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With 4 Figures

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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 expressions 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 projection 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 co-editor were most helpful.

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Stuttgart, Autumn 1981 *Hermann Grabert*

# Contents

# 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.

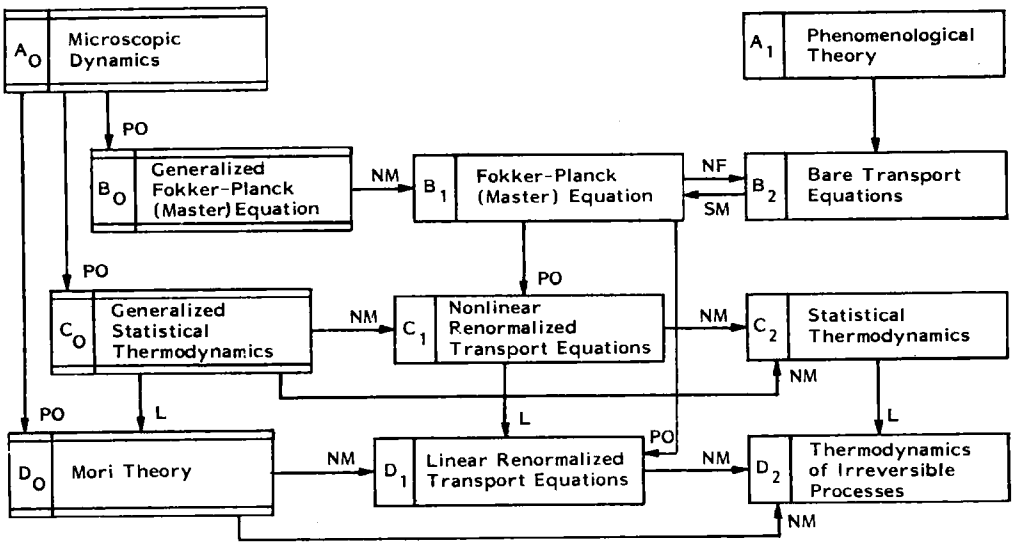
For most macroscopic systems the discrete nature of the microscopic states can safely be neglected, and they are well described on the macroscopic level by a continuous stochastic process. In a pioneering work GREEN [1] derived a *Fokker-Planck equation* for such nonequilibrium systems which explicitly 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-

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".




Theories:

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

2 In quantum-statistical mechanics $\rho$ is also referred to as the density matrix or statistical operator.