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Projection Operator Techniques in Nonequilibrium Statistical Mechanics

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Preface

Ever since the time of Boltzmann, the desire to understand how macroscopic irreversible behavior arises out of the complexity of the underlying microscopic processes has been driving the development of the statistical mechanical theory of many-body systems. While most of the "fundamental" questions associated with irreversible processes have yet to be answered to the satisfaction of all physicists, the theory has obtained valuable results for "down-to-earth" physics by giving molecular expression for those quantities encountered in macroscopic evolution laws. Most of those questions concerning the general form of macroscopic evolution equations, their features and symmetries, and their connection with the molecular process can be answered quite generally, independent of particular models, on different levels of approximation, each level being related to the others by a hierachical structure.

These questions can be approached in an elegant manner by utilizing the projectio operator technique, which will be presented in detail in this volume. This method is employed to derive transport equations for the relaxation of the mean, Langevin equations for the fluctuations about the mean, and, further, on a more detailed level, Fokker-Planck and master equations. The relations between the various evolution equations will be discussed and the equations themselves will be illustrated by applying them to specific models.

The emphasis of this article is on the unifying aspects of the different statistical mechanical theories of relaxation and fluctuation in many-body systems. However, the work does not treat those approaches which begin particularly close to the molecular level, such as the Boltzmann equation, because these approaches, of necessity, depend on details of particular models.

I am grateful to the many colleagues who have added to my insights and understanding. In particular, I am indebted to those with whom I have had the pleasure of close collaboration: W. Eidlich, P. Talkner, P. Hanggi, R. Graham, and, especially, the late M.S. Green.

Special thanks are also due to H. Haken whose suggestions and efforts as a coeditor were most helpful.

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Finally, it is a pleasure to thank Ms. E. Effenberg for the skillful preparation of the manuscript.

Stuttgart, Autumn 1981 *Hermann Grabert*

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1. Introduction and Survey

Many-body systems composed of a great number of identical constituents exhibit on the macroscopic level a rather simple behavior described by equations of motion for a few macroscopic variables. Examples are the Navier-Stokes equations for fluids, the Bloch equations for magnetic relaxation, the Fokker-Planck equation for a Brownian particle, and the master equation for atoms interacting with a radiation field. The statistical mechanical theory relates this macroscopic dynamics with the underlying microscopic process. In spite of its complexity in detail, the microscopic process has simple formal properties: it is a reversible dynamical process which is determined completely by the Hamiltonian H and the initial probability density $\rho(t_0)$ from which all properties of the system can be calculated, at least in principle.

Because of the common structure of the microscopic dynamics, the macroscopic evolution laws of nonequilibrium systems possess common features as well. Among those is most notably the fact that the macroscopic evolution equations can be cast into the form of transport equations[1] which are determined by a thermodynamic potential and a matrix of transport coefficients. The underlying molecular nature of the system is primarily manifest in this particular form. The irreversible part of the transport equations is related to correlations of molecular fluxes by GREEN-KUBO-type formulae [1,2], while the reversible part has a Poisson bracket (or commutator) structure [3,4]. Kinetic equations seemingly as different as the Navier-Stokes equations and the Pauli master equation display their common features when they are cast into the form of transport laws. The analogy is not complete, but it is extremely helpful if one wants to borrow techniques developed to understand one system for the study of another one.

In this article we make an attempt to develop a general foundation of the statistical mechanics of irreversible processes and to provide a theoretical framework within which the correspondence between the macroscopic relaxation and fluctuation behavior of a rich variety of many-body systems can be assessed. The approach is based on macroscopic kinetic equations of the form of (possibly generalized) trans-

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[1] We shall use the term transport equation in a broader sense than usual.

port equations which are derived from the underlying molecular dynamics by means of the *projection operator technique*. At no stage shall we resort to an *a priori* introduction of purely stochastic elements.

Before beginning a systematic exposition, it may be worthwhile to elaborate on some aspects of the problem we wish to address. When dealing with macroscopic evolution equations for a many-body system, we have to bear in mind that there is not just *one* macroscopic evolution law but rather a whole hierarchy of kinetic equations, each of which gives a valid description of the macroscopic behavior under certain physical conditions and is bound to fail if these conditions are not met.

Nonequilibrium systems, when they deviate only slightly from equilibrium, and when they are not close to phase transitions, are well described on the macroscopic level by a Gauss-Markov process. The statistical-mechanical theory of irreversible processes, which began with EINSTEIN [5] and developed through the work of a number of authors [6-16], realized the intimate connection between fluctuations and irreversible behavior. This brings about common features of the near equilibrium Gauss-Markov processes crystallizing in ONSAGER's reciprocal relations [11,12] and the fluctuation-dissipation theorem [10,14]. The whole theory is subsumed in the *thermodynamics of irreversible processes*, which is now a well-settled matter of textbooks [17-19].

Clearly a macroscopic description by a Gauss-Markov process can only be an approximation, since nonlinearities, which are met within all real systems, produce non-Gaussian stochastics, and the finite correlation times of microscopic variables lead to non-Markovian corrections. Considering the time evolution of *equilibrium* correlation functions, MORI [20] has shown that all these corrections can exactly be accounted for if the transport coefficients are replaced by time-retarded transport kernels. In frequency space this means that the transport coefficients are made frequency dependent. Essentially the same findings have been obtained by KADANOFF and MARTIN [21]. These generalized transport coefficients, which are actually functions of frequency or time, are now often referred to as renormalized transport coefficients. When they are replaced by constants, thus disregarding the memory effects, one recovers the standard theory of near equilibrium irreversible processes [17-19]. The differences are particularly pronounced near critical points where the latter theory fails. An excellent review of *Mori theory* including many applications has more recently been given by FORSTER [22].

A significant body of work published during the last three decades has searched for a nonlinear generalization of the theory of linear irreversible processes. Such a generalization is needed to treat *nonequilibrium* systems when they deviate sufficiently from equilibrium. ROBERTSON [23] has shown that the exact time evolution of the macroscopic state is governed by generalized transport equations which differ from those of Mori theory in two resepcts. The thermodynamic potential is a nonlinear function of the state variables and cannot be truncated after the bilinear terms, and the transport kernels pick up a functional dependence on the past history of the macroscopic state when the systems leaves the vicinity of the equilibrium state, thus rendering the transport laws nonlinear. Closely related results have been obtained by McLENNAN [24] and ZUBAREV [25].

More recently, this author [26,27] has shown that the fluctuations about the mean obey exact generalized Langevin equations whose systematic terms are determined by the transport laws and whose stochastic terms are related to the transport kernels by a generalized fluctuation-dissipation theorem. These Langevin equations are linear but nonstationary in general. By *generalized statistical thermodynamics*, we mean a theory describing the relaxation and fluctuation behavior of nonequilibrium systems by means of these generalized transport and Langevin equations. When the theory is linearized about equilibrium, one recovers Mori theory. On the other hand, when the memory effects are disregarded, one obtains an approximate description of nonequilibrium systems in terms of a nonstationary Gauss-Markov process. We shall refer to this approximate theory as *statistical thermodynamics*. Various authors [28-34] have proposed such a theory on the basis of phenomenological arguments. The statistical-mechanical foundation of statistical thermodynamics [35] leads to common features of the nonstationary Gauss-Markov processes which correspond to those of Onsager's theory. Of course, the latter is obtained by linearizing statistical thermodynamics about equilibrium (Fig.1.1).

While statistical thermodynamics extends the range of validity of the theory of linear irreversible processes to the nonlinear regime far from equilibrium, it still breaks down near equilibrium phase transitions if the memory effects are disregarded. Away from equilibrium there are additional nonequilibrium instabilities, like the Bénard instability [36] and the Gunn instability [37], which also are described only roughly by a mean-field-type approximation. While these shortcomings can be corrected by including the memory effects, it is rather cumbersome to evaluate the molecular expressions for the retarded transport kernels even approximately, and a more straightforward method for the calculation of renormalized transport coefficients is needed.

It has been realized during recent years that the most important contributions to the memory effects in generalized statistical thermodynamics are not caused by the finite correlation time of the microscopic variables but rather come from nonlinear couplings between fluctuations of the macroscopic variables [38-42]. These nonlinearities are disguised in the frequency dependence of the renormalized transport coefficients. As a consequence, it seems natural to seek for an extended theory of irreversible processes which retains the Markovian property but gives up the Gaussian property. Such a non-Gaussian Markov process is governed by a Fokker-Planck equation or a master equation, according to whether the process is continuous or not.

For most macroscopic systems the discrete nature of the microscopic states can safely be neglected, and they are well described on the macroscopic level by a continuous stochastic process. In a pioneering work GREEN [1] derived a *Fokker-Planck equation* for such nonequilibrium systems which explicitly displays the nonlinearities since the drift vector may be a nonlinear function of the state variables and since the diffusion matrix is not necessarily constant. He further established molecular expressions and common features for the bare transport coefficients entering the Fokker-Planck equation. Later ZWANZIG [43] showed that the macroscopic dynamics can be exactly described by a *generalized Fokker-Planck equation* containing memory effects. In as much as non-Gaussian stochastics is accounted for by the nonlinearities, these memory effects reflect non-Markovian corrections alone. When the memory effects are disregarded one recovers Green's results.

The Fokker-Planck equation gives a more complete description of nonequilibrium systems than statistical thermodynamics, because it treats the state variables and the nonlinear functions of the state variables on an equal footing, while the latter are not considered relevant variables in the theory of statistical thermodynamics. As a consequence of this and the nonlinearities, however, the Fokker-Planck approach does not yield directly closed equations of motion for the mean values and the correlation functions of the state variables. These have to be determined by what is now commonly referred to as a renormalization. By renormalizing the Fokker-Planck process one obtains *renormalized transport laws* with retarded transport kernels of the same type as those met within generalized statistical thermodynamics, but the transport kernels are in fact approximated since non-Markovian effects are not included in the Fokker-Planck equation.[2]

The renormalized transport laws derived from the Fokker-Planck equation or a set of stochastically equivalent nonlinear Langevin equations [44- 46] lie between statistical thermodynamics and generalized statistical thermodynamics (Fig.1.1); they do contain the major corrections to statistical thermodynamics though. Mostly, authors have looked for renormalized transport equations in the linearized form in order to determine equilibrium correlation functions [38-42,47,48]. This is the approach which has been so successful in explaining the dynamical behavior in the vicinity of equilibrium phase transitions [4,49-51]. In the study of nonequilibrium systems, however, the renormalized transport laws become nonlinear [53-55].

Particularly in systems where quantal effects are important, it may be necessary to take into account the fact that the macroscopic variables can take on values out of a discrete set only. The Fokker-Planck equation is then replaced by a quantum-

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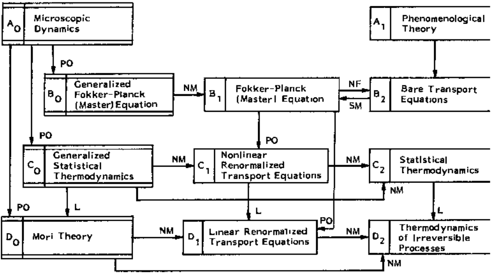
[2] To distinguish the two kinds of renormalized transport equations one could call those derived from the Fokker-Planck equation "fluctuation renormalized" and those met within the theory of generalized statistical thermodynamics "fully renormalized".



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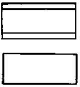

exact

approximate

Connections:

PO : projection operator technique
L : linearization about equilibrium
NM : neglecting memory effects
NF : neglecting flutuations
SM : stochastic modeling

Discussion in this Article:

$A_0 \rightarrow B_0$: Sects.4.1-3 (5.1-3)
$A_0 \rightarrow C_0$: Sects.3.1-3
$B_0 \rightarrow B_1$: Sect.4.4 (5.4,5)
$B_1 \rightarrow C_1$: Sects.4.5,6 (5.6)
$C_0 \rightarrow D_0$: Sect.3.4
$C_0 \rightarrow C_2$: Sects.3.5,6

Connections including a simple linearization about equilibrium are not always discussed explicitly.

Fig.1.1. Levels of description and their connections

mechanical *master equation.*[3] This approach traces back to PAULI [59], was improved later by VAN HOVE [60], PRIGOGINE [61,62], NAKAJIMA [63], ZWANZIG [64-66], and others [67-72], and has been reviewed by HAAKE [73] and SPOHN [74]. Very recently, objections against the standard approach have been raised on the basis of fundamental considerations [75,76]. To cope with these, we have found it necessary to abandon the usual factorization assumptions [73,74] and to bring the master equation into the form of a transport equation. This form has not been used so far. The master equation approach may then be developed in close analogy with the Fokker-Planck equation approach.

The various macroscopic evolution laws and their mutual dependence are depicted schematically in Fig.1.1. The hierarchical character is apparent in the one-way connections which either lead downwards to a theory that has more microscopic details left out, or rightwards to a theory that has more approximations built in. Clearly, the scheme in Fig.1.1 is not complete since there are further levels of description lying between a fully microscopic treatment and the level of nonlinear Markov processes, that is, between level A and B in Fig.1.1.

The usual Fokker-Planck description is not appropriate for a study of phenomena occuring on a length or time scale close to a microscopic scale. One must then either take non-Markovian effects into account [77,78] or utilize a more microscopic method (e.g., a *Boltzmann equation* approach [78-81]). Although this approach may also be analyzed in a language very similar to one given here, a discussion of it would be beyond the scope of this article. This is because the closer one approaches the microscopic level, less universal the findings are, and because different physical systems require different treatment. We shall concentrate on the structural aspects of the macroscopic theory of many-body systems.and, in particular, on those aspects that are independent of a specific model.

Moreover, we shall not discuss the field of *nonequilibrium instabilities* [46,70, 82-85] which has received so much attention recently. In general, these phenomena do not demand statistical-mechanical techniques different from those treated in this article; rather one starts from the equations of motion derived here. Often, a complete macroscopic description of a nonequilibrium system requires a large set of macroscopic variables, particularly in inhomogeneous systems, where the macroscopic variables are local variables. In the vicinity of a nonequilibrium instability, however, the set of relevant variables can greatly be reduced because a separation of time scales between the "stable" and the "unstable" modes occurs. Indeed, HAKEN [85,86] eliminates the stable modes and derives a close subdynamics for the unstable modes only. While this *second coarse graining* can partly be performed by

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[3] Clearly, there are also classical systems which can approximately be described by master equations. In particular, well-stirred ideal mixtures undergoing chemical reactions have frequently been studied [56-58]. Most of the fundamental questions raised by quantal master equations are not present in the classical case.

means of the techniques developed here for the *first coarse graining*, it is important to notice that the effective evolution equations for the unstable modes do not necessarily share the features that our equations of motion possess.

In practice, macroscopic phenomena are frequently studied by means of phenomenological methods. Indeed, from phenomenological considerations one often obtains a set of deterministic equations of motion for the macroscopic variables (e.g., [87]). The question of how to account for fluctuations thus arises. In particular, in the interesting case of nonlinear systems, this problem of *stochastic modeling* has extensively been discussed in the literature. Recently, some proposals have been critically investigated by HANGGI [88]. Considerations on the basis of statistical-mechanical arguments show that, at least for continuous processes, the stochastic description by means of a Fokker-Planck equation can be reconstructed from the limiting deterministic laws [89,90]. Some macroscopic theories discussed in this article can, hence, also be approached from the phenomenological point of view (Fig.1.1). For a recent review of the phenomenological approach see [91].

The *outline* of this article is the following. The paper is divided into two parts, A and B, each of which has several chapters. Each chapter opens with a brief summary of its content. While the material is presented in a systematic way, all chapters after Chap.3 are to a large extent self-contained. This made it necessary to repeat occasionally an argument already given in a previous chapter, but it certainly facilitates the use of the article as a source of reference for the various approaches discussed in it. A general idea about the organization of the article can also be obtained by glancing at Fig.1.1 and its caption.

Part A is devoted to the derivation of macroscopic evolution equations starting from a microscopic theory. To this purpose we make use of the *projection operator technique* which has been introduced into statistical physics by NAKAJIMA [63] and ZWANZIG [64]. In particular ZWANZIG [43,65,66,92] developed the technique into a powerful tool for the derivation of formally exact equations of motion for classical or quantal probability densities. Later MORI [20] put forward a projection operator technique in the Heisenberg picture, which leads to generalized linear Langevin equations. Both approaches have been reviewed by HYNES and DEUTSCH [93]. Using an extended time-dependent projection operator technique, ROBERTSON [23] was able to derive closed nonlinear equations for mean values. This approach was supplemented later by the author [26], who derived exact evolution equations for the fluctuations about the mean. The latter technique can be shown to cover the previous ones.

Since most of the specialized applications of the projection operator technique are best appreciated when the central elements of this method have been understood, we reserve Chap.2 for a detailed presentation of the basic ideas and the general scheme. The presentation is more general than is needed for the following chapters, but the characteristics thus become particularly clear, and the approach also covers applications not explicitly discussed here [81,94,95].

In Chaps.3, 4, and 5, we then apply the technique to derive the various types of macroscopic evolution equations mentioned above. Molecular expressions for the quantities entering the transport laws are derived, and general properties and symmetries of these quantities are proved. We further discuss the mutual connections between the different equations of motion. In Chap.6 we study the response of the system to an applied time-dependent perturbation, both from a microscopic and macroscopic point of view. We show how the macroscopic evolution equations are modified by the external perturbation and emphasize the connection with the preceding results

Part B contains some select applications of the general formalism which are intended to illustrate the methods discussed in Part A. Chapter 7 is concerned with the statistical-mechanical theory of a classical nonlinear oscillator in interaction with a heat bath. This investigation is based on the Fokker-Planck equation approach The special cases of a Brownian particle in a fluid and a mass impurity in a harmonic lattice are discussed in some detail, and the renormalization of transport equations is illustrated by using the Duffing oscillator as an example.

In Chap.8, statistical thermodynamics is applied to simple classical fluids. We start out from general considerations of systems described by local densities and derive exact equations of motion for the hydromechanic modes. The nonlinear Navier-Stokes equations are recovered in an approximation. Langevin equations for the spontaneous fluctuations are obtained and used to calculate the structure factor for light scattering in the presence of a steady temperature gradient. In Chap.9, we discuss spin relaxation using the master equation approach. The master equation for the coarse-grained spin probability density and the Bloch equations for the mean spin relaxation are derived. Finally, we determine the linear response to an alternating applied magnetic field.

While the present article is based on the projection operator technique, it is not intended to give a comprehensive review of all recent developments related to projector methods, nor is an extensive or even complete list of literature provided. The emphasis is on a coherent presentation of those methods which have proved to be particularly powerful tools for the development of a statistical-mechanical foundation of irreversible processes in many-body systems.

Part A. General Theory

2. The Projection Operator Technique

In this chapter we present the basic ideas and the general scheme of the projection operator technique.[1] We show how the method extracts exact equations of motion for a few macroscopic variables from the microscopic process involving all variables of the system.

The foundations of the method are formed by the particular structure of the microscopic dynamics governed by a Hamiltonian and by the concept of the relevant probability density. The important properties of the microscopic dynamics, as far as we shall need them, are recapitulated in Sect.2.1. On the macroscopic level the system is described by a set of macroscopic variables. The ability to choose the appropriate set for a given problem is where physical insight is required. For a given set of macroscopic variables we introduce a relevant probability density which is macroscopically equivalent to the full microscopic probability density. Section 2.2 summarizes the basic properties of a relevant probability density, while its particular form is left open during the general considerations of this part of the article.

As soon as the set of macroscopic variables and the relevant probability density have been fixed on the basis of physical arguments, the continuation of the projection operator method is determined by a mathematical elimination procedure removing the microscopic variables from the equations of motion. First, in Sect.2.3 we introduce a projection operator acting in the space of all variables and projecting out the macroscopic variables. The form of this projection operator is specified in terms of the relevant probability density. In Sect.2.4 we come to the fundamental mathematical identity. The microscopic time evolution operator is decomposed with the help of the projection operator into a sum of three terms, where the first term is completely determined by the instantaneous values of the macroscopic variables, the second term by their past history, and the third term is of microscopic origin leading to the irregular motion of macroscopic quantities.

The fundamental identity is used in Sect.2.5 to derive the generalized transport equations. They form an exact closed system of integro-differential equations for

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[1] We essentially follow [26].

the mean values of the macroscopic variables. In these equations the microscopic variables are eliminated completely in favor of after-effect functions describing a retarded interaction among the macroscopic variables.

In Sect.2.6 we derive the generalized Langevin equations describing the dynamics of fluctuations about the mean path. The Langevin equations are nonstationary if the mean values depend on time. The fluctuations of the macroscopic variables are driven by random forces, the stochastics of which depends on the mean path. Section 2.7 contains some concluding, as well as additional, remarks on the projection operator technique.

2.1 Microscopic Dynamics

Statistical-mechanical theory relates the macroscopic dynamics of a large system composed of great numbers of identical constituents with the underlying microscopic or molecular process. Clearly, the microscopic process is very complex in detail, and the laws governing this process might be known only approximately since we do not always know the molecular constituents of a system and their mutual interactions precisely. On the other hand, the microscopic process has simple formal properties: it is a special Markovian process which is completely determined by the Hamiltonian of the system and the initial probability density. These formal properties of the microscopic process lead to a definite structure of the macroscopic dynamics. In this section we summarize some of the general properties of microscopic processes.

The microscopic dynamics determines the time evolution of a microscopic state of the system in a unique, deterministic way. However, by macroscopic observation or measurements we obtain only incomplete information about the microscopic state of a macroscopic system. We have to consider an ensemble of identical systems which have been under the influence of identical external conditions (identical preparation of the initial state) and ask for the ensemble probability of events. In practice, an ensemble of systems can also be formed by repeating the same process very often with the same system, or, in the case of stationary processes, by measuring for a sufficiently long time.

An ensemble of systems is described by a probability density ρ. In classical-statistical mechanics ρ is a distribution function in the phase space Φ, while for quantum-mechanical systems ρ is an operator[2] acting in the Hilbert space H. In the following we shall often suppress the ensemble point of view and call ρ the microscopic probability of the system. The probability density ρ is positive

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[2] In quantum-statistical mechanics ρ is also referred to as the density matrix or statistical operator.

$$\rho \geq 0 \text{ , i.e.. } \begin{cases} \rho(\Gamma) \geq 0 & \text{(classical)} \\ \langle\psi|\rho|\psi\rangle \geq 0 & \text{(quantal)} \end{cases} \tag{2.1.1}$$

and normalized

$$\mathrm{tr}[\rho] = 1, \text{ i.e., } \begin{cases} \int d\Gamma\rho(\Gamma) = 1 & \text{(classical)} \\ \sum_i \langle\varphi_i|\rho|\varphi_i\rangle = 1 & \text{(quantal)} \end{cases} \quad . \tag{2.1.2}$$

In classical-statistical mechanics the value of the phase function $\rho(\Gamma)$ is positive in every point Γ of the phase space Φ, and tr denotes the integration over all phase space. In quantum-statistical mechanics the matrix element $\langle\psi|\rho|\psi\rangle$ is positive for every state $|\psi\rangle$ in the Hilbert space H, and tr denotes the trace over a complete orthonormal basis $\{\varphi_i\}$ of H.

We consider isolated systems. If necessary, this can be achieved, at least approximately, by enlarging the system to include the interacting surroundings. The time evolution of the microscopic probability ρ of an isolated system is governed by the Liouville equation

$$\dot{\rho}(t) = -i\mathbf{L}\rho(t) \quad . \tag{2.1.3}$$

In classical physics the Liouvillian **L** acts upon a phase function X as Poisson bracket with the Hamilton function H, while the quantum-mechanical Liouvillian acts upon a Hilbert space operator X as commutator with the Hamilton operator H:

$$\begin{aligned} \mathbf{L}X &= i\{H,X\} && \text{(classical)} \\ \mathbf{L}X &= \frac{1}{\hbar}[H,X] && \text{(quantal)} \quad . \end{aligned} \tag{2.1.4}$$

The formal solution of the Liouville equation reads

$$\rho(t) = e^{-i\mathbf{L}t}\rho(0) \tag{2.1.5}$$

where $\rho(0)$ is the initial microscopic probability.[3]

A variable (observable) F of the system is represented as a phase function in classical statistical mechanics and as a self-adjoint Hilbert space operator in quantum statistics. The microscopic probability $\rho(t)$ determines the mean value (expectation value) of a variable F at time t

$$\langle F(t)\rangle = \mathrm{tr}\{F\rho(t)\} \quad . \tag{2.1.6}$$

While in the Schrödinger picture the probability density is a function of time, the Heisenberg picture treats the variables as time-dependent phase functions,

$$F(t) = e^{i\mathbf{L}t}F \quad , \quad F \equiv F(0) \quad , \tag{2.1.7}$$

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[3] In quantum-statistical mechanics (2.1.5) can also be written $\rho(t) = \exp[-(i/\hbar)Ht]\rho(0)\exp[(i/\hbar)Ht]$.

and the mean values reads

$$\langle F(t)\rangle = \mathrm{tr}\{F(t)\rho(0)\} \quad . \tag{2.1.8}$$

The representations (2.1.6) and (2.1.8) are equivalent since the Liovillian has the property

$$\mathrm{tr}\{F\mathbf{L}\rho\} = -\mathrm{tr}\{\rho\mathbf{L}F\} \quad , \quad \text{i.e.,} \quad \mathbf{L}^T = -\mathbf{L} \quad , \tag{2.1.9}$$

which can be used to transfer the time dependence from the probability density to the variables, and vice versa.

The Heisenberg picture is particularly useful if we want to consider correlations of variables $F_i (i = 1, \ldots, p)$ at different times t_i. In classical statistical mechanics the correlation function is given by

$$\langle F_1(t_1)\ldots F_p(t_p)\rangle = \mathrm{tr}\{F_1(t_1)\ldots F_p(t_p)\rho(0)\} \quad . \tag{2.1.10}$$

Phase functions under the classical phase space integral tr may be permuted in an arbitrary way, whereas the quantum-mechanical trace tr is only invariant under cycli permutations of the Hilbert space operators. Consequently, there are different multitime expectations of Heisenberg operators $F_i(t_i)$ which reduce to the same classical correlation function (2.1.10) in the classical limit. The differences between those multitime expectations are a consequence of the quantum-mechanical dispersion, which introduces an additional stochastic element beyond the scope of classical stochastic processes. It is merely a matter of convenience which of the various multitime expectations is called correlation function. In fact, several definitions of quantum-mechanical correlation functions have been introduced in different contexts [14,17,70,96-102]. Some convenient choices will be discussed later.

2.2 Macroscopic Variables and Relevant Probability Density

Macroscopic systems exhibit on a macroscopic level a rather simple behavior described by equations of motion for a few macroscopic variables. The appropriate choice of these macroscopic variables is one of the most important steps in a statistical-mechanical theory of many-body systems. Frequently, the existence of slow variables can be traced back to conservation laws or, in the case of ordered systems, to continuous broken symmetries; the associated macroscopic variables are then densities of conserved quantities and order parameters [22,49,103]. There may be additional variables though: e.g., in systems undergoing slow chemical reactions, the concentrations of the reacting constituents are among the macroscopic variables although they are not conserved [104-106]. For concrete systems the macroscopic variables are generally known by experience. In a kinetic model the macroscopic variables are mostly algebraic sums of molecular variables.

The set of macroscopic variables $A = (A_1,\ldots,A_i,\ldots)$ is supposed to be large enough to specify the macroscopic or thermodynamic state of the system. Naturally, given the mean values

$$a_i(t) = \langle A_i(t)\rangle = \mathrm{tr}\{A_i\rho(t)\} \qquad (2.2.1)$$

of the macroscopic variables at time t, we can not construct the true microscopic probability density $\rho(t)$ in detail. This would require the mean values of a complete set of variables. We introduce instead a relevant probability density $\bar{\rho}(t)$ with the properties

a) $\bar{\rho}(t)$ has the general properties (2.1.1,2) of a probability density, in particular

$$\mathrm{tr}\{\bar{\rho}(t)\} = 1 \quad , \qquad (2.2.2)$$

b) $\bar{\rho}(t)$ is completely specified by the mean values of the macroscopic variables

$$\bar{\rho}(t) = \bar{\rho}[a(t)] \quad , \qquad (2.2.3)$$

c) $\bar{\rho}(t)$ and the true probability density $\rho(t)$ are macroequivalent

$$\mathrm{tr}\{A_i\bar{\rho}(t)\} = \mathrm{tr}\{A_i\rho(t)\} = a_i(t) \quad , \qquad (2.2.4)$$

d) the initial probability density $\rho(0)$ is a relevant probability density

$$\rho(0) = \bar{\rho}(0) \quad . \qquad (2.2.5)$$

In this section we will not elaborate much on the appropriate choice of the relevant probability density since several concrete examples will be given in subsequent chapters. However, it may be worthwhile to stress the following: the projection operator technique outlined below leads to formally exact equations of motion for the macroscopic variables A regardless of the particular choice of the relevant probability density $\bar{\rho}$, provided the conditions (2.2.2-4) are satisfied, but the resulting equations may have a rather complicated structure. To obtain tractable macroscopic laws it is essential that the true probability density $\rho(t)$ be well approximated by the relevant probability density $\bar{\rho}(t)$. Hence, the macroscopic variables A and the relevant probability distribution $\bar{\rho}$ associated with their mean values a have to be chosen carefully by taking into consideration the particular physical process one wants to describe.

For instance, a useful relevant probability density $\bar{\rho}$ may be found by making plausible assumptions about the microscopic distribution ρ (like a factorization assumption in the case of weakly interacting subsystems) so that the distribution would be of the relevant form $\bar{\rho}$ if those assumptions were true. On the other hand, the projection operator technique does not rely on the validity of assumptions that might have motivated the defintion of $\bar{\rho}$. Quite to the contrary, the deviations of the true microscopic probability density ρ from the relevant form $\bar{\rho}$ are determined systematically, and the final result is formally exact.

2.3 Projection Operator

The macroscopic variables A and the "unity" 1 are supposed to form a set of linearly independent variables which span a macroscopically relevant subspace in the space of all variables. One of the characteristic features of the macroscopic level of description, the restriction to a comparatively small number of macroscopic variables, can be characterized mathematically as a projection of the space of all variables upon the macroscopically relevant subspace. Only the projected image $\bar{F}$ of a variable F is dealt with in macroscopic physics.

We describe this projection by means of a projection operator of the form [26]

$$P[a]F = \bar{F}[a] = \mathrm{tr}\{\bar{\rho}[a]F\} + \sum_i (A_i - a_i)\,\mathrm{tr}\left\{\frac{\partial\bar{\rho}[a]}{\partial a_i}F\right\} \quad . \tag{2.3.1}$$

Note that this projection operator is determined if we have fixed the set of macroscopic variables and the form of the relevant probability density. The particular form of P can be motivated by the particular properties of the so-defined projection. The projected image $\bar{F}$ of a variable F is a linear combination of the macroscopic variables A and the unity 1 with coefficients which may be functions of the macroscopic state a. The projection $F \rightarrow \bar{F}$ has the properties

a) $\overline{\alpha F + \beta G} = \alpha\bar{F} + \beta\bar{G}$, (2.3.2)

b) $\bar{\bar{F}} = \bar{F}$,

c) $F = c_0 + \sum_i c_i A_i \Leftrightarrow F = \bar{F}$,

d) $\mathrm{tr}\{\rho\bar{F}\} = \mathrm{tr}\{\bar{\rho}F\}$,

e) $\mathrm{tr}\left\{\rho\,\frac{\partial\bar{F}}{\partial a_i}\right\} = 0$.

These properties are a consequence of (2.2.2,4) and the relations

$$\mathrm{tr}\left\{\frac{\partial\bar{\rho}}{\partial a_j}\right\} = 0 \quad , \quad \mathrm{tr}\left\{A_i\,\frac{\partial\bar{\rho}}{\partial a_j}\right\} = \delta_{ij} \tag{2.3.3}$$

which follow from (2.2.2,4) by differentiation.

The properties a) - c) are just the general properties of a projection upon the macroscopically relevant subspace.[4] Because of d), the projection is chosen in such

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[4] The properties a) - c) alone do not characterize the projection uniquely since we have not defined an orthogonality relation in the space of variables. Only the properties d) and e) specify the "direction" of the projection.

a way that the reduction of the variables by projection corresponds to a change from the true probability density ρ to the macro-equivalent relevant probability density $\bar{\rho}$. In general, this latter property can only be obtained if the projection is allowed to depend on the macroscopic state a. However, this state dependence is a weak as possible since the averages of the derivatives $\partial\bar{F}/\partial a_i$ vanish according to property e). It can be shown that the properties (2.3.2) specify the projection (2.3.1) uniquely.

Clearly, the properties (2.3.2) of the projection can also be expressed as properties of the projection operator **P**. In particular, one shows that **P** projects out the macroscopic variables

$$\mathbf{P}[a]A_i = A_i \quad . \tag{2.3.4}$$

Further, we have

$$\mathbf{P}[a]\mathbf{P}[a'] = \mathbf{P}[a'] \quad , \tag{2.3.5}$$

which includes the projection operator property (idempotent operator) for a = a', and which also gives

$$\mathbf{P}[a](\mathbf{1}-\mathbf{P}[a]) = (\mathbf{1}-\mathbf{P}[a])\mathbf{P}[a] = 0 \quad . \tag{2.3.6}$$

By means of the projection operator every variable F can uniquely be decomposed into a sum of two parts

$$F = \mathbf{P}[a]F + (\mathbf{1}-\mathbf{P}[a])F \tag{2.3.7}$$

which may be viewed as the macroscopic and the microscopic parts of F, respectively.

In a nonstationary process the mean values a are time dependent so that the projection operator becomes a function of time $\mathbf{P}(t) \equiv \mathbf{P}[a(t)]$, and we have

$$\mathbf{P}(t)F = \mathrm{tr}[\bar{\rho}(t)F] + \sum_i [A_i - a_i(t)]\mathrm{tr}\left\{\frac{\partial\bar{\rho}(t)}{\partial a_i(t)} F\right\} \quad . \tag{2.3.8}$$

Equation (2.3.5) may now be written

$$\mathbf{P}(t)\mathbf{P}(t') = \mathbf{P}(t') \quad . \tag{2.3.9}$$

From (2.3.8) we obtain for the time derivative of the projection operator

$$\dot{\mathbf{P}}(t)F = \sum_{i,j} [A_i - a_i(t)]\dot{a}_j(t)\ \mathrm{tr}\left\{\frac{\partial^2\bar{\rho}(t)}{\partial a_i(t)\partial a_j(t)} F\right\} \tag{2.3.10}$$

which has the property

$$\dot{\mathbf{P}}(t) = \mathbf{P}(t)\dot{\mathbf{P}}(t)(\mathbf{1}-\mathbf{P}(t)) \quad . \tag{2.3.11}$$

This follows most easily from (2.3.9) by differentiation.

There is a transposed projection operator $\mathbf{P}^T(t)$ acting in the space of densities μ defined by

$$\mathrm{tr}\{\mu\mathbf{P}(t)F\} = \mathrm{tr}\{F\mathbf{P}^T(t)\mu\} \quad . \tag{2.3.12}$$

From (2.3.8) we get explicitely [107]

$$\mathbf{P}^T(t)\mu = \bar{\rho}(t)\mathrm{tr}\{\mu\} + \sum_i \frac{\partial\bar{\rho}(t)}{\partial a_i(t)} [\mathrm{tr}\{A_i\mu\} - a_i(t)\mathrm{tr}\{\mu\}] \quad . \tag{2.3.13}$$

This operator projects out the relevant probability density

$$\bar{\rho}(t) = \mathbf{P}^T(t)\rho(t) \quad . \tag{2.3.14}$$

Its time derivative has the form

$$\dot{\mathbf{P}}^T(t)\mu = \sum_{i,j} \frac{\partial^2\bar{\rho}(t)}{\partial a_i(t)\partial a_j(t)} \dot{a}_i(t) \; [\mathrm{tr}\{A_j\mu\} - a_j(t)\mathrm{tr}\{\mu\}] \tag{2.3.15}$$

from which we see that

$$\dot{\mathbf{P}}^T(t)\rho(t) = \dot{\mathbf{P}}^T(t)\bar{\rho}(t) = 0 \quad . \tag{2.3.16}$$

This means that the projection operator $\mathbf{P}^T(t)$ and the time derivative commute when acting upon the probability density [108]

$$\left[\frac{\partial}{\partial t} \, , \, \mathbf{P}^T(t)\right]\rho(t) = 0 \quad . \tag{2.3.17}$$

2.4 Decomposition of the Time Evolution Operator

By means of the projection operator, the time evolution operator $\exp(i\mathbf{L}t)$ for variables in the Heisenbarg representation can be decomposed into a sum of three terms

$$\begin{aligned} e^{i\mathbf{L}t} = {} & e^{i\mathbf{L}t}\mathbf{P}(t) \\ & + \int_s^t du \; e^{i\mathbf{L}u}\mathbf{P}(u)[i\mathbf{L} - \dot{\mathbf{P}}(u)][\mathbf{1} - \mathbf{P}(u)]\mathbf{G}(u,t) \\ & + e^{i\mathbf{L}s}[\mathbf{1} - \mathbf{P}(s)]\mathbf{G}(s,t) \quad , \end{aligned} \tag{2.4.1}$$

where s is an arbitrary time in the interval $[0, t]$, while $\mathbf{G}(t',t)$ is a time-ordered exponential

$$\mathbf{G}(t',t) = T_- \exp\left\{\int_{t'}^t du \; i\mathbf{L}[\mathbf{1} - \mathbf{P}(u)]\right\} \quad , \tag{2.4.2}$$

where operators are ordered from left to right as time increases. $\mathbf{G}(t',t)$ is an operator valued functional of the mean path $\{a(u), t' \le u \le t\}$ since the projection operator is a function of the mean values.

The identity (2.4.1) is easily proven by differentiation. Here, we give an alternative derivation which points to the physical relevance of the decomposition. First we decompose the time evolution operator into a sum of two terms

$$e^{i\mathbf{L}t} = e^{i\mathbf{L}t}\mathbf{P}(t) + e^{i\mathbf{L}t}[\mathbf{1} - \mathbf{P}(t)] \quad . \tag{2.4.3}$$

If we apply the first term to an arbitrary variable F, we obtain with (2.1.7) and (2.3.8)

$$e^{i\mathbf{L}t}\mathbf{P}(t)F = \mathrm{tr}(\bar{\rho}(t)F) + \sum_i [A_i(t) - a_i(t)]\,\mathrm{tr}\left\{\frac{\partial\bar{\rho}(t)}{\partial a_i(t)}F\right\} \quad , \tag{2.4.4}$$

which is a linear combination of the macroscopic variables at time t. About the "microscopic" term

$$\mathbf{Z}(t) = e^{i\mathbf{L}t}[\mathbf{1} - \mathbf{P}(t)] \tag{2.4.5}$$

of the decomposition (2.4.3) we want to obtain some macroscopically available information by taking into account the past history of the macroscopic variables. To this purpose we decompose the time rate of change

$$\dot{\mathbf{Z}}(t) = e^{i\mathbf{L}t}\{i\mathbf{L}[\mathbf{1} - \mathbf{P}(t)] - \dot{\mathbf{P}}(t)\} \tag{2.4.6}$$

into two terms

$$\begin{aligned}\dot{\mathbf{Z}}(t) &= \mathbf{Z}(t)i\mathbf{L}[\mathbf{1} - \mathbf{P}(t)] \\ &\quad + e^{i\mathbf{L}t}\mathbf{P}(t)[i\mathbf{L} - \dot{\mathbf{P}}(t)][\mathbf{1} - \mathbf{P}(t)] \quad ,\end{aligned} \tag{2.4.7}$$

where we have used (2.3.11). Because of (2.4.4), the second term is a linear combination of the macroscopic variables and can be considered as a known inhomogeneity in the differential equation (2.4.7). The solution of the homogeneous equation reads

$$\mathbf{Z}_{\mathrm{hom}}(t) = \mathbf{Z}(s)\mathbf{G}(s,t) \quad , \tag{2.4.8}$$

where $\mathbf{G}(s,t)$ has been defined previously, and the solution of the inhomogeneous equation with initial condition $\mathbf{Z}(s) = e^{i\mathbf{L}s}[\mathbf{1} - \mathbf{P}(s)]$ follows in the usual way

$$\begin{aligned}\mathbf{Z}(t) &= e^{i\mathbf{L}s}[\mathbf{1} - \mathbf{P}(s)]\mathbf{G}(s,t) \\ &\quad + \int_s^t du\, e^{i\mathbf{L}u}\mathbf{P}(u)[i\mathbf{L} - \dot{\mathbf{P}}(u)][\mathbf{1} - \mathbf{P}(u)]\mathbf{G}(u,t) \quad .\end{aligned} \tag{2.4.9}$$

If this expression for the second term in equation (2.4.3) is inserted there, we obtain the identity (2.4.1).

There is a corresponding decomposition of the time evolution operator $\exp(i\mathbf{L}t)$ in the Schrödinger picture. The transpose of (2.4.2) is the exponential

$$\mathbf{G}^{T}(t,t') = T_{+}\exp\left\{-\int_{t'}^{t} du[\mathbf{1} - \mathbf{P}^{T}(u)]i\mathbf{L}\right\} \quad , \tag{2.4.10}$$

where operators are ordered from right to left as time increases. We now take the transpose of (2.4.1) and obtain with (2.1.9), (2.3.12) and (2.4.10) a decomposition of the time evolution operator in the Schrödinger picture

$$e^{-i\mathbf{L}t} = \mathbf{P}^{T}(t)\, e^{-i\mathbf{L}t} \tag{2.4.11}$$

$$- \int_s^t du\, \mathbf{G}^T(t,u)[\mathbf{1} - P^T(u)][i\mathbf{L} + \dot{P}^T(u)]P^T(u)\, e^{-i\mathbf{L}u}$$

$$+ \mathbf{G}^T(t,s)[\mathbf{1} - P^T(s)]\, e^{-i\mathbf{L}s} \quad .$$

The usefulness of the identities (2.4.1,11) lies in the fact that they express the microscopic time evolution partly in terms of the time evolution of macroscopic quantities. The macroscopically available information about the microscopic dynamics is cast into a mathematical relation. This relation constitutes the mathematical basis of the projection operator technique.

2.5 Generalized Transport Equations

By means of the identity (2.4.1), the time rate of change of a macroscopic variable at time t

$$\dot{A}_i(t) = e^{i\mathbf{L}t}\dot{A}_i \quad , \quad \dot{A}_i = i\mathbf{L}A_i \tag{2.5.1}$$

may be decomposed into a sum of three terms

$$\begin{aligned} \dot{A}_i(t) = {} & e^{i\mathbf{L}t}\mathbf{P}(t)\dot{A}_i \\ & + \int_s^t du\, e^{i\mathbf{L}u}\mathbf{P}(u)[i\mathbf{L} - \dot{P}(u)][\mathbf{1} - P(u)]\mathbf{G}(u,t)\dot{A}_i \\ & + F_i(t,s) \quad , \end{aligned} \tag{2.5.2}$$

where the third term reads

$$F_i(t,s) = e^{i\mathbf{L}s}[\mathbf{1} - P(s)]\mathbf{G}(s,t)\dot{A}_i \quad . \tag{2.5.3}$$

The first two terms in (2.5.2) are linear combinations of the macroscopic variables at time t and at previous times u in the interval [s,t], respectively. This becomes explicit if we make use of (2.3.10,11) and (2.4.4) to write (2.5.2) in the form

$$\begin{aligned} \dot{A}_i(t) = {} & v_i(t) + \sum_j \Omega_{ij}(t)\delta A_j(t) \\ & + \int_s^t du \Big[K_i(t,u) + \sum_j \Phi_{ij}(t,u)\delta A_j(u) \Big] \\ & + F_j(t,s) \quad , \end{aligned} \tag{2.5.4}$$

where the

$$\delta A_i(t) = A_i(t) - a_i(t) \tag{2.5.5}$$

are the fluctuations of the macroscopic variables about their mean values, and where we have introduced the organized drift

$$v_i(t) = \mathrm{tr}\{\bar{\rho}(t)\dot{A}_i\} \quad , \tag{2.5.6}$$

the collective frequencies

$$\Omega_{ij}(t) = \mathrm{tr}\left\{\frac{\partial\bar{\rho}(t)}{\partial a_j(t)}\dot{A}_i\right\} \quad , \tag{2.5.7}$$

the after-effect functions

$$K_i(t,s) = \mathrm{tr}\{\bar{\rho}(s) iL[1 - P(s)]G(s,t)\dot{A}_i\} \quad , \tag{2.5.8}$$

and the memory functions

$$\Phi_{ij}(t,s) = \mathrm{tr}\left\{\frac{\partial\bar{\rho}(s)}{\partial a_j(s)} iL[1 - P(s)]G(s,t)\dot{A}_i\right\} \tag{2.5.9}$$

$$- \sum_k \dot{a}_k(s)\ \mathrm{tr}\left\{\frac{\partial\bar{\rho}(s)}{\partial a_j(s)\partial a_k(s)} G(s,t)\dot{A}_i\right\} \quad .$$

The meaning of these quantities will become clear below.

First, we average (2.5.4) over the initial probability density $\rho(0)$. Since $<\delta A_i(t)> = 0$, we have

$$\dot{a}_i(t) = v_i(t) + \int_s^t du K_i(t,u) + f_i(t,s) \quad , \tag{2.5.10}$$

where

$$f_i(t,s) = <F_i(t,s)> = \mathrm{tr}\{\rho(0)F_i(t,s)\} \quad . \tag{2.5.11}$$

This term may also be written

$$f_i(t,s) = \mathrm{tr}\{\delta\rho(s)\, G(s,t)\dot{A}_i\} \quad , \tag{2.5.12}$$

where

$$\delta\rho(s) = \rho(s) - \bar{\rho}(s) = [1 - P^T(s)]\rho(s) \tag{2.5.13}$$

is the deviation of the true microscopic probability density $\rho(s)$ from the relevant form. In passing from (2.5.11) to (2.5.12), we have made use of (2.1.5), (2.3.14), and (2.5.3).

The decomposition (2.5.10) expresses the time rate of change of the mean value of a macroscopic variable as a sum of three terms. The first term, the organized drift $v_i(t)$, is the average of the microscopic flux $\dot{A}_i$ over the relevant probability density $\bar{\rho}(t)$. Like $\bar{\rho}(t)$ this term depends on t only via the mean values

$$v_i(t) \equiv v_i[a(t)] \tag{2.5.14}$$

so that $v_i(t)$ is completely determined by the instantaneous macroscopic state. The remaining terms form the disorganized drift

$$\gamma_i(t) = \int_s^t du\ K_i(t,u) + f_i(t,s) \tag{2.5.15}$$

which is due to the deviation $\delta\rho(t)$ of the microscopic probability density $\rho(t)$ from the relevant form. This contribution to $\dot{a}_i(t)$ is again split into two pieces:

a functional of the mean path $\{a(u),\ s \leq u \leq t\}$ which the system has run through in the preceeding time interval $[s,t]$, and a term due to the deviation $\delta\rho(s)$ at the earlier time s.

So far we have made use of the properties (2.2.2-4) of the relevant probability density only. The remaining property (2.2.5) requires that the initial probability density $\rho(0)$ be of the relevant form. This should be looked upon as a condition for an adequate definition of the relevant probability density rather than a restriction of initial states. Because of (2.2.5) and (2.5.12), we obtain from (2.5.15) by taking into account the whole past history from the initial time $t_0 = 0$ to the present time t an expression for the disorganized drift $\gamma_i(t)$ in terms of the aftereffect function $K_i(t,u)$:

$$\gamma_i(t) = \gamma_i\{a(u),\ 0 \leq u \leq t\} = \int_0^t du\ K_i(t,u) \tag{2.5.16}$$

$$= \int_0^t du\ \mathrm{tr}\{\bar{\rho}(u) i\mathbf{L}[1 - P(u)]\mathbf{G}(u,t)\dot{A}_i\} \quad .$$

This expression determines the disorganized drift completely as a functional of the mean path.

The time rate of change of the mean values may now be written

$$\dot{a}_i(t) = v_i[a(t)] + \gamma_i\{a(u),\ 0 \leq u \leq t\} \quad . \tag{2.5.17}$$

These equations form a closed set of equations of motion for the mean values of the macroscopic variables and will be referred to as generalized transport equations. They describe the mean relaxation of an ensemble of systems initially characterized by a probability density $\rho(0)$ of the relevant form. The derivation of such closed exact equations of motion for a reduced set of variables is one of the main results of the projection operator technique.

To shed some additional light on the statistical-mechanical background of the generalized transport equations, we also give an alternative derivation within the Schrödinger representation. We use the identity (2.4.11) with $s = 0$ to get from (2.1.5) an expression for $\rho(t)$. This expression can be simplified by means of (2.2.5) and (2.3.14,16) to yield

$$\rho(t) = \bar{\rho}(t) - \int_0^t du\ \mathbf{G}^T(t,u)[1 - P^T(u)]i\mathbf{L}\bar{\rho}(u) \quad . \tag{2.5.18}$$

This formula represents the true probability density $\rho(t)$ as the sum of the relevant probability density $\bar{\rho}(t)$ and the deviation $\delta\rho(t)$ from the relevant form expressed as an integral over the past history of the macroscopic variables.

With (2.5.18) the time rate of change of the mean value $a_i(t)$ may be written

$$\dot{a}_i(t) = \mathrm{tr}\{\dot{A}_i\rho(t)\}$$

$$= \mathrm{tr}\{\dot{A}_i\bar{\rho}(t)\} - \int_0^t du\ \mathrm{tr}\{\dot{A}_i\mathbf{G}^T(t,u)[1 - P^T(u)]i\mathbf{L}\bar{\rho}(u)\} \quad . \tag{2.5.19}$$

This equation coincides with (2.5.17) if we write $v_i(t)$ and $\gamma_i(t)$ in terms of molecular expressions by means of (2.5.6,8,16). Note that the order of the transposed operators in the trace in the integrand of (2.5.19) has to be reverse to the order in (2.5.8).

2.6 Generalized Langevin Equations

So far we have considered only the average of the fundamental decomposition (2.5.4) of the time rate of change $\dot{A}_i(t)$. We now subtract the average relation (2.5.10) from (2.5.4) to get

$$\delta\dot{A}_i(t) = \sum_j \Omega_{ij}(t)\delta A_j(t) + \int_s^t du \sum_j \Phi_{ij}(t,u)\delta A_j(u) + \delta F_i(t,s) \quad , \tag{2.6.1}$$

where

$$\delta F_i(t,s) = F_i(t,s) - f_i(t,s) \quad . \tag{2.6.2}$$

Equation (2.6.1) gives the time rate of change of the fluctuations of the macroscopic variables as a sum of three terms. The first two terms are completely determined by macroscopic quantities. The collective frequencies $\Omega_{ij}(t)$ are functions of the mean values, and they are related to the organized drift $v_i(t)$ of the generalized transport equations by

$$\Omega_{ij}[a] = \frac{\partial v_i[a]}{\partial a_j} \quad , \quad \Omega_{ij}(t) = \Omega_{ij}[a(t)] \quad . \tag{2.6.3}$$

This follows immediately from the molecular expressions (2.5.6,7). The memory functions $\Phi_{ij}(t,u)$ are defined in (2.5.9) as functionals of the mean path, and they can be expressed as functional derivatives of the disorganized drift $\gamma_i(t)$ of the generalized transport equations [26,27]

$$\Phi_{ij}(t,s) = \frac{\delta\gamma_i\{a(u),\ 0 \leq u \leq t\}}{\delta a_j(s)} \quad . \tag{2.6.4}$$

To prove this relation we have to express $\gamma_i(t)$ as a statistical-mechanical average by means of (2.5.8,16). Then the functional derivative can be calculated explicitly, and the result coincides with the molecular expression (2.5.9) for the memory functions. Details are given at the end of this section.

Given a solution of the generalized transport equations (2.5.17), the collective frequencies $\Omega_{ij}(t)$ and the memory functions $\Phi_{ij}(t,u)$ may be looked upon as given functions of time so that the first two terms of the decomposition (2.6.1) depend only on the instantaneous fluctuations and their past history in the time interval $[s,t]$. The third term $\delta F_i(t,s)$ gives the influence of microscopic processes and of macroscopic fluctuations prior to time s, and it has the properties

$$\langle\delta F_i(t,s)\rangle = 0 \tag{2.6.5}$$

$$\mathrm{tr}\left\{\frac{\partial\bar{\rho}(s)}{\partial a_j(s)}\, e^{-iLs}\, \delta F_i(t,s)\right\} = 0 \quad ,$$

following from (2.5.3) and (2.6.2).

Going back to the initial time of preparation $t_0 = 0$, we get from (2.6.1) the generalized Langevin equations [26]:

$$\delta\dot{A}_i(t) = \sum_j \Omega_{ij}(t)\delta A_j(t) + \int_0^t du \sum_j \Phi_{ij}(t,u)\delta A_j(u) + F_i(t) \quad , \tag{2.6.6}$$

where the random forces

$$F_i(t) \equiv F_i(t,0) = \delta F_i(t,0) \tag{2.6.7}$$

have the properties

$$\langle F_i(t)\rangle = 0 \quad , \quad \mathrm{tr}\left\{\frac{\partial\bar{\rho}(0)}{\partial a_j(0)}\, F_i(t)\right\} = 0 \quad . \tag{2.6.8}$$

The generalized Langevin equations (2.6.6) determine the stochastic process of the fluctuations $\delta A(t)$ of the macroscopic variables in terms of another process, the stochastic process of the random forces $F(t)$. This means that we have to know the stochastic process of the random forces in order to determine the stochastic process of the fluctuations. The properties (2.6.8) of the random forces are not sufficient to obtain interesting quantities like time correlations of fluctuations from the generalized Langevin equations. One has to determine further properties of the random forces using their molecular expressions. Since these properties depend on the particular form of the relevant density matrix, we will postpone further discussion to the following sections where we deal with particular forms of $\bar{\rho}$.

We now give a derivation of (2.6.4). From (2.3.8) it follows that

$$\frac{\partial\mathbf{P}(t)}{\partial a_i(t)}\, F = \sum_j [A_j - a_j(t)]\ \mathrm{tr}\left\{\frac{\partial^2\bar{\rho}(t)}{\partial a_i(t)\partial a_j(t)}\, F\right\} \quad . \tag{2.6.9}$$

Further, the functional derivatives of the operator valued functional (2.4.2) read

$$\begin{aligned}\frac{\delta\mathbf{G}(t',t)}{\delta a_i(u)}\, F &= -\mathbf{G}(t',u)iL\,\frac{\partial\mathbf{P}(u)}{\partial a_i(u)}\,\mathbf{G}(u,t)F \\ &= -\sum_j \mathbf{G}(t',u)\dot{A}_j\ \mathrm{tr}\left\{\frac{\partial^2\bar{\rho}(u)}{\partial a_i(u)\partial a_j(u)}\,\mathbf{G}(u,t)F\right\} \quad .\end{aligned} \tag{2.6.10}$$

We then obtain for the functional derivatives of the disorganized drift (2.5.16)

$$\begin{aligned}\frac{\partial\gamma_i\{a(u),\ 0 \le u \le t\}}{\delta a_j(u)} &= \mathrm{tr}\left\{\frac{\partial\bar{\rho}(u)}{\partial a_j(u)}\, iL[1-\mathbf{P}](u)\,\mathbf{G}(u,t)\dot{A}_i\right\} \\ &\quad - \sum_k \mathrm{tr}\{\bar{\rho}(u)\dot{A}_k\}\,\mathrm{tr}\left\{\frac{\partial^2\bar{\rho}(u)}{\partial a_j(u)\partial a_k(u)}\,\mathbf{G}(u,t)\dot{A}_i\right\}\end{aligned}$$

$$- \int_0^u dt' \sum_k \mathrm{tr}\{\bar{\rho}(t') i\mathbf{L}[1 - \mathbf{P}(t')]\mathbf{G}(t',u)\dot{A}_k\} \mathrm{tr}\left\{\frac{\partial^2 \bar{\rho}(u)}{\partial a_j(u) \partial a_k(u)} \mathbf{G}(u,t)\dot{A}_i\right\}$$

$$= \mathrm{tr}\left\{\frac{\partial \bar{\rho}(u)}{\partial a_j(u)} i\mathbf{L}[1 - \mathbf{P}(u)]\mathbf{G}(u,t)\dot{A}_i\right\}$$

$$- \sum_k [v_k(u) + \gamma_k(u)] \mathrm{tr}\left\{\frac{\partial^2 \bar{\rho}(u)}{\partial a_j(u) \partial a_k(u)} \mathbf{G}(u,t)\dot{A}_i\right\} \quad , \tag{2.6.11}$$

where we have made use of the fact that $\mathbf{G}(t',t)$ does not depend on mean values $a(u)$ for times $u < t'$, and the second transformation follows by virtue of (2.5.6,16)

Finally, with (2.5.17), the relations (2.5.9) and (2.6.11) combine to give (2.6.4). An alternative derivation, pointing to the physical meaning of (2.6.4), may be found in [27,109].

2.7 More on Projection Operator Methods

The generalized transport equations (2.5.17) for the mean values and the generalized Langevin equations (2.6.6) for the fluctuations about the mean path are exact for every choice of the relevant probebility density $\bar{\rho}$ provided (2.2.2-5) hold. The equations of motion (2.5.17) and (2.6.6) display the universal structure of exact equations of motion in nonequilibrium statistical mechanics. For the investigation of particular irreversible processes the general frame has to be adapted by choosing a particular form of the relevant probebility density. The various projection operator methods which have been put forward in the last two decades are just such special cases of the general approach outlined in the preceeding sections.

Scalar Products. Sometimes authors have preferred to specify the projection (2.3.1) of the space of all variables upon the macroscopically relevant subspace by means of a scalar product defined in the space of variables as compared to a specification by means of a relevant probability density. In such a case one requires that the direction of the projection be orthogonal to the macroscopically relevant subspace instead of the properties d) and e) in (2.3.2). Various definitions of such a scalar product have been found useful in different contexts [20,110,111]. It can be shown [112] that the definition of a scalar product in the space of variables is in fact equivalent to the introduction of a relevant probability density, and it is basically a matter of taste as to which is regarded as primary. Often an adequate choice of $\bar{\rho}$ emerges very naturally from physical considerations so that we shall remain with $\bar{\rho}$.

Modified Projection Operators. By inspecting the molecular expressions (2.4.2) and (2.5.6-9) which define the quantities that appear in the equations of motion (2.5.17) and (2.6.6), we see that in these formulas the projection operator $\mathbf{P}(t)$

appears only in the combination $\mathbf{LP}(t)$. Thus, we could introduce a somewhat modified projection operator $\tilde{\mathbf{P}}(t)$ so that

$$\mathbf{L}\tilde{\mathbf{P}}(t) = \mathbf{LP}(t) \tag{2.7.1}$$

without changing the final result. If we work with the transposed operator we have

$$\tilde{\mathbf{P}}^T(t)\mathbf{L} = \mathbf{P}^T(t)\mathbf{L} \tag{2.7.2}$$

instead of (2.7.1). Consequently, the same equation of motion can be derived by means of two different projection operators related by (2.7.1) or (2.7.2) (compare e.g. [23] and [107]).

The Unity as a Macroscopic Variable. Sometimes there arises a situation where the chosen set of macroscopic variables A already includes the unity 1 as a certain linear combination

$$1 = \sum_i \xi_i A_i \quad . \tag{2.7.3}$$

Naturally, we always could split off the unity explicitly and use the previous scheme but this is often unsuitable, and we will shortly discuss the modifications necessary if we want to allow for (2.7.3). In this case the normalization (2.2.2) of the relevant probability density is included in (2.2.4), from which we get

$$\mathrm{tr}\left\{A_i \frac{\partial\tilde{\rho}}{\partial a_j}\right\} = \delta_{ij} \tag{2.7.4}$$

Further, with (2.7.3)

$$\mathrm{tr}\left\{\frac{\partial\tilde{\rho}}{\partial a_j}\right\} = \xi_j \quad , \tag{2.7.5}$$

which is now valid instead of (2.3.3). With (2.7.4,5) it is readily shown that the properties (2.3.2) of the projection (2.3.1) are still valid if the macroscopic state a is compatible with the normalization

$$\sum_i \xi_i a_i = 1 \quad . \tag{2.7.6}$$

Hence, we can use the same projection operator (2.3.1) to deal with macroscopic variables A which include the unity as a linear combination, and the equations of motion (2.5.17) and (2.6.6) remain unchanged.

Time-Independent Projection Operators. The earlier work on projection operator methods was based on relevant probability densities $\tilde{\rho}[a]$ which are linear functions of the mean values a. In this case $\tilde{\rho}[a]$ is of the form

$$\tilde{\rho}[a] = \hat{\rho} + \sum_i \rho_i(a_i - \hat{a}_i) \quad , \tag{2.7.7}$$

where the $\hat{a}$ are suitably chosen reference values. Because of (2.2.4) we have

$$\mathrm{tr}\{\hat{\rho}A_i\} = \hat{a}_i \quad , \quad \mathrm{tr}\{A_i\rho_j\} = \delta_{ij} \quad . \tag{2.7.8}$$

Now, the projection operator (2.3.1) is particularly simple:

$$PF = \mathrm{tr}\{\hat{\rho}F\} + \sum_i (A_i - \hat{a}_i)\mathrm{tr}\{\rho_i F\} \quad . \tag{2.7.9}$$

Note that $\mathbf{P}$ does not depend on the macroscopic state a and, consequently, it is time-independent in a dynamical process.

Since we can omit the time ordering prescription in (2.4.2), the molecular expressions (2.5.6-9) simplify considerably. The organized drift (2.5.6) reads

$$v_i[a] = \hat{v}_i + \sum_j \Omega_{ij}(a_j - \hat{a}_j) \quad , \tag{2.7.10}$$

where

$$\hat{v}_i = \mathrm{tr}\{\hat{\rho}\dot{A}_i\} \quad . \tag{2.7.11}$$

while the

$$\Omega_{ij} = \mathrm{tr}\{\rho_j \dot{A}_i\} \tag{2.7.12}$$

are the collective frequencies (2.5.7) which are now independent of the macroscopic state. The after-effect functions (2.5.8) read

$$K_i(t,s) = \hat{\Phi}_i(t - s) + \sum_j \Phi_{ij}(t - s)(a_j(s) - \hat{a}_j) \quad . \tag{2.7.13}$$

where

$$\hat{\Phi}_i(t) = \mathrm{tr}\left\{\hat{\rho}i\mathbf{L}(\mathbf{1} - \mathbf{P})\, e^{i\mathbf{L}(\mathbf{1}-\mathbf{P})t}\dot{A}_i\right\} \quad , \tag{2.7.14}$$

while the

$$\Phi_{ij}(t) = \mathrm{tr}\left\{\rho_j i\mathbf{L}(\mathbf{1} - \mathbf{P})\, e^{i\mathbf{L}(\mathbf{1}-\mathbf{P})t}\dot{A}_i\right\} \tag{2.7.15}$$

are the memory functions (2.5.9) which are now independent of the mean path.

The generalized transport equations (2.5.17) are linear in the mean values

$$\begin{aligned} \dot{a}_i(t) = \hat{v}_i &+ \sum_j \Omega_{ij}(a_j(t) - \hat{a}_j) \\ &+ \int_0^t du\left[\hat{\Phi}_i(t - u) + \sum_j \Phi_{ij}(t - u)(a_j(u) - \hat{a}_j)\right] \quad , \end{aligned} \tag{2.7.16}$$

and the generalized Langevin equations (2.6.6) assume the form

$$\delta A_i(t) = \sum_j \Omega_{ij}\delta A_i(t) + \int_0^t du \sum_j \Phi_{ij}(t - u)\delta A_j(u) + F_i(t) \quad , \tag{2.7.17}$$

where the random forces

$$F_i(t) = (\mathbf{1} - \mathbf{P})\, e^{i\mathbf{L}(\mathbf{1}-\mathbf{P})t}\dot{A}_i \tag{2.7.18}$$

have the properties

$$\mathrm{tr}\{\hat{\rho}F_i(t)\} = 0 \quad , \quad \mathrm{tr}\{\rho_j F_i(t)\} = 0 \quad . \tag{2.7.19}$$

By adding the evolution equations (2.7.16) and (2.7.17) we get

$$\dot{A}_i(t) = \hat{v}_i + \sum_j \Omega_{ij}(A_j(t) - \hat{a}_j) \tag{2.7.20}$$

$$+ \int_0^t du\left[\phi_i(t - u) + \sum_j \phi_{ij}(t - u)(A_j(u) - \hat{a}_j)\right] + F_i(t) \quad ,$$

which is the same equation as (2.7.16) except that the mean values are replaced by the fluctuating variables and a random source term $F_i(t)$ has been added. This means that in a system where the mean values obey a linear law, fluctuations of the state variables can be taken into account simply by adding random forces to the systematic fluxes. This is not true if the transport equations are nonlinear.

Clearly, the exact equations of motion which are obtained with the help of a relevant probability density linearly dependent on the mean values a have a much simpler structure than those more general equations derived previously, and one might ask why do we not restrict ourselves to the linear case. First, the initial states of a process under consideration can not always be written in the simple form (2.7.7), in particular if these states are far from equilibrium. Second, since the equations of motions are linear, physically important couplings among the macroscopic variables may be hidden under a complicated structure of the memory functions. In such a case a time-dependent projection operator approach which allows for nonlinear evolution laws may turn out to be simpler in the long run.

3. Statistical Thermodynamics

In this chapter we study the relaxation of a system which has been displaced from equilibrium by means of external forces. The initial state may be far from thermal equilibrium, and we shall not restrict ourselves to linearizations about equilibrium. To a macroscopic nonequilibrium state described by the mean values a of the macroscopic variables A, we assign a relevant probability density $\bar{\rho}$ of the generalized canonical form. Since this relevant probability density is a natural generalization of the equilibrium probability density, we can use it to extend relations familiar from equilibrium thermodynamics in a natural way to nonequilibrium systems. We shall employ the projection operator technique to determine the effects of the deviation of the true microscopic state from the generalized canonical form.

In Sect.3.1 we introduce the generalized canonical probability density [23,113-116] and use it to define a nonequilibrium free energy F as a function of the macroscopic state a. The derivatives $\mu_i = \partial F/\partial a_i$ of the free energy have the meaning of thermodynamic forces conjugate to the fluxes $\dot{a}_i$. In Sect.3.2 the generalized transport equations [23] governing the time evolution of the mean values are cast into a special form where the fluxes $\dot{a}$ are expressed in terms of the forces μ and of transport coefficients which depend on the preceeding mean path. In Sect.3.3 we give the associated Langevin equations [27] governing the time evolution of fluctuations about the mean, and we derive a generalized fluctuation-dissipation theorem of the second kind. If the mean values assume their stationary equilibrium values, the Langevin equations reduce to MORI's Langevin equations [20]. The main features of the Mori theory are summarized in Sect.3.4.

In order to use the equations of motion of generalized statistical thermodynamics to describe the motion of a given system, the rather involved formal expressions for the transport coefficients and the correlations of the random forces have to be evaluated explicitly first. In most cases this can only be done approximately. In Sects.3.5 and 3.6 we present such an approximation where the time rates of change of the macroscopic variables are used as small quantities [35]. In the lowest nontrivial order the approximate equations of motion have a particularly simple structure: the mean values obey the nonlinear transport equations

$$\dot{a}_i(t) = -\sum_j L_{ij}(t)\mu_j(t) = m_i(t) \quad ; \quad \mu_i = \frac{\partial F}{\partial a_i} \quad ,$$

where the L_{ij} are the transport coefficients; the fluctuations about the mean obey the linear nonstationary Langevin equations

$$\delta\dot{A}_i(t) = \sum_j \frac{\partial m_i(t)}{\partial a_j(t)} \delta A_j(t) + F_i(t) \quad ,$$

where the random forces have the properties

$$\langle F_i(t)\rangle = 0 \quad , \quad \langle F_i(t)\delta A_j(s)\rangle = 0 \quad \text{for} \quad t > s$$

$$\langle F_i(t)F_j(s)\rangle = k_BT(L_{ij}(t) + L_{ji}(t))\delta(t - s) \quad .$$

The last relation is a fluctuation-dissipation theorem of the second kind.[1] In Sect.3.7 we show that the time-reversal symmetry leads to

$$F[\tilde{a}] = F[a]$$

and the reciprocal relations

$$L_{ij}[\tilde{a}] = \varepsilon_i\varepsilon_j L_{ji}[a] \quad ,$$

where ε_i is the time-reversal signature of A_i so that $\tilde{a}_i = \varepsilon_i a_i$.

The approximate equations of motion have the nice property of being specified completely in terms of the thermodynamic potential $F[a]$, which is an even function of the state variables a, and the matrix of transport coefficients $L_{ij}[a]$, which satisfies the reciprocal relations. The theory goes beyond usual thermodynamics by including fluctuations and beyond standard thermodynamics of irreversible processes by extending it to the nonlinear regime. It will be referred to as statistical thermodynamics. Although the theory is valid far from equilibrium, the nonlinearities show only in the large mean deviations from equilibrium, i.e., the transport equations are nonlinear, but the small fluctuations about the mean behave quasi linear. Clearly, this can only be valid approximately and the approximation may be poor, especially if the system is near critical points or boundaries of the state space. In order to improve the theory, the transport coefficients and the correlations of the random forces have to be determined more precisely, and we have to keep some of the retardation effects included in the exact form of the equations of motion. We shall return to this problem in Chap.4.

The theory in this chapter is presented within the framework of quantum statistical mechanics. Everything can be done in a completely analogous way within the frame work of classical statistical mechanics. The corresponding classical formulas are obtained by replacing the commutator $(1/i\hbar)[X,Y]$ by the Poisson bracket $\{X,Y\}$, and by noting that phase functions under the classical phase space integral tr may be

---

[1] Equations of motion of a similar structure have been put forward by a number of authors on the basis of phenomenological arguments [28-34].

permuted in an arbitrary way, leading often to a considerable simplification of the classical formulas.

3.1 Generalized Canonical Probability Density

We consider a quantum-mechanical system described on the macroscopic level by the dynamical variables A which are represented as self-adjoint Hilbert space operators, i.e., $A^+ = A$, and whose dynamics is governed by the Hamiltonian H. By external forces h which couple to the macroscopic variables according to

$$H_h = H - \sum_i h_i A_i \quad . \tag{3.1.1}$$

we may displace the system from thermal equilibrium. If the forces are constant in time, the system will settle down to a new stationary state described by a generalized canonical (g.c.) probability density of the form

$$\rho_h = \frac{e^{-\beta(H-\sum h_i A_i)}}{\mathrm{tr}\, e^{-\beta(H-\sum h_i A_i)}} \quad , \tag{3.1.2}$$

where $\beta = 1/k_B T$ is the inverse temperature.[2] We then release the system at t = 0 by switching off the external forces and study the subsequent relaxation process.

In every instant of time $t \geq 0$ we may choose a relevant probability density $\tilde{\rho}(t)$ of the g.c. form [23,27,113-116]:

$$\tilde{\rho}(t) = Z^{-1}(t)\; e^{-\beta(H-\sum \mu_i(t) A_i)} \quad . \tag{3.1.3}$$

where the parameters $\mu_i(t)$ and the normalization factor Z(t) are determined by

$$\mathrm{tr}\{\tilde{\rho}(t)\} = 1$$

$$\mathrm{tr}\{A_i \tilde{\rho}(t)\} = a_i(t) \tag{3.1.4}$$

as functions of the mean values a(t). The g.c. probability density (3.1.3) has the general properties (2.2.2-4) of a relevant probability density, and it also satisfies (2.2.5) since the initial state (3.1.2) is of the g.c. form.

---

[2] For a system which consists of a subsystem described by the A and a reservoir, T is the reservoir temperature. More generally we may define T as the temperature of the equilibrium state corresponding to the average values of the extensive constants of motion. If the A are local variables, the local temperature in the g.c. state can be quite different from T. The introduction of a temperature can be avoided by including the Hamiltonian H into the set A (see [27]). For macroscopic systems this makes no difference in the resulting equations of motion.

to yield

It is natural to introduce a coarse-grained free energy by

$$F(t) = \mathrm{tr}\{\tilde{\rho}(t)H\} + k_B T\, \mathrm{tr}\{\tilde{\rho}(t) \ln\tilde{\rho}(t)\} \quad . \tag{3.1.5}$$

Like $\tilde{\rho}(t)$, the free energy $F(t)$ is a function of time only via the mean values $a(t)$ or the parameters $\mu(t)$,

$$F(t) = F[a(t)] = F[\mu(t)] \quad . \tag{3.I.6}$$

The relation between the mean values $a(t)$ and the parameters $\mu(t)$ may then be written

$$\mu_i(t) = \frac{\partial F(t)}{\partial a_i(t)} \quad , \quad a_i(t) = k_B T \frac{\partial \ln Z(t)}{\partial \mu_i(t)} \quad . \tag{3.1.7}$$

The time rate of change of the free energy reads

$$\dot{F}(t) = \sum_i \mu_i(t)\dot{a}_i(t) \quad . \tag{3.1.8}$$

This bilinear form shows that the parameters μ are the forces conjugate to the fluxes $\dot{a}$.

Using the formula[3]

$$\frac{d}{dx} e^{A(x)} = \int_0^I d\varphi\, e^{\varphi A(x)} \frac{dA(x)}{dx} e^{(I-\varphi)A(x)} \tag{3.1.9}$$

and (3.I.7), we get from (3.I.3)

$$\frac{\partial\tilde{\rho}(t)}{\partial\mu_i(t)} = \int_0^\beta d\alpha\; e^{-\alpha H_t}[A_i - a_i(t)]\, e^{\alpha H_t}\, \tilde{\rho}(t) \quad , \tag{3.I.10}$$

where

$$H_t = H - \sum_i \mu_i(t)A_i \quad . \tag{3.I.11}$$

Equation (3.1.10) combines with (3.I.4) to yield

$$\frac{\partial a_i(t)}{\partial\mu_j(t)} = \int_0^\beta d\alpha\; \mathrm{tr}\Big\{\tilde{\rho}(t)[A_i - a_i(t)]\, e^{-\alpha H_t}[A_j - a_j(t)]\, e^{\alpha H_t}\Big\} \quad . \tag{3.I.12}$$

---

[3] To prove this formula we first verify the identity

$$e^{\nu(A+\delta A)} = e^{\nu A} + \int_0^\nu d\varphi\; e^{\varphi(A+\delta A)}\delta A\; e^{(\nu-\varphi)A}$$

by differentiating with respect to ν and showing that both sides satisfy the same differential equation. Then, using this identity for $\nu = I$ in connection with

$$\frac{d}{dx} e^{A(x)} = \lim_{\varepsilon\to 0} \frac{I}{\varepsilon} \left(e^{A(x)+\delta A(x)} - e^{A(x)}\right)$$

where $\delta A(x) = (dA(x)/dx)\varepsilon$, we obtain (3.1.9).

The right-hand side suggests the introduction of a g.c. correlation function of time-dependent variables $X(t)$ and $Y(s)$ with $t \geq s$ by[4] [27]

$$(X(t),Y(s)) = (Y(s),X(t))$$

$$= \frac{1}{\beta}\int_0^\beta d\alpha \; \mathrm{tr}\left\{\bar{\rho}(s)[e^{-i\mathbf{L}s}X(t)] \; e^{-\alpha H_t}[e^{-i\mathbf{L}s}Y(s)] \; e^{\alpha H_t}\right\} \quad . \tag{3.1.13}$$

This correlation function is particularly simple for the dynamical variables $X(t) = \exp(i\mathbf{L}t)X$ and $Y(s) = \exp(i\mathbf{L}s)Y$, where it takes the simple form

$$(X(t),Y(s)) = \frac{1}{\beta}\int_0^\beta d\alpha \; \mathrm{tr}\left\{\bar{\rho}(s)X(t - s) \; e^{-\alpha H_t} \, Y \; e^{\alpha H_t}\right\} \quad . \tag{3.1.14}$$

This shows that the g.c. correlation is a natural generalization to nonequilibrium states of KUBO's canonical correlation function [101,102]. If the state at the earlier time s is of the g.c. form, (3.1.14) reduces in the classical limit to the correct classical two-time correlation (2.1.10).

Equation (3.1.12) may now be written

$$\frac{\partial a_i(t)}{\partial \mu_j(t)} = \beta(\delta A_i(t), \; \delta A_j(t)) \quad , \tag{3.1.15}$$

where $(\delta A_i(t),\delta A_j(t))$ is the variance matrix in the g.c. state $\bar{\rho}(t)$. Because of (3.1.7), the variance matrix is related to the second-order derivatives of the free energy by[5]

$$(\delta A_i(t),\delta A_j(t)) = k_B T \left\{\frac{\partial^2 F[a(t)]}{\partial a_i(t)\partial a_j(t)}\right\}^{-1} \quad . \tag{3.1.16}$$

From (3.1.10,13) we get for arbitrary time-dependent variables $X(t)$

$$\mathrm{tr}\left\{\frac{\partial \bar{\rho}(s)}{\partial \mu_i(t)} \; e^{-i\mathbf{L}s}X(t)\right\} = \beta(X(t),\delta A_i(s)) \quad . \tag{3.1.17}$$

Using the chain rule

$$\frac{\partial \bar{\rho}(t)}{\partial a_i(t)} = \sum_j \frac{\partial \mu_j(t)}{\partial a_i(t)} \, \frac{\partial \bar{\rho}(t)}{\partial \mu_j(t)} \tag{3.1.18}$$

as well as (3.1.15,17), we easily see that for the present choice of the relevant probability density, the projection operator (2.3.8) projecting out the macroscopic

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[4] Unless otherwise stated variables of the system are always assumed to be represented by self-adjoint operators. Then, the g.c. correlation function is a real quantity. Of course, the generalization to non-Hermitian operators is straightforward.

[5] In our notation X^{-1}_{ij} is the inverse of the matrix X_{ij} and not the inverse of a particular matrix element.

variables may be written [27]

$$P(t)X = \mathrm{tr}\{\tilde{\rho}(t)X\} + \sum_{i,j} (A_i - a_i(t))(\delta A_i(t), \delta A_j(t))^{-1} (e^{iLt}X, \delta A_j(t)) \quad . \tag{3.1.19}$$

3.2 Transport Equations

The mean relaxation from the initial nonequilibrium state (3.1.2) to equilibrium is governed by the generalized transport equations (2.5.17), i.e.,

$$\dot{a}_i(t) = v_i[a(t)] + \gamma_i\{a(u),\ 0 \le u \le t\} \quad . \tag{3.2.1}$$

The organized drift v_i and the disorganized drift γ_i are defined in Sect.2.5 for a general relevant probability density, and these expressions can now be evaluated further when we put in the particular form (3.1.3) of the relevant probability density.

We write the Hamiltonian in the form

$$H = \Big[H - \sum_i \mu_i(t)A_i\Big] + \sum_i \mu_i(t)A_i \quad , \tag{3.2.2}$$

where the first term commutes with the relevant probability density (3.1.3). By use of (3.2.2) the expression (2.5.6) for $v_i(t)$ may be transformed to read

$$v_i[a(t)] = -\sum_j V_{ij}[a(t)]\mu_j(t) \quad , \tag{3.2.3}$$

where the V_{ij} are given by the commutator relations

$$V_{ij}[a] = \mathrm{tr}\Big\{\tilde{\rho}[a]\ \frac{i}{\hbar}\ [A_i, A_j]\Big\} \quad . \tag{3.2.4}$$

Because of the antisymmetry

$$V_{ij}[a] = -V_{ji}[a] \quad , \tag{3.2.5}$$

we have

$$\sum_i v_i(t)\mu_i(t) = 0 \quad , \tag{3.2.6}$$

so that the organized drift does not contribute to the time rate of change of the free energy (3.1.8).

Next we wish to transform the expression for the disorganized drift. The identity[6] [101]

$$[A, e^B] = \int_0^1 d\varphi\ e^{\varphi B}[A,B]\ e^{(1-\varphi)B} \tag{3.2.7}$$

---

[6] To prove the identity we start by noting $A\exp(B) - \exp(B)A = C(0) - C(1) = -\int_0^1 d\varphi (dC(\varphi)/d\varphi)$, where $C(\varphi) = \exp(\varphi B)\, A \exp[(1-\varphi)B]$. By inserting $dC(\varphi)/d\varphi = -\exp(\varphi B)[A,B]\exp[(1-\varphi)B]$, we obtain (3.2.7).

yields with (3.1.3,11)

$$iL\tilde{\rho}(t) = \sum_i \int_0^\beta d\alpha \, e^{-\alpha H_t} \dot{A}_i \, e^{\alpha H_t} \tilde{\rho}(t)\mu_i(t) \quad . \tag{3.2.8}$$

With (2.1.9) and (3.2.8) the after-effect functions (2.5.8) may be transformed to read

$$K_i(t,s) = -\sum_j R_{ij}(t,s)\mu_j(s) \quad , \tag{3.2.9}$$

where the R_{ij} are given by Green-Kubo type formulae

$$R_{ij}(t,s)$$

$$= \int_0^\beta d\alpha \, \mathrm{tr}\left\{\tilde{\rho}(s) \, e^{\alpha H_s}[(1 - \mathbf{P}(s)\mathbf{G}(s,t)\mathring{A}_i]e^{-\alpha H_s}\mathring{A}_j\right\} \quad . \tag{3.2.10}$$

When (3.2.9) is put into (2.5.16), we get [23,107]

$$\gamma_i(t) = -\int_0^t ds \sum_j R_{ij}(t,s)\mu_j(t) \quad . \tag{3.2.11}$$

With (3.2.3,11) the transport equations (3.2.1) read

$$\mathring{a}_i(t) = -\sum_j V_{ij}(t)\mu_j(t) - \int_0^t ds \sum_j R_{ij}(t,s)\mu_j(s) \quad . \tag{3.2.12}$$

These equations express the mean fluxes $\mathring{a}$ in terms of driving forces μ and generalized transport coefficients. There is an instantaneous reaction of the fluxes upon the instantaneous values of the forces and a retarded reaction upon the forces at earlier times. Correspondingly the matrix of generalized transport coefficients consists of two parts. $V_{ij}(t)$ describes the instantaneous transport. These coefficients are functions of the instantaneous mean values, i.e., $V_{ij}(t) = V_{ij}[a(t)]$. The second part $R_{ij}(t,s)$ describes the retarded transport caused by the forces at the earlier time s. The coefficients $R_{ij}(t,s)$ are functionals of the mean path in the time interval [s,t] i.e., $R_{ij}(t,s) = R_{ij}\{a(u), s \leq u \leq t\}$. Equations (3.2.4,10) give exact expressions for the generalized transport coefficients in terms of molecular quantities.

In the transport equation (3.2.12) the driving forces μ are derivatives of the free energy F. For closed systems it may seem more natural to use the entropy as the adequate thermodynamic potential. Defining a coarse-grained entropy S(t) by

$$S(t) = -k_B \, \mathrm{tr}\{\tilde{\rho}(t) \ln\tilde{\rho}(t)\} \quad , \tag{3.2.13}$$

we obtain from (3.1.5) the usual connection between the entropy and the free energy:

$$F(t) = \langle H \rangle - TS(t) \quad . \tag{3.2.14}$$

T is the temperature of the equilibrium state corresponding to the given mean value of the energy <H> and possibly other extensive constants of motion. Then, we have

$$\mu_i(t) = \frac{\partial F(t)}{\partial a_i(t)} = - T \frac{\partial S(t)}{\partial a_i(t)} \quad , \tag{3.2.15}$$

and the transport equations (3.2.12) could also be written

$$\dot{a}_i(t) = \sum_j V'_{ij}(t) \frac{\partial S(t)}{\partial a_j(t)} + \int_0^t ds \sum_j R'_{ij}(t - s) \frac{\partial S(s)}{\partial a_j(s)} \quad , \tag{3.2.16}$$

where

$$V'_{ij} = TV_{ij} \quad , \quad R'_{ij}(t) = TR_{ij}(t) \quad . \tag{3.2.17}$$

References to applications of the generalized transport equations may be found in a recent review article by ROBERTSON [116].

3.3 Langevin Equations

The fluctuations about the mean path obey the generalized Langevin equations (2.6.6), i.e.,

$$\delta\dot{A}_i(t) = \sum_j \Omega_{ij}(t)\delta A_j(t) + \int_0^t ds \sum_j \Phi_{ij}(t,s)\delta A_j(s) + F_i(t) \quad . \tag{3.3.1}$$

The collective frequencies $\Omega_{ij}(t)$ and the memory functions $\Phi_{ij}(t,s)$ are related to derivatives of the organized drift $v_i(t)$ and the disorganized drift $\gamma_i(t)$ by (2.6.3,4), respectively. Because of (3.1.17,18), the properties (2.6.8) of the random forces read

$$<F_i(t)> = 0 \quad , \quad (F_i(t),\delta A_j(0)) = 0 \quad . \tag{3.3.2}$$

The second relation shows that the random forces are statistically independent of the initial fluctuations.

Defining a matrix $M_{ij}(t,s)$ by

$$\frac{\partial}{\partial t} M_{ij}(t,s) = \sum_k \Omega_{ik}(t)M_{kj}(t,s) + \int_s^t du \sum_k \Phi_{ik}(t,u)M_{kj}(u,s) \tag{3.3.3}$$

and

$$M_{ij}(s,s) = \delta_{ij} \quad , \tag{3.3.4}$$

the formal solution of the Langevin equations (3.3.1) may be written

$$\delta A_i(t) = \sum_j M_{ij}(t,0)\delta A_j(0) + \int_0^t du \sum_j M_{ij}(t,u)F_j(u) \quad . \tag{3.3.5}$$

This relation gives the fluctuations as a function of their initial values and as a functional of the random forces. The evolution matrix $M_{ij}(t,s)$ is related to the g.c. correlations of the fluctuations by

$$(\delta A_i(t),\delta A_j(s)) = \sum_k M_{ik}(t,s)(\delta A_k(s),\delta A_j(s)) \quad , \tag{3.3.6}$$

because the g.c. correlations satisfy the same evolution law (3.3.3) with a different initial condition. This follows from (2.6.1,5) if we note that (2.6.5) may be transformed with (3.1.17,18) to read

$$<\delta F_i(t,s)> = 0 \quad , \quad (\delta F_i(t,s),\delta A_j(s)) = 0 \quad . \tag{3.3.7}$$

We now define a quantum-mechanical correlation function of time-dependent variables $X(t),Y(s)$ by [35]

$$\begin{aligned} &<X(t)Y(s)> = <Y(s)X(t)> \\ &= \int_0^1 d\varphi \; \mathrm{tr}\left\{e^{\varphi\sigma(0)}X(t) \; e^{(1-\varphi)\sigma(0)}Y(s)\right\} \quad , \end{aligned} \tag{3.3.8}$$

where

$$\rho(0) = e^{\sigma(0)} \tag{3.3.9}$$

is the initial probability density. In the classical limit the correlation function (3.3.8) reduces to (2.1.10). The correlation function (3.3.8) may also be written

$$\begin{aligned} &<X(t)Y(s)> \\ &= \int_0^1 d\varphi \; \mathrm{tr}\left\{e^{\varphi\sigma(s)}\{e^{-iLs}X(t)]e^{(1-\varphi)\sigma(s)}[e^{-iLs}Y(s)]\right\} \quad , \end{aligned} \tag{3.3.10}$$

where

$$\rho(s) = e^{\sigma(s)} \tag{3.3.11}$$

is the probability density at time $s \leq t$. From this form we see that $<X(t)Y(s)>$ coincides with the g.c. correlation function if the true probability density at the earlier time s is of the g.c. form (3.1.3), but the correlation functions (3.1.13) and (3.3.8) will be different otherwise.

Because of (2.2.5), we have with (3.3.2)

$$<F_i(t)\delta A_j(0)> = 0 \quad . \tag{3.3.12}$$

Using (3.3.12) and the formal solution (3.3.5) of the Langevin equations, we obtain for the correlations of the fluctuations

$$\begin{aligned} <\delta A_i(t)\delta A_j(s)> = &\sum_{k,l} M_{ik}(t,0)M_{jl}(s,0)<\delta A_k(0)\delta A_l(0)> \\ &+ \int_0^t du \int_0^s du' \sum_{k,l} M_{ik}(t,u)M_{jl}(s,u')<F_k(u)F_l(u')> \quad . \end{aligned} \tag{3.3.13}$$

This expresses the correlations in terms of the initial correlations and the correlations of the random forces. It should be noted that the evolution matrix

$M_{ij}(t,s)$ can be determined if we know the transport equations (3.2.12) governing the mean relaxation, i.e., the time evolution of the one-time averages of the macroscopic variables. The basic new quantities needed to determine two-time averages are the correlations of the random forces. In general, the $\langle F_i(t)F_j(s)\rangle$ cannot be related exactly to quantities already appearing on the mean value level; rather, the $\langle F_i(t)F_j(s)\rangle$ have to be determined by using the molecular expressions.

On the other hand, there is a relation between the correlations of the forces $F_i(t,s)$ defined in (2.5.3) and the retarded parts $R_{ij}(t,s)$ of the transport coefficients. With (2.5.3), (3.1.13), and (3.2.10) it is readily shown that [27]

$$R_{ij}(t,s) = \beta(F_i(t,s),F_j(s,s)) \quad . \tag{3.3.14}$$

This relation will be referred to as "generalized fluctuation-dissipation theorem" (of the second kind). A relation similar to (3.3.14) has also been obtained by FURUKAWA [34,111]. The evolution equations (3.2.12), (3.3.1), the theorems (2.6.3,4) (3.3.14), and the molecular expressions (2.5.3), (3.1.5,7), (3.2.4,10) are the basis of generalized statistical thermodynamics.

3.4 Mori Theory

In equilibrium the forces μ vanish, $\hat{\mu} = 0$, and the mean values a assume their equilibrium values $\hat{a}$ which depend on the equilibrium temperature T. If the initial nonequilibrium state is near equilibrium, the $\mu(t)$ are small for all $t \geq 0$, and we may linearize the transport equations (3.2.12). Thus, we can evaluate the generalized transport coefficients (3.2.4,10) at equilibrium to yield

$$\hat{V}_{ij} = tr\left\{\hat{\rho}\ \frac{i}{\hbar}\,[A_i,A_j]\right\} \tag{3.4.1}$$

and

$$\hat{R}_{ij}(t-s) = \int_0^\beta d\alpha\ tr\left\{\hat{\rho}e^{\alpha H}[(1-\hat{\mathbf{P}})\hat{\mathbf{G}}(t-s)\dot{\hat{A}}_i]e^{-\alpha H}\dot{\hat{A}}_j\right\} \quad , \tag{3.4.2}$$

where

$$\hat{\rho} = \tilde{\rho}[\mu = 0] = Z^{-1}\, e^{-\beta H} \tag{3.4.3}$$

is the canonical probability density, and where $\hat{\mathbf{P}}$ and $\hat{\mathbf{G}}(t-s)$ are $\mathbf{P}(t)$ and $\mathbf{G}(s,t)$ for equilibrium mean values $a(u) = \hat{a}$, respectively. Hence

$$\hat{\mathbf{P}}X = tr\{\hat{\rho}X\} + \sum_{i,j} \delta\hat{A}_i(\delta\hat{A}_i,\delta\hat{A}_j)_M^{-1}(\delta\hat{A}_j,X)_M \tag{3.4.4}$$

and

$$\hat{\mathbf{G}}(t-s) = e^{iL(\mathbf{1}-\hat{\mathbf{P}})(t-s)} \tag{3.4.5}$$

where

$$\delta\hat{A}_i = A_i - \hat{a}_i \tag{3.4.6}$$

are the fluctuations about equilibrium, while [20,101,102]

$$(X,Y)_M = \frac{1}{\beta}\int_0^\beta d\alpha \; \mathrm{tr}\left\{\hat{\rho} X \, e^{-\alpha H} Y \, e^{\alpha H}\right\} \tag{3.4.7}$$

is MORI's scalar product or KUBO's canonical correlation to which (3.1.13) reduces in equilibrium. Because of (2.7.1), we could omit the first term on the right-hand side of (3.4.4). The second term is the Mori projection operator [20].

In the considered approximation the transport equations (3.2.12) read

$$\dot{a}_i(t) = -\sum_j \hat{V}_{ij}\mu_j(t) - \int_0^t ds \sum_j \hat{R}_{ij}(t-s)\mu_j(s) \quad . \tag{3.4.8}$$

With (3.1.15) we have to linear order in the deviations from equilibrium

$$a_i(t) - \hat{a}_i = \sum_j \beta\hat{\sigma}_{ij}\mu_j(t) \quad , \tag{3.4.9}$$

where

$$\hat{\sigma}_{ij} = (\delta\hat{A}_i, \delta\hat{A}_j)_M \tag{3.4.10}$$

is the equilibrium variance matrix. Hence, the transport equations governing the mean relaxation in the linear regime near equilibrium may be written

$$\dot{a}_i(t) = \sum_j \hat{\Omega}_{ij}(a_j(t) - \hat{a}_j) + \int_0^t ds \sum_j \hat{\Phi}_{ij}(t-s)(a_j(s) - \hat{a}_j) \quad , \tag{3.4.11}$$

where

$$\hat{\Omega}_{ij} = -\sum_k \frac{1}{\beta}\hat{V}_{ik}\hat{\sigma}^{-1}_{kj} \quad , \tag{3.4.12}$$

and

$$\hat{\Phi}_{ij}(t) = -\sum_k \frac{1}{\beta}\hat{R}_{ik}(t)\hat{\sigma}^{-1}_{kj} \quad . \tag{3.4.13}$$

While the transport equations (3.4.11) are valid in the linear approximation only, they yield exact expressions for the derivatives of the organized drift and the disorganized drift at equilibrium, so that we can use (3.4.11) in connection with (2.6.3,4) to determine the equilibrium collective frequencies and the memory functions exactly. Consequently, the fluctuations about equilibrium obey the Langevin equations [20,22]:

$$\delta\dot{\hat{A}}_i(t) = \sum_j \hat{\Omega}_{ij}\delta\hat{A}_j(t) + \int_0^t ds \sum_j \hat{\Phi}_{ij}(t-s)\delta\hat{A}_j(s) + \hat{F}_i(t) \quad , \tag{3.4.14}$$

where $\hat{F}_i(t)$ is $F_i(t)$ for equilibrium mean values:

$$\hat{F}_i(t) = (1 - \hat{P})\hat{\mathbf{G}}(t)\dot{A}_i = (1 - \hat{P})\, e^{iL(1-\hat{P})t}\,\dot{A}_i \quad . \tag{3.4.15}$$

The equilibrium random forces $\hat{F}_i(t)$ have the properties

$$\mathrm{tr}\{\hat{\rho}\hat{F}_i(t)\} = 0 \quad , \quad (\hat{F}_i(t), \delta\hat{A}_j(0))_M = 0 \quad , \tag{3.4.16}$$

and theorem (3.3.14) gives at equilibrium

$$\hat{R}_{ij}(t - s) = \beta(\hat{F}_i(t - s),\hat{F}_j(0))_M = \beta(\hat{F}_i(t),\hat{F}_j(s))_M \quad . \tag{3.4.17}$$

This is the fluctuation-dissipation theorem associated with MORI's Langevin equation (3.4.14). The last transformation follows from (3.4.15) by noting that the Liouville operator **L** is antisymmetric with respect to the Mori scalar product (3.4.7),

$$(X,\mathbf{L}Y)_M = -(\mathbf{L}X,Y)_M \quad , \tag{3.4.18}$$

while the projector operator (3.4.4) is symmetric,

$$(X,\hat{\mathbf{P}}Y)_M = (\hat{\mathbf{P}}X,Y)_M \quad . \tag{3.4.19}$$

In equilibrium the correlation function (3.3.8) coincides with the Mori scalar product of the correlated variables. Because of (3.4.16), we immediately get from (3.4.14) an evolution equation for the correlations

$$C_{ij}(t) = (\delta\hat{A}_i(t),\delta\hat{A}_j(0))_M = (\delta\hat{A}_i(t+s),\delta\hat{A}_j(s))_M \tag{3.4.20}$$

of fluctuations about equilibrium of the form

$$\dot{C}_{ij}(t) = \sum_k \hat{\Omega}_{ik}C_{kj}(t) + \int_0^t ds \sum_k \hat{\Phi}_{ik}(t - s)C_{kj}(s) \quad . \tag{3.4.21}$$

Comparing (3.4.11,21), we see that the mean relaxation from a nonequilibrium state in the vicinity of the equilibrium state and the time evolution of correlations of fluctuations about equilibrium are governed by the same law [20]. This proves ONSAGER's regression hypothesis [11] in the general case.

3.5 Approximate Transport Equations

The transport equations (3.2.12) and the Langevin equations (3.3.1) are formally exact but their evaluation is very complicated since the retarded parts of the transport coefficients $R_{ij}(t,s)$ and the correlations of the random forces $\langle F_i(t)F_j(s)\rangle$ are given in terms of rather involved molecular expressions. Clearly, equations of motion used in the phenomenological theory of many-body systems have a much simpler structure. Such simpler equations of motion can be valid only approximately. The approximation is based on a characteristic property of macroscopic variables, namely, that they are varying only slowly in time.

In the following we shall regard the time rates of change $\dot{A}$ of the macroscopic variables as small quantities, and we shall disregard those tarms in the equations of motion that contain $\dot{A}$ to the third or higher powers. At present such an approximation is based mainly on intuitive grounds; it can partly be justified by the a posteriori success of the resulting theory. We basically follow [35]. An approximation along similar lines has previously been used by ZWANZIG [43] in a different context.

The $R_{ij}(t,s)$, defined in (3.2.10), are functionals of the mean path $\{a(u),\ s \leq u \leq t\}$, and they are explicitly of second order in $\mathring{A}$. Since any variation of the mean values $a(u)$ in the time interval $[s,t]$ is at least of the first order in $\mathring{A}$, we may replace the actual mean path by the quasi-stationary path $\{a(u) \equiv a(t),\ s \leq u \leq t\}$ to yield

$$R_{ij}(t,s)$$

$$= \int_0^\beta d\alpha\ \mathrm{tr}\left\{\bar{\rho}(t)\ e^{\alpha H_t}[e^{i\mathbf{L}(t-s)}(\mathbf{1} - \mathbf{P}(t))\mathring{A}_i]e^{-\alpha H_t}\mathring{A}_j\right\} + \mathcal{O}(\mathring{A}^3) \quad , \tag{3.5.1}$$

where we have used (2.4.2) and the fact that $i\mathbf{LP}(t)$ is of the order $\mathring{A}$.

The approximation (3.5.1) effectively replaces $a(s)$ by $a(t)$, so that it can be a reasonable approximation only if the retardation time $t - s$ is much smaller than the characteristic time τ_c within which the macroscopic variables change appreciably. The $R_{ij}(t,s)$ have to decay within a characteristic retardation time $\tau_r \ll \tau_c$. Hence, by neglecting terms of the third order in $\mathring{A}$, we tacitly assume that there is a clear-cut separation of two time scales, one characterizing the slow macroscopic processes and the other characterizing the fast processes of the eliminated degrees of freedom.

In the second term on the right-hand side of the transport equations (3.2.12) we may replace $\mu_j(s)$ by $\mu_j(t)$ since the $R_{ij}(t,s)$ are already of the second order in $\mathring{A}$. Further, for $t > \tau_r$, we may extend the time integral to $s = -\infty$ since the $R_{ij}(t,s)$ vanish for $t - s > \tau_r$ so that

$$\int_0^t ds \sum_j R_{ij}(t,s)\mu_j(s) \doteq \sum_j O_{ij}(t)\mu_j(t) \quad , \tag{3.5.2}$$

where $O_{ij}(t) = O_{ij}[a(t)] \equiv O_{ij}[\mu(t)]$ is given by

$$O_{ij}[a] = \int_0^\infty ds \int_0^\beta d\alpha\ \mathrm{tr}\left\{\bar{\rho}[a]e^{\alpha(H-\sum\mu_k A_k)}[e^{i\mathbf{L}s}(\mathbf{1} - \mathbf{P}[a])\mathring{A}_i]e^{-\alpha(H-\sum\mu_k A_k)}\mathring{A}_j\right\} \quad . \tag{3.5.3}$$

Hence, by neglecting terms of the third order in $\mathring{A}$, the transport equations (3.2.12) assume the form

$$\dot{a}_i(t) \doteq -\sum_j L_{ij}(t)\mu_j(t) \quad , \tag{3.5.4}$$

where the

$$L_{ij}(t) = V_{ij}(t) + D_{ij}(t) \tag{3.5.5}$$

are the transport coefficients. Equations (3.5.4) specify the time rates of change of the mean values completely in terms of the instantaneous mean values without referring back to earlier times. We may write

$$\dot{a}_i(t) = m_i[a(t)] \quad , \tag{3.5.6}$$

where

$$m_i[a(t)] \equiv m_i(t) = - \sum_j L_{ij}(t)\mu_j(t) \quad . \tag{3.5.7}$$

The present approximation disregards retardation effects, but it is not an approximation restricted to the regime near thermal equilibrium. The transport equations (3.5.6) are generally nonlinear because the transport coefficients L_{ij} may depend on the state a and the forces μ_j are not necessarily linear in the deviations of the mean values from their equilibrium values.

For a given system the derivation of the approximate equations of motion (3.5.4) can often be based on firmer grounds, in particular if the time rates of change $\dot{A}$ are proportional to a small dimensionless parameter of the problem. Frequently, the time rates of change $\dot{A}$ are not necessarily small because the reversible organized motion is not slow. In such a case the part of the time rates of change due to the interaction with the eliminated degrees of freedom may be small, though. Then we can look upon the projected fluxes $(1 - P(t))\dot{A}$ as small quantities. The above approximation can be extended to this case leading again to transport laws of the form (3.5.4). However, the molecular expression (3.5.3) for the coefficients D_{ij} is modified.

3.6 Approximate Langevin Equations

Because of the general relations (2.6.3,4), the Langevin equations (3.3.1) associated with the transport equations (3.5.6) read

$$\delta\dot{A}_i(t) \doteq \sum_j \frac{\partial m_i(t)}{\partial a_j(t)} \delta A_j(t) + F_i(t) \quad . \tag{3.6.1}$$

The present approximation neglects memory effects. The memory functions $\Phi_{ij}(t,s)$ decay within the same characteristic time τ_r as the $R_{ij}(t,s)$, and τ_r is assumed to be small compared to the macroscopic time scale characterized by τ_c. In view of (2.6.1), the present approximation implies that the forces $F_i(t,s)$ rapidly forget their s dependence, so that

$$F_i(t,s) \doteq \delta F_i(t,s) \doteq F_i(t) \tag{3.6.2}$$

for $t - s > \tau_r$. Consequently, on account of (3.3.7), the random forces $F_i(t)$ have the properties

$$\langle F_i(t) \rangle = 0 \tag{3.6.3}$$

and

$$(F_i(t),\ \delta A_j(s)) \doteq 0 \tag{3.6.4}$$

for $t - s > \tau_r$. Hence, the random forces $F_i(t)$ are uncorrelated with the fluctuation $\delta A_j(s)$ for *all* times $s < t - \tau_r$.

Our next aim is a special version of the generalized fluctuation-dissipation formula (3.3.14) which is valid in the present approximation. With (2.5.3) and (3.1.13) we have a molecular expression for $(F_i(t,s-\tau),F_j(s,s-\tau))$. Making the same kind of approximations that have led us from (3.2.10) to (3.5.1), and using

$$(X(t),LY(s)) = -(LX(t),Y(s)) + \mathcal{O}(\dot{A}) \quad , \tag{3.6.5}$$

we find

$$(F_i(t,s-\tau),F_j(s,s-\tau)) = (F_i(t,s),F_j(s,s)) + \mathcal{O}(\dot{A}^3) \quad . \tag{3.6.6}$$

We now choose $\tau > \tau_r$ and make use of (3.6.2). Then, (3.3.14) and (3.6.6) may be combined to yield

$$R_{ij}(t,s) \doteq \beta(F_i(t),F_j(s)) \quad . \tag{3.6.7}$$

Since the right-hand side is the integrand in (3.5.3), we have

$$D_{ij}(t) \doteq \beta \int_{-\infty}^{t} ds(F_i(t),F_j(s)) \quad . \tag{3.6.8}$$

The mean values $a(t)$ are quasi stationary on the time scale characterized by the decay time τ_r of the integrand in (3.6.8) so that

$$(F_i(t),F_j(t-\tau)) \doteq (F_i(t+\tau),F_j(t)) = (F_j(t),F_i(t+\tau)) \quad . \tag{3.6.9}$$

Consequently, (3.6.8) may be transformed to read

$$D_{ij}(t) \doteq \beta \int_{t}^{\infty} ds(F_j(t),F_i(s)) \quad . \tag{3.6.10}$$

Because of (2.5.18), deviations $\delta\rho$ of the microscopic probability density ρ from the g.c. form $\bar{\rho}$ are at least of the first order in $\dot{A}$. Since the random forces $F_i(t)$ are themselves of the first order in $\dot{A}$, we may, in the present approximation, identify the g.c. correlations of the random forces with the quantum-mechanical correlations (3.3.8). Then, in the limit $\tau_r \to 0$ (3.6.8,10) combine to give [35]

$$\begin{aligned} \langle F_i(t)F_j(s)\rangle &\doteq k_B T[D_{ij}(t) + D_{ji}(t)]\delta(t-s) \\ &= k_B T[L_{ij}(t) + L_{ji}(t)]\delta(t-s) \quad , \end{aligned} \tag{3.6.11}$$

where the last transformation follows from (3.2.5) and (3.5.5). This is the fluctuation-dissipation theorem associated with the Langevin equations (3.6.1).

When we put (3.6.11) into (3.3.13), we get

$$<\delta A_i(t)\delta A_j(s)> = \sum_{k,l} M_{ik}(t,0)M_{jl}(s,0)<\delta A_k(0)\delta A_l(0)> \\ + k_BT \int_0^s du \sum_{k,l} M_{ik}(t,u)M_{jl}(s,u)(\mathbf{L}_{kl}(u) + \mathbf{L}_{lk}(u)) \quad , \tag{3.6.12}$$

where the evolution matrix $M_{ij}(t,s)$ is the solution of

$$\frac{\partial}{\partial t} M_{ij}(t,s) = \sum_k \frac{\partial m_i(t)}{\partial a_k(t)} M_{kj}(t,s) \quad . \quad M_{ij}(s,s) = \delta_{ij} \quad . \tag{3.6.13}$$

This follows from (3.3.3,4) in the present approximation.

The evolution law for the correlations of the fluctuations is obtained from (3.6.12,13) as

$$\frac{\partial}{\partial t} <\delta A_i(t)\delta A_j(s)> = \sum_k \frac{\partial m_i(t)}{\partial a_k(t)} <\delta A_k(t)\delta A_j(s)> \quad , \tag{3.6.14}$$

which has to be solved with the initial condition

$$<\delta A_i(s)\delta A_j(s)> = \sigma_{ij}(s) \quad , \tag{3.6.15}$$

where $\sigma_{ij}(s)$ is the variance. Equation (3.6.14) follows directly from the Langevin equation (3.6.1) and

$$<F_i(t)\delta A_j(s)> = 0 \quad \text{for} \quad t > s \quad . \tag{3.6.16}$$

The last equation is a consequence of (3.6.4) in the limit $\tau_r \to 0$ since $\delta\rho(s)$ has no influence upon the random forces $F_i(t)$ for $t - s > \tau_r$. From (3.6.12,13) we also obtain an equation of motion for the variance

$$\frac{\partial}{\partial t} \sigma_{ij}(t) = \sum_k \frac{\partial m_i(t)}{\partial a_k(t)} \sigma_{kj}(t) + \sum_k \sigma_{ik}(t) \frac{\partial m_j(t)}{\partial a_k(t)} + k_BT[\mathbf{L}_{ij}(t) + \mathbf{L}_{ji}(t)] \quad . \tag{3.6.17}$$

Equations (3.6.14,17) determine the time evolution of the two-time correlations of the fluctuations completely. With (3.5.6,7) they are the basis of statistical thermodynamics meaning an approximate description of nonequilibrium systems in terms of a nonstationary Gauss-Markov process.

3.7 Time-Reversal Symmetry

The time-reversal transformation reverses the sign of the molecular momenta and spins while it leaves the coordinates unchanged. Let us assume that the Hamiltonian H is invariant under this transformation,[7] while the macroscopic variables are

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[7] The generalization to more general situations, like systems in an external magnetic field, is straightforward. For a detailed discussion of the time reversal transformation see [117].

either even or odd with respect to time reversal:

$$\tilde{H} = H \quad , \quad \tilde{A}_i = \epsilon_i A_i \quad , \tag{3.7.1}$$

where ϵ_i is +1 or -1 for even or odd A_i, accordingly. Then, we have with (3.1.3,4)

$$\tilde{a}_i = \epsilon_i a_i \quad , \tag{3.7.2}$$

$$\tilde{\mu}_i = \epsilon_i \mu_i \quad , \tag{3.7.3}$$

and

$$\widetilde{\rho[a]} = \tilde{\rho}[\tilde{a}] \quad , \tag{3.7.4}$$

which yields with (3.1.6)

$$F[\tilde{a}] = F[a] \quad . \tag{3.7.5}$$

Hence, the free energy is time-reversal invariant. Further, using (3.2.4), we get

$$V_{ij}[\tilde{a}] = \epsilon_i \epsilon_j V_{ji}[a] \quad , \tag{3.7.6}$$

which combines with (3.2.3) and (3.7.3) to yield

$$v_i[\tilde{a}] = -\epsilon_i v_i[a] \quad . \tag{3.7.7}$$

This shows that the organized drift is reversible.

The retarded parts $R_{ij}(t,s)$ of the transport coefficients do not have simple time-reversal symmetries except in two special cases. The equilibrium coefficients defined in (3.4.2) have the symmetry

$$\hat{R}_{ij}(t) = \epsilon_i \epsilon_j \hat{R}_{ji}(t) \quad . \tag{3.7.8}$$

This follows from (3.4.2) with (3.4.18,19) and

$$\widetilde{iLX} = -iL\tilde{X} \tag{3.7.9}$$

as well as

$$(\tilde{X},\tilde{Y})_M = (X,Y)_M \quad , \tag{3.7.10}$$

which holds for all variables X, Y represented by self-adjoint operators. The last relation implies

$$\widetilde{\hat{P}X} = \hat{P}\tilde{X} \quad . \tag{3.7.11}$$

Because of (3.7.10), variables with different time-reversal signature are orthogonal in the Mori scalar product. Hence, the equilibrium variance (3.4.10) has the symmetry

$$\hat{\sigma}_{ij} = \hat{\sigma}_{ji} = \epsilon_i \epsilon_j \hat{\sigma}_{ij} \quad . \tag{3.7.12}$$

This is also a consequence of (3.7.5) and (3.1.16) evaluated at equilibrium.

Away from equilibrium, simple time-reversal symmetries for the transport coefficients only hold if we disregard terms of the third order in $\mathring{A}$. Using (3.7.9) and

$$\widetilde{P[a]X} = P[\tilde{a}]\tilde{X} \quad , \tag{3.7.13}$$

which follows from (3.1.19) with (3.1.13) and (3.7.2-4), the right-hand side of (3.5.3) may be transformed to yield

$$O_{ij}[a] = \varepsilon_i\varepsilon_j \int_0^\infty ds \int_0^\beta d\alpha \tag{3.7.14}$$

$$\cdot\, \mathrm{tr}\left\{\bar{\rho}[\tilde{a}]e^{\alpha(H-\sum\tilde{\mu}_k A_k)}[e^{-iLs}(1 - P[\tilde{a}])\mathring{A}_i]e^{-\alpha(H-\sum\mu_k A_k)}\mathring{A}_j\right\} \quad .$$

Neglecting terms of the third order in $\mathring{A}$, this may be transformed further to read

$$O_{ij}[a] = \varepsilon_i\varepsilon_j \int_0^\infty ds \int_0^\beta d\alpha \tag{3.7.15}$$

$$\cdot\, \mathrm{tr}\left\{\bar{\rho}[\tilde{a}]e^{\alpha(H-\sum\tilde{\mu}_k A_k)}\mathring{A}_i\; e^{-\alpha(H-\sum\tilde{\mu}_k A_k)}[e^{iLs}(1 - P[\tilde{a}])\mathring{A}_j]\right\} \quad ,$$

which combines with (3.5.3) to

$$O_{ij}[\tilde{a}] = \varepsilon_i\varepsilon_j O_{ji}[a] \quad . \tag{3.7.16}$$

Finally, (3.5.5) and (3.7.6,16) give the ONSAGER-CASIMIR symmetry of the transport coefficients (reciprocal relations)

$$L_{ij}[\tilde{a}] = \varepsilon_i\varepsilon_j L_{ji}[a] \quad . \tag{3.7.17}$$

It should be notad that this is not an exact symmetry in a nonequilibrium state but holds only if retardation effects in the equations of motion can be neglected.

From (3.4.1) and (3.7.6) it follows that

$$\hat{V}_{ij} = \varepsilon_i\varepsilon_j\hat{V}_{ji} \quad . \tag{3.7.18}$$

The symmetries (3.7.8,12,18) are necessary and sufficient conditions for the detailed balance symmetry

$$C_{ij}(t) = \varepsilon_i\varepsilon_j C_{ji}(t) \tag{3.7.19}$$

of the equilibrium correlations. To see this explicitly we consider the Laplace transformed correlations

$$C_{ij}(z) = \int_0^\infty dt\; e^{-zt}C_{ij}(t) \quad . \tag{3.7.20}$$

Then, using (3.4.12,13) we obtain from (3.4.21)

$$zC_{ij}(z) - \hat{\sigma}_{ij} = -\frac{1}{\beta}\sum_{k,l}\;[\hat{V}_{ik} + \hat{R}_{ik}(z)]\hat{\sigma}^{-1}_{kl}C_{lj}(z) \quad , \tag{3.7.21}$$

where we have also made use of $C_{ij}(t = 0) = \hat{\sigma}_{ij}$. Equation (3.7.21) leads to

$$C^{-1}_{ij}(z) = z\hat{\sigma}^{-1}_{ij} + \frac{1}{\beta}\sum_{k,l}\;\hat{\sigma}^{-1}_{ik}[\hat{V}_{kl} + \hat{R}_{kl}(z)]\hat{\sigma}^{-1}_{lj} \tag{3.7.22}$$

from which it follows that

$$C^{-1}_{ij}(z) = \epsilon_i \epsilon_j C^{-1}_{ji}(z) \quad , \tag{3.7.23}$$

because the right-hand side of (3.7.22) has this symmetry by virtue of (3.7.8,12, 18). From (3.7.23) we obtain (3.7.19).

In this derivation of (3.7.19) we did not make use of the precise form of the retarded transport coefficients $\hat{R}_{ij}(t)$ but only of their time-reversal symmetry. Hence, the detailed balance symmetry of the equilibrium correlations is not lost if the memory effects are neglected as in Sects.3.5 and 3.6.

4. The Fokker-Planck Equation Approach

The approximate equations of motion for the mean values of the macroscopic variables and for the fluctuations about the mean which we have obtained in Chap.3 describe "normal" features of irreversible processes in many-body systems in a satisfactory way, but there are important phenomena where the approximations involved are too crude. For instance, the linear Langevin equations (3.6.1) will not be adequate to describe the dynamics near critical points where nonlinear couplings between fluctuations become important. The exact Langevin equations (3.3.1) describe these nonlinear interactions in terms of the memory functions, and we can improve the approximate equations of motion by taking into account these retardation effects.

Clearly, we have to worry about retardation effects if there are slowly varying quantities among the eliminated degrees of freedom which may cause a slow decay of the transport kernels. The eliminated degrees of freedom include the nonlinear functions of the macroscopic variables which are themselves comparatively slowly varying quantities. Hence, the transport kernels (3.5.1) may have a slowly decaying part if the fluxes $\dot{A}$ couple to nonlinear functions of the A [38-41]. We could try to determine this part by an improved evaluation of the molecular expressions for the transport kernels. It is often advantageous, however, not to go back directly to the molecular level but to tackle the problem by starting out from a more detailed macroscopic level lying between the molecular level and statistical thermodynamics.

Such an intermediate level is obtained by enlarging the set of macroscopic variables to include the nonlinear functions of the A. In quantum mechanics there is an ordering problem associated with the definition of nonlinear functions of noncommuting variables. We postpone this problem to Chap.5 and restrict ourselves to classical statistical mechanics for the present. Then, the linear and nonlinear functions of the A span a well-defined subspace of state functions in the space of all phase functions. In Sect.4.1 we construct a projection operator projecting out these state functions, and we use the projection operator technique in Sect.4.2 to extract an exact subdynamics for the state functions. Some properties of quantities to be found in the exact equations of motion are summarized in Sect.4.3.

The enlarged set of variables included into the present macroscopic description is more likely to exhaust the reservoir of slowly varying quantities of the system, so that we may often disregard retardation effects in the new equations of motion even in cases where we have to allow for retardation effects on the level of statistical thermodynamics. In Sect.4.4 we work out a corresponding approximation where again the time rates of change of the macroscopic variables are used as small quantities. It is shown that in the lowest nontrivial order, the dynamics of the state functions are governed by a Fokker-Planck equation of the form [1]

$$p(\alpha,t) = -\sum_i \frac{\partial}{\partial\alpha_i} K_i(\alpha)p(\alpha,t) + \sum_{i,j} \frac{\partial^2}{\partial\alpha_i\partial\alpha_j} K_{ij}(\alpha)p(\alpha,t) \quad ,$$

where the drift vector $K_i(\alpha)$ and the diffusion matrix $K_{ij}(\alpha)$ are given in terms of a "bare" free energy $F^*(\alpha)$, and a matrix of "bare" transport coefficients $L^*_{ij}(\alpha)$ by [89]

$$K_i(\alpha) = -\sum_j L^*_{ij}(\alpha) \frac{\partial F^*(\alpha)}{\partial\alpha_j} + k_BT \sum_j \frac{\partial L^*_{ij}(\alpha)}{\partial\alpha_j}$$

and

$$K_{ij}(\alpha) = \frac{1}{2} k_BT[L^*_{ij}(\alpha) + L^*_{ji}(\alpha)] \quad .$$

The bare free energy is related to the stationary probability density $p_\beta(\alpha)$ in the conventional way:

$$p_\beta(\alpha) \propto e^{-\beta F^*(\alpha)} \quad , \quad \beta = \frac{1}{k_BT} \quad .$$

We further show that the time-reversal symmetry leads to

$$F^*(\tilde{\alpha}) = F^*(\alpha)$$

and

$$L^*_{ij}(\tilde{\alpha}) = \varepsilon_i\varepsilon_j L^*_{ji}(\alpha) \quad .$$

Naturally, the bare quantities F^* and L^*_{ij} have to be distinguished from the "renormalized" quantities F and L_{ij} introduced in Chap.3. In Sects.4.5 and 4.6 we start out from the Fokker-Planck dynamics to determine the renormalized thermodynamic potential F and the renormalized transport coefficients L_{ij} in terms of the corresponding bare quantities. This renormalization procedure is again carried out with the help of the projection operator technique. We find that the renormalized transport coefficients contain a retarded part due to the coupling of the fluxes $\dot{A}$ to nonlinear state functions, so that the Fokker-Planck equation approach leads in a natural way to an improvement of those equations of motion derived in Chap.3 by disregarding retardation effects on the level of statistical thermodynamics. Finally, Sect.4.7 contains some additional remarks on the Fokker-Planck equation approach.

The main results of this chapter have been obtained by GREEN [1]. For the most part, our presentation follows ZWANZIG [43], while Sects.4.5 and 4.6 contain results obtained by WEIDLICH and the author [54]. The statistical mechanical derivation of the Fokker-Planck equation has also been studied in several more recent publications [118-122], which we take partly into account, and various aspects of the renormalization of transport laws are discussed in [47-55]. We shall not discuss here the sophisticated techniques [123-126] that must often be used to obtain concrete results from Fokker-Planck equations if the nonlinearities cannot be treated in a perturbative way. Various methods have been developed for the numerous applications of the Fokker-Planck equation or equivalent Langevin equations to many-body systems. This includes applications to critical systems [49-52], metastable and unstable systems [127-134], and systems in nonequilibrium steady states [46,55,83,135-138], to mention only a tiny portion of recent work based on Fokker-Planck or closely related methods.

4.1 Relevant Probability Density

We confine ourselves to classical statistical mechanics. The macroscopic state of the system will be described by a set of macroscopic variables $A = (A_1,\dots,A_i,\dots)$ which represent coordinates in the state space Σ. On the molecular level the macroscopic variables are represented by phase functions $A(\Gamma)$. A microscopic state Γ in the phase space Φ is macroscopically described by the state $\alpha = A(\Gamma)$ in the state space Σ. Clearly, there is a huge number of microscopic states Γ which are molecular realizations of the same macroscopic state α. In the phase space Φ these realizations constitute the hypersurface $\Xi(\alpha)$ on which the phase functions $A(\Gamma)$ assume the values α (Fig.4.1).

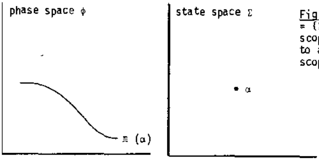

Fig.4.1. The hypersurface $\Xi(\alpha) = \{\Gamma \in \Phi | A(\Gamma) = \alpha\}$ in the microscopic phase space Φ corresponds to a single point α in the macroscopic state space Σ.

In a macroscopic description of the system we want to determine the macroscopic state $\alpha(t)$ at time t. Even if we know the initial macroscopic state $\alpha(0)$, we cannot determine the future state $\alpha(t)$ with certainty since we will have only probabilis-

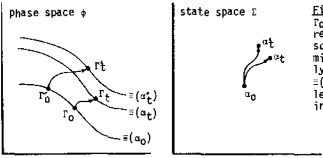

Fig.4.2. Two microscopic states Γ_0 and Γ_0' which are molecular realizations of the same macroscopic state α_0 evolve into microscopic states Γ_t and Γ_t' lying on different hypersurfaces $\Xi(\alpha_t)$ and $\Xi(\alpha_t')$ in general. This leads to the stochastic motion in the macroscopic state space Σ

tic information about the molecular realization of the initial state. This means that the macroscopic variables describing the state have to be considered as stochastic variables (Fig.4.2).

In Chap.3 we singled out the mean values a(t) of the macroscopic variables and obtained an exact closed subdynamics for these mean values, namely, the transport equations (3.2.12). Now, we are going to keep the mean values of all nonlinear functions of the macroscopic variables, and we shall aim at a closed subdynamics for this enlarged set of variables.

A function of the macroscopic variables, i.e., a state function $g(\alpha)$, is represented on the molecular level by the phase function

$$G(\Gamma) = g(A(\Gamma)) = \int d\alpha\, g(\alpha)\Psi_\alpha(\Gamma) \quad , \tag{4.1.1}$$

where

$$\Psi_\alpha(\Gamma) = \prod_i \delta(A_i(\Gamma) - \alpha_i) = \delta(A(\Gamma) - \alpha) \quad . \tag{4.1.2}$$

Hence, a state function is a linear combination of the Ψ_α. The Ψ_α form a set of variables with continuous index α. They have the property

$$\Psi_\alpha\Psi_{\alpha'} = \delta(\alpha - \alpha')\Psi_\alpha \quad , \tag{4.1.3}$$

and their mean values

$$\begin{aligned} p(\alpha,t) &= \mathrm{tr}\{\Psi_\alpha\rho(t)\} \\ &= \int d\Gamma\, \delta(A(\Gamma) - \alpha)\rho(\Gamma,t) \end{aligned} \tag{4.1.4}$$

give the macroscopic probability density $p(\alpha,t)$ in the state space Σ. $p(\alpha,t)d\alpha$ is the probability that the macroscopic variables assume values in the state space volume element $d\alpha$ around α at time t, and the mean value of a state function reads

$$\langle g(\alpha)\rangle = \mathrm{tr}\{G\rho(t)\} = \int d\alpha\, g(\alpha)p(\alpha,t) \quad . \tag{4.1.5}$$

Because of (4.1.1) nonlinear functions of the macroscopic variables are linear functions of the Ψ_α. We shall now look upon the Ψ_α as the "set of macroscopic variables" in the sense of the previous chapters. Then, by projecting out the macroscopically relevant subspace formed by the linear combinations of the Ψ_α, we project out the linear and nonlinear functions of the A, i.e., the state functions.

Replacing A_i by the enlarged set Ψ_α, we obtain from (3.1.3) a relevant probability density of the form

$$\begin{aligned}\bar{\rho}(\Gamma,t) &= Z^{-1}(t)\, e^{-\beta[H(\Gamma)-\int d\alpha\mu(\alpha,t)\Psi_\alpha(\Gamma)]} \\ &= Z^{-1}(t)\, e^{-\beta H(\Gamma)} \int d\alpha\, e^{\beta\mu(\alpha,t)}\Psi_\alpha(\Gamma) \quad ,\end{aligned} \tag{4.1.6}$$

where $\beta = 1/k_BT$, and where the last transformation follows from (4.1.3). Since $p(\alpha,t)$ is the mean value of Ψ_α, conditions (2.2.2,3) give

$$\begin{aligned}Z(t) &= \int d\alpha\, e^{\beta\mu(\alpha,t)} \mathrm{tr}\{e^{-\beta H}\Psi_\alpha\} \quad , \\ p(\alpha,t) &= Z^{-1}(t)\, e^{\beta\mu(\alpha,t)} \mathrm{tr}\{e^{-\beta H}\Psi_\alpha\} \quad .\end{aligned} \tag{4.1.7}$$

We introduce the canonical distribution

$$\rho_\beta(\Gamma) = Z_\beta^{-1}\, e^{-\beta H(\Gamma)} \quad , \quad Z_\beta = \mathrm{tr}\{e^{-\beta H}\} \tag{4.1.8}$$

and the associated macroscopic probability density

$$p_\beta(\alpha) = \mathrm{tr}\{\rho_\beta\Psi_\alpha\} = \int d\Gamma\, \delta(A(\Gamma) - \alpha)\rho_\beta(\Gamma) \quad . \tag{4.1.9}$$

Then the relevant probability density (4.1.6) may be transformed to read

$$\bar{\rho}(\Gamma,t) = \rho_\beta(\Gamma) \int d\alpha\, \frac{p(\alpha,t)}{p_\beta(\alpha)}\, \Psi_\alpha(\Gamma) \quad . \tag{4.1.10}$$

By construction, the relevant probability density $\bar{\rho}(t)$ yields the correct macroscopic probability density

$$p(\alpha,t) = \mathrm{tr}\{\Psi_\alpha\rho(t)\} = \mathrm{tr}\{\Psi_\alpha\bar{\rho}(t)\} \quad . \tag{4.1.11}$$

In an ensemble described by $\bar{\rho}(\Gamma,t)$ the occupation probability of a hypersurface $\Xi(\alpha)$ in the phase space Φ is determined by the macroscopic probability density $p(\alpha,t)$, while the relative weight of molecular realizations Γ within a given hypersurface is determined by the Boltzmann weighting factor $\exp(-\beta H(\Gamma))$.

4.2 Generalized Fokker-Planck Equation

Since the relevant probability density (4.1.10) is a special case of the g.c. probability density (3.1.3) for the set Ψ_α of macroscopic variables, we could proceed by specializing the results of Chap.3 to this particular case. Or, by noting that $\bar{\rho}(t)$ depends linearly on the mean values of the Ψ_α, namely, the macroscopic probability distribution $p(\alpha,t)$, we could specialize (2.7.20) to obtain the evolution law for the Ψ_α. However, in order to make this chapter more self-contained, we shall give a brief derivation of the evolution law for the Ψ_α starting from the Liouville equation directly.

To this purpose we introduce the projection operator[1]

$$\mathbf{P}X(\Gamma) = \int d\alpha \, \frac{\mathrm{tr}\{\rho_\beta \Psi_\alpha X\}}{p_\beta(\alpha)} \Psi_\alpha(\Gamma) \tag{4.2.1}$$

which has the projection operator property

$$\mathbf{P}^2 = \mathbf{P} \tag{4.2.2}$$

because of (4.1.3,9). $\mathbf{P}$ projects out the Ψ_α:

$$\mathbf{P}\Psi_\alpha(\Gamma) = \Psi_\alpha(\Gamma) \quad . \tag{4.2.3}$$

Hence, it reduces the set of all phase functions to the subset of those which are state functions.

The transposed projection operator $\mathbf{P}^T$ defined by

$$\mathrm{tr}\{\mu \mathbf{P} X\} = \mathrm{tr}\{X \mathbf{P}^T \mu\} \tag{4.2.4}$$

reads

$$\mathbf{P}^T \mu(\Gamma) = \rho_\beta(\Gamma) \int d\alpha \, \frac{\mathrm{tr}\{\Psi_\alpha \mu\}}{p_\beta(\alpha)} \Psi_\alpha(\Gamma) \quad , \tag{4.2.5}$$

and its projects out the relevant probability density

$$\bar{\rho}(\Gamma,t) = \mathbf{P}^T \rho(\Gamma,t) \quad . \tag{4.2.6}$$

Clearly, the two projection operators are also related by

$$\mathbf{P}^T(\rho_\beta X) = \rho_\beta \mathbf{P} X \quad . \tag{4.2.7}$$

The time evolution operator for variables in the Heisenberg representation may be split into

$$\begin{aligned} e^{iLt} &= e^{iLt}\mathbf{P} \\ &\quad + i \int_0^t du \, e^{iLu} \mathbf{P} L (\mathbf{1} - \mathbf{P}) e^{iL(\mathbf{1}-\mathbf{P})(t-u)} + (\mathbf{1} - \mathbf{P}) e^{iL(\mathbf{1}-\mathbf{P})t} \quad . \end{aligned} \tag{4.2.8}$$

This is a special version of (2.4.1) for a time-independent projection operator. Equation (4.2.8) can be proved directly by showing that both sides satisfy the same differential equation and coincide initially.

If we put (4.2.8) into

$$\frac{\partial}{\partial t} \Psi_\alpha(t) = e^{iLt} iL\Psi_\alpha = e^{iLt} \dot{\Psi}_\alpha \quad , \tag{4.2.9}$$

we obtain with (4.2.1) an equation of motion for the Ψ_α:

$$\frac{\partial}{\partial t} \Psi_\alpha(t) = \int d\alpha' \, \frac{\mathrm{tr}\{\rho_\beta \Psi_{\alpha'} \dot{\Psi}_\alpha\}}{p_\beta(\alpha')} \Psi_{\alpha'}(t) \tag{4.2.10}$$

---

[1] This projection operator follows from the general form (2.3.1) by (4.1.10)

$$+\int_0^t ds \int d\alpha' \frac{\mathrm{tr}\{\rho_\beta \Psi_{\alpha'}, iLF_\alpha(t-s)\}}{p_\beta(\alpha')} \Psi_{\alpha'}(s) + F_\alpha(t) \quad ,$$

where the random forces are

$$F_\alpha(t) = (1 - P)e^{iL(1-P)t}\, \dot{\Psi}_\alpha \quad . \tag{4.2.11}$$

We now want to evaluate some expressions appearing in (4.2.10) more explicitly. The classical Liouville operator (2.1.4) acts upon a phase function as a sum of first-order differential operators. Hence, the fluxes $\dot{\Psi}_\alpha$ of the variables (4.1.2) read

$$\dot{\Psi}_\alpha = iL\Psi_\alpha = -\sum_i \frac{\partial}{\partial \alpha_i} \Psi_\alpha iLA_i = -\sum_i \frac{\partial}{\partial \alpha_i} \Psi_\alpha \dot{A}_i \quad . \tag{4.2.12}$$

Then, (4.2.11) may be written

$$F_\alpha(t) = -\sum_i \frac{\partial}{\partial \alpha_i} R_i(\alpha,t) \quad , \tag{4.2.13}$$

where

$$R_i(\alpha,t) = (1 - P)e^{iL(1-P)t}\Psi_\alpha \dot{A}_i \quad . \tag{4.2.14}$$

Further, we find with (4.1.3)

$$\frac{\mathrm{tr}\{\rho_\beta \Psi_{\alpha'}, \dot{\Psi}_\alpha\}}{p_\beta(\alpha')} = -\sum_i \frac{\partial}{\partial \alpha_i} v_i(\alpha)\delta(\alpha - \alpha') \quad , \tag{4.2.15}$$

where we have introduced the drift vector

$$v_i(\alpha) = \frac{\mathrm{tr}\{\rho_\beta \Psi_\alpha \dot{A}_i\}}{p_\beta(\alpha)} \quad . \tag{4.2.16}$$

Finally, using (2.1.9), (4.1.3), (4.2.12,13), and

$$L\rho_\beta X = \rho_\beta LX \quad , \tag{4.2.17}$$

we get

$$\mathrm{tr}\{\rho_\beta \Psi_{\alpha'}, iLF_\alpha(t - s)\}$$

$$= -\sum_{i,j} \frac{\partial}{\partial \alpha_i} \frac{\partial}{\partial \alpha'_j} \mathrm{tr}\{\rho_\beta \Psi_{\alpha'} \dot{A}_j R_i(\alpha, t - s)\} \quad , \tag{4.2.18}$$

which may be transformed further with the help of (4.2.4,7.14) to read

$$\mathrm{tr}\{\rho_\beta \Psi_\alpha, iLF_\alpha(t - s)\}$$

$$= -\sum_{i,j} \frac{\partial}{\partial \alpha_i} \frac{\partial}{\partial \alpha'_j} D_{ij}(\alpha, \alpha', t - s) p_\beta(\alpha') \quad , \tag{4.2.19}$$

where we have introduced the diffusion kernels

$$O_{ij}(\alpha,\alpha',t-s) = \frac{\mathrm{tr}\{\rho_\beta R_i(\alpha,t)R_j(\alpha',s)\}}{p_\beta(\alpha')} \quad . \tag{4.2.20}$$

When we put (4.2.15) and (4.2.19) into (4.2.10) and integrate partially with respect to α', the equation of motion takes the form

$$\begin{aligned}\frac{\partial}{\partial t}\Psi_\alpha(t) = &- \sum_i \frac{\partial}{\partial \alpha_i} v_i(\alpha)\Psi_\alpha(t) \\ &+ \int_0^t ds \sum_{i,j} \frac{\partial}{\partial \alpha_i} \int d\alpha' O_{ij}(\alpha,\alpha',t-s)p_\beta(\alpha') \frac{\partial}{\partial \alpha'_j} \frac{\Psi_{\alpha'}(s)}{p_\beta(\alpha')} + F_\alpha(t) \quad .\end{aligned} \tag{4.2.21}$$

Because of (4.2.3,7,11) the random forces $F_\alpha(t)$ have the property

$$\mathrm{tr}\{\rho_\beta \Psi_{\alpha'} F_\alpha(t)\} = 0 \tag{4.2.22}$$

for all α'. Hence, $F_\alpha(t)$ is not correlated with the initial values of all state functions.

By displacing the system from thermal equilibrium by means of external forces which couple to the macroscopic degrees of freedom, we can prepare an initial nonequilibrium probability density $\rho(0)$ which is of the relevant form; i.e., $\rho(0) = \bar{\rho}(0)$. We now average (4.2.21) over this initial microscopic probability density. The average of $\Psi_\alpha(t)$ yields the macroscopic probability density $p(\alpha,t)$, while the average of $F_\alpha(t)$ vanishes because of (4.2.22). Consequently, the average of (4.2.21) reads [43]

$$\begin{aligned}\frac{\partial}{\partial t} p(\alpha,t) = &- \sum_i \frac{\partial}{\partial \alpha_i} v_i(\alpha)p(\alpha,t) \\ &+ \int_0^t ds \sum_{i,j} \frac{\partial}{\partial \alpha_i} \int d\alpha' O_{ij}(\alpha,\alpha',t-s)p_\beta(\alpha') \frac{\partial}{\partial \alpha'_j} \frac{p(\alpha',s)}{p_\beta(\alpha')} \quad .\end{aligned} \tag{4.2.23}$$

This is the generalized Fokker-Planck equation. The time rate of change of the macroscopic probability density is expressed as a sum of two terms. The first term is local in time and local in state space and is characterized by the drift v_i. The second term is nonlocal in time (retarded) and nonlocal in state space. This term is characterized by the diffusion kernels O_{ij} and the stationary probability p_β.

The equilibrium correlation function of two state functions $g_1(\alpha)$, $g_2(\alpha)$ with associated phase functions $G_1(\Gamma)$, $G_2(\Gamma)$ of the form (4.1.1) reads

$$\langle G_1(t)G_2(0)\rangle = \int d\alpha d\alpha' g_1(\alpha)g_2(\alpha')p_\beta^{(2)}(\alpha,\alpha',t) \quad , \tag{4.2.24}$$

where

$$p_\beta^{(2)}(\alpha,\alpha',t) = \mathrm{tr}\{\rho_\beta\Psi_\alpha(t)\Psi_{\alpha'}(0)\} \tag{4.2.25}$$

is the stationary macroscopic joint probability density. Because of (4.1.3) we have

$$p_\beta^{(2)}(\alpha,\alpha',0) = \delta(\alpha-\alpha')p_\beta(\alpha') \quad . \tag{4.2.26}$$

Using (4.2.21,22), it is easily shown that (4.2.25) satisfies the generalized Fokker-Planck equation (4.2.23) with the initial condition (4.2.26). Hence, the generalized Fokker-Planck equation does not only determine the time evolution of state functions during a relaxation process from a nonequilibrium state towards equilibrium, but it also determines the time evolution of correlations of state functions at equilibrium.

4.3 Properties of Drift and Diffusion Kernels

Because of the chain rule, the Poisson bracket of a macroscopic variable A_i with the canonical distribution (4.1.8) reads

$$\{A_i,\rho_\beta\} = -\beta\rho_\beta\{A_i,H\} = -\beta\rho_\beta\dot{A}_i \quad , \tag{4.3.1}$$

and the Poisson bracket with Ψ_α may be written

$$\{A_i,\Psi_\alpha] = -\sum_j \frac{\partial}{\partial\alpha_j}\Psi_\alpha\{A_i,A_j] \quad . \tag{4.3.2}$$

Using these relations, we may transform the right-hand side of (4.2.16) to read

$$v_i(\alpha) = \frac{1}{p_\beta(\alpha)}\sum_j \frac{\partial}{\partial\alpha_j}\pi_{ij}(\alpha)p_\beta(\alpha) \quad , \tag{4.3.3}$$

where we have introduced the antisymmetric matrix

$$\pi_{ij}(\alpha) = -\pi_{ji}(\alpha) = \frac{1}{\beta}\,\frac{\mathrm{tr}[\rho_\beta\Psi_\alpha\{A_j,A_i\}]}{p_\beta(\alpha)} \quad . \tag{4.3.4}$$

This connection between the drift v_i and the Poisson brackets of the macroscopic variables A is often very useful. In particular, (4.3.3) shows that

$$\sum_i \frac{\partial}{\partial\alpha_i}v_i(\alpha)p_\beta(\alpha) = 0 \quad , \tag{4.3.5}$$

so that $p_\beta(\alpha)$ is in fact the stationary solution of the generalized Fokker-Planck equation.

We now assume that the Hamiltonian function H is invariant under the time-reversal transformation and that the macroscopic variables have a definite time-reversal signature:

$$\tilde{H} = H \quad , \quad \tilde{A}_i = \varepsilon_i A_i \quad , \tag{4.3.6}$$

where ε_i is +1 or -1. Then, we easily find that

$$\tilde{\Psi}_\alpha = \Psi_{\tilde{\alpha}} \quad , \tag{4.3.7}$$

where

$$\tilde{\alpha}_i = \varepsilon_i\alpha_i \quad . \tag{4.3.8}$$

Further, using

$$\widetilde{\{X,Y\}} = -\{\tilde{X},\tilde{Y}\} \tag{4.3.9}$$

and

$$\mathrm{tr}\ \tilde{X} = \mathrm{tr}\ X \quad , \tag{4.3.10}$$

it is straightforward to show that

$$\widetilde{iLX} = -iL\tilde{X} \quad , \tag{4.3.11}$$

and, using

$$\tilde{\rho}_\beta = \rho_\beta \quad , \tag{4.3.12}$$

that

$$p_\beta(\tilde{\alpha}) = p_\beta(\alpha) \quad . \tag{4.3.13}$$

We may also show that quantities projected out by the operators (4.2.1,5) transform according to

$$\widetilde{\mathbf{P}X} = \mathbf{P}\tilde{X} \tag{4.3.14}$$

and

$$\widetilde{\mathbf{P}^T\mu} = \mathbf{P}^T\tilde{\mu} \quad . \tag{4.3.15}$$

With the above relations we obtain from (4.3.4)

$$\pi_{ij}(\tilde{\alpha}) = \varepsilon_i\varepsilon_j\pi_{ji}(\alpha) \quad , \tag{4.3.16}$$

and from (4.2.14)

$$\tilde{R}_i(\alpha,t) = -\varepsilon_i R_i(\tilde{\alpha},-t) \quad . \tag{4.3.17}$$

Now, because of (4.3.13,16), the drift vector (4.3.3) has the symmetry

$$v_i(\tilde{\alpha}) = -\varepsilon_i v_i(\alpha) \quad . \tag{4.3.18}$$

Hence, $v_i(\alpha)$ is a reversible drift vector. Because of (4.3.17), we obtain from (4.2.20)

$$D_{ij}(\alpha,\alpha',t)p_\beta(\alpha') = \varepsilon_i\varepsilon_j D_{ij}(\tilde{\alpha},\tilde{\alpha}',-t)p_\beta(\tilde{\alpha}') \quad . \tag{4.3.19}$$

On the other hand, (4.2.20) implies

$$D_{ij}(\alpha,\alpha',t)p_\beta(\alpha') = D_{ji}(\alpha',\alpha,-t)p_\beta(\alpha) \quad , \tag{4.3.20}$$

which combines with (4.3.19) to give

$$D_{ij}(\tilde{\alpha},\tilde{\alpha}',t)p_\beta(\tilde{\alpha}') = \varepsilon_i\varepsilon_j D_{ji}(\alpha',\alpha,t)p_\beta(\alpha) \quad . \tag{4.3.21}$$

Equations (4.3.13,18,21) give the time-reversal symmetries of those quantities that determine the form of the generalized Fokker-Planck equation (4.2.23). Because of these symmetries the solution of the generalized Fokker-Planck equation with initial condition (4.2.26), namely, the stationary joint probability density, has the symmetry

$$p_\beta^{(2)}(\alpha,\alpha',t) = p_\beta^{(2)}(\tilde{\alpha}',\tilde{\alpha},t) \quad . \tag{4.3.22}$$

This is the well-known detailed balance symmetry. Naturally, the symmetry (4.3.22) follows directly from the molecular expression (4.2.25). However, by connecting (4.3.22) with (4.3.13,18,21) we avoid going back to the molecular level. The latter relations can be looked upon as "generalized potential conditions" for the generalized Fokker-Planck process (4.2.23).

4.4 Fokker-Planck Equation

We shall now approximate the generalized Fokker-Planck equation using a characteristic property of macroscopic variables, namely, that they are varying only slowly in time. To this purpose we shall regard the time rates of change $\dot{A}$ as small quantities, and we shall disregard terms of the third order in $\dot{A}$ in the equation of motion (4.2.23).

First we note that the diffusion kernels (4.2.20) are explicitly of the second order in $\dot{A}$ since the R_i are explicitly of the first order. Therefore, we may approximate (4.2.14) by

$$R_i(\alpha,t) = (\mathbf{1} - \mathbf{P})\Psi_\alpha \dot{A}_i(t) + O(\dot{A}^2) \quad , \tag{4.4.1}$$

where we have used the fact the $\mathbf{LP}$ is at least of the first order in $\dot{A}$ and that

$$e^{iLt}\Psi_\alpha X = \Psi_\alpha e^{iLt} X + O(\dot{A}) \quad . \tag{4.4.2}$$

With (4.1.3) and (4.2.1,15) we obtain from (4.4.1)

$$R_i(\alpha,t) = \Psi_\alpha[\dot{A}_i(t) - v_i(\alpha)] + O(\dot{A}^2) \quad . \tag{4.4.3}$$

When we put this into (4.2.20) we get

$$D_{ij}(\alpha,\alpha',t-s)$$

$$= \delta(\alpha-\alpha')\,\frac{\mathrm{tr}\{\rho_\beta\Psi_\alpha[\dot{A}_i(t)-v_i(\alpha)][\dot{A}_j(s)-v_j(\alpha)]\}}{p_\beta(\alpha)} + O(\dot{A}^3) \quad . \tag{4.4.4}$$

Hence, in the present approximation, the diffusion kernels are local in state space. Introducing a shorthand notation for the average over a hypersurface $\Xi(\alpha)$ in the state space Φ by

$$\langle X;\alpha\rangle = \frac{\mathrm{tr}\{\rho_\beta\Psi_\alpha X\}}{p_\beta(\alpha)} = \frac{\int d\Gamma\,\delta(A(\Gamma)-\alpha)e^{-\beta H(\Gamma)}X(\Gamma)}{\int d\Gamma\,\delta(A(\Gamma)-\alpha)e^{-\beta H(\Gamma)}} \quad , \tag{4.4.5}$$

we have

$$D_{ij}(\alpha,\alpha',t-s)$$

$$= \delta(\alpha-\alpha')\langle[\dot{A}_i(t)-\langle\dot{A}_i(t);\alpha\rangle][\dot{A}_j(s)-\langle\dot{A}_j(s);\alpha\rangle];\alpha\rangle + O(\dot{A}^3) \quad , \tag{4.4.6}$$

which gives the diffusion kernels in terms of a hypersurface correlation function of so-called subtracted fluxes $\dot{A}_i - <\dot{A}_i;\alpha>$. The subtracted fluxes are internal degrees of freedom on the hypersurface $\Xi(\alpha)$. Under the assumption that those internal hypersurface correlations decay on a short microscopic time scale, we can disregard the retardation in the generalized Fokker-Planck equation (4.2.23) to derive from (4.4.6) an approximate equation of motion of the form

$$\frac{\partial}{\partial t} p(\alpha,t) = - \sum_i \frac{\partial}{\partial \alpha_i} v_i(\alpha) p(\alpha,t) + \sum_{i,j} \frac{\partial}{\partial \alpha_i} \xi_{ij}(\alpha) p_\beta(\alpha) \frac{\partial}{\partial \alpha_j} \frac{p(\alpha,t)}{p_\beta(\alpha)} \quad , \tag{4.4.7}$$

where the ξ_{ij} are given by a formula due to GREEN [1]:

$$\xi_{ij}(\alpha) = \int_0^\infty ds < [\dot{A}_i(s) - <\dot{A}_i(s);\alpha>][\dot{A}_j - <\dot{A}_j;\alpha>];\alpha> \quad . \tag{4.4.8}$$

By (4.3.13,21), we observe that the ξ_{ij} have the symmetry

$$\xi_{ij}(\tilde{\alpha}) = \varepsilon_i \varepsilon_j \xi_{ji}(\alpha) \quad . \tag{4.4.9}$$

Equation (4.4.7) is a Fokker-Planck equation which may also be written in the more familiar form

$$\frac{\partial}{\partial t} p(\alpha,t) = - \sum_i \frac{\partial}{\partial \alpha_i} K_i(\alpha) p(\alpha,t) + \sum_{i,j} \frac{\partial^2}{\partial \alpha_i \partial \alpha_j} K_{ij}(\alpha) p(\alpha,t) \quad , \tag{4.4.10}$$

with the Fokker-Planck drift

$$K_i(\alpha) = v_i(\alpha) + \frac{1}{p_\beta(\alpha)} \sum_j \frac{\partial}{\partial \alpha_j} \xi_{ij}(\alpha) p_\beta(\alpha) \tag{4.4.11}$$

and the diffusion matrix

$$K_{ij}(\alpha) = \frac{1}{2} [\xi_{ij}(\alpha) + \xi_{ji}(\alpha)] \quad . \tag{4.4.12}$$

While this form of the Fokker-Planck equation is frequently used in the phenomenological theory, the statistical-mechanical origin of the Fokker-Planck equation is primarily manifest in another form given below.

Let us introduce a "bare" free energy $F^*(\alpha)$ in a conventional way by

$$p_\beta(\alpha) \propto e^{-\beta F^*(\alpha)} \tag{4.4.13}$$

which defines $F^*(\alpha)$ up to an irrelevant additive constant. Using (4.1.9) we may give a statistical-mechanical definition of $F^*(\alpha)$ by

$$F^*(\alpha) = -k_B T \ln \int d\Gamma \, \delta(A(\Gamma) - \alpha) \, e^{-(1/k_B T) H(\Gamma)} \quad . \tag{4.4.14}$$

The bare free energy F^* has to be distinguished from the free energy F introduced in (3.1.5). To avoid confusion the latter will be referred to as the renormalized free energy henceforth. Because of (3.1.16), the renormalized free energy F[a] is a convex function of the mean values a, while the bare free energy $F^*(\alpha)$ is a function of the fluctuating variables α which is not necessarily convex.

Furthermore, we introduce a matrix of "bare" transport coefficients $L^*_{ij}(\alpha)$ by

$$k_B T\, L^*_{ij}(\alpha) = \pi_{ij}(\alpha) + \xi_{ij}(\alpha) \quad . \tag{4.4.15}$$

The two matrices $\pi_{ij}(\alpha)$ and $\xi_{ij}(\alpha)$ are defined in statistical mechanics as certain averages over the phase space hypersurface $\Xi(\alpha)$. The matrix $\pi_{ij}(\alpha)$ is given by the Poisson bracket relations

$$\pi_{ij}(\alpha) = k_B T \langle \{A_j, A_i\};\alpha\rangle \tag{4.4.16}$$

while $\xi_{ij}(\alpha)$ is defined by the Green-Kubo formula (4.4.8). Clearly, the L^*_{ij} have to be distinguished from the renormalized coefficients L_{ij} introduced in Chap.3

Now, using (4.3.3) and the definitions (4.4.13,15), the Fokker-Planck equation (4.4.7) can be recast into the form [89,90]

$$\frac{\partial}{\partial t} p(\alpha,t) = \sum_{i,j} \frac{\partial}{\partial \alpha_i} L^*_{ij}(\alpha) \left[\frac{\partial F^*(\alpha)}{\partial \alpha_j} + k_B T \frac{\partial}{\partial \alpha_j}\right] p(\alpha,t) \tag{4.4.17}$$

which gives the Fokker-Planck dynamics in terms of a bare thermodynamic potential $F^*(\alpha)$ and a matrix of bare transport coefficients $L^*_{ij}(\alpha)$. In terms of these quantities the Fokker-Planck drift (4.4.11) reads

$$K_i(\alpha) = -\sum_j L^*_{ij}(\alpha) \frac{\partial F^*(\alpha)}{\partial \alpha_j} + k_B T \sum_j \frac{\partial L^*_{ij}(\alpha)}{\partial \alpha_j} \quad . \tag{4.4.18}$$

while the diffusion matrix (4.4.12) has the form

$$K_{ij}(\alpha) = \frac{1}{2} k_B T [L^*_{ij}(\alpha) + L^*_{ji}(\alpha)] \quad . \tag{4.4.19}$$

From (4.3.13,16) and (4.4.9) we get the time-reversal symmetry

$$F^*(\tilde{\alpha}) = F^*(\alpha) \tag{4.4.20}$$

and the reciprocal relations

$$L^*_{ij}(\tilde{\alpha}) = \varepsilon_i \varepsilon_j L^*_{ji}(\alpha) \quad . \tag{4.4.21}$$

Because of these symmetries the Fokker-Planck equation (4.4.17) can be shown to satisfy the potential conditions for detailed balance [139].

The Fokker-Planck equation describes an irreversible, generally non-Gaussian, Markov process. Using (4.4.8) we obtain from (4.4.12)

$$K_{ij}(\alpha) = \frac{1}{2} \int_{-\infty}^{+\infty} ds \, \langle [\dot{A}_i(s) - \langle \dot{A}_i(s);\alpha\rangle][\dot{A}_j(0) - \langle \dot{A}_j(0);\alpha\rangle];\alpha\rangle \quad , \tag{4.4.22}$$

where we have made use of the fact that the integrand in (4.4.8) is a stationary correlation function in the approximation under consideration. With (4.4.22) we have

$$\sum_{i,j} K_{ij}(\alpha)x_i x_j = \frac{1}{2}\int_{-\infty}^{+\infty} ds\, <X(s)X(0);\alpha> \geq 0 \quad , \tag{4.4.23}$$

where

$$X(s) = \sum_i x_i[\mathring{A}_i(s) - <\mathring{A}_i(s);\alpha>] \quad . \tag{4.4.24}$$

The right-hand side of (4.4.23) is positive since the Fourier transform of a stationary autocorrelation function is positive. Consequently, the diffusion matrix $K_{ij}(\alpha)$ is positive.

We now define a functional $F(p(\alpha,t))$ of the macroscopic probability density $p(\alpha,t)$ by

$$F(p(\alpha,t)) = F_\beta + k_B T \int d\alpha\, p(\alpha,t) \ln \frac{p(\alpha,t)}{p_\beta(\alpha)} \quad . \tag{4.4.25}$$

On writing the Fokker-Planck equation (4.4.17) in the form

$$\frac{\partial}{\partial t} p(\alpha,t) = \sum_{i,j} \frac{\partial}{\partial \alpha_i} k_B T\, L^*_{ij}(\alpha) p_\beta(\alpha) \frac{\partial}{\partial \alpha_j} \frac{p(\alpha,t)}{p_\beta(\alpha)} \quad , \tag{4.4.26}$$

we easily find for the time rate of change of $F(p)$

$$\dot{F}(p) = -k_B T \int d\alpha\, p(\alpha,t) \sum_{i,j} K_{ij}(\alpha)\sigma_i(\alpha,t)\sigma_j(\alpha,t) \leq 0 \quad , \tag{4.4.27}$$

where we have made use of (4.4.19), and where

$$\sigma_i(\alpha,t) = \frac{\partial}{\partial \alpha_i} \ln \frac{p(\alpha,t)}{p_\beta(\alpha)} \quad . \tag{4.4.28}$$

Hence $F(p)$ decreases in time and it reaches its minimum for the stationary probability density $p_\beta(\alpha)$, which is approached as $t \to \infty$.

4.5 Renormalization of Thermodynamic Forces

In terms of the macroscopic probability density $p(\alpha,t)$ the mean values a of the macroscopic variables are given by

$$a_i(t) = \int d\alpha\, \alpha_i p(\alpha,t) \quad . \tag{4.5.1}$$

In Chap.3 we have derived a closed set of equations of motion for these mean values, namely, the generalized transport equations (3.2.12), by starting directly from the Liouville equation. In the remainder of this chapter we shall derive the evolution law for the mean values from the Fokker-Planck equation (4.4.17) (the treatment following [54]).

Using (4.4.10), we find for the time rates of change of the mean values

$$\dot{a}_i(t) = \int d\alpha\, K_i(\alpha)p(\alpha,t) \quad . \tag{4.5.2}$$

If the Fokker-Planck drift $K_i(\alpha)$ is a nonlinear function of the α, the mean values are coupled to the fluctuations of the α. From (4.4.18) we see that nonlinearities may have two origins: first, thermodynamic nonlinearities which arise if the thermodynamic potential $F^*(\alpha)$ is not a bilinear function of the α leading to a non-Gaussian stationary probability density $p_\beta(\alpha)$; second, dynamical nonlinearities which arise if the transport coefficients $L^*_{ij}(\alpha)$ depend on the state α.

The effects of fluctuations are disregarded in the deterministic theory which may be obtained from the stochastic theory in a certain limit where the Boltzmann constant k_B formally approaches zero with the transport coefficients L^*_{ij} and the thermodynamic potential F^* kept constant [89,90]. In this limit the Fokker-Planck equation (4.4.17) reduces to the pure drift equation

$$\frac{\partial}{\partial t} p(\alpha,t) = - \sum_i \frac{\partial}{\partial \alpha_i} f_i(\alpha)p(\alpha,t) \quad , \tag{4.5.3}$$

where

$$f_i(\alpha) = - \sum_j L^*_{ij}(\alpha) \frac{\partial F^*(\alpha)}{\partial \alpha_j} \tag{4.5.4}$$

is the deterministic drift vector. The evolution equation (4.5.3) does not lead to a broadening of an initially sharp probability density, and the center of such a probability density moves according to the deterministic equations of motion

$$\dot{a}_i(t) = f_i(a(t)) = - \sum_j L^*_{ij}(a(t))\mu^*_j(t) \quad , \tag{4.5.5}$$

where we have introduced the bare thermodynamic forces

$$\mu^*_i(\alpha) = \frac{\partial F^*(\alpha)}{\partial \alpha_i} \quad . \tag{4.5.6}$$

Equation (4.5.5) will also be referred to as bare transport equations. Note that they are given in terms of the same quantities L^*_{ij} and F^* as the Fokker-Planck equation (4.4.17), so that the Fokker-Planck dynamics can be reconstructed from the limiting deterministic law (4.5.5) (stochastic modeling). The bare transport equations (4.5.5) have the same structure as the generalized transport equation (3.2.12) but in a nonlinear system they provide only a lowest-order approximation to the latter. To obtain closed equations of motion for the mean values alone, we have to reduce the set of all state functions contained in the Fokker-Planck dynamics to the subset of the linear functions of the α.

The nonlinear state functions can be eliminated with the help of the projection operator technique. To this purpose we first have to define a relevant macroscopic probability density $\bar{p}(\alpha,t)$ which is a function of time only via the mean values $a(t)$. It is natural to choose as $\bar{p}(\alpha,t)$ the macroscopic probability density associated with a microscopic probability density of the generalized canonical form (3.1.3) by (4.1.4); i.e.,

$$\bar{p}(\alpha,t) = Z^{-1}(t)\mathrm{tr}\{\psi_\alpha e^{-\beta(H-\Sigma\mu_i(t)A_i)}\} \quad . \tag{4.5.7}$$

Using (4.1.2,9) we have[2]

$$\bar{p}(\alpha,t) = Z^{-1}(t)Z_\beta p_\beta(\alpha)e^{\beta\Sigma\mu_i(t)\alpha_i} \quad . \tag{4.5.8}$$

The parameters $Z(t)$ and $\mu(t)$ are determined by

$$\int d\alpha\, \bar{p}(\alpha,t) = 1 \quad , \quad \int d\alpha\, \alpha_i\bar{p}(\alpha,t) = a_i(t) \quad . \tag{4.5.9}$$

In particular, we get

$$Z(t) = Z_\beta \int d\alpha\ p_\beta(\alpha)e^{\beta\Sigma\mu_i(t)\alpha_i} \quad . \tag{4.5.10}$$

In terms of the relevant macroscopic probability density $\bar{p}(\alpha,t)$ the renormalized free energy (3.1.5) may be written as

$$F(t) = F_\beta + k_BT\int d\alpha\ \bar{p}(\alpha,t)\ \ln\frac{\bar{p}(\alpha,t)}{p_\beta(\alpha)} \quad , \tag{4.5.11}$$

where

$$F_\beta = -k_BT \ln Z_\beta \tag{4.5.12}$$

is the equilibrium free energy. By (4.5.8,9) we get

$$F(t) = -k_BT \ln Z(t) + \sum_i \mu_i(t)a_i(t) \quad , \tag{4.5.13}$$

and, using (4.5.10), the renormalized thermodynamic forces read

$$\mu_i(t) = \frac{\partial F(t)}{\partial a_i(t)} \tag{4.5.14}$$

while the mean values may be written as

$$a_i(t) = k_BT\frac{\partial \ln Z(t)}{\partial\mu_i(t)} \quad , \tag{4.5.15}$$

which coincides with our earlier result (3.1.7).

The above relations are more transparent if we express the equilibrium probability density in terms of the bare free energy $F^*(\alpha)$ by

$$p_\beta(\alpha) = Z_\beta^{-1}\ e^{-\beta F^*(\alpha)} \quad , \tag{4.5.16}$$

where

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[2] $\bar{p}(\alpha,t)$ is also the probability density minimizing the functional (4.4.25) under the constraints (4.5.9).

$$Z_\beta = \int d\alpha\, e^{-\beta F^*(\alpha)} \quad . \tag{4.5.17}$$

Now, (4.5.8,10) read

$$\bar{p}(\alpha,t) = Z^{-1}(t)\; e^{-\beta(F^*(\alpha)-\Sigma\mu_i(t)\alpha_i)} \tag{4.5.18}$$

$$Z(t) = \int d\alpha\, e^{-\beta(F^*(\alpha)-\Sigma\mu_i(t)\alpha_i)} \tag{4.5.19}$$

We may use (4.5.19) in connection with (4.5.15) to determine the μ as functions of the mean values a. Then (4.5.13) gives the renormalized free energy F[a] in terms of the bare free energy $F^*(\alpha)$.

If the stationary probability density is Gaussian, which means that $F^*(\alpha)$ is a bilinear function of the α, the integral (4.5.19) can be done exactly, and the renormalized free energy coincides with the bare free energy apart from an irrelevant additive constant. Non-Gaussian behavior of the fluctuations in the stationary state leads to a renormalization of the thermodynamic potential; i.e., the bare thermodynamic forces $\mu^*(\alpha)$ are renormalized by nonlinear fluctuations to yield the renormalized thermodynamic forces $\mu[a]$. Near critical points, (4.5.19) can not be evaluated by just expanding the exponential about a Gaussian; rather, renormalization group techniques [52,140,141] must be used. In this context the renormalized thermodynamic potential F[a] is usually referred to as the generating functional for vertex functions.

4.6 Renormalization of Transport Coefficients

We may write the Fokker-Planck equation (4.4.10) in a form which resembles the Liouville equation (2.1.3):

$$\frac{\partial}{\partial t}\, p(\alpha,t) = -i\mathcal{L}p(\alpha,t) \quad , \tag{4.6.1}$$

where $\mathcal{L}$ is given by

$$\begin{aligned} -i\mathcal{L}X(\alpha) &= -\sum_i \frac{\partial}{\partial\alpha_i}\, K_i(\alpha)X(\alpha) + \sum_{i,j} \frac{\partial^2}{\partial\alpha_i\partial\alpha_j}\, K_{ij}(\alpha)X(\alpha) \\ &= \sum_{i,j} \frac{\partial}{\partial\alpha_i}\, L^*_{ij}(\alpha) \left[\frac{\partial F^*(\alpha)}{\partial\alpha_j} + k_B T\, \frac{\partial}{\partial\alpha_j}\right] X(\alpha) \quad . \end{aligned} \tag{4.6.2}$$

Further, in analogy to (2.3.13), we may introduce a projection operator $\mathcal{P}(t)$ by [54]

$$\mathcal{P}(t)X(\alpha) = \bar{p}(\alpha,t) \int d\alpha X(\alpha) + \sum_i \frac{\partial\bar{p}(\alpha,t)}{\partial a_i(t)} \int d\alpha[\alpha_i - a_i(t)]X(\alpha) \quad , \tag{4.6.3}$$

which projects out the relevant macroscopic probability density

$$\tilde{p}(\alpha,t) = P(t)p(\alpha,t) \quad . \tag{4.6.4}$$

Moreover, we may easily convince ourselves that the validity of the decomposition (2.4.11) does not depend on the particular forms of the Liouville and projection operators to be found therein, so that we may write

$$\begin{aligned} e^{-iLt} &= P(t)\, e^{-iLt} \\ &- \int_0^t du\; G(t,u)[1 - P(u)][iL + \dot{P}(u)]P(u)\, e^{-iLu} + G(t,0)[1 - P(0)] \quad , \end{aligned} \tag{4.6.5}$$

where $G(t,t')$ is defined analogously to (2.4.10) by

$$G(t,t') = T_+ \exp\left\{- \int_{t'}^{t} du[1 - P(u)]iL\right\} \quad . \tag{4.6.6}$$

An initial nonequilibrium state of the generalized canonical form (3.1.2) is described on the macroscopic level by a probability density of the form (4.5.8), i.e.,

$$p(\alpha,0) = \tilde{p}(\alpha,0) \quad . \tag{4.6.7}$$

When we apply (4.6.5) to an initial macroscopic probability density of the relevant form, we obtain

$$p(\alpha,t) = \tilde{p}(\alpha,t) - \int_0^t ds\, G(t,s)[1 - P(s)]iL\tilde{p}(\alpha,s) \quad , \tag{4.6.8}$$

where we have used (4.6.4) and

$$\dot{P}(t)p(\alpha,t) = \dot{P}(t)\tilde{p}(\alpha,t) = 0 \tag{4.6.9}$$

which corresponds to (2.3.16). Equation (4.6.8) gives the true macroscopic probability density $p(\alpha,t)$ in terms of $\tilde{p}(\alpha,t)$ and its past history.

When we insert (4.6.8) into (4.5.2), we find for the time rates of change of the mean values

$$\begin{aligned} \dot{a}_i(t) &= \int d\alpha\, K_i(\alpha)\tilde{p}(\alpha,t) \\ &- \int_0^t ds \int d\alpha\, K_i(\alpha)G(t,s)[1 - P(s)]iL\tilde{p}(\alpha,s) \quad . \end{aligned} \tag{4.6.10}$$

Since the time dependence of $\tilde{p}(\alpha,t)$ and of the projection operator $P(t)$ arises only through $a(t)$, so does the time dependence of $G(t,s)$, and the right-hand side of (4.6.10) is completely determined by the mean values $a(t)$ and their past history. Consequently, the (4.6.10) provide a closed set of equations of motion for the mean values.

Equations (4.6.10) are not yet of the standard form where the fluxes are expressed in terms of transport coefficients and driving thermodynamic forces. In order to obtain this form, we make some transformations. With (4.4.18) and (4.5.18) we find after a partial integration

$$\int d\alpha\, K_i(\alpha)\bar{p}(\alpha,t) = -\sum_j \bar{L}_{ij}(t)\mu_j(t) \quad , \tag{4.6.11}$$

where

$$\bar{L}_{ij}(t) = \int d\alpha\, \bar{p}(\alpha,t)L^*_{ij}(\alpha) \quad . \tag{4.6.12}$$

Further, we get from (4.5.18) and (4.6.2) by use of (4.4.18,19)

$$-iL\bar{p}(\alpha,t) = \sum_{i,j} \frac{\partial}{\partial\alpha_i} L^*_{ij}(\alpha)\bar{p}(\alpha,t)\mu_j(t) \quad , \tag{4.6.13}$$

so that

$$\int d\alpha\, K_i(\alpha)G(t,s)[1 - P(s)]iL\bar{p}(\alpha,s) = \sum_j \Lambda_{ij}(t,s)\mu_j(s) \quad , \tag{4.6.14}$$

where

$$\Lambda_{ij}(t,s) = -\sum_k \int d\alpha\, K_i(\alpha)G(t,s)[1 - P(s)]\, \frac{\partial}{\partial\alpha_k} L_{kj}(\alpha)\bar{p}(\alpha,t) \quad . \tag{4.6.15}$$

Using (4.6.11,14), the equations of motion (4.6.10) may be written

$$\dot{a}_i(t) = -\sum_j \bar{L}_{ij}(t)\mu_j(t) - \int_0^t ds\, \Lambda_{ij}(t,s)\mu_j(s) \quad . \tag{4.6.16}$$

Here the mean fluxes $\dot{a}$ are given in terms of the renormalized thermodynamic forces μ. There is an instantaneous reaction of the fluxes upon the instantaneous forces and a retarded reaction upon the forces at earlier times. Correspondingly, the renormalized transport coefficients consist of an instantaneous part $\bar{L}_{ij}(t)$ which is a function of the instantaneous mean values, $\bar{L}_{ij}(t) = \bar{L}_{ij}[a(t)]$, and a retarded part $\Lambda_{ij}(t,s)$ which is a functional of the mean path in the time interval $[s,t]$, i.e., $\Lambda_{ij}(t,s) = \Lambda_{ij}\{a(u),\ s \leq u \leq t\}$. By means of (4.6.12,15) the renormalized transport coefficients are given in terms of the bare transport coefficients $L^*_{ij}(\alpha)$ and the bare thermodynamic potential $F^*(\alpha)$.

The renormalized transport equations (4.6.16) have the same form as the transport equations (3.2.12). When comparing the two sets of equations, we first note that (3.2.12) is formally exact while (4.6.16) is valid in the Fokker-Planck approximation only[3]. In this approximation a part of the retarded coefficient $R_{ij}(t,s)$ in (3.2.12) is approximated by an instantaneous coefficient which is added to $V_{ij}(t)$ to yield the instantaneous transport coefficient $\bar{L}_{ij}(t)$ in (4.6.16). This may be seen explicitly if we insert (4.4.15) into (4.6.12) to yield with (4.1.10) and (4.3.4) $\bar{L}_{ij}(t) = \mathrm{tr}[\bar{\rho}(t)\{A_j,A_i\}]+\beta\int d\alpha\, \bar{p}(\alpha,t)\xi_{ij}(\alpha)$, where the first term coincides with $V_{ij}(t)$ for classical systems.

On the other hand, the Fokker-Planck approximation leading to (4.6.16) is more accurate than the approximation used in Chap.3 in order to obtain (3.5.4) where all retardation effect are disregarded. To obtain (4.6.16) we had to assume that

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[3] (3.2.12), (4.6.16), and (3.5.4) correspond to C_0, C_1, and C_2 in Fig.I.1.

the state functions $g(\alpha)$ are slowly varying compared to the remaining degrees of freedom, whereas in order to obtain (3.5.4) we had to assume that the linear functions of α already form a set of slowly varying variables with a characteristic time scale well separated from the time scale of the other degrees of freedom. As a consequence, (4.6.16) cover a wider range than (3.5.4). In particular, they are still useful at and in the vicinity of critical points.

4.7 More on the Fokker-Planck Equation Approach

Nonlinear Langevin Equations. Instead of a Fokker-Planck equation, one may use a set of Langevin equations to describe the dynamics of the macroscopic variables. The equivalence of the two approaches is well known [44,46,91], but there are some ambiguities associated with nonlinear Langevin equations. That is why we have preferred to base this part of the article upon the Fokker-Planck equation where such ambiguities do not arise. However, for completeness, we shall give the form of the Langevin equations associated with the Fokker-Planck process (4.4.7).

When the stochastic integral is defined in the ITO sense [142], the process may be described by the Langevin equations (stochastic differential equations)

$$\dot{\alpha}_i(t) = K_i(\alpha(t)) + \sum_j g_{ij}(\alpha(t))\zeta_j(t) \quad , \tag{4.7.1}$$

where $K_i(\alpha)$ is the Fokker-Planck drift (4.4.18), while the $g_{ij}(\alpha)$ obey the relations

$$\sum_k g_{ik}(\alpha)g_{jk}(\alpha) = 2K_{ij}(\alpha) \quad , \tag{4.7.2}$$

where $K_{ij}(\alpha)$ is the Fokker-Planck diffusion matrix (4.4.19). The $\zeta_i(t)$ are Gaussian, δ-correlated fluctuating quantities with the averages

$$\langle\zeta_i(t)\rangle = 0 \quad , \quad \langle\zeta_i(t)\zeta_j(t')\rangle = \delta_{ij}\delta(t - t') \quad . \tag{4.7.3}$$

Note that the drift vector $K_i(\alpha)$ in the Langevin equations (4.7.1) does not coincide with the deterministic drift vector (4.5.4) in general.

When the stochastic integral is defined in the STRATONOVICH sense [44], the Langevin equations have the form

$$\dot{\alpha}_i(t) = K_i^S(\alpha(t)) + \sum_j g_{ij}(\alpha(t))\zeta_j(t) \quad , \tag{4.7.4}$$

where the Stratonovich drift $K_i^S(\alpha)$ reads

$$K_i^S(\alpha) = K_i(\alpha) - \frac{1}{2}\sum_{jk} \frac{\partial g_{ij}(\alpha)}{\partial \alpha_k} g_{kj}(\alpha) \quad . \tag{4.7.5}$$

It is customary to make the g_{ij} symmetric,

$$g_{ij}(\alpha) = g_{ji}(\alpha) \quad , \tag{4.7.6}$$

since without this condition the form of the Langevin equations is rather arbitrary [143]. Again, the Stratonovich drift (4.7.5) differs from the deterministic drift (4.5.4) in general.[4] In linear systems there is no ambiguity associated with the Langevin equations and the Langevin drift vector is indeed the deterministic drift vector.

Fokker-Planck Equation Without Temperature. So far, the theory in this chapter has made use of a temperature T defined as the equilibrium temperature corresponding to the given mean value of the energy. The temperature dependence of the equations of motion automatically disappears if the Hamiltonian H is included in the set of macroscopic variables A. Then, we have $H(\Gamma) = H(A(\Gamma))$ and we find with (4.1.2,8,9)

$$\frac{\mathrm{tr}\{\rho_\beta \Psi_\alpha X\}}{p_\beta(\alpha)} = \frac{\mathrm{tr}\{\Psi_\alpha X\}}{\mathrm{tr}\{\Psi_\alpha\}} = \langle X;\alpha\rangle \quad , \tag{4.7.7}$$

since the Boltzmann factor $\exp[-\beta H(\Gamma)]$ can be brought as $\exp[-\beta H(\alpha)]$ in front of the trace where it cancels. Consequently, the temperature dependence disappears from all quantities to be found in the exact equations of motion (4.2.10).

The further evaluation of (4.2.10) is somewhat simplified by (4.7.7) leading, instead of to (4.2.23), to the generalized Fokker-Planck equation

$$\begin{aligned}\frac{\partial}{\partial t} p(\alpha,t) = &- \sum_i \frac{\partial}{\partial \alpha_i} v_i(\alpha) p(\alpha,t) \\ &+ \int_0^t ds \sum_{i,j} \frac{\partial}{\partial \alpha_i} \int d\alpha' D'_{ij}(\alpha,\alpha',t-s) w(\alpha') \frac{\partial}{\partial \alpha'_j} \frac{p(\alpha',s)}{w(\alpha')}\end{aligned} \tag{4.7.8}$$

where

$$w(\alpha) = \mathrm{tr}\{\Psi_\alpha\} = \int d\Gamma \delta(A(\Gamma) - \alpha) \quad , \tag{4.7.9}$$

$$v_i(\alpha) = \langle \dot{A}_i;\alpha\rangle = \frac{\int d\Gamma \delta(A(\Gamma)-\alpha)\dot{A}_i(\Gamma)}{w(\alpha)} \quad , \tag{4.7.10}$$

$$D'_{ij}(\alpha,\alpha',t-s) = \frac{\mathrm{tr}\{R_i(\alpha,t)R_j(\alpha',s)\}}{w(\alpha')} \quad . \tag{4.7.11}$$

It is convenient to redefine the A in such a way that $A_0 = H$ while $A_1, A_2, \ldots$ are the macroscopic variables used earlier. Since $\dot{A}_0 = 0$, we then have $v_0 = D'_{0i} = D'_{i0} = 0$ Consequently, in the generalized Fokker-Planck equation (4.7.8) all terms with $i = 0$ or $j = 0$ vanish. Henceforth it is implied that the indices i,j run through $1,2,\ldots$ only.

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[4] This means that the widely used procedure to introduce fluctuations by simply adding fluctuating forces to the deterministic equations is subject to pitfalls in nonlinear systems [89,144].

The drift vector (4.7.10) may be written

$$v_i(\alpha) = \frac{1}{w(\alpha)} \sum_j \frac{\partial}{\partial \alpha_j} \pi'_{ij}(\alpha) w(\alpha) \quad , \tag{4.7.12}$$

where

$$\pi'_{ij}(\alpha) = \frac{\mathrm{tr}\left[\Theta(\alpha_0 - H) \prod_{k=1}^{n} \delta(A_k - \alpha_k)\{A_j, A_i\}\right]}{w(\alpha)} . \tag{4.7.13}$$

$\Theta(x)$ is the unit step function

$$\Theta(x) = \begin{cases} 1 & \text{for} \quad x > 0 \\ 0 & \text{for} \quad x < 0 \quad . \end{cases} \tag{4.7.14}$$

When we make the same kind of approximations as in Sect.4.4, the generalized Fokker-Planck equation (4.7.8) simplifies to

$$\frac{\partial}{\partial t} p(\alpha,t) = - \sum_i \frac{\partial}{\partial \alpha_i} v_i(\alpha) p(\alpha,t)$$

$$+ \sum_{i,j} \frac{\partial}{\partial \alpha_i} \xi'_{ij}(\alpha) w(\alpha) \frac{\partial}{\partial \alpha_j} \frac{p(\alpha,t)}{w(\alpha)} \quad , \tag{4.7.15}$$

where the $\xi'_{ij}(\alpha)$ are given by (4.4.8) except that the hypersurface average $<X;\alpha>$ is now defined as in (4.7.7) so that the ξ'_{ij} do not depend on the temperature T but on the total energy α_0 instead.

The Fokker-Planck equation (4.7.15) may be written

$$\frac{\partial}{\partial t} p(\alpha,t) = \sum_{i,j} \frac{\partial}{\partial \alpha_i} L'_{ij}(\alpha) \left[- \frac{\partial S'(\alpha)}{\partial \alpha_j} + k_B \frac{\partial}{\partial \alpha_j}\right] p(\alpha,t) \quad , \tag{4.7.16}$$

where

$$S'(\alpha) = k_B \ln w(\alpha) \tag{4.7.17}$$

is the bare entropy, while the

$$L'_{ij}(\alpha) = \frac{1}{k_B} \{\pi'_{ij}(\alpha) + \xi'_{ij}(\alpha)\} \tag{4.7.18}$$

are the corresponding bare transport coefficients.

The Fokker-Planck equation (4.7.16) has the same form as (4.4.17) except that the quantities to be found in (4.4.17) depend on the temperature T, while the quantities to be found in (4.7.16) depend on the total energy α_0. It may be shown that they are related by

$$\exp\left[- \frac{1}{k_B T} F^*(T,\alpha_i)\right] \propto \int d\alpha_0 \exp\left[\frac{1}{k_B} S'(\alpha_0,\alpha_i) - \frac{1}{k_B T} \alpha_0\right] \tag{4.7.19}$$

and

$$T L^*_{ij}(T,\alpha_k) = \frac{\int d\alpha_0 \exp\left[\frac{1}{k_B} S'(\alpha_0,\alpha_k) - \frac{1}{k_B T} \alpha_0\right] L'_{ij}(\alpha_0,\alpha_k)}{\int d\alpha_0 \exp\left[\frac{1}{k_B} S'(\alpha_0,\alpha_k) - \frac{1}{k_B T} \alpha_0\right]} \quad . \tag{4.7.20}$$

If the A_i describe local properties of the system or properties of small subsystems, it does not matter whether the total energy is microcanonically sharp or distributed canonically if the system is only sufficiently large. For large systems

$$\exp\left\{\frac{1}{k_B} S' - \frac{1}{k_B T} \alpha_D\right\}$$

is a very sharply peaked function of α_D, and (4.7.19,20) yield as approximate relations

$$F^*(T,\alpha_i) = \alpha_D - TS'(\alpha_D,\alpha_i) \tag{4.7.21}$$

and

$$TL^*_{ij}(T,\alpha_k) = L'_{ij}(\alpha_D,\alpha_k) \quad , \tag{4.7.22}$$

where α_D is related to T by

$$\frac{\partial S'}{\partial \alpha_D} = \frac{1}{T} \quad . \tag{4.7.23}$$

In this case the Fokker-Planck equations (4.4.17) and (4.7.16) are equivalent.

5. The Master Equation Approach

The macroscopic variables A of a quantum system are generally noncommuting; that is, the product of two macroscopic variables has a different meaning depending on the order of the two variables. Hence, if we follow the line of reasoning of Chap.4 and enlarge the set of macroscopic variables to include the nonlinear functions of the A, we will encounter new problems not present on the level of classical statistical mechanics. As a consequence, the Fokker-Planck equation approach described previously cannot be easily applied to quantum systems. The difficulty lies in the fact that, because of the quantum-mechanical dispersion, there is no quantum analogue of the classical hypersurface $\Xi(\alpha)$ on which all macroscopic variables A assume given values α.

Often the macroscopic variables A describe properties of a subsystem S with Hilbert space $\mathcal{H}_S$. The Hilbert space $\mathcal{H}$ of the entire system may then be written as a tensor product of $\mathcal{H}_S$ and a Hilbert space $\mathcal{H}_R$, where R stands for "reservoir" or "remaining degrees of freedom". In this chapter we shall consider quantum systems with this property. This concept is not general enough to account for all situations of interest. For instance, in a crystal the long-wavelength phonons may constitute the system S, while the short-wavelength phonons belong to the reservoir. The corresponding Hilbert spaces are not just factors of the Hilbert space $\mathcal{H}$ of the entire system. The approach given in this chapter can, however, be extended to systems where the macroscopic variables are projected out by a more general coarse-graining operator. To keep things simple, the general case is not discussed here, but an example is given in Chap.9.

Instead of just projecting out the macroscopic variables A as in Chap.3, we shall now proceed in a way similar to Chap.4 and enlarge the set of relevant variables to include all operators acting in $\mathcal{H}_S$ while leaving $\mathcal{H}_R$ invariant. This enlarged set contains the nonlinear functions of the A since the A act in $\mathcal{H}_S$ only. To put it differently, we keep all variables of the system S and eliminate those of the reservoir R.

In Sect.5.1 we define a relevant probability density $\bar{\rho}(t)$ which yields the same reduced probability density $\rho_S(t) = \mathrm{tr}_R\{\rho(t)\}$ of the subsystem S as the true probability density $\rho(t)$, and we use the associated projection operator in Sect.5.2 to study the dynamics of the open system S moving under the influence of the reservoir

The reduced probability density $\rho_S(t)$ is shown to obey a generalized master equation. In contrast to previous work on the same problem [68-74, 145-147], we do not assume that the system S and the reservoir R are uncorrelated initially. The advantage of the present approach lies in the fact that the generalized master equation describes, in addition to the mean relaxation towards equilibrium, the time evolution of stationary canonical correlations. Some properties of the stochastic operators to be found in the generalized master equation are summarized in Sect.5.3.

In Sect.5.4 we study the limit of a weak coupling between S and R and show that under certain assumptions about the decay of reservoir correlations the dynamics of the open system S is described by a master equation of the form

$$\dot{\rho}_S(t) = -\frac{i}{\hbar}[H_S,\rho_S(t)] + \Lambda_S\rho_S(t) \quad .$$

The first term describes the free motion of S, and the dissipative Liouville operator Λ_S describes the influence of the reservoir. While the free motion is described by a commutator, the dissipative Liouville operator is shown to have a double commutator structure. Some properties of the master equation and in particular the consequences of the time-reversal symmetry are discussed in Sect.5.5.

Finally, Sect.5.6 is concerned with the problem of deriving fluctuation renormalized transport equations for the set A of macroscopic variables of the open system S by starting from the master equation describing the time evolution of all variables of S. The resulting transport equations contain a retarded part due to the internal interaction in S and are compared with those derived in Chap.3.

5.1 Relevant Probability Density

We consider a closed quantum system composed of two interacting parts S and R. The subsystem S is of experimental relevance while R is a reservoir. We want to describe the dynamics of S moving under the influence of R. Each of the two subsystems has its own Hilbert space $\mathcal{H}_S$ and $\mathcal{H}_R$, respectively, and the Hilbert space $\mathcal{H}$ of the entire system is the tensor product $\mathcal{H} = \mathcal{H}_S \otimes \mathcal{H}_R$. The Hamiltonian H consists of three parts[1]

$$H = H_S + H_R + gH_{SR} \quad , \tag{5.1.1}$$

where H_S and H_R are the Hamiltonians of S and R, respectively, while H_{SR} is the interaction where we have split off a coupling constant g for later convenience.

---

[1] Our notation does not distinguish between the operator X_S acting in $\mathcal{H}_S$ and the operator $X_S \otimes 1_R$ acting in $\mathcal{H}$, where 1_R is the unity in $\mathcal{H}_R$. We shall always use the symbol X_S since no ambiguity will arise. Correspondingly, we shall use Y_R instead of $1_S \otimes Y_R$.

Correspondingly, the Liouville operator $\mathbf{L} = \frac{1}{\hbar}[H,\cdot/.]$ divides into three pieces

$$\mathbf{L} = \mathbf{L}_S + \mathbf{L}_R + g\mathbf{L}_{SR} \quad . \tag{5.1.2}$$

The state of the subsystem S is described by the reduced probability density

$$\rho_S(t) = \mathrm{tr}_R\{\rho(t)\} \quad , \tag{5.1.3}$$

where $\rho(t)$ is the probability density of the entire system while tr_R denotes the partial trace over a complete set of orthonormal functions in H_R. Since the trace operator tr can be carried out in two steps

$$\mathrm{tr} = \mathrm{tr}_S\, \mathrm{tr}_R \quad , \tag{5.1.4}$$

we find for the mean value of any variable X_S of the subsystem S

$$\langle X_S(t)\rangle = \mathrm{tr}\{X_S\rho(t)\} = \mathrm{tr}_S\{X_S\, \mathrm{tr}_R[\rho(t)]\} = \mathrm{tr}_S\{X_S\rho_S(t)\} \quad . \tag{5.1.5}$$

Hence, the reduced probability density $\rho_S(t)$ just determines the mean values of those variables which we want to project out, and it contains no additional information.

In thermal equilibrium the state of the system is described by a canonical probability density

$$\rho_\beta = Z_\beta^{-1}\, e^{-\beta H} \quad , \quad Z_\beta = \mathrm{tr}\{e^{-\beta H}\} \; , \tag{5.1.6}$$

where $\beta = 1/k_BT$ is the inverse reservoir temperature. The corresponding reduced probability density reads

$$\rho_{S\beta} = Z_\beta^{-1}\, \mathrm{tr}_R\{e^{-\beta H}\} \quad . \tag{5.1.7}$$

If the equilibrium state is perturbed by external forces which are constant in time and couple to the subsystem S only, the system will settle down to a new stationary state of the form

$$\rho_{st} = \frac{e^{-\beta(H+H_S')}}{\mathrm{tr}\{e^{-\beta(H+H_S')}\}} \quad , \tag{5.1.8}$$

where H_S' describes the coupling to the applied forces. For weak perturbations we have up to terms of higher order in H_S'

$$\rho_{st} = \frac{1}{\beta}\int_0^\beta d\alpha\, Z_\beta^{-1}\, e^{-\alpha H}[1 - \beta H_S' + \beta\langle H_S'\rangle_\beta]e^{-(\beta-\alpha)H} \quad , \tag{5.1.9}$$

where

$$\langle H_S'\rangle_\beta = \mathrm{tr}\{\rho_\beta H_S'\} \quad . \tag{5.1.10}$$

We want to study the relaxation of initial nonequilibrium states of the form (5.1.9).[2] (Footnote see next page.) To this purpose we introduce a relevant probability density

$$\bar{\rho}(t) = \frac{1}{\beta}\int_0^\beta d\alpha\, Z_\beta^{-1}\, e^{-\alpha H}\, \Psi_S(t)\, e^{-(\beta-\alpha)H} \quad , \tag{5.1.11}$$

where the operator $\Psi_S(t)$, which acts in the subspace H_S only, is determined by the requirement

$$\mathrm{tr}_R\{\bar{\rho}(t)\} = \mathrm{tr}_R\{\rho(t)\} = \rho_S(t) \quad . \tag{5.1.12}$$

Hence, as far as the state of the subsystem S is concerned, the relevant probability density $\bar{\rho}(t)$ and the true probability density $\rho(t)$ are equivalent. Further, the relevant probability density has been defined in such a way that the equilibrium state ρ_β and those states obtained by weak perturbations of the subsystem S are of the relevant form.[3]

On defining a transformation $\mathbf{\Sigma}$ by

$$\mathbf{\Sigma}X = \frac{1}{\beta}\int_0^\beta d\alpha\, Z_\beta^{-1}\, e^{-\alpha H} X\, e^{-(\beta-\alpha)H} \quad , \tag{5.1.13}$$

where X is any operator acting in H, the relevant probability density may be written

$$\bar{\rho}(t) = \mathbf{\Sigma}\Psi_S(t) \quad . \tag{5.1.14}$$

We further introduce a transformation Σ_S which transforms the variables of the subsystem S, that is, operators X_S acting in H_S only:

$$\Sigma_S X_S = \mathrm{tr}_R\{\Sigma X_S\} \quad . \tag{5.1.15}$$

Then, (5.1.12) may be written

$$\Sigma_S \Psi_S(t) = \rho_S(t) = \mathrm{tr}_R\{\rho(t)\} \quad . \tag{5.1.16}$$

Combining (5.1.14,16), the relevant probability density $\bar{\rho}(t)$ may formally be expressed in terms of the true probability density

$$\bar{\rho}(t) = \mathbf{P}^T \rho(t) \quad , \tag{5.1.17}$$

where

---

[2] It is important to note that we do not assume that the system S and the reservoir R are uncorrelated initially.

[3] We may also study the relaxation of initial states of the form (5.1.8) where the perturbation H_S' is not necessarily weak. In this case, we define a relevant probability density of the form $\bar{\rho}(t) \propto \exp\{-\beta[H - \mu_S(t)]\}$ where $\mu_S(t)$ is determined by the requirement $\mathrm{tr}_R\{\bar{\rho}(t)\} = \rho_S(t)$. Following the general scheme given in Chap.3, we may derive an equation of motion for $\rho_S(t)$ which then describes the relaxation from initial states possibly far from thermal equilibrium. This extended theory, which we shall not discuss here, gives the same results for the linear relaxation near equilibrium and, in particular, for the dynamics of equilibrium correlations as the present, somewhat simpler, approach.

$$\mathbf{P}^T X = \Sigma\, \Sigma_S^{-1}\, \mathrm{tr}_R\{X\} \tag{5.1.18}$$

is a projection operator satisfying $(\mathbf{P}^T)^2 = \mathbf{P}^T$. The transposed projection operator defined by

$$\mathrm{tr}\{X\mathbf{P}^T Y\} = \mathrm{tr}\{Y\mathbf{P}X\} \tag{5.1.19}$$

reads

$$\mathbf{P}X = \Sigma_S^{-1}\, \mathrm{tr}_R\{\Sigma X\} \quad , \tag{5.1.20}$$

which is easily shown by using (5.1.4) and

$$\mathrm{tr}\{X\Sigma Y\} = \mathrm{tr}\{Y\Sigma X\} \quad . \tag{5.1.21}$$

Note that Σ_S has been defined as a transformation of operators X_S acting in H_S only, whereas $\mathrm{tr}_R\Sigma$ may be applied to any operator X acting in $H = H_S \times H_R$. The transformation $\mathrm{tr}_R\Sigma$ reduces operators acting in H to operators acting in H_S only, and it has no inverse. However, the two transformations $\mathrm{tr}_R\Sigma$ and Σ_S coincide when they are applied to variables X_S of the subsystem S. The projection operator (5.1.20) projects out these variables

$$\mathbf{P}X_S = X_S \quad . \tag{5.1.22}$$

Clearly, the projection operators (5.1.18,20) are also related by

$$\mathbf{P}^T\Sigma = \Sigma\mathbf{P} \quad . \tag{5.1.23}$$

5.2 Generalized Master Equation

To determine the dynamics of the open system S, we make use of the operator identity

$$\begin{aligned} e^{-i\mathbf{L}t} &= \mathbf{P}^T e^{-i\mathbf{L}t} \\ &\quad - i\int_0^t ds\, e^{-i(\mathbf{1}-\mathbf{P}^T)\mathbf{L}(t-s)}(\mathbf{1} - \mathbf{P}^T)\mathbf{L}\mathbf{P}^T e^{-i\mathbf{L}s} \\ &\quad + e^{-i(\mathbf{1}-\mathbf{P}^T)\mathbf{L}t}(\mathbf{1} - \mathbf{P}^T) \quad , \end{aligned} \tag{5.2.1}$$

which is a version of (2.4.11) for a time-independent projection operator. Equation (5.2.1) may be verified directly by showing that both sides satisfy the same differential equation and coincide initially. Putting (5.2.1) into

$$\dot{\rho}_S(t) = \mathrm{tr}_R\{\dot{\rho}(t)\} = -i\,\mathrm{tr}_R\{\mathbf{L}e^{-i\mathbf{L}t}\rho(0)\} \quad , \tag{5.2.2}$$

we find for the time rate of change of the reduced probability density

$$\begin{aligned} \dot{\rho}_S(t) &= -i\,\mathrm{tr}_R\{\mathbf{L}\mathbf{P}^T\rho(t)\} \\ &\quad - \int_0^t ds\, \mathrm{tr}_R\Big\{\mathbf{L}\, e^{-i(\mathbf{1}-\mathbf{P}^T)\mathbf{L}(t-s)}(\mathbf{1} - \mathbf{P}^T)\mathbf{L}\mathbf{P}^T\rho(s)\Big\} \end{aligned} \tag{5.2.3}$$

$$- i \, \mathrm{tr}_R \left\{ \mathbf{L} \, e^{-i(\mathbf{1}-\mathbf{P}^T)\mathbf{L}t} (\mathbf{1} - \mathbf{P}^T) \rho(0) \right\} \quad .$$

We study the relaxation of initial states $\rho(0)$ of the form (5.1.9). Then, we have $\rho(0) = \bar{\rho}(0)$ and thus

$$(\mathbf{1} - \mathbf{P}^T)\rho(0) = 0 \quad . \tag{5.2.4}$$

Further, by noting

$$\mathbf{P}^T \rho(t) = \bar{\rho}(t) = \Sigma \, \Sigma_S^{-1} \, \rho_S(t) \quad , \tag{5.2.5}$$

(5.2.3) gives

$$\dot{\rho}_S(t) = \Omega_S \rho_S(t) + \int_0^t ds \, \Phi_S(t - s) \rho_S(s) \quad , \tag{5.2.6}$$

where we have introduced the stochastic operators

$$\Omega_S X_S = - i \, \mathrm{tr}_R \left\{ \mathbf{L} \Sigma \Sigma_S^{-1} \, X_S \right\} \tag{5.2.7}$$

and

$$\Phi_S(t) X_S = -\mathrm{tr}_R \left\{ \mathbf{L} \, e^{-i(\mathbf{1}-\mathbf{P}^T)\mathbf{L}t} (\mathbf{1} - \mathbf{P}^T) \mathbf{L} \Sigma \, \Sigma_S^{-1} \, X_S \right\} . \tag{5.2.8}$$

These stochastic operators act within the space of probability densities of the subsystem S. Equation (5.2.6) is a generalized master equation which provides an exact evolution law for the reduced probability density $\rho_S(t)$ in the linear regime near equilibrium.[4] Hence, the projection operator technique has eliminated the reservoir variables completely in favor of memory terms described by $\Phi_S(t - s)$.

Let us define an operator $\mu_S(t)$ acting in H_S by

$$\mu_S(t) = \frac{1}{\beta} \left(\Psi_S(t) - 1 \right) \tag{5.2.9}$$

where $\Psi_S(t)$ has been introduced in (5.1.14). With (5.1.16), we have

$$\mu_S(t) = \frac{1}{\beta} \left[\Sigma_S^{-1} \, \rho_S(t) - 1 \right] \quad . \tag{5.2.10}$$

Further, from (5.1.13,15) we get

$$\Sigma 1 = \rho_\beta \ , \quad \Sigma_S 1 = \rho_{S\beta} \quad , \tag{5.2.11}$$

so that (5.2.10) may be written

$$\mu_S(t) = \frac{1}{\beta} \, \Sigma_S^{-1} \left[\rho_S(t) - \rho_{S\beta} \right] \quad . \tag{5.2.12}$$

Clearly, $\mu_S(t)$ characterizes the deviation from equilibrium.

---

[4] The restriction to the linear regime near equilibrium is due to the fact that the initial state $\rho(0)$ has been assumed to be of the form (5.1.9), which is obtained from the more general expression (5.1.8) with linear order in the perturbation H_S' only.

The operator $\mu_S(t)$ can also be viewed as a thermodynamic force operator conjugate to the reduced probability density $\rho_S(t)$ in the following sense. Introducing a coarse-grained nonequilibrium free energy $F^*(t)$ as a function of the reduced probability density $\rho_S(t)$ by[5]

$$F^*(t) = F_\beta + \frac{1}{2\beta}\, \mathrm{tr}_S\{[\rho_S(t) - \rho_{S\beta}]\Sigma_S^{-1}[\rho_S(t) - \rho_{S\beta}]\} \tag{5.2.13}$$

where F_β is the equilibrium free energy, we have

$$\frac{\delta F^*(t)}{\delta \rho_S(t)} = \mu_S(t) \quad . \tag{5.2.14}$$

With (5.2.12) the free energy $F^*(t)$ may also be written as

$$F^*(t) = F_\beta + \frac{\beta}{2}\, \mathrm{tr}_S\{\mu_S(t)\Sigma_S\mu_S(t)\} \tag{5.2.15}$$

$$= F_\beta + \frac{\beta}{2}\, (\mu_S(t),\mu_S(t)) \quad ,$$

where

$$(X,Y) = \mathrm{tr}\{X\Sigma Y\} = \mathrm{tr}\{Y\Sigma X\} \tag{5.2.16}$$

$$= \frac{1}{\beta}\int_0^\beta d\alpha\, \mathrm{tr}\{\rho_\beta X\, e^{-\alpha H} Y\, e^{\alpha H}\}$$

is the canonical correlation already introduced in (3.4.7).

Now, with the help of (5.2.7,8,12) and

$$\Sigma\Sigma_S^{-1}\rho_{S\beta} = \rho_\beta \quad , \tag{5.2.17}$$

the generalized master equation (5.2.6) may be transformed to read

$$\dot{\rho}_S(t) = -\mathbf{V}_S\mu_S(t) - \int_0^t ds\, \mathbf{R}_S(t-s)\mu_S(s) \quad , \tag{5.2.18}$$

where we have introduced the transport operators

$$\mathbf{V}_S X_S = i\beta\, \mathrm{tr}_R\{\mathbf{L}\,\Sigma X_S\} \tag{5.2.19}$$

and

$$\mathbf{R}_S(t)X_S = \beta\, \mathrm{tr}_R\left\{\mathbf{L}\, e^{-i(\mathbf{1}-\mathbf{P}^T)\mathbf{L}t}(\mathbf{1} - \mathbf{P}^T)\mathbf{L}\,\Sigma X_S\right\} \tag{5.2.20}$$

which are related to the stochastic operators (5.2.7,8) by

$$\mathbf{\Omega}_S = -\frac{1}{\beta}\,\mathbf{V}_S\Sigma_S^{-1} \tag{5.2.21}$$

$$\mathbf{\Phi}_S(t) = -\frac{1}{\beta}\,\mathbf{R}_S(t)\Sigma_S^{-1} \quad . \tag{5.2.22}$$

Equation (5.2.18) shows that the generalized master equation actually has the same structure as the transport equations discussed earlier.

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[5] This expression for the free energy is obtained if we seek the minimum of the functional $F\{\rho(t)\}=\mathrm{tr}\{\rho(t)H\}+k_BT\,\mathrm{tr}\{\rho(t)\ln\rho(t)\}$ under the constraint $\mathrm{tr}_R\{\rho(t)\}=\rho_S(t)$ and neglect terms of the third order in $\rho_S(t)-\rho_{S\beta}$.

In equilibrium the canonical correlation of two variables X_S and Y_S of the subsystem S reads

$$(X_S(t + s), Y_S(s)) = (X_S(t), Y_S(0)) \qquad (5.2.23)$$

$$= \mathrm{tr}\{X_S\, e^{-i\mathbf{L}t} \Sigma Y_S\} \quad .$$

Using (5.1.4), we see that this correlation function may be written

$$(X_S(t), Y_S) = \mathrm{tr}_S\{X_S \mathbf{G}_S(t) Y_S\} \quad , \qquad (5.2.24)$$

where we have introduced

$$\mathbf{G}_S(t) X_S = \mathrm{tr}_R\{e^{-i\mathbf{L}t} \Sigma X_S\} \quad , \qquad (5.2.25)$$

which may be viewed as the quantum analogue of the stationary joint-probability density of classical statistical mechanics.

If we insert the identity (5.2.1) into

$$\dot{\mathbf{G}}_S(t) X_S = -i\, \mathrm{tr}_R\{\mathbf{L}\, e^{-i\mathbf{L}t} \Sigma X_S\} \qquad (5.2.26)$$

and make use of

$$(\mathbf{1} - \mathbf{P}^T) \Sigma X_S = \Sigma (\mathbf{1} - \mathbf{P}) X_S = 0 \qquad (5.2.27)$$

and the relations (5.1.18) and (5.2.7,8), we find that $\mathbf{G}_S(t)$ satisfies the generalized master equation (5.2.6), i.e.,

$$\dot{\mathbf{G}}_S(t) = \boldsymbol{\Omega}_S \mathbf{G}_S(t) + \int_0^t ds\, \boldsymbol{\Phi}_S(t - s) \mathbf{G}_S(s) \qquad (5.2.28)$$

with the initial condition

$$\mathbf{G}_S(0) = \Sigma_S \quad . \qquad (5.2.29)$$

Consequently, the generalized master equation (5.2.6) does not only determine the relaxation of the reduced probability density $\rho_S(t)$ from a nonequilibrium state towards equilibrium but it also governs the time evolution of correlations of variables of the open system S in equilibrium.

Finally, we note that the time evolution of $\rho_S(t)$ can be expressed in terms of $\mathbf{G}_S(t)$. Since (5.1.14) leads to

$$\rho(0) = \tilde{\rho}(0) = \Sigma \Psi_S(0) \quad , \qquad (5.2.30)$$

we get with (5.2.25)

$$\rho_S(t) = \mathrm{tr}_R\{e^{-i\mathbf{L}t} \rho(0)\} = \mathbf{G}_S(t) \Psi_S(0) \qquad (5.2.31)$$

$$= \mathbf{G}_S(t)\, \Sigma_S^{-1} \rho_S(0) \quad .$$

For the last transformation we have made use of (5.1.16).

5.3 Properties of the Stochastic Operators

From the identity (3.2.7) and the definition (5.1.13) we get

$$[X,\rho_\beta] = -\int_0^\beta d\alpha\, Z_\beta^{-1}\, e^{-\alpha H}[X,H]e^{-(\beta-\alpha)H} \tag{5.3.1}$$

$$= \hbar\beta\, \Sigma \mathbf{L} X \quad .$$

Further, we have

$$\mathbf{L}\Sigma = \Sigma\mathbf{L}. \tag{5.3.2}$$

Using these relations, the expression (5.2.19) for $\mathbf{V}_S$ may be transformed to read

$$\mathbf{V}_S X_S = \frac{i}{\hbar}\, \mathrm{tr}_R\{[X_S,\rho_\beta]\} = -\frac{i}{\hbar}[\rho_{S\beta},X_S] \quad . \tag{5.3.3}$$

It is now readily shown that the instantaneous part of the time rate of change of $\rho_S(t)$, that is, $-\mathbf{V}_S\mu_S(t)$, does not contribute to the time rate of change of the free energy

$$\dot{F}^*(t) = \mathrm{tr}_S\{\mu_S(t)\dot{\rho}_S(t)\} \tag{5.3.4}$$

since

$$\mathrm{tr}_S\{\mu_S(t)\mathbf{V}_S\mu_S(t)\} = 0 \quad . \tag{5.3.5}$$

Further, from (5.3.5) it is easily seen that the transposed operator $\mathbf{V}_S^T$ defined by

$$\mathrm{tr}_S\{Y_S\mathbf{V}_S X_S\} = \mathrm{tr}_S\{X_S\mathbf{V}_S^T Y_S\} \tag{5.3.6}$$

is given by

$$\mathbf{V}_S^T = -\mathbf{V}_S \quad . \tag{5.3.7}$$

Using (5.1.19,21) and (5.2.20), we obtain for the operator $\mathbf{R}_S^T(t)$, transpose to $\mathbf{R}_S(t)$,

$$\mathbf{R}_S^T(t)X_S = \beta\,\mathrm{tr}_R\{\Sigma\,\mathbf{L}(\mathbf{1}-\mathbf{P})\, e^{i\mathbf{L}(\mathbf{1}-\mathbf{P})t}\mathbf{L}X_S\} \quad , \tag{5.3.8}$$

which may be transformed further by use of (5.1.23) and (5.3.2) to give

$$\mathbf{R}_S^T(t) = \mathbf{R}_S(-t) \quad . \tag{5.3.9}$$

We now assume that the Hamiltonian H is invariant under the time-reversal transformation, i.e.,

$$\tilde{H} = H \quad . \tag{5.3.10}$$

Then, we get from (5.1.13,15)

$$\widetilde{\Sigma X} = \Sigma\tilde{X} \quad ; \quad \widetilde{\Sigma_S X_S} = \Sigma_S\tilde{X}_S \quad , \tag{5.3.11}$$

which implies

$$\widetilde{\Sigma_S X_S} = \Sigma_S^T \tilde{X}_S \tag{5.3.12}$$

since $\Sigma_S^T = \Sigma_S$. As a consequence of (5.3.12), the free energy $F^*(t)$ is time-reversal invariant. Further, with (5.1.18,20) we find

$$\widetilde{\mathbf{P}X} = \mathbf{P}\tilde{X} \quad ; \quad \widetilde{\mathbf{P}^T X} = \mathbf{P}^T \tilde{X} \quad . \tag{5.3.13}$$

The Liouville operator transforms as

$$\widetilde{i\mathbf{L}X} = -i\mathbf{L}\tilde{X} \quad , \tag{5.3.14}$$

and $\mathbf{V}_S$ transforms accordingly since it is a commutator with a time-reversal invariant operator, too:

$$\widetilde{\mathbf{V}_S X} = -\mathbf{V}_S \tilde{X} \quad . \tag{5.3.15}$$

This combines with (5.3.7) to give

$$\widetilde{\mathbf{V}_S X} = \mathbf{V}_S^T \tilde{X} \quad . \tag{5.3.16}$$

Using (5.3.11,13,14), we obtain

$$\widetilde{\mathbf{R}_S(t) X_S} = \mathbf{R}_S(-t) \tilde{X}_S \quad , \tag{5.3.17}$$

which combines with (5.3.9) to give

$$\widetilde{\mathbf{R}_S(t) X_S} = \mathbf{R}_S^T(t) \tilde{X}_S \quad . \tag{5.3.18}$$

The relations (5.3.12,16,18) are the detailed balance conditions associated with the generalized master equation. These conditions guarantee that $\mathbf{G}_S(t)$ transforms as

$$\widetilde{\mathbf{G}_S(t) X_S} = \mathbf{G}_S^T(t) \tilde{X}_S \quad , \tag{5.3.19}$$

which leads in connection with (5.2.24) to the symmetry of detailed balance

$$(X_S(t), Y_S) = (\tilde{Y}_S(t), \tilde{X}_S) \quad . \tag{5.3.20}$$

This symmetry is a consequence of the microscopic reversibility.

To see the connection between (5.3.19) and the detailed balance conditions explicitly, it is convenient to Laplace transform (5.2.28). With (5.2.29) we find

$$z\mathbf{G}_S(z) - \Sigma_S = \mathbf{\Omega}_S \mathbf{G}_S(z) + \mathbf{\Phi}_S(z) \mathbf{G}_S(z) \quad , \tag{5.3.21}$$

where

$$\mathbf{G}_S(z) = \int_0^\infty dt\, e^{-zt} \mathbf{G}_S(t) \quad . \tag{5.3.22}$$

Other Laplace-transformed quantities are defined accordingly. Using (5.2.21,22), we get

$$\mathbf{G}_S^{-1}(z) = \Sigma_S^{-1}\left[z + \frac{1}{\beta}\,\mathbf{V}_S\Sigma_S^{-1} + \frac{1}{\beta}\,\mathbf{R}_S(z)\Sigma_S^{-1}\right] \quad . \tag{5.3.23}$$

Now, we may easily determine $\overparen{\mathbf{G}_S^{-1}(z)X}$ and $(\mathbf{G}_S^{-1}(z))^T\tilde{X}$. On comparing the two expressions, which we do not write down explicitly, we find that they are identical provided (5.3.12,16,18) hold. Thus, the detailed balance conditions imply (5.3.19).

Instead of (5.3.16,19), we may give conditions for the stochastic operators $\mathbf{\Omega}_S$ and $\Phi_S(t)$. With (5.2.21,22) we get

$$\overparen{\mathbf{\Omega}_S\Sigma_S X} = \Sigma_S\Omega_S^T\tilde{X}_S \tag{5.3.24}$$

and

$$\overparen{\Phi_S(t)\Sigma_S X} = \Sigma_S\Phi_S^T(t)\tilde{X}_S \quad . \tag{5.3.25}$$

However, the symmetries of the process become particularly clear when expressed as before in terms of Σ_S (or F^*) and the transport operators $\mathbf{V}_S$ and $\mathbf{R}_S(t)$. The reason is that Σ_S characterizes the statics of the system while the transport operators do not affect the statics; they determine the relaxational behavior. Such a separation of static and dynamic quantities is very useful in the study of formal properties of a macroscopic process.

5.4 Weak Coupling Limit

We shall now approximate the generalized master equation (5.2.6) under the assumption that the coupling of the system S to the reservoir R is weak. To this purpose we first provide some useful relations. We split the Hamiltonian and the Liouville operator according to (5.1.1) and (5.1.2), respectively. It is easy to see that

$$\mathrm{tr}_R\{\mathbf{L}_S X\} = \mathbf{L}_S\ \mathrm{tr}_R\{X\} \tag{5.4.1}$$

and

$$\mathrm{tr}_R\{\mathbf{L}_R X\} = 0 \quad . \tag{5.4.2}$$

Thus, (5.2.7) gives

$$\mathbf{\Omega}_S X_S = -i\mathbf{L}_S X_S - ig\ \mathrm{tr}_R\{\mathbf{L}_{SR}\,\Sigma\Sigma_S^{-1}X_S\} \quad . \tag{5.4.3}$$

From (5.1.18) and (5.2.7) we get

$$\begin{aligned} -i\ \mathrm{tr}_R\{\mathbf{L}\mathbf{P}^T X\} &= -i\ \mathrm{tr}_R\{\mathbf{L}\,\Sigma\Sigma_S^{-1}\ \mathrm{tr}_R\{X\}\} \\ &= \mathbf{\Omega}_S\ \mathrm{tr}_R\{X\} = \mathrm{tr}_R\{\mathbf{\Omega}_S X\} \quad . \end{aligned} \tag{5.4.4}$$

Further, with (5.1.20) we find

$$\mathbf{\Omega}_S^T X_S = i\Sigma_S^{-I}\ \mathrm{tr}_R\{\Sigma\mathbf{L}X_S\} = i\mathbf{P}\mathbf{L}X_S \quad , \tag{5.4.5}$$

which gives with (5.1.23) and (5.3.2)

$$i(\mathbf{1} - \mathbf{P}^{T})\mathbf{L}\,\Sigma X_S = i\,\Sigma(\mathbf{1} - \mathbf{P})\mathbf{L}X_S = \Sigma(i\mathbf{L} - \Omega_S^{T})X_S \quad . \tag{5.4.6}$$

Using (5.4.4,6), the expression (5.2.20) for $\mathbf{R}_S(t)$ may be transformed to read

$$\mathbf{R}_S(t)X_S = \beta\,\mathrm{tr}_R\left\{(-\,i\mathbf{L} - \Omega_S)e^{-i(\mathbf{1}-\mathbf{P}^{T})\mathbf{L}t}\;\Sigma(i\mathbf{L} - \Omega_S^{T})X_S\right\} \quad . \tag{5.4.7}$$

So far, all relations are exact. We now expand in terms of the coupling constant g. From (5.1.13) we get

$$\Sigma X = \hat{\Sigma}X + \mathcal{O}(g) \quad , \tag{5.4.8}$$

where

$$\hat{\Sigma}X = \frac{1}{\beta}\int_0^\beta d\alpha\,\frac{1}{\mathrm{tr}\{e^{-\beta H_0}\}}\,e^{-\alpha H_0}\,X\,e^{-(\beta-\alpha)H_0} \tag{5.4.9}$$

with

$$H_0 = H_S + H_R \quad . \tag{5.4.10}$$

Using (5.1.15) and (5.4.8), we find

$$\Sigma_S X_S = \hat{\Sigma}_S X_S + \mathcal{O}(g) \quad , \tag{5.4.11}$$

where

$$\hat{\Sigma}_S X_S = \frac{1}{\beta}\int_0^\beta d\alpha\,\frac{1}{\mathrm{tr}_S\{e^{-\beta H_S}\}}\,e^{-\alpha H_S}\,X_S\,e^{-(\beta-\alpha)H_S} \quad , \tag{5.4.12}$$

which combines with (5.4.9) to yield

$$\hat{\Sigma}X_S = \hat{\rho}_{R\beta}\hat{\Sigma}_S X_S \tag{5.4.13}$$

with

$$\hat{\rho}_{R\beta} = \frac{e^{-\beta H_R}}{\mathrm{tr}_R\{e^{-\beta H_R}\}} \quad . \tag{5.4.14}$$

Now, from (5.1.18) we have

$$\mathbf{P}^{T} = \hat{\mathbf{P}}^{T} + \mathcal{O}(g) \quad , \tag{5.4.15}$$

where [69][6]

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[6] Although our projection operator $\mathbf{P}^{T}$ reduces to the Argyres-Kelley projection operator $\hat{\mathbf{P}}^{T}$ for $g \to 0$, the resulting master equation is somewhat different from the Argyres-Kelley master equation [69,73]. Recent criticism [75,76] concerning the compatibility of the master equation with the fluctuation-dissipation theorem does not apply to the present approach. See also Sect.6.5.

$$\hat{\mathbf{P}}^T X = \hat{\rho}_{R\beta} \mathrm{tr}_R\{X\} \qquad (5.4.16)$$

is the Argyres-Kelley projection operator. Next, we introduce the Liouville operator $\mathbf{L}_0$ of the uncoupled systems

$$\mathbf{L}_0 = \mathbf{L}_S + \mathbf{L}_R \quad . \qquad (5.4.17)$$

Using (5.4.1,2) and $\mathbf{L}_R \hat{\rho}_{R\beta} = 0$, we find that $\mathbf{L}_0$ commutes with $\hat{\mathbf{P}}^T$:

$$\mathbf{L}_0 \hat{\mathbf{P}}^T = \hat{\mathbf{P}}^T \mathbf{L}_0 \quad . \qquad (5.4.18)$$

We wish to examine the dynamics of the open system S in the limit of a vanishing coupling to the reservoir R. From (5.1.7), in the limit g → 0, it is seen that the stationary solution $\rho_{S\beta}$ of the exact master equation (5.2.6) approaches a canonical probability density of the free system S

$$\hat{\rho}_{S\beta} = \frac{e^{-\beta H_S}}{\mathrm{tr}_S\{e^{-\beta H_S}\}} \quad , \qquad (5.4.19)$$

where β is determined by the reservoir temperature. Clearly, the interaction with the reservoir leads to deviations from the canonical form, but we shall disregard these corrections to (5.4.19) in the following. The operator $\boldsymbol{\Sigma}_S$ characterizing the stationary equal-time correlations is then approximated by $\hat{\boldsymbol{\Sigma}}_S$.

The operator $\mathbf{V}_S$ governs the reversible dynamics of the open system S. From (5.3.3) we obtain in the approximation under consideration, that is, by substituting $\hat{\rho}_{S\beta}$ for $\rho_{S\beta}$,

$$\hat{\mathbf{V}}_S X_S = -\frac{i}{\hbar}[\hat{\rho}_{S\beta}, X_S] = i\beta \hat{\boldsymbol{\Sigma}}_S \mathbf{L}_S X_S \quad , \qquad (5.4.20)$$

where the last transformation follows by use of a relation analogous to (5.3.1). Since

$$\hat{\boldsymbol{\Sigma}}_S \mathbf{L}_S = \mathbf{L}_S \hat{\boldsymbol{\Sigma}}_S \quad , \qquad (5.4.21)$$

we find

$$\hat{\boldsymbol{\Omega}}_S = -\frac{1}{\beta} \hat{\mathbf{V}}_S \hat{\boldsymbol{\Sigma}}_S^{-1} = -i\mathbf{L}_S \quad . \qquad (5.4.22)$$

Hence, the instantaneous and reversible part of the generalized master equation (5.2.6) reduces in the limit g → 0 to the free motion of the system S.

The approximation of the retarded part of the dynamics characterized by $\mathbf{R}_S(t)$ is a somewhat more subtle problem. From (5.4.3) we obtain with (5.4.8,11,13)

$$\boldsymbol{\Omega}_S X_S = -i\mathbf{L}_S X_S - ig\, \mathrm{tr}_R\{\mathbf{L}_{SR} \hat{\rho}_{R\beta} X_S\} + O(g^2) \quad , \qquad (5.4.23)$$

which may be transformed to read

$$\boldsymbol{\Omega}_S X_S = -\,i\mathbf{L}_S X_S - \frac{ig}{\hbar}[\mathrm{tr}_R\{\hat{\rho}_{R\beta} H_{SR}\}, X_S] + O(g^2) \quad . \qquad (5.4.24)$$

We now expand (5.4.7) for $\mathbf{R}_S(t)$ in terms of g. With (5.4.2,8,17,18,24) we obtain

$$\mathbf{R}_S(t)X_S = g^2\beta \mathrm{tr}_R\{\delta\mathbf{L}_{SR}\, e^{-i\mathbf{L}_0 t}\hat{\Sigma}\, \delta\mathbf{L}_{SR}X_S\} + \mathcal{O}(g^3) \quad , \tag{5.4.25}$$

where

$$\delta\mathbf{L}_{SR}X = \frac{1}{\hbar}\,[\delta H_{SR}, X] \tag{5.4.26}$$

with

$$\delta H_{SR} = H_{SR} - \mathrm{tr}_R\{\rho_{R\beta}H_{SR}\} \quad . \tag{5.4.27}$$

Although $\mathbf{R}_S(t)$ is of the second order in g, we cannot disregard it altogether in the limit $g \to 0$. The reason is that the spectrum of the Liouville operator $\mathbf{L}_S$ is highly degenerate. Let

$$H_S = \sum_n \epsilon_n |n\rangle\langle n| \tag{5.4.28}$$

be the spectral decomposition of the Hamiltonian H_S. Then the spectral decomposition of $\mathbf{L}_S$ is given by

$$\mathbf{L}_S = \sum_\omega \omega \Pi_\omega \quad , \tag{5.4.29}$$

where the sum runs over all energy differences, and where

$$\Pi_\omega X_S = \sum_{\epsilon_n - \epsilon_m = \hbar\omega} |n\rangle\langle n|X_S|m\rangle\langle m| \quad . \tag{5.4.30}$$

Therefore we have

$$e^{-i\mathbf{L}_S t}\, X_S = \sum_\omega e^{-i\omega t}\Pi_\omega X_S \quad . \tag{5.4.31}$$

Thus, all matrix elements $\langle n|X_S|m\rangle$ that contribute to $\Pi_\omega X_S$ oscillate with a coherent phase $\exp(-i\omega t)$. In the lowest order in g the memory terms in the generalized master equation will just destroy this phase coherence.

To find the stochastic operator which destroys the coherent phase oscillations in the weak coupling limit, we replace the stochastic operator $\Phi_S(t)$ by [148]

$$\Phi_S'(t) = \sum_\omega \Pi_\omega \Phi_S(t)\Pi_\omega \quad , \tag{5.4.32}$$

where each term of the sum acts within a subspace of degenerate eigenoperators of $\mathbf{L}_S$. Since

$$\Pi_\omega \hat{\Sigma}_S = \hat{\Sigma}_S \Pi_\omega \quad , \tag{5.4.33}$$

we get from (5.2.22)

$$\Phi_S'(t) = -\frac{1}{\beta}\,\mathbf{R}_S'(t)\hat{\Sigma}_S^{-1} \quad , \tag{5.4.34}$$

where

$$\mathbf{R}_S'(t) = \sum_\omega \Pi_\omega \mathbf{R}_S(t)\Pi_\omega \quad . \tag{5.4.35}$$

It is useful to write the interaction in the form

$$H_{SR} = \sum_{\nu} R_{\nu} S_{\nu} \quad , \tag{5.4.36}$$

where the R_{ν} are operators acting in $\mathcal{H}_R$, while the S_{ν} are operators acting in $\mathcal{H}_S$ with the property

$$\mathbf{L}_S S_{\nu} = \omega_{\nu} S_{\nu} \quad . \tag{5.4.37}$$

Such a representation of the interaction is always possible.[7] Then, we get from (5.4.26,27)

$$\delta \mathbf{L}_{SR} X = \frac{1}{\hbar} \sum_{\nu} [\delta R_{\nu} S_{\nu}, X] \quad , \tag{5.4.38}$$

where

$$\delta R_{\nu} = R_{\nu} - \mathrm{tr}_R\{\hat{\rho}_{R\beta} R_{\nu}\} \quad . \tag{5.4.39}$$

Further, it is easy to show that because of (5.4.37)

$$S_{\nu}(\Pi_{\omega} X_S) = \Pi_{\omega+\omega_{\nu}}(S_{\nu} X_S) \tag{5.4.40}$$

and

$$(\Pi_{\omega} X_S) S_{\nu} = \Pi_{\omega+\omega_{\nu}}(X_S S_{\nu}) \tag{5.4.41}$$

Using (5.4.9,38), we obtain from (5.4.25)

$$\mathbf{R}_S(t)\, e^{i\mathbf{L}_S t}\, X_S = \sum_{\nu,\mu} [S_{\nu}, \beta \mathbf{K}_{\nu\mu}(t)[S_{\mu}, X_S]] + \mathcal{O}(g^3) \quad , \tag{5.4.42}$$

where

$$\mathbf{K}_{\nu\mu}(t) X_S = \frac{g^2}{\hbar^2} \frac{1}{\beta} \int_0^{\beta} d\alpha\, e^{-i\omega_{\mu} t}$$

$$\times\, \mathrm{tr}_R\{\hat{\rho}_{R\beta} \delta R_{\nu}(t)\, e^{-\alpha H_R}\, \delta R_{\mu}\, e^{\alpha H_R}\} e^{-\alpha H_S}\, X\, e^{\alpha H_S}\, \hat{\rho}_{S\beta} \quad . \tag{5.4.43}$$

On inserting (5.4.42) into (5.4.35) we find

$$\mathbf{R}_S'(t)\, e^{i\mathbf{L}_S t} X_S = \sum_{\omega_{\nu}+\omega_{\mu}=0} [S_{\nu}, \beta \mathbf{K}_{\nu\mu}(t)[S_{\mu}, X_S]] + \mathcal{O}(g^3) \quad , \tag{5.4.44}$$

where we have made use of (5.4.33,40,41) and

$$\mathbf{K}_{\nu\mu}(t) \Pi_{\omega} = \Pi_{\omega} \mathbf{K}_{\nu\mu}(t) \quad . \tag{5.4.45}$$

Now, we are in a position to approximate the memory term in the generalized master equation (5.2.6) in the weak coupling limit. Noting that

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[7] A general, but clumsy, representation of the form (5.4.36) is $H_{SR} = \sum_{nm} R_{nm} S_{nm}$, where $R_{nm} = \langle n | H_{SR} | m \rangle$, $S_{nm} = | n \rangle \langle m |$, and $\omega_{nm} = (\varepsilon_n - \varepsilon_m)/\hbar$.

$$\rho_S(s) = e^{i\mathbf{L}_S(t-s)}\rho_S(t) + \mathcal{O}(g) \quad , \tag{5.4.46}$$

we obtain from (5.4.34,44)

$$\int_0^t ds\, \Phi'_S(t - s)\rho_S(s) \tag{5.4.47}$$

$$= - \int_0^t ds \sum_{\omega_\nu+\omega_\mu=0} [S_\nu,\mathbf{K}_{\nu\mu}\,(t - s)[S_\mu, \hat{\Sigma}_S^{-1}\rho_S(t)]] + \mathcal{O}(g^3) \quad .$$

Under the assumption that the correlations of the reservoir operators δR_ν decay on a short microscopic time scale, we can extend the integration over s from s = 0 to s = ∞. With (5.4.22) we then get the Markovian master equation

$$\dot{\rho}_S(t) = - i\mathbf{L}_S\rho_S(t) + \Lambda_S\rho_S(t) \quad , \tag{5.4.48}$$

where we have introduced the dissipative Liouville operator

$$\Lambda_S X_S = - \sum_{\omega_\nu+\omega_\mu=0} [S_\nu,\mathbf{K}_{\nu\mu}[S_\nu, \hat{\Sigma}_S^{-1} X_S]] \tag{5.4.49}$$

with

$$\mathbf{K}_{\nu\mu} = \int_0^\infty dt\, \mathbf{K}_{\nu\mu}(t) \quad . \tag{5..4.50}$$

5.5 Properties of the Master Equation

The master equation (5.4.48) which describes the dynamics of the open system S moving under the influence of a weakly coupled reservoir has several important properties. These properties follow partly from properties of the generalized master equation discussed in Sect.5.3, but they may also be verified directly. First we note that the dissipative Liouville operator Λ_S conserves probability since

$$\mathrm{tr}_S\{\Lambda_S X_S\} = 0 \quad . \tag{5.5.1}$$

Further, Λ_S commutes with Π_ω:

$$\Lambda_S \Pi_\omega = \Pi_\omega \Lambda_S \quad . \tag{5.5.2}$$

This follows from (5.4.49) by means of (5.4.33,40,41,45). Consequently, we also have

$$\Lambda_S \mathbf{L}_S = \mathbf{L}_S \Lambda_S \quad . \tag{5.5.3}$$

The interaction H_{SR} is self-adjoint and time-reversal invariant. Thus, in a representation of H_{SR} of the form (5.4.36) the adjoint operators S_ν^+, R_ν^+ and the time-reversed operators $\tilde{S}_\nu$, $\tilde{R}_\nu$ will occur as elements of the set of the S_ν and R_ν

operators. With the notation

$$S_\nu^+ = S_{\nu'} \quad , \quad R_\nu^+ = R_{\nu'} \tag{5.5.4}$$

and

$$\tilde{S}_\nu = S_{\tilde{\nu}} \quad , \quad \tilde{R}_\nu = R_{\tilde{\nu}} \tag{5.5.5}$$

the interaction may then be written

$$H_{SR} = \sum_\nu S_\nu R_\nu = \sum_{\nu'} S_{\nu'} R_{\nu'} = \sum_{\tilde{\nu}} S_{\tilde{\nu}} R_{\tilde{\nu}} \quad . \tag{5.5.6}$$

Using (5.4.43) and $\omega_{\mu'} = -\omega_\mu$, it is easily shown that

$$(\mathbf{K}_{\nu\mu}(t)X_S)^+ = \mathbf{K}_{\nu'\mu'}(t)X^+ \quad , \tag{5.5.7}$$

which gives by virtue of (5.4.49,50)

$$(\Lambda_S X_S)^+ = \Lambda_S X_S^+ \quad . \tag{5.5.8}$$

Thus Λ_S maps self-adjoint operators to self-adjoint operators.

From (5.4.49) we see that we need $\mathbf{K}_{\nu\mu}$ for indices ν,μ with $\omega_\nu + \omega_\mu = 0$ only. Then it is readily shown from (5.4.43) that

$$\mathbf{K}_{\nu\mu}^T(t) = \mathbf{K}_{\mu\nu}(-t) \quad . \tag{5.5.9}$$

Further, by noting $\omega_{\tilde{\mu}} = \omega_\mu$ we find

$$\widetilde{\mathbf{K}_{\nu\mu}(t)X_S} = \mathbf{K}_{\tilde{\nu}\tilde{\mu}}(-t)\tilde{X}_S \quad , \tag{5.5.10}$$

which combines with (5.5.9) to give

$$\widetilde{\mathbf{K}_{\nu\mu}(t)X_S} = \mathbf{K}_{\tilde{\mu}\tilde{\nu}}^T(t)\tilde{X}_S \quad . \tag{5.5.11}$$

Now, it follows from (5.4.49,50) that

$$\widetilde{\Lambda_S \hat{\Sigma}_S X_S} = \hat{\Sigma}_S \Lambda_S^T \tilde{X}_S \quad . \tag{5.5.12}$$

Together with

$$\widetilde{\hat{\Sigma}_S X_S} = \hat{\Sigma}_S^T \tilde{X}_S = \hat{\Sigma}_S \tilde{X}_S \tag{5.5.13}$$

and

$$\widetilde{-i\mathbf{L}_S \hat{\Sigma}_S X_S} = i\, \hat{\Sigma}_S \mathbf{L}_S \tilde{X}_S \quad , \tag{5.5.14}$$

the property (5.5.12) guarantees that the stationary process described by the master equation (5.4.48) has the symmetry of detailed balance.

Suppose now, the spectrum of H_S is nondegenerate. Then we have from (5.4.30)

$$\Pi_0 \rho_S(t) = \sum_n p_n(t)|n\rangle\langle n| \quad , \tag{5.5.15}$$

where

$$p_n(t) = \langle n|\rho_S(t)|n\rangle \qquad (5.5.16)$$

is the occupation probability of the nth energy level. With (5.4.29) and (5.5.2) we obtain from (5.4.48) an equation of motion for the diagonal part of $\rho_S(t)$ in energy representation:

$$\Pi_0\dot{\rho}_S(t) = \Lambda_S\Pi_0\rho_S(t) \quad . \qquad (5.5.17)$$

To evaluate this further, we first provide some useful relations. From (5.4.12) we get

$$\hat{\Sigma}_S|n\rangle\langle n| = \hat{p}_n|n\rangle\langle n| \quad , \qquad (5.5.18)$$

where

$$\hat{p}_n = \langle n|\hat{\rho}_{S\beta}|n\rangle = \frac{e^{-\beta\varepsilon_n}}{\sum\limits_n e^{-\beta\varepsilon_n}} \qquad (5.5.19)$$

is the canonical occupation probability of the nth energy level. From (5.4.37) we have

$$e^{-\alpha H_S}\, S_\mu\, e^{\alpha H_S} = e^{-\alpha\hbar L_S}\, S_\mu = e^{-\alpha\hbar\omega_\mu}\, S_\mu \quad . \qquad (5.5.20)$$

Further, by use of (5.4.43,50) and (5.5.20) we obtain

$$\mathbf{K}_{\nu\mu}[S_\mu, |n\rangle\langle n|] = \gamma_{\nu\mu}[S_\mu, |n\rangle\langle n|]\hat{\rho}_{S\beta} \quad , \qquad (5.5.21)$$

where

$$\gamma_{\nu\mu} = \frac{g^2}{\hbar^2}\int\limits_0^\infty dt\, \frac{1}{\beta}\int\limits_0^\infty d\alpha\, e^{-i\omega_\mu(t-i\alpha\hbar)} \qquad (5.5.22)$$

$$\times\, \mathrm{tr}_R\{\hat{\rho}_{R\beta}\delta R_\nu(t)\, e^{-\alpha H_R}\, \delta R_\mu\, e^{\alpha H_R}\} \quad .$$

Recalling $\omega_\nu + \omega_\mu = 0$, it may be shown that the coefficients $\gamma_{\nu\mu}$ have the properties

$$\gamma_{\nu\mu} = e^{-\beta\hbar\omega_\mu}\, \gamma^*_{\nu'\mu'} \qquad (5.5.23)$$

and

$$\gamma_{\nu\mu} = e^{-\beta\hbar\omega_\mu}\, \gamma^*_{\tilde{\mu}\tilde{\nu}} \quad . \qquad (5.5.24)$$

Let us turn now to the investigation of the right-hand side of (5.5.17). Using (5.4.49) and (5.5.15,18,21), we find after some simple transformations

$$\Lambda_S\Pi_0\rho_S(t) = \sum_{n,m}\, [W_{nm}p_m(t) - W_{mn}p_n(t)]|n\rangle\langle n| \quad , \qquad (5.5.25)$$

where

$$W_{mn} = \sum_{\nu,\mu}\left(\gamma_{\nu\mu} + \gamma_{\mu\nu}\frac{\hat{p}_m}{\hat{p}_n}\right)\langle n|S_\nu|m\rangle\langle m|S_\mu|n\rangle \qquad (5.5.26)$$

is the transition probability from the nth to the mth energy level. Note that the terms of the sum are vanishing unless $\omega_\nu = -\omega_\mu = (\varepsilon_n - \varepsilon_m)/\hbar$. It may be shown that the W_{mn} have the properties

$$W_{mn} \geq 0 \tag{5.5.27}$$

and

$$W_{mn}\hat{p}_n = W_{nm}\hat{p}_m \quad . \tag{5.5.28}$$

Using (5.5.25), the evolution equation (5.5.17) for the diagonal part of the probability density can be cast into the form of a Pauli master equation [59]:

$$\dot{p}_n(t) = \sum_m [W_{nm}p_m(t) - W_{mn}p_n(t)] \tag{5.5.29}$$

which has the canonical occupation probabilities $\hat{p}_n$ as a stationary solution.

5.6 Renormalized Transport Equations

Let A be the set of macroscopic variables of the open system S with mean values

$$a_i(t) = \mathrm{tr}_S\{A_i\rho_S(t)\} \quad . \tag{5.6.1}$$

The reduced probability density $\rho_S(t)$ is assumed to obey the master equation (5.4.48), which we write in the form

$$\dot{\rho}_S(t) = -i\mathcal{L}_S\rho_S(t) \tag{5.6.2}$$

with

$$\mathcal{L}_S = \mathbf{L}_S + i\Lambda_S \quad . \tag{5.6.3}$$

The probability density $\rho_S(t)$ contains information about any variable of S including the nonlinear functions of the A. We now want to keep only the macroscopic variables A and eliminate all the other variables of the system S. To this purpose we introduce a relevant reduced probability density

$$\bar{\rho}_S(t) = \hat{\Sigma}_S\Big[1 + \sum_i \beta\mu_i(t)(A_i - \hat{a}_i)\Big] \quad , \tag{5.6.4}$$

where the $\hat{a}$ are the equilibrium values of the macroscopic variables

$$\hat{a}_i = \mathrm{tr}_S\{A_i\hat{\rho}_{S\beta}\} \quad . \tag{5.6.5}$$

and where the parameters $\mu(t)$ are determined by the requirements

$$\mathrm{tr}_S\{A_i\bar{\rho}_S(t)\} = a_i(t) \quad . \tag{5.6.6}$$

Note, that an initial state of the form (5.1.8) gives a reduced probability density of the relevant form (5.6.4) in the limit of a weak coupling to the reservoir ($g \to 0$) and to first order in a weak perturbation of the form $H_S' = -\sum_i\mu_iA_i$.

Introducing the canonical equilibrium correlation

$$\begin{aligned}(X_S,Y_S)_S &= \frac{1}{\beta}\int_0^\beta d\alpha\ \mathrm{tr}_S\{\hat{\rho}_{S\beta}X_S\, e^{-\alpha H_S}\, Y_S\, e^{\alpha H_S}\} \\ &= \mathrm{tr}_S\{X_S\,\hat{\Sigma}_S Y_S\} \quad ,\end{aligned} \tag{5.6.7}$$

we obtain from (5.6.4,6)

$$a_i(t) = \hat{a}_i + \sum_j (\hat{\delta}A_i, \hat{\delta}A_j)_S \, \beta\mu_j(t) \quad , \tag{5.6.8}$$

where there

$$\hat{\delta}A_i = A_i - \hat{a}_i \tag{5.6.9}$$

are the fluctuations about equilibrium. Equation (5.6.8) determines the $\mu(t)$ in terms of the mean values $a(t)$, and vice versa. With (5.6.8) it is easily shown that the projection operator

$$\mathcal{P}X_S = \hat{\Sigma}_S\Big[\mathrm{tr}_S\{X_S\} + \sum_{i,j} \hat{\delta}A_i(\hat{\delta}A_i, \hat{\delta}A_j)_S^{-1} \, \mathrm{tr}_S\{\hat{\delta}A_j X_S\}\Big] \tag{5.6.10}$$

projects out the relevant probability density

$$\bar{\rho}_S(t) = \mathcal{P}\rho_S(t) \quad . \tag{5.6.11}$$

We now take advantage of the fact that the identity (5.2.1) holds independent from the particular form of the operators **L** and $\mathbf{P}^T$ to be found therein, so that we also have

$$e^{-i\mathcal{L}t} = \mathcal{P}\, e^{-i\mathcal{L}t} - i \int_0^t ds \; e^{-i(1-\mathcal{P})\mathcal{L}(t-s)}(1 - \mathcal{P})\mathcal{L}\mathcal{P}\, e^{-i\mathcal{L}s} \tag{5.6.12}$$

$$+ \, e^{-i(1-\mathcal{P})\mathcal{L}t}(1 - \mathcal{P}) \quad .$$

When we insert this identity into

$$\rho_S(t) = e^{-i\mathcal{L}t}\rho_S(0) \quad , \tag{5.6.13}$$

where the initial state $\rho_S(0)$ is the relevant form

$$\rho_S(0) = \mathcal{P}\rho_S(0) = \tilde{\rho}_S(0) \quad , \tag{5.6.14}$$

we obtain

$$\rho_S(t) = \bar{\rho}_S(t) - i \int_0^t ds \; e^{-i(1-\mathcal{P})\mathcal{L}(t-s)}(1 - \mathcal{P})\mathcal{L}\tilde{\rho}_S(s) \quad , \tag{5.6.15}$$

which gives when put into

$$\dot{a}_i(t) = -i \; \mathrm{tr}_S\{A_i \mathcal{L}\rho_S(t)\} \tag{5.6.16}$$

an evolution law for the mean values of the macroscopic variables

$$\dot{a}_i(t) = -i \; \mathrm{tr}_S\{A_i \mathcal{L}\bar{\rho}_S(t)\} \tag{5.6.17}$$

$$- \int_0^t ds \; \mathrm{tr}_S\{A_i \mathcal{L}\, e^{-i(1-\mathcal{P})\mathcal{L}(t-s)}(1 - \mathcal{P})\mathcal{L}\bar{\rho}_S(s)\} \quad .$$

Since the time dependence of $\bar{\rho}_S(t)$ arises only through $a(t)$ the right-hand side is completely determined by the instantaneous mean values and their past history.

While (5.6.17) is the closed set of evolution equations for the mean values we were looking for, these equations are not yet of the standard form of transport laws. To obtain this form we first note that (5.4.49) and (5.6.4) give

$$-iL\bar{\rho}_S(t) = -i \sum_j (\beta L \hat{\Sigma}_S A_i)\mu_j(t) \quad . \tag{5.6.18}$$

With this result (5.6.17) may be transformed to read

$$\dot{a}_i(t) = - \sum_j \hat{L}_{ij}\mu_j(t) - \int_0^t ds \sum_j \hat{\Lambda}_{ij}(t - s)\mu_j(s) \quad , \tag{5.6.19}$$

where

$$\hat{L}_{ij} = i\beta \, \mathrm{tr}_S\{A_i L \hat{\Sigma}_S A_j\} \tag{5.6.20}$$

and

$$\hat{\Lambda}_{ij}(t) = \beta \, \mathrm{tr}_S\{A_i L \, e^{-i(1-P)Lt}(1 - P)L\hat{\Sigma}_S A_j\} \quad . \tag{5.6.21}$$

In (5.6.19) the time rates of change of the mean values are given in terms of (renormalized) thermodynamic forces $\mu_j(t)$ and in terms of (renormalized) transport coefficients consisting of an instantaneous part $\hat{L}_{ij}$ and a retarded part $\hat{\Lambda}_{ij}(t)$. The renormalized transport equations (5.6.19) govern the relaxation of the mean values in the linear regime near equilibrium. This restriction to the linear regime is due to the fact that we have treated initial states of the form (5.6.4) only.

Besides the relaxation towards equilibrium, the master equation (5.4.48) also governs the time evolution of canonical equilibrium correlations of the open system S, and it follows that the renormalized transport equations (5.6.19) also determine the time evolution of canonical equilibrium correlations of the macroscopic variables A. Using (5.6.8), the transport equation (5.6.19) may be written

$$\dot{a}_i(t) = \sum_j \omega_{ij}(a_j(t) - \hat{a}_j) + \int_0^t ds \sum_j \varphi_{ij}(t - s)(a_j(s) - \hat{a}_j) \quad , \tag{5.6.22}$$

where

$$\omega_{ij} = - \sum_k \frac{1}{\beta} \hat{L}_{ik}\hat{\sigma}^{-1}_{kj} \tag{5.6.23}$$

and

$$\varphi_{ij}(t) = - \sum_k \frac{1}{\beta} \hat{\Lambda}_{ik}(t)\hat{\sigma}^{-1}_{kj} \tag{5.6.24}$$

with the canonical equilibrium variance

$$\hat{\sigma}_{ij} = (\hat{\delta}A_i, \hat{\delta}A_j)_S \quad . \tag{5.6.25}$$

Then, the evolution laws for the canonical equilibrium correlations of the macroscopic variables read

$$\frac{d}{dt} (\hat{\delta}A_i(t), \hat{\delta}A_j)_S = \sum_k \omega_{ik}(\hat{\delta}A_k(t), \hat{\delta}A_j)_S + \int_0^t ds \sum_k \varphi_{ik}(t - s)(\hat{\delta}A_k(s), \hat{\delta}A_j)_S \; . \tag{5.6.26}$$

The renormalized transport equations obtained in this section are closely related to those of Mori theory treated in Chap.3. If we replace the Liouville operator L of the open system S by the Liouville operator L_S of the closed system S in (5.6.20,21), (5.6.19) reduces to (3.4.8) for the closed system S (that is, the molecular expressions in Chap.3 are read with H_S as Hamiltonian and tr_S instead of tr). Hence, the internal dynamics of the open system S are treated exactly in (5.6.19).

On the other hand, the influence of the reservoir is treated only approximately in (5.6.19). On using (3.4.8) for the closed system $S \otimes R$ (that is, the molecular expressions in Chap.3 are now read with $H_S + H_R + gH_{SR}$ as Hamiltonian and $tr = tr_S tr_R$) we obtain exact renormalized transport equations. These exact equations describe memory effects due to the internal dynamics of S as well as memory effects coming from the reservoir dynamics. The latter are disregarded in (5.6.19) and a weak coupling to the reservoir is assumed. However, since effects of nonlinear couplings within S are treated correctly, the approximate transport laws (5.6.19) are useful in many situations where a complete disregard of memory effects as in (3.5.4) is not possible. For a discussion of various applications of the master equation approach we refer to HAAKE's review [73].

Finally we mention that the master equation approach given in this chapter is novel and differs from earlier approaches [68-74] in two respects. First, we have utilized a relevant probability density defined in such a way that the equilibrium probability density is of the relevant form, while usually a factorizing relevant probability density is used. Even in the weak coupling limit the present approach leads to an expression for the dissipative Liouvillian different from expressions given previously. Since in our approach the irrelevant part $\rho(t) - \bar{\rho}(t)$ of the probability density is dying out for $t \to \infty$, we obtain the correct long time behavior (which is chiefly of interest). Second, in the Markov approximation correlatio functions are usually determined with the help of a "quantum regression hypothesis" or equivalent assumptions. These assumptions are not compatible with the symmetries of the process [75]. In our approach the master equation is intimately connected with the dynamics of canonical correlation functions. As will be shown in Chap. 6 symmetrized and antisymmetrized correlation functions (the latter being response functions) can also be determined from the master equation, but the rules how to compute these quantities differ from schemes put forward previously. For further details we refer to [149].

6. Response Theory

The response to an applied time-dependent perturbation gives valuable information about the nonequilibrium properties of a system. To investigate this reponse we first have to extend the scope of the methods studied so far, since up to now we have considered closed systems only. On the microscopic level an applied perturbation is described by a time-dependent Hamiltonian $H'(t)$ which is added to the Hamiltonian H governing the internal motion. For the most part we will assume that the perturbation is caused by external forces h coupling to the macroscopic variables A of the system. Then

$$H'(t) = -\sum_i h_i(t) A_i \quad .$$

In Sect.6.1 we review standard microscopic response theory [2,102] and derive molecular expressions for the response functions χ_{ij} relating the response of the mean values a to the applied forces h causing it:

$$\Delta a_i(t) = \int_0^t ds \sum_j \chi_{ij}(t,s) h_j(s) \quad .$$

The response tensor $\chi_{ij}(t)$ of an equilibrium system with temperature T is shown to be related to the canonical equilibrium correlations $C_{ij}(t)$ by the fluctuation-dissipation theorem of the first kind [14,102,150]

$$\chi_{ij}(t) = -\frac{1}{k_B T}\, \Theta(t) \dot{C}_{ij}(t) \quad .$$

In order to study the response from a macroscopic point of view, we have to know how the coupling of the applied forces comes out in the macroscopic evolution laws. This crucial question is investigated in Sect.6.2 for the method of statistical thermodynamics, where the macroscopic evolution laws are furnished by the generalized transport equations studied in Chap.3. We find that the coupling of the applied forces arises in two ways. First, the applied forces h are subtracted from the thermodynamic forces μ so that the fluxes $\dot{a}$ are now caused by the differences between the thermodynamic and the applied forces. This change can be taken into account by adding the mean value of the perturbation $H'(t)$ to the free energy

$$F(t) \rightarrow F(t) - \sum_i h_i(t) a_i(t) \quad .$$

Second, the retarded parts of the transport coefficients pick up a functional dependence on the applied forces in general.

In Sect.6.3 we use the modified transport equations to reexamine the linear response of an equilibrium system from a macroscopic point of view. We show that the modification of the retarded parts of the transport coefficients does not contribute to the linear response, and we obtain macroscopic expressions for the response functions χ_{ij} in terms of the free energy and the transport coefficients. The fluctuation-dissipation theorem of the first kind is recovered. The response theory given in Sect.6.3 does not make use of the particular forms of the transport coefficients and the free energy, so that the method is insensitive to approximations of these quantities that preserve their basic symmetries. The method can immediately be applied to macroscopic evolution laws in which the memory effects have been neglected.

In Sects.6.4 and 6.5 an applied perturbation is incorporated into the Fokker-Planck equation approach and the master equation approach, respectively. The evolution equations are again modified in two ways. The average energy of the perturbation is added to the free energy, and the transport quantities describing the memory effects become functionals of the applied forces. We also study the response of an equilibrium system and derive expressions for the response functions.

6.1 Microscopic Response Theory

We consider a system with Hamiltonian H, the microscopic state of which is described by the probability density $\rho(t)$. When an external perturbation is applied to it, the dynamics of the system is governed by a time-dependent Hamiltonian

$$H(t) = H + H'(t) \quad , \tag{6.1.1}$$

and an initial probability density $\rho(0)$ evolves in time according to

$$\rho(t) = \mathbf{U}(t,0)\rho(0) \quad . \tag{6.1.2}$$

The time-ordered exponential $(t \geq t')$

$$\mathbf{U}(t,t') = T_+ \exp\left\{-i \int_{t'}^{t} ds\mathbf{L}(s)\right\} \quad , \tag{6.1.3}$$

in which operators are ordered from right to left as time increases, is the time evolution operator in the Schrödinger picture with

$$\mathbf{L}(t)X = (\mathbf{L}+\mathbf{L}'(t))X = \begin{cases} i\{H(t),X\} & \text{(classical)} \\ \frac{1}{\hbar}[H(t),X] & \text{(quantal)} \quad . \end{cases} \tag{6.1.4}$$

The effect of the perturbation $H'(t)$ upon the state of the system is described by

$$\Delta\rho(t) = \rho(t) - \rho_0(t) \quad , \tag{6.1.5}$$

where

$$\rho_0(t) = e^{-iLt}\rho(0) \tag{6.1.6}$$

is the state evolving from $\rho(0)$ by the natural motion of the system. Using the identity

$$U(t,0) = e^{-iLt} - i \int_0^t ds\, U(t,s)L'(s)\, e^{-iLs} \quad , \tag{6.1.7}$$

which is clearly true for $t = 0$ and may therefore be verified by showing that both sides satisfy the same differential equation, we get

$$\Delta\rho(t) = -i \int_0^t ds\, U(t,s)L'(s)\rho_0(s) \quad . \tag{6.1.8}$$

We now assume that the applied perturbation is caused by external forces h coupling to the macroscopic variables A of the system. Then

$$H(t) = H - \sum_i h_i(t)A_i \tag{6.1.9}$$

and (6.1.8) becomes[1]

$$\Delta\rho(t) = \int_0^t ds \sum_i \frac{i}{\hbar} U(t,s)[A_i,\rho_0(s)]h_i(s) \quad . \tag{6.1.10}$$

The response of the system to the applied forces h as observed in the average change of the macroscopic variables is given by

$$\begin{aligned} \Delta a_i(t) &= \mathrm{tr}\{A_i\Delta\rho(t)\} \\ &= \int_0^t ds \sum_j \frac{i}{\hbar} \mathrm{tr}\{A_i U(t,s)[A_j,\rho_0(s)]\}h_j(s) \quad . \end{aligned} \tag{6.1.11}$$

To the first order in the applied forces (6.1.11) gives [102]

$$\Delta a_i(t) = \int_0^t ds \sum_j \chi_{ij}(t,s)h_j(s) \quad , \tag{6.1.12}$$

where for $t \geq s$

$$\begin{aligned} \chi_{ij}(t,s) &= \frac{i}{\hbar}\, \mathrm{tr}\{[A_i(t-s),A_j]\rho_0(s)\} \\ &= \frac{i}{\hbar}\, \mathrm{tr}\{[A_i(t),A_j(s)]\rho(0)\} \end{aligned} \tag{6.1.13}$$

is the response tensor. Here $A(t)$ represents the unperturbed motion in the Heisenberg picture:

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[1] To be definite we work in the framework of quantum statistical mechanics. The corresponding classical formulas are obtained by replacing $(-i/\hbar)[X,Y]$ by $\{X,Y\}$.

$$A_i(t) = e^{iLt} A_i \quad , \tag{6.1.14}$$

so that the response tensor depends on the internal dynamics of the system only. Higher-order corrections to the linear response can be obtained by making repeated use of (6.1.7) to get an approximate expression for **U**(t,s) in the desired order and then inserting it into (6.1.11).

If the system is initially in thermal equilibrium, that is, if

$$\rho(0) = \hat{\rho} = \frac{e^{-\beta H}}{\mathrm{tr}(e^{-\beta H})} \quad , \tag{6.1.15}$$

the response tensor (6.1.13) becomes

$$\begin{aligned} \chi_{ij}(t - s) &= \frac{i}{\hbar}\,\mathrm{tr}\{[A_i(t),A_j(s)]\hat{\rho}\} \\ &= \frac{i}{\hbar}\,\mathrm{tr}\{[A_i(t - s),A_j]\hat{\rho}\} \quad . \end{aligned} \tag{6.1.16}$$

The response tensor of an equilibrium system is related in a simple way to the equilibrium correlations defined by [cf. (3.4.10)]

$$C_{ij}(t) = \frac{1}{\beta}\int_0^\beta d\alpha\ \mathrm{tr}[\hat{\delta}A_i(t)\ e^{-\alpha H}\ \hat{\delta}A_j\ e^{\alpha H}\ \hat{\rho}\} \quad , \tag{6.1.17}$$

where the δA are the fluctuations about equilibrium. Using the identity (3.2.7) we find

$$[A_j,\hat{\rho}] = -\int_0^\beta d\alpha\ e^{-\alpha H}[A_j,H]e^{\alpha H}\hat{\rho} \quad . \tag{6.1.18}$$

Thus for t ≥ 0 the response tensor may be written

$$\begin{aligned} \chi_{ij}(t) &= \int_0^\beta d\alpha\ \mathrm{tr}\{A_i(t)\ e^{-\alpha H}\ \dot{A}_j\ e^{\alpha H}\ \hat{\rho}\} \\ &= -\int_0^\beta d\alpha\ \mathrm{tr}\{\dot{A}_i(t)\ e^{-\alpha H}\ A_j\ e^{\alpha H}\ \hat{\rho}\} \ , \end{aligned} \tag{6.1.19}$$

which combines with (6.1.17) to yield [102]

$$\chi_{ij}(t) = -\,\Theta(t)\beta\dot{C}_{ij}(t) \quad . \tag{6.1.20}$$

This relation between the response tensor and the time rates of change of the equilibrium correlation functions is the fluctuation-dissipation theorem of the first kind. The unit step function

$$\Theta(t) = \begin{cases} 1 & \text{for} \quad t > 0 \\ 0 & \text{for} \quad t < 0 \end{cases} \tag{6.1.21}$$

takes care of the fact that the response tensor is nonvanishing for t > 0 only. For later use, we note that since

$$C_{ij}(t) = C_{ji}(-t) \quad , \tag{6.1.22}$$

the fluctuation-dissipation theorem (6.1.20) is equivalent to

$$\chi_{ij}(t) - \chi_{ji}(-t) = -\beta\dot{C}_{ij}(t) \quad . \tag{6.1.23}$$

It should be noted that the fluctuation-dissipation theorem (6.1.20) takes the same form in the classical and the quantal case. This is due to the fact that we have used the canonical correlation defined by (6.1.17). In the quantal case the canonical correlation must be distinguished from other sorts of correlation functions such as the symmetrized correlation

$$S_{ij}(t) = \frac{1}{2}\,\mathrm{tr}\{[\hat{\delta}A_i(t)\hat{\delta}A_j + \hat{\delta}A_j\hat{\delta}A_i(t)]\hat{\rho}\} \quad . \tag{6.1.24}$$

The relation between (6.1.17) and (6.1.24) is most easily expressed in terms of the associated spectral functions

$$C_{ij}(\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\ e^{-i\omega t}\ C_{ij}(t) \tag{6.1.25}$$

and

$$S_{ij}(\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\ e^{-i\omega t}\ S_{ij}(t) \quad . \tag{6.1.26}$$

The symmetrized spectral function $S_{ij}(\omega)$ is sometimes called the scattering function since the differential cross sections observed in inelastic scattering of light, electrons, etc. are related to quantities of this kind.[2] The canonical and symmetrized spectral functions are connected by

$$S_{ij}(\omega) = \beta E_\beta(\omega) C_{ij}(\omega) \quad , \tag{6.1.27}$$

where

$$E_\beta(\omega) = \frac{1}{2}\hbar\omega\,\coth\!\left(\frac{1}{2}\beta\hbar\omega\right) \tag{6.1.28}$$

is the average energy of a harmonic oscillator with frequency ω at temperature $T = 1/k_B\beta$. To verify (6.1.27) it is best to write down each expression in terms of the matrix elements of $\hat{\delta}A_i$ and $\hat{\delta}A_j$ in the representation diagonalizing the Hamiltonian H. Clearly in the classical limit ($\hbar\omega \ll k_BT$) the difference between $S_{ij}(\omega)$ and $C_{ij}(\omega)$ disappears.

Introducing the dynamic susceptibility

$$\chi_{ij}(\omega) = \int_{-\infty}^{+\infty} dt\ e^{-i\omega t}\ \chi_{ij}(t) = \int_{0}^{\infty} dt\ e^{-i\omega t}\ \chi_{ij}(t) \quad , \tag{6.1.29}$$

we obtain from (6.1.23) the form of the fluctuation-dissipation theorem in frequency space:

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[2] A nice and brief discussion of scattering is given, for example, in [22], Appendix A.

$$\chi''_{ij}(\omega) = \pi\beta\omega C_{ij}(\omega) = \frac{\pi\omega}{E_\beta(\omega)} S_{ij}(\omega) \quad , \tag{6.1.30}$$

where

$$\chi''_{ij}(\omega) = \frac{i}{2} [\chi_{ij}(\omega) - \chi_{ji}(-\omega)] \tag{6.1.31}$$

is the dissipative part of the dynamic susceptibility.

Finally we note that for macroscopic variables A_i having time-reversal signature[3] ε_i, there follows from (6.1.16) the symmetry

$$\chi_{ij}(t) = \varepsilon_i \varepsilon_j \chi_{ji}(t) \quad . \tag{6.1.32}$$

6.2 Macroscopic Coupling of Applied Forces

In this section we study the effect of an external perturbation upon the macroscopic evolution laws. As in Chap.2 we consider a system described on the macroscopic level by a relevant probability density $\bar{\rho}(t)$ which is projected out by a projection operator $\mathbf{P}^T(t)$

$$\bar{\rho}(t) = \mathbf{P}^T(t)\rho(t) \quad . \tag{6.2.1}$$

$\mathbf{P}^T$ has the properties (see Sect.2.3 for details)

$$\dot{\mathbf{P}}^T(t) = [\mathbf{1} - \mathbf{P}^T(t)]\dot{\mathbf{P}}^T(t)\mathbf{P}^T(t) \tag{6.2.2}$$

and

$$\dot{\mathbf{P}}^T(t)\rho(t) = \dot{\mathbf{P}}^T(t)\bar{\rho}(t) = 0 \quad . \tag{6.2.3}$$

Unlike in Chap.2, we now allow for an external perturbation applied to the system. Then the microscopic time evolution is governed by (6.1.2-4).

With the help of the projection operator $\mathbf{P}^T(t)$, the time evolution operator (6.1.3) may be decomposed into three pieces:

$$\begin{aligned} \mathbf{U}(t,0) = {} & \mathbf{P}^T(t)\mathbf{U}(t,0) \\ & - \int_0^t ds\, \mathbf{G}^T(t,s)[\mathbf{1} - \mathbf{P}^T(s)][i\mathbf{L}(s) + \dot{\mathbf{P}}^T(s)]\mathbf{P}^T(s)\mathbf{U}(s,0) \\ & + \mathbf{G}^T(t,0)[\mathbf{1} - \mathbf{P}^T(0)] \end{aligned} \tag{6.2.4}$$

where for $t \geq t'$

$$\mathbf{G}^T(t,t') = T_+ \exp\left\{- i \int_{t'}^{t} du [\mathbf{1} - \mathbf{P}^T(u)]\mathbf{L}(u)\right\} \quad . \tag{6.2.5}$$

---

[3] See Sect.3.7 for a definition of the time-reversal transformation.

The identity (6.2.4) can be verified by differentiating with respect to t and showing that because of (6.2.2) both sides satisfy the same differential equation. If we apply (6.2.4) to an initial state $\rho(0)$ of the relevant form,

$$\rho(0) = \bar{\rho}(0) , \text{ i.e.,} \quad [\mathbf{1} - \mathbf{P}^T(0)]\rho(0) = 0 \quad , \tag{6.2.6}$$

we obtain by virtue of (6.2.1,3)

$$\rho(t) = \bar{\rho}(t) - i \int_0^t ds\, \mathbf{G}^T(t,s)[\mathbf{1} - \mathbf{P}^T(s)]\mathbf{L}(s)\bar{\rho}(s) \quad . \tag{6.2.7}$$

This generalizes (2.5.18) for systems with a time-dependent Hamiltonian.

We now assume that the Hamiltonian $H(t)$ is of the form (6.1.9) so that its time-dependence arises through applied forces $h(t)$. The time rates of change of the mean values $a(t)$ of the macroscopic variables A read

$$\dot{a}_i(t) = - i \, \mathrm{tr}\{A_i \mathbf{L}(t)\rho(t)\} \quad . \tag{6.2.8}$$

On inserting (6.2.7) we obtain

$$\dot{a}_i(t) = v_i[a(t),h(t)] + \gamma_i\{a(s),h(s),\ 0 \leq s \leq t\} \quad , \tag{6.2.9}$$

where

$$v_i(t) \equiv v_i[a(t),h(t)] = - i \, \mathrm{tr}\{A_i \mathbf{L}(t)\bar{\rho}(t)\} \tag{6.2.10}$$

is the organized drift, while

$$\begin{aligned} \gamma_i(t) &\equiv \gamma_i\{a(s),h(s),\ 0 \leq s \leq t\} \\ &= - \int_0^t ds\ \mathrm{tr}\{A_i \mathbf{L}(t)\mathbf{G}^T(t,s)[\mathbf{1} - \mathbf{P}^T(s)]\mathbf{L}(s)\bar{\rho}(s)\} \quad . \end{aligned} \tag{6.2.11}$$

is the disorganized drift. Equation (6.2.9) extends the previously derived transport laws (2.5.17) to include the effects of applied forces. The organized drift $v_i(t)$ is now a function of the instantaneous mean values $a(t)$ and the applied forces $h(t)$, while the disorganized drift $\gamma_i(t)$ is a functional of their past history. While the microscopic coupling of the applied forces is determined by (6.1.9), the macroscopic coupling arises through the dependence of v_i and γ_i on the applied forces.

For the remainder of this section the relevant probability density $\bar{\rho}(t)$ is taken to be of the generalized canonical (g.c.) form [cf. (3.1.3)]:

$$\bar{\rho}(t) = Z^{-1}(t)\ e^{-\beta(H - \Sigma\mu_i(t)A_i)} \quad . \tag{6.2.12}$$

Then, (6.2.9) may be evaluated further. We first provide some useful relations. The time-dependent Hamiltonian (6.1.9) may be written

$$H(t) = \Big\{H - \sum_i \mu_i(t)A_i\Big\} + \Big\{\sum_i [\mu_i(t) - h_i(t)]A_i\Big\} \quad , \tag{6.2.13}$$

where the first term commutes with $\bar{\rho}(t)$. With (6.2.13) we get from (6.1.4) and (6.2.12) in the quantal case

$$iL(t)\bar{\rho}(t) = \frac{i}{\hbar} \sum_i [A_i, \bar{\rho}(t)][\mu_i(t) - h_i(t)] \quad . \tag{6.2.14}$$

Here and in the following the corresponding classical formulas are again obtained by replacing the commutator $(-i/\hbar)[X,Y]$ by the Poisson bracket $\{X,Y\}$. We find another expression for $iL(t)\bar{\rho}(t)$ by taking advantage of the identity (3.2.7)

$$iL(t)\bar{\rho}(t) = \frac{1}{\beta} \int_0^\beta d\alpha \; e^{-\alpha H_t} \frac{i}{\hbar} [H - \sum_i h_i(t)A_i , -\beta H_t] e^{\alpha H_t} \bar{\rho}(t) \quad , \tag{6.2.15}$$

where

$$H_t = H - \sum_i \mu_i(t)A_i \quad . \tag{6.2.16}$$

On noting that

$$\frac{i}{\hbar} [H - \sum_i h_i(t)A_i , H_t] = - i \sum_i L(t)A_i[\mu_i(t) - h_i(t)] \quad , \tag{6.2.17}$$

(6.2.15) becomes

$$iL(t)\bar{\rho}(t) = \sum_i \int_0^\beta d\alpha \; e^{-\alpha H_t} \; (iL(t)A_j) \; e^{\alpha H_t} \bar{\rho}(t)[\mu_j(t) - h_j(t)] \quad . \tag{6.2.18}$$

We now put (6.2.14) into (6.2.10) to give

$$v_i(t) = - \sum_j V_{ij}(t)[\mu_j(t) - h_j(t)] \quad , \tag{6.2.19}$$

where the

$$V_{ij}(t) = V_{ij}[a(t)] = \mathrm{tr}\{\bar{\rho}(t) \frac{i}{\hbar} [A_i, A_j]\} \tag{6.2.20}$$

are the instantaneous parts of the generalized transport coefficients. Further, using (6.2.18), we obtain from (6.2.11)

$$\gamma_i(t) = - \int_0^t ds \sum_j R_{ij}(t,s)[\mu_j(s) - h_j(s)] \quad , \tag{6.2.21}$$

where the

$$R_{ij}(t,s) = \int_0^\beta d\alpha \; \mathrm{tr}\{(iL(t)A_1)G^T(t,s)[1 - P^T(s)]e^{-\alpha H_s}(iL(s)A_j)e^{\alpha H_s}\bar{\rho}(s)\} \tag{6.2.22}$$

are the retarded parts of the generalized transport coefficients. With (6.2.19,21) the generalized transport equations (6.2.9) read

$$\dot{a}_i(t) = - \sum_j V_{ij}(t)[\mu_j(t) - h_j(t)] - \int_0^t ds \sum_j R_{ij}(t,s)[\mu_j(s) - h_j(s)] \quad . \tag{6.2.23}$$

On comparing (6.2.23) with (3.2.12) we see that the effects of the applied forces are of two kinds. First, the fluxes $\dot{a}$ are now caused by the differences $\mu - h$ between the thermodynamic forces μ and the applied forces h. This is natural, since the g.c. probability density $\bar{\rho}[\mu = h]$ is the stationary probability density in the presence of constant applied forces h. Second, the transport coefficients are modified. There is no change in the instantaneous parts $V_{ij}(t)$ but the retarded parts $R_{ij}(t,s)$ become functionals of the applied forces h(u) in the time interval $s \le u \le t$.

The first modification can be taken into account by simply changing the free energy function [cf. (3.1.5-7)]:

$$F(t) \rightarrow F_h(t) = F(t) - \sum_i h_i(t)a_i(t) \quad . \tag{6.2.24}$$

Then, the derivatives of $F_h(t)$ with respect to the mean values a(t),

$$\frac{\partial F_h(t)}{\partial a_i(t)} = \mu_i(t) - h_i(t) \quad , \tag{6.2.25}$$

are just the appropriate driving forces. This change in the free energy makes allowance for the effects of applied forces on the statics of the system. The second modification, the dependence of the retarded transport coefficients $R_{ij}(t,s)$ on the applied forces, may arise in a complicated way. However, this purely dynamical effect of applied forces must generally be taken into account in the study of the response of nonequilibrium systems and the nonlinear response of equilibrium systems

6.3 Linear Response of Equilibrium Systems

In this section we consider a system that is initially in thermal equilibrium and then disturbed by applied forces h(t). Using the macroscopic evolution laws, we calculate the response of the system to the first order in the applied perturbation. In equilibrium the thermodynamic forces μ vanish, that is, $\hat{\mu} = 0$. Consequently, if we start out from equilibrium at time $t_0 = 0$, the thermodynamic forces μ(t) at later times t > 0 are at least of the first order in the applied forces h(t) and the transport laws (6.2.23) give

$$\dot{a}_i(t) = - \sum_j \hat{V}_{ij}[\mu_j(t) - h_j(t)] - \int_0^t ds \sum_j \hat{R}_{ij}(t-s)[\mu_j(s) - h_j(s)] + \mathcal{O}(h^2) \quad , \tag{6.3.1}$$

where $\hat{V}_{ij}$ and $\hat{R}_{ij}(t)$ are the transport coefficients for vanishing thermodynamic and applied forces. These coefficients have been introduced previously in (3.4.1,2). In disregarding terms of the second order in h in the equations of motion, we entirely disregard the dependence of the retarded transport coefficients on the applied forces. Clearly, this particularly simple situation generally occurs only if the thermodynamic forces μ are at least of the first order in the applied forces h, that is, for systems which are initially in equilibrium.

Near equilibrium the thermodynamic forces μ are related to the mean values a by [cf. (3.4.9)]

$$\Delta a_i(t) = \sum_j \beta\hat{\sigma}_{ij}\mu_j(t) \quad , \tag{6.3.2}$$

where the

$$\Delta a_i(t) = a_i(t) - \hat{a}_i \tag{6.3.3}$$

are the deviations of the mean values $a(t)$ from their initial equilibrium values $\hat{a}$, while $\hat{\sigma}_{ij}$ is the equilibrium variance matrix introduced in (3.4.10). When we express the thermodynamic forces μ in terms of the Δa, we obtain from (6.3.1) the transport equations of Mori theory in the presence of applied forces

$$\begin{aligned}\Delta\dot{a}_i(t) = {} & \sum_j \hat{\Omega}_{ij}\Delta a_j(t) + \int_0^t ds\ \hat{\Phi}_{ij}(t-s)\Delta a_j(s) \\ & + \sum_j \hat{V}_{ij}h_j(t) + \int_0^t ds \sum_j \hat{R}_{ij}(t-s)h_j(s) + O(h^2) \quad ,\end{aligned} \tag{6.3.4}$$

where [cf. also (3.4.12,13)]

$$\hat{\Omega}_{ij} = -\sum_k \frac{1}{\beta}\hat{V}_{ik}\hat{\sigma}^{-1}_{kj} \quad , \quad \hat{\Phi}_{ij}(t) = -\sum_k \frac{1}{\beta}\hat{R}_{ik}(t)\hat{\sigma}^{-1}_{kj} \quad . \tag{6.3.5}$$

In terms of the evolution matrix $M_{ij}(t)$ satisfying

$$\frac{\partial}{\partial t}M_{ij}(t) = \sum_k \hat{\Omega}_{ik}M_{kj}(t) + \int_0^t ds\,\hat{\Phi}_{ik}(t-s)M_{kj}(s) \tag{6.3.6}$$

and

$$M_{ij}(0) = \delta_{ij} \quad , \tag{6.3.7}$$

the formal solution of (6.3.4) with initial condition $\Delta a_i(0) = 0$ reads

$$\Delta a_i(t) = \int_0^t ds \sum_{j,k} M_{ij}(t-s)\left[\hat{V}_{jk}h_k(s) + \int_0^s du\ \hat{R}_{jk}(s-u)h_k(u)\right] \quad . \tag{6.3.8}$$

This result may be written

$$\Delta a_i(t) = \int_0^t ds \sum_j \chi_{ij}(t-s)h_j(s) \quad , \tag{6.3.9}$$

where for $t \geq 0$

$$\chi_{ij}(t) = \sum_k M_{ik}(t)\hat{V}_{kj} + \int_0^t ds \sum_k M_{ik}(t-s)\hat{R}_{kj}(s) \tag{6.3.10}$$

is the response tensor. Equation (6.3.9) gives the linear response of an equilibrium system to an applied perturbation as a superposition of the delayed effects.

The Laplace transform of (6.3.6) reads

$$M_{ij}(z) - \delta_{ij} = \sum_k [\hat{\Omega}_{ik} + \hat{\Phi}_{ik}(z)]M_{kj}(z) \quad . \tag{6.3.11}$$

If we multiply this relation by $M_{mi}(z)$ from the left and by $M^{-1}_{jn}(z)$ from the right and then sum over the indices i and j, we get

$$M_{mn}(z) - \delta_{mn} = \sum_i M_{mi}(z)[\hat{\Omega}_{in} + \hat{\Phi}_{in}(z)] \quad , \tag{6.3.12}$$

which is the Laplace transform of

$$\dot{M}_{ij}(t) = \sum_k M_{ik}(t)\hat{\Omega}_{kj} + \int_0^t ds \sum_k M_{ik}(t - s)\hat{\Phi}_{kj}(s) \quad . \tag{6.3.13}$$

We now take advantage of (6.3.5) to express $\hat{V}_{kj}$ and $\hat{R}_{kj}(s)$ in (6.3.10) in terms of $\hat{\Omega}_{kj}$ and $\hat{\Phi}_{kj}(s)$. Then by virtue of (6.3.13) the response tensor emerges as

$$\chi_{ij}(t) = -\Theta(t)\beta \sum_k \dot{M}_{ik}(t)\hat{\sigma}_{kj} \quad . \tag{6.3.14}$$

Since the evolution law (3.4.21) for the canonical equilibrium correlations $C_{ij}(t)$ coincides with the evolution law (6.3.6) for the $M_{ij}(t)$, the two quantities differ only by their initial conditions, and we have for $t \geq 0$

$$C_{ij}(t) = \sum_k M_{ik}(t)\hat{\sigma}_{kj} \quad . \tag{6.3.15}$$

Thus the response tensor (6.3.14) is related to the correlation functions by the fluctuation-dissipation theorem of the first kind (6.1.20). Further, the time-reversal symmetry (6.1.32) of the response tensor can easily be obtained from the transformation properties of the transport equations. As shown in Sect.3.7, the latter imply the detailed balance symmetry

$$C_{ij}(t) = \varepsilon_i\varepsilon_j C_{ji}(t) \tag{6.3.16}$$

of the equilibrium correlations. Then, we obtain (6.1.32) by virtue of the fluctuation-dissipation theorem.

It should be noted that in this section the response tensor has been determined by starting out from the macroscopic evolution laws, and (6.3.10) gives the response tensor virtually in terms of the free energy and the transport coefficients. If these solely macroscopic quantities are now approximated, as in Sect.3.5 for example, the line of reasoning in this section remains practically unchanged. Again we recognize the advantage of writing the transport laws in terms of transport coefficients and forces derived from a thermodynamic potential. Then it is easy to make approximations in such a way that basic symmetries and properties of the process, such as the fluctuation-dissipation theorem, are not destroyed.

6.4 Fokker-Planck Equation Approach

We now address the problem of accounting for the effects of applied forces in the Fokker-Planck equation approach. As mentioned in Sect.4.2, the Fokker-Planck equatio is formally obtained from the transport equations of statistical thermodynamics by replacing the set A of macroscopic variables by the enlarged set $\Psi_\alpha = \delta(A - \alpha)$. Hence, the arguments in Sects.6.2 and 6.3 can be transfered to the Fokker-Planck formalism in a rather straightforward manner.

We start by noting that the relevant probability density is of the form (see Sects.4.1 and 4.2 for further details)

$$\bar{\rho}(t) = \rho_\beta \int d\alpha \, \frac{p(\alpha,t)}{p_\beta(\alpha)} \Psi_\alpha \quad , \tag{6.4.1}$$

where $p(\alpha,t)$ is the macroscopic probability density. The associated projection operator $\mathbf{P}^T$ is time-independent and given explicitly in (4.2.5). Now, by inserting the general formula (6.2.7) into

$$\frac{\partial}{\partial t} p(\alpha,t) = - i \, \mathrm{tr}\{\Psi_\alpha \mathbf{L}(t)\rho(t)\} \quad , \tag{6.4.2}$$

we obtain for the time rate of change of the macroscopic probability density

$$\begin{aligned} \frac{\partial}{\partial t} p(\alpha,t) = &- i \, \mathrm{tr}\{\Psi_\alpha \mathbf{L}(t)\bar{\rho}(t)\} \\ &- \int_0^t ds \, \mathrm{tr}\{\Psi_\alpha \mathbf{L}(t)\mathbf{G}^T(t,s)[\mathbf{1} - \mathbf{P}^T]\mathbf{L}(s)\bar{\rho}(s)\} \quad . \end{aligned} \tag{6.4.3}$$

The time-dependent Hamiltonian $H(t)$, describing the internal motion and the applied perturbation, is taken to be

$$H(t) = H + H'(t) = H + \int d\alpha \, H'(\alpha,t)\Psi_\alpha \quad . \tag{6.4.4}$$

This includes (6.1.9) as the special case:

$$H'(\alpha,t) = - \sum_i h_i(t)\alpha_i \quad . \tag{6.4.5}$$

Using (6.4.1,4), we find

$$\begin{aligned} -i\mathbf{L}(t)\bar{\rho}(t) &= \{H(t),\bar{\rho}(t)\} \\ &= \int d\alpha \left[\{\Psi_\alpha,\rho_\beta\} \frac{1}{\beta} \frac{p(\alpha,t)}{p_\beta(\alpha)} + \{\Psi_\alpha,\bar{\rho}(t)\}H'(\alpha,t) \right] \quad , \end{aligned} \tag{6.4.6}$$

where we have made use of

$$\{H,\rho_\beta\Psi_\alpha\} = \rho_\beta\{H,\Psi_\alpha\} = - \frac{1}{\beta} \{\rho_\beta,\Psi_\alpha\} \quad . \tag{6.4.7}$$

From (6.4.6) we get

$$-i\ \mathrm{tr}[\Psi_\alpha \mathbf{L}(t)\bar{\rho}(t)\}$$

$$= \int d\alpha' \Big(\mathrm{tr}[\{\Psi_\alpha,\Psi_{\alpha'}\}\rho_\beta] \, \frac{1}{\beta} \, \frac{p(\alpha',t)}{p_\beta(\alpha')} + \mathrm{tr}[\{\Psi_\alpha,\Psi_{\alpha'}\}\bar{\rho}(t)] H'(\alpha',t) \Big) \quad . \tag{6.4.8}$$

From (6.4.1) and

$$\{\Psi_\alpha,\Psi_{\alpha'}\} = -\sum_i \frac{\partial}{\partial\alpha_i} \Psi_\alpha\{A_i,\Psi_{\alpha'}\} = \sum_{i,j} \frac{\partial^2}{\partial\alpha_i\partial\alpha_j'} \delta(\alpha-\alpha')\Psi_\alpha\{A_i,A_j\} \tag{6.4.9}$$

(6.4.8) can be written

$$-i\ \mathrm{tr}\{\Psi_\alpha \mathbf{L}(t)\bar{\rho}(t)\}$$

$$= \sum_{i,j} \frac{\partial}{\partial\alpha_i} \pi_{ij}(\alpha)\Big[p_\beta(\alpha) \frac{\partial}{\partial\alpha_j} \frac{p(\alpha,t)}{p_\beta(\alpha)} + \beta p(\alpha,t) \frac{\partial H'(\alpha,t)}{\partial\alpha_j}\Big] \quad , \tag{6.4.10}$$

where the π_{ij} are given by the Poisson bracket relations

$$\pi_{ij}(\alpha) = -\pi_{ji}(\alpha) = \frac{\mathrm{tr}[\Psi_\alpha\rho_\beta[A_j,A_i\}]}{\beta p_\beta(\alpha)} \quad . \tag{6.4.11}$$

On the other hand, we have

$$-i\mathbf{L}(t)\bar{\rho}(t) = \{H(t),\bar{\rho}(t)\} = \int d\alpha\ \{H(t),\rho_\beta\Psi_\alpha\} \, \frac{p(\alpha,t)}{p_\beta(\alpha)} \quad . \tag{6.4.12}$$

Using

$$\{H(t),\rho_\beta\Psi_\alpha\} = \rho_\beta\{H(t),\Psi_\alpha\} + \Psi_\alpha\{H(t),\rho_\beta\}$$

$$= -\sum_i \frac{\partial}{\partial\alpha_i} \rho_\beta\Psi_\alpha\{H(t),A_i\} - \beta\rho_\beta\Psi_\alpha\{H(t),H\} \quad .. \tag{6.4.13}$$

and

$$\{H(t),H\} = \{H'(t),H(t)\}$$

$$= \int d\alpha\ H'(\alpha,t)[\Psi_\alpha,H(t)\} = \int d\alpha\ \frac{\partial H'(\alpha,t)}{\partial\alpha_i} \Psi_\alpha\{A_i,H(t)\} \quad , \tag{6.4.14}$$

(6.4.12) gives

$$-i\mathbf{L}(t)\bar{\rho}(t) = -\int d\alpha\ \rho_\beta\Psi_\alpha(i\mathbf{L}(t)A_i) \Big[\frac{\partial}{\partial\alpha_i} \frac{p(\alpha,t)}{p_\beta(\alpha)} + \beta \, \frac{p(\alpha,t)}{p_\beta(\alpha)} \frac{\partial H'(\alpha,t)}{\partial\alpha_i}\Big] \quad . \tag{6.4.15}$$

Now, by virtue of (6.4.15) and

$$-i\ \mathrm{tr}[\Psi_\alpha \mathbf{L}(t)X\} = \mathrm{tr}[\{\Psi_\alpha,H(t)\}X\}$$

$$= -\sum_i \frac{\partial}{\partial\alpha_i} \mathrm{tr}[\Psi_\alpha(i\mathbf{L}(t)A_i)X\} \quad , \tag{6.4.16}$$

the integrand in (6.4.3) becomes

$$-\mathrm{tr}\{\Psi_\alpha \mathbf{L}(t)\mathbf{G}^T(t,s)[\mathbf{1} - \mathbf{P}^T]\mathbf{L}(s)\bar{\rho}(s)\}$$

$$= \sum_{i,j} \frac{\partial}{\partial \alpha_i} \int d\alpha' \, D_{ij}(\alpha,t;\alpha',s)\left[p_\beta(\alpha') \frac{\partial}{\partial \alpha'_j} \frac{p(\alpha',s)}{p_\beta(\alpha')} + \beta p(\alpha',s) \frac{\partial H'(\alpha',s)}{\partial \alpha'_j}\right] \quad , \tag{6.4.17}$$

where the

$$D_{ij}(\alpha,t;\alpha',s) = \frac{\mathrm{tr}\{\Psi_\alpha[i\mathbf{L}(t)A_i]\mathbf{G}^T(t,s)(\mathbf{1} - \mathbf{P}^T)\rho_\beta \Psi_{\alpha'} i\mathbf{L}(s)A_j\}}{p_\beta(\alpha')} \tag{6.4.18}$$

are the diffusion kernels in the presence of an applied perturbation.

Finally, because of (6.4.10,17) we obtain from (6.4.3) the generalized Fokker-Planck equation

$$\frac{\partial}{\partial t} p(\alpha,t) = \sum_{i,j} \frac{\partial}{\partial \alpha_i} \beta \pi_{ij}(\alpha) \left[\frac{\partial F^*(\alpha)}{\partial \alpha_j} + \frac{\partial H'(\alpha,t)}{\partial \alpha_j} + \frac{1}{\beta}\frac{\partial}{\partial \alpha_j}\right] p(\alpha,t)$$

$$+ \sum_{i,j} \frac{\partial}{\partial \alpha_i} \int_0^t ds \int d\alpha' \beta D_{ij}(\alpha,t;\alpha',s) \left[\frac{\partial F^*(\alpha')}{\partial \alpha'_j} + \frac{\partial H'(\alpha',s)}{\partial \alpha'_j} + \frac{1}{\beta}\frac{\partial}{\partial \alpha'_j}\right] p(\alpha',s) \tag{6.4.19}$$

where

$$F^*(\alpha) = -\frac{1}{\beta} \ln p_\beta(\alpha) \tag{6.4.20}$$

is the bare free energy. Again the applied perturbation appears in two ways. The first change, which accounts for the effects of the perturbation upon the statics of the system, is taken into account by changing the free energy

$$F^*(\alpha) \to F^*(\alpha) + H'(\alpha,t) \quad . \tag{6.4.21}$$

Secondly, the diffusion kernels $D_{ij}(\alpha,t;\alpha',s)$ have picked up a functional dependence on the perturbation.

In the remainder of this section we study the linear response of an equilibrium system. Since

$$\left[\frac{\partial F^*(\alpha)}{\partial \alpha_j} + \frac{1}{\beta}\frac{\partial}{\partial \alpha_j}\right] p_\beta(\alpha) = 0 \quad , \tag{6.4.22}$$

we then can disregard the modification of the diffusion kernels. Further, we shall restrict ourselves to situations where the memory effects in (6.4.19) can be disregarded.[4] In that case the generalized Fokker-Planck equation (6.4.19) reduces to the Fokker-Planck equation

$$\frac{\partial}{\partial t} p(\alpha,t) = \sum_{i,j} \frac{\partial}{\partial \alpha_i} L^*_{ij}(\alpha) \left[\frac{\partial F^*(\alpha)}{\partial \alpha_j} + \frac{\partial H'(\alpha,t)}{\partial \alpha_j} + \frac{1}{\beta}\frac{\partial}{\partial \alpha_j}\right] p(\alpha,t) \quad , \tag{6.4.23}$$

---

[4] The following discussion can easily be generalized to systems with memory by using the same Laplace-transform techniques as in Sect.6.3. Compare also [151].

where the bare transport coefficients $L^*_{ij}(\alpha)$ have been defined previously in Sect.4.4.

Introducing the conditional probability $p(\alpha,t|\alpha')$ of the unperturbed system, that is, the solution of the unperturbed Fokker-Planck equation with initial condition $p(\alpha,0|\alpha') = \delta(\alpha - \alpha')$,[5] we obtain from (6.4.23) by first-order perturbation theory

$$\begin{aligned}\Delta p(\alpha,t) &= p(\alpha,t) - p_\beta(\alpha)\\ &= \int_0^t ds \int d\alpha' p(\alpha,t-s|\alpha') \sum_{i,j} \frac{\partial}{\partial\alpha'_i} L^*_{ij}(\alpha') \frac{\partial H'(\alpha',s)}{\partial\alpha'_j} p_\beta(\alpha') \quad , \qquad (6.4.24)\end{aligned}$$

where we have assumed that the system is initially at time $t_0 = 0$ in equilibrium. Because of (6.4.22) we have

$$\begin{aligned}\sum_{i,j} \frac{\partial}{\partial\alpha_i} L^*_{ij}(\alpha) \frac{\partial H'(\alpha,s)}{\partial\alpha_j} p_\beta(\alpha) &= \sum_{i,j} \frac{\partial}{\partial\alpha_i} L^*_{ij}(\alpha) \left[\frac{\partial F^*(\alpha)}{\partial\alpha_j} + \frac{1}{\beta}\frac{\partial}{\partial\alpha_j}\right]\beta H'(\alpha,s)p_\beta(\alpha)\\ &= -i\mathcal{L}\beta H'(\alpha,s)p_\beta(\alpha) \quad . \qquad (6.4.25)\end{aligned}$$

Since the operator acting upon $\beta H'(\alpha,s)p_\beta(\alpha)$ in the last expression is the unperturbed Fokker-Planck operator (4.6.2) governing the time evolution of the conditional probability, we obtain by putting (6.4.25) into (6.4.24)

$$\Delta p(\alpha,t) = -\int_0^t ds \int d\alpha' \chi(\alpha,\alpha',t-s)H'(\alpha',s) \quad , \qquad (6.4.26)$$

where

$$\chi(\alpha,\alpha',t) = -\beta\Theta(t) \frac{\partial}{\partial t} p^{(2)}_\beta(\alpha,\alpha',t) \qquad (6.4.27)$$

is the response kernel, while

$$p^{(2)}_\beta(\alpha,\alpha',t) = p(\alpha,t|\alpha')p_\beta(\alpha') \qquad (6.4.28)$$

is the equilibrium joint probability density. Equation (6.4.27) implies the fluctuation-dissipation theorem of the first kind.

For an external perturbation of the form (6.4.5) the response of the mean values $a(t)$ reads

$$\Delta a_i(t) = \int d\alpha\, \alpha_i \Delta p(\alpha,t) = \int_0^t ds \sum_j \chi_{ij}(t-s)h_j(s) \quad , \qquad (6.4.29)$$

where

$$\chi_{ij}(t) = \int d\alpha\, d\alpha' \alpha_i \alpha'_j \chi(\alpha,\alpha',t) \quad . \qquad (6.4.30)$$

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[5] The conditional probability density can also be viewed as the kernel of the evolution operator $\exp(-i\mathcal{L}t)$, where $-i\mathcal{L}$ is the unperturbed Fokker-Planck operator (4.6.2).

is the response tensor. Because of (6.4.27) we have

$$\chi_{ij}(t) = -\beta\Theta(t)\dot{C}_{ij}(t) \tag{6.4.31}$$

with the equilibrium correlation functions

$$C_{ij}(t) = \int d\alpha d\alpha' \delta\alpha_i \delta\alpha_j' p_\beta^{(2)}(\alpha,\alpha',t) \quad , \tag{6.4.32}$$

where the $\delta\alpha$ are the deviations from the equilibrium values. Hence we recover our previous results.

6.5 Master Equation Approach

In this section we study how the master equation changes when an external perturbation is applied to the system. The line of reasoning is very similar to the one pursued in the preceeding sections so that we can be briefer this time. The relevant probability density is of the form (see Sects.5.1 and 5.2 for details)

$$\bar{\rho}(t) = \Sigma\Sigma_S^{-1}\rho_S(t) \quad , \tag{6.5.1}$$

where

$$\rho_S(t) = \mathrm{tr}_R\{\rho(t)\} = \mathrm{tr}_R\{\bar{\rho}(t)\} \tag{6.5.2}$$

is the reduced probability density describing the state of the subsystem S. The projection operator $\mathbf{P}^T$ projecting out the relevant probability density is time independent. The Hamiltonian H(t) is taken to be

$$H(t) = H + H_S'(t) \quad , \tag{6.5.3}$$

where $H_S'(t)$ describes an applied perturbation acting upon the subsystem S only.

On inserting (6.2.7) into

$$\dot{\rho}_S(t) = -i\,\mathrm{tr}_R\{\mathbf{L}(t)\rho(t)\} \quad , \tag{6.5.4}$$

we obtain

$$\dot{\rho}_S(t) = -i\,\mathrm{tr}_R\{\mathbf{L}(t)\bar{\rho}(t)\} - \int_0^t ds\,\mathrm{tr}_R\{\mathbf{L}(t)\mathbf{G}^T(t,s)[1-\mathbf{P}^T]\mathbf{L}(s)\bar{\rho}(s)\} \quad . \tag{6.5.5}$$

For further evaluation we restrict ourselves to the accuracy necessary to describe the linear response of the equilibrium system correctly. We then have

$$\mathbf{L}(t)\bar{\rho}(t) = \mathbf{L}\bar{\rho}(t) + \mathbf{L}_S'(t)\rho_\beta + O(H_S'^2) \quad . \tag{6.5.6}$$

Next we note that

$$\mathbf{L}\bar{\rho}(t) = \mathbf{L}\Sigma\Sigma_S^{-1}\rho_S(t) = \beta\mathbf{L}\Sigma\mu_S(t) \quad , \tag{6.5.7}$$

where the operator $\mu_S(t)$, conjugate to $\rho_S(t)$, has been introduced in Sect.5.2. Further, because of (5.3.1,2), we have

$$\mathbf{L}_S^{\prime}(t)\rho_\beta = \frac{1}{\hbar}[H_S^{\prime}(t),\rho_\beta] = \beta\mathbf{L}\Sigma H_S^{\prime}(t) \quad , \tag{6.5.8}$$

which combines with (6.5.7) to yield

$$\mathbf{L}(t)\bar{\rho}(t) = \beta\mathbf{L}\Sigma[\mu_S(t) + H_S^{\prime}(t)] + \mathcal{O}(H_S^{\prime 2}) \quad . \tag{6.5.9}$$

We now insert (6.5.9) into both terms on the right-hand side of (6.5.5) and observe that in the considered approximation we may disregard any further dependence of the memory term on the applied perturbation. Then we obtain

$$\dot{\rho}_S(t) = -\mathbf{V}_S[\mu_S(t) + H_S^{\prime}(t)\} - \int_0^t ds\, \mathbf{R}_S(t-s)[\mu_S(s) + H_S^{\prime}(s)] \quad , \tag{6.5.10}$$

where the transport operators $\mathbf{V}_S$ and $\mathbf{R}_S(t)$ have been defined in (5.2.19,20). Clearly the external perturbation $H_S^{\prime}(t)$ is just added to the thermodynamic force operator $\mu_S(t)$. In view of (5.2.14) this change can be accounted for by changing the free energy

$$F^*(t) \rightarrow F^*(t) + \mathrm{tr}_S\{\rho_S(t)H_S^{\prime}(t)\} \quad . \tag{6.5.11}$$

Generally the retarded transport operator $\mathbf{R}_S(t)$ will also be modified by the external perturbation, but this change does not contribute to the linear response.

Provided $\rho_S(0) = \rho_{S\beta}$, we get from (6.5.10) by first-order perturbation theory

$$\begin{aligned} \Delta\rho_S(t) &= \rho_S(t) - \rho_{S\beta} & (6.5.12)\\ &= -\int_0^t ds\, \mathbf{G}_S(t-s)\,\Sigma_S^{-1}\Big[\mathbf{V}_S H_S^{\prime}(s) + \int_0^s du\, \mathbf{R}_S(s-u)H_S^{\prime}(u)\Big] \quad , \end{aligned}$$

where we have used the fact that a solution of the unperturbed master equation is of the form (5.2.31). This result may be written

$$\Delta\rho_S(t) = -\int_0^t ds\, \chi_S(t-s)H_S^{\prime}(s) \quad , \tag{6.5.13}$$

where for $t \geq 0$

$$\chi_S(t) = \mathbf{G}_S(t)\,\Sigma_S^{-1}\mathbf{V}_S + \int_0^t ds\, \mathbf{G}_S(t-s)\,\Sigma_S^{-1}\mathbf{R}_S(s) \tag{6.5.14}$$

is the response operator. From (5.3.21) we get

$$\begin{aligned} z\mathbf{G}_S(z) - \Sigma_S &= \mathbf{G}_S(z)\,\Sigma_S^{-1}[\Omega_S + \Phi_S(z)]\Sigma_S \\ &= -\frac{1}{\beta}\mathbf{G}_S(z)\,\Sigma_S^{-1}[\mathbf{V}_S + \mathbf{R}_S(z)] \quad , & (6.5.15) \end{aligned}$$

where the last transformation follows by virtue of (5.2.,21,22). Since (6.5.15) is the Laplace transform of

$$\dot{\mathbf{G}}_S(t) = -\frac{1}{\beta}\mathbf{G}_S(t)\,\Sigma_S^{-1}\mathbf{V}_S - \frac{1}{\beta}\int_0^t ds\, \mathbf{G}_S(t-s)\,\Sigma_S^{-1}\mathbf{R}_S(s) \tag{6.5.16}$$

the response operator (6.5.14) may ba written

$$\chi_S(t) = -\beta\Theta(t)\dot{\mathbf{G}}_S(t) \quad . \tag{6.5.17}$$

~~This~~ relation implies the fluctuation-dissipation theorem of the first kind in as much as $\mathbf{G}_S(t)$ determines the dynamics of canonical equilibrium correlations.

If the perturbation is of the form

$$H_S'(t) = -\sum_i A_i h_i(t) \quad , \tag{6.5.18}$$

the response of the mean values a(t) reads

$$\Delta a_i(t) = \mathrm{tr}_S\{A_i \Delta\rho_S(t)\} = \int_0^t ds\; \chi_{ij}(t-s) h_j(s) \quad . \tag{6.5.19}$$

where

$$\chi_{ij}(t) = \mathrm{tr}_S\{A_i \chi_S(t) A_j\} \tag{6.5.20}$$

is the response tensor. Because of (6.5.17), the $\chi_{ij}(t)$ are related to the canonical correlations [see (5.2.24)]

$$C_{ij}(t) = \mathrm{tr}_S[\hat{\delta}A_i \mathbf{G}_S(t) \hat{\delta}A_j\} \tag{6.5.11}$$

of the fluctuations $\hat{\delta}A_i$ about equilibrium by (6.1.20).

Since the results following (6.5.10) have been obtained without making use of the precise form of the stochastic operators, we expect that they still hold if the stochastic operators are approximated as in Sect.5.4. We shall not go through the arguments in detail but only mention that (6.5.10) reduces in the weak coupling limit to

$$\dot{\rho}_S(t) = -i\mathcal{L}_S[\rho_S(t) + \beta\hat{\Sigma}_S H_S'(t)\} \quad , \tag{6.5.22}$$

where $\mathcal{L}_S$ has been defined in (5.6.3), while $\hat{\Sigma}_S$ has been introduced in (5.4.12). Clearly, the approximate equation (6.5.22) can only be used if the applied perturbation $H_S'(t)$ is slowly varying in time. From (6.5.22) we easily obtain for the response operator

$$\chi_S(t) = i\beta\Theta(t)\, e^{-i\mathcal{L}_S t}\mathcal{L}_S \hat{\Sigma}_S = -\beta\Theta(t)\dot{\mathbf{G}}_S(t) \quad . \tag{6.5.23}$$

where

$$\mathbf{G}_S(t) = e^{-i\mathcal{L}_S t}\hat{\Sigma}_S \tag{6.5.24}$$

determines the canonical equilibrium correlations by virtue of (5.2.24).

Part B. Select Applications

7. Damped Nonlinear Oscillator

In this chapter we shall deal with the theory of a damped nonlinear oscillator from a statistical-mechanical point of view. Our treatment is presented as a simple application of the Fokker-Planck equation approach given in Chap.4. We first introduce in Sect.7.1 a class of microscopic models where an oscillator moving in a field of force (not necessarily linear) interacts with a reservoir of bath particles. This class comprises physically important systems like the damped harmonic oscillator, the Brownian particle in a fluid, the mass impurity in a lattice, and the diffusing particle in a periodic potential. Starting out from the exact evolution law for the oscillator distribution function, we reexamine the Markovian approximation in Sect.7.2 and obtain a Fokker-Planck equation in the limit where the mass of the oscillator is large compared with the mass of the bath particles.

The special cases of a Brownian particle in a fluid and a mass impurity in a harmonic lattice are studied in Sect.7.3. Important early contributions to the theory of Brownian movement have been compiled by WAX [152]. We follow essentially the statistical-mechanical approach by LEBOWITZ and RÉSIBOIS [153] and by MAZUR and OPPENHEIM [154]. The subject has also been presented in various books and review articles [22,93,155]. The mass impurity in a harmonic lattice has frequently been studied [156-161] since this model can be solved exactly for simple couplings and thus makes a detailed study of the Markovian limit possible.

The focus of the last two sections is on damped nonlinear oscillators, where the non-Gaussian fluctuations lead to a renormalization of the transport equations. Expressions for the renormalized thermodynamic forces and transport coefficients are derived in Sect.7.4, and explicit perturbation theoretical results for the Duffing oscillator are given in Sect.7.5. The Duffing oscillator has been studied in greater detail by BIXON and ZWANZIG [162] using numerical methods, and some aspects of this and related problems have recently been reviewed by ZWANZIG [163].

7.1 Microscopic Model and Generalized Fokker-Planck Equation

The damping of an oscillator is due to the interaction between the oscillator and its surroundings. As a simple model we study a mechanical oscillator in interaction with a reservoir consisting of N particles. The Hamiltonian of the closed system formed by the oscillator and the reservoir is taken to be

$$H = H_0 + H_R + V \quad . \tag{7.1.1}$$

Here

$$H_0(\vec{P},\vec{Q}) = \frac{\vec{P}^2}{2M} + U(\vec{Q}) \tag{7.1.2}$$

is the Hamiltonian of an oscillator with mass M and momentum $\vec{P}$ at position $\vec{Q}$ moving in a pinning potential $U(\vec{Q})$. Denoting by $\vec{p}_i$ and $\vec{q}_i$ the position and momentum of the i^{th} reservoir particle of mass m, we can write the reservoir Hamiltonian in the form

$$H_R(\vec{p}_i,\vec{q}_i) = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + U_R(\vec{q}_i) \quad . \tag{7.1.3}$$

Finally, $V(\vec{Q},\vec{q}_i)$ describes the interaction between the oscillator and the reservoir. We treat the system on the basis of classical statistical mechanics using the Fokker-Planck method given in Chap.4.

Since we are interested in the motion of the oscillator moving under the influence of the reservoir, we choose its momentum $\vec{P}$ and position $\vec{Q}$ as the macroscopic variables. The time rates of change of these variables read

$$\dot{\vec{Q}} = iL\vec{Q} = \{\vec{Q},H\} = \frac{\vec{P}}{M} \tag{7.1.4}$$

and

$$\vec{P} = iL\vec{P} = \{\vec{P},H\} = -\frac{\partial U}{\partial \vec{Q}} + \vec{K}_R \quad , \tag{7.1.5}$$

where

$$\vec{K}_R(\vec{Q},\vec{q}_i) = -\frac{\partial V(\vec{Q},\vec{q}_i)}{\partial \vec{Q}} \tag{7.1.6}$$

is the force which the reservoir exerts on the oscillator.

In equilibrium the state of the entire system is described by the canonical probability density

$$\rho_\beta = Z_\beta^{-1}\, e^{-\beta H} \quad , \tag{7.1.7}$$

where $\beta = 1/k_BT$ is the inverse reservoir temperature, while the state of the oscillator is described by the macroscopic probability density[1]

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[1] In this chapter the macroscopic probability density is denoted by f to avoid confusion with the momentum p.

$$f_\beta(\vec{p},\vec{q}) = \mathrm{tr}\{\psi_{\vec{p}\vec{q}}\rho_\beta\} \quad , \tag{7.1.8}$$

where

$$\psi_{\vec{p}\vec{q}} = \delta(\vec{P} - \vec{p})\,\delta(\vec{Q} - \vec{q}) \quad . \tag{7.1.9}$$

Using (7.1.1-3), we find [cf. (4.4.13)]

$$f_\beta(\vec{p},\vec{q}) = e^{-\beta F^*(\vec{p},\vec{q})} \tag{7.1.10}$$

with the bare free energy

$$F^*(\vec{p},\vec{q}) = \frac{\vec{p}^{\,2}}{2M} + U(\vec{q}) + \Delta U(\vec{q}) \quad . \tag{7.1.11}$$

Here

$$\Delta U(\vec{q}) = -\frac{1}{\beta}\ln\int dq_i\; e^{-\beta[U_R(\vec{q}_i)+V(\vec{q},\vec{q}_i)]} \tag{7.1.12}$$

is a potential for the average force exerted by the reservoir on the oscillator when it is fixed at the position $\vec{Q} = \vec{q}$. This average force vanishes in the important case where the potentials $U_R(\vec{q}_i)$ and $V(\vec{q},\vec{q}_i)$ depend on the distance vectors $\vec{q}_i - \vec{q}_j$ and $\vec{q} - \vec{q}_i$ only. In the general case we can always add the potential $\Delta U(\vec{q})$ to the pinning potential $U(\vec{q})$ so that we may assume

$$\Delta U(\vec{q}) = 0 \tag{7.1.13}$$

henceforth.

The reversible dynamics of the oscillator is determined by the antisymmetric matrix (4.3.4). Since the Poisson brackets read

$$\{Q^\nu, P^\mu\} = \delta^{\nu\mu} \quad , \tag{7.1.14}$$

where ν and μ label the space components, we find

$$\pi_{p^\nu q^\nu} = -\pi_{q^\nu p^\nu} = \frac{1}{\beta} \tag{7.1.15}$$

and the remaining coefficients vanish. To evaluate the diffusion kernels (4.2.20) which determine the irreversible dynamics, we start by noting that

$$\mathbf{P}\psi_{\vec{p}\vec{q}}\vec{K}_R = \psi_{\vec{p}\vec{q}}\,\frac{\mathrm{tr}\{e^{-\beta H}\psi_{\vec{p}\vec{q}}\vec{K}_R\}}{\mathrm{tr}\{e^{-\beta H}\psi_{\vec{p}\vec{q}}\}} = -\psi_{\vec{p}\vec{q}}\,\frac{\partial\Delta U(\vec{q})}{\partial\vec{q}} \quad , \tag{7.1.16}$$

where we have made use of (4.2.1) and (7.1.6,12). Equation (7.1.16) in connection with (7.1.13) gives

$$\mathbf{P}\vec{K}_R = 0 \quad . \tag{7.1.17}$$

Further, from (4.2.2) and (7.1.4) we get

$$(1 - \mathbf{P})\Psi_{\vec{p}\vec{q}}\overset{\bullet}{\vec{Q}} = 0 \quad , \tag{7.1.18}$$

and from (7.1.5) we obtain in view of (7.1.17)

$$(1 - \mathbf{P})\Psi_{\vec{p}\vec{q}}\overset{\bullet}{\vec{P}} = \Psi_{\vec{p}\vec{q}}\vec{K}_R \quad . \tag{7.1.19}$$

Thus, using (4.2.14,20), we find that the only nonvanishing diffusion kernels are

$$\begin{aligned} O_{p^\nu p^\mu}(\vec{p},\vec{q},\vec{p}',\vec{q}',t) &= \frac{1}{\beta}\,\gamma^{\nu\mu}(\vec{p},\vec{q},\vec{p}',\vec{q}',t) \\ &= \frac{\mathrm{tr}[\rho_\beta \Psi_{\vec{p}',\vec{q}'}\, K_R^\mu\, e^{i\mathbf{L}(1-\mathbf{P})t}\Psi_{\vec{p}\vec{q}}\, K_R^\nu\}}{\mathrm{tr}[\rho_\beta \Psi_{\vec{p}',\vec{q}'}\}} \quad . \end{aligned} \tag{7.1.20}$$

This expression is a modified correlation function of the force exerted on the oscillator by the reservoir.

Having investigated the free energy and the transport kernels, we turn to the generalized Fokker-Planck equation, which is of the form

$$\begin{aligned} \frac{\partial}{\partial t} f(\vec{p},\vec{q},t) &= \sum_\nu \frac{\partial}{\partial p^\nu}\, \pi_{p^\nu q^\nu}\left[\beta\,\frac{\partial F^*(\vec{p},\vec{q})}{\partial q^\nu} + \frac{\partial}{\partial q^\nu}\right] f(\vec{p},\vec{q},t) \\ &+ \sum_\nu \frac{\partial}{\partial q^\nu}\, \pi_{q^\nu p^\nu}\left[\beta\,\frac{\partial F^*(\vec{p},\vec{q})}{\partial p^\nu} + \frac{\partial}{\partial p^\nu}\right] f(\vec{p},\vec{q},t) \\ &+ \int_0^t ds \sum_{\nu\mu} \frac{\partial}{\partial p^\nu} \int dp'dq'\, O_{p^\nu p^\mu}(\vec{p},\vec{q},\vec{p}',\vec{q}',s)\left[\beta\,\frac{\partial F^*(\vec{p}',\vec{q}')}{\partial p'^\mu} + \frac{\partial}{\partial p'^\mu}\right] \\ &\qquad \cdot \quad f(\vec{p}',\vec{q}',t - s) \quad . \end{aligned} \tag{7.1.21}$$

Thus, by virtue of (7.1.11,13,15,20), we obtain

$$\begin{aligned} \frac{\partial}{\partial t} f(\vec{p},\vec{q},t) &= \left(\frac{\partial}{\partial \vec{p}} \cdot \frac{\partial U(\vec{q})}{\partial \vec{q}} - \frac{\partial}{\partial \vec{q}} \cdot \frac{\vec{p}}{M}\right) f(\vec{p},\vec{q},t) \\ &+ \int_0^t ds\, \frac{\partial}{\partial \vec{p}} \cdot \int dp'dq'\, \overleftrightarrow{\gamma}(\vec{p},\vec{q},\vec{p}',\vec{q}',s) \cdot \left(\frac{\vec{p}'}{M} + k_B T\,\frac{\partial}{\partial \vec{p}'}\right) f(\vec{p}',\vec{q}',t - s) \quad . \end{aligned} \tag{7.1.22}$$

This is an exact evolution law for the macroscopic probability density.

7.2 Fokker-Planck Approximation

In order to make use of the generalized Fokker-Planck equation (7.1.22) we have to determine the diffusion kernels (7.1.20) more explicitly. This can be done exactly only for simple models while we have to resort to approximations in general.

It is useful to decompose the Liouville operator into four pieces:

$$\mathbf{L} = \mathbf{L}_0 + \mathbf{L}_R + \mathbf{L}_{0\to R} + \mathbf{L}_{R\to 0} \quad , \tag{7.2.1}$$

where

$$i\mathbf{L}_0 X = \{X,H_0\} \tag{7.2.2}$$

and

$$i\mathbf{L}_R X = \{X,H_R\} \tag{7.2.3}$$

describe the internal dynamics of the oscillator and the reservoir, respectively,

$$i\mathbf{L}_{0\to R} X = -\sum_{i=1}^{N} \frac{\partial X}{\partial \vec{p}_i} \cdot \frac{\partial V}{\partial \vec{q}_i} \tag{7.2.4}$$

describes the action of the oscillator on the reservoir, and

$$i\mathbf{L}_{R\to 0} X = -\frac{\partial X}{\partial \vec{P}} \cdot \frac{\partial V}{\partial \vec{Q}} = \frac{\partial X}{\partial \vec{P}} \cdot \vec{K}_R \tag{7.2.5}$$

describes the reverse, the action of the reservoir on the oscillator.

We now assume that the mass M of the oscillator is much larger than the mass m of the reservoir particles. Then, the mean thermal velocity $(k_B T\, M)^{1/2}$ of the oscillator is by a factor $(m/M)^{1/2}$ smaller than the mean thermal velocity $(k_B T\, m)^{1/2}$ of the lighter reservoir particles. Hence the position $\vec{Q}$ of the oscillator is a slowly varying quantity on the time scale set by the reservoir motion. Further, the momentum transfer in a collision between a reservoir particle and the oscillator is, for $M \gg m$, of the order of the mean thermal momentum of a reservoir particle, that is, $(k_B T\, m)^{1/2}$. This momentum transfer is small compared to the mean thermal momentum $(k_B T\, M)^{1/2}$ of the oscillator so that $\vec{P}$ is a slowly varying quantity too. Thus, we can approximate the generalized Fokker-Planck equation (7.1.21) according to the method given in Sect.4.4.[2] The above arguments can be sharpened by introducing scaled dimensionless momenta $\vec{P}^0 = \vec{P}(k_B T\, M)^{-1/2}$ and $\vec{p}_i^{\,0} = \vec{p}_i(k_B T\, m)^{-1/2}$. Then it is easily shown that

$$\mathbf{L} = \mathbf{L}_R + \mathbf{L}_{0\to R} + \mathcal{O}\left[\left(\frac{m}{M}\right)^{1/2}\right] \quad , \tag{7.2.6}$$

from where we see that the time rates of change of the macroscopic variables $\vec{P}$ and $\vec{Q}$ are of the order $(m/M)^{1/2}$.

Since $\mathbf{L}_R$ and $\mathbf{L}_{0\to R}$ act upon the reservoir variables only, we have

$$\mathbf{L}_R \mathbf{P} = \mathbf{L}_{0\to R} \mathbf{P} = 0 \tag{7.2.7}$$

which in connection with (7.2.6) yields

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[2] If we use the Fokker-Planck equation to calculate the relaxation from an initial nonequilibrium state we also have to assume that the initial velocity of the oscillator is small compared to the mean thermal velocity of the reservoir particles

$$e^{i\mathbf{L}(1-P)t} = e^{i(\mathbf{L}_R + \mathbf{L}_{0\to R})t} + \mathcal{O}\left[\left(\frac{m}{M}\right)^{1/2}\right] \quad . \tag{7.2.8}$$

Now, the matrix $\overleftrightarrow{\gamma}$ is explicitly of the second order in $\dot{\vec{P}}$, that is, of the order m/M. Thus, on inserting (7.2.8) into (7.1.20), we obtain by use of (4.1.3)

$$\gamma^{\nu\mu}(\vec{p},\vec{q},\vec{p}',\vec{q}',t) = \delta(\vec{p} - \vec{p}')\delta(\vec{q} - \vec{q}')\gamma_\infty^{\nu\mu}(\vec{q},t) + \mathcal{O}\left[\left(\frac{m}{M}\right)^{3/2}\right] \quad , \tag{7.2.9}$$

where

$$k_B T \gamma_\infty^{\nu\mu}(\vec{q},t) = \langle K_\infty^\nu(t) K_\infty^\mu(0);\vec{q}\rangle \quad . \tag{7.2.10}$$

Here

$$\vec{K}_\infty(t) = e^{i(\mathbf{L}_R + \mathbf{L}_{0\to R})t}\,\vec{K}_R \tag{7.2.11}$$

is the force exerted by the reservoir on an oscillator held fixed at the position $\vec{Q} = \vec{q}$. $\vec{K}_\infty(t)$ can also be looked upon as the force exerted on an infinitely heavy oscillator. The average in (7.2.10) is defined by

$$\begin{aligned} \langle K_\infty^\nu(t) K_\infty^\mu(0);\vec{q}\rangle &= \frac{\mathrm{tr}\{\rho_\beta \Psi_{\vec{p}\vec{q}} K_\infty^\nu(t) K_\infty^\mu(0)\}}{\mathrm{tr}\{\rho_\beta \Psi_{\vec{p}\vec{q}}\}} \\ &= \frac{\int dp_i dq_i\; e^{-\beta(H_R + V(\vec{q},\vec{q}_i)}\; K_\infty^\nu(t) K_\infty^\mu(0)}{\int dp_i dq_i\; e^{-\beta(H_R + V(\vec{q},\vec{q}_i))}} \quad , \end{aligned} \tag{7.2.12}$$

that is, an average over the equilibrium state of the reservoir in the presence of the oscillator acting as a force center at the position q.

Now, since

$$f(\vec{p},\vec{q},t - s) = f(\vec{p},\vec{q},t) + \mathcal{O}\left[\left(\frac{m}{M}\right)^{1/2}\right] \quad , \tag{7.2.13}$$

we obtain by inserting (7.2.9) into (7.1.22) the Fokker-Planck equation

$$\begin{aligned} \frac{\partial}{\partial t} f(\vec{p},\vec{q},t) &= \left(\frac{\partial}{\partial \vec{p}} \cdot \frac{\partial U(\vec{q})}{\partial \vec{q}} - \frac{\partial}{\partial \vec{q}} \cdot \frac{\vec{p}}{M}\right) f(\vec{p},\vec{q},t) \\ &\quad + \frac{\partial}{\partial \vec{p}} \cdot \overleftrightarrow{\zeta}(\vec{q}) \cdot \left(\frac{\vec{p}}{M} + k_B T \frac{\partial}{\partial \vec{p}}\right) f(\vec{p},\vec{q},t) + \mathcal{O}\left[\left(\frac{m}{M}\right)^{3/2}\right] \quad , \end{aligned} \tag{7.2.14}$$

where the $\zeta^{\nu\mu}$ are given by the Green-Kubo formula

$$k_B T\, \zeta^{\nu\mu}(\vec{q}) = \int_0^\infty ds\, \langle K_\infty^\nu(s) K_\infty^\mu(0);\vec{q}\rangle \quad . \tag{7.2.15}$$

In deriving (7.2.14) we have assumed that the time t is large compared with the decay time of the force correlation function (7.2.12). However, this correlation function will rapidly decay to zero because it contains only the rapid dynamical process of the light reservoir particles. Thus, (7.2.14) holds on the macroscopic time scale.

Clearly, the Fokker-Planck equation (7.2.14) follows straightforwardly from (4.4.7), and the formula (7.2.15) for the matrix $\overleftrightarrow{\zeta}$ is just a special case of

(4.4,8). We have reexamined here the formal approximation of Sect.4.4 in some detail for a concrete model where the Fokker-Planck approximation emerges naturally in a certain limit, namely, the limit $M \gg m$, thereby showing that the approach of Sect.4.4 can indeed be based on firmer grounds.

7.3 Brownian Motion and Impurity in a Harmonic Lattice

The only quantity to ba found in the Fokker-Planck equation (7.2.14) not yet explicitly known is the matrix $\overleftrightarrow{\zeta}$. However, in order to obtain further results from (7.2.15) we first have to specify the model in greater detail. Let us consider two special cases.

Brownian Motion. A heavy Brownian particle is immersed into a fluid of light particles. If we treat both the Brownian particle and the fluid particles as mass points, we are led to a microscopic model of Brownian motion belonging to the class of models introduced in Sect.7.1. There is no pinning potential $U(\vec{Q})$, and the internal interaction of the host fluid can be written

$$U_R(\vec{q}_i) = \frac{1}{2}\sum_{i\neq j} u(|\vec{q}_i - \vec{q}_j|) \quad , \tag{7.3.1}$$

while the interaction between the Brownian particle and the fluid reads

$$V(\vec{Q},\vec{q}_i) = \sum_i v(|\vec{Q} - \vec{q}_i|) \quad . \tag{7.3.2}$$

Here $u(r)$ and $v(r)$ are spherically symmetrical interaction potentials.

The Hamiltonian H of the system is invariant under translations and rotations. Consequently, (7.1.13) is automatically satisfied, and the force $\vec{K}_R$ depends on the distances $|\vec{Q} - \vec{q}_i|$ only. Thus, the correlation (7.2.12) is now independent of $\vec{q}$ and proportional to $\delta^{\nu\mu}$ so that the matrix (7.2.15) is of the form

$$\zeta^{\nu\mu}(\vec{q}) = \zeta\delta^{\nu\mu} \quad , \tag{7.3.3}$$

where ζ is a constant given by

$$\zeta = \frac{1}{3k_BT}\int_0^\infty ds\, \langle \vec{K}_\infty(s)\cdot\vec{K}_\infty(0)\rangle \quad . \tag{7.3.4}$$

This formula has first been derived by KIRKWOOD [13] on quite different lines. The Fokker-Planck equation (7.2.14) now takes the form

$$\left(\frac{\partial}{\partial t} + \frac{\vec{p}}{M}\cdot\frac{\partial}{\partial\vec{q}}\right)f(\vec{p},\vec{q},t) = \zeta\,\frac{\partial}{\partial\vec{p}}\cdot\left(\frac{\vec{p}}{M} + k_BT\,\frac{\partial}{\partial\vec{p}}\right)f(\vec{p},\vec{q},t) \quad . \tag{7.3.5}$$

Generally one puts in ζ as a phenomenological parameter since the evaluation of (7.3.4) is rather complicated.

A detailed discussion of the Fokker-Planck equation (7.3.5) is given in the review article of CHANDRASEKHAR [164]. If we integrate over $\vec{q}$, we obtain from (7.3.5) an equation for the momentum probability density $f(\vec{p},t)$ of the form

$$\frac{\partial}{\partial t} f(\vec{p},t) = \zeta \frac{\partial}{\partial \vec{p}} \cdot \left(\frac{\vec{p}}{M} + k_B T \frac{\partial}{\partial \vec{p}}\right) f(\vec{p},t) \quad . \tag{7.3.6}$$

The conditional momentum probability, that is, the Green's function of (7.3.6), is found to be

$$f(\vec{p},t|\vec{p}') = [2\pi\sigma(t)]^{-d/2} \exp\left\{- \frac{[\vec{p} - \vec{p}'(t)]^2}{2\sigma(t)}\right\} \quad , \tag{7.3.7}$$

where

$$\vec{p}'(t) = \vec{p}' \, e^{-(\zeta/M)t} \quad , \; \sigma(t) = k_B T \, M(1 - e^{-(2\zeta/M)t}) \quad . \tag{7.3.8}$$

Since the stationary momentum probability density reads

$$f_\beta(\vec{p}) = (2\pi k_B T \, M)^{-d/2} \exp\left\{- \frac{\vec{p}^2}{2k_B T \, M}\right\} \quad , \tag{7.3.9}$$

we obtain for the momentum autocorrelation function

$$\begin{aligned} \langle p^\nu(t) p^\mu(0) \rangle &= \int dp dp' \, p^\nu p'^\mu f(\vec{p},t|\vec{p}') f_\beta(\vec{p}') \\ &= \delta^{\nu\mu} k_B T \, M \, e^{-(\zeta/M)t} \quad . \end{aligned} \tag{7.3.10}$$

Other quantities of interest can also be calculated easily.

Impurity in a Harmonic Lattice. As a second example we consider a heavy impurity in a harmonic lattice consisting of N lighter particles. The Hamiltonian is taken to be

$$H = \frac{\vec{P}^2}{2M} + \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m} + U'(\vec{Q}) + U_R(\vec{q}_i) + V'(\vec{Q},\vec{q}_i) \quad . \tag{7.3.11}$$

$\vec{Q}$ and $\vec{q}_i$ are the deviations of the particles from their equilibrium positions. $U_R(\vec{q}_i)$ is the interaction of the harmonic lattice with the impurity held fixed at the position $\vec{Q} = 0$, and it is of the form

$$U_R(\vec{q}_i) = \frac{1}{2} \sum_{i,j,\nu,\mu} u_{ij}^{\nu\mu} q_i^\nu q_j^\mu \quad , \tag{7.3.12}$$

where $u_{ij}^{\nu\mu}$ is a positive and symmetric matrix

$$u_{ij}^{\nu\mu} = u_{ji}^{\mu\nu} \tag{7.3.13}$$

which has an inverse $n_{ij}^{\nu\mu}$ defined by

$$\sum_{j,\mu} n_{ij}^{\nu\mu} u_{jk}^{\mu\lambda} = \delta_{ik} \delta^{\nu\lambda} \quad . \tag{7.3.14}$$

$V'(\vec{Q},\vec{q}_i)$ is a bilinear interaction between the lattice and the impurity

$$V'(\vec{Q},\vec{q}_i) = \sum_{i,\nu,\mu} v_i^{\nu\mu} q_i^{\nu} Q^{\mu} \quad , \tag{7.3.15}$$

The potential $U'(\vec{Q})$ is not necessarily harmonic. The Hamiltonian can always be written in the form (7.3.11) if the internal interaction of the N lattice particles and their couplings to the impurity are harmonic.

The requirement (7.1.13) is not automatically satisfied. We add

$$\Delta U(\vec{Q}) = \frac{1}{2} \sum_{\nu,\mu} c^{\nu\mu} Q^{\nu} Q^{\mu} \tag{7.3.16}$$

with

$$c^{\nu\mu} = \sum_{i,j,\lambda,\sigma} n_{ij}^{\lambda\sigma} v_i^{\lambda\nu} v_j^{\sigma\mu} \tag{7.3.17}$$

to the potential $U'(\vec{Q})$ and subtract it from the bilinear interaction $V'(\vec{Q},\vec{q}_i)$ to give

$$U(\vec{Q}) = U'(\vec{Q}) + \Delta U(\vec{Q}) \tag{7.3.18}$$

and

$$V(\vec{Q},\vec{q}_i) = \sum_{i,\nu,\mu} v_i^{\nu\mu} \Big(q_i^{\nu} + \frac{1}{2} \sum_{\lambda} d_i^{\nu\lambda} Q^{\lambda} \Big) Q^{\mu} \quad , \tag{7.3.19}$$

where[3]

$$d_i^{\nu\lambda} = \sum_{j,\mu} n_{ij}^{\nu\mu} v_j^{\mu\lambda} \quad . \tag{7.3.20}$$

On adding (7.3.12,19) we obtain

$$U_R(\vec{q}_i) + V(\vec{Q},\vec{q}_i) = \frac{1}{2} \sum_{i,j,\nu,\mu} u_{ij}^{\nu\mu} \hat{q}_i^{\nu} \hat{q}_j^{\mu} \quad , \tag{7.3.21}$$

where

$$\hat{q}_i^{\nu} = q_i^{\nu} + \sum_{\mu} d_i^{\nu\mu} Q^{\mu} \quad . \tag{7.3.22}$$

Now, (7.1.12) gives only an irrelevant constant, and we are in the position to make use of our previous results.

From (7.3.19) we obtain by virtue of (7.3.20,22)

$$K_R^{\nu} = -\frac{\partial V}{\partial Q^{\nu}} = -\sum_{j,\mu} v_j^{\mu\nu} \hat{q}_j^{\mu} \quad . \tag{7.3.23}$$

The time evolution of the force $\vec{K}_{\infty}(t)$ introduced in (7.2.11) has to be calculated with the impurity held fixed at the position $\vec{Q} = \vec{q}$. Then, (7.3.22) is a time-independent transformation. In view of (7.3.21,23) this transformation removes the dependence on $\vec{Q}$ from the evolution law for $\vec{K}_{\infty}(t)$ and from the average (7.2.12).

---

[3] We note in passing that if the Hamiltonian (7.3.11) is invariant under translations of all coordinates $\vec{Q},\vec{q}_i$, e.g., if the interaction depends on the distances only, we simply have $d_i^{\nu\mu} = -\delta^{\nu\mu}$.

As a consequence the matrix $\overleftrightarrow{\zeta}$ is independent of $\vec{q}$, and (7.2.15) gives

$$k_B T \zeta^{\nu\mu} = \int_0^\infty ds \sum_{i,j,\lambda,\sigma} v_i^{\lambda\nu} v_j^{\sigma\mu} \langle q_i^\lambda(s) q_j^\sigma(0) \rangle \quad , \tag{7.3.24}$$

where the $\langle q_i^\nu(s) q_j^\mu(0) \rangle$ are the stationary correlations of the harmonic lattice with the impurity held fixed at $\vec{Q} = 0$. For some special cases, where the interaction (7.3.12) is particularly simple, the integrand of (7.3.24) has been calculated explicitly [156-160].

If we restrict ourselves to a one-dimensional lattice, we obtain a Fokker-Planck equation of the form

$$\frac{\partial}{\partial t} f(p,q,t) = \left(\frac{\partial}{\partial p}\frac{\partial U(q)}{\partial q} - \frac{\partial}{\partial q}\frac{p}{M}\right) f(p,q,t) + \zeta \frac{\partial}{\partial p}\left(\frac{p}{M} + k_B T \frac{\partial}{\partial p}\right) f(p,q,t) \quad . \tag{7.3.25}$$

As noted above, the potential $U(q)$ is not necessarily harmonic, so that the Fokker-Planck equation (7.3.25) may contain nonlinearities.

7.4 Renormalization of Transport Equations

In this section we study a system described by the Fokker-Planck equation (7.3.25). The potential $U(q)$ is symmetric in q and arbitrary otherwise, but later, the form

$$U(q) = \frac{r}{2} q^2 + \frac{u}{4} q^4 \tag{7.4.1}$$

will be used for explicit calculations. Introducing a state vector $\vec{\alpha} = (p,q)$, the Fokker-Planck equation (7.3.25) may be written in the standard form (4.4.17); that is,

$$\frac{\partial}{\partial t} f(\vec{\alpha},t) = \frac{\partial}{\partial \vec{\alpha}} \cdot \overleftrightarrow{L}^* \cdot \left[\frac{\partial F^*(\vec{\alpha})}{\partial \vec{\alpha}} + k_B T \frac{\partial}{\partial \vec{\alpha}}\right] f(\vec{\alpha},t) \quad , \tag{7.4.2}$$

where

$$F^*(\vec{\alpha}) = \frac{p^2}{2M} + U(q) \tag{7.4.3}$$

is the bare free energy, while

$$\overleftrightarrow{L}^* = \begin{pmatrix} \zeta & 1 \\ -1 & 0 \end{pmatrix} \tag{7.4.4}$$

is the matrix of bare transport coefficients.

The bare thermodynamic forces (4.5.6) read

$$\vec{\mu}^* = \frac{\partial F^*}{\partial \vec{\alpha}} = \left(\frac{p}{M} , \frac{\partial U}{\partial q}\right) \quad , \tag{7.4.5}$$

and the bare transport laws (4.5.5) are

$$\dot{\vec{a}} = -\overleftrightarrow{L}^{*} \cdot \vec{\mu}^{*}(\vec{\alpha}) \tag{7.4.6}$$

or more explicitly

$$\dot{p} = -\frac{\partial U}{\partial q} - \frac{\zeta}{M}\, p \quad ,$$

$$\dot{q} = \frac{1}{M}\, p \quad . \tag{7.4.7}$$

These are the familiar phenomenological equations of motion for a damped nonlinear oscillator. To obtain the renormalized transport equations we have to carry out the renormalization procedure discussed in Sects.4.5 and 4.6. Here, we shall restrict ourselves to the linear regime near equilibrium.

For the present problem the partition function (4.5.19) reads

$$Z(\vec{\mu}) = \int d\alpha \; e^{-\beta(F^{*}(\vec{\alpha}) - \vec{\mu}\cdot\vec{\alpha})} \tag{7.4.8}$$

where $\vec{\mu}$ is the vector of renormalized thermodynamic forces which is determined as a function of the mean values $\langle\vec{\alpha}\rangle$ by [cf. (4.5.15)]

$$\langle\vec{\alpha}\rangle = k_B T \, \frac{\partial \ln Z(\vec{\mu})}{\partial \vec{\mu}} \quad . \tag{7.4.9}$$

At equilibrium the mean values vanish, and we obtain from (7.4.8) and (7.4.9) by disregarding terms of the second order in $\langle q\rangle$

$$\vec{\mu} = \left(\frac{\langle p\rangle}{M} \, , \, \frac{\langle q\rangle}{\beta\sigma}\right) \quad , \tag{7.4.10}$$

where

$$\sigma = \frac{\int dq \, q^2 \, e^{-\beta U(q)}}{\int dq \, e^{-\beta U(q)}} = \langle q^2\rangle_\beta \tag{7.4.11}$$

is the equilibrium variance of q. Clearly, there is no renormalization of the thermodynamic force conjugate to the momentum since the stationary momentum probability density is Gaussian.

The bare transport matrix $\overleftrightarrow{L}^{*}$ does not depend on the state $\vec{\alpha}$. Hence, it follows from (4.6.12) that the instantaneous part of the renormalized transport matrix coincides with the bare transport matrix

$$\overleftrightarrow{L} = \overleftrightarrow{L}^{*} = \begin{pmatrix} \zeta & 1 \\ -1 & 0 \end{pmatrix} \quad . \tag{7.4.12}$$

The retarded part, $\overleftrightarrow{\Lambda}(t-s)$, of the renormalized transport matrix is a functional of the mean values $\langle\vec{\alpha}(u)\rangle$ in the time interval $s \leq u \leq t$. However, as far as the linear transport laws are concerned, we can evaluate (4.6.15) for equilibrium mean values $\langle\vec{\alpha}(u)\rangle_\beta = 0$. To this end we first provide some useful relations.

For vanishing mean values the projection operator (4.6.3) reduces to $P_\beta \equiv P[\langle\vec{\alpha}\rangle = 0]$, which is of the form

$$P_\beta X(\vec{\alpha}) = f_\beta(\vec{\alpha})\Big(\int d\alpha\, X(\vec{\alpha}) + \frac{p}{k_B T M}\int d\alpha\, pX(\vec{\alpha}) + \frac{q}{\sigma}\int d\alpha\, qX(\vec{\alpha})\Big) \quad , \tag{7.4.13}$$

where

$$f_\beta(\vec{\alpha}) = \frac{e^{-\beta F^*(\vec{\alpha})}}{Z(\vec{\mu} = 0)} \tag{7.4.14}$$

is the equilibrium probability density. In deriving (7.4.13) we have made use of

$$\left.\frac{\partial \bar{f}(\vec{\alpha},\langle\vec{\alpha}\rangle)}{\partial\langle p\rangle}\right|_{\langle\vec{\alpha}\rangle=0} = \frac{p}{k_B T M} f_\beta(\vec{\alpha}) \quad , \quad \left.\frac{\partial \vec{f}(\alpha,\langle\vec{\alpha}\rangle)}{\partial\langle q\rangle}\right|_{\langle\vec{\alpha}\rangle=0} = \frac{q}{\sigma} f_\beta(\vec{\alpha}) \quad , \tag{7.4.15}$$

where

$$\bar{f}(\vec{\alpha},\langle\vec{\alpha}\rangle) = \frac{f_\beta(\vec{\alpha})\; e^{\beta\vec{\mu}\cdot\vec{\alpha}}}{\int d\alpha\, f_\beta(\vec{\alpha})\; e^{\beta\vec{\mu}\cdot\vec{\alpha}}} \tag{7.4.16}$$

is the relevant probability density introduced in (4.5.8). From (7.4.14) we obtain by virtue of (7.4.5)

$$\frac{\partial}{\partial\vec{\alpha}} f_\beta(\vec{\alpha}) = -\beta f_\beta(\vec{\alpha})\vec{\mu}^*(\vec{\alpha}) \quad , \tag{7.4.17}$$

and further, by use of (7.4.13)

$$(1 - P_\beta)\,\frac{\partial}{\partial p}\, f_\beta(\vec{\alpha}) = 0 \tag{7.4.18}$$

$$(1 - P_\beta)\,\frac{\partial}{\partial q}\, f_\beta(\vec{\alpha}) = -\beta f_\beta(\vec{\alpha})\Delta\mu(q) \quad ,$$

where

$$\Delta\mu(q) = \frac{\partial U(q)}{\partial q} - \frac{q}{\beta\sigma} \quad . \tag{7.4.19}$$

The right-hand sides of (7.4.18) are proportional to the differences between the bare and the renormalized thermodynamic forces.

From (4.4.18) we see that for the present model the Fokker-Planck drift coincides with the deterministic drift:

$$\vec{K}(\vec{\alpha}) = (K_p(\vec{\alpha}),\, K_q(\vec{\alpha})) = -\overleftrightarrow{L}^*(\vec{\alpha})\cdot\vec{\mu}^*(\vec{\alpha}) \quad . \tag{7.4.20}$$

Further we find by use of (7.4.6,7,13,19)

$$\int d\alpha\, K_p(\vec{\alpha})(1 - P_\beta)X(\vec{\alpha}) = -\int d\alpha\, \Delta\mu(q)X(\vec{\alpha}) \quad ,$$

$$\int d\alpha\, K_q(\vec{\alpha})(1 - P_\beta)X(\vec{\alpha}) = 0 \quad . \tag{7.4.21}$$

Now, from (7.4.18,21) it is readily seen that for vanishing mean values, $\langle\vec{\alpha}(u)\rangle = 0$, the retarded part (4.6.15) of the renormalized transport matrix takes the form

$$\overleftrightarrow{\Lambda}(t-s) = \begin{pmatrix} \zeta_r(t-s) & 0 \\ 0 & 0 \end{pmatrix} , \tag{7.4.22}$$

where

$$\zeta_r(t) = \beta \int d\alpha\, \Delta\mu(q)\, e^{-i(1-\mathcal{P}_\beta)\mathcal{L}t} \Delta\mu(q) f_\beta(\vec{\alpha}) \quad . \tag{7.4.23}$$

On combining (7.4.10,12,22) we obtain for the renormalized transport equation (4.6.16) in the linear approximation

$$\frac{\partial}{\partial t}\langle p(t)\rangle = -\frac{1}{\beta\sigma}\langle q(t)\rangle - \frac{\zeta}{M}\langle p(t)\rangle - \int_0^t ds\, \frac{\zeta_r(t-s)}{M}\langle p(s)\rangle \quad , \tag{7.4.24}$$

$$\frac{\partial}{\partial t}\langle q(t)\rangle = \frac{1}{M}\langle p(t)\rangle \quad .$$

These equations govern the mean relaxation in the vicinity of the equilibrium state, and they are actually of the same form as (3.4.11) discussed earlier. However, while (3.4.11) are formally exact, (7.4.24) hold in the Fokker-Planck approximation only. The renormalized transport equations (7.4.24) also determine the dynamics of correlations of fluctuations about equilibrium. The corresponding evolution laws, which are immediately written down in analogy to (3.4.21), are an exact consequence of the Fokker-Planck equation (7.4.2).

Notice that by simply linearizing the Fokker-Planck equation (7.4.2) we obtain

$$\frac{\partial}{\partial t}\langle p(t)\rangle = -r\langle q(t)\rangle - \frac{\zeta}{M}\langle p(t)\rangle \quad ,$$

$$\frac{\partial}{\partial t}\langle q(t)\rangle = \frac{1}{M}\langle p(t)\rangle \quad , \tag{7.4.25}$$

where we have assumed that the potential U(q) is of the form (7.4.1). On comparing (7.4.24,25) we see that the nonlinearity renormalizes r and leads to a retarded renormalized damping.[4] It might be worth mentioning that this memory term does not describe non-Markovian effects. Rather it is entirely due to the nonlinearity of the Markovian Fokker-Planck model under consideration.

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[4] When (7.4.24) is written in Fourier space, the memory term in (7.4.24) gives rise to a frequency-dependent damping.

7.5 Expansion in Terms of k_B

To make use of the renormalized transport equations (7.4.24) we have to determine σ and $\zeta_r(t)$ explicitly. The potential $U(q)$ is taken to be of the form (7.4.1) with r and u positive. This system is also known as the Duffing oscillator [162]. Since the bare transport equations (7.4.7) and the renormalized transport equations (7.4.24) have both the stable stationary solution $p = q = 0$, we expect that the effects of fluctuations leading to the renormalization of the transport laws can be treated in a perturbative way.[5] The effects of fluctuations vanish in the deterministic limit $k_B \to 0$. Hence the explicit k_B dependence of the Fokker-Planck equation can be used to set up a perturbation scheme where k_B is used as an expansion parameter in order to calculate fluctuation corrections to the deterministic theory [54].

With (7.4.1) we obtain from (7.4.11) after an obvious change of the integration variable

$$\sigma = \langle q^2\rangle_\beta = \frac{k_B T}{r}\,\frac{\int d\xi\,\xi^2\,e^{-\frac{1}{2}\xi^2-\frac{1}{4}\tilde{u}\xi^4}}{\int d\xi\,e^{-\frac{1}{2}\xi^2-\frac{1}{4}\tilde{u}\xi^4}}\quad, \tag{7.5.1}$$

where

$$\tilde{u} = \frac{k_B T\,u}{r^2}\quad. \tag{7.5.2}$$

By expanding in terms of k_B we find

$$\sigma = \frac{k_B T}{r}\,(1 - 3\tilde{u} + 24\tilde{u}^2) + O(k_B^4)\quad. \tag{7.5.3}$$

Here a formal expansion in terms of k_B amounts to an expansion in terms of the dimensionless nonlinearity parameter $\tilde{u}$.

Next we observe that (7.4.23) may be transformed to read

$$\zeta_r(t) = \beta\langle\Delta\mu\, e^{-iL^T(1-P_\beta^T)t}\,\Delta\mu\rangle_\beta\quad, \tag{7.5.4}$$

where $\langle\ldots\rangle_\beta$ denotes the average over the equilibrium probability density (7.4.14). P_β^T is transposed to the projection operator (7.4.13), that is,

$$P_\beta^T X(\vec{a}) = \langle X\rangle_\beta + \frac{p}{k_B T M}\langle pX\rangle_\beta + \frac{q}{\sigma}\langle qX\rangle_\beta\quad, \tag{7.5.5}$$

while $-iL^T$ is transposed to the Fokker-Planck operator (4.6.2). Using (7.4.1,3,4) we find

$$-iL^T X(\vec{a}) = \left[\left(-rq-uq^3-\frac{\zeta}{M}\,p\right)\frac{\partial}{\partial p} + \frac{p}{M}\frac{\partial}{\partial q} + k_B T\zeta\,\frac{\partial^2}{\partial p^2}\right]X(\vec{a})\quad. \tag{7.5.6}$$

---

[5] This is not so in the bistable case $r < 0$ where naive perturbation methods fail [127-134].

This operator is also called the backward Fokker-Planck operator.

For further evaluation it is convenient to write $\zeta_r(t)$ in the form

$$\zeta_r(t) = \beta\langle\Delta\mu\lambda(t)\rangle_\beta \quad , \tag{7.5.7}$$

where

$$\lambda(\vec{\alpha},t) = e^{-iL^T(1-P_\beta^T)t}\Delta\mu(q) \quad . \tag{7.5.8}$$

Using (7.4.1), we obtain from (7.4.19)

$$\Delta\mu(q) = (r - \frac{1}{\beta\sigma})q + uq^3 \quad , \tag{7.5.9}$$

and (7.4.17) gives

$$\frac{\partial}{\partial q}\, f_\beta(\vec{\alpha}) = -\beta f_\beta(\vec{\alpha})(rq + uq^3) \quad . \tag{7.5.10}$$

Thus we find by inserting (7.5.9) into (7.5.7)

$$\zeta_r(t) = \left\langle\frac{\partial\lambda(t)}{\partial q}\right\rangle_\beta - \frac{1}{\sigma}\langle q\lambda(t)\rangle_\beta \quad . \tag{7.5.11}$$

The equilibrium averages on the right-hand side of (7.5.11) can now be expanded in terms of k_B. With (7.5.3) we get

$$\zeta_r(t) = \frac{k_B^2T^2u}{r^3}\left[\frac{\partial^3}{\partial q^3}\,\lambda(\vec{\alpha},t)\right]_{\vec{\alpha}=0} + O(k_B^3) \quad . \tag{7.5.12}$$

Furthermore, in this approximation the time evolution of $\lambda(\vec{\alpha},t)$ can be determined from the bare linearized transport laws:

$$\dot{p}(t) = -\,rq(t) - \frac{\zeta}{M}\,p(t) \quad , \quad \dot{q}(t) = \frac{1}{M}\,p(t) \quad , \tag{7.5.13}$$

which have for $p(0) = 0$ the solution

$$q(t) = q(0)\;e^{-(\zeta t/2M)}\left(\mathrm{ch}\,\frac{\eta t}{2M} + \frac{\zeta}{\eta}\,\mathrm{sh}\,\frac{\eta t}{2M}\right) \quad , \tag{7.5.14}$$

where

$$\eta = (\zeta^2 - 4rM)^{1/2} \quad . \tag{7.5.15}$$

Equation (7.5.14) holds for real and imaginary η and also in the aperiodic case for $\eta \to 0$.

Using (7.5.8,9,14), we obtain

$$\left[\frac{\partial^3}{\partial q^3}\,\lambda(\vec{\alpha},t)\right]_{\vec{\alpha}=0} = u\;e^{-(3\zeta t/2M)}\left(\mathrm{ch}\,\frac{\eta t}{2M} + \frac{\zeta}{\eta}\,\mathrm{sh}\,\frac{\eta t}{2M}\right)^3 + O(k_B) \quad , \tag{7.5.16}$$

which combines with (7.5.12) to give

$$\zeta_r(t) \approx \tilde{u}^2 r\, e^{-(3\zeta t/2M)} \left(\mathrm{ch}\,\frac{\eta t}{2M} + \frac{\zeta}{} \,\mathrm{sh}\,\frac{\eta t}{2M}\right)^3 + O(k_B^3) \quad . \tag{7.5.17}$$

Again the expansion is actually in terms of the nonlinearity parameter $\tilde{u}$ introduced in (7.5.2). Equations (7.5.3,17) give the first nontrivial terms of a perturbative calculation of the renormalized thermodynamic forces and transport coefficients.

8. Simple Fluids

Our objective in this chapter is to derive by statistical-mechanical methods a generalization of the phenomenological equations of motion for simple one-component fluids and to show how the phenomenological equations themselves can be recovered as an approximation. Our treatment is presented as an application of statistical thermodynamics, which has been discussed from a general point of view in Chap.3. Also, since the macroscopic variables of a fluid are local densities of conserved quantities, it is shown how the general theory applies to systems described by local variables.

In Sect.8.1 we summarize some general results for systems with local conservation laws and bring the equations of motion put forward in Chap.3 into a form which is appropriate for systems with a fluctuating local energy density. In Sect.8.2 we derive the conservation laws in simple fluids and obtain molecular expressions for the local fluxes of the conserved quantities. The properties of the generalized canonical probability density for fluids are discussed in Sect.8.3. We then evaluate the molecular expressions for the organized fluxes explicitly in Sect.8.4. This yields Euler's equations of motion for ideal adiabatic fluids.

In Sect.8.5 the disorganized motion is evaluated in an approximation where terms of the third order in the wavenumber k are disregarded. We show that in this approximation the fluid is described by the nonlinear phenomenological equations of hydromechanics [87]. Finally, in Sect.8.6, we obtain Langevin equations for the fluctuations about the mean. The theory is illustrated by applying it to a steady-state nonequilibrium fluid. In particular, the structure factor for light scattering in the presence of a temperature gradient is determined.

Our approach [165] has features in common with several other works. Exact evolution equations for the mean values of the hydrodynamic variables have been put forward by PICCIRELLI [166] and studied in greater detail by KAWASAKI and GUNTON [107] and ERNST et al. [167]. While these papers do not obtain Langevin equations for the fluctuations, the transport kernels are evaluated in [107,167] in approximations going beyond the one discussed in Sect.8.5. Our investigation is also related to the recent work by OPPENHEIM and LEVINE [168]. We avoid the introduction of a reference equilibrium temperature, however, and relate some more details to the dynamics of fluctuations.

By disregarding memory effects on the level of statistical thermodynamics one ignores the complicated nonanalytic structure of the renormalized transport coefficients, which is particularly important near the gas-liquid critical point, but which also leads to nontrivial but small corrections outside of the critical regime [78,169]. Rather than evaluating the retarded transport kernels more precisely [107,167], one may start out from a more complete Fokker-Planck description of fluids which is implicit in the work of GREEN [170]. Fokker-Planck models ignoring the sound modes have been used in the study of the gas-liquid critical point [4,49], and noncritical fluids have been treated by Fokker-Planck methods in the incompressible [169,171] and isothermal [172] approximations. More recently, Fokker-Planck equations or equivalent nonlinear Langevin equations have also been employed to treat nonequilibrium fluids [138,173].

We shall not discuss the Fokker-Planck description of fluids explicitly here. A Fokker-Planck equation can, however, be derived in a rather straightforward manner by applying the theory in Chap.4. The resulting equation of motion in the Markovian approximation is given in the appendix of [138]. It should be noted that in a Fokker-Planck description the spatial variation of the hydrodynamic variables has to be restricted by introducing a cutoff wavenumber [170] because otherwise singular behavior in the averaged quantities is found [174]. This is not necessary on the level of statistical thermodynamics, since the spatial variations contributing to the molecular expressions are controlled by the variations of the conjugate thermodynamic fields.

8.1 Systems with Local Conversation Laws

In this section we consider some general properties of classical systems where the macroscopic variables $A_i(\vec{x},t)$ are local densities of conserved quantities and where the energy density is among the macroscopic variables.[1] The conservation laws read

$$A_i(\vec{x},t) = i\mathbb{L}A_i(\vec{x},t) = -\sum_{\nu} \frac{\partial}{\partial x^{\nu}} J_i^{\nu}(\vec{x},t) \quad , \tag{8.1.1}$$

where ν labels the space components, while the $\vec{J}_i(\vec{x},t)$ are the local fluxes of the conserved quantities. The exact equations of motion derived in Chap.3 are easily transcribed for systems with macroscopic variables labeled by the continuous index $(i,\vec{x})$, and some minor modifications are appropriate. We only give the basic definitions and results for later use.

---

[1] Often the energy density is not included into the set of macroscopic variables and the system is treated in an isothermal approximation. For isothermal models some modifications of the general approach explained below (like the replacement of the free energy functional by an entropy functional) are not necessary and the previous results can be used directly.

Since the energy density is one of the conserved densities, the Hamiltonian H is among the macroscopic variables, and the generalized canonical probability density (3.1.3) may now be written

$$\bar{\rho}(t) = Z^{-1}(t)\,\exp\left\{-\frac{1}{k_B}\int dx \sum_i \lambda_i(\vec{x},t)A_i(\vec{x})\right\} \quad , \tag{8.1.2}$$

where $\lambda_i(\vec{x},t)$ and $Z(t)$ are determined by

$$\mathrm{tr}\{\bar{\rho}(t)\} = 1$$

$$\mathrm{tr}\{\bar{\rho}(t)A_i(\vec{x},t)\} = \mathrm{tr}\{\rho(t)A_i(\vec{x},t)\} = a_i(\vec{x},t) \quad . \tag{8.1.3}$$

Further, the proper thermodynamic potential is now the entropy functional

$$S(t) = -k_B\,\mathrm{tr}\{\bar{\rho}(t)\ln\bar{\rho}(t)\} \quad , \tag{8.1.4}$$

and we have

$$\lambda_i(\vec{x},t) = \frac{\delta S(t)}{\delta a_i(\vec{x},t)} \quad ; \quad a_i(\vec{x},t) = -k_B\,\frac{\delta \ln Z(t)}{\delta\lambda_i(\vec{x},t)} \quad . \tag{8.1.5}$$

With (8.1.1) the organized drift (2.5.6) takes the form

$$v_i(\vec{x},t) = -\sum_\nu \frac{\partial}{\partial x^\nu}\langle J_i^\nu(\vec{x},t)\rangle_{or} \quad , \tag{8.1.6}$$

where

$$\langle\vec{J}_i(\vec{x},t)\rangle_{or} = \mathrm{tr}\{\bar{\rho}(t)\vec{J}_i(\vec{x})\} \tag{8.1.7}$$

is the mean organized flux.[2] Using (8.1.2), we get

$$iL\bar{\rho}(t) = -\frac{1}{k_B}\,\bar{\rho}(t)\int dx \sum_i \lambda_i(\vec{x},t)\; iLA_i(\vec{x}) \quad , \tag{8.1.8}$$

and by virtue of the conservation laws (8.1.1)

$$iL\bar{\rho}(t) = -\frac{1}{k_B}\,\bar{\rho}(t)\int dx \sum_{i,\nu} J_i^\nu(\vec{x})\,\frac{\partial}{\partial x^\nu}\lambda_i(\vec{x},t) \quad . \tag{8.1.9}$$

Because of (8.1.1,9), the disorganized drift (2.5.16) may be written

$$\gamma_i(\vec{x},t) = -\sum_\nu \frac{\partial}{\partial x^\nu}\langle J_i^\nu(\vec{x},t)\rangle_{di} \tag{8.1.10}$$

where the mean disorganized flux is given by

$$\langle J_i^\nu(\vec{x},t)\rangle_{di} = \int_0^t ds \int dy \sum_{j,\mu} R_{ij}^{\nu\mu}(\vec{x}t,\vec{y}s)\,\frac{\partial}{\partial y^\mu}\lambda_j(\vec{y},s) \tag{8.1.11}$$

with

$$R_{ij}^{\nu\mu}(\vec{x}t,\vec{y}s) = \frac{1}{k_B}\,\mathrm{tr}\{\bar{\rho}(s)J_j^\mu(\vec{y})[1-P(s)]G(s,t)J_i^\nu(\vec{x})\} \quad . \tag{8.1.12}$$

---

[2] Since the energy density is among the macroscopic variables, the representation (3.2.3,4) of the organized drift is not appropriate here. For fluids a corresponding representation will be given later.

The generalized transport equations (3.2.1) for the mean values $a_i(x,t)$ of the macroscopic variables are

$$\frac{\partial}{\partial t} a_i(\vec{x},t) = - \sum_{\nu} \frac{\partial}{\partial x^{\nu}} \Big[\langle J_i^{\nu}(\vec{x},t)\rangle_{or} + \int_0^t ds \int dy \sum_{j,\mu} R_{ij}^{\nu\mu}(\vec{x}t,\vec{y}s) \frac{\partial}{\partial y^{\mu}} \lambda_j(\vec{y},s) \Big] \quad . \tag{8.1.13}$$

These exact equations of motion are nonlocal in time and space. In general, even the organized fluxes $\langle\vec{J}_i(\vec{x},t)\rangle_{or}$ depend on the $a_j(\vec{y},t)$ at different positions $\vec{y}$. The disorganized fluxes $\langle\vec{J}_i(\vec{x},t)\rangle_{di}$ are caused by the gradients of the $\lambda_j(\vec{y},s)$ at different positions $\vec{y}$ and earlier times s. The effect of these gradients on the time rates of change at position $\vec{x}$ and time t is determined by the $R_{ij}^{\nu\mu}(\vec{x}t,\vec{y}s)$ which are functionals of the $a_i(\vec{x},t)$.

Finally, the Langevin equations (3.3.1) are obtained by linearizing the generalized transport equations about the mean path and adding the random forces. Hence

$$\frac{\partial}{\partial t} \delta A_i(\vec{x},t) = - \sum_{\nu} \frac{\partial}{\partial x^{\nu}} \Bigg[\int dy \sum_j \frac{\delta\langle J_i^{\nu}(\vec{x},t)\rangle_{or}}{\delta a_j(\vec{y},t)} \delta A_j(\vec{y},t) + \int_0^t ds \int dy \sum_j \frac{\delta\langle J_i^{\nu}(\vec{x},t)\rangle_{di}}{\delta a_j(\vec{y},s)} \delta A_j(\vec{y},s) + \xi_j^{\nu}(\vec{x},t) \Bigg] \quad , \tag{8.1.14}$$

where we have taken into account the fact that the random forces are of the form

$$F_i(\vec{x},t) = - \sum_{\nu} \frac{\partial}{\partial x^{\nu}} \xi_i^{\nu}(\vec{x},t) \quad , \tag{8.1.15}$$

where the

$$\vec{\xi}_i(\vec{x},t) = [1 - P(0)]G(0,t)\vec{J}_i(\vec{x}) \tag{8.1,16}$$

are the random fluxes with the properties

$$\langle\vec{\xi}_i(\vec{x},t)\rangle = 0$$

$$(\vec{\xi}_i(\vec{x},t) \;,\; \delta A_j(\vec{y},0)) = 0 \quad . \tag{8.1.17}$$

8.2 Conservation Laws in Simple Fluids

We consider a simple one-component classical fluid described by the Hamiltonian

$$H = \sum_a \frac{\vec{p}_a^{\,2}}{2m} + \frac{1}{2} {\sum_{a,b}}' \varphi(r_{ab}) \quad , \tag{8.2.1}$$

where $\vec{p}_a$, $\vec{x}_a$ are the phase space variables of the a^th particle. The sums run over all particles, and a prime indicates that terms with a = b are omitted. $\varphi(r)$ is a spherically symmetric potential depending on the distance

$$r_{ab} = |\vec{x}_a - \vec{x}_b| \qquad (8.2.2)$$

only. The macrovariables $A_i(\vec{x})$, $(i = 0,1,\ldots,4 = 0,\nu,4)$ and the conjugate thermodynamic fields $\lambda_i(\vec{x})$ are given by

$$\begin{array}{c|c|c} i & A_i(\vec{x}) & \lambda_i(\vec{x}) \\ \hline 0 & n(\vec{x}) & -\dfrac{\nu(\vec{x})}{T(\vec{x})} \\ \nu & g^\nu(\vec{x}) & -\dfrac{v^\nu(\vec{x})}{T(\vec{x})} \\ 4 & e(\vec{x}) & \dfrac{1}{T(\vec{x})} \end{array} \qquad (8.2.3)$$

where

$$n(\vec{x}) = \sum_a \delta(\vec{x} - \vec{x}_a) \qquad (8.2.4)$$

defines the particle density,

$$g^\nu(\vec{x}) = \sum_a p_a^\nu \delta(\vec{x} - \vec{x}_a) \qquad (8.2.5)$$

defines the momentum density, and

$$e(\vec{x}) = \sum_a \left[\frac{\vec{p}_a^{\,2}}{2m} + \frac{1}{2}\sum_b{}' \varphi(r_{ab})\right]\delta(\vec{x} - \vec{x}_a) \qquad (8.2.6)$$

defines the energy density. The meaning of the conjugate fields $\lambda_i(\vec{x})$ will be clear from below.

The time rates of change of the macroscopic variables are given by

$$\dot{A}_i(\vec{x}) = iLA_i(\vec{x}) = \{A_i(\vec{x}),H\} \quad . \qquad (8.2.7)$$

These Poisson brackets can be evaluated with the use of

$$\{\delta(\vec{x} - \vec{x}_a),H\} = -\sum_\nu \frac{\partial}{\partial x^\nu}\frac{p_a^\nu}{m}\delta(\vec{x} - \vec{x}_a) \qquad (8.2.8)$$

and

$$\delta(\vec{x} - \vec{x}_a) - \delta(\vec{x} - \vec{x}_b)$$

$$= -\sum_\nu \frac{\partial}{\partial x^\nu}\frac{x_a^\nu - x_b^\nu}{r_{ab}}\int_0^{r_{ab}} dr\,\delta\left(\vec{x} - \vec{x}_a - r\,\frac{\vec{x}_b - \vec{x}_a}{r_{ab}}\right) \quad . \qquad (8.2.9)$$

In this way we find the conservation laws:

$$\dot{n}(\vec{x}) = -\sum_{\nu} \frac{\partial}{\partial x^{\nu}} \frac{1}{m} g^{\nu}(\vec{x}) \quad ,$$

$$\dot{g}^{\nu}(\vec{x}) = -\sum_{\mu} \frac{\partial}{\partial x^{\mu}} \sigma^{\nu\mu}(\vec{x}) \quad ,$$

$$\dot{e}(\vec{x}) = -\sum_{\nu} \frac{\partial}{\partial x^{\nu}} \tau^{\nu}(\vec{x}) \quad , \tag{8.2.10}$$

where

$$\sigma^{\nu\mu}(\vec{x}) = \sum_{a} \frac{p_a^{\nu} p_a^{\mu}}{m} \delta(\vec{x} - \vec{x}_a) - \frac{1}{2} \sum_{a,b}{}' \frac{(x_a^{\nu} - x_b^{\nu})(x_a^{\mu} - x_b^{\mu})}{r_{ab}^2} \frac{d\varphi(r_{ab})}{dr_{ab}} \; . \times \int_0^{r_{ab}} dr\, \delta\left(\vec{x} - \vec{x}_a - r\, \frac{\vec{x}_b - \vec{x}_a}{r_{ab}}\right) \tag{8.2.11}$$

defines the stress tensor and

$$\tau^{\nu}(\vec{x}) = \sum_{a} \frac{p_a^{\nu}}{m} \left[\frac{\vec{p}_a^{\,2}}{2m} + \frac{1}{2} \sum_{b}{}' \varphi(r_{ab})\right] \delta(\vec{x} - \vec{x}_a) - \frac{1}{4} \sum_{a,b}{}' \sum_{\mu} \frac{(x_a^{\nu} - x_b^{\nu})(x_a^{\mu} - x_b^{\mu})}{r_{ab}^2} \frac{p_a^{\mu} + p_b^{\mu}}{m} \frac{d\varphi(r_{ab})}{dr_{ab}} \; . \times \int_0^{r_{ab}} dr\, \delta\left(\vec{x} - \vec{x}_a - r\, \frac{\vec{x}_b - \vec{x}_a}{r_{ab}}\right) \tag{8.2,12}$$

defines the energy flux.

8.3 Generalized Canonical Probability Density

Introducing the inverse tamperature field

$$\beta(\vec{x},t) = \frac{1}{k_B T(\vec{x},t)} \quad , \tag{8.3.1}$$

we obtain from (8.1.2) and (8.2.3) for the generalized canonical probability density the form

$$\bar{\rho}(t) = Z^{-1}(t) \exp\left\{-\int dx\, \beta(\vec{x},t)[e(\vec{x}) - \vec{v}(\vec{x},t) \cdot \vec{g}(\vec{x}) - \nu(\vec{x},t) n(\vec{x})]\right\} \quad . \tag{8.3.2}$$

On defining a transformation $\mathbf{S}(t)$ of phase functions $X(\vec{p}_a,\vec{x}_a)$ by

$$\mathbf{S}(t) X(\vec{p}_a,\vec{x}_a) = X(\vec{p}_a - m\vec{v}(\vec{x}_a,t),\vec{x}_a) \quad , \tag{8.3.3}$$

one easily establishes that

$$\mathrm{tr}\{\mathbf{S}(t)X\} = \mathrm{tr}\{X\} \ , \tag{8.3.4}$$

$$\mathbf{S}(t)n(\vec{x}) = n(\vec{x}) \ , \tag{8.3.5}$$

$$\mathbf{S}(t)\vec{g}(\vec{x}) = \vec{g}(\vec{x}) - m\vec{v}(\vec{x},t)n(\vec{x}) \ , \tag{8.3.6}$$

$$\mathbf{S}(t)e(\vec{x}) = e(\vec{x}) - \vec{v}(\vec{x},t)\cdot\vec{g}(\vec{x}) + \frac{m}{2}v^2(\vec{x},t)n(\vec{x}) \ . \tag{8.3.7}$$

Now, the generalized canonical probability density matrix may be written

$$\tilde{\rho}(t) = \mathbf{S}(t)\hat{\rho}(t) \ , \tag{8.3.8}$$

where

$$\hat{\rho}(t) = Z^{-1}(t)\exp\left\{-\int dx\,\beta(\vec{x},t)[e(\vec{x}) - \mu(\vec{x},t)n(\vec{x})]\right\} \tag{8.3.9}$$

with

$$\mu(\vec{x},t) = \nu(\vec{x},t) + \frac{m}{2}v^2(\vec{x},t) \ . \tag{8.3.10}$$

Since $e(\vec{x})$ is quadratic in the momenta, the probability density $\hat{\rho}(t)$ is Gaussian with respect to the momenta and we have

$$\begin{aligned}\mathrm{tr}\{\hat{\rho}(t)\vec{g}(\vec{x})\} &= \mathrm{tr}\{\tilde{\rho}(t)\mathbf{S}(t)\vec{g}(\vec{x})\} \\ &= \langle\vec{g}(\vec{x},t)\rangle - \vec{v}(\vec{x},t)m\langle n(\vec{x},t)\rangle = 0 \ ,\end{aligned} \tag{8.3.11}$$

where we have made use of (8.3,4,6,8) and the fact that $\tilde{\rho}(t)$ yields correct mean values of the macroscopic variables. From (8.3.11) we see that

$$\vec{v}(\vec{x},t) = \frac{\langle\vec{g}(\vec{x},t)\rangle}{m\langle n(\vec{x},t)\rangle} \tag{8.3.12}$$

is the flow velocity. Using (8.3,5,7,11), we also find

$$\mathrm{tr}\{\hat{\rho}(t)n(\vec{x})\} = \langle n(\vec{x},t)\rangle \tag{8.3.13}$$

and

$$\mathrm{tr}\{\hat{\rho}(t)e(\vec{x})\} = \langle\varepsilon(\vec{x},t)\rangle \ , \tag{8.3.14}$$

where

$$\begin{aligned}\langle\varepsilon(\vec{x},t)\rangle &= \langle e(\vec{x},t)\rangle - \frac{1}{2m}\frac{\langle\vec{g}(\vec{x},t)\rangle^2}{\langle n(\vec{x},t)\rangle} \\ &= \langle e(\vec{x},t)\rangle - \frac{m}{2}v^2(\vec{x},t)\langle n(\vec{x},t)\rangle\end{aligned} \tag{8.3.15}$$

is the mean density of intrinsic energy.

Equation (8.3.8,9) show that the generalized canonical probability density $\tilde{\rho}(t)$ describes a state of local equilibrium [114] of small cells with temperature $T(\vec{x},t)$ and chemical potential $\mu(\vec{x},t)$ moving with the flow velocity $\vec{v}(\vec{x},t)$. Because of (8.3.13,14), the temperature field $T(\vec{x},t)$ and the nonuniform chemical potential $\mu(\vec{x},t)$ are functionals of the mean particle density $\langle n(\vec{x},t)\rangle$ and the mean density of intrinsic energy $<\varepsilon(\vec{x},t)>$, while (8.3.12) gives the flow velocity $\vec{v}(\vec{x},t)$ as a function of the local mean densities. Finally, the quantities $T(\vec{x},t)$, $\mu(\vec{x},t)$ and $\vec{v}(\vec{x},t)$ are related to the conjugate thermodynamic fields $\lambda_i(\vec{x},t)$ by (8.2.3) and (8.3.10).

It should be noted that our generalized canonical probability density $\tilde{\rho}(t)$ is of the grand canonical type. The total particle number is not fixed but rather a fluctuating quantity. Only the mean particle number coincides with the actual particle number of the fluid system.[3] Correspondingly, in expressions where averages over $\tilde{\rho}$ or $\hat{\rho}$ are taken, the trace is a "grand trace" involving a summation over all particle numbers.

8.4 Ideal Fluids

The organized (ideal) motion of fluids is determined by the mean organized fluxes introduced in (8.1.7). They read

$$<g^{\nu}(\vec{x},t)>_{or} = \mathrm{tr}\{\tilde{\rho}(t)g^{\nu}(\vec{x})\} = <g^{\nu}(\vec{x},t)> \quad , \qquad (8.4.1)$$

$$<\sigma^{\nu\mu}(\vec{x},t)>_{or} = \mathrm{tr}\{\tilde{\rho}(t)\sigma^{\nu\mu}(\vec{x})\} \quad , \qquad (8.4.2)$$

$$<\tau^{\nu}(\vec{x},t)>_{or} = \mathrm{tr}\{\tilde{\rho}(t)\tau^{\nu}(\vec{x})\} \quad . \qquad (8.4.3)$$

The first relation expresses the fact that the particle flux $\vec{g}(\vec{x},t)/m$ has no disorganized motion part since $\vec{g}(\vec{x},t)$ is itself a macroscopic variable. To evaluate (8.4.2) we make use of the transformation $\mathbf{S}(t)$ defined in (8.3.3). With (8.3.4,8) we have

$$<\sigma^{\nu\mu}(\vec{x},t)>_{or} = \mathrm{tr}\{\hat{\rho}(t)\mathbf{S}^{-1}(t)\sigma^{\mu\nu}(\vec{x})\} \quad . \qquad (8.4.4)$$

On applying $\mathbf{S}^{-1}(t)$ to (8.2.11) we find

$$\mathbf{S}^{-1}(t)\sigma^{\nu\mu}(\vec{x})$$
$$= \sigma^{\nu\mu}(\vec{x}) + v^{\nu}(\vec{x},t)g^{\mu}(\vec{x}) + v^{\mu}(\vec{x},t)g^{\nu}(\vec{x}) + mv^{\nu}(\vec{x},t)v^{\mu}(\vec{x},t)n(\vec{x}) \quad . \qquad (8.4.5)$$

Using (8.3.11), the right-hand side of (8.4.4) can be evaluated further to yield

$$<\sigma^{\nu\mu}(\vec{x},t)>_{or} = mv^{\nu}(\vec{x},t)v^{\mu}(\vec{x},t)<n(\vec{x},t)> + p^{\nu\mu}(\vec{x},t) \quad , \qquad (8.4.6)$$

where $p^{\nu\mu}(\vec{x},t)$ is the pressure tensor defined by

$$p^{\nu\mu}(\vec{x},t) = \mathrm{tr}\{\hat{\rho}(t)\sigma^{\nu\mu}(\vec{x})\} \quad . \qquad (8.4.7)$$

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[3] In this respect our approach differs from PICCIRELLI's work [166]. That is why we have a normalization factor $Z(t)$ in (8.3.2). ln $Z(t)$ is related to the space integral over the pressure [cf. (8.1.5) and (8.4.18)].

We now insert (8.2.11) into (8.4.7) to give

$$p^{\nu\mu}(\vec{x},t) = \frac{<n(\vec{x},t)>}{\beta(\vec{x},t)}\,\delta^{\nu\mu} \tag{8.4.8}$$

$$- \frac{1}{2} \int dy\, \frac{y^\nu y^\mu}{|y|^2} \frac{d\varphi(|y|)}{d|y|} \int_0^{|y|} dr \int dy'\,\delta\!\left(\vec{x} - \vec{y}' - \frac{r}{|y|}\,\vec{y}\right) g_t^{(2)}(\vec{y}',\vec{y}' + \vec{y})$$

with

$$g_t^{(2)}(\vec{x},\vec{y}) = \sum_{a,b}{}' \ \mathrm{tr}\{\hat{\rho}(t)\delta(\vec{x} - \vec{x}_a)\delta(\vec{y} - \vec{x}_b)\} \quad . \tag{8.4.9}$$

This relation determines the pressure tensor as a generally nonlocal function of $T(\vec{x},t)$ and $\mu(\vec{x},t)$. However, the second term in (8.4.8) gives a contribution only for distances $|y|$ within the range r_0 of the interparticle potential $\varphi(|y|)$. The functions $T(\vec{x},t)$ and $\mu(\vec{x},t)$ are substantially constant on this scale, and we can replace $g_t^{(2)}(\vec{y}',\vec{y}' + \vec{y})$ by the corresponding quantity $g_{eq}^{(2)}(|y|;T,\mu)$ of an equilibrium fluid characterized by the intensive variables T and μ matched with the local values $T(\vec{x},t)$ and $\mu(\vec{x},t)$. We then find

$$p^{\nu\mu}(\vec{x},t) = p(\vec{x},t)\delta^{\nu\mu} \equiv p_{eq}(T(\vec{x},t),\mu(\vec{x},t))\delta^{\nu\mu} \quad , \tag{8.4.10}$$

where

$$p_{eq}(T,\mu) = k_B T<n> - \frac{2\pi}{3} \int_0^\infty dr\, r^3\, \frac{d\varphi(r)}{dr}\, g_{eq}^{(2)}(r;T,\mu) \tag{8.4.11}$$

is a familiar expression for the equilibrium pressure. Equations (8.4.6,10) combine to give

$$<\sigma^{\nu\mu}(\vec{x},t)>_{or} = mv^\nu(\vec{x},t)v^\mu(\vec{x},t)<n(\vec{x},t)> + p(\vec{x},t)\delta^{\nu\mu} \quad . \tag{8.4.12}$$

The right-hand side of (8.4.3) can be transformed in the same way to read

$$<\tau^\nu(\vec{x},t)>_{or} = v^\nu(\vec{x},t)\left[<e(\vec{x},t)> + \frac{<n(\vec{x},t)>}{\beta(\vec{x},t)}\right] \tag{8.4.13}$$

$$- \frac{1}{2} \int dy \sum_\mu \frac{y^\nu y^\mu}{|y|^2} \frac{d\varphi(|y|)}{d|y|} \int_0^{|y|} dr \int dy'\,v^\mu(\vec{y}',t)\,\delta\!\left(\vec{x} - \vec{y}' - \frac{r}{|y|}\,\vec{y}\right)$$

$$g_t^{(2)}(\vec{y}',\vec{y}' + \vec{y}) \quad .$$

Assuming that $v^\mu(\vec{x},t)$ is substantially constant within the range r_0 of the interparticle potential and replacing

$$g_t^{(2)}(\vec{y}',\vec{y}' + \vec{y}) \quad \text{by} \quad g_{eq}^{(2)}(|y|;T(\vec{x},t),\mu(\vec{x},t)) \quad ,$$

we find by virtue of (8.4.11)

$$<\tau^\nu(\vec{x},t)>_{or} = v^\nu(\vec{x},t)[<e(\vec{x},t)> + p(\vec{x},t)] \quad . \tag{8.4.14}$$

With (8.4.1,12,14) the equations of organized motion take the form

$$\frac{\partial}{\partial t}\langle n\rangle = -\frac{1}{m}\sum_{\nu}\frac{\partial}{\partial x^{\nu}}\langle g^{\nu}\rangle \quad ,$$

$$\frac{\partial}{\partial t}\langle g^{\nu}\rangle = -\sum_{\mu}\frac{\partial}{\partial x^{\mu}}\, m v^{\nu} v^{\mu}\langle n\rangle - \frac{\partial}{\partial x^{\nu}}\, p \quad , \tag{8.4.15}$$

$$\frac{\partial}{\partial t}\langle e\rangle = -\sum_{\nu}\frac{\partial}{\partial x^{\nu}}\,(\langle e\rangle + p)\, v^{\nu} \quad ,$$

where we have omitted the $(\vec{x},t)$ dependence of all quantities. Under the assumption that the local temperature and the local chemical potential can approximately be expressed as functions of the local mean particle and intrinsic energy densities,[4] the right-hand sides of (8.4.15) are local functions of the mean densities. Then (8.4.15) is a closed set of reversible, local equations of motion for the conserved densities. These are just Euler's equations of motion for an ideal adiabatic fluid.

Equations (8.4.15) can be cast into a form which makes it apparent that the fluxes are caused by the conjugate thermodynamic forces λ_i. From (8.2.3) and (8.3.10) we get

$$T = \frac{1}{\lambda_4} \quad , \quad \mu = -\frac{\lambda_0}{\lambda_4} + \frac{m}{2}\sum_{\nu}\frac{\lambda_{\nu}^2}{\lambda_4^2} \quad , \quad v^{\nu} = -\frac{\lambda_{\nu}}{\lambda_4} \tag{8.4.16}$$

This, in connection with the well-known relations

$$\left(\frac{\partial p}{\partial T}\right)_{\mu} = s = \frac{\langle\varepsilon\rangle + p - \mu\langle n\rangle}{T} \tag{8.4.17}$$

$$\left(\frac{\partial p}{\partial \mu}\right)_{T} = \langle n\rangle$$

where s is the entropy density, gives

$$\frac{\partial p}{\partial \lambda_0} = -T\langle n\rangle \quad ,$$

$$\frac{\partial p}{\partial \lambda_{\nu}} = -Tmv^{\nu}\langle n\rangle \quad ,$$

$$\frac{\partial p}{\partial \lambda_4} = -T(\langle e\rangle + p) \quad . \tag{8.4.18}$$

Here p is considered to be a function of the λ_i.

The mean values $a_i(\vec{x},t) = \langle A_i(\vec{x},t)\rangle$ of the macroscopic variables (8.2.3) form a five-component field of mean densities. The reversible equations of motion (8.4.15) for this field can be written

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[4] Near the gas-liquid critical point the mean values $\langle n\rangle$ and $\langle\varepsilon\rangle$ become nonlocal functionals of T and μ, and gradient terms are of importance [4,49].

$$\frac{\partial}{\partial t} a_i(\vec{x},t) = \int dy \sum_j V_{ij}(\vec{x},\vec{y})\lambda_j(\vec{y},t) \quad , \tag{8.4.19}$$

where $V_{ij}(\vec{x},\vec{y})$ is an antisymmetric matrix

$$V_{ij}(\vec{x},\vec{y}) = -V_{ji}(\vec{y},\vec{x}) \tag{8.4.20}$$

which can be expressed in terms of derivatives of the pressure with respect to the λ_i [138]:

$$V_{ij}(\vec{x},\vec{y}) = \begin{array}{cc} & \rightarrow j \\ \downarrow i & \left[\begin{array}{c|c|c} 0 & -\frac{\partial}{\partial x^\mu}\frac{\partial p}{\partial \lambda_0} & 0 \\ \hline \frac{\partial}{\partial y^\nu}\frac{\partial p}{\partial \lambda_0} & -\frac{\partial}{\partial x^\mu}\frac{\partial p}{\partial \lambda_\nu} + \frac{\partial}{\partial y^\nu}\frac{\partial p}{\partial \lambda_\mu} & \frac{\partial}{\partial y^\nu}\frac{\partial p}{\partial \lambda_4} \\ \hline 0 & -\frac{\partial}{\partial x^\mu}\frac{\partial p}{\partial \lambda_4} & 0 \end{array}\right] \end{array} \delta(\vec{x}-\vec{y}) \quad . \tag{8.4.21}$$

Here the index i runs through $0,\nu$ and 4, while j runs through $0,\mu$ and 4 with $\nu,\mu = 1,2,3$. The equivalence of (8.4.19) and (8.4.15) follows from (8.2.3) and (8.4.18,21) after some familiar thermodynamic manipulations.

It is worth mentioning that except for a factor T, the components with i and $j \neq 4$ of the matrix (8.4.21) are just the local equilibrium averages of the Poisson brackets between the macroscopic variables $A_i(\vec{x})$ and $A_j(\vec{y})$. However, the components with i or $j = 4$ are not related to Poisson brackets with the energy density $A_4(\vec{x})$. This is as it should be since the local equilibrium averages of the Poisson brackets between the macroscopic variables and the energy density already determine the organized fluxes completely so that a representation of the organized fluxes in terms of *all* Poisson brackets would be redundant.

The representation (8.4.19) of the reversible fluxes can be viewed as a modification of (3.2.3) which makes allowance for the fact that the energy density is among the macroscopic variables. Further results obtain in Chap.3 are easily transcribed for the present case. For instance, instead of (3.2.6) we now find that the organized motion does not contribute to the time rate of change of the entropy. This may also be shown directly using (8.1.5) and (8.4.19,20).

8.5 Viscous Fluids

The irreversibility of the fluid motion is due to the disorganized fluxes (8.1.11) which are given in terms of the transport kernels (8.1.12). To evaluate the latter we start by noting that they may be written

$$R^{\nu\mu}_{ij}(\vec{x}t,\vec{y}s) = \frac{1}{k_B}\, \mathrm{tr}\{\bar{\rho}(s)\hat{J}^{\nu}_{i}(\vec{x},t,s)\hat{J}^{\mu}_{j}(\vec{y},s,s)\} \quad , \tag{8.5.1}$$

where

$$\hat{J}_i^{\nu}(x,t,s) = [1 - P(s)]G(s,t)[1 - P(t)]J_i^{\nu}(\vec{x}) \quad . \tag{8.5.2}$$

In obtaining (8.5.1) from (8.1.12) we have inserted operators $[1 - P(t)]$, this being permitted because of (2.3.9), and we have made use of

$$\mathrm{tr}\{\bar{\rho}(t)XP(t)Y\} = \mathrm{tr}\{\bar{\rho}(t)YP(t)X\} \quad , \tag{8.5.3}$$

which can easily be shown to hold for classical systems. Equation (8.5.1) is a modification of the generalized fluctuation-dissipation theorem (3.3.14), and it avoids the introduction of a global temperature, desirable trait considering the fact that the energy density is among the macroscopic variables.

The quantities (8.5.2) will be referred to as subtracted fluxes, henceforth. Because $\vec{g}(\vec{x}) = P(t)\vec{g}(\vec{x})$, there is no subtracted particle flux. The subtracted stress tensor and the subtracted energy flux read

$$\hat{\sigma}^{\nu\mu}(\vec{x},t,s) = [1 - P(s)]G(s,t)[1 - P(t)]\sigma^{\nu\mu}(\vec{x}) \tag{8.5.4}$$

and

$$\hat{\tau}^{\nu}(\vec{x},t,s) = [1 - P(s)]G(s,t)[1 - P(t)]\tau^{\nu}(\vec{x}) \quad . \tag{8.5.5}$$

To get rid of a purely kinematical correlation between the momentum flux and the energy flux, we put

$$\hat{\tau}^{\nu}(\vec{x},t,s) = \sum_{\mu} \hat{\sigma}^{\nu\mu}(\vec{x},t,s)v^{\mu}(\vec{x},s) + \hat{q}^{\nu}(\vec{x},t,s) \quad , \tag{8.5.6}$$

which defines the subtracted heat flux $\hat{q}^{\nu}(\vec{x},t,s)$. Then, using (8.4.1) and the form (8.2.3) of the conjugate thermodynamic fields, the mean disorganized fluxes (8.1.11) read

$$<g^{\nu}(\vec{x},t)>_{di} = 0 \quad , \tag{8.5.7}$$

$$\begin{aligned}<\sigma^{\nu\mu}(\vec{x},t)>_{di} = - \int_0^t ds \int dy \Bigg[&\sum_{\lambda,\pi} \frac{\mathrm{tr}\{\bar{\rho}(s)\hat{\sigma}^{\nu\mu}(\vec{x},t,s)\hat{\sigma}^{\lambda\pi}(\vec{y},s,s)\}}{k_B T(\vec{y},s)} \frac{\partial}{\partial y^{\lambda}} v^{\pi}(\vec{y},s) \\ &+ \sum_{\lambda} \frac{\mathrm{tr}\{\bar{\rho}(s)\hat{\sigma}^{\nu\mu}(\vec{x},t,s)\hat{q}^{\lambda}(\vec{y},s,s)\}}{k_B T^2(\vec{y},s)} \frac{\partial}{\partial y^{\lambda}} T(\vec{y},s) \Bigg] \quad ,\end{aligned} \tag{8.5.8}$$

$$\begin{aligned}<\tau^{\nu}(\vec{x},t)>_{di} = - \int_0^t ds \int dy \Bigg[&\sum_{\lambda,\pi} \frac{\mathrm{tr}\{\bar{\rho}(s)\hat{q}^{\nu}(\vec{x},t,s)\hat{\sigma}^{\lambda\pi}(\vec{y},s,s)\}}{k_B T(\vec{y},s)} \frac{\partial}{\partial y^{\lambda}} v^{\pi}(\vec{y},s) \\ &+ \sum_{\lambda} \frac{\mathrm{tr}\{\bar{\rho}(s)\hat{q}^{\nu}(\vec{x},t,s)\hat{q}^{\lambda}(\vec{y},s,s)\}}{k_B T^2(\vec{y},s)} \frac{\partial}{\partial y^{\lambda}} T(\vec{y},s) \\ &+ \sum_{\mu} v^{\mu}(\vec{x},s) \cdot \text{integrand of (8.5.8)} \Bigg] \quad .\end{aligned} \tag{8.5.9}$$

We shall not write down the formally exact equations of motion that follow from these expressions. Instead, we turn directly to the approximate transport equations discussed in Sect.3.5. Since for the present system the time rates of change of the macroscopic variables are proportional to the wavenumber k in a Fourier space representation, an approximation along the lines of Sect.3.5 amounts to neglecting terms of the third order in k in the retarded parts of the exact transport laws. In real space this means that the right-hand sides of (8.5.8,9), which are functionals of the conjugate thermodynamic fields, have to be eavluated up to terms of the first order in the spatial derivatives of the thermodynamic fields. Since all terms are explicitly of the first order in these derivatives, the traces can be evaluated for a homogeneous system characterized by constant thermodynamic fields matched with their local values.

By way of example we consider the first term on the right-hand side of (8.5.8). Using the transformation (8.3.3) and (8.5.4), we find

$$\begin{aligned}&\mathrm{tr}\{\bar{\rho}(s)\hat{\sigma}^{\nu\mu}(\vec{x},t,s)\hat{\sigma}^{\lambda\pi}(\vec{y},s,s)\} \\ &\quad = \mathrm{tr}\{\hat{\rho}(s)[\mathbf{S}^{-1}(s)(\mathbf{1}-\mathbf{P}(s))\mathbf{G}(s,t)(\mathbf{1}-\mathbf{P}(t))\sigma^{\nu\mu}(\vec{x})][\mathbf{S}^{-1}(s)(\mathbf{1}-\mathbf{P}(s))\sigma^{\lambda\pi}(\vec{y})]\} \quad . \end{aligned} \tag{8.5.10}$$

The projected part of the stress tensor reads

$$\mathbf{P}(t)\sigma^{\nu\mu}(\vec{x}) = \left\{1 + \int dy \sum_i [A_i(\vec{y}) - a_i(\vec{y},t)] \frac{\delta}{\delta a_i(\vec{y},t)}\right\} \mathrm{tr}\{\bar{\rho}(t)\sigma^{\nu\mu}(\vec{x})\} \quad , \tag{8.5.11}$$

where we have specified the projection operator (2.3.8) for the set (8.2.3) of macroscopic variables. The local equilibrium average (8.4.2) of the stress tensor has been evaluated previously. With the result (8.4.12) we obtain from (8.5.11)

$$\begin{aligned}\mathbf{P}(t)\sigma^{\nu\mu} &= mv^\nu v^\mu\langle n\rangle + p\delta^{\nu\mu} + v^\nu(g^\mu - \langle g^\mu\rangle) \\ &\quad + v^\mu(g^\nu - \langle g^\nu\rangle) - mv^\nu v^\mu(n - \langle n\rangle) + \frac{\partial p}{\partial\langle n\rangle}(n - \langle n\rangle)\delta^{\nu\mu} \\ &\quad + \frac{\partial p}{\partial\langle\varepsilon\rangle}\left[e - \langle\varepsilon\rangle - \sum_\lambda v^\lambda(g^\lambda - \langle g^\lambda\rangle) + \frac{m}{2}v^2(n - \langle n\rangle)\right]\delta^{\nu\mu} \quad . \end{aligned} \tag{8.5.12}$$

Here phase functions are to be taken in the Schrödinger representation, and we have omitted the space and time arguments. Using (8.4.5) and (8.5.12) one finds that

$$\begin{aligned}\Delta\sigma^{\nu\mu} &= \mathbf{S}^{-1}(t)[\mathbf{1} - \mathbf{P}(t)]\sigma^{\nu\mu} \\ &= \sigma^{\nu\mu} - \left[p + \frac{\partial p}{\partial\langle\varepsilon\rangle}(e - \langle\varepsilon\rangle) + \frac{\partial p}{\partial\langle n\rangle}(n - \langle n\rangle)\right]\delta^{\nu\mu} \quad . \end{aligned} \tag{8.5.13}$$

$\Delta\sigma^{\nu\mu}$ is the intrinsic subtracted part of the stress tensor which is expressed completely in terms of quantities defined in the local rest frame.

Since $i\mathbf{L}\mathbf{P}(t)$ is of order $\dot{A}$, that is, of order k in a Fourier space representation, we obtain from (8.5.10) by use of (2.4.2) and (8.5.13)

$$\mathrm{tr}\{\bar{\rho}(s)\hat{\sigma}^{\nu\mu}(\vec{x},t,s)\hat{\sigma}^{\lambda\pi}(\vec{y},s,s)\}$$

$$= \mathrm{tr}\Big\{\hat{\rho}(s)[\exp\{\mathbf{S}^{-1}(s)i\mathbf{L}\mathbf{S}(s)(t-s)\}\Delta\sigma^{\nu\mu}(\vec{x})]\Delta\sigma^{\lambda\pi}(\vec{y})\Big\} + \mathcal{O}(\text{Å}) \quad . \tag{8.5.14}$$

Next we notice that

$$\exp\{\mathbf{S}^{-1}i\mathbf{L}\mathbf{S}u\}X(\vec{p}_a,\vec{x}_a - \vec{x})$$

$$= e^{iLu}\, X(\vec{p}_a,\vec{x}_a - \vec{x} + u\vec{v}) + \mathcal{O}\left(\frac{\partial v}{\partial X}\right) \quad , \tag{8.5.15}$$

where X is any phase function describing local properties at position $\vec{x}$. Equation (8.5.15) is proven easily with the definition of **S** and the Poisson bracket structure of i**L**. The additional terms in (8.5.15) are of order k and can be omitted. We then obtain from (8.5.14)

$$\mathrm{tr}\{\bar{\rho}(s)\hat{\sigma}^{\nu\mu}(\vec{x},t,s)\hat{\sigma}^{\lambda\pi}(\vec{y},s,s)\}$$

$$= \mathrm{tr}\{\hat{\rho}(s)\Delta\sigma^{\nu\mu}(\vec{x} - (t-s)\vec{v},s)\Delta\sigma^{\lambda\pi}(\vec{y},0)\} \quad . \tag{8.5.16}$$

Here, the right-hand side is expressed in terms of quantities defined in the local rest frame. As mentioned earlier, for the present approximation it is sufficient to evaluate this expression for a homogeneous system characterized by a particle density <n> and a density of intrinsic energy <ε> matched with their local values. We then find after an obvious change of the integration variables

$$\int_0^t ds \int dy\ \mathrm{tr}\{\bar{\rho}(s)\hat{\sigma}^{\nu\mu}(\vec{x},t,s)\hat{\sigma}^{\lambda\pi}(\vec{y},s,s)\}\ \frac{1}{T(\vec{y},s)}\ \frac{\partial}{\partial y^\lambda}\, v^\pi(\vec{y},s)$$

$$= \int_0^t ds \int dy <\Delta\sigma^{\nu\mu}(\vec{x}-\vec{y},s)\Delta\sigma^{\lambda\pi}(\vec{0},0)|\vec{x},t>\ \frac{1}{T(\vec{y}-s\vec{v},t-s)}\ \frac{\partial}{\partial y^\lambda}\, v^\pi(\vec{y}-s\vec{v},t-s) \quad , \tag{8.5.17}$$

where the average $<\ldots|\vec{x},t>$ is over the grand canonical distribution

$$\rho_{gc}(\vec{x},t) = Z^{-1}(\vec{x},t)\ \exp\left\{-\frac{1}{k_B T(\vec{x},t)}[H - \mu(\vec{x},t)N]\right\} \quad . \tag{8.5.18}$$

Here $T(\vec{x},t)$ and $\mu(\vec{x},t)$ are determined by $<\epsilon(\vec{x},t)>$ and $<n(\vec{x},t)>$. Note that in (8.5.18 $\vec{x}$ and t are fixed parameters, and the distribution describes a homogeneous equilibrium fluid.

The retardation in time and the nonlocality in space of (8.5.17) can be disregarded if the equilibrium correlations of the $\Delta\sigma^{\nu\mu}$ decay on a time and length scale well separated from the characteristic time and length scale of the macroscopic motion (in the local rest frame where possibly large convective parts of the time rates of change of the conserved densities are absent).[5] We then obtain

(Footnote 5 see next page)

$$\int_0^t ds \int dy\ \mathrm{tr}\{\bar{\rho}(s)\hat{\sigma}^{\nu\mu}(\vec{x},t,s)\hat{\sigma}^{\lambda\pi}(\vec{y},s,s)\}\ \frac{1}{k_B T(\vec{y},s)}\ \frac{\partial}{\partial y^\lambda}\, v^\pi(\vec{y},s)$$

$$\doteq\ \Xi^{\nu\mu,\lambda\pi}(\vec{x},t)\ \frac{\partial}{\partial x^\lambda}\, v^\pi(\vec{x},t) \quad , \tag{8.5.19}$$

where

$$\Xi^{\nu\mu,\lambda\pi}(\vec{x},t) = \frac{1}{k_B T(\vec{x},t)} \int_0^\infty ds \int dy < \Delta\sigma^{\nu\mu}(\vec{y},s)\Delta\sigma^{\lambda\pi}(\vec{0},0)\,|\vec{x},t> \quad . \tag{8.5.20}$$

The tensor $\Xi^{\nu\mu,\lambda\pi}$ fulfills quite a few symmetry relations that follow from the symmetry of the stress tensor, from the reciprocal relations, and from the isotropy of the state (8.5.18) over which the integrand of (8.5.20) is averaged. These symmetrie lead to the following form of $\Xi^{\nu\mu,\lambda\pi}$:

$$\Xi^{\nu\mu,\lambda\pi} = \eta(\delta^{\nu\lambda}\delta^{\mu\pi} + \delta^{\nu\pi}\delta^{\mu\lambda}) + (\zeta - \frac{2}{3}\eta)\delta^{\nu\mu}\delta^{\lambda\pi} \quad . \tag{8.5.21}$$

where η and ζ are the shear and bulk viscosities, respectively, and are scalar functions of the local values of $<n>$ and $<\varepsilon>$. Green-Kubo formulae for η and ζ are easily obtained from (8.5.20) by appropriate contractions of indices.

By the same method the other terms on the right-hand sides of (8.5.8,9) can be evaluated approximately. The second term on the right-hand side of (8.5.8) is approximated by

$$\int_0^t ds \int dy\ \mathrm{tr}\{\bar{\rho}(s)\hat{\sigma}^{\nu\mu}(\vec{x},t,s)\hat{q}^{\lambda}(\vec{y},s,s)\}\ \frac{1}{k_B T^2(\vec{y},s)}\ \frac{\partial}{\partial y^\lambda}\, T(\vec{y},s)$$

$$\doteq \Psi^{\nu\mu,\lambda}(\vec{x},t)\ \frac{1}{T(\vec{x},t)}\ \frac{\partial}{\partial y^\lambda}\, T(\vec{x},t) \quad , \tag{8.5.22}$$

where

$$\Psi^{\nu\mu,\lambda}(\vec{x},t) = \frac{1}{k_B T(\vec{x},t)} \int_0^\infty ds \int dy < \Delta\sigma^{\nu\mu}(\vec{y},s)\Delta q^{\lambda}(\vec{0},0)\,|\vec{x},t> \quad , \tag{8.5.23}$$

and

$$\Delta q^\nu = \mathbf{S}^{-1}(\mathbf{1} - \mathbf{P})\Big(\tau^\nu - \sum_\mu \sigma^{\nu\mu}v^\mu\Big)$$

$$= \tau^\nu - \frac{<\varepsilon> + p}{m<n>}\, g^\nu \quad . \tag{8.5.24}$$

Symmetry arguments show that

$$\Psi^{\nu\mu,\lambda} = 0 \quad , \tag{8.5.25}$$

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5 We remark that such a separation of time and length scales does not really occur even in the hydrodynamic limit. We are disregarding here some small effects associated with the long-time tail phenomena [78]. To include these effects one has to evaluate the renormalized transport kernels more precisely. They can also be obtained, however, from the Fokker-Planck description of fluids in a more straightforward manner [169,171].

which means that there is no correlation between the random stress tensor and the random heat flux in the approximation under consideration.

The second term on the right-hand side of (8.5.9) is approximated as follows:

$$\int_0^t ds \int dy \, \mathrm{tr}\{\bar{\rho}(s)\hat{q}^{\nu}(\vec{x},t,s)\hat{q}^{\mu}(\vec{y},s,s)\} \frac{1}{k_B T^2(\vec{y},s)} \frac{\partial}{\partial y^{\mu}} T(\vec{y},s)$$

$$\doteq K^{\nu\mu}(\vec{x},t) \frac{1}{T(\vec{x},t)} \frac{\partial}{\partial x^{\mu}} T(\vec{x},t) \quad , \tag{8.5.26}$$

where

$$K^{\nu\mu}(\vec{x},t) = \frac{1}{k_B T(\vec{x},t)} \int_0^{\infty} ds \int dy < \Delta q^{\nu}(\vec{y},s) \Delta q^{\mu}(\vec{0},0) | \vec{x},t> \quad . \tag{8.5.27}$$

Symmetry arguments show that

$$K^{\nu\mu} = \varkappa T \delta^{\nu\mu} \quad , \tag{8.5.28}$$

where $\varkappa$ is the heat conductivity which is a scalar function of the local values of $<n>$ and $<\varepsilon>$. (8.5.27) immediately gives a Green-Kubo formula for $\varkappa$.

The remaining terms in (8.5.8,9) do not lead to new coefficients. Finally, (8.5.8,9) reduce in the present approximation to

$$<\sigma^{\nu\mu}>_{di} \doteq - \sum_{\lambda,\pi} \underline{\underline{\eta}}^{\nu\mu,\lambda\pi} \frac{\partial v^{\pi}}{\partial x^{\lambda}}$$

$$= -\eta\left(\frac{\partial v^{\nu}}{\partial x^{\mu}} + \frac{\partial v^{\mu}}{\partial x^{\nu}} - \frac{2}{3}\delta^{\nu\mu} \sum_{\lambda} \frac{\partial v^{\lambda}}{\partial x^{\lambda}}\right) - \zeta\delta^{\nu\mu} \sum_{\lambda} \frac{\partial v^{\lambda}}{\partial x^{\lambda}} \quad , \tag{8.5.29}$$

and

$$<\tau^{\nu}>_{di} \doteq \sum_{\mu} <\sigma^{\nu\mu}>_{di} v^{\mu} - \varkappa \frac{\partial T}{\partial x^{\nu}} \quad . \tag{8.5.30}$$

On adding the mean disorganized fluxes (8.5.29,30) to the mean organized fluxes on the right-hand sides of (8.4.15), we obtain the transport laws for the mean densities of the conserved quantities:

$$\frac{\partial}{\partial t} <n> \doteq - \frac{1}{m} \sum_{\nu} \frac{\partial}{\partial x^{\nu}} <g^{\nu}> \quad , \tag{8.5.31}$$

$$\frac{\partial}{\partial t} <g^{\nu}> \doteq - \sum_{\mu} \frac{\partial}{\partial x^{\mu}} m v^{\nu} v^{\mu} <n> - \frac{\partial}{\partial x^{\nu}} p + \frac{\partial}{\partial x^{\nu}} \left(\zeta - \frac{2}{3}\eta\right) \sum_{\mu} \frac{\partial v^{\mu}}{\partial x^{\mu}}$$

$$+ \sum_{\mu} \frac{\partial}{\partial x^{\mu}} \eta\left(\frac{\partial v^{\nu}}{\partial x^{\mu}} + \frac{\partial v^{\mu}}{\partial x^{\nu}}\right) \quad ,$$

$$\frac{\partial}{\partial t} <e> = - \sum_{\nu} \frac{\partial}{\partial x^{\nu}} (<e> + p) v^{\nu} + \sum_{\nu} \frac{\partial}{\partial x^{\nu}} \varkappa \frac{\partial}{\partial x^{\nu}} T$$

$$+ \sum_{\nu,\mu} \frac{\partial}{\partial x^{\nu}} \left[\left(\zeta - \frac{2}{3}\eta\right) \frac{\partial v^{\mu}}{\partial x^{\mu}} v^{\nu} + \eta\left(\frac{\partial v^{\nu}}{\partial x^{\mu}} + \frac{\partial v^{\mu}}{\partial x^{\nu}}\right) v^{\mu}\right] \quad .$$

These are the usual nonlinear equations of motion for isotropic fluids which are well-known from phenomenological theory [87].

We want to cast the transport equations into the standard form (3.2.16). For the reversible motion this has been done in (8.4.19). The dissipative motion can be expressed in terms of the conjugate thermodynamic fields λ_i and a symmetric matrix

$$O_{ij}(\vec{x},\vec{y}) = O_{ji}(\vec{y},\vec{x}) \qquad (8.5.32)$$

of the form

$$O_{ij}(\vec{x},\vec{y}) = -\sum_{\lambda\pi} \frac{\partial}{\partial x^{\lambda}} \Delta^{i\lambda,j\pi}(\vec{x}) \frac{\partial}{\partial x^{\pi}} \delta(\vec{x}-\vec{y}) \quad , \qquad (8.5.33)$$

where

$$\Delta^{i\lambda,j\pi} = \overset{\downarrow i \;\rightarrow j}{\left[\begin{array}{c:c:c} 0 & 0 & 0 \\ \hdashline 0 & T\equiv^{\nu\lambda,\mu\pi} & T\sum_{\rho}\equiv^{\nu\lambda,\rho\pi}v^{\rho} \\ \hdashline 0 & T\sum_{\sigma}\equiv^{\sigma\lambda,\mu\pi}v^{\sigma} & T\sum_{\sigma\rho}\equiv^{\sigma\lambda,\rho\pi}v^{\sigma}v^{\rho} + T^{2}\kappa\delta^{\lambda\pi} \end{array}\right]} \quad . \qquad (8.5.34)$$

Again the index i runs through $0,\nu$, and 4, while j runs through $0,\mu$, and 4 with $\nu,\mu = 1,2,3$. Then, in terms of the transport matrix

$$L_{ij}(\vec{x},\vec{y}) = V_{ij}(\vec{x},\vec{y}) + O_{ij}(\vec{x},\vec{y}) \quad , \qquad (8.5.35)$$

the transport equations (8.5.31) take the form

$$\dot{a}_i(\vec{x},t) = \int dy \sum_j L_{ij}(\vec{x},\vec{y})\lambda_j(\vec{y},t) \quad . \qquad (8.5.36)$$

These are transport equations for the mean motion.[6]

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[6] We remark that the transport matrix is local in time and space as a consequence of the approximation made. Nonlocal corrections can be obtained by looking upon (8.5.36) as the deterministic equations of motion associated with a Fokker-Planck equation of the form (4.7.16). Then the coefficients to be found in (8.5.36) have to be looked upon as bare coefficients and the renormalized coefficients are obtained by carrying out a renormalization along the lines of Sects.4.5 and 4.6. This avoids a complicatad molecular calculation beyond the approximations made in this section.

8.6 Fluctuations in Nonequilibrium Fluids

On the level of statistical thermodynamics the fluctuations obey linear Langevin equations of the form (3.6.1), (8.1.14), with random forces, the strength of which is determined by the symmetric part of the transport matrix. For fluids the Langevin equations resulting from (8.5.31) take the form

$$\frac{\partial}{\partial t}\delta n = -\frac{1}{m}\sum_{\nu}\frac{\partial}{\partial x^{\nu}}\delta g^{\nu} \quad , \tag{8.6.1}$$

$$\begin{aligned}\frac{\partial}{\partial t}\delta g^{\nu} = &-\sum_{\mu}\frac{\partial}{\partial x^{\mu}}\left[v^{\nu}\delta g^{\mu} + v^{\mu}\,\delta g^{\nu} - m v^{\nu} v^{\mu}\delta n\right] - \frac{\partial}{\partial x^{\nu}}\,\delta p \\ &+ \frac{\partial}{\partial x^{\nu}}\left[\sum_{\mu}\frac{\partial v^{\mu}}{\partial x^{\mu}}\,(\delta\zeta - \frac{2}{3}\,\delta\eta) + (\zeta - \frac{2}{3}\,\eta)\,\frac{\partial}{\partial x^{\mu}}\,\delta v^{\mu}\right] \\ &+ \sum_{\mu}\frac{\partial}{\partial x^{\mu}}\left[\left(\frac{\partial v^{\nu}}{\partial x^{\mu}} + \frac{\partial v^{\mu}}{\partial x^{\nu}}\right)\delta\eta + \eta\left(\frac{\partial}{\partial x^{\mu}}\,\delta v^{\nu} + \frac{\partial}{\partial x^{\nu}}\,\delta v^{\mu}\right)\right] \\ &- \sum_{\mu}\frac{\partial}{\partial x^{\mu}}\,\xi^{\nu\mu}\end{aligned} \tag{8.6.2}$$

$$\begin{aligned}\frac{\partial}{\partial t}\delta e = &-\sum_{\nu}\frac{\partial}{\partial x^{\nu}}\,[v^{\nu}(\delta e + \delta p) + (\langle e\rangle + p)\delta v^{\nu}] \\ &+ \sum_{\nu}\frac{\partial}{\partial x^{\nu}}\left[\frac{\partial T}{\partial x^{\nu}}\,\delta\kappa + \kappa\,\frac{\partial}{\partial x^{\nu}}\,\delta T\right] \\ &+ \sum_{\nu,\mu}\frac{\partial}{\partial x^{\nu}}\left[v^{\nu}\,\frac{\partial v^{\mu}}{\partial x^{\mu}}\,(\delta\zeta - \frac{2}{3}\,\delta\eta) + (\zeta - \frac{2}{3}\,\eta)v^{\nu}\,\frac{\partial}{\partial x^{\mu}}\,\delta v^{\mu}\right. \\ &\left. + (\zeta - \frac{2}{3}\,\eta)\,\frac{\partial v^{\mu}}{\partial x^{\mu}}\,\delta v^{\nu}\right] \\ &+ \sum_{\nu,\mu}\frac{\partial}{\partial x^{\nu}}\left[\left(\frac{\partial v^{\nu}}{\partial x^{\mu}} + \frac{\partial v^{\mu}}{\partial x^{\nu}}\right)(v^{\mu}\delta\eta + \eta\delta v^{\mu}) + \eta v^{\mu}\left(\frac{\partial}{\partial x^{\mu}}\,\delta v^{\nu} + \frac{\partial}{\partial x^{\nu}}\,\delta v^{\mu}\right)\right] \\ &- \sum_{\nu}\frac{\partial}{\partial x^{\nu}}\left[\sum_{\mu}\xi^{\nu\mu}v^{\mu} + \xi^{\nu}\right] \; .\end{aligned} \tag{8.6.3}$$

Here we have introduced the abbreviations

$$\delta v^{\nu} = \frac{1}{m\langle n\rangle}\,(\delta g^{\nu} - m v^{\nu}\delta n) \quad ,$$

$$\delta f = \left(\frac{\partial f}{\partial\langle\varepsilon\rangle}\right)_{\langle n\rangle}(\delta e - \vec{v}\cdot\delta\vec{g} + \frac{m}{2}\,v^{2}\delta n) + \left(\frac{\partial f}{\partial\langle n\rangle}\right)_{\langle\varepsilon\rangle}\delta n \quad , \tag{8.6.4}$$

where f is p, η, ζ, κ, or T.

The properties of the random fluxes follow from the (3.6.11,16) when the factor T is absorbed into the definition of the transport matrix as in (3.2.17). This modification comes from the fact that we use the entropy as thermodynamic potential. One finds

$$<\xi^{\nu\mu}(\vec{x},t)> = <\xi^{\nu}(\vec{x},t)> = 0 \tag{8.6.5}$$

and

$$<\xi^{\nu\mu}(\vec{x},t)\delta A_i(\vec{y},s)> = <\xi^{\nu}(\vec{x},t)\delta A_i(\vec{y},s)> = 0 \tag{8.6.6}$$

for $t > s$. Furthermore, since the random energy flux has been decomposed into a purely convective contribution from the random stress tensor $\xi^{\nu\mu}$ and the random heat flux ξ^{ν}, we have

$$<\xi^{\nu\mu}(\vec{x},t)\xi^{\lambda\pi}(\vec{x},s)> = 2k_B T(\vec{x},t)\Xi^{\nu\mu,\lambda\pi}(\vec{x},t)\delta(\vec{x} - \vec{y})\delta(t - s) \quad , \tag{8.6.7}$$

$$<\xi^{\nu}(\vec{x},t)\xi^{\mu}(\vec{y},s)> = 2k_B T^2(\vec{x},t)\kappa(\vec{x},t)\delta(\vec{x} - \vec{y})\delta(t - s) \quad , \tag{8.6.8}$$

$$<\xi^{\nu\mu}(\vec{x},t)\xi^{\lambda}(\vec{y},s)> = 0 \quad . \tag{8.6.9}$$

These correlations of the random fluxes were first derived by LANDAU and LIFSHITZ [87] in a phenomenological way.

In order to illustrate the theory we consider a particular nonequilibrium steady state: two heat baths at different temperatures maintain a constant temperature gradient $\vec{G}$ in a fluid layer of thickness L. This nonequilibrium state is a stationary solution of the transport equation (8.5.31) characterized by

$$\begin{aligned} v^{\nu}(\vec{x}) &= 0 \quad , \\ p(\vec{x}) &= p_0 \quad , \\ T(\vec{x}) &= T_0 + \sum_{\nu} G^{\nu}x^{\nu} \quad . \end{aligned} \tag{8.6.10}$$

The origin of the coordinate system lies at the center of the fluid system. To keep things as simple as possible we disregard the temperature and pressure dependence of κ, ζ, and η.

The Langevin equations (8.6.1-3) for the fluctuations about the nonequilibrium steady state (8.6.10) take the form

$$\frac{\partial}{\partial t}\delta n = -\frac{1}{m}\sum_{\nu}\frac{\partial}{\partial x^{\nu}}\delta g^{\nu} \quad , \tag{8.6.11}$$

$$\begin{aligned} \frac{\partial}{\partial t}\delta g^{\nu} = &-\frac{\partial}{\partial x^{\nu}}\left(\frac{\partial p}{\partial <\varepsilon>}\delta e + \frac{\partial p}{\partial <n>}\delta n\right) \\ &+ \sum_{\mu}\left(\zeta + \frac{1}{3}\eta\right)\frac{\partial^2}{\partial x^{\nu}\partial x^{\mu}}\frac{1}{m<n>}\delta g^{\mu} \\ &+ \sum_{\mu}\eta\frac{\partial^2}{\partial x^{\mu}\partial x^{\mu}}\frac{1}{m<n>}\delta g^{\nu} - \sum_{\mu}\frac{\partial}{\partial x^{\mu}}\xi^{\nu\mu} \quad , \end{aligned} \tag{8.6.12}$$

$$\frac{\partial}{\partial t}\,\delta e = -\sum_\nu \frac{\partial}{\partial x^\nu}\frac{<e> + p}{m<n>}\,\delta g^\nu$$

$$+ \varkappa \sum_\nu \frac{\partial^2}{\partial x^\nu \partial x^\nu}\left(\frac{\partial T}{\partial <\varepsilon>}\,\delta e + \frac{\partial T}{\partial <n>}\,\delta n\right) - \sum_\nu \frac{\partial}{\partial x^\nu}\,\xi^\nu \quad . \tag{8.6.13}$$

Notice that the strength of the random fluxes $\xi^{\nu\mu}$ and ξ^ν, which is determined by (8.6.7-9), is nonuniform because of the nonuniform temperature field.

Fluctuations about the nonequilibrium state under consideration have been studied experimentally by means of Brillouin scattering of light [175] (Fig.8.1). Since the coupling of the thermal mode to the sound modes has only a small influence upon the structure factor for Brillouin scattering [176], we shall neglect this coupling by making the assumption that the pressure is a function of the density $<n>$ only, i.e., $\partial p/\partial <\varepsilon> = 0$. We also introduce a Fourier space representation of the fluctuations

$$a_i(\vec{k}) = \frac{1}{V^{1/2}} \int dx\; e^{i\vec{k}\cdot\vec{x}}\,\delta a_i(\vec{x}) \quad , \tag{8.6.14}$$

where V is the volume. The requirement that the fluctuating variables not be influenced by the boundary of the system restricts the k vector to values with $|k| \gg 1/L$.[7]

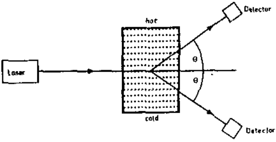

Fig.8.1. *Light scattering from a fluid with a temperature gradient. For small scattering angles θ the two detectors show unequal intensities*

We then obtain from (8.6.11,12)

$$\frac{\partial}{\partial t}\,n(\vec{k},t) = -\frac{i}{m}\,|k|g_\parallel(\vec{k},t) \quad ,$$

$$\frac{\partial}{\partial t}\,|k|g_\parallel(\vec{k},t) = -\,ic^2k^2mn(\vec{k},t) - \nu_\parallel k^2|k|g_\parallel(k,t) - i\xi(\vec{k},t) \quad , \tag{8.6.15}$$

where $g_\parallel(\vec{k},t) - |k|^{-1}\sum_\nu k^\nu g^\nu(\vec{k},t)$ is the longitudinal momentum,

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[7] Clearly the Langevin equations (8.6.1-3) can only be used to describe fluctuations in the interior of the system while they have to be modified near the boundaries. In nonequilibrium systems, boundary effects can often not be eliminated by means of a formal thermodynamic limit. In the presence of a given temperature gradient we can not let the size of the system tend to infinity since this would lead to unphysical temperature differences.

$$c = \left(\frac{\partial p}{m\partial\langle n\rangle}\right)^{1/2} \tag{8.6.16}$$

is the sound velocity, and

$$\nu_\parallel = \frac{\zeta + \frac{4}{3}\eta}{m\langle n\rangle} \tag{8.6.17}$$

is the longitudinal diffusion constant. The random force $\xi(\vec{k},t)$ is defined by

$$\xi(\vec{k},t) = \sum_{\nu,\mu} k^\nu k^\mu \xi^{\nu\mu}(\vec{k},t) \quad , \tag{8.6.18}$$

and it follows from (8.5.21) and (8.6.7,10) that

$$\langle\xi(\vec{k},t)\xi(\vec{l},s)\rangle$$
$$= 2k_B[2\eta(\vec{k}\cdot\vec{l})^2 + (\zeta - \tfrac{2}{3}\eta)k^2l^2]\left(T_0 - i\sum_\nu G^\nu \frac{\partial}{\partial k^\nu}\right)\delta(\vec{k}+\vec{l}) \quad . \tag{8.6.19}$$

The determination of the particle density autocorrelation function from (8.6.15, 19) is standard, and one finds that

$$C_{nn}(\vec{k},\vec{l},\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\, e^{-i\omega t}\langle n(\vec{k},t)n(\vec{l},0)\rangle \tag{8.6.20}$$

is given by

$$C_{nn}(\vec{k},\vec{l},\omega) = \frac{k_B}{\pi m^2}\,\frac{2\eta(\vec{k}\cdot\vec{l})^2+(\zeta-\frac{2}{3}\eta)k^2l^2}{(\omega^2-c^2k^2-i\nu_\parallel\omega k^2)(\omega^2-c^2l^2+i\nu_\parallel\omega l^2)} \tag{8.6.21}$$
$$\times \left(T_0 - i\sum_\nu G^\nu \frac{\partial}{\partial k^\nu}\right)\delta(\vec{k}+\vec{l}) \quad .$$

The particle density autocorrelation function is related to the structure factor $S(k,\omega)$ for light scattering by

$$S(\vec{k},\omega) = \frac{1}{B^2}\int dl\, dl'\, B(\vec{k}-\vec{l})B(\vec{k}+\vec{l}')C_{nn}(\vec{l},\vec{l}',\omega) \quad , \tag{8.6.22}$$

where $B(\vec{k}) = B(-\vec{k})$ is a weighting function which depends on the bandwidth of the light source focused on a spot around $\vec{x} = 0$, and where $B^2 = \int dk\, B(\vec{k})B(-\vec{k})$. Using (8.6.21), we find

$$S(\vec{k},\omega) = \frac{1}{B^2}\int dl\, B(\vec{k}-\vec{l})^2 I(\vec{l},\omega) \tag{8.6.23}$$

with

$$I(\vec{k},\omega) = \frac{k_B\langle n\rangle}{\pi m}\,\frac{k^4}{(\omega^2-c^2k^2)^2+\nu_\parallel^2\omega^2k^4}\left(T_0 - \frac{2\nu_\parallel\omega^3\sum_\nu G^\nu k^\nu}{(\omega^2-c^2k^2)^2+\nu_\parallel^2\omega^2k^4}\right) \quad . \tag{8.6.24}$$

Since the light source should only illuminate a small portion of the fluid in the interior, the bandwidth Δk has to be large compared to L^{-1} but it may still be small compared to $|k|$. In this case the average over $B(\vec{k}-\vec{l})^2$ can be neglected in

(8.6.23) and we have [176-178]

$$S(\vec{k},\omega) = I(\vec{k},\omega) \quad . \tag{8.6.25}$$

The structure factor (8.6.25) has two peaks at $\omega = \pm c|k|$. At equilibrium, where $\vec{G}$ vanishes, the peaks have equal intensity,[8] while the temperature gradient leads to an asymmetry of the nonequilibrium spectrum. From (8.6.24) we obtain for the relative height difference ε of the two peaks

$$\varepsilon = -\frac{2c}{T\nu_* k^2} \sum_\nu G^\nu \frac{k^\nu}{|k|} \quad , \tag{8.6.26}$$

which has a pronounced $1/k^2$ dependence [179].[9] This nonequilibrium phenomenon can be traced back to the fact that the symmetrical part of the transport matrix of fluids is not constant but temperature dependent [138]. Since $1/k^2$ in Fourier space means $1/r$ in real space, there are long-range density correlations in the nonequilibrium fluid. This has first been predicted by RONIS et al. [179] and was further studied by various authors [138,176-181]. The asymmetry in the spectrum has experimentally been confirmed by BEYSENS et al. [175].

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[8] We have treated the fluid by classical statistical mechanics and miss a small asymmetry of the equilibrium spectrum which is a quantum effect. Quantum effects are very small, however, for $\hbar\omega \ll k_B T$.

[9] The wavenumber $|k|$ is related to the scattering angle θ by $|k| = 2|k_i|\sin(\theta/2)$ wher $|k_i|$ is the wavenumber of the incident light beam.

9. Spin Relaxation

There are two important relaxation theories for spin systems. The Bloch-Wangsness-Redfield theory [145,182,183] constructs a master equation for the reduced spin probability density, and the Kubo-Tomita theory [184] focuses on the linear response of the system. We first reformulate the master equation approach by applying the results obtained in Chap.5 to a coupled spin-reservoir system. The scope of the general theory in Chap.5 is extended, however, because we eliminate not only the reservoir variables but also the molecular spins, keeping only the bulk spin variables. While this modification, aimed immediately at a genuine macroscopic description, is not required in order to develop the master equation approach to magnetic relaxation problems, we also intend to show how the previous approach can be extended in a straightforward manner to situations where the macroscopic variables do not form a complete set of variables of a subsystem. The necessary changes are discussed in Sect.9.1.

In Sect.9.2 we derive the generalized master equation for the coarse-grained spin probability density and evaluate it further for a simple model where the spin-reservoir coupling is bilinear. For the treatment of more complicated coupling Hamiltonians we must refer to the books by ABRAGAM [185] and SLICHTER [186] and recent review articles [187-190]. Proceeding from the master equation, we derive the Bloch equations [191] for the mean relaxation in Sect. 9.3. Because of the particular simple model studied, these renormalized transport laws do not contain memory effects which will occur, however, if nonlinear spin interactions are taken into account. Finally, in Sect.9.4, we determine the dynamic susceptibility describing the linear response to an applied alternating magnetic field.

9.1 Macroscopic Variables and Relevant Probability Density

We consider a macroscopic system which may be composed of various constituents but does contain N identical molecules carrying a spin 1/2 angular momentum. Upon denoting the spin angular momentum of the l^{th} molecule by $\hbar\vec{s}_l$, the components s_l^ν satisfy

$$[s_l^\nu, s_{l'}^\mu] = i \sum_\lambda \varepsilon^{\nu\mu\lambda} \delta_{ll'} s_l^\lambda \qquad (9.1.1)$$

and

$$\vec{s}_l^{\,2} = \frac{3}{4} \quad . \qquad (9.1.2)$$

The Hilbert space H of the system may be written as a tensor product of a spin Hilbert space H_S and a Hilbert space H_L associated with the other degrees of freedom

$$H = H_S \otimes H_L \quad . \qquad (9.1.3)$$

For instance, if the spin carrying molecules are in a crystal, H_L is the lattice Hilbert space.

The spin Hilbert space H_S is a tensor product of single spin Hilbert spaces:

$$H_S = \prod_l \otimes H_l \quad , \qquad (9.1.4)$$

where H_l is a two-dimensional Hilbert space spanned by eigenstates of $\vec{s}_l^{\,2}$ and s_l^z:

$$\vec{s}_l^{\,2} |\sigma_l\rangle = \frac{3}{4} |\sigma_l\rangle \quad , \quad s_l^z |\sigma_l\rangle = \sigma_l |\sigma_l\rangle \qquad (9.1.5)$$

with $\sigma_l = \pm 1/2$. Later, the coordinates will be chosen such that the z axis is paralle to an applied magnetic field $\vec{h}_0$. We also introduce the spin flip operators

$$s_l^\pm = s_l^x \pm i\, s_l^y \quad . \qquad (9.1.6)$$

The macroscopic variables of the system are the components of the bulk spin

$$\vec{R} = \sum_l \vec{s}_l \qquad (9.1.7)$$

and are related to the bulk magnetization $\vec{M}$ by

$$\vec{M} = \gamma\hbar\vec{R} \quad , \qquad (9.1.8)$$

where γ is the gyromagnetic ratio. The components R^ν of the bulk spin satisfy

$$[R^\nu, R^\mu] = i \sum_\lambda \varepsilon^{\nu\mu\lambda} R^\lambda \quad . \qquad (9.1.9)$$

It is convenient to introduce the bulk spin raising and lowering operators

$$R^\pm = \sum_l s_l^\pm \quad , \qquad (9.1.10)$$

and the square of the bulk spin

$$R^2 = R^+R^- + R^z(R^z - 1) = R^-R^+ + R^z(R^z + 1) \quad . \qquad (9.1.11)$$

These operators satisfy the commutation relations

$$[R^+, R^-] = 2R^z \quad , \qquad (9.1.12)$$

$$[R^z, R^\pm] = \pm R^\pm \quad , \qquad (9.1.13)$$

$$[\vec{R}^2, R^\pm] = [\vec{R}^2, R^z] = 0 \quad . \qquad (9.1.14)$$

The spin operators $\vec{s}_1^{\,2}$ and s_1^z of the N molecular spins commute mutually and their simultaneous eigenstates form a complete basis in the spin Hilbert space $\mathcal{H}_S$. On the other hand, there is a basis $|r,m,\alpha\rangle$ of simultaneous eigenstates of the bulk spin operators $\vec{R}^2$ and R^z:

$$\vec{R}^2|r,m,\alpha\rangle = r(r+1)|r,m,\alpha\rangle \quad , \qquad (9.1.15)$$

$$R^z|r,m,\alpha\rangle = m|r,m,\alpha\rangle \quad ,$$

where $r = N/2,\ N/2-1, \ldots,\ 1/2$ or 0, $m = -r, -r+1, \ldots, +r$, and where the degeneracy index α runs through $d(r)$ values with

$$d(r) = \frac{N!(2r+1)}{(\frac{N}{2}+r+1)!(\frac{N}{2}-r)!} \quad . \qquad (9.1.16)$$

The α can be chosen in such a way that for $m < r$

$$|r,m+1,\alpha\rangle = \frac{1}{\sqrt{r(r+1)-m(m+1)}}\, R^+|r,m,\alpha\rangle \qquad (9.1.17)$$

with the same value of α. The normalization factor follows from (9.1.11).

The microscopic spin degrees of freedom can be eliminated by means of the coarse-graining operator

$$\mathbf{C}X = \sum_{r,m,m',\alpha} |r,m,\alpha\rangle\left(\frac{1}{d(r)}\sum_{\alpha'} \langle r,m,\alpha'|X|r,m',\alpha'\rangle\right)\langle r,m',\alpha| \qquad (9.1.18)$$

which has the property

$$\mathbf{C}^2 = \mathbf{C} \quad . \qquad (9.1.19)$$

The usefulness of the coarse-graining operator lies in the fact that the macroscopic state of the system is described by the coarse-grained reduced probability density

$$\rho_C(t) = \mathbf{C}\,\mathrm{tr}_L\{\rho(t)\} \quad , \qquad (9.1.20)$$

where tr_L is the trace over a complete set of orthonormal functions in $\mathcal{H}_L$. For a variable F which is not necessarily a linear function of the bulk spin operators, we have

$$\mathrm{tr}\{F\rho(t)\} = \mathrm{tr}_S\{F\rho_C(t)\} \quad , \qquad (9.1.21)$$

where tr_S is the trace over a complete basis in $\mathcal{H}_S$.

To define a relevant probability density associated with $\rho_C(t)$, we cannot follow the line of reasoning of Chap.5 literally, since $\rho_C(t)$ is not just the reduced probability density $\rho_S(t) = \mathrm{tr}_L\{\rho(t)\}$ for all spin degrees of freedom; rather, the microscopic spin degrees of freedom have been eliminated, too. However, the theory of Chap.5 is easily generalized to allow for the present more complex situation. We introduce a transformation

$$\mathbf{Z}_C X_C = \mathbf{C}\,\mathrm{tr}_L\{\mathbf{\Sigma}\mathbf{C}\,X_C\} \qquad (9.1.22)$$

where Σ is the transformation of operators acting in H introduced previously in (5.1.13). The transformation $\mathbf{Z}_C$ acts within the subspace of spin operators X_C of the coarse-grained form (9.1.18).

Now the relevant probability density is taken to be

$$\bar{\rho}(t) = P^T\rho(t) \quad , \tag{9.1.23}$$

where

$$P^T X = \Sigma \mathbf{Z}_C^{-1} \mathbf{C}\,\mathrm{tr}_L\{X\} \tag{9.1.24}$$

is a projection operator satisfying

$$(P^T)^2 = P^T \tag{9.1.25}$$

and

$$\mathbf{C}\,\mathrm{tr}_L\{P^T X\} = \mathbf{C}\,\mathrm{tr}_L\{X\} \tag{9.1.26}$$

so that

$$\mathbf{C}\,\mathrm{tr}_L\{\bar{\rho}(t)\} = \mathbf{C}\,\mathrm{tr}_L\{\rho(t)\} = \rho_C(t) \quad . \tag{9.1.27}$$

The relevant probability density is defined in such a way that the equilibrium probability density and those states obtained by applying weak uniform magnetic fields are of the relevant form.

9.2 Master Equation

A master equation for the coarse-grained reduced probability density $\rho_C(t)$ is obtained by following our procedure in Sect.5.2 with the projection operator P^T replaced by (9.1.24). Instead of (5.2.6), we now obtain

$$\dot{\rho}_C(t) = \Omega_C\rho_C(t) + \int_0^t ds\, \Phi_C(t-s)\rho_C(s) \quad , \tag{9.2.1}$$

where

$$\Omega_C X_C = -i\mathbf{C}\,\mathrm{tr}_L\{L\Sigma \mathbf{Z}_C^{-1} X_C\} \tag{9.2.2}$$

and

$$\Phi_C X_C = -\mathbf{C}\,\mathrm{tr}_L\{L\, e^{-i(1-P^T)Lt}(1-P^T)L\Sigma \mathbf{Z}_C^{-1} X_C\} \quad . \tag{9.2.3}$$

The master equation (9.2.1) has the stationary solution

$$\rho_{C\beta} = \mathbf{C}\,\mathrm{tr}_L\{\rho_\beta\} \quad , \tag{9.2.4}$$

where ρ_β is the canonical probability density (5.1.6) of the system.

In analogy to (5.2.12) we define a thermodynamic force operator $\mu_C(t)$ conjugate to $\rho_C(t)$ by

$$\mu_C(t) = \frac{1}{\beta}\mathbf{Z}_C^{-1}(\rho_C(t) - \rho_{C\beta}) \quad .$$

Then the master equation (9.2.1) may be transformed to read

$$\dot{\rho}_C(t) = -\mathbf{V}_C\mu_C(t) - \int_0^t ds\, \mathbf{R}_C(t-s)\mu_C(s) \quad , \tag{9.2.6}$$

where the transport operators are defined by

$$\mathbf{V}_C X_C = i\beta\, \mathbf{C}\, \mathrm{tr}_L\{\mathbf{L}\,\mathbf{\Sigma}\, X_C\} \tag{9.2.7}$$

and

$$\mathbf{R}_C(t) X_C = \beta\, \mathbf{C}\, \mathrm{tr}_L\{\mathbf{L}\, e^{-i(1-\mathbf{P}^T)\mathbf{L}t}(1 - \mathbf{P}^T)\mathbf{L}\,\mathbf{\Sigma}\, X_C\} \quad . \tag{9.2.8}$$

The form (9.2.6) of the evolution law is particularly useful if we want to study the linear response of the system to an applied magnetic field $\vec{h}_1(t)$. Such a perturbation is described by an additional term in the Hamiltonian of the form

$$H'(t) = -\gamma\hbar\vec{R}\cdot\vec{h}_1(t) = -\vec{M}\cdot\vec{h}_1(t) \quad . \tag{9.2.9}$$

As shown in Sect.6.5 the perturbation $H'(t)$ can just be added to $\mu_C(t)$ in (9.2.6).

The general properties of the master equation discussed in Chap.5 and Sect.6.5 apply to the present case accordingly. It must be noted, however, that the time-reversal transformation reverses the direction of an external magnetic field. For explicit evaluations we now provide some useful relations.

By virtue of (5.3.1,2) and (9.2.4) the transport operator (9.2.7) may be transformed to read

$$\mathbf{V}_C X_C = -\frac{i}{\hbar}\,[\rho_{C\beta}, X_C] \quad . \tag{9.2.10}$$

On defining a coarse-grained Hamiltonian H_C by

$$\rho_{C\beta} = e^{-\beta H_C} \quad , \tag{9.2.11}$$

(9.2.10) takes the form

$$\mathbf{V}_C X_C = i\beta\mathbf{L}_C\, \mathbf{\Sigma}_C X_C \quad , \tag{9.2.12}$$

where

$$\mathbf{L}_C X_C = \frac{1}{\hbar}\,[H_C, X_C] \tag{9.2.13}$$

and

$$\mathbf{\Sigma}_C X_C = \frac{1}{\beta}\int_0^\beta d\alpha\, e^{-\alpha H_C}\, X_C\, e^{\alpha H_C}\, \rho_{C\beta} \quad . \tag{9.2.14}$$

The stochastic operator $\mathbf{\Omega}_C = (-1/\beta)\mathbf{V}_C\mathbf{Z}_C^{-1}$ now becomes

$$\mathbf{\Omega}_C = -i\mathbf{L}_C\, \mathbf{\Sigma}_C \mathbf{Z}_C^{-1} \quad . \tag{9.2.15}$$

The transport operator (9.2.8) can be written in a form corresponding to (5.4.7). From (9.1.24) and (9.2.7) we find

$$\mathbf{P}^T\mathbf{L}\Sigma X_C = \frac{1}{i\beta}\Sigma \mathbf{Z}_C^{-1}\mathbf{V}_C X_C \quad , \qquad (9.2.16)$$

which gives by virtue of (9.2.12,15)

$$\mathbf{P}^T\mathbf{L}\Sigma X_C = -i\Sigma\Omega_C^T X_C \quad . \qquad (9.2.17)$$

Equation (9.2.8) can then be shown to take the form

$$\mathbf{R}_C(t)X_C = \beta\,\mathbf{C}\,\mathrm{tr}_L\left\{(-i\mathbf{L}-\Omega_C)\, e^{-i(1-\mathbf{P}^T)\mathbf{L}t}\,\Sigma(i\mathbf{L}-\Omega_C^T)X_C\right\} \quad , \qquad (9.2.18)$$

which is a suitable starting point for explicit calculations.

For the further evaluation we split the Hamiltonian H into

$$H = H_S + H_L + gH_{SL} \quad . \qquad (9.2.19)$$

The pure spin Hamiltonian H_S is taken to be the Zeeman interaction

$$H_S = \hbar\omega_0 R^z \quad , \qquad (9.2.20)$$

where

$$\omega_0 = \gamma h_0 \qquad (9.2.21)$$

is the Larmor frequency in a magnetic field $\vec{h}_0 = (0,0,-h_0)$ of strength h_0 applied along the -z axis. H_L governs the molecular motions independent of the spins, and gH_{SL} is the interaction with the spins. For most interactions of interest we have

$$\langle H_{SL}\rangle_L = \frac{\mathrm{tr}_L\{e^{-\beta H_L}\,H_{SL}\}}{\mathrm{tr}_L\{e^{-\beta H_L}\}} = 0 \quad . \qquad (9.2.22)$$

We now expand in terms of the coupling constant g. Most transformations are parallel to those carried out in Sect.5.4. Because of (9.2.22), we obtain from (9.2.4,11)

$$H_C = H_S + O(g^2) \quad , \qquad (9.2.23)$$

which gives in connection with (9.1.22) and (9.2.14)

$$\mathbf{Z}_C = \Sigma_C + O(g^2) \quad . \qquad (9.2.24)$$

Thus, using (9.2.15) we find

$$\Omega_C = -\,i\mathbf{L}_C + O(g^2) = -\,i\mathbf{L}_S + O(g^2) \quad . \qquad (9.2.25)$$

Further, (9.2.18) gives

$$\mathbf{R}_C(t)X_C = g^2\beta\mathbf{C}\,\mathrm{tr}_L\{\mathbf{L}_{SL}\, e^{-i(\mathbf{L}_S+\mathbf{L}_L)t}\,\hat{\Sigma}\mathbf{L}_{SL}X_C\} + O(g^3) \quad , \qquad (9.2.26)$$

where $\hat{\Sigma}$ is Σ for vanishing g.

One simple example for H_{SL} is the interaction

$$H_{SL} = g\sum_l \vec{I}_l\cdot\vec{s}_l \quad , \qquad (9.2.27)$$

where the operators $\vec{\Gamma}_l$ depend on molecular degrees of freedom independent of the spins. We assume that the variables Γ_l^{ν} behave quasi classically with mean values

$$\langle\Gamma_l^{\nu}(t)\rangle_L = 0 \tag{9.2.28}$$

and correlations

$$\langle\Gamma_l^{\nu}(t)\Gamma_{l'}^{\mu}(s)\rangle_L = \delta_{ll'}\delta^{\nu\mu}\varphi_L(|t-s|) \quad . \tag{9.2.29}$$

The interaction Hamiltonian (9.2.27) may be written

$$H_{SL} = g\sum_l (\Gamma_l^z s_l^z + \Gamma_l^+ s_l^- + \Gamma_l^- s_l^+) \tag{9.2.30}$$

where

$$\Gamma_l^{\pm} = \frac{1}{2}(\Gamma_l^x \pm i\Gamma_l^y) \quad . \tag{9.2.31}$$

Then, the correlations (9.2.29) become

$$\langle\Gamma_l^z(t)\Gamma_{l'}^{\pm}(s)\rangle = \langle\Gamma_l^+(t)\Gamma_{l'}^+(s)\rangle = \langle\Gamma_l^-(t)\Gamma_{l'}^-(s)\rangle = 0 \quad , \tag{9.2.32}$$

$$\langle\Gamma_l^z(t)\Gamma_{l'}^z(s)\rangle = 2\langle\Gamma_l^+(t)\Gamma_{l'}^-(s)\rangle = \delta_{ll'}\varphi_L(|t-s|) \quad .$$

By utilizing (9.2.30,32) and

$$\mathbf{L}_S s_l^z = 0 \quad , \quad \mathbf{L}_S s_l^{\pm} = \pm\omega_0 s_l^{\pm} \quad , \tag{9.2.33}$$

we obtain from (9.2.26)

$$\begin{aligned}\mathbf{R}_C(t)\, e^{i\mathbf{L}_S t} X_C = \frac{g^2\beta}{\hbar^2}\varphi_L(t)\mathbf{C}\sum_l \Big\{ & [s_l^z, \Sigma_S[s_l^z, X_C]] \\ & + \frac{1}{2} e^{i\omega_0 t}[s_l^+, \Sigma_S[s_l^-, X_C]] + \frac{1}{2} e^{-i\omega_0 t}[s_l^-, \Sigma_S[s_l^+, X_C]]\Big\} + O(g^3) \quad ,\end{aligned} \tag{9.2.34}$$

where Σ_S coincides with Σ_C for the present approximation.

In a coordinate frame rotating about the z axis with the Larmor frequency ω_0, a change of the coarse-grained probability density arises only through the interaction $g\,H_{SL}$. Hence, for weak interactions the characteristic time for a change of the macroscopic state will be large compared with the decay time of $\varphi_L(t)$. We then can disregard the memory effect in the master equation (9.2.1). Using $\Phi_C(t) = -(1/\beta)\mathbf{R}_C(t)\mathbf{Z}_C^{-1}$ and (9.2.24,25,34), we may proceed as in Sect.5.4. We then arrive at an approximate master equation of the form

$$\dot{\rho}_C(t) = -i\mathbf{L}_S\rho_C(t) + \Lambda_C\rho_C(t) \quad , \tag{9.2.35}$$

where

$$\begin{aligned}\Lambda_C X_C = -\mathbf{C}\sum_l \Big\{ & \varkappa_0[s_l^z, \Sigma_S[s_l^z, \Sigma_S^{-1}X_C]] \\ & + \frac{1}{2}(\varkappa' + i\varkappa'')[s_l^+, \Sigma_S[s_l^-, \Sigma_S^{-1}X_C]] + \frac{1}{2}(\varkappa' - i\varkappa'')[s_l^-, \Sigma_S[s_l^+, \Sigma_S^{-1}X_C]]\Big\} \quad .\end{aligned} \tag{9.2.36}$$

The real parameters $\varkappa_0, \varkappa'$, and $\varkappa''$ are defined by

$$\varkappa_0 = \frac{g^2}{\hbar^2} \int_0^\infty ds\, \varphi_L(s) \tag{9.2.37}$$

and

$$\varkappa' + i\varkappa'' = \frac{g^2}{\hbar^2} \int_0^\infty ds\, e^{i\omega_0 s} \varphi_L(s) \quad . \tag{9.2.38}$$

9.3 The Bloch Equations

The master equation (9.2.35) can be used to derive relaxation equations for the mean values $\langle\vec{R}(t)\rangle$ of the macroscopic variables. Since we have taken particularly simple examples for the spin Hamiltonian H_S and the interaction $g\, H_{SL}$, the master equation (9.2.35) is uncomplicated enough to allow for a determination of the relaxation laws without utilizing the renormalization techniques presented in Sect.5.6. With

$$\mathsf{L}_S R^z = 0 \quad , \quad \mathsf{L}_S R^\pm = \pm\omega_0 R^\pm \tag{9.3.1}$$

and

$$\mathrm{tr}_S\{\vec{R}\mathsf{C}X_S\} = \mathrm{tr}_S\{\vec{R}X_S\} \quad , \tag{9.3.2}$$

we obtain from (9.2.35,36)

$$\begin{aligned} \frac{\partial}{\partial t} \langle R^z(t)\rangle = - \sum_l \mathrm{tr}_S\Big\{&\frac{1}{2}(\varkappa' + i\varkappa'')[R^z, s_l^+]\, \Sigma_S[s_l^-, \Sigma_S^{-1}\rho_C(t)] \\ &+ \frac{1}{2}(\varkappa' - i\varkappa'')[R^z, s_l^-]\, \Sigma_S[s_l^+, \Sigma_S^{-1}\rho_C(t)]\Big\} \end{aligned} \tag{9.3.3}$$

and

$$\begin{aligned} \frac{\partial}{\partial t} \langle R^+(t)\rangle = i\omega_0\langle R^+(t)\rangle - \sum_l \mathrm{tr}_S\Big\{&\varkappa_0[R^+, s_l^z]\, \Sigma_S[s_l^z, \Sigma_S^{-1}\rho_C(t)] \\ &+ \frac{1}{2}(\varkappa' - i\varkappa'')[R^+, s_l^-]\, \Sigma_S[s_l^+, \Sigma_S^{-1}\rho_C(t)]\Big\} \quad . \end{aligned} \tag{9.3.4}$$

The equation for $\langle R^-(t)\rangle$ is the complex conjugate of (9.3.4).

The spin operators obey the relations

$$\begin{aligned} &[s_l^z, s_{l'}^\pm] = \pm\delta_{ll'} s_l^\pm , \quad [s_l^+, s_{l'}^-] = 2\delta_{ll'} s_l^z \quad , \\ &s_l^+ s_l^+ = s_l^- s_l^- = 0 \ , \quad s_l^z s_l^z = \frac{1}{4} \ , \quad s_l^\pm s_l^z + s_l^z s_l^\pm = 0 \quad , \end{aligned} \tag{9.3.5}$$

which may be used to show that

$$\Sigma_S^{-1}[s_l^z, \Sigma_S\, s_l^\pm] = \pm s_l^\pm \quad , \tag{9.3.6}$$

$$\Sigma_S^{-1}[s_l^\pm, \Sigma_S\, s_l^z] = \mp \frac{\hbar\omega_0}{2k_B T} \coth\left(\frac{\hbar\omega_0}{2k_B T}\right) s_l^\pm \quad ,$$

$$\Sigma_S^{-1}[s_1^+, \Sigma_S\, s_1^-] = -\Sigma_S^{-1}[s_1^-, \Sigma_S\, s_1^+]$$

$$= 2\,\frac{k_BT}{\hbar\omega_0}\,\mathrm{sh}\left(\frac{\hbar\omega_0}{k_BT}\right)\left[s_1^z + \frac{1}{2}\,\mathrm{th}\left(\frac{\hbar\omega_0}{2k_BT}\right)\right] \quad .$$

By utilizing (9.1.7), (9.3.5), and $\Sigma_S^T = \Sigma_S$, the right-hand sides of (9.3.3,4) can be transformed into expressions which are readily evaluated by virtue of (9.3.6). We then arrive at

$$\frac{\partial}{\partial t}\langle R^z(t)\rangle = -\frac{1}{T_1}\left(\langle R^z(t)\rangle - \langle R^z\rangle_\beta\right) \tag{9.3.7}$$

and

$$\frac{\partial}{\partial t}\langle R^\pm(t)\rangle = \pm i(\omega_0 + \Delta\omega)\langle R(t)\rangle - \frac{1}{T_2}\langle R^\pm(t)\rangle \quad , \tag{9.3.8}$$

where

$$\langle R^z\rangle_\beta = -\frac{N}{2}\,\mathrm{th}\left(\frac{\hbar\omega_0}{2k_BT}\right) \tag{9.3.9}$$

is the equilibrium value of R^z,

$$\frac{1}{T_1} = 2\kappa'\,\frac{k_BT}{\hbar\omega_0}\,\mathrm{sh}\left(\frac{\hbar\omega_0}{k_BT}\right) \tag{9.3.10}$$

and

$$\frac{1}{T_2} = \kappa_0 + \kappa'\,\frac{\hbar\omega_0}{2k_BT}\,\coth\left(\frac{\hbar\omega_0}{2k_BT}\right) \tag{9.3.11}$$

are relaxation times, and

$$\Delta\omega = \kappa''\,\frac{\hbar\omega_0}{2k_BT}\,\coth\left(\frac{\hbar\omega_0}{2k_BT}\right) \tag{9.3.12}$$

is a frequency shift. Equations (9.3.7,8) are commonly referred to as the Bloch equations [191].

In most relaxation problems, it is possible to make the high-temperature approximation, which is valid when $\hbar\omega_0 \ll k_BT$. To proceed further we shall also assume a simple exponential correlation function for the $\vec{\Gamma}_1(t)$ with correlation time τ_c:

$$\frac{g^2}{\hbar^2}\,\varphi_L(t) = A\,e^{-|t|/\tau_c} \quad . \tag{9.3.13}$$

We then obtain from (9.2.37,38)

$$\kappa_0 = A\tau_c \;, \quad \kappa' = \frac{A\tau_c}{1+\omega_0^2\tau_c^2} \;, \quad \kappa'' = \frac{A\omega_0\tau_c^2}{1+\omega_0^2\tau_c^2} \quad , \tag{9.3.14}$$

and thus from (9.3.10-12) in the high-temperature approximation

$$\frac{1}{T_1} = \frac{2A\tau_c}{1+\omega_0^2\tau_c^2} \quad , \tag{9.3.15}$$

$$\frac{1}{T_2} = A\tau_c\left(1 + \frac{1}{1+\omega_0^2\tau_c^2}\right) \quad ,$$

and

$$\Delta\omega = \frac{A\omega_0\tau_c^2}{1+\omega_0^2\tau_c^2} \quad . \tag{9.3.16}$$

Of course, the master equation (9.2.35) and the Bloch equations derived from it are only valid if $\tau_c \ll T_1, T_2$. We remark that in the limit of very rapid molecular motion ($\tau_c \ll 1/\omega_0$) the relaxation times T_1 and T_2 are equal, as is often observed in low viscosity fluids.

9.4 Dynamic Susceptibility

In Sect.5.6 we have shown that the equations (5.6.22) for the mean relaxation lead to the evolution laws (5.6.26) for the canonical correlations of the macroscopic variables. Hence, the Bloch equations (9.3.7,8) can be used to determine the time evolution of canonical correlations

$$C^{\nu\mu}(t) = (\delta R^\nu(t), \delta R^\mu) \tag{9.4.1}$$

of the bulk spin. By disregarding the frequency shift, we find

$$C^{zz}(t) = \sigma_\parallel \, e^{-|t|/T_1} \quad , \tag{9.4.2}$$

$$C^{xx}(t) = C^{yy}(t) = \sigma_\perp \, e^{-|t|/T_2} \cos(\omega_0 t) \quad ,$$

$$C^{yx}(t) = -C^{xy}(t) = \sigma_\perp \, e^{-|t|/T_2} \sin(\omega_0 t) \quad .$$

In the high-temperature approximation the equilibrium variances $\sigma_\parallel$ and $\sigma_\perp$ are given by

$$\sigma_\parallel = \sigma_\perp = \frac{N}{4} \quad . \tag{9.4.3}$$

Let us now assume that an applied alternating field $\vec{h}_1(t)$ is present, giving an extra term (9.2.9) in the Hamiltonian. We study the linear response of the bulk magnetization to this perturbation. By utilizing (9.1.8), (9.2.9), and the fluctuation-dissipation theorem (6.1.20), we find

$$\Delta\langle M^\nu(t)\rangle = \int_0^t ds \sum_\mu \chi^{\nu\mu}(t-s) h_1^\mu(s) \quad , \tag{9.4.4}$$

where the response functions are given by

$$\chi^{\nu\mu}(t) = -\theta(t)\,\frac{\gamma^2\hbar^2}{k_B T}\,\dot{C}^{\nu\mu}(t) \quad . \tag{9.4.5}$$

In particular, the response to a field

$$\vec{h}_1(t) = (h_1,0,0)\,e^{i\omega t} \tag{9.4.6}$$

applied along the x axis is found to be

$$\Delta\langle M^+(t)\rangle = \Delta\langle M^x(t)\rangle + i\Delta\langle M^y(t)\rangle = \chi_\perp(\omega)h_1 e^{i\omega t} \quad , \tag{9.4.7}$$

where we have neglected the transient term. The complex susceptibility $\chi_\perp(\omega)$ is given by

$$\chi_\perp(\omega) = \chi_\perp\,\frac{1 - i\omega_0 T_2}{1 - i(\omega_0 - \omega)T_2} \quad , \tag{9.4.8}$$

where

$$\chi_\perp = \frac{\gamma^2\hbar^2}{k_B T}\,\sigma_\perp \tag{9.4.9}$$

is the static transverse susceptibility.

It should be noted that the 1 in the numerator of (9.4.8) is generally omitted [185,186] since it can be neglected for $\omega \approx \omega_0$, if $\omega_0 T_2 \gg 1$. From (9.4.8) we obtain, however, the correct static susceptibility in the limit $\omega \to 0$.

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