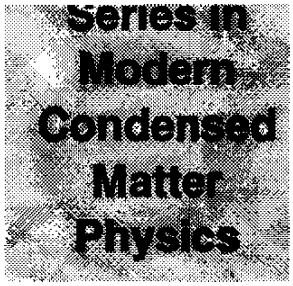

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QUANTUM DISSIPATIVE SYSTEMS

Second Edition

Ulrich Weiss

Institute for Theoretical Physics
University of Stuttgart

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Preface

Since the first publication of this book in 1993, there have been enormous research activities in quantum dissipative mechanics both experimentally and theoretically. For this reason, it has been highly desirable after the book has been sold out almost three years ago to undergo a number of extensions and improvements. I have been encouraged by the positive reception of this book by a large community and by many colleagues to write not simply an updated second edition. What came out now after all is almost a new book of roughly double content.

In an extensive rewriting, the 19 Chapters of the First Edition have been expanded by about one third to better meet the desires of both the newcomers to the field and the advanced readership, and I have added 7 new chapters. The most relevant extensions are as follows. In the first part, I have added a section on stochastic dynamics in Hilbert space and I have extended the discussion of relevant microscopic global models considerably. Now, there are also treated acoustic phonons with two-phonon coupling, a microscopic model for tunneling between surfaces, charging and environmental effects in normally conducting and superconducting tunnel junctions, and nonlinear quantum environments. Part II now contains an extended discussion of the damped harmonic oscillator (e.g., a study of the density of states is added), and new chapters on the thermodynamic variational approach and variational perturbation expansion method, and on the quantum decoherence problem. Part III, which deals with quantum-statistical decay, is extended by two chapters. In the new edition, the turnover theory to the energy-diffusion limited regime is discussed, and the treatment of dissipative quantum tunneling has been extended and improved. Ample space is now provided in Part IV to a thorough discussion of the dissipative two-state system. A number of new results on the thermodynamics and dynamics of this archetypal system are presented. An extensive discussion of electron transfer in a solvent, incoherent tunneling in the nonadiabatic regime, and single-charge tunneling is provided in a unified framework. Regarding dynamics, new sections on exact master equations, improved approximation schemes, and recent results on correlation functions have been written, and a new chapter on the driven dissipative two-state is included. Part V, which deals with the dissipative multi-state system, is completely rewritten. It now contains four chapters on quantum Brownian motion in a cosine potential, multi-state dynamics, duality symmetry, and tunneling of charge through an impurity in a quantum wire. Many new results available only very recently are presented. The about 460 references are suggestions for additional reading on particular subjects and are not intended as a comprehensive bibliography.

Stuttgart
December 1998 *Ulrich Weiss*

Acknowledgements

A number of colleagues and friends have made valuable remarks on the first edition. In this regard, I am especially grateful to Theo Costi, Thorsten Dröse, Reinhold Egger, Hermann Grabert, Peter Hänggi, Gert-Ludwig Ingold, Chi Mak, Maura Sassetti, Rolf Schilling, Herbert Spohn, and Wilhelm Zwerger. In writing the new edition, discussions with Pino Falci, Igor Goychuk, Milena Grifoni, Gunther Lang, Elisabetta Paladino, and Manfred Winterstetter have been extremely profitable, and I wish to thank them for their suggestions and for tracking down misprints. I also would like to acknowledge the preparation of a number of figures by Jochen Bauer, Gunther Lang. Jörg Rollbühler, and Manfred Winterstetter. Finally, I would like to thank Mrs. Karen Yeo as the responsible Editor of World Scientific Publishing Co. for her useful advice.

Preface to the First Edition

This book is an outgrowth of a series of lectures which I taught at the ICTP at Trieste and at the University of Stuttgart during the spring and summer of 1991. The purpose of my lectures was to present the approaches and techniques that accurately treat quantum processes in the presence of frictional influences.

The problem of *open* quantum systems has been around since the beginnings of quantum mechanics. Important contributions to this general area have been made by researchers working in fields as diverse as solid-state physics, chemical physics, biophysics, quantum measurement theory, quantum optics, nuclear and particle physics. Often, there has been used, and still is used, a language well known in one context or one field, yet sufficiently different from others that it is not altogether easy to make out the connection. Here, I offer a collection of ideas and examples rather than a comprehensive review of the topic and the history.

The central theme is the space-time functional integral or path integral formulation of quantum theory. This approach is particularly well suited for treating the quantum generalization of friction. Here we are faced to understand the behavior of a system with few quantal degrees of freedom coupled to a thermal reservoir. After integrating out the bath while keeping the system's coordinates fixed we get the influence functional describing the influence of the many bath degrees of freedom on the few relevant ones. This leads to an effective action weighting the paths of the open system in the functional integral description. Indeed, if one wishes to perform numerical computations on a rigorous level, there are no alternatives to this approach at present.

Path integration in condensed matter and chemical physics has become a growth industry in the last one or two decades. A newcomer to this thriving field may not yet be very familiar with the path integral method. Here, I do assume a knowledge of standard text book quantum mechanics and statistical mechanics augmented by a knowledge of Feynman's approach on a first introductory level. The books by Baym [1], Chandler [2], Feynman and Hibbs [3], and by Feynman [4] provide the elementary material in this regard. Further background and supplementary material on the path integral method are contained in the books by Schulman [5] and by Kleinert [6]. However, advanced mastery of these subjects is not necessary.

Some of the more sophisticated concepts, such as preparation functions, propagating functions, and correlation functions, are basic to the development as it is presented here. To cover this material at an introductory level, I make frequent use of simplified models. In this way, I can keep the mathematics relatively simple.

Many of the problems, methods, and ideas which are discussed here have become essential to the current understanding of quantum statistical mechanics. I have made

a considerable effort to make the material largely self-contained. Thus, although the theoretical tools are not developed systematically and in its full beauty, the material may be useful to many graduate students to become familiar with the field and learn the methods. For the most part, I refrain from just quoting results without explaining where they come from. With regard to citations, I have tried to give references to the historical development and also to provide a selection of the very recent important ones. But the list is surely not a comprehensive bibliography.

This book exists because of the physics I learned and enjoyed from the fertile collaboration with Hermann Grabert, Peter Hänggi, Gert-Ludwig Ingold, Peter Riseborough, and Maura Sassetti. I am particularly indebted to Maura who took time off her research to weed out points of confusion and who persistently encouraged me to finish this venture. I am also grateful to my students Reinhold Egger, Manfried Milch, Jürgen Stockburger, and Dietmar Weinmann for helpful comments concerning the presentation of many subjects discussed here and for preparing the figures.

In writing this book, I have benefited from the discussion with many companions; in particular Uli Eckern, Enrico Galleani d'Agliano, Anthony J. Leggett, Hajo Leschke, Franco Napoli, Albert Schmid, Gerd Schön, Larry Schulman, Peter Talkner, Valerio Tognetti, Andrei Zaikin, and Wilhelm Zwerger, who helped me in increasing my understanding of many of the subjects which are discussed here.

It is a pleasure to thank my teacher, colleague, and friend Wolfgang Weidlich for many fruitful discussions over the years.

Finally, and most importantly, I am deeply grateful to my wife Christel and my children Ulrike, Jan, and Meike for their infinite patience and omnipresent sympathy.

Stuttgart
October 1992 *Ulrich Weiss*

Contents

1. Introduction

Quantum-statistical mechanics is a very rich and checkered field. It is the theory dealing with the dynamical behavior of spontaneous quantal fluctuations.

When probing dynamical processes in complex many-body systems, one usually employs an external force which drives the system slightly or far away from equilibrium, and then measures the time-dependent response to this force. The standard experimental methods are quasielastic and inelastic scattering of light, electrons, or neutrons off a sample, and the system's dynamics is analyzed from the line shapes of the corresponding spectra. Other experimental tools are, e. g., spin relaxation experiments, studies of the absorptive and dispersive acoustic behavior, and investigations of transport properties. In such experiments, the system's response gives information about the dynamical behavior of the spontaneous fluctuations. Theoretically, the response is rigorously described in terms of time correlation functions. Therefore, time correlation functions are the center of interest in theoretical studies of the relaxation of non-equilibrium systems.

This book deals with the theories of open quantum systems with emphasis on phenomena in condensed matter. An essential ingredient of any particular real dissipative quantum system is the separation of a global quantum system into a subsystem, usually called the relevant part, and the environment, called the irrelevant part. In most cases of practical interest, the environment is thought to be in thermal equilibrium. The coupling to a quantum statistical environment results in a fluctuating force acting on the relevant system and reflecting the characteristics of the heat reservoir. It is the very nature of the fluctuating forces to cause decoherence and damping, and to drive everything to disorder.

While quantum mechanics was conceived as a theory for the microcosm, there is apparently no contradiction with this theory in the mesoscopic and macroscopic world. The understanding of the appearance of classical behavior within quantum mechanics is of fundamental importance. This issue is intimately connected with the understanding of decoherence. Despite the stunning success of quantum theory, there is still no general agreement on the interpretation. The main disputes circle around "measurement" and "observation".

Decoherence is the phenomenon that the superposition of macroscopically distinct states decays on a short time scale. It is omnipresent because information about quantum interference is carried away in some physical form into the surroundings. In a sense, the environmental coupling acts as a continuous measuring apparatus, leading to an incessant destruction of phase correlations. The relevance of this coupling for macroscopic systems is nowadays generally accepted by the respectable community.

An attempt is made to present the problem of dissipation in quantum mechanics in a unified form. A general framework is developed which can deal with weak and strong dissipation, and with all kinds of memory effects. The reader will find a presentation of the relevant ideas and theoretical concepts, and a discussion of a wide collection

of microscopic models. In the models and applications, emphasis is put on condensed matter physics. We have tried to use vocabulary and notation which should be fairly familiar to scientists working in chemical and condensed matter physics.

The book is divided into five parts. The following sequence of topics is adopted. The first part of the book is devoted to the general theory of open quantum systems. In Chapter 2, we review traditional approaches, such as formulations by master equations for weak coupling, operator-valued and quasiclassical Langevin equations. We also discuss attempts to interpret the dynamics of an open quantum system in terms of a stochastic process in the Hilbert space of state vectors pertaining to the reduced system. In Chapter 3, various global models are introduced. They are partly connected with microscopic models which are of relevance in condensed matter physics. Chapter 4 is devoted to the equilibrium statistical mechanics for the relevant subsystems of these models using the imaginary-time path integral approach. Chapter 5 concerns dynamics — quantum-mechanical motion, decoherence and relaxation of macroscopic systems that are far from or close to equilibrium. In particular, we discuss the concepts of preparation functions, propagating functions, and correlation functions and derive the corresponding exact formal solutions using the path integration method.

Part II with Chapters 6 – 9 covers a discussion of exactly solvable damped linear quantum systems (damped harmonic oscillator and free Brownian particle), the useful thermodynamic variational approach with extension to open nonlinear quantum systems, and a semiclassical treatment of the quantum decoherence problem for a particle traveling in a medium.

Part III deals with quantum-statistical metastability: a problem of fundamental importance in chemical physics and reaction theory. After an introduction into the problem in Chapter 10, the relevant theoretical concepts and the characteristic features of the decay are discussed in Chapters 11 to 17 . The treatment mainly relies on a thermodynamic method in which the decay rate is related to the imaginary part of the analytically continued free energy of the damped system. This allows for a uniform theoretical description in the entire temperature range. The discussion extends from high temperatures where thermal activation prevails down to zero temperature where the system can only decay by quantum-mechanical tunneling out of the ground state in the metastable well. Results in analytic form are presented where available.

In Part IV, we consider the thermodynamics and dynamics of the dissipative two-state or spin-boson system, which is the simplest nonlinear system that allows to study the interplay between quantum coherence, quantal and thermal fluctuations, and friction. After an introduction into the model in Chapter 18, the discussion in Chapter 19 is focused on equilibrium properties for a general form of the system-reservoir coupling. In particular, the partition function is discussed and the specific heat and static susceptibility are studied. The relationship with Kondo and Ising models is explained. Chapter 20 is devoted to the electron transfer problem in a solvent, nonadiabatic tunneling under exchange of energy, and single charge tunneling in the presence of an electromagnetic environment. Chapter 21 deals with the dissi-

pative two-state dynamics. Different kinds of initial preparations of the system-plus-reservoir complex are treated and exact formal expressions for the system's dynamics in the form of series expressions and generalized master equations are derived. Ample space is devoted to the discussion of non-equilibrium and equilibrium correlation functions, and to adequate approximate treatments in the various regions of the parameter space. Part IV is concluded with a chapter on the dynamics of the dissipative two-state system under exposure to time-dependent external fields.

The last part reviews quantum transport in a dissipative multi-state system. In Chapters 23 and 24, we introduce the relevant global models, develop the general formalism and derive exact formal expressions describing the system's dynamics for factorizing and thermal initial states. Chapter 25 provides a discussion of a duality symmetry between the weak- and strong-binding representations which becomes an exact self-duality in the so-called Ohmic scaling limit. We show that self-duality offers the possibility to construct the exact scaling function for the nonlinear mobility at zero temperature. The book closes with a chapter on charge transport across a weak or strong impurity in a quantum wire. It is shown that this model maps on the multi-well system coupled to an Ohmic heat bath. Thus, the results of the latter model can be directly transferred to the impurity scattering problem.

We have tried to concentrate on models which are simple enough to be largely tractable by means of analytical methods. There are, however, important examples where numerical computations have given clues to the analytical solution of a problem. If one wishes to calculate the full dynamics of the global system, one is faced with the problem that the number of basis states is growing exponentially. Therefore, even on supercomputers, the number of reservoir modes which can be treated numerically exactly, is rather limited. When the number of bath modes is above ten or even tends to infinity, an inclusive description of the environmental effects, e.g., in terms of the influence functional method (cf. Chapters 4 and 5) is indispensable. Various numerical schemes developed within the framework of the influence functional approach are available. The most valuable numerical tool in many-body quantum theory is probably the path integral Monte Carlo simulation method. Unfortunately, in simulations of the real-time quantum dynamics, the numerical stability of long-time propagation is spoilt by the destructive interference of different paths contributing to the path sum. This so-called *dynamical sign problem* is intrinsic in real-time quantum mechanics, and is characterized by an exponential drop of the signal-to-noise ratio with increasing propagation time.

In recent years, considerable progress in reducing the sign problem has been achieved by implementation of blocking algorithms in quantum Monte Carlo simulations based on a Trotter split-up of the elementary propagator. A possible strategy consists in sampling "blocks" of which the corresponding average sign is nonzero, instead of single states. This method always reduces the sign problem [C. H. Mak and R. Egger, Adv. Chem. Phys. **93**, 39 (1996)]. Alternatively, one may use iterative procedures which are based on systematic approximations. In the so-called tensor-

propagator approach, a maximal correlation time of the influence functional interactions is introduced [N. Makri, J. Math. Phys. **36**, 2430 (1995)]. In the so-termed path class approach, the exact summation of a class of paths is approximated by a low-order cumulant expansion of averages of the path class history [M. Winterstetter and W. Domcke, Chem. Phys. Letters **236**, 455 (1995)]. We have refrained from adding sections which deal with numerical methods in detail. Where appropriate, we give relevant information and literature.

After all, the reader may not find a comprehensive account of what interests him most. Since the number of articles in this general field has become enormous in recent years, a somewhat arbitrary choice among the various efforts is inevitable. My choice of topics is just one possibility. It reflects, to some extent, the author's personal valuation of an active and rapidly developing area in science.

PART I
GENERAL THEORY OF OPEN QUANTUM SYSTEMS

2. Diverse limited approaches: a brief survey

Often in condensed phases, a rather complex physical situation can adequately be described by a global model system consisting of only one or few relevant dynamical variables in contact with a huge environment, of which the number of degrees of freedom is very large or even infinity. If we are interested in the physical properties of the *small* relevant system alone, we have to handle this system as an open system. In recent years, a variety of theoretical methods for open quantum systems has been developed and employed. The emphasis in this book is on the functional integral approach to open quantum systems. This method has turned out to be very powerful and has found broad application. Nevertheless, I find it appropriate to begin with a brief survey of various other formalisms. Clearly, the short discussion given subsequently can not do justice to all of them. However, I hope that the interested reader will be able to get a line along the given references for deeper studies. I find it appropriate to begin with a brief discussion of the classical regime.

2.1 Classical Langevin equation

The dynamics of a classical open system is conveniently described by a Langevin equation in which the effects of the environment are encapsulated in a frictional force and in a fluctuating force. Consider for simplicity an open system with a single degree of freedom $q(t)$. For *linear*, i.e., state-independent dissipation, the frictional force is a linear functional of the history of the velocity $\dot{q}(t)$. The stochastic force $\xi(t)$ obeys Gaussian statistics and is therefore fully characterized by the ensemble averages

$$\langle \xi(t) \rangle \;=\; 0\,, \qquad \langle \xi(t)\xi(t') \rangle_{\rm cl} \;\equiv\; \mathcal{X}_{\rm cl}(t-t')\,. \tag{2.1}$$

For a white noise source, which originates from a heat reservoir at temperature T with zero memory time, the stochastic force is δ-correlated according to

$$\mathcal{X}_{\rm cl}(t-t') \;=\; 2M\gamma k_{\rm B}T\delta(t-t')\,, \tag{2.2}$$

and the friction force is local in time. Thus the classical Langevin equation reads

$$M\ddot{q}(t) + M\gamma\,\dot{q}(t) + V'(q) \;=\; \xi(t)\,. \tag{2.3}$$

A time-local friction term which is proportional to the velocity is usually called Ohmic because of the correspondence with a series resistor in an electrical circuit. The dynamical equation (2.3) describes, for example, a heavy Brownian particle with mass M immersed in a fluid of light particles and driven by a systematic force $-V'(q)$, where $V(q)$ is an externally applied potential. Equation (2.3) together with the relations (2.1) and (2.2) forms the basis for the theory of Brownian motion since the seminal studies by Einstein, Langevin and Smoluchowski. The early work on Brownian motion theory was reviewed in an excellent article by Chandrasekhar [7].

In many cases of practical interest, the heat reservoir is a source of noise with a finite memory time. For colored noise, the dynamics is described by the generalized Langevin equation

$$M\ddot{q}(t) + M\int_{-\infty}^{t} dt'\,\gamma(t-t')\,\dot{q}(t') + V'(q) \;=\; \xi(t)\,. \tag{2.4}$$

The mean effect of the reservoir on the heavy particle is contained in the memory friction force expressed in terms of the causal damping kernel, $\gamma(t) = 0$ for $t < 0$. The fluctuating force $\xi(t)$ thus vanishes on average. The stochastic nature of $\xi(t)$ is again described by the autocorrelation function $\langle\xi(t)\xi(0)\rangle_{\rm cl}$. The frequency-dependent damping coefficient[1] [$\tilde{\gamma}'(\omega) = \mathrm{Re}\,\tilde{\gamma}(\omega)$ and $\tilde{\gamma}''(\omega) = \mathrm{Im}\,\tilde{\gamma}(\omega)$]

$$\tilde{\gamma}(\omega) \;\equiv\; \tilde{\gamma}'(\omega) + i\,\tilde{\gamma}''(\omega) \;=\; \int_{-\infty}^{\infty} dt\,\gamma(t)\,e^{i\omega t} \tag{2.5}$$

is connected with $\langle\xi(t)\xi(0)\rangle_{\rm cl}$ by the Green-Kubo formula [8]

$$\tilde{\gamma}(\omega) \;=\; \frac{1}{Mk_{\rm B}T}\int_{0}^{\infty} dt\,\langle\xi(t)\xi(0)\rangle_{\rm cl}\,e^{i\omega t}\,. \tag{2.6}$$

Hence the power spectrum of the classical stochastic force

$$\tilde{\mathcal{X}}_{\rm cl}(\omega) \;\equiv\; \int_{-\infty}^{\infty} dt\,\mathcal{X}_{\rm cl}(t)\cos(\omega t) \;=\; \int_{-\infty}^{\infty} dt\,\langle\xi(t)\xi(0)\rangle_{\rm cl}\cos(\omega t) \tag{2.7}$$

is given in terms of the real part $\tilde{\gamma}'(\omega)$ of the damping function by the relation

$$\tilde{\mathcal{X}}_{\rm cl}(\omega) \;=\; 2Mk_{\rm B}T\,\tilde{\gamma}'(\omega)\,. \tag{2.8}$$

This is a version of the classical fluctuation-dissipation or Nyquist theorem.

As any phenomenological equation, Eq. (2.4) has a restricted range of validity. It can hold, at best, only for times long compared to the memory times of the environment, as it will become clear in Subsection 3.1.3. On the other hand, we expect that at sufficiently low temperatures all types of quantum effects should occur. Now, since the standard procedure of quantization relies upon the existence of a Lagrangian or a Hamiltonian function for the system, the question arises: how can one reconcile dissipation with the canonical scheme of quantization?

[1] Throughout this book, we use for the Fourier transform the normalization and sign convention in the exponent as in Eq. (2.5).

2.2 New schemes of quantization

The equation of damped motion (2.3) can not be obtained from the application of Hamilton's principle unless the Lagrangian has an explicit time dependence. The use of time-dependent Lagrangians or Hamiltonians would permit us to use the standard schemes of quantization directly. Historically, the first researchers taking this path were Caldirola [9] and Kanai [10] who employed a time-dependent mass chosen in such a way that a friction term appears in the corresponding classical equation of motion. However, this procedure does not properly handle the uncertainty principle [11]. As the resumé of diverse studies, it is generally accepted now that dissipation cannot be described adequately by simply introducing a time-dependent mass.

Many approaches to open quantum systems were introduced over the last thirty years. The variety of attempts falls into three main categories. One either modifies the procedure of quantization, or one uses the system-plus-reservoir approach, or a stochastic Schrödinger equation for state vectors is employed. The third category is discussed in Section 2.4. Among the first group, Dekker [12] proposed a theory with a canonical quantization procedure for complex variables, thereby reproducing the Fokker-Planck equation for the Wigner distribution function. However, some *ad hoc* assumptions in the theory seem questionable, such as the introduction of noise sources in the equations of position and momentum. Kostin [13] introduced a theory with a nonlinear Schrödinger equation. The same equation was found later by Yasue [14] using Nelson's stochastic quantization procedure [15]. However, this theory violates the superposition principle, and also yields some dubious results such as stationary damped states. Apart from the fact that the theoretical foundations are completely unclear, these approaches can reproduce, at best, known results only for very special cases, such as weakly damped linear systems. Therefore, all attempts of the first group can be assessed to have failed. We shall not consider them further here.

The more natural, and also more successful approach has been to regard the system and the environment as the constituents of a conservative global system which obeys the standard rules of quantization. In this picture, friction comes about by the transfer of energy from the "small" system to the "large" environment. The energy, once transferred, dissipates into the environment and is not given back within any physically relevant period of time.

2.3 Traditional system–plus–reservoir methods

Common approaches to open quantum systems based on system-plus-reservoir models are generally divided into two classes. Working in the Schrödinger picture, the dynamics is conventionally described in terms of generalized quantum master equations for the reduced density matrix or density operator [16] – [18]. Working in the Heisenberg picture, the description is given in terms of generalized Langevin equations for the relevant set of operators of the reduced system [19] – [21].

2.3.1 *Quantum-mechanical master equations for weak coupling*

The starting point of this method is the familiar Liouville equation of motion for the density operator $W(t)$ of the global system,

$$\dot{W} \;=\; -(i/\hbar)\,[\,H, W(t)\,] \;\equiv\; \mathcal{L}\,W(t)\,, \tag{2.9}$$

where H is the Hamiltonian of the total system, and where the second equality defines the Liouville operator $\mathcal{L}$. Next, assume that the Hamiltonian H and the Liouvillian $\mathcal{L}$ of the total system are decomposed as

$$H \;=\; H_{\rm S} + H_{\rm R} + H_{\rm I}\,; \qquad \mathcal{L} \;=\; \mathcal{L}_{\rm S} + \mathcal{L}_{\rm R} + \mathcal{L}_{\rm I}\,. \tag{2.10}$$

The individual parts refer to the free motion of the relevant system and of the reservoir, and to the interaction term, respectively. Employing a certain projection operator P, chosen as to project on the relevant part of the density matrix, the full density operator is reduced to an operator acting only in the space of the macroscopically relevant variables,

$$\rho(t) \;=\; PW(t)\,. \tag{2.11}$$

The operator $\rho(t)$ is usually called *reduced density* operator. For systems with the Hamiltonian form (2.10), the projection operator contains a trace operation over the reservoir coordinates. By means of the projection operator P, the density operator can be decomposed into the relevant part $\rho(t)$ and the irrelevant part $(1-P)W(t)$,

$$W(t) \;=\; \rho(t) + (1-P)W(t)\,; \qquad P^2 \;=\; P\,. \tag{2.12}$$

Upon substituting the decomposition (2.12) into Eq. (2.9), and acting on the resulting equation from the left with the operator P and with the operator $1-P$, respectively, we obtain two coupled equations for the relevant part $\rho(t)$ and the irrelevant part $(1-P)W(t)$. A closed equation for $\rho(t)$ is obtained by inserting the formal integral for $(1-P)W(t)$ into the first equation. We then finally arrive at the formally exact generalized master equation, the *Nakajima-Zwanzig equation* [16, 17]

$$\begin{aligned}\dot{\rho}(t) \;&=\; P\mathcal{L}\,\rho(t) + \int_0^t dt'\, P\mathcal{L}\,\exp[(1-P)\mathcal{L}\,t']\,(1-P)\mathcal{L}\,\rho(t-t') \\ &\quad + P\mathcal{L}\,\exp[(1-P)\mathcal{L}\,t]\,(1-P)W(0)\,.\end{aligned} \tag{2.13}$$

The generalized master equation is an inhomogeneous integro-differential equation in time. It describes the dynamics of the open (damped) system in contact with the reservoir $\mathcal{R}$. Observe that the inhomogeneity in Eq. (2.13) still depends on the initial value of the irrelevant part $(1-P)W(0)$. In applications, it is attempted to choose the projection operator in such a way that the irrelevant part of the initial state $(1-P)W(0)$ can be disregarded. Assuming further that P commutes with $\mathcal{L}_{\rm S}$ one then finds the homogeneous time-retarded master equation

$$\dot{\rho}(t) \;=\; P(\mathcal{L}_{\rm S} + \mathcal{L}_{\rm I})\rho(t) \;+\; \int_0^t dt'\, P\mathcal{L}_{\rm I}\, e^{(1-P)\mathcal{L}\,t'}\,(1-P)\mathcal{L}_{\rm I}\rho(t-t')\,. \tag{2.14}$$

The first (instantaneous) term describes the reversible motion of the relevant system while the second (time-retarded) term brings on irreversibility. Equation (2.14) is still too complicated for explicit evaluation. First, the kernel of (2.14) contains any power of $\mathcal{L}_{\rm I}$. Secondly, the dynamics of ρ at time t depends on the whole history of the density matrix. In order to surmount these difficulties, one usually considers the kernel of Eq. (2.14) only to second order in $\mathcal{L}_{\rm I}$. Disregarding also retardation effects, one finally arrives at the Born-Markov master equation

$$\dot{\rho}(t) \;=\; P(\mathcal{L}_{\rm S}+\mathcal{L}_{\rm I})\rho(t) \;+\; \int_0^t dt'\, P\mathcal{L}_{\rm I}\, e^{(1-P)(\mathcal{L}_{\rm S}+\mathcal{L}_{\rm R})\,t'}\,(1-P)\mathcal{L}_{\rm I}\,\rho(t)\;. \qquad (2.15)$$

Master equations of this form were successfully used to describe weak-damping phenomena, for instance in quantum optics or spin dynamics. Various excellent reviews of this sort of approach including many applications are available in Refs. [22] – [30]. While the Markov assumption can easily be dropped, the more severe limitation of this method is the Born approximation for the kernel. The truncation of the Born series at second order in the interaction $\mathcal{L}_{\rm I}$ effectively restricts the application of these generalized master equations to weakly damped systems with relaxation times that are large compared to the relevant time scales of the reversible dynamics.

In the eigenstate basis of $H_{\rm S}$, the density matrix obeys in the Born-Markov limit the so-called *Redfield* equations [31, 26, 32]

$$\dot{\rho}_{nm}(t) \;=\; -i\omega_{nm}\rho_{nm}(t) - \sum_{k,l} R_{nmkl}\rho_{kl}(t)\;. \qquad (2.16)$$

The first term represents the reversible motion in terms of the transition frequencies ω_{nm}, and the second term describes relaxation. The Redfield relaxation tensor reads

$$R_{nmkl} \;=\; \delta_{lm}\sum_r \Gamma^{(+)}_{nrrk} + \delta_{nk}\sum_r \Gamma^{(-)}_{lrrm} - \Gamma^{(+)}_{lmnk} - \Gamma^{(-)}_{lmnk}\;. \qquad (2.17)$$

The rates are given by the Golden Rule expressions

$$\begin{aligned}
\Gamma^{(+)}_{lmnk} &= \hbar^{-2}\int_0^\infty dt\, e^{-i\omega_{nk}t}\langle \tilde{H}_{{\rm I},lm}(t)\tilde{H}_{{\rm I},nk}(0)\rangle\;,\\
\Gamma^{(-)}_{lmnk} &= \hbar^{-2}\int_0^\infty dt\, e^{-i\omega_{lm}t}\langle \tilde{H}_{{\rm I},lm}(0)\tilde{H}_{{\rm I},nk}(t)\rangle\;.
\end{aligned} \qquad (2.18)$$

Here, $\tilde{H}_{\rm I}(t) \;=\; \exp(iH_{\rm R}t/\hbar)H_{\rm I}\exp(-iH_{\rm R}t/\hbar)$ is the interaction in the interaction picture, and the bracket denotes thermal average of the bath degrees of freedom.

The Redfield equations (2.16) are well-established in wide areas of physics and chemistry, e.g., in nuclear magnetic resonance (NMR), in optical spectroscopy, and in laser physics. In NMR, one deals with the externally driven dynamics of the density matrix for the nuclear spin [33, 34, 35]. In optical spectroscopy, a variant of the Redfield equations are the optical Bloch equations [36, 37].

Multilevel Redfield theory has been applied to the electron transfer dynamics in condensed phase reactions by several authors [38].

Markovian reduced density matrix (RDM) theory has been also utilized in the diabatic state representation [39]. Denoting electronic-vibrational direct-product states in the diabatic representation[2] by α, $\beta, \cdots$, the RDM equations of motion read

$$\dot{\rho}_{\alpha\beta}(t) = -i\omega_{\alpha\beta}\rho_{\alpha\beta}(t) - \frac{i}{\hbar}\sum_{\nu}[V_{\alpha\nu}\rho_{\nu\beta}(t) - V_{\nu\beta}\rho_{\alpha\nu}(t)] - \sum_{\nu,\sigma} R_{\alpha\beta\nu\sigma}\rho_{\nu\sigma}(t) . \quad (2.19)$$

The $\omega_{\alpha\beta}$ are the transition frequencies between unperturbed diabatic surfaces, the $V_{\alpha\beta}$ are the matrix elements of the diabatic interstate coupling, and the relaxation tensor $R_{\alpha\beta\nu\sigma}$ describes relaxation of the diabatic electronic-vibrational states. For electron transfer processes, the diabatic surfaces can often be taken as harmonic, which simplifies the calculation of the relaxation tensor drastically. The master equation (2.19) in the diabatic basis is especially useful when the interstate coupling is weak or moderate. In contrast to Redfield theory in the system's eigenstate basis, the computation of the Redfield tensor in the diabatic basis, Eq. (2.19), is without difficulties even for multimode vibronic-coupling systems [42]. When the RDM approach is applied to complex systems, the dimension N of the Hilbert space of the relevant system H_S is possibly very large. Since the density matrix scales with N^2 and the relaxation tensor with N^4, the computational problem may become easily nontrivial. The so-called Monte-Carlo wave function propagation or quantum jump method discussed below in Section 2.4, which is equivalent to the Born-Markov RDM method, provides a considerably more favorable scaling of the computational costs with the number of states than the direct integration of the Redfield equations.

Within the conception of quantum mechanics, the time evolution of the density operator of a closed system is a unitary map. If the system is open, the possible transformations are thought to be "completely positive" [43, 29], $\rho \to \sum_n O_n \rho O_n^\dagger$. Here $\{O_n\}$ is a set of linear operators on the reduced state space, restricted only by $\sum_n O_n^\dagger O_n = 1$, which guarantees that $\mathrm{tr}\,\rho$ does not change. The most general form of generators $\mathcal{L}$, $\dot{\rho}(t) = \mathcal{L}\rho(t)$, preserving complete positivity of density operators and conveying time-directed irreversibility is established by the Lindblad theory [43]. The Lindblad form of the quantum master equation for an open system reads

$$\frac{d\rho(t)}{dt} = -\frac{i}{\hbar}[H_S, \rho(t)] + \frac{1}{2}\sum_j \left\{[L_j\rho(t), L_j^\dagger] + [L_j, \rho(t)L_j^\dagger]\right\} . \quad (2.20)$$

The first term represents the reversible dynamics of the relevant system. The Lindblad operators L_j describe the effect of the environment on the system in Born-Markov approximation. In concrete applications of Eq. (2.20), the L_j transmit emission and absorption processes. For linear dissipation, the simplest form of a Lindblad operator is a linear combination of a coordinate and a momentum operator [44],

$$L = \mu q + i\nu p , \qquad L^\dagger = \mu q - i\nu p , \quad (2.21)$$

where μ and ν are c-numbers. Explicit temperature-dependent expressions for μ and ν are obtained for the damped harmonic quantum oscillator by matching the dissipation

[2] The concepts of diabatic states are discussed in recent reviews [40, 41, 42].

terms of the Lindblad master equation with corresponding expressions of this exactly solvable model (cf. Chapter 6) in the Born-Markov limit [45].

Complete positivity of reduced density operators is considered as a strict guideline by researchers working on stochastic Schrödinger equations (see Section 2.4). However, complete positivity of the RDM is an artefact of the product initial condition $W = \rho \otimes \rho_R$ for the global density operator, as shown by Pechukas [46, a]. Product initial conditions are only appropriate to weak coupling. For correlated initial states, the reduced dynamics need not be completely positive. This is consistent with the discovery in Ref. [46, b] that a fast "slippage" of the initial condition must occur before the reduced dynamics looks Markovian. The slippage captures the effects of the actual non-Markovian evolution in a short transient regime (see also [46, c]). The Markovian master equation holds only in a subspace in which fast components are disregarded. These findings have been confirmed in a recent study of the exactly solvable damped harmonic oscillator [47]. Using the exact path integral solution, it has been shown that in general there is no exact dissipative Liouville operator describing the dynamics of the oscillator in terms of an exact master equation that is independent of the initial preparation. Exact non-stationary Liouville operators can be found only for particular preparations. Time-independent Liouville operators which are valid for arbitrary preparation of the initial state can be extracted only in a sub-space where the fast transient components have already decayed. However, the Liouville operators are still not of the Lindblad form. The Lindblad master equation is obtained only when the weak-coupling limit is performed and a coarse graining in time is carried out. It is perfectly obvious from the study of this exactly solvable model that one should not attach the fundamental significance to the Lindblad master equation as attributed by circles of the "stochastic Schrödinger equation" community. Besides the Markov approximation and the weak-coupling limit, there is another severe limitation of the usefulness of the above quantum master equations. Namely, the relaxation dynamics towards the equilibrium state $\rho_\beta = P W_\beta$ [$W_\beta = Z_\beta^{-1} \exp(-\beta H)$ is the canonical equilibrium density matrix of the global system] is correctly described only when the system's relaxation times are large compared to the thermal time $\hbar\beta$. The latter time scale enters into the problem through the Matsubara frequencies. However, this limitation is easily violated for low temperatures, in particular when relaxation occurs by quantum tunneling (cf. , e.g., the discussion in Chapters 6 and 17).

In conclusion, the Born-Markov quantum master equation method provides a reasonable description in many cases, such as in NMR, in laser physics, and in a variety of chemical reactions. However, this method turned out to be not useful in most problems of solid state physics at low temperatures for which neither the Born approximation is valid nor the Markov assumption holds.

2.3.2 Operator Langevin equations for weak coupling

Just as we projected the density matrix $W(t)$ of the global system onto the relevant part $\rho(t)$, we may proceed in the Heisenberg picture by projecting the operators of

the global system on the set of macroscopically relevant operators. The various efforts in studying the dynamics of these operators have been described by Gardiner [49].

Let us denote the set of operators of the global system by $\{X\}$ and the set of macroscopically relevant operators governing the open system by $\{Y\}$. Now consider the operators X_i and Y_μ as elements $|X_i)$ and $|Y_\mu)$ in the Liouville space Λ.[3] At time $t = 0$, the operators $\{Y\}$ span a subspace Λ_Y of the Liouville space Λ. We use the convention that an operator in the Heisenberg representation without time argument denotes the operator at time zero. Next, it is convenient to define a time-independent projection operator which projects onto Λ_Y,

$$\mathcal{P} = \sum_{\mu,\nu} |Y_\mu)\, g_{\mu\nu}\, (Y_\nu| \,; \qquad \mathcal{P}^2 = \mathcal{P} \,. \tag{2.22}$$

The metric $g_{\mu\nu}$ is the inverse of the scalar product $(Y_\mu|Y_\nu)$ which has to be chosen appropriately in practical calculations. For quantum statistical linear response and relaxation problems, a suitable form is the Mori scalar product [21, 48]

$$(Y_\mu|Y_\nu) \equiv \beta^{-1} \int_0^\beta d\lambda \, \langle \exp(-\lambda H)\, Y_\mu^\dagger \exp(\lambda H)\, Y_\nu \rangle \,. \tag{2.23}$$

The angular brackets denote average with respect to the canonical ensemble of the global system $W_\beta = Z_\beta^{-1} \exp(-\beta H)$, and $\beta = 1/k_B T$. The superoperator $\mathcal{P}$ projects onto the subspace Λ_Y according to

$$\mathcal{P}\,|X_i) = \sum_{\mu,\nu} |Y_\mu)\, g_{\mu\nu}\, (Y_\nu|X_i) \,. \tag{2.24}$$

Acting now from the left with $\mathcal{P}$ and with $1-\mathcal{P}$ on the Heisenberg equation of motion

$$|\dot{X}_i) = \mathcal{L}\,|X_i) \,, \tag{2.25}$$

where $\mathcal{L}$ is the Liouville superoperator, and eliminating $(1-\mathcal{P})|X_i)$ with the aid of the exact formal solution, it is straightforward to derive for $Y_\mu(t)$ the generalized Langevin equation

$$\dot{Y}_\mu(t) = i \sum_\nu Y_\nu(t)\, \Omega_{\nu\mu}(t) - \sum_\nu \int_0^t ds\, Y_\nu(t-s)\, \gamma_{\nu\mu}(s) + \xi_\mu(t) \,. \tag{2.26}$$

These equations form a system of coupled integro-differential equations for the set of operators $\{Y\}$. They have been popularized in the literature as the Mori equations. The generally temperature-dependent drift matrix $\Omega_{\nu\mu}(t)$ is given by

$$i\,\Omega_{\nu\mu}(t) = \sum_\rho g_{\nu\rho}\, (Y_\rho|\dot{Y}_\mu(t)) \,. \tag{2.27}$$

The stochastic force $\xi_\nu(t)$ is a functional of the *irrelevant* operators,

[3] See Ref. [48] for a review of the formulation of quantum mechanics in Liouville space.

$$\xi_\nu(t) \;=\; \exp[(1-\mathcal{P})\mathcal{L}\,t\,](1-\mathcal{P})\dot{X}_\nu(t)\;. \tag{2.28}$$

Finally, the memory matrix is expressed in terms of the correlation function of the stochastic force as

$$\gamma_{\nu\mu}(t) \;=\; \sum_\rho g_{\nu\rho}(\xi_\rho|\xi_\mu(t))\;. \tag{2.29}$$

The actual computation of the fluctuating force and of the memory matrix is again restricted to weak coupling. Altogether, this approach is subject to exactly the same limitations we encountered above in the master equation method.

In conclusion, it is important in the Mori formalism that the complete set of macrovariables spans the subspace. Otherwise, the fluctuating force contains slowly varying components, and the separation of time scales is incomplete.

2.3.3 Quantum and quasiclassical Langevin equation

One further approach consists in attempting to generalize the classical Langevin equation for a Brownian particle to the quantum case [20, 50, 51]. The quantum mechanical version of the Langevin equation for the coordinate operator reads[4]

$$M\frac{d^2\widehat{q}(t)}{dt^2} + M\int_{t_0}^{t} dt'\,\gamma(t-t')\frac{d\widehat{q}(t')}{dt'} + V'(\widehat{q}) \;=\; \widehat{\xi}(t)\;, \tag{2.30}$$

where $\widehat{\xi}(t)$ is the Gaussian random force operator with correlation expectation value [we define $\langle\widehat{O}\rangle \equiv \mathrm{tr}_{\mathrm{R}}\{e^{-\beta\widehat{H}_{\mathrm{R}}}\widehat{O}\}$ where R refers to the reservoir]

$$\langle\widehat{\xi}(t)\widehat{\xi}(0)\rangle \;=\; \frac{\hbar M}{\pi}\int_0^\infty d\omega\,\omega\widetilde{\gamma}'(\omega)\Big(\coth(\omega\hbar\beta/2)\cos(\omega t) - i\sin(\omega t)\Big)\;. \tag{2.31}$$

The equation (2.30) can be derived, e. g., for the linear response oscillator model discussed below in Section 3.1 [50]. One can even show that the form (2.31) of the correlation is a general result of the fluctuation-dissipation theorem (cf. Section 6.2) and is therefore independent of the model.[5] Benguria and Kac [52], and Ford and Kac [50] argued that the system approaches the correct equilibrium state for the form (2.30) with (2.31) and Gaussian noise. Recently, the quantum Langevin equation (2.30) has been derived for the white-noise case from the Feynman-Vernon forward-backward path integral discussed below in Section 5.1 [53].

In the *quasiclassical* Langevin equation (QLE) [19, 54], the operator-valued quantities in Eq. (2.30) are replaced by c-numbers, but the Gaussian property of the stochastic force and the correlation (2.31) are retained. We then end up at the generalized classical Langevin equation (2.4) in which the power spectrum of the symmetrized force autocorrelation function has the quantum mechanical form

$$\widetilde{\mathcal{X}}(\omega) \;\equiv\; \int_{-\infty}^{\infty} dt\,\langle\xi(t)\xi(0)\rangle\cos(\omega t) = M\hbar\omega\coth\left(\frac{\hbar\omega}{2k_{\mathrm{B}}T}\right)\widetilde{\gamma}'(\omega)\;. \tag{2.32}$$

[4] Here we dropped a term which depends on the initial condition and which decays on a time scale given by the memory time of the reservoir (See the discussion in Subsection 3.1.3).

[5] The Gaussian property of the force operator does not seem to follow from such general considerations, but is implied by a harmonic oscillator reservoir.

In Section 5.5 we briefly sketch the derivation of the QLE within the path integral method following the approach by Schmid [54]. It will become clear from the derivation that the QLE is exact (apart from disregarding a term describing the initial transient behavior) when the external force is harmonic (see also Ref. [19]). The QLE gives a reasonable description for systems which are nearly harmonic [55, 56]. However, the predictions of the QLE are unreliable when the unharmonicity of the potential is of crucial importance like, for instance, in quantum tunneling. The mere insertion of the quantum noise (2.32) into a classical equation is insufficient to render a proper description of the quantum statistical decay of a metastable state [55].

When the unharmonicity of the potential is relevant, the most successful approach is the functional integral description. Like in the classical regime, the dissipative system is considered to interact with a complex environment, and the "complete universe" formed by the system plus environment is assumed to be conservative so that it can be quantized in the standard way. For equations of motion which are linear in the bath coordinates, the environment can easily be eliminated. Thus one obtains closed equations for the damped system alone. In the path integral description, the environment reveals itself through an influence functional depending on the spectral properties of the environmental coupling and on temperature. A general discussion of the influence functional method is presented in Chapters 4 and 5.

2.3.4 Phenomenological methods

Often, a physical or chemical system cannot be characterized by a simple model Hamiltonian of the form (2.10), or the Hamiltonian is simply unknown. In such situations, it is sometimes useful to describe the dissipative quantum dynamics on a phenomenological level. For instance, one may introduce a dynamical description of the system in terms of occupation probabilities $p_n(t)$ of energy levels or of spatially localized states, etc., rather than in terms of complex probability amplitudes or wave functions, or the full reduced density matrix $\rho_{nn'}$. Then, the relaxation dynamics of a macroscopic system is described by a *Pauli master equation* for $p_n(t) \equiv \rho_{nn}(t)$,

$$\dot{p}_n(t) \;=\; \sum_m \left[\, A_{nm}\, p_m(t) - A_{mn}\, p_n(t) \,\right] . \tag{2.33}$$

The first term on the r.h.s. describes the gain and the second term the loss of probability in the state n. In this formulation, knowledge of the full set of transition rates $\{A_{nm}\}$ is requisite in order to have a complete description of the relaxation process. The transition rates may be inferred, e. g., from standard quantum mechanical perturbation theory, or from experimental data, or they may be chosen by a phenomenological ansatz. The Pauli master equation (2.33) has found widespread application to the study of rate dynamics in physics, chemical kinetics, and biology.

In the quantum coherence regime, off-diagonal matrix elements of the density matrix become relevant. Nevertheless, the full coherent dynamics of the populations can still be formulated in terms of dynamical equations for diagonal matrix elements. However, the corresponding master equation is time-nonlocal (see Section 21.3).

2.4 Stochastic dynamics in Hilbert space

In recent years, there have been made numerous attempts to postulate non-Hamiltonian dynamics as a fundamental modification of the Schrödinger equation in order to explain the spontaneous stochastic collapse of the wave function and the appearance of a "classical world" (cf. for a survey the article by I.-O. Stamatescu in Ref. [57]). In these approaches, the non-unitary dynamics of open quantum systems is interpreted in terms of a fundamental stochastic process in the Hilbert space of state vectors pertaining to the system. To retain the standard probability rules, the respective dynamical equations become inevitably nonlinear. The evolution of state vectors is considered as a stochastic Markov process, and the covariance matrix of the state vector is taken as the density operator. The stochastic process is usually constructed in such a way that the equation of motion of the density operator is the familiar Markovian quantum master equation in Lindblad form (2.20), e.g., the optical Bloch equations [36, 37]. First of all, the approaches of this type were introduced on phenomenological grounds. Later on, a fundamental significance has been allocated to the "stochastic Schrödinger equations" by several authors, in particular to propose explanation of the omnipresent decoherence phenomena observed in real quantum systems. The above scheme does not lead to a definite stochastic representation of the dynamics of the reduced system in Hilbert space, even though the Markov approximation is made, since the stochastic process is not unambiguously determined by merely fixing the covariance. An infinity of different realizations is possible. Basically, one may distinguish two classes of stochastic models for the evolution of state vectors in the Schrödinger picture. In the first class of stochastic Schrödinger equations, the stochastic increment is a diffusion process, the so-called Wiener process. In the second class, the evolution of the state vector is represented as a stochastic process of which the realizations are piecewise deterministic paths, and the smooth segments are interruped by stochastic sudden jump processes [58].

The *quantum-state diffusion* (QSD) method proposed by Gisin [59] and developed further by Gisin, Percival and coworkers [60, 61] belongs to the first class. The QSD method is based upon a correspondence between the solutions of the master equation for the ensemble density operator ρ and the solutions of a Langevin-Itô diffusion equation for the normalized pure state vector $|\psi>$ of an individual system of the ensemble. If the master equation has the Lindblad form (2.20), then the corresponding QSD equation is the nonlinear stochastic differential equation

$$|d\psi> = -\frac{i}{\hbar} H|\psi> dt + \sum_j \Big(< L_j^\dagger > L_j - \tfrac{1}{2} L_j^\dagger L_j - \tfrac{1}{2} < L_j^\dagger >< L_j > \Big)|\psi> dt + \sum_j \Big(L_j - < L_j > \Big)|\psi> d\xi_j \,, \tag{2.34}$$

where $< L_j > \equiv <\psi|L_j|\psi>$ is the quantum expectation.[6] The first sum describes the nonlinear drift of the state vector in the state space and the second sum the random

[6] We constantly use the symbol $|\cdots>$ for a pure state, and $\langle\cdots\rangle$ for an ensemble average.

fluctuations. The $d\xi_j$ are complex differential variables of a Wiener process satisfying

$$\langle d\xi_j \rangle = 0 \,, \qquad \langle d\xi_j \, d\xi_k \rangle = 0 \,, \qquad \langle d\xi_j^* \, d\xi_k \rangle = \delta_{j,k} \, dt \,, \tag{2.35}$$

where $\langle \cdots \rangle$ represents a mean over the ensemble. The density operator is given by the mean over the projectors onto the quantum states of the ensemble

$$\rho \;=\; \langle \, |\psi><\psi| \, \rangle \,. \tag{2.36}$$

A relativistic quantum state diffusion model has been proposed in Ref. [62].

There have been made also attempts to describe the stochastic evolution of the state vector in terms of a stochastic differential equation with a linear drift [63].

The Monte-Carlo wave function simulation or *quantum jump methods* proposed by Diósi [64], by Dalibard, Castin, and Mølmer [65], by Zoller and coworkers [66], and by Carmichael *et al.* [67] belong to the second class. In these related methods, the Schrödinger equation is supplemented by a non-Hermitean term and by a stochastic term undergoing a Poisson jump process. Because of the non-unitary time evolution of the state vector under a non-Hermitean Hamiltonian, the trace of the density operator is no more conserved. Conservation of probability is restored again and again by imposing stochastically chosen quantum jumps (see Refs. [65, 66, 68]). In the Monte Carlo algorithm by Mølmer *et al.* [69], the deviation of the norm δp of the wave function from unity after a certain time step is compared with a number ϵ, which is randomly chosen from the interval [0, 1]. If $\delta p > \epsilon$, a quantum jump occurs by which the wave function is renormalized to unity. A comparison of some of the quantum jump and state diffusion models was given in Ref. [70].

Recently, Breuer and Petruccione showed that a unique stochastic process in Hilbert space for the dynamics of the open system may be derived directly from the underlying microscopic system-plus-reservoir model [71]. They employed a description of quantum mechanical ensembles in terms of probability distributions on projective Hilbert space. In order to eliminate the reservoir, they made the Markovian approximation, and they employed second-order perturbation theory in the system-reservoir coupling. They then obtained a Liouville-master functional equation for the reduced probability distribution. The Liouville part of this equation corresponds to a deterministic Schrödinger-type equation with a non-Hermitean Hamiltonian which is intrinsically nonlinear in order to preserve the norm. The master part of this equation describes gain and loss of the probabilities for individual states due to discontinuous quantum jumps. In this description, the realization of the stochastic process is very similar to those generated by the piecewise deterministic quantum jump method [65] – [67]. Therefore, the stochastic simulation algorithms of all these approaches are very similar likewise. The equation of motion for the reduced density matrix derived from the Liouville-master equation is exactly of the Lindblad form (2.20).

In the first place, the stochastic wave function methods are computational tools with which the solution of the Born-Markov master equation is simulated by using Monte Carlo importance-sampling techniques [68]. The stochastic methods are numerically superior to the conventional integration of the master equation when the

rank of the reduced density matrix is large. Over and above the computational advantage of stochastic wave function methods for Born-Markov processes, some groups are presuming to claim that the instantaneous discontinuous processes are *real* and provide a natural description of individual quantum jump events (and not only of their statistics) as observed, e.g., in experiments with single ions in radio-frequency traps [72, 73]. Against that, we wish to point out that the assignment of definite states to a subsystem is *incompatible* with standard quantum theory, and has been proven wrong, e.g., in Einstein-Rosen-Podolsky experiments. Moreover, there is no experimental indication for non-standard phenomena (e.g., spontaneous collapse) in connection with the explanation of classical properties. Hence there is no phenomenological necessity for the introduction of a stochastic equation for state vectors.

Besides computational advantages in the simulation of Born-Markov processes, the quantum-state diffusion method provides an alternative approach to measurement theory. In this method, a continuous measurement process, by which the system is steadily reduced within a certain time period to an eigenstate, is an integral part of the dynamical description. In conclusion, the stochastic wave function approaches provide efficient numerical simulations of quantum master equations which are of the Lindblad form. However, since the Markov and the Born approximation are made, the application of these methods to solid state physics problems is as limited as the Born-Markov quantum master equation approach.

In the sequel, we move on firm ground taking the conservative view that the Hamiltonian dynamics of a global system induces a non-unitary dynamics for a subsystem.

3. System–plus–reservoir models

For many complex systems we do not have a clear understanding of the microscopic origin of damping. However, sometimes one might be able to acquire knowledge of the power spectrum of the stochastic force in the classical regime. Therefore, it is interesting to set up phenomenological system-plus-reservoir models which reduce in the appropriate limit to a description of the stochastic process in terms of a quasi-classical Langevin equation of the form (2.4). The simplest model of a dissipative quantum mechanical system that one can envisage is a damped quantum mechanical linear oscillator: a central harmonic oscillator is coupled linearly via its displacement coordinate q to a fluctuating dynamical reservoir or bath. If the bath is only weakly perturbed by the system, it can be considered as linear and therefore be described by harmonic oscillators. Then the statistics is exactly Gaussian. This model has been introduced and discussed in a series of four papers by Ullersma [74]. Zwanzig generalized the model to the case in which the central particle moves in an anharmonic potential and studied the classical regime [75]. Caldeira and Leggett [76] were among the first who applied this model to quantum mechanical tunneling of a macroscopic variable. The relevant model is considered in this chapter.

In the first section of this chapter we introduce the model and we track down the relations between the parameters of the model and the quantities appearing on the classical phenomenological level. Subsequent to this, we discuss a number of physically important particle-reservoir systems for which we can base the description to some extent on a microscopic footing. We cannot, in this chapter, deal with these systems in any detail. We shall only outline the underlying Hamiltonians and postpone the path integral formulation of the quantum statistical mechanics until the next chapter. In the last section, we briefly go into the discussion of nonlinear quantum environments.

3.1 Harmonic oscillator bath with linear coupling

In this section, we first introduce the most general Hamiltonian underlying a dissipative system obeying Eq. (2.4), and explain the important generalization to the case where the viscosity is state-dependent. After that, we determine the relation between the parameters of the global model and the phenomenological frequency-dependent friction coefficient $\tilde{\gamma}(\omega)$.

3.1.1 The Hamiltonian of the global system

Consider a system with one or few degrees of freedom which is coupled to a huge environment and imagine that the environment is represented by a bath of harmonic excitations above a stable ground state. The interaction of the system with each individual degree of freedom of the reservoir is proportional to the inverse of the volume of the reservoir. Hence, *the coupling to an individual bath mode is weak for a geometrically macroscopic environment.* Therefore, it is physically reasonable for macroscopic global systems to assume that the system-reservoir coupling is a *linear* function of the bath coordinates. This property is nice since it allows to eliminate the environment exactly. Importantly, the weak perturbation of any individual bath mode does not necessarily mean that the dissipative influence of the reservoir on the system is weak as well since the couplings of the bath modes add up and the number of modes can be very large.

The most general form of the Hamiltonian for the global system complying with these properties (barring pathological cases) is (see Ref. [76], Appendix C)

$$H = H_{\rm S} + H_{\rm R} + H_{\rm I} \,, \tag{3.1}$$

where

$$H_{\rm S} = p^2/2M + V(q) \tag{3.2}$$

is the Hamiltonian of the relevant system with a generalized coordinate q,

$$H_{\rm R} = \sum_{\alpha=1}^{N} \left(\frac{1}{2}\frac{p_\alpha^2}{m_\alpha} + \frac{1}{2} m_\alpha \omega_\alpha^2 x_\alpha^2 \right) \tag{3.3}$$

describes the reservoir consisting of N harmonic oscillators, and

$$H_{\rm I} \;=\; -\sum_{\alpha=1}^{N} F_\alpha(q)x_\alpha + \Delta V(q) \tag{3.4}$$

is the interaction term which by construction is linear in the bath coordinates. For later purposes, we have added a counter-term $\Delta V(q)$ which depends on the parameters m_α, ω_α of the environment, and on $F_\alpha(q)$, but not on the dynamical variables x_α of the reservoir. The additional potential term $\Delta V(q)$ is introduced in order to compensate a renormalization of the potential $V(q)$ which is caused by the linear coupling in x_α in $H_{\rm I}$ [the first term in Eq. (3.4)]. In the absence of $\Delta V(q)$, the minimum of the potential surface of the global system for given q is at $x_\alpha = F_\alpha(q)/m_\alpha\omega_\alpha^2$ for all α. The "effective" potential renormalized by the coupling is then given by

$$V_{\rm eff}(q) \;=\; V(q) - \sum_{\alpha=1}^{N} \frac{F_\alpha^2(q)}{2m_\alpha\omega_\alpha^2}\,. \tag{3.5}$$

In the special case $F_\alpha(q) = c_\alpha q$, the second term in Eq. (3.5) causes a negative shift $(\Delta\omega)^2 = -\sum_\alpha c_\alpha^2/Mm_\alpha\omega_\alpha^2$ in the squared frequency ω_0^2 of small oscillations about the minimum. Such coupling-induced renormalization effects can be very large, and if $\omega_{\rm eff}^2 = \omega_0^2+(\Delta\omega)^2 < 0$, they even change the potential qualitatively. If we wish that the coupling to the reservoir solely introduces dissipation — and not a renormalization of the potential $V(q)$ — we must compensate the second term in Eq.(3.5) and put

$$\Delta V(q) \;=\; \sum_{\alpha=1}^{N} \frac{F_\alpha^2(q)}{2m_\alpha\omega_\alpha^2}\,. \tag{3.6}$$

The special case of a *separable* interaction

$$F_\alpha(q) \;=\; c_\alpha F(q) \tag{3.7}$$

with $F(q)$ independent of α is of particular interest. Thus, considering a system weakly coupled to its environment as specified above, the most general translational invariant Hamiltonian with a separable interaction is

$$H \;=\; \frac{p^2}{2M} + V(q) + \frac{1}{2}\sum_{\alpha=1}^{N}\left[\frac{p_\alpha^2}{m_\alpha} + m_\alpha\omega_\alpha^2\left(x_\alpha - \frac{c_\alpha}{m_\alpha\omega_\alpha^2}F(q)\right)^2\right]. \tag{3.8}$$

For a nonlinear function $F(q)$, the open system undergoes a state-dependent dissipation process. This case is important, e.g., for *rotational tunneling systems.* It has been argued [77] that the periodicity of a hindering potential in a rotational tunneling system is an exact symmetry which cannot be destroyed whatever the external influences are. The argument applies when several identical particles are tunneling at the same time, as e.g., in a rotating molecule complex. If there are N identical particles coherently tunneling [e.g., $N = 3$ for a methyl-(CH_3-)group], both the potential $V(\varphi)$ and the coupling function $F(\varphi)$ [φ is the dynamical angular variable] belong to the same symmetry group C_N, i.e., $V(\varphi) = V(\varphi + 2\pi/N)$ and $F(\varphi) = F(\varphi + 2\pi/N)$.

Quasiparticle tunneling in Josephson systems is another important case. Then the coordinate q is again identified with a phase variable φ. In a phenomenological modeling of charge tunneling between superconductors the interaction term is [78]

$$H_{\rm I} = \sin(\varphi/2)\sum_\alpha c_\alpha^{(1)} x_\alpha^{(1)} + \cos(\varphi/2)\sum_\alpha c_\alpha^{(2)} x_\alpha^{(2)} , \tag{3.9}$$

where $\{x_\alpha^{(1)}\}$ and $\{x_\alpha^{(2)}\}$ represent two independent sets of oscillators. For a discussion of the microscopic theory, see Subsection 4.2.10.

If we require that the dissipation be *strictly* linear, we must constrain $F_\alpha(q)$ as

$$F_\alpha(q) = c_\alpha q , \tag{3.10}$$

which is the case of state-independent dissipation. The form (3.10) describes an ideal measurement of the particle's position by the reservoir in von Neumann's sense.

Substituting Eq. (3.10) into Eq. (3.1), the Hamiltonian takes the form

$$H = \frac{p^2}{2M} + V(q) + \frac{1}{2}\sum_{\alpha=1}^{N}\left[\frac{p_\alpha^2}{m_\alpha} + m_\alpha\omega_\alpha^2\left(x_\alpha - \frac{c_\alpha}{m_\alpha\omega_\alpha^2}q\right)^2\right] . \tag{3.11}$$

For later convenience, we rewrite the Hamiltonian (3.11) as

$$H = \frac{p^2}{2M} + \sum_{\alpha=1}^{N}\frac{p_\alpha^2}{2m_\alpha} + V(q,\boldsymbol{x}) , \tag{3.12}$$

$$V(q,\boldsymbol{x}) = V(q) + \frac{1}{2}\sum_{\alpha=1}^{N} m_\alpha\omega_\alpha^2\left(x_\alpha - \frac{c_\alpha}{m_\alpha\omega_\alpha^2}q\right)^2 . \tag{3.13}$$

Here, $V(q,\boldsymbol{x})$ is the potential of the global system, and $\boldsymbol{x}$ represents the set of bath coordinates $\{x_\alpha\}$. The Hamiltonian (3.11) has been used to model dissipation for about thirty years. Early studies were limited to a harmonic potential $V(q)$. Probably the first who showed that Eq. (3.11) leads to dissipation was Magalinskiĭ [79]. Shortly later studies include the work by Rubin [80] for classical systems, and Senitzky [19], Ford *et al.* [20], and Ullersma [74] for quantum systems. In the more recent literature, the model described by Eq. (3.11) is often referred to as the Caldeira-Leggett model.

3.1.2 The road to the classical generalized Langevin equation

The equations of motion for a global system described by the Hamiltonian (3.8) read

$$M\ddot{q} + V'(q) + \sum_\alpha \left(c_\alpha^2/m_\alpha\omega_\alpha^2\right)F(q)F'(q) = F'(q)\sum_\alpha c_\alpha x_\alpha , \tag{3.14}$$

$$m_\alpha\ddot{x}_\alpha + m_\alpha\omega_\alpha^2 x_\alpha = c_\alpha F(q) , \tag{3.15}$$

where $V'(q) = \partial V/\partial q$ and $F'(q) = \partial F/\partial q$. The dynamical equation for the oscillator position $x_\alpha(t)$ is an ordinary second order linear differential equation with inhomogeneity $c_\alpha F(q)$. This can be easily solved for $x_\alpha(t)$ by standard Green's function techniques. The solution for general initial values $x_\alpha^{(0)}$ and $p_\alpha^{(0)}$ at $t = 0$ reads

$$x_\alpha(t) \;=\; x_\alpha^{(0)}\cos(\omega_\alpha t)+\frac{p_\alpha^{(0)}}{m_\alpha\omega_\alpha}\sin(\omega_\alpha t)+\frac{c_\alpha}{m_\alpha\omega_\alpha}\int_0^t dt'\sin[\,\omega_\alpha(t-t')\,]\,F[q(t')]\;. \quad (3.16)$$

Next, it is convenient to rewrite Eq. (3.16) as a functional of the particle's velocity. Integrating the last term by parts, we get

$$\begin{aligned} x_\alpha(t) \;&=\; x_\alpha^{(0)}\cos(\omega_\alpha t)+\frac{p_\alpha^{(0)}}{m_\alpha\omega_\alpha}\sin(\omega_\alpha t)+\frac{c_\alpha}{m_\alpha\omega_\alpha^2}\Big(F[q(t)]-\cos(\omega_\alpha t)F[q(0)]\Big) \\ &\quad -\frac{c_\alpha}{m_\alpha\omega_\alpha^2}\int_0^t dt'\cos[\,\omega_\alpha(t-t')\,]\,F'[q(t')]\dot q(t')\;. \end{aligned} \quad (3.17)$$

We can eliminate the bath degrees of freedom by substituting Eq. (3.17) into Eq. (3.14). Then, the last term of the l.h.s. in Eq. (3.14) originating from the counter term in Eq. (3.4) cancels out. The dynamical equation for $q(t)$ alone is found to read

$$\begin{aligned} &M\ddot q(t)+MF'[q(t)]\int_0^t dt'\,\gamma(t-t')F'[q(t')]\dot q(t')+V'(q) \\ &\qquad =\; -\,MF'[q(t)]\gamma(t)F[q(0)]+F'[q(t)]\zeta(t)\;. \end{aligned} \quad (3.18)$$

Here we have introduced the memory-friction kernel

$$\gamma(t-t') \;=\; \Theta(t-t')\,\frac{1}{M}\sum_\alpha\frac{c_\alpha^2}{m_\alpha\omega_\alpha^2}\cos[\omega_\alpha(t-t')]\;, \quad (3.19)$$

and the force

$$\zeta(t) \;=\; \sum_\alpha c_\alpha\left(x_\alpha^{(0)}\cos(\omega_\alpha t)+\frac{p_\alpha^{(0)}}{m_\alpha\omega_\alpha}\sin(\omega_\alpha t)\right)\;. \quad (3.20)$$

Taking the average of the initial values $x_\alpha^{(0)}$, $p_\alpha^{(0)}$ with respect to the canonical classical equilibrium density of the unperturbed reservoir

$$\rho_{\rm R}^{(0)} \;=\; Z^{-1}\exp\left[\,-\beta\sum_\alpha\left(\frac{p_\alpha^{(0)\,2}}{2m_\alpha}+\frac{m_\alpha\omega_\alpha^2}{2}x_\alpha^{(0)\,2}\right)\right]\;, \quad (3.21)$$

the force $\zeta(t)$ becomes a fluctuating force with colored noise and Gaussian statistical properties [for a generalization to the quantum regime, see Eq. (2.31)]

$$\langle\zeta(t)\rangle_{\rho_{\rm R}^{(0)}} \;=\; 0\;, \qquad \langle\zeta(t)\zeta(t')\rangle_{\rho_{\rm R}^{(0)}} \;=\; Mk_{\rm B}T\gamma(t-t')\;. \quad (3.22)$$

The second relation is the classical fluctuation-dissipation theorem.

The dynamical equation (3.18) is a Langevin-type equation with a memory-friction force and a random force. When $F'(q)$ is q-dependent, the damping force in Eq. (3.18) describes nonlinear (state-dependent) memory friction and the random force exhibits multiplicative noise. As important examples for state-dependent noise, we mention quasiparticle tunneling between superconductors and strong electron tunneling through a mesoscopic junction [cf. Subsections 4.2.10 and 5.5.3].

In the remainder of this subsection, we restrict the attention to the case of *linear dissipation*, $F(q) = q$. Then, the dynamical equation (3.18) reduces to an ordinary Langevin equation with a linear memory-friction force and additive noise,

$$M\ddot{q}(t) + M\int_0^t dt'\,\gamma(t-t')\dot{q}(t') + V'(q) \;=\; \zeta(t) - M\gamma(t)q(0)\,. \tag{3.23}$$

The stochastic equation of motion (3.23) still contrasts with the usual form of the Langevin equation by the spurious term $-M\gamma(t)q(0)$. This term is a transient depending on the initial value $q(0)$.

Upon strengthening an observation by Bez [81], it has been argued [82] that the initial transient slippage is an artefact of the decoupled thermal initial state (3.21).

The annoying term in Eq. (3.23) can be eliminated by a suitable definition of the thermal average as follows. In the first step of the elimination, the term $-M\gamma(t)q(0)$ is absorbed by a corresponding shift of the random force $\zeta(t)$,

$$\xi(t) \;=\; \zeta(t) - M\gamma(t)q(0)\,. \tag{3.24}$$

The modified random force $\xi(t)$ does not vanish on average when the mean value is taken with respect to $\rho_{\rm R}^{(0)}$. In the second step, $\xi(t)$ is reconciled with the usual properties of a Gaussian random force by performing the thermal average in the initial state of the reservoir with the shifted canonical equilibrium distribution

$$\rho_{\rm R} \;=\; Z^{-1}\exp\left\{-\beta\sum_\alpha\left[\frac{p_\alpha^{(0)\,2}}{2m_\alpha} + \frac{m_\alpha\omega_\alpha^2}{2}\left(x_\alpha^{(0)} - \frac{c_\alpha}{m_\alpha\omega_\alpha^2}q(0)\right)^2\right]\right\}. \tag{3.25}$$

Upon averaging $x_\alpha^{(0)}$ and $p_\alpha^{(0)}$ with the weight function (3.25), the random force $\xi(t)$ exhibits proper statistical behavior,

$$\langle\xi(t)\rangle_{\rho_{\rm R}} \;=\; 0\,, \qquad \langle\xi(t)\xi(t')\rangle_{\rho_{\rm R}} \;=\; Mk_{\rm B}T\gamma(t-t')\,. \tag{3.26}$$

Thus we arrive at the standard form of the generalized Langevin equation,

$$M\ddot{q}(t) + V'(q) + M\int_0^t dt'\,\gamma(t-t')\dot{q}(t') \;=\; \xi(t)\,. \tag{3.27}$$

From the above we see that care has to be taken if one refers to statistical properties of a random force [82]. We have been able to remove the initial transient slippage by taking the thermal average in the initial state with respect to bath modes which are shifted by the coupling to the particle.

3.1.3 Phenomenological modeling

For a small number N of bath oscillators, the time on which the transferred energy is feeded back to the small system is of the order of other relevant time scales. However, when N is about 20 or larger, the Poincaré recurrence time is found to be practically infinity. Then we may take the limit $N \to \infty$ and replace the sum of bath modes

by an integral over a continuous spectral density. With these preliminary remarks, it is straightforward to establish the connection of the frequency-dependent damping coefficient $\tilde{\gamma}(\omega)$ defined in Eq. (2.5) with the parameters of the Hamiltonian (3.8) or (3.11). The Fourier transform of the retarded memory-friction kernel (3.19) is

$$\tilde{\gamma}(\omega) \;=\; \lim_{\epsilon\to 0^+} -i\,\frac{\omega}{M}\sum_{\alpha=1}^{N}\frac{c_\alpha^2}{m_\alpha\omega_\alpha^2}\,\frac{1}{\omega_\alpha^2-\omega^2-i\epsilon\,\mathrm{sgn}\,(\omega)}\;. \tag{3.28}$$

In order to deal with a real heat bath causing dissipation, we introduce the spectral density of the environmental coupling

$$J(\omega) \;=\; \frac{\pi}{2}\sum_{\alpha}\frac{c_\alpha^2}{m_\alpha\omega_\alpha}\delta(\omega-\omega_\alpha)\;, \tag{3.29}$$

and we eventually regard $J(\omega)$ as a smooth function of ω. In the continuum limit, the sum in Eq. (3.28) is replaced by the integral

$$\tilde{\gamma}(\omega) \;=\; \lim_{\epsilon\to 0^+}\frac{-i\omega}{M}\,\frac{2}{\pi}\int_0^\infty d\omega'\,\frac{J(\omega')}{\omega'}\,\frac{1}{\omega'^{\,2}-\omega^2-i\epsilon\,\mathrm{sgn}\,(\omega)}\;. \tag{3.30}$$

By this extension, the function $\tilde{\gamma}(\omega)$ acquires a smooth real part,

$$\tilde{\gamma}'(\omega) \;=\; J(\omega)/M\omega\;. \tag{3.31}$$

For frequency-dependent damping, it is sometimes convenient to consider the Laplace transform $\hat{\gamma}(z)$ of the damping kernel $\gamma(t)$. The damping functions $\hat{\gamma}(z)$ and $\tilde{\gamma}(\omega)$ are related by analytic continuation,

$$\hat{\gamma}(z) \;=\; \tilde{\gamma}(\omega=iz)\;; \qquad \tilde{\gamma}(\omega) \;=\; \lim_{\epsilon\to 0^+}\hat{\gamma}(z=-i\omega+\epsilon)\;. \tag{3.32}$$

According to Eq. (3.30) we then have

$$\hat{\gamma}(z) \;=\; \frac{z}{M}\sum_{\alpha=1}^{N}\frac{c_\alpha^2}{m_\alpha\omega_\alpha^2}\,\frac{1}{(\omega_\alpha^2+z^2)} \;=\; \frac{z}{M}\,\frac{2}{\pi}\int_0^\infty d\omega'\,\frac{J(\omega')}{\omega'}\,\frac{1}{\omega'^2+z^2}\;. \tag{3.33}$$

As far as we are interested in properties of the particle alone, the dynamics is fully determined by the mass M, the potential $V(q)$, and the spectral density $J(\omega)$. We see from Eq. (3.31) that $J(\omega)$ is uniquely determined by the classical frequency-dependent damping coefficient $\tilde{\gamma}(\omega)$. With the roles reversed, we can also express the microscopic characteristics in terms of the phenomenological real-time damping kernel $\gamma(t)$. Using Eq. (3.30), we can give the damping kernel $\gamma(t)$ in terms of the spectral density $J(\omega)$ of the environmental coupling,

$$\gamma(t) \;=\; \Theta(t)\,\frac{1}{M}\,\frac{2}{\pi}\int_0^\infty d\omega\,\frac{J(\omega)}{\omega}\,\cos(\omega t)\;. \tag{3.34}$$

The inversion of the Fourier integral (3.34) gives

$$J(\omega) \;=\; M\omega \int_0^\infty dt\, \gamma(t) \cos(\omega t)\,. \tag{3.35}$$

The spectral density $J(\omega)$ may also be expressed in terms of the Laplace transform of the damping kernel. From Eq. (3.35) we find

$$J(\omega) \;=\; \lim_{\epsilon \to 0^+} M\omega[\,\widehat{\gamma}(\epsilon + i\omega) + \widehat{\gamma}(\epsilon - i\omega)\,]/2\,. \tag{3.36}$$

We conclude with an important remark: The spectral density $J(\omega)$, and later on quantum mechanics, is determined by quantities that appear already in the classical phenomenological equation of motion [83, 84]. This property holds in the case of strict linear dissipation, i.e., damping itself does not depend on the state of the system. For instance, a conventional molecular dynamics simulation may be used to compute $\widetilde{\gamma}'(\omega)$, which then determines $J(\omega)$ by Eq. (3.31). Therefore, this relation plays a fundamental role in the phenomenological modeling of dissipative quantum systems.

3.1.4 Ohmic and frequency-dependent damping

In the strict *Ohmic* case (Markovian limit), damping is frequency-independent,

$$\widetilde{\gamma}(\omega) \;=\; \gamma\,. \tag{3.37}$$

We see from Eq. (3.35) or from Eq. (3.36) that strict Ohmic damping is described by the model (3.11) with the spectral density $J(\omega)$ in the form [76]

$$J(\omega) \;=\; \eta\omega \;=\; M\gamma\omega \tag{3.38}$$

for all frequencies ω. In the first equality, we have introduced the familiar viscosity coefficient η. The relation (3.38) implies memoryless friction $\gamma(t) = 2\gamma\delta(t)$.[1] This, of course, is an idealized situation. In reality, any particular real spectral density $J(\omega)$ falls off in the limit $\omega \to \infty$. Otherwise, certain physical quantities, e.g. the momentum dispersion, would diverge (cf. the discussion in Section 7.3). There is always a microscopic memory time setting the time scale for inertia effects in the reservoir. In the simplest form, the damping kernel $\gamma(t)$ in the classical equation of motion (2.4) is regularized with a memory time $\tau_{\rm D} = 1/\omega_{\rm D}$,

$$\gamma(t) \;=\; \gamma\omega_{\rm D}\Theta(t) \exp(-\omega_{\rm D} t)\,, \tag{3.39}$$

which is known as *Drude regularization*. We then have

$$\widetilde{\gamma}(\omega) \;=\; \gamma/[\,1 - i\omega/\omega_{\rm D}\,]\,, \qquad \text{and} \qquad \widehat{\gamma}(z) \;=\; \gamma/[\,1 + z/\omega_{\rm D}\,]\,. \tag{3.40}$$

For this choice, the imaginary part of $\widetilde{\gamma}(\omega)$ is smaller than the real part by a factor of $\omega/\omega_{\rm D}$. The Drude form (3.40) comes from a spectral density with algebraic cutoff,

[1] In the integral in Eq. (2.4) the δ-function counts only half, and thus the damping term reduces to the Ohmic form $M\gamma\dot{q}(t)$ in Eq. (2.3).

$$J(\omega) \;=\; M\gamma\omega/[\,1+\omega^2/\omega_{\rm D}^2\,]\,. \tag{3.41}$$

The damping kernel brings in memory-friction effects on the time scale $\tau_{\rm D} = \omega_{\rm D}^{-1}$. When the relevant frequencies of the system are much lower than the Drude cutoff frequency $\omega_{\rm D}$, the reservoir described by (3.41) behaves like an Ohmic heat bath with effective damping strength $\gamma_{\rm eff} = \int_0^\infty dt\,\gamma(t) = \gamma$.

Next, consider the extension to general frequency-dependent damping. It is convenient to assume (though it is not strictly necessary) that the function $J(\omega)$ has a power law form at low frequencies, $J(\omega) \propto \omega^s$. It will become clear later on that the dissipative influences can be classified by the power s. Negative values of s are excluded since otherwise the counterterm (3.6) or the quantity $\gamma(0)$ would diverge which is pathological. The power-law form is assumed to hold in the frequency range $0 \le \omega \lesssim \omega_{\rm c}$, where $\omega_{\rm c}$ is much less than a characteristic cutoff frequency $\omega_{\rm ch}$, which is of the order of the Drude, Debye, or Fermi frequency etc., depending on the model. For frequencies of the order of or greater than $\omega_{\rm ch}$, the behavior of $J(\omega)$ may be complicated and may not easily be inferable either from the classical motion or from microscopic considerations. However, the important point now is that, as long as we are interested in times $t \gg \omega_{\rm c}^{-1}$, the effect of the environmental modes with $\omega \gtrsim \omega_{\rm c}$ can be absorbed into a renormalization of parameters appearing in the Hamiltonian $H_{\rm S}$ of the system. The only additional property we need to postulate is that $J(\omega)$ falls off at least with some negative power of ω in the limit $\omega \to \infty$. The minimal decrease of $J(\omega)$ required depends on the physical quantity under consideration.

To make the discussion quantitative, we decompose $J(\omega)$ into a low-frequency and a high-frequency contribution,

$$J(\omega) \;=\; J_{\rm lf}(\omega) + J_{\rm hf}(\omega)\,, \tag{3.42}$$

$$J_{\rm lf}(\omega) \;=\; J(\omega) f(\omega/\omega_{\rm c})\,, \tag{3.43}$$

$$J_{\rm hf}(\omega) \;=\; J(\omega)\,[\,1 - f(\omega/\omega_{\rm c})\,]\,. \tag{3.44}$$

Here, $f(\omega/\omega_{\rm c})$ is a cutoff function defined in such a way that $J_{\rm hf}(\omega)$ is negligibly small for $\omega \ll \omega_{\rm c}$ and $J_{\rm lf}(\omega)$ negligibly small for $\omega \gg \omega_{\rm c}$. Depending on convenience, we may choose either a sharp cutoff $f(\omega/\omega_{\rm c}) = \Theta(1-\omega/\omega_{\rm c})$, or a smooth exponential or algebraic cutoff. Expedient forms are a Gaussian, an exponential, or the Drude form $f(\omega/\omega_{\rm c}) = 1/[\,1+(\omega/\omega_{\rm c})^2\,]$.

We shall consider in most applications the case in which $J_{\rm lf}(\omega)$ has a power-law form with an exponential cutoff,

$$J_{\rm lf}(\omega) \;=\; \eta_s \omega_{\rm ph}^{1-s} \omega^s\, e^{-\omega/\omega_{\rm c}}\,, \qquad\qquad \eta_s \;=\; M\gamma_s\,. \tag{3.45}$$

Here we have introduced for $s \neq 1$ a "phononic" reference frequency $\omega_{\rm ph}$, so that the coupling constant η_s has the usual dimension of viscosity for all s. We shall distinguish the frequency $\omega_{\rm ph}$ from the cutoff frequency $\omega_{\rm c}$. For notational convenience, we shall sometimes use the corresponding temperature scales

$$T_{\rm ph} \;\equiv\; \hbar\omega_{\rm ph}/k_{\rm B}\,, \qquad\qquad T_{\rm c} \;\equiv\; \hbar\omega_{\rm c}/k_{\rm B}\,. \tag{3.46}$$

In many physical situations, the frequency ω_c at which the power law $J_{\rm lf}(\omega) \propto \omega^s$ is cut off is very large compared with all other relevant frequencies of the system. A number of analytic results will be available in this limit.

The partial spectral density $J_{\rm hf}(\omega \to 0) \propto \omega^s$ contributes to the damping function $\tilde{\gamma}(\omega)$ in the limit $\omega \to 0$ the term

$$\tilde{\gamma}_{\rm hf}(\omega \to 0) \;=\; -i\omega\, \Delta M_{\rm hf}/M \;, \tag{3.47}$$

$$\Delta M_{\rm hf} \;=\; \frac{2}{\pi} \int_0^\infty d\omega' \, \frac{J_{\rm hf}(\omega')}{\omega'^3} \;, \tag{3.48}$$

as follows from (3.30). With (3.47), the Fourier transform $-i\omega\tilde{\gamma}_{\rm hf}(\omega)\tilde{q}(\omega)$ of the memory-friction force reduces at low frequencies to the form $-\Delta M_{\rm hf}\,\omega^2\tilde{q}(\omega)$. This term, however, may be added to the kinetic term $-M\omega^2\tilde{q}(\omega)$. Thus for times $t \gg \omega_c^{-1}$, the partial spectral density $J_{\rm hf}(\omega)$ manifests itself simply as mass renormalization,

$$M_{\rm r} \;=\; M + \Delta M_{\rm hf} \,. \tag{3.49}$$

From this we conclude that if we are not interested in the time regime $t < 1/\omega_c$, we may treat $J_{\rm hf}(\omega)$ in the adiabatic approximation. If not stated differently, we will eliminate $J_{\rm hf}(\omega)$ from the explicit description, and we will regard the mass M as a renormalized mass which is already dressed by the reservoir's high-frequency modes.

The integral (3.48) is convergent also for the spectral density $J_{\rm lf}(\omega)$ when the power s in Eq. (3.43) is larger than 2. For this case, the full spectral density results in no more than mass renormalization for times $t \to \infty$. Further discussion of this point is given in Section 7.4.

Upon inserting the form (3.43) of the spectral density with a sharp cutoff into the representation (3.33), the spectral damping function takes the exact form [85]

$$\hat{\gamma}(z) \;=\; \frac{2\gamma_s}{\pi s} \left(\frac{\omega_c}{\omega_{\rm ph}}\right)^{s-1} \frac{\omega_c}{z}\, {}_2{\rm F}_1\!\left(1,\, \tfrac{1}{2}s;\, 1+\tfrac{1}{2}s;\, -\omega_c^2/z^2\right), \tag{3.50}$$

where ${}_2{\rm F}_1(a,\, b;\, c;\, x)$ is a hypergeometric function [86]. The explicit form of the spectral damping function $\hat{\gamma}(z)$ for $z \ll \omega_c$ is found from the asymptotic expansion of the hypergeometric function. This may be calculated upon using standard transformation formulas of the hypergeometric function. Putting $\lambda_s \equiv \gamma_s/\sin(\pi s/2)$, we find

$$\hat{\gamma}(z) \;=\; \begin{cases} \lambda_s \left(z/\omega_{\rm ph}\right)^{s-1} \,, & 0 < s < 2 \,, \\ (\gamma_2/\pi)(z/\omega_{\rm ph}) \ln\left(1 + \omega_c^2/z^2\right) \,, & s = 2 \,, \\ z\left[\Delta M/M \,+\, (\lambda_s/\omega_{\rm ph})(z/\omega_{\rm ph})^{s-2} + \mathcal{O}\left(\frac{z^2}{\omega_c^2}\right)\right] \,, & 2 < s < 4 \,, \\ z\left[\Delta M/M + \mathcal{O}\left(\frac{z^2}{\omega_c^2}\right)\right] \,, & s \geq 4 \,. \end{cases} \tag{3.51}$$

In the regime $0 < s < 2$, we have disregarded terms depending on ω_c. From these results we see that in the most interesting regime $0 < s < 2$ the damping function

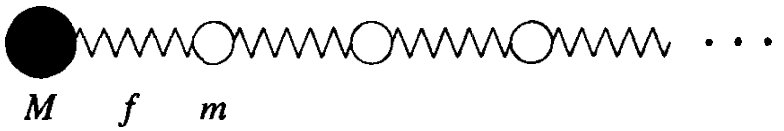

Figure 3.1: Pictorial sketch of the mechanical analogue of the Rubin model.

$\hat{\gamma}(z)$ behaves as z^{s-1}. In the case $2 < s < 4$, we have also given the next to leading order term in order to study the behavior beyond simple mass renormalization. This term is relevant in the transient time regime.

As we have discussed already, the case $s = 1$ in Eq. (3.43) describes Ohmic friction. The cases $0 < s < 1$ and $s > 1$ have been popularized as *sub-Ohmic* and *super-Ohmic*, respectively [87]. We shall see in the next section that the case of Ohmic friction is important, e. g., for charged interstitials in metals, while a phonon bath in d spatial dimensions corresponds to the case $s = d$ or $s = d + 2$ depending on the symmetry properties of the strain field. Nonintegral values of s may be relevant for fractal environments.

3.1.5 Rubin model

In Rubin's model, a heavy particle of mass M and coordinate q is bilinearly coupled to a half-infinite chain of harmonic oscillators with masses m and spring constants $f = m\omega_{\rm R}^2/4$ [88], as sketched in Fig. 3.1. The Hamiltonian of the global model is

$$H = \frac{p^2}{2M} + V(q) + \sum_{n=1}^{\infty}\left(\frac{p_n^2}{2m} + \frac{f}{2}(x_{n+1} - x_n)^2\right) + \frac{f}{2}(q - x_1)^2 . \tag{3.52}$$

The model is not yet of the standard form (3.11) since the harmonic bath modes are coupled with each other. The bath is diagonalized with the transformation

$$x_n = \sqrt{2/\pi}\int_0^{\pi} dk\, \sin(kn)\, X(k) . \tag{3.53}$$

In the normal mode representation of the reservoir, the Hamiltonian reads

$$H = \frac{p^2}{2M} + V(q) + \frac{f}{2}q^2 + \int_0^{\pi} dk\left(\frac{P^2(k)}{2m} + \frac{m}{2}\omega^2(k)X^2(k) - c(k)X(k)\,q\right) , \tag{3.54}$$

where the eigenfrequencies $\omega(k)$ and the coupling function $c(k)$ are given by

$$\omega(k) = \omega_{\rm R}\sin(k/2) , \qquad c(k) = \sqrt{2/\pi}\,[m\omega_{\rm R}^2/4]\sin(k) . \tag{3.55}$$

The frequency $\omega_{\rm R}$ is the highest frequency of the reservoir modes. Substituting Eq. (3.55) into Eq.(3.29), the spectral density of the coupling is found as

$$J(\omega) = \frac{m\omega_{\rm R}^3}{16}\int_0^{\pi} dk\,\frac{\sin^2(k)}{\sin(\frac{1}{2}k)}\,\delta\left[\omega - \omega(k)\right] = \frac{m\omega_{\rm R}}{2}\,\omega\Big(1 - \frac{\omega^2}{\omega_{\rm R}^2}\Big)^{1/2}\Theta(\omega_{\rm R} - \omega) ,$$