics leads to two equations instead of one GLE: an equation for the mean values of the macrovariables and another one for the fluctuations. It should also be noted that Grabert's formalism doesn't specifically depend on the heat bath to be in equilibrium, though its form was derived with the generalised canonical density in mind.

In the next sections, we will introduce Grabert's formalism based on *Grabert* (1977), *Grabert* (1978) and *Grabert* (1982).

5.2 Derivation

5.2.1 Microscopic and Macroscopic Variables

As in the former chapters, we would like to represent the equations of motion for macroscopic variables $A(\Gamma)$ by a decomposition in two parts. Hence,

$$A_i(t) = \overline{A_i}(t) + \gamma_i(t), \tag{5.2.1}$$

and likewise for the time rate of change

$$\dot{A}_i(t) = \overline{\dot{A}_i}(t) + \dot{\gamma}_i(t). \tag{5.2.2}$$

In order to achieve such a decomposition, Grabert's formalism goes further then the other projection operator methods and decomposes the probability density function $\rho(\Gamma, t)$ itself.

5.2.2 Relevant Probability Density and Projection Operator

Grabert's formalism is centred around the notion of a relevant probability density function $\bar{\rho}(\Gamma, t)$. In the introduction sec. 1.2.6, it was shown that the mean value α_j of a macroscopic variable A_j is given by

$$\alpha_j(t) = \langle A_j(t) \rangle = \mathrm{tr}\left(\rho(\Gamma, t) A_j\right), \tag{5.2.3}$$

with $\rho(\Gamma, t)$ being the probability density function of the whole system and the trace tr being defined by

$$\mathrm{tr}\,(X) := \int d\Gamma\ X \tag{5.2.4}$$

for arbitrary X. Grabert introduced a so called relevant probability density function $\bar{\rho}(\Gamma, t)$, which approximates the probability density function of the system. The formalism doesn't specify the exact functional form of $\bar{\rho}(\Gamma, t)$ (though the use of the generalised canonical density simplifies calculations a lot), but restricts it with the following properties:

- $\bar{\rho}(\Gamma, t)$ is a probability density function, i.e. it is always positive $\bar{\rho}(\Gamma, t) \geq 0$ and normalised with $\mathrm{tr}\left(\bar{\rho}(\Gamma, t)\right) = 1$.
- $\rho(\Gamma, t)$ and $\bar{\rho}(\Gamma, t)$ yield the same mean values for the macroscopic variables at all times t, i.e.

$$\mathrm{tr}\left(A_j \bar{\rho}(\Gamma, t)\right) = \alpha_j(t) = \mathrm{tr}\left(A_j \rho(\Gamma, t)\right). \tag{5.2.5}$$

Grabert coined the term "macroequivalency" for this property.

- The time-dependence of $\bar{\rho}(\Gamma, t)$ arises only through the time-dependence of the mean values α_j, i.e.

$$\bar{\rho}(\Gamma, t) = \bar{\rho}(\Gamma, \alpha(t)), \tag{5.2.6}$$

where $\alpha(t)$ represents all mean values $\alpha_j(t)$.

- An optional, though very useful, property is

$$\rho(\Gamma, 0) = \bar{\rho}(\Gamma, 0) \tag{5.2.7}$$

which explicitly takes care of the preparation procedure and will simplify terms containing the "random force".

Given a relevant probability density function $\bar{\rho}(\Gamma, t)$ with the properties defined as above, it is possible to separate an arbitrary microscopic or macroscopic variable $X(t)$ into a macroscopic part $\overline{X}(t)$ and a fluctuation $\delta X(t)$, i.e.

$$X(t) = \overline{X}(t) + \delta X(t). \tag{5.2.8}$$

The macroscopic part $\overline{X}(t)$ shall be defined by

$$\overline{X}(t) := \overline{\langle X(t)\rangle} + \sum_j \frac{\partial \overline{\langle X(t)\rangle}}{\partial \alpha_j(t)} (A_j - \alpha_j(t)), \tag{5.2.9}$$

where the so called macroscopic value

$$\overline{\langle X(t)\rangle} := \mathrm{tr}\left(X \bar{\rho}(\Gamma, \alpha_j(t))\right) \tag{5.2.10}$$

looks formally similar to the mean value $\langle X(t)\rangle = \mathrm{tr}\left(X\rho(\Gamma, t)\right)$, but only depends on the mean values of the set of macroscopic variables $\{A_j(\Gamma)\}$. Because of eq. (5.2.9),

$$\overline{\langle X(t)\rangle} = \mathrm{tr}\left(X \bar{\rho}(\Gamma, t)\right) = \mathrm{tr}\left(\overline{X}(t)\rho(\Gamma, t)\right) \tag{5.2.11}$$

holds. Therefore, we define a projection operator $\mathcal{P}(t)$, which projects an arbitrary variable X onto its macroscopic part by

$$\begin{aligned} \mathcal{P}(t)X &:= \mathrm{tr}\left(\bar{\rho}(\Gamma, t)X\right) + \sum_j (A_j - \alpha_j(t))\mathrm{tr}\left(\frac{\partial \bar{\rho}(\Gamma, \alpha_j(t))}{\partial \alpha_j(t)} X\right) \\ &= \overline{X}(t). \end{aligned} \tag{5.2.12}$$

In case of a time-independent relevant probability density $\bar{\rho}(\Gamma, \alpha)$, the projection operator reduces to

$$\mathcal{P}X = \mathrm{tr}\left(\bar{\rho}(\Gamma,\alpha)X\right) + \sum_j (A_j - \alpha_j)\mathrm{tr}\left(\frac{\partial\bar{\rho}(\Gamma,\alpha_j)}{\partial\alpha_j}X\right). \tag{5.2.13}$$

The projection operator $\mathcal{P}(t)$ is for different times t and t' idempotent in the sense of

$$\mathcal{P}(t)\mathcal{P}(t') = \mathcal{P}(t'). \tag{5.2.14}$$

This can be proved by using the definition of $\mathcal{P}$ and an arbitrary variable X, i.e.

$$\begin{aligned}
\mathcal{P}(t)\mathcal{P}(t')X &= \mathcal{P}(t)\left[\mathrm{tr}\left(\bar{\rho}(\Gamma,t')X\right) + \sum_j (A_j - \alpha_j(t'))\mathrm{tr}\left(\frac{\partial\bar{\rho}(\Gamma,t')}{\partial\alpha_j}X\right)\right] \\
&= \mathrm{tr}\left(\bar{\rho}(\Gamma,t')X\right) + \sum_j (\alpha_j(t) - \alpha_j(t'))\mathrm{tr}\left(\frac{\partial\bar{\rho}(\Gamma,t')}{\partial\alpha_j}X\right) \\
&\quad + \sum_{j,k}(A_k - \alpha_k(t))\mathrm{tr}\left(\frac{\partial\bar{\rho}(\Gamma,t)}{\partial\alpha_k}A_j\right)\mathrm{tr}\left(\frac{\partial\bar{\rho}(\Gamma,t')}{\partial\alpha_j}X\right) \\
&= \mathrm{tr}\left(\bar{\rho}(\Gamma,t')X\right) + \sum_j (A_j - \alpha_j(t'))\mathrm{tr}\left(\frac{\partial\bar{\rho}(\Gamma,t')}{\partial\alpha_j}X\right) \\
&= \mathcal{P}(t')X.
\end{aligned} \tag{5.2.15}$$

The time derivative of $\mathcal{P}(t)$ can be directly calculated from eq. (5.2.12) and results in

$$\dot{\mathcal{P}}(t)X = \sum_{i,j}(A_i - \alpha_i)\dot{\alpha_j}(t)\ \mathrm{tr}\left(\frac{\partial^2\bar{\rho}(\Gamma,t)}{\partial\alpha_i(t)\partial\alpha_j(t)}X\right). \tag{5.2.16}$$

5.2.3 Decomposition of the Dynamics

With the aid of the projection operator $\mathcal{P}(t)$ as defined in the last section, the decomposition of the dynamics in organised and disorganised motion can be accomplished.

As in the former chapters, we are interested in the dynamics of an arbitrary variable $X(t)$ for which the time rate of change can be expressed through the Liouville-propagator, i.e.

$$\dot{X}(t) := e^{i\mathcal{L}t}\dot{X} \tag{5.2.17}$$

(remember the notation $B = B(0)$ for arbitrary $B(t)$). The Liouville-propagator in eq. (5.2.17) can be decomposed with the use of the projection operator according to

$$\begin{aligned}
e^{i\mathcal{L}t} =& e^{i\mathcal{L}t}\mathcal{P}(t) \\
&+ \int_s^t du\ e^{i\mathcal{L}u}\mathcal{P}(u)\left(i\mathcal{L} - \dot{\mathcal{P}}(u)\right)(1 - \mathcal{P}(u))\,G(u,t) \\
&+ e^{i\mathcal{L}s}\,(1 - \mathcal{P}(s))\,G(s,t),
\end{aligned} \tag{5.2.18}$$

where s is arbitrary in the interval $[0,t]$ and $G(t',t)$ is the anti-time-ordered exponential defined by

$$G(t',t) = T_{-} \exp\left\{ i \int_{t'}^{t} ds\ \mathcal{L}(1-\mathcal{P}(s)) \right\} \qquad (t \geq t') \tag{5.2.19}$$

In contrast to the other decompositions in the former chapters, the need for the time-ordered exponential arises through the time-dependence of the projection operator. Eq. (5.2.18) can be proved by differentiation and an alternative derivation is also given in *Grabert* (1982).

By inserting eq. (5.2.18) in eq. (5.2.17), we arrive at the exact decomposed equation of motion for an arbitrary variable $X(t)$

$$\begin{aligned} \dot{X}(t) = e^{i\mathcal{L}t}\mathcal{P}(t)\dot{X} + \int_0^t ds\ e^{i\mathcal{L}s}\mathcal{P}(s)\left[i\mathcal{L} - \dot{\mathcal{P}}(s) \right](1-\mathcal{P}(s))G(s,t)\dot{X} \\ + (1-\mathcal{P}(0))G(0,t)\dot{X}. \end{aligned} \tag{5.2.20}$$

5.2.4 Generalised Transport and Langevin Equations

With eq. (5.2.20), the derivation of the generalised Langevin equations is almost complete. It remains to apply the results to the set of macrovariables $A_j(t)$, with which this sections deals.

As usual, fluctuations $\delta A_j(t)$ of the macrovariables $A_j(t)$ are defined by deviations from their mean values $\alpha_j(t)$, thus

$$\delta A_j(t) = A_j(t) - \alpha_j(t). \tag{5.2.21}$$

Further on, we can evaluate the propagator/projector terms in eq. (5.2.20)

$$e^{i\mathcal{L}t}\mathcal{P}(t)X = \mathrm{tr}\left(\bar{\rho}(\Gamma,t)X\right) + \sum_j \delta A_j(t)\mathrm{tr}\left(\frac{\partial\bar{\rho}(\Gamma,t)}{\partial\alpha_j(t)}X \right), \tag{5.2.22a}$$

$$e^{i\mathcal{L}t}\dot{\mathcal{P}}(t)X = \sum_{j,k} \delta A_j(t)\dot{a}_k(t)\mathrm{tr}\left(\frac{\partial}{\partial a_k(t)}\frac{\partial\bar{\rho}(\Gamma,t)}{\partial\alpha_j(t)}X \right) \tag{5.2.22b}$$

to arrive at

$$\begin{aligned} \dot{A}_j(t) = \mathrm{tr}\left(\bar{\rho}(\Gamma,t)\dot{A}_j(t)\right) + \sum_k \Omega_{jk}(t)\delta A_k(t) \\ + \int_0^t ds\ \mathrm{tr}\left(\bar{\rho}(s)i\mathcal{L}(1-\mathcal{P}(s))G(s,t)\dot{A}_j\right) \\ + \int_0^t ds\ \sum_k \Phi_{jk}(t,s)\delta A_k(s) + F_j(t) \end{aligned} \tag{5.2.23}$$

with the definitions

$$\Omega_{jk}(t) := \mathrm{tr}\left(\frac{\partial\bar{\rho}(\Gamma,t)}{\partial a_k(t)}\dot{A}_j\right), \tag{5.2.24a}$$

$$\Phi_{jk}(t,s) := \mathrm{tr}\left(\frac{\partial\bar{\rho}(\Gamma,s)}{\partial a_k(s)}i\mathcal{L}(1-\mathcal{P}(s))G(s,t)\dot{A}_j\right) \tag{5.2.24b}$$

$$-\sum_l \dot{a}_l(s)\mathrm{tr}\left(\frac{\partial}{\partial a_l(s)}\frac{\partial\bar{\rho}(\Gamma,s)}{\partial a_k(s)}G(s,t)\dot{A}_j\right), \tag{5.2.24c}$$

$$F_j(t) := (1-\mathcal{P}(0))G(0,t)\dot{A}_j. \tag{5.2.24d}$$

Eq. (5.2.23) would be the starting point for comparisons with the δ and Mazur-Oppenheim projection operator procedures. Mori's formalism, however, yields equations for the fluctuations $\delta A_j(t)$ which will be derived subsequently. In order to do so, the equations for the mean values $\alpha_j(t)$ have to be derived. After that is done, they can be plugged into eq. (5.2.21) together with (5.2.23) to yield the equations for $\delta\dot{A}_j(t)$.

The mean values $\dot{\alpha}_j(t)$ are determined by averaging eq. (5.2.23) with the initial probability density function $\rho(\Gamma,0)$. Because of

$$\mathrm{tr}\left(X\bar{\rho}(\Gamma,t)\right) = \mathrm{tr}\left((\mathcal{P}(t)X)\rho(\Gamma,t)\right), \tag{5.2.25}$$

(see eq. (5.2.11)) the general relation

$$\mathrm{tr}\left(((1-\mathcal{P}(0))X)\bar{\rho}(\Gamma,0)\right) = 0 \tag{5.2.26}$$

holds for every variable X. Therefore,

$$\langle F_j(t)\rangle = \mathrm{tr}\left(F_j(t)\rho(\Gamma,0)\right) = 0, \tag{5.2.27}$$

where we have additionally used the preparation property eq. (5.2.7) of the relevant probability density function. It is that step which justifies this otherwise useless property. Thus, in the mean value equation, the "random force" term $F_j(t)$ doesn't appear, and we can write

$$\dot{a}_j(t) = \mathrm{tr}\left(\bar{\rho}(\Gamma,t)\dot{A}_j\right) + \int_0^t ds\ \mathrm{tr}\left(\bar{\rho}(\Gamma,s)i\mathcal{L}(1-\mathcal{P}(s))G(s,t)\dot{A}_j\right), \tag{5.2.28}$$

because the terms containing fluctuations $\delta A_j(t)$ also vanish (obviously, as the average of $\delta A_j(t)$ vanishes).

It remains to insert the result into eq. (5.2.23) to obtain the generalised Langevin equation

$$\delta\dot{A}_j(t) = \sum_k \Omega_{jk}(t)\delta A_k(t) + \int_0^t ds\ \sum_k \Phi_{jk}(t,s)\delta A_k(s) + F_j(t). \tag{5.2.29}$$

5.3 Relation to other projection operators

Four different projection operators have been discussed up to this point, and one might wonder if there is a relationship between them. There is, and it is Grabert's formalism from which all other three formalism are derived by the special choice of a relevant probability density $\bar{\rho}(\Gamma)$.

In the following discussion, we will not derive the generalised Langevin equations of the preceding chapters, as it suffices to derive the different projection operators. The relationship between Mori's formalism and Grabert's formalism was shown in *Grabert* (1982), where also the relation to the δ-projector was hinted at. The relation to Mazur and Oppenheim's projection operator is given by us.

5.3.1 Mori's projection operator

Grabert's projection operator for time-independent relevant probability densities is

$$\mathcal{P}X = \mathrm{tr}\left(\bar{\rho}X\right) + \sum_i (\Delta A_i - \alpha_i)\mathrm{tr}\left(\frac{\partial\bar{\rho}}{\partial\alpha_i}X\right), \tag{5.3.1}$$

where we have already replaced A_i by Mori's relevant variables ΔA_i. We choose Mori's non-equilibrium ensemble density (for negligible $O(h^2)$) as our relevant probability density

$$\begin{aligned}\bar{\rho}(\Gamma) &= \rho_{eq}(\Gamma)\left(1 + \sum_j h_j \Delta A_j\right) \\ &= \rho_{eq}(\Gamma) + \sum_{j,k} \rho_{eq}(\Gamma)(\Delta A_j, \Delta A_k)^{-1}\Delta A_j \alpha_k,\end{aligned} \tag{5.3.2}$$

where the expression for h_j has been taken from eq. (2.2.2). By using eq. (5.3.2) in eq. (5.3.1), we get

$$\mathcal{P}X = \mathrm{tr}\left(\rho_{eq}X\right) + \sum_{i,j}\alpha_j(\Delta A_i, \Delta A_j)^{-1}\mathrm{tr}\left(\rho_{eq}\Delta A_i X\right) + \sum_i(\Delta A_i - \alpha_i)\mathrm{tr}\left(\frac{\partial\bar{\rho}}{\partial\alpha_i}X\right), \tag{5.3.3}$$

and because

$$\frac{\partial\bar{\rho}}{\partial\alpha_i} = \sum_{i,j}\rho_{eq}(\Delta A_j, \Delta A_i)^{-1}\Delta A_j, \tag{5.3.4}$$

the projection operator finally reads

$$\begin{aligned}\mathcal{P}X &= \mathrm{tr}\left(\rho_{eq}X\right) + \sum_{i,j}(\Delta A_i, \Delta A_j)^{-1}\alpha_j \mathrm{tr}\left(\rho_{eq}\Delta A_i X\right) \\ &\quad + \sum_{i,j}(\Delta A_i - \alpha_i)(\Delta A_j, \Delta A_i)^{-1}\mathrm{tr}\left(\rho_{eq}\Delta A_j X\right) \\ &= \mathrm{tr}\left(\rho_{eq}X\right) + \sum_{i,j}\Delta A_i(\Delta A_j, \Delta A_i)^{-1}\mathrm{tr}\left(\rho_{eq}\Delta A_j X\right)\end{aligned} \tag{5.3.5}$$

The second term is already Mori's projection operator, and because the projection operator always appears with the Liouville operator in the GLEs (see eq. (5.2.29) with the definitions eqs. (5.2.24)), one could find a projection operator $\tilde{\mathcal{P}}$ which satisfies

$$i\mathcal{L}\tilde{\mathcal{P}} = i\mathcal{L}\mathcal{P}. \tag{5.3.6}$$

That is the case when we drop the first term of eq. (5.3.5), because the trace is independent of Γ, but the Liouville operator includes derivatives $\frac{\partial}{\partial\Gamma}$. Therefore, we have shown that Mori's formalism is a special case of Grabert's.

5.3.2 δ-projection operator

In general, if a relevant probability density is linear in the mean values α_i, it satisfies

$$\bar{\rho}(\Gamma) = \sum_i \alpha_i \frac{\partial\bar{\rho}}{\partial\alpha_i}, \tag{5.3.7}$$

and Grabert's time-independent projection operator eq. (5.2.13) simplifies by direct substitution of eq. (5.3.7) to

$$\mathcal{P}X = \sum_i A_i \ \mathrm{tr}\left(\frac{\partial\bar{\rho}}{\partial\alpha_i}X\right). \tag{5.3.8}$$

In the case of the δ-projector, the relevant variables are $G_a(\Gamma)$ and their mean values are the macroscopic probability density $p(a)$. The time-independent relevant probability density of the δ-projection operator is because of $\bar{\rho}(\Gamma, 0) = \rho(\Gamma, 0)$ (see eq. (3.2.1) and eq. (3.2.5))

$$\bar{\rho}(\Gamma) = \rho_{eq}(\Gamma)\int da\ \frac{p(a)}{p_{eq}(a)}G_a(\Gamma) \tag{5.3.9}$$

and is linear in the macroscopic probability density $p(a)$. Therefore, we have to change the projection operator in eq. (5.3.8) according to the replacements $A_i \to G_a(\Gamma)$, $\sum_i \to \int da$, and because the mean values α_i are now given by the functions $p(a)$, we are replacing $\alpha_i \to p(a)$.

The original derivative $\frac{\partial\bar{\rho}}{\partial\alpha_i}$ is now a functional derivative of $\bar{\rho}$ with respect to $p(a)$, i.e. $\frac{\delta\bar{\rho}}{\delta p(a)} = \rho_{eq}(\Gamma)\frac{1}{p_{eq}(a)}G_a(\Gamma)$. Hence, the projection operator becomes

$$\mathcal{P}X = \int da\ G_a \mathrm{tr}\left(\frac{\delta\bar{\rho}}{\delta p(a)}X\right). \tag{5.3.10}$$

Using this result we get immediately the δ-projector

$$\mathcal{P}X = \int da\ (G_a, X)G_a. \tag{5.3.11}$$

5.3.3 Mazur & Oppenheim's projection operator

In the case of Mazur & Oppenheim's projection operator, the time-independent relevant probability density

$$\bar{\rho}(\Gamma) = \delta(\mathbf{R}-\mathbf{R_0})\delta(\mathbf{P}-\mathbf{P_0})\rho_0(\Gamma), \tag{5.3.12}$$

where $\rho_0(\Gamma)$ is defined as in eq. (4.2.11), has to be used in Grabert's time-independent projection operator

$$\mathcal{P}X = \mathrm{tr}\,(\bar{\rho}X) + (\phi(\mathbf{R_0},\mathbf{P_0}) - \langle\phi(\mathbf{R},\mathbf{P})\rangle)\,\mathrm{tr}\left(\frac{\partial\bar{\rho}}{\partial\alpha}X\right), \tag{5.3.13}$$

with $\alpha = \langle\phi(\mathbf{R},\mathbf{P})\rangle$. As the potential V in $\mathscr{H}_0$ only depends on the absolute value $|\mathbf{r_i}-\mathbf{R}|$ (see eq. (4.2.4)), the expectation value of $\phi(\mathbf{R},\mathbf{P})$ is equal to $\phi(\mathbf{R_0},\mathbf{P_0})$ and the second term in eq. (5.3.13) vanishes.

This leads immediately to the result

$$\mathcal{P}X = \int d\Gamma_0\ \rho_0(\Gamma_0)X. \tag{5.3.14}$$

In eq. (5.3.14), Γ_0 denotes the phase space variables for the heat bath (i.e. Γ without $\mathbf{R}$ and $\mathbf{P}$). This result concludes the comparison of the four projection operators.

Appendices

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Abstract

The method of projection operators in statistical mechanics describes the separation of equations of motions for properties of interest in a relevant and a fluctuating part, where the fluctuating part consists of constituents which are individually not important. With these techniques, it is possible to derive generalised Langevin equations or generalised Fokker-Planck equations, which extend and motivate known phenomenological equations.

In this thesis, we describe the concept of projection operators in statistical mechanics, review four specific choices of them and show that Grabert's formalism (*Grabert* (1982)) is a generalisation of the others. Examples are given and relationships to the method of partially solving the equations of motion as described in *Zwanzig* (1973) are pointed out.

Zusammenfassung

Die Methode der Projektionsoperatoren in der Statistischen Mechanik beschreibt die Aufteilung von Bewegungsgleichungen physikalisch interessanter Größen in einen relevanten und einen fluktuierenden Teil, wobei die Bestandteile des fluktuierenden Teils im Einzelnen nicht maßgeblich sind. Mit dieser Methode ist es möglich, verallgemeinerte Langevin- oder Fokker-Planck-Gleichungen herzuleiten, die bereits bekannte phänomenologische Gleichungen erweitern.

In dieser Masterarbeit wird die Methode der Projektionsoperatoren in der Statistischen Mechanik beschrieben und anhand von vier unterschiedlichen Formalismen näher betrachtet. Es wird gezeigt, dass Graberts Formalismus (*Grabert* (1982)) eine Verallgemeinerung der anderen betrachteten Projektionsoperator-Formalismen ist. Zusätzlich werden Beispiele behandelt und Verbindungen zu der Methode der teilweisen Lösung der Bewegungsgleichungen aus *Zwanzig* (1973) hergestellt.

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