

the relevant system and the reservoir are the constituents of an energy-conserving 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 “huge” 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,

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

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

$$H = H_S + H_R + H_I; \quad \mathcal{L} = \mathcal{L}_S + \mathcal{L}_R + \mathcal{L}_I. \quad (2.10)$$

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 relevant variables,

$$\rho(t) = PW(t) \quad (2.11)$$

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 $(1 - P)W(t)$,

$$W(t) = \rho(t) + (1 - P)W(t); \quad P^2 = P. \quad (2.12)$$

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 quantum master equation, the *Nakajima-Zwanzig equation* [16, 17]

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

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 $\mathcal{L}_S$ one then finds the homogeneous time-retarded quantum master equation

$$\dot{\rho}(t) = P(\mathcal{L}_S + \mathcal{L}_I)\rho(t) + \int_0^t dt' P\mathcal{L}_I e^{(1-P)\mathcal{L}t'} (1 - P)\mathcal{L}_I\rho(t - t') . \quad (2.14)$$

The first (instantaneous) term describes the reversible motion of the relevant system while the second (time-retarded) term brings on irreversibility. It describes all possible effects the reservoir may exert on the system, such as relaxation, decoherence and energy shifts. Equation (2.14) is still too complicated for explicit evaluation. First, the kernel of (2.14) contains any power of $\mathcal{L}_I$. 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 $\mathcal{L}_I$. Disregarding also retardation effects, one finally arrives at the quantum master equation in Born-Markov approximation

$$\dot{\rho}(t) = P(\mathcal{L}_S + \mathcal{L}_I)\rho(t) + \int_0^t dt' P\mathcal{L}_I e^{(1-P)(\mathcal{L}_S + \mathcal{L}_R)t'} (1 - P)\mathcal{L}_I\rho(t) . \quad (2.15)$$

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 $\mathcal{L}_I$ 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.

When the Born-Markov quantum master equation (2.15) is given in the energy eigenstate basis of H_S , it is usually referred to as *Redfield equation* [31, 26, 32]

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

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

$$R_{nmkl} = \delta_{lm} \sum_r \Gamma_{nr rk}^{(+)} + \delta_{nk} \sum_r \Gamma_{lr rm}^{(-)} - \Gamma_{lm nk}^{(+)} - \Gamma_{lm nk}^{(-)}. \quad (2.17)$$

The rates are given by the Golden Rule expressions

$$\begin{aligned} \Gamma_{lm nk}^{(+)} &= \hbar^{-2} \int_0^\infty dt e^{-i\omega_{nk}t} \langle \tilde{H}_{l,lm}(t) \tilde{H}_{l,nk}(0) \rangle_R, \\ \Gamma_{lm nk}^{(-)} &= \hbar^{-2} \int_0^\infty dt e^{-i\omega_{lm}t} \langle \tilde{H}_{l,lm}(0) \tilde{H}_{l,nk}(t) \rangle_R. \end{aligned} \quad (2.18)$$

Here, $\tilde{H}_I(t) = \exp(iH_R t/\hbar) H_I \exp(-iH_R t/\hbar)$ 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 representation² by $\alpha, \beta, \dots$, 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 approach, 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

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

transformations are thought to be “completely positive” [43, 29], $\rho \rightarrow \sum_n O_n \rho O_n^\dagger$. 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 $\text{tr } \rho$ 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 raising and lowering operator, or equivalently of a coordinate and a momentum operator [44],

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

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 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, as argued by Pechukas [46, a], complete positivity of the RDM is an artefact of product initial conditions $W^{(i)} = \rho^{(i)} \otimes \rho_R^{(i)}$ for the global density matrix. Product initial conditions are only appropriate in the weak-coupling limit. In general, reduced dynamics need not be completely positive. It is known that the Redfield-Bloch master equation may break the positivity of the density matrix. Violation of positivity may occur if memory effects are not adequately taken into account at the initial stage of the time evolution. Then some “slippage” of the initial conditions must occur before the reduced dynamics looks Markovian [46, b]. The slippage captures the effects of the actual non-Markovian evolution in a short transient regime of the order of the reservoir’s memory time. (see also [46, c]). The Markovian master equation holds only in a subspace in which rapidly decaying components of the density matrix are disregarded, whereas Lindblad theory requires validity for *any* reduced density matrix. These findings have been confirmed in a 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 attribute fundamental significance to the Lindblad master equation.

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 $\rho_\beta = P W_\beta$, where W_β is the thermal equilibrium density matrix of the global system, is correctly described only when the system's relaxation times are large compared to the thermal time $\hbar\beta$ (see, e.g., the discussion in Chapters 6 and 17).

In conclusion, the Born-Markov quantum master equation approach provides a reasonable description in many cases, e. g. in NMR, in quantum optics, and in a variety of chemical reactions. However, this method is not applicable 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 $|X_i\rangle$ and $|Y_\mu\rangle$ 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 the subspace Λ_Y ,

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

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]

$$(Y_\mu|Y_\nu) \equiv \frac{1}{\beta} \quad d\lambda \langle e^{-\lambda H} Y_\mu^\dagger e^{\lambda H} Y_\nu \rangle. \quad (2.23)$$

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

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

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

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

$$|\dot{X}_i\rangle = \mathcal{L} |X_i\rangle , \quad (2.25)$$

where $\mathcal{L}$ is the Liouville superoperator, and eliminating $(1 - \mathcal{P})|X_i\rangle$ with the aid of the exact formal solution, it is straightforward to derive for $Y_\mu(t)$ a system of coupled integro-differential equations, which have been popularized as the Mori equations.

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

The generally temperature-dependent drift matrix $\Omega_{\nu\mu}(t)$ is given by

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

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

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

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

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

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 reads⁴

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

where $\hat{\xi}(t)$ is the Gaussian random force operator with autocorrelation

$$\langle \hat{\xi}(t) \hat{\xi}(0) \rangle = \frac{\hbar M}{\pi} \int_0^\infty d\omega \omega \tilde{\gamma}(\omega) \left(\coth(\beta \hbar \omega / 2) \cos(\omega t) - i \sin(\omega t) \right) . \quad (2.31)$$

⁴Here 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).

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 force autocorrelation function has the quantum mechanical form

$$\tilde{\chi}(\omega) \equiv \int_{-\infty}^{\infty} dt \langle \xi(t)\xi(0) \rangle \cos(\omega t) = M\hbar\omega \coth\left(\frac{\hbar\omega}{2k_B T}\right) \tilde{\gamma}'(\omega). \quad (2.32)$$

The derivation of this expression from a quantum statistical ensemble average is given in Subsection 3.1.4. In addition, we briefly sketch in Section 5.5 the derivation of the QLE within the path integral method following the approach by Schmid [54]. There, it will turn out that the QLE is exact (apart from disregarding a term describing the initial transient behaviour) if 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 anharmonicity 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 energy-conserving 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 sit-

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

uations, 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, 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 $p_n(t) \equiv \rho_{nn}(t)$,

$$\dot{p}_n(t) = \sum_m [A_{nm} p_m(t) - A_{mn} p_n(t)] . \quad (2.33)$$

The first term on the r.h.s. describes the gain and the second term the loss of probability to occupy 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 21.2.6).

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 interrupted 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 $|\psi\rangle$ 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

$$\begin{aligned} |d\psi\rangle = & -\frac{i}{\hbar} H|\psi\rangle dt + \sum_j \left(\langle L_j^\dagger \rangle L_j - \frac{1}{2} L_j^\dagger L_j - \frac{1}{2} \langle L_j^\dagger \rangle \langle L_j \rangle \right) |\psi\rangle dt \\ & + \sum_j \left(L_j - \langle L_j \rangle \right) |\psi\rangle d\xi_j, \end{aligned} \quad (2.34)$$

where $\langle L_j \rangle \equiv \langle \psi | L_j | \psi \rangle$ 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 fluctuations. The $d\xi_j$ are complex differential variables of a Wiener process satisfying

$$\langle d\xi_j \rangle = 0, \quad \langle d\xi_j d\xi_k \rangle = 0, \quad \langle d\xi_j^* d\xi_k \rangle = \delta_{j,k} dt, \quad (2.35)$$

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

$$\rho = \langle |\psi\rangle \langle \psi| \rangle. \quad (2.36)$$

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

Attempts have also been made 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 ,

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

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, 72]. 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-Hermitian 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 in 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 [73, 74]. 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. Upon performing a reduction of the global system to the relevant subsystem, all effects of the environmental coupling are put into an influence functional. Non-Markovian generalizations of quantum state diffusion and related stochastic Schrödinger equations can be found by a stochastic unraveling of the influence functional. The related discussion is given in Section 5.6.

3. System-plus-reservoir models

For many complex quantum systems we do not have a clear understanding of the microscopic origin of damping. In some systems, however, it is possible to track down the power spectrum of the stochastic force in the classical regime, and hence the spectral damping function $\tilde{\gamma}(\omega)$. Therefore, it is very important to have phenomenological system-plus-reservoir models which on the one hand open up the full quantum mechanical treatment, and on the other hand reduce in the classical limit to a description of the stochastic process in terms of a 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 equilibrium state of the reservoir is only weakly perturbed by the central oscillator, its classical dynamics can be represented by linear equations. Therefore, it can be described in terms of a bosonic field or a (infinite) set of harmonic oscillators. Then the noise statistics of the stochastic process induced by the reservoir is strictly Gaussian. This simple system-plus-reservoir model has been introduced and discussed in a series of four papers by Ullersma [75]. Zwanzig generalized the model to the case in which the central particle moves in an anharmonic potential and studied the classical regime [76]. Caldeira and Leggett [77] were among the first who applied this model to a study of 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-plus-reservoir systems for which we can base the description to some extent on a microscopic footing. In this chapter, we cannot deal with these systems in any detail. We shall outline only the underlying Hamiltonians and postpone the path integral formulation of the quantum statistical mechanics until the next chapter. In the last section, we touch on 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) in the classical limit, and we 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 very reasonable for macroscopic global systems to assume that the system-reservoir coupling is a *linear* function of the bath coordinates. This property is favourable 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 individual bath modes add up and the number of modes can be very large.

The general form of the Hamiltonian for the global system complying with these properties (barring pathological cases) is (see Ref. [77], Appendix C)

$$H = H_S + H_R + H_I. \quad (3.1)$$

Here, H_S is the Hamiltonian of the relevant system. For simplicity, we imagine a particle of mass M moving in a potential $V(q)$,

$$H_S = p^2/2M + V(q). \quad (3.2)$$

The reservoir consists of a set of harmonic oscillators,

$$H_R = \sum_{\alpha=1}^N \left(\frac{p_{\alpha}^2}{2m_{\alpha}} + \frac{1}{2} m_{\alpha} \omega_{\alpha}^2 x_{\alpha}^2 \right), \quad (3.3)$$

and the system-bath interaction H_I is assumed to be linear in the bath coordinates,

$$H_I = - \sum_{\alpha=1}^N F_{\alpha}(q) x_{\alpha} + \Delta V(q) \quad (3.4)$$

For specific purpose we have added a counter-term $\Delta V(q)$ which depends on $F_{\alpha}(q)$, and on the parameters m_{α} , ω_{α} of the reservoir, but not on its dynamical variables $x_{\alpha}(t)$. 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 coupling term linear in x_α in the interaction H_I . In the absence of $\Delta V(q)$, the minimum of the potential surface of the global system for fixed q in x_α -direction is at $x_\alpha = F_\alpha(q)/m_\alpha\omega_\alpha^2$. Thus, the “effective” potential renormalized by the coupling is given by

$$V_{\text{eff}}(q) = V(q) - \sum_{\alpha=1}^N \frac{F_\alpha^2(q)}{2m_\alpha\omega_\alpha^2} \quad (3.5)$$

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 circular frequency ω_0^2 of small oscillations about the minimum. This coupling-induced renormalization of the potential can be very large, and, if $\omega_{\text{eff}}^2 = \omega_0^2 + (\Delta\omega)^2 < 0$, it changes the potential even qualitatively.

If we wish that the coupling of the relevant system to the reservoir solely introduces dissipation — and not in addition a renormalization of the potential $V(q)$ — we must compensate the second term in Eq. (3.5) by a suitable choice of $\Delta V(q)$. Full compensation of the coupling-induced potential distortion is achieved if we put

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

The specific choice of *separable* interaction

$$F_\alpha(q) = c_\alpha F(q), \quad (3.7)$$

where $F(q)$ is independent of α , is of particular interest. Thus, under the assumptions specified above, the most general translational invariant Hamiltonian with a separable interaction is

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

The case of a nonlinear function $F(q)$ occurs e.g. in rotational tunneling systems, in polaron systems and in Josephson systems.

It has been argued [78] 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 $F(\varphi)$, where φ is the dynamical angular variable, belong to the same symmetry group C_N , i.e., $V(\varphi) = V(\varphi + 2\pi/N)$ and $F(\varphi) = F(\varphi + 2\pi/N)$.

In a polaron system, the particle’s interaction energy due to linear lattice distortions is nonlinear in the particle’s coordinate according to $F_{\mathbf{k}}(\mathbf{q}) = e^{i\mathbf{k} \cdot \mathbf{q}}$ [cf. Sec. 3.3].

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 [79]

$$H_I = \sin(\varphi/2) \sum_{\alpha} c_{\alpha}^{(1)} x_{\alpha}^{(1)} + \cos(\varphi/2) \sum_{\alpha} c_{\alpha}^{(2)} x_{\alpha}^{(2)}, \quad (3.9)$$

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

$$F_{\alpha}(q) = c_{\alpha} q. \quad (3.10)$$

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

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

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

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

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

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

Here, $V(q, \mathbf{x})$ is the potential of the global system, and $\mathbf{x}$ 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 [80]. Shortly later studies include the work by Rubin [81] for classical systems, and Senitzky [19], Ford *et al.* [20], and Ullersma [75] for quantum systems. In the more recent literature, the model described by Eq. (3.11) is usually 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 (3.11) read

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

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

where $V'(q) = \partial V/\partial q$. The dynamical equation for the oscillator position $x_{\alpha}(t)$ is an ordinary second order linear differential equation with inhomogeneity $c_{\alpha} q(t)$. This equation is solved by standard Green's function techniques. In Fourier space, a particular solution of the inhomogeneous equation reads

$$\tilde{x}_{\alpha}(\omega) = \tilde{\chi}_{\alpha}(\omega) c_{\alpha} \tilde{q}(\omega), \quad \text{where} \quad \tilde{\chi}_{\alpha}(\omega) = \lim_{\epsilon \rightarrow 0^+} \frac{1}{m_{\alpha}} \frac{1}{\omega_{\alpha}^2 - \omega^2 - i\omega\epsilon} \quad (3.16)$$

is the dynamical susceptibility of an individual bath oscillator. Of particular later interest is the absorptive part $\text{Im } \tilde{\chi}_\alpha(\omega) \equiv \tilde{\chi}_\alpha''(\omega) = (\pi/m_\alpha) \text{sgn}(\omega) \delta(\omega_\alpha^2 - \omega^2)$. For simplicity we fix the initial time to $t_0 = 0$. The solution evolving from the initial values $x_\alpha^{(0)}$ and $p_\alpha^{(0)}$ reads

$$x_\alpha(t) = x_\alpha^{(0)} \cos(\omega_\alpha t) + \frac{p_\alpha^{(0)}}{m_\alpha \omega_\alpha} \sin(\omega_\alpha t) + \frac{c_\alpha}{m_\alpha \omega_\alpha} \int_0^t dt' \sin[\omega_\alpha(t-t')] q(t'). \quad (3.17)$$

It is convenient to rewrite Eq. (3.17) as a functional of the particle's velocity. Integrating the last term by parts, we get

$$\begin{aligned} x_\alpha(t) = & x_\alpha^{(0)} \cos(\omega_\alpha t) + \frac{p_\alpha^{(0)}}{m_\alpha \omega_\alpha} \sin(\omega_\alpha t) + \frac{c_\alpha}{m_\alpha \omega_\alpha^2} \left(q(t) - \cos(\omega_\alpha t) q(0) \right) \\ & - \frac{c_\alpha}{m_\alpha \omega_\alpha^2} \int_0^t dt' \cos[\omega_\alpha(t-t')] \dot{q}(t'). \end{aligned} \quad (3.18)$$

Next, we eliminate the bath degrees of freedom by substituting Eq. (3.18) 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

$$M\ddot{q}(t) + M \int_0^t dt' \gamma(t-t') \dot{q}(t') + V'(q) = \zeta(t) - M\gamma(t-t_0)q(0). \quad (3.19)$$

Here we have introduced the memory-friction kernel

$$\gamma(t) = \Theta(t) k(t), \quad \text{where} \quad k(t) = \frac{1}{M} \sum_\alpha \frac{c_\alpha^2}{m_\alpha \omega_\alpha^2} \cos(\omega_\alpha t), \quad (3.20)$$

and the force

$$\zeta(t) = \sum_\alpha c_\alpha \left(x_\alpha^{(0)} \cos(\omega_\alpha t) + \frac{p_\alpha^{(0)}}{m_\alpha \omega_\alpha} \sin(\omega_\alpha t) \right). \quad (3.21)$$

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

$$\rho_R^{(0)} = Z^{-1} \exp \left[-\beta \sum_\alpha \left(\frac{p_\alpha^{(0)2}}{2m_\alpha} + \frac{m_\alpha \omega_\alpha^2}{2} x_\alpha^{(0)2} \right) \right], \quad (3.22)$$

the force $\zeta(t)$ becomes a stochastic force with stationary Gaussian statistics,

$$\langle \zeta(t) \rangle_{\rho_R^{(0)}} = 0, \quad \langle \zeta(t) \zeta(0) \rangle_{\rho_R^{(0)}} \equiv \mathcal{X}_{\text{cl}}(t) = Mk_B T k(t). \quad (3.23)$$

The second relation is the classical fluctuation-dissipation theorem. Upon Fourier-transformation of the second relation we obtain the power spectrum of the random force as $\tilde{\mathcal{X}}(\omega) = 2Mk_B T \tilde{\gamma}'(\omega)$, given already earlier in Eq. (2.8). From this we see that in the case of memory-friction the stochastic force $\xi(t)$ is not anymore delta-correlated. Since $\tilde{\mathcal{X}}(\omega)$ is frequency-dependent, this case is usually referred to as coloured noise.

The dynamical equation (3.19) is a Langevin equation with a linear memory-friction force and a random force representing additive noise. The generalization to quantum-thermal noise is given in Subsection 3.1.4.

The stochastic equation of motion (3.19) 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 position $q(0)$.

Upon strengthening an observation by Bez [82], it has been argued [83] that the initial transient slippage is an artefact of the decoupled thermal initial state (3.22).

The annoying term in Eq. (3.19) 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 $\zeta(t)$,

$$\xi(t) = \zeta(t) - M\gamma(t)q(0). \quad (3.24)$$

The modified random force $\xi(t)$ does not vanish on average when the mean value is taken with respect to $\rho_R^{(0)}$. 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

$$\rho_R = Z^{-1} \exp \left\{ -\beta \sum_{\alpha} \left[\frac{p_{\alpha}^{(0)2}}{2m_{\alpha}} + \frac{m_{\alpha}\omega_{\alpha}^2}{2} \left(x_{\alpha}^{(0)} - \frac{c_{\alpha}}{m_{\alpha}\omega_{\alpha}^2} q(t_0) \right)^2 \right] \right\}. \quad (3.25)$$

Upon averaging $x_{\alpha}^{(0)}$ and $p_{\alpha}^{(0)}$ with the weight function (3.25) $\xi(t)$ becomes a random force with the same statistical properties as the random force $\zeta(t)$,

$$\langle \xi(t) \rangle_{\rho_R} = 0, \quad \langle \xi(t)\xi(0) \rangle_{\rho_R} = Mk_B T k(t). \quad (3.26)$$

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

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

anticipated in Section 2.1.

From the above we see that care has to be taken if one refers to statistical properties of a random force [83]. 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.

If we had started at the Hamiltonian (3.8), we would have reached the form

$$M\ddot{q}(t) + MF'[q(t)] \int_0^t dt' \gamma(t-t') F'[q(t')] \dot{q}(t') + V'(q) = F'[q(t)] \xi(t). \quad (3.28)$$

In this modified Langevin equation the damping force describes nonlinear (state-dependent) memory friction and the random force represents multiplicative noise.

As important examples for state-dependent dissipation, we mention quasiparticle tunneling through a barrier between superconductors (Josephson contact) and strong electron tunneling through a mesoscopic junction [cf. Subsections 4.2.10 and 5.5.3].

3.1.3 Phenomenological modeling

If the number N of the bath oscillators is small, the period of time, in which the energy transferred to the bath is fed back to the central 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. In such cases it is appropriate to replace the sum over the discrete bath modes by a frequency integral with a continuous spectral density of the reservoir coupling.

With these preliminary remarks it is now straightforward to establish the connection of the frequency-dependent damping function $\tilde{\gamma}(\omega)$ 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 (3.20) is

$$\tilde{\gamma}(\omega) = \lim_{\epsilon \rightarrow 0^+} -i \frac{\omega}{M} \sum_{\alpha=1}^N \frac{c_{\alpha}^2}{m_{\alpha} \omega_{\alpha}^2} \frac{1}{\omega_{\alpha}^2 - \omega^2 - i \omega \epsilon} . \quad (3.29)$$

Next we introduce the spectral density of the environmental coupling

$$J(\omega) = \frac{\pi}{2} \sum_{\alpha} \frac{c_{\alpha}^2}{m_{\alpha} \omega_{\alpha}} \delta(\omega - \omega_{\alpha}) . \quad (3.30)$$

For a set of discrete modes, the spectral density consists of a sequence of δ -peaks. In order to work on a genuine heat bath, we assume that the eigenfrequencies ω_{α} are so dense as to form a continuous spectrum. In the continuum limit, $J(\omega)$ becomes a smooth function of ω , and the sum in Eq. (3.29) is replaced by the integral

$$\tilde{\gamma}(\omega) = \lim_{\epsilon \rightarrow 0^+} \frac{-i\omega}{M} \frac{2}{\pi} \int_0^{\infty} d\omega' \frac{J(\omega')}{\omega'} \frac{1}{\omega'^2 - \omega^2 - i \omega \epsilon} \quad (3.31)$$

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

$$\tilde{\gamma}'(\omega) = J(\omega)/M\omega . \quad (3.32)$$

The real and imaginary parts of $\tilde{\gamma}(\omega)$ are related by Kramers-Kronig relations, as required for a response function.

Sometimes it is convenient to consider the Laplace transform $\hat{\gamma}(z)$ of the damping kernel $\gamma(t)$. The damping function $\hat{\gamma}(z)$ is related to the Fourier transform $\tilde{\gamma}(\omega)$ by analytic continuation,

$$\hat{\gamma}(z) = \tilde{\gamma}(\omega = iz) ; \quad \tilde{\gamma}(\omega) = \lim_{\epsilon \rightarrow 0^+} \hat{\gamma}(z = -i\omega + \epsilon) . \quad (3.33)$$

Upon using Eqs. (3.29) and (3.31) we then get

$$\hat{\gamma}(z) = \frac{z}{M} \sum_{\alpha=1}^N \frac{c_{\alpha}^2}{m_{\alpha} \omega_{\alpha}^2} \frac{1}{(\omega_{\alpha}^2 + z^2)} = \frac{z}{M} \frac{2}{\pi} \int_0^{\infty} d\omega' \frac{J(\omega')}{\omega'} \frac{1}{\omega'^2 + z^2} . \quad (3.34)$$

We may express $\tilde{\gamma}(\omega)$ and $J(\omega)$ in terms of the dynamical susceptibilities of the individual reservoir modes given in Eq. (3.16). The resulting expressions are

$$\tilde{\gamma}(\omega) = \frac{1}{-i\omega M} \sum c_\alpha^2 \left(\tilde{\chi}_\alpha(0) - \tilde{\chi}_\alpha(\omega) \right), \quad (3.35)$$

and

$$J(\omega) = \Theta(\omega) \sum_{\alpha=1}^N c_\alpha^2 \tilde{\chi}_\alpha''(\omega) \quad (3.36)$$

We see from Eq. (3.35) that the aforementioned counter term serves to eliminate a contribution from the static susceptibility. These forms pave the way for situations in which the bath modes are effectively nonlinear, as discussed below in Section 3.5.

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. (3.32) 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. (3.31), we can give the damping kernel $\gamma(t)$ in terms of the spectral density $J(\omega)$ of the environmental coupling,

$$\gamma(t) = \Theta(t) \frac{1}{M} \frac{2}{\pi} \int_0^\infty d\omega \frac{J(\omega)}{\omega} \cos(\omega t). \quad (3.37)$$

The inversion of the Fourier integral (3.37) gives

$$J(\omega) = M\omega \int_0^\infty dt \gamma(t) \cos(\omega t). \quad (3.38)$$

The spectral density $J(\omega)$ may also be expressed in terms of the Laplace transform of the damping kernel. From Eq. (3.38) we find

$$J(\omega) = \lim_{\epsilon \rightarrow 0^+} M\omega [\hat{\gamma}(\epsilon + i\omega) + \hat{\gamma}(\epsilon - i\omega)]/2. \quad (3.39)$$

We conclude this subsection 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 [84, 85]. This property holds exactly in the case of strict linear (i.e. state-independent) dissipation. For instance, a conventional molecular dynamics simulation may be used to compute $\tilde{\gamma}'(\omega)$, which then determines $J(\omega)$ by Eq. (3.32). Therefore, this relation plays a fundamental role in the phenomenological modeling of dissipative quantum systems.

3.1.4 Quasiclassical Langevin equation

The quasiclassical Langevin equation looks formally the same as the classical Langevin equation (3.27). The generalization is that the random force $\xi(t)$ bears the quantum statistical fluctuations of the reservoir instead of the pure classical ones. To account for quantum statistical behaviour in a simple way, we assign to the random force $\xi(t)$ operator character via $x_\alpha^{(0)}$ and $p_\alpha^{(0)}$. Next, we write these operators in terms of creation and annihilation operators,

$$x_\alpha^{(0)} = \left(\frac{\hbar}{2m_\alpha \omega_\alpha} \right)^{1/2} (b_\alpha + b_\alpha^\dagger) , \quad p_\alpha^{(0)} = i \left(\frac{m_\alpha \omega_\alpha \hbar}{2} \right)^{1/2} (b_\alpha^\dagger - b_\alpha) , \quad (3.40)$$

which obey the usual commutator relations

$$(b_\alpha, b_\gamma) = (b_\alpha^\dagger, b_\gamma^\dagger) = 0 , \quad \text{and} \quad (b_\alpha, b_\gamma^\dagger) = \delta_{\alpha\gamma} . \quad (3.41)$$

In the language of these operators, the random force (3.21) reads¹

$$\xi(t) = \sum_\alpha c_\alpha \left(\frac{\hbar}{2m_\alpha \omega_\alpha} \right)^{1/2} (e^{i\omega_\alpha t} b_\alpha^\dagger + e^{-i\omega_\alpha t} b_\alpha) \quad (3.42)$$

The relevant quantum statistical equilibrium averages of these operators are

$$\begin{aligned} \langle b_\alpha \rangle_\beta &= \langle b_\alpha^\dagger \rangle_\beta = \langle b_\alpha b_\gamma \rangle_\beta = \langle b_\alpha^\dagger b_\gamma^\dagger \rangle_\beta = 0 , \\ \langle b_\alpha^\dagger b_\gamma \rangle_\beta &= \delta_{\alpha\gamma} n(\omega_\alpha) , \quad \langle b_\alpha b_\gamma^\dagger \rangle_\beta = \delta_{\alpha\gamma} [1 + n(\omega_\alpha)] , \end{aligned} \quad (3.43)$$

where $n(\omega)$ is the single-particle Bose distribution

$$n(\omega) = \frac{1}{e^{\beta\hbar\omega} - 1} . \quad (3.44)$$

With these ensemble averages the random force obeys Gaussian statistics

$$\langle \xi(t) \rangle_\beta = 0 , \quad \langle \xi(t) \xi(0) \rangle_\beta = \mathcal{X}(t) , \quad (3.45)$$

and the force correlator takes the form

$$\mathcal{X}(t) = \hbar \sum_\alpha \frac{c_\alpha^2}{2m_\alpha \omega_\alpha} \{ e^{-i\omega_\alpha t} [1 + n(\omega_\alpha)] + e^{i\omega_\alpha t} n(\omega_\alpha) \} . \quad (3.46)$$

From this expression we see that the force correlator conveys absorption to and emission from the reservoir of a single quantum of energy $\hbar\omega_\alpha$. Since we have

$$\frac{n(\omega)}{1 + n(\omega)} = e^{-\beta\hbar\omega} , \quad (3.47)$$

emission and absorption are related by detailed balance. Upon introducing the continuous spectral density of the coupling (3.30), the force correlator is found to read

$$\mathcal{X}(t) = \frac{\hbar}{\pi} \int_0^\infty d\omega J(\omega) [\coth(\beta\hbar\omega/2) \cos(\omega t) - i \sin(\omega t)] . \quad (3.48)$$

From this we find with Eq. (3.32) that the power spectrum of the random force is

$$\tilde{\mathcal{X}}(\omega) \equiv \int_{-\infty}^\infty dt \mathcal{X}(t) \cos(\omega t) = M\hbar\omega \coth(\beta\hbar\omega/2) \tilde{\gamma}'(\omega) , \quad (3.49)$$

which is a version of the quantum-mechanical fluctuation-dissipation theorem. This form has been anticipated above in Eq. (2.32).

One remark is appropriate. We see from the classical fluctuation-dissipation theorem (3.23), or from the classical limit of Eq. (3.49), that classical noise is δ -correlated for strict Ohmic friction. On the other hand, Eq. (3.49) tells us that quantum statistical noise stays coloured even when friction becomes Ohmic.

¹For simplicity we disregard here the initial transient slippage $-M\gamma(t)q(0)$.

3.1.5 Ohmic and frequency-dependent damping

In the strict *Ohmic* (instant response) limit, damping is frequency-independent,

$$\tilde{\gamma}(\omega) = \gamma. \quad (3.50)$$

We see from Eq. (3.38) or from Eq. (3.39) that strict Ohmic damping is described by the model (3.11) in which the spectral density $J(\omega)$ is chosen as [77]

$$J(\omega) = \eta\omega = M\gamma\omega \quad (3.51)$$

for all frequencies ω . In the first equality, we have introduced the familiar viscosity coefficient η . The relation (3.51) implies memoryless friction $\gamma(t) = 2\gamma\Theta(t)\delta(t)$.² This, of course, is an idealized situation. In reality, any particular spectral density $J(\omega)$ of physical origin falls off in the limit $\omega \rightarrow \infty$, because there is always a microscopic memory time setting the time scale for inertia effects in the reservoir. If $J(\omega)$ would grow steadily with ω , certain physical quantities, e.g. the momentum dispersion, would be divergent (cf. the discussion in Section 7.3).

In the simplest form, the damping kernel $\gamma(t)$ in the classical equation of motion (2.4) is regularized with a Drude memory time $\tau_D = 1/\omega_D$,

$$\gamma(t) = \gamma\omega_D\Theta(t)\exp(-\omega_D t), \quad (3.52)$$

which is known as *Drude regularization*. We then have in the frequency domain

$$\tilde{\gamma}(\omega) = \gamma/[1 - i\omega/\omega_D], \quad \text{and} \quad \hat{\gamma}(z) = \gamma/[1 + z/\omega_D]. \quad (3.53)$$

In the Drude case, the imaginary part of $\tilde{\gamma}(\omega)$ differs from the real part by a factor of ω/ω_D . Hence it is small well below the Drude frequency.

The Drude form (3.53) originates from a spectral density with algebraic cutoff,

$$J(\omega) = M\gamma\omega/[1 + \omega^2/\omega_D^2]. \quad (3.54)$$

The damping kernel brings in memory-friction on the time scale $\tau_D = \omega_D^{-1}$. When the relevant frequencies of the system are much lower than the Drude cutoff frequency ω_D , the reservoir described by (3.54) behaves like an Ohmic heat bath with effective damping strength $\gamma_{\text{eff}} = \int_0^\infty dt \gamma(t) = \gamma$.

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 counter term (3.6) or the quantity $\gamma(0)$ would diverge which is pathological. The power-law form is assumed to hold in the frequency range $0 \leq \omega \lesssim \omega_c$, where ω_c is much less than a characteristic cutoff frequency ω_{ch} , which is of the order of the Drude, Debye, or Fermi frequency etc., depending on the model.

²In 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).

For frequencies of the order of or greater than ω_{ch} , the behaviour of $J(\omega)$ may be complicated and may not easily be inferable from the classical motion or from microscopic considerations. The important point, however, is that, as long as we are interested in times $t \gg \omega_c^{-1}$, the effect of the environmental modes with $\omega \gtrsim \omega_c$ can be absorbed into a renormalization of parameters appearing in the Hamiltonian H_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 $\omega \rightarrow \infty$. 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,

$$J(\omega) = J_{\text{lf}}(\omega) + J_{\text{hf}}(\omega), \quad (3.55)$$

$$J_{\text{lf}}(\omega) = J(\omega) f(\omega/\omega_c), \quad (3.56)$$

$$J_{\text{hf}}(\omega) = J(\omega) [1 - f(\omega/\omega_c)]. \quad (3.57)$$

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

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

$$J_{\text{lf}}(\omega) = \eta_s \omega_{\text{ph}}^{1-s} \omega^s e^{-\omega/\omega_c}, \quad \eta_s = M\gamma_s. \quad (3.58)$$

Here we have introduced for $s \neq 1$ a “phononic” reference frequency ω_{ph} , so that the coupling constant η_s has dimension of viscosity for all s . We shall distinguish the frequency ω_{ph} from the cutoff frequency ω_c . Where convenient, we shall use the respective temperature scales

$$T_{\text{ph}} \equiv \hbar\omega_{\text{ph}}/k_B, \quad T_c \equiv \hbar\omega_c/k_B. \quad (3.59)$$

In many physical situations, the frequency ω_c at which the power law $J_{\text{lf}}(\omega) \propto \omega^s$ 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 $J_{\text{hf}}(\omega)$ adds to the damping function $\tilde{\gamma}(\omega)$ in the regime $\omega \ll \omega_c$ the contribution

$$\tilde{\gamma}_{\text{hf}}(\omega) = -i\omega \Delta M_{\text{hf}}/M, \quad (3.60)$$

$$\Delta M_{\text{hf}} = \frac{2}{\pi} \int_0^\infty d\omega' \frac{J_{\text{hf}}(\omega')}{\omega'^3}, \quad (3.61)$$

as follows from Eq. (3.31). With (3.60), the Fourier transform of the memory-friction force $-i\omega \tilde{\gamma}_{\text{hf}}(\omega) \tilde{q}(\omega)$ reduces at low frequencies to the form $-\Delta M_{\text{hf}} \omega^2 \tilde{q}(\omega)$. This term,

however, simply adds to the kinetic term $-M\omega^2\tilde{q}(\omega)$. Thus for times $t \gg \omega_c^{-1}$, the partial spectral density $J_{\text{hf}}(\omega)$ manifests itself just as mass renormalization,

$$M_{\text{r}} = M + \Delta M_{\text{hf}}. \quad (3.62)$$

From this we conclude that if we are not interested in the time regime $t < 1/\omega_c$, we may treat $J_{\text{hf}}(\omega)$ in the adiabatic approximation. If not stated differently, we will eliminate $J_{\text{hf}}(\omega)$ 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 (3.61) is convergent also for the spectral density $J_{\text{f}}(\omega)$ when the power s in Eq. (3.56) is larger than 2. For this case, the full spectral density results in no more than mass renormalization for asymptotic times. Further discussion of this point is given in Section 7.4.

Upon inserting the form (3.56) of the spectral density with a sharp cutoff into the representation (3.34), the spectral damping function takes the exact form [86]

$$\hat{\gamma}(z) = \frac{2\gamma_s}{\pi s} \left(\frac{\omega_c}{\omega_{\text{ph}}} \right)^{s-1} \frac{\omega_c}{z} {}_2F_1\left(1, \frac{1}{2}s; 1 + \frac{1}{2}s; -\omega_c^2/z^2\right), \quad (3.63)$$

where ${}_2F_1(a, b; c; x)$ is a hypergeometric function [87, 88]. 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. It may be calculated upon using standard transformation formulas of the hypergeometric function. Putting $\lambda_s \equiv \gamma_s/\sin(\pi s/2)$, we find

$$\hat{\gamma}(z) = \begin{cases} \lambda_s (z/\omega_{\text{ph}})^{s-1}, & 0 < s < 2, \\ (\gamma_2/\pi)(z/\omega_{\text{ph}}) \ln(1 + \omega_c^2/z^2), & s = 2, \\ z \left[\Delta M/M + (\lambda_s/\omega_{\text{ph}})(z/\omega_{\text{ph}})^{s-2} + \mathcal{O}\left(\frac{z^2}{\omega_c^2}\right) \right], & 2 < s < 4, \\ z \left[\Delta M/M + \mathcal{O}\left(\frac{z^2}{\omega_c^2}\right) \right], & s \geq 4 \end{cases} \quad (3.64)$$

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

As we have discussed already, the case $s = 1$ in Eq. (3.56) describes Ohmic friction. The cases $0 < s < 1$ and $s > 1$ have been dubbed *sub-Ohmic* and *super-Ohmic*, respectively [89]. We shall present in Sections 3.3 and 4.2 various microscopic models and consider the respective spectral densities of the coupling. We anticipate that an Ohmic friction contribution is almost ubiquitously met in real physical systems at low temperatures. The Ohmic case is important, e.g., for tunneling systems in a metallic environment. A phonon bath in d spatial dimensions corresponds to the case $s = d$ or $s = d + 2$, depending on the underlying symmetry of the strain field. Irrational values of s may occur for environments with fractal dimension.

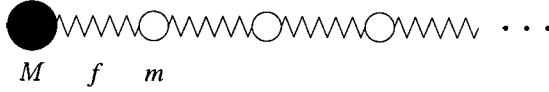


Figure 3.1: Pictorial sketch of the mechanical analogue of the Rubin model.

3.1.6 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 $f = m\omega_R^2/4$ [90], as sketched in Fig. 3.1. The Hamiltonian of the global model is

$$H = \frac{p^2}{2M} + V(q) + \sum_{n=1}^{\infty} \left(\frac{p_n^2}{2m} + \frac{f}{2}(x_{n+1} - x_n)^2 \right) + \frac{f}{2}(q - x_1)^2. \quad (3.65)$$

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

$$x_n = \sqrt{2/\pi} \int_0^\pi dk \sin(kn) X(k). \quad (3.66)$$

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

$$H = \frac{p^2}{2M} + V(q) + \frac{f}{2}q^2 + \int_0^\pi dk \left(\frac{P^2(k)}{2m} + \frac{m}{2}\omega^2(k)X^2(k) - c(k)X(k)q \right), \quad (3.67)$$

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

$$\omega(k) = \omega_R \sin(k/2), \quad c(k) = \sqrt{2/\pi} [m\omega_R^2/4] \sin(k). \quad (3.68)$$

The frequency ω_R is the highest frequency of the reservoir modes. Substituting Eq. (3.68) into Eq.(3.30), the spectral density of the coupling is found as

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

which is Ohmic for $\omega \ll \omega_R$. With this form, the damping kernel (3.37) emerges as

$$\gamma(t) = \frac{m}{2M} \omega_R \frac{J_1(\omega_R t)}{t}, \quad (3.69)$$

where $J_1(z)$ is a Bessel function of the first kind. Thus, the damping kernel of the Rubin model oscillates with time, and for asymptotic times $t \gg 1/\omega_R$, it decays algebraically,

$$\gamma(t) = \frac{m}{2M} \sqrt{2\omega_R/\pi} \frac{\sin(\omega_R t - \pi/4)}{t^{3/2}} \quad (3.70)$$

This behaviour drastically differs from the exponential decay of the Drude kernel (3.52). Finally, observe that the memory time of the Rubin kernel is of the order of $1/\omega_R$.