

FLUCTUATIONS IN SYSTEMS FAR
FROM EQUILIBRIUM

BY

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A unified formulation of transport and fluctuations in a nonequilibrium fluid is described at both the kinetic and the hydrodynamic levels. The method is based on the analysis of a generating functional for the fluctuations of the set of observables of interest around their average values. It is shown that the first functional derivatives of such a generating functional obey an inhomogeneous form of the macroscopic regression laws (nonlinear Boltzmann equation or nonlinear Navier-Stokes equations). From this equation the dynamics of multi-space and -time fluctuations may be obtained by suitable functional differentiation. In particular the equations for the second order correlation functions of fluctuations at different and equal times are obtained to illustrate the method. The dynamics of a nonequilibrium fluid is governed by three sets of coupled equations: (1) nonlinear equations for the macroscopic observables, (2) linear homogeneous equations for the two-time correlation functions, and (3) linear

inhomogeneous equations for the equal time correlation functions. The description obtained constitutes a precise statement of the generalization to nonequilibrium states of Onsager's assumption on the regression of fluctuations. The results apply to general nonstationary nonequilibrium states, either stable or unstable. The description of nonequilibrium fluctuations obtained rests on the same theoretical basis as the macroscopic description of the system (Boltzmann kinetic theory for a low density gas and hydrodynamics for a general fluid).

CHAPTER I INTRODUCTION

A large class of macroscopic irreversible processes in many-body systems is adequately described in terms of relatively few (compared to the number of degrees of freedom) macroscopic variables, changing continuously in time.¹ This description applies when the time scale of interest is large compared to a microscopic time scale characteristic of the problem and the system considered. The macroscopic variables can be identified with the quantities measured in an experiment, and their values at a time t completely characterize the state of the system at that time. Examples of such a set of observables are the hydrodynamic densities in a fluid and the concentrations describing a chemical reaction. On this macroscopic scale static and dynamic properties of the system are expected to be governed by a closed set of macroscopic laws. In particular the time dependent properties should obey a set of differential equations of first order in time. It is then a deterministic description in the sense that the equations assign fixed values to all the macroscopic variables, once the values at $t=0$ have been given. The completeness of a set of macroscopic observables for the description of a particular problem on a particular time scale is difficult to determine a priori and is established only by the derivation of the macroscopic equations themselves.*

*The complete set of observables often coincides with the set of conserved variables in the system. However nonlinear coupling between the hydrodynamic modes in a fluid can lead to the appearance of memory

The role of statistical mechanics consists in providing a microscopic basis for the macroscopic description, defining its limit of applicability, and establishing a precise connection between the dynamics of the observables and the time evolution of the positions and momenta of all the particles in the system.

A derivation of the macroscopic laws from the microscopic dynamics, governed by the Liouville equation, can be accomplished by introducing the idea of several well separated time scales in nonequilibrium fluids.³ A system in an arbitrary nonequilibrium state is considered. On a very short time scale, of the order of or smaller than the duration of a collision, the dynamics of a system of N particles is very complex and a large number of variables (the $6N$ coordinates and momenta of the particles in the system or, alternatively, all the reduced distribution functions) is necessary to describe it. However, after a microscopic time, of the order of the duration of a collision, or mean collision time, τ_c^* , the system relaxes to a kinetic regime, where the dynamics may be described more simply in terms of the average density in the single particle phase space.^{4,5} Therefore, when the time scale of interest is large compared to τ_c , a contraction of the formal description of the dynamics of the N -body problem to a description in terms of the one-particle distribution function is obtained.

effects in the macroscopic equations of motion: this indicates that the chosen set of variables is not complete and needs to be enlarged (for a discussion and references on this point see Ref. 2).

*For intermolecular forces with a finite and nonvanishing range, τ_c is defined as the ratio of the force range, σ , and the mean thermal speed of the molecules, v_0 , -i.e. $\tau_c = \sigma/v_0$.

At larger time scales (for gases larger than the time between collisions, or mean free time, t_f ,*) a further contraction of the description takes place. The system relaxes to a state near local equilibrium and its dynamics is described in terms of an even smaller number of variables, identified with the local conserved densities, e.g., mass density, energy density, flow velocity.⁶ This is the hydrodynamic regime, which describes variations on time scales of the order, for example, of the time required by a sound wave in a fluid to cross a region of macroscopic interest.⁷

The macroscopic regression laws governing the relaxation of a system displaced from equilibrium can be derived in principle by averaging the microscopic equations of motion and introducing approximations suitable for the time scale of interest. For example, in the limit of times large compared to a collision time (i.e., the kinetic regime), the nonlinear Boltzmann equation for the one-particle distribution function is obtained by a low density closure of the BBGKY hierarchy.^{5,8} The Chapman-Enskog expansion provides then a systematic method for deriving the hydrodynamic equations for the average densities in the gas, on the longer time scale.^{8,9} Alternatively, the hydrodynamic equations can be obtained directly by averaging the microscopic conservation laws, bypassing consideration of the kinetic stage.^{6,10}

The contraction of the description of the dynamics of a many-particle system in terms of few average variables naturally introduces the concept of fluctuations. From a microscopic point of view in fact

*Defined as $t_f = \lambda/v$, where λ is the mean free path of the molecules. For liquids, t_f can be of the order of τ_c and the separation of time scales is no longer useful.

the dynamical variables fluctuate instantaneously around their average values. The physical origin of the fluctuations can be different for different systems. In general, however, the amplitude of their space and time correlations controls the adequacy of the macroscopic description and can be measured in a variety of experiments. Thus the statistical mechanics of irreversible processes in a many-particle system should also provide a framework to describe fluctuations in an arbitrary nonequilibrium state.

The description of fluctuations in equilibrium systems is well established from both phenomenological considerations,¹¹ and first principles calculations for some limiting cases (e.g., low density gases).¹² A precise connection between the spontaneous fluctuations in the equilibrium state and the macroscopic response of the system to a small external perturbation is established by the fluctuation-dissipation theorem.^{13,14} This result is concisely expressed in Onsager's assumption on the regression of fluctuations,¹⁵ which states that spontaneous fluctuations around the equilibrium value decay in time according to the same linear laws governing the relaxation of a macroscopic state close to equilibrium. In other words the linearized regression laws apply regardless of whether the nonequilibrium condition is prepared or occurs spontaneously. The adequacy of this assumption is a consequence of the fact that the size of the equilibrium fluctuations is limited by their thermal origin. Furthermore the space correlation of the equal time fluctuations can be calculated directly from the equilibrium ensemble.

The relationship of correlation functions and response functions to a great number of measurable properties of macroscopic systems in equilibrium is also well understood and a wide variety of experiments is available for comparison.¹⁶ The interpretation of Rayleigh-Brillouin light scattering experiments in fluids¹⁷ constitutes a well known example of the success of the equilibrium fluctuations theory. The detailed evaluation of time dependent correlation functions remains in many cases a difficult many-body problem, but the theoretical formulation can be stated clearly and is founded on the basic principles of statistical mechanics.

The corresponding theoretical and experimental study of fluctuations in a nonequilibrium system is much less complete and several new problems arise, even from a purely theoretical viewpoint, in addition to the difficult computational aspects.

The systems considered are in general open systems, in contact with several reservoirs, which are not in equilibrium among themselves.^{3,6} These reservoirs impose external forces and fluxes on the system, preventing it from reaching thermodynamic equilibrium and keeping it in a nonequilibrium state, which is stationary if the external forces are time independent. In contrast to the equilibrium system, which is specified by a unique thermodynamic state, a large class of nonequilibrium states must now be considered. The first problem encountered when dealing with systems out of equilibrium is therefore the adequate characterization of the particular nonequilibrium phenomenon of interest.

Furthermore, the formulation of the macroscopic description of the system and the derivation of the nonlinear regression laws for a

complete set of observables, such as the nonlinear hydrodynamic equations, presents several difficulties. At the hydrodynamic level the evaluation of the form of the macroscopic fluxes as functionals of the thermodynamic forces is required. These constitutive relationships are highly nonlinear and only a formal expression can be provided in the general case.^{10,19} An explicit evaluation has only been performed in specific model cases (shear flow^{10,19-24}) or under precise limiting conditions (Burnett coefficients^{18,20}). On the other hand, in near equilibrium situations the formalism of linear response theory provides expressions for susceptibilities and transport coefficients in terms of the correlation functions of equilibrium fluctuations (Green-Kubo relations).^{3,6} Nonlinear transport phenomena also can be related to nonequilibrium fluctuations by introducing the concept of nonlinear response functions. The understanding of the dynamics of fluctuations in the nonequilibrium state is therefore intimately related to the description of energy, momentum, mass and charge transport in systems far from equilibrium.

Other characteristic nonequilibrium phenomena where fluctuations play an important role are the appearance of instabilities, bifurcations and turbulences, and the related onset of nonequilibrium phase transitions.²⁵ A system macroscopically displaced from equilibrium and brought outside the region of applicability of the linear response theory (into a region where the macroscopic regression laws are nonlinear) evolves through a succession (or branch) of nonequilibrium states as the magnitude of the parameter measuring the strength of the external perturbation increases. At some critical value of this parameter the state of the system may become unstable. The system will then make a

transition into a new branch of states. The occurrence of such instabilities may lead to a change of symmetry of the stable state of the system. In this sense the phenomenon is analogous to a phase transition in a system in thermodynamic equilibrium. Therefore, as the mechanism of equilibrium phase transition can be understood by recognizing the importance of the fluctuations near the transition point, the occurrence of bifurcations (and other nonequilibrium phase transitions) is intimately related to the fluctuations in the system at the instabilities.

A large variety of physical systems shows this general behavior. The most popular hydrodynamic example is the Bénard instability, occurring in a liquid layer heated from below in the gravitational field. Other examples are found in nonlinear optics, autocatalytic reactions and biological systems. The formulation of a theory of nonequilibrium fluctuations which does not impose restrictions on the size of the fluctuations and applies near instabilities is an essential starting point for the understanding of all these nonequilibrium phenomena.

However, even for the simplest case of hydrodynamic fluctuations, it is not obvious how Onsager's assumption should be generalized for such nonequilibrium states. Because of the nonlinear character of the average regression laws, the dynamics of the macroscopic observables is no longer the same as that of their fluctuations. Furthermore a non-trivial problem is the determination of the source of the fluctuations, which may no longer be simply thermal in origin and whose knowledge is required for the specification of the equal time correlation functions.

There have been several recent studies of fluctuations in nonequilibrium stationary states that are similar in spirit and objectives to

the present discussion. It therefore seems instructive to put the present work in context by presenting a brief overview of these approaches. They can be classified in general into two broad categories: stochastic approaches,²⁶⁻³³ where the microscopic fluctuating variables are assumed to define a random process, characterized by a set of probability densities, and microscopic approaches,³⁴⁻⁴⁶ which attempt to derive from first principles the dynamics of nonequilibrium fluctuations.

The stochastic formulations are essentially based on a generalization of the Onsager-Machlup regression hypothesis to the nonequilibrium case. The time-dependent properties of the system are governed by a set of equations for the probability densities (Fokker Planck equations) or for the stochastic variables themselves (Langevin equations).

A stochastic theory of hydrodynamic fluctuations has been developed by Tremblay, Arai and Siggia²⁶ by assuming that the fluctuating hydrodynamic equations proposed by Landau and Lifschitz^{47,48} can be applied to describe not only fluctuations in the equilibrium state, but also small fluctuations around a nonequilibrium stationary state. The time evolution of the fluctuating variables is then governed by a linear Langevin equation whose coefficients depend on the nonequilibrium state of the system. The correlation of the random forces is chosen to have the same form as in equilibrium, except with local thermodynamic variables for the nonequilibrium state. The characteristic feature of the Langevin theory is the separation of the time variation into a slowly varying and a rapidly varying part. The basic assumption is that the correlations of the fast variables are determined by a local equilibrium ensemble. This Langevin theory has been successfully

applied by several authors^{26,49-51} to the evaluation of the scattering of light from a fluid with a temperature gradient and/or in shear flow.* However the limitation on the size of the fluctuations clearly restricts its applicability to regions far from instabilities and critical points. Furthermore in Ref. 26 the example of a case where the theory fails is given: electrons scattering off impurities to which a potential difference is applied. Presumably this is a case when the local equilibrium assumption for the fast variables does not apply.

A formal theory of nonequilibrium fluctuations and nonlinear irreversible processes has been developed by Grabert, Graham and Green.^{27,28} Their approach generalizes to the nonlinear regime the functional integral expression for the transition probability between two macroscopic states introduced by Onsager and Machlup^{1,15} as an extension to the time dependent domain of Boltzmann's relationship between entropy and probability. The basic assumption of the theory is that the probability of a given fluctuation from one state to another is measured by the minimum increase in action associated with the change among the two states considered. This minimum principle provides the possibility of constructing a path integral expression for the conditional probability which appears as a natural generalization of the Onsager-Machlup functional. However this minimum principle is purely an assumption and has not been justified on any microscopic basis. Only a posteriori can it be seen that the results obtained agree with those derived through different formulations. In particular the conditional

*It should be pointed out that the results of Ref. 50 for the Brillouin scattering in temperature gradient are not in agreement with the results of the other calculations.^{26,49}

probability can be shown to satisfy a Fokker-Planck equation. This equation has also been applied by Grabert²⁸ to evaluate the spectrum for light scattering from a fluid in a temperature gradient. His results agree with those derived by other methods.

Within the framework of this generalized Onsager-Machlup theory, Graham²⁵ has also analyzed in detail problems associated with the stability and the breaking of symmetry in nonequilibrium stationary states.

Several authors²⁹⁻³² have formulated studies of nonequilibrium fluctuations based on a master equation in an appropriate stochastic space. With the aim of generalizing Landau-Lifshitz's fluctuating hydrodynamics to the nonlinear region, Keizer³⁰ has rewritten the microscopic conservation laws in a fluid in the form of master equations by describing the fluid in terms of elementary molecular processes. His results support the Langevin theory proposed in Ref. 26. Coarse grained master equations for inhomogeneous systems* have been assumed as the starting point to describe phase space fluctuations by Onuki³¹ and Ueyama.³² For systems near equilibrium the linearized Boltzmann-Langevin equation⁵³ is recovered. Furthermore by using the Chapman-Enskog expansion method fluctuating hydrodynamics can be derived. Finally, van Kampen²⁹ has applied the method of expansion in the size of the system to the solution of master equations for several problems, from the Boltzmann equation to the rate equations governing chemical reactions. The principal limitations of the master equation approaches are the necessity of assuming (instead of deriving from first

*This is in effect a generalization of an analogous master equation proposed by Logan and Kac⁵² for homogeneous systems.

principles) the basic equation, and the strong dependence of this equation on the model considered.

Finally, a generalization to the nonlinear regime of the linearized Boltzmann-Langevin equation⁵³ has been proposed³³ to describe nonequilibrium phase space fluctuations in low density gases. This method is similar in spirit to the fluctuating hydrodynamics of Ref. 26, since the correlation of the random forces is again assumed to have a local equilibrium form.

The microscopic studies are based on several different techniques. First of all the methods of the kinetic theory of gases have been used³⁴⁻³⁸ to describe phase space fluctuations. To make any progress with the formal theory the limitation of low density has in general to be imposed. This restriction, however, allows the introduction of controlled approximations. Furthermore, the kinetic theory is more general than the hydrodynamic description since it describes fluctuations on shorter space and time scales and it incorporates the latter. In particular Ernst and Cohen³⁷ have applied the methods of the nonequilibrium cluster expansion to derive kinetic equations for the equal and unequal time two-point correlations of phase space fluctuations for a gas of hard spheres. The meaning and adequacy of their expansion will be discussed in Chapter IV and Appendix D, where an alternative method, leading to equivalent results, is presented.

An alternative microscopic theory of fluctuations in nonequilibrium steady states has been developed by an M.I.T. group.³⁹⁻⁴² For states not too far from equilibrium (up to second order in the parameters measuring the deviations from equilibrium) they apply the method of nonlinear response theory to express nonequilibrium averages and

correlation functions in terms of higher order equilibrium correlation functions.⁴⁰ These correlation functions are then evaluated (in the hydrodynamic case) by assuming a separation of time scales in the system, implying that the correlations involving the dissipative fluxes decay on a time scale shorter than the macroscopic time scale of interest. Their results are also generalized to nonequilibrium stationary states arbitrarily far from equilibrium by employing the projection operator techniques.⁴¹ They conclude that in general a simple generalization of the equilibrium fluctuation-dissipation theorem to a local equilibrium form does not hold. The formalism used however obscures many of the physical hypotheses entering the derivation. Furthermore the separation in fast and slow variables is not well founded for states arbitrarily far from equilibrium.

Finally Kirkpatrick, Cohen and Dorfman⁴³⁻⁴⁶ developed a hydrodynamic theory of nonequilibrium fluctuations in stationary states based on the use of projection operator techniques and on the Kadanoff-Swift mode-coupling theory for the evaluation of the equal time correlation functions. They also have applied their description of hydrodynamic fluctuations to the problem of light scattering from a fluid subject to a temperature gradient, for both the cases of small and large gradient.

The formulations briefly described here suffer from several limitations. Their applicability is often restricted to nonequilibrium stationary states and to small fluctuations around the states. The latter condition implies that the system has to be far from instabilities and critical points. A precise connection between the stochastic and the microscopic approaches, as is possible for the case

of equilibrium fluctuations, has not been established. In the stochastic methods it is often not clear how the macroscopic information on the nonequilibrium state, as specified in an experiment, enters the problem. In general there is a need for developing an exact treatment of nonequilibrium systems whose validity extends to both the kinetic and hydrodynamic regimes and that establishes a precise connection between the theoretical and the experimental description.

The objective of the present work is to provide a unified formulation of the description of nonequilibrium fluctuations founded on a microscopic basis and constituting a precise statement of the generalization of Onsager's assumption on the regression of fluctuations to arbitrary nonequilibrium states. The problems mentioned above are addressed explicitly. An open system in contact with external reservoirs is considered. The reservoirs prepare or maintain the system in a general nonequilibrium state. The results derived apply to nonstationary states, either stable or unstable.

The method rests on the definition of a generating functional whose first functional derivatives are directly related to the complete set of macroscopic nonequilibrium observables relevant to the problem considered. Higher order functional differentiation generates the correlation functions of the fluctuations of the chosen dynamical variables around their average values. The first advantage of this approach is that it makes it possible to discuss the problems of average behavior and fluctuations in a unified context. Characterizing the nonequilibrium state amounts to providing a statistical mechanical derivation of the macroscopic regression laws. This can be accomplished both at the

kinetic and hydrodynamic level in such a way that the properties of the generating functional are preserved.

A set of nonlinear equations for the first functional derivatives is first obtained: these equations have the same form as the macroscopic regression laws, the only difference being the appearance of additional contributions arising from transient effects in the system whose lifetime is short compared to the time scale of interest. By functionally differentiating these equations, equations for the correlation functions are obtained.

After defining precisely in Chapter II the class of problems considered and the general form of the associated generating functional, the specific cases of hydrodynamic and kinetic regimes are analyzed in Chapter III and Chapter IV, respectively.

The appropriate macroscopic variables for the hydrodynamic description are the five average conserved densities. For simplicity attention is limited to a simple fluid whose nonequilibrium state is adequately described by the nonlinear Navier-Stokes equations. The set of equations for the first functional derivatives can be derived by using the nonlinear response theory, as shown in Appendix A. The equations are an inhomogeneous form of the nonlinear Navier-Stokes equations. Additional contributions appear as extra terms in the irreversible heat and momentum fluxes. By functionally differentiating these generalized Navier-Stokes equations, a set of linear equations for the correlation functions is obtained. The additional contributions to the irreversible fluxes survive only in the equations for the equal time correlation functions, derived by a limiting procedure on the equations for the multitime fluctuations.

A similar procedure is carried through at the kinetic level in Chapter IV. Here the macroscopic variable of interest is the one-particle distribution function, interpreted as the average of the microscopic phase space density. A low density kinetic equation for the first functional derivative of the associated generating functional is derived in Appendix C by following closely the nonequilibrium cluster expansion used to obtain the Boltzmann equation from the BBGKY hierarchy. Again the equation obtained differs from the nonlinear Boltzmann equation by the presence of extra short-lived terms that only contribute to the equations for the equal time correlations. The equations for the correlation functions are obtained by functional differentiation of this generalized Boltzmann equation.

At both levels of description, kinetic and hydrodynamic, the same structure is obtained: nonlinear equations for the averages and linear equations for the correlation functions. The coefficients in the linear equations depend on the solution of the nonlinear problem: the dynamics of the fluctuations is then entirely governed by the nonequilibrium state. The amplitude of the noise, or source of fluctuations, enters in the form of an inhomogeneous term in the equations for the equal time correlation functions and is derived without introducing any assumptions other than the ones entering in the derivation of the macroscopic equations.

The formulation presented here starts from the Liouville equation for the system, but all the equations considered for the macroscopic description involve only averaged quantities, either observables or correlation functions. The information on the nonequilibrium state enters through boundary and initial conditions for such macroscopic variables: these are the parameters controlled in an experiment.

The linear character of the equations for the correlation functions appears as a general result in the present discussion, not as the outcome of a linearization around the nonequilibrium state, applicable only when the fluctuations are small in size. In this sense the results obtained here agree with the conclusions of the M.I.T. group: the dynamics of the fluctuations is, as in equilibrium, determined by the state of the system in a form that naturally generalizes Onsager's regression hypothesis.

As an application of the general description of nonequilibrium fluctuations obtained by the generating functional method, the velocity-velocity autocorrelation function of a tagged particle in a fluid in shear flow is evaluated in Chapter V, for arbitrarily large shear rate. Substantial simplifications occur in the problem as the result of three conditions: (1) low density, (2) uniform shear rate and (3) Maxwell molecules. In fact it is well known that the irreversible part of the stress tensor may be evaluated exactly from the nonlinear Boltzmann equation for a gas of Maxwell molecules in uniform shear flow.⁵⁴ Consequently, the hydrodynamic problem can be solved exactly to all orders in the shear rate.¹⁹⁻²⁴

Here the velocity-velocity correlation function is evaluated by solving the appropriate set of coupled kinetic equations. The velocity correlations do not decay to zero at long times, since the asymptotic velocity of the particle is equal to the velocity of the fluid at the position of the particle. Nonvanishing position velocity correlations are then present in the fluid at large t . Also, due to the presence of the shear in the fluid, equal time correlation functions which are zero in equilibrium are now nonvanishing.

CHAPTER II
NONEQUILIBRIUM STATISTICAL MECHANICS OF CLASSICAL SYSTEMS

II.1 The Nonequilibrium Distribution Function:
Average Values and Fluctuations

To prepare or maintain a system in a nonequilibrium state external forces have to be introduced in general; nonequilibrium statistical mechanics involves the description of a system in interaction with its surroundings in addition to specified initial conditions.^{3,6} The external forces are assumed to have the character of reservoirs, in the sense that they can be specified independently of the state of the system. In the case of a fluid, for example, the most general situation is represented by interaction with particle, energy and momentum reservoirs.

In classical mechanics a system of N interacting particles enclosed in a volume V is described in terms of the canonical coordinates, $\vec{q}_1, \dots, \vec{q}_N$, and the canonical momenta, $\vec{p}_1, \dots, \vec{p}_N$, of the particles. The state of the system is represented by a point in the $6N$ -dimensional space of the canonical coordinates.

In the language of statistical mechanics the state of the system at the time t is described by the N -particle distribution function,

$$\rho_N(x_1, \dots, x_N, t) = \rho_N(x_1(-t), \dots, x_N(-t)) , \quad (2.1)$$

where $x_i = (\vec{q}_i, \vec{p}_i)$. Here $x_i(t)$ are the canonical coordinates of the i -th particle as evolved from their initial value $x_i(0) \equiv x_i$, according to the dynamics of the system interacting with its surroundings. The

distribution function ρ_N represents the probability that the system lies in a neighborhood $d\Gamma = dx_1 \dots dx_N$ of the phase space point $\Gamma = (x_1, \dots, x_N)$ at time t . The time evolution of the distribution function is governed by the Liouville equation for a system in interaction with its surroundings,^{3,6}

$$\left\{ \frac{\partial}{\partial t} + \mathcal{L} \right\} \rho_N + \rho_N \frac{\partial \vec{F}_n}{\partial \vec{p}_n} = 0 , \quad (2.2)$$

where here and in the following summation over repeated indices is understood. The operator \mathcal{L} in Eq.(2.2) is

$$\mathcal{L} = L(x_1, \dots, x_N) + \vec{F}_n \cdot \frac{\partial}{\partial \vec{p}_n} , \quad (2.3)$$

where L is the Liouville operator for the isolated system, defined as

$$L\rho_N = \{ \rho_N, H \} . \quad (2.4)$$

Here $\{\dots\}$ indicates the classical Poisson bracket and H is the Hamiltonian of the system. \vec{F}_n is an external force representing the effect of the reservoirs on the n -th particle of the system: it depends in principle on all the degrees of freedom of the system and reservoirs and on the details of their interaction. The force \vec{F}_n is in general nonconservative and time dependent, and can be assumed to be applied everywhere at the boundary of the system. This assumption does not constitute a serious restriction since it corresponds to most experimental situations of interest.

Equation (2.2) can be integrated formally when supplemented by an initial condition at $t=0$,

$$\rho_N(x_1, \dots, x_N, 0) = \rho_{N,0}(x_1(0), \dots, x_N(0)) . \quad (2.5)$$

In general $\rho_{N,0}$ will be assumed to represent an arbitrary nonequilibrium state. Also, the distribution function ρ_N is normalized at all times,

$$\sum_{N=0}^{\infty} \int dx_1 \dots dx_N \rho_N(x_1, \dots, x_N, t) = 1 . \quad (2.6)$$

As already mentioned in Chapter I, a macroscopic description of a many-body system only involves a set of relatively few (compared to the number of microscopic degrees of freedom) conveniently chosen variables. The appropriate set of observables depends on the system considered and on the macroscopic space and time scales of interest: the one-particle distribution function is the object to consider in the kinetic theory of gases and the five average conserved densities are the appropriate set of variables to describe hydrodynamics in a simple fluid. In any case the choice is guided by the requirement that the macroscopic description is closed on some time scale when given in terms of the variables considered. A discussion of this point can be found for example in Ref. 1.

Within the formalism of statistical mechanics the macroscopic measurable quantities are defined as ensemble averages of corresponding microscopic dynamical variables, $\{\hat{A}_\alpha(x_1, \dots, x_N)\}_{1 \leq \alpha \leq s}$, functions of the phase space coordinates,

$$A_{\alpha}(t) = \langle \hat{A}_{\alpha}(x_1, \dots, x_N); t \rangle, \quad (2.7)$$

where $\langle \dots; t \rangle$ indicates an average over the nonequilibrium distribution function at time t ,

$$\langle \hat{A}_{\alpha}; t \rangle = \int d\Gamma \hat{A}_{\alpha}(x_1, \dots, x_N) \rho_N(x_1, \dots, x_N, t) \quad (2.8)$$

and $\int d\Gamma \equiv \sum_{N=0}^{\infty} \int dx_1 \dots dx_N$. Here and in the following a caret indicates the microscopic variable as opposed to the averaged one.

An alternative expression of Eq.(2.8) is obtained by observing that the time evolution of the dynamical variables $\{\hat{A}_{\alpha}\}$ is governed by the equation of motion,

$$\left\{ \frac{\partial}{\partial t} - \right\} \hat{A}_{\alpha}(\Gamma, t) = 0, \quad (2.9)$$

where the operator $\left\{ \frac{\partial}{\partial t} - \right\}$ has been defined in Eq.(2.3). Equation (2.9) can be formally integrated with the result,

$$\hat{A}_{\alpha}(\Gamma, t) = T(t, 0) \hat{A}_{\alpha}(\Gamma) . \quad (2.10)$$

The time evolution operator $T(t, t')$ is the solution of the equation,

$$\left\{ \frac{\partial}{\partial t} - \right\} T(t, t') = 0, \quad (2.11)$$

with initial condition $T(t', t') = 1$. It also has the property,

$$T(t, t') T(t', t'') = T(t, t'') . \quad (2.12)$$

Equations (2.2) and (2.9) differ because in a nonconservative system a region of phase space does not maintain a fixed volume as it evolves in time. This can be seen explicitly by evaluating the Jacobian of the transformation of an element of volume in phase space as it evolves in time,

$$J = \frac{\partial(\{x_i(t)\})}{\partial(\{x_i(0)\})} . \quad (2.13)$$

For a conservative system, $J=1$. Here J satisfies the equation,

$$\left\{ \frac{\partial}{\partial t} + \mathcal{L} \right\} J = J \frac{\partial \vec{F}_n}{\partial \vec{p}_n} \quad (2.14)$$

and therefore its change in time accounts for the difference in the time evolution of the distribution function and the dynamical variables.

The average values of the dynamical variables \hat{A}_α can then be written

$$\langle \hat{A}_\alpha; t \rangle = \int d\Gamma \hat{A}_\alpha(x_1, \dots, x_N, t) \rho_N(x_1, \dots, x_N, 0) . \quad (2.15)$$

The possibility of shifting the time from the distribution function onto \hat{A}_α will be useful in the following to display some properties of the time-correlation functions.

At this point the dynamics of the macroscopic set $\{A_\alpha\}$ is determined through the time evolution of the distribution function. In this sense Eq.(2.8) has only the meaning of a formal definition.

On a microscopic scale \hat{A}_α fluctuates instantaneously around its average value. The microscopic fluctuations are defined as

$$\hat{\delta A}_\alpha(\Gamma; t) = \hat{A}_\alpha(\Gamma) - \langle \hat{A}_\alpha; t \rangle . \quad (2.16)$$

A complete description of the system should incorporate a systematic analysis of the fluctuations and of their space- and time-correlation functions of any order.

The second order equal time correlation function is defined as

$$\begin{aligned} M_{\alpha\beta}(t) &\equiv \langle \hat{\delta A}_\alpha \hat{\delta A}_\beta; t \rangle \\ &= \int d\Gamma \hat{\delta A}_\alpha(\Gamma) \hat{\delta A}_\beta(\Gamma) \rho_N(\Gamma, t) , \end{aligned} \quad (2.17)$$

and, in general, the k-th order correlation function is

$$M_{\alpha_1 \dots \alpha_k}(t) = \langle \hat{\delta A}_{\alpha_1} \hat{\delta A}_{\alpha_2} \dots \hat{\delta A}_{\alpha_k}; t \rangle . \quad (2.18)$$

Again, as for the average quantities, the time evolution of the equal time correlation functions is determined through the ensemble.

The amplitude of the equal time correlation functions is a measure of the width of the probability distribution of the fluctuations of a variable around its average value. The fluctuations can be viewed as the result of a stochastic force which represents explicitly the effect of instantaneous molecular collisions not accounted for in the macroscopic description and averages to zero over a time long compared to the microscopic collision time. In the language of stochastic processes the fluctuations are then the result of the "noise" in the system and the equal time correlation functions measure the size of this noise. It should be pointed out however that, even if here and in the following

some of the terminology of stochastic processes is used, the description presented here is entirely macroscopic and always deals with averaged quantities.

In equilibrium, away from critical points, the probability of fluctuations is Gaussian and only second order correlations are important.⁵⁵ Their amplitude is proportional to $k_B T$, where T is the temperature and k_B is the Boltzmann constant, as suggested from the fact that in the equilibrium state spontaneous fluctuations can only be thermal in origin. In systems driven out of equilibrium new sources of noise may become available, in a way strongly dependent on the particular state considered. Furthermore in a nonequilibrium state equal time fluctuations are dynamical variables: the clear separation of static and dynamic properties that appears natural in equilibrium does not apply to this case.

The correlation of fluctuations at different times are measured in terms of multitime correlation functions. The most general definition of a two-time correlation function is

$$M_{\alpha\beta}(t_1, t_2; t) = \langle \delta\hat{A}_\alpha(t_1) \delta\hat{A}_\beta(t_2); t \rangle . \quad (2.19)$$

By using Eqs.(2.8) and (2.15) to translate the time arguments, this can also be written as

$$\langle \delta\hat{A}_\alpha(t_1) \delta\hat{A}_\beta(t_2); t \rangle = \langle \delta\hat{A}_\alpha(t_1 - t) \delta\hat{A}_\beta(t_2 - t); 0 \rangle . \quad (2.20)$$

Therefore the two-time correlation function really depends on two time arguments and on the initial time. In the following the dependence on

the initial time will not be indicated explicitly, unless needed. An average over the initial nonequilibrium ensemble will simply be written

$$\langle \hat{A} \rangle \equiv \sum_{N=0}^{\infty} \int d\Gamma \hat{A}(\Gamma) \rho_N(\Gamma, 0) . \quad (2.21)$$

The k-time correlation function is then

$$M_{\alpha_1 \dots \alpha_k}(\tau_1, \dots, \tau_k) = \langle \delta \hat{A}_{\alpha_1}(\tau_1) \delta \hat{A}_{\alpha_2}(\tau_2) \dots \delta \hat{A}_{\alpha_k}(\tau_k) \rangle . \quad (2.22)$$

The macroscopic variables and the correlation functions of their fluctuations around the average value have been expressed here as nonequilibrium averages of the corresponding microscopic quantities. In the next chapters equations describing the dynamics of the observables here defined will be derived in two specific macroscopic conditions.

II.2 Reduced Distribution Function Formalism

In the special case when the dynamical variables $\{\hat{A}_\alpha\}$ are sum of single particle functions, two-particle functions, etc.,

$$\hat{A}_\alpha(x_1, \dots, x_N) = \sum_{i=1}^N \hat{a}_\alpha(x_i) + \sum_{i=1}^N \sum_{\substack{j=1 \\ i \neq j}}^N \hat{b}_\alpha(x_i, x_j) + \dots , \quad (2.23)$$

their averages and correlation functions are conveniently represented in terms of reduced distribution functions. Many of the physical variables of interest in real systems, such as the microscopic mass, energy and momentum density in fluids, have the form (2.23).

A set of microscopic phase space densities is defined as

$$\hat{f}_1(x_1, t) = \sum_{i=1}^N \delta(x_1 - x_i(t))$$

$$\hat{f}_2(x_1, x_2, t) = \sum_{i=1}^N \sum_{\substack{j=1 \\ i \neq j}}^N \delta(x_1 - x_i(t)) \delta(x_2 - x_j(t)) \quad (2.24)$$

etc.

The reduced distribution functions usually defined in kinetic theory,^{56,57}

$$n^s f_s(x_1, \dots, x_s, t) = \sum_{N \geq s} \frac{N!}{(N-s)!} \int dx_{s+1} \dots dx_N \rho_N(x_1, \dots, x_N, t) \quad (2.25)$$

can be interpreted as averages of the phase space densities over the nonequilibrium ensemble,

$$n^s f_s(x_1, \dots, x_s, t) = \langle \hat{f}_s(x_1, \dots, x_s, t) \rangle . \quad (2.26)$$

In particular the one-particle distribution function is defined as

$$\begin{aligned} n f_1(x_1, t) &= \langle \hat{f}_1(x_1, t) \rangle \\ &= \sum_{N \geq 1} \frac{N!}{(N-1)!} \int dx_2 \dots dx_N \rho_N(x_1, x_2, \dots, x_N, t) . \end{aligned} \quad (2.27)$$

The reduced distribution function f_s represents the probability density that, at the time t , the positions and momenta of particle 1 through s lie in a neighborhood $dx_1 \dots dx_s$ of the point $\{x_1, \dots, x_s\}$, regardless of the positions and momenta of the other particles in the system.

The average of a variable \hat{A}_α of the form given in Eq.(2.23) is then written as

$$\begin{aligned} \langle \hat{A}_\alpha; t \rangle &= n \int dx_1 \hat{a}_\alpha(x_1) f_1(x_1, t) \\ &+ n^2 \int dx_1 dx_2 \hat{b}_\alpha(x_1, x_2) f_2(x_1, x_2, t) + \dots \end{aligned} \quad (2.28)$$

For simplicity only the expressions for the correlation functions of variables that are sums of single particle functions will be derived here. The extension to more general cases is straightforward.

The correlation functions of the $\{\hat{A}_\alpha\}$ can then be expressed in terms of the correlation functions of the fluctuations of the one-particle phase space density around its average value, C_S , with the result,

$$M_{\alpha\beta}(t) = \int dx_1 dx_2 \hat{a}_\alpha(x_1) \hat{a}_\beta(x_2) C_2(x_1, t; x_2, t) , \quad (2.29)$$

and

$$M_{\alpha\beta}(t_1, t_2) = \int dx_1 dx_2 \hat{a}_\alpha(x_1) \hat{a}_\beta(x_2) C_2(x_1, t_1; x_2, t_2) . \quad (2.30)$$

In general the k -th order correlation function is given by

$$M_{\alpha_1 \dots \alpha_k}(t_1, \dots, t_k) = \int \dots \int \prod_{i=1}^k \{ dx_i \hat{a}_{\alpha_i}(x_i) \} C_k(x_1, t_1; \dots; x_k, t_k) . \quad (2.31)$$

Equivalent expressions for the correlation functions of more general variables involving also two-particle functions, etc., will involve correlations of higher order phase space densities.

The equal time correlation functions of phase space fluctuations introduced in Eqs.(2.29-30) are defined as

$$C_s(x_1, t; \dots; x_s, t) = \langle \hat{\delta f}_1(x_1, t) \dots \hat{\delta f}_1(x_s, t) \rangle, \quad (2.32)$$

where

$$\hat{\delta f}_1(x, t) = \hat{f}_1(x, t) - \langle \hat{f}_1(x); t \rangle. \quad (2.33)$$

It is immediately seen that these correlation functions can be expressed in terms of the reduced distribution functions f_s .

Similarly, the multitime correlation functions introduced in Eq.(2.31) are given by

$$C_s(x_1, t_1; \dots; x_s, t_s) = \langle \hat{\delta f}_1(x_1, t_1) \dots \hat{\delta f}_1(x_s, t_s) \rangle. \quad (2.34)$$

The one-particle distribution function and the fluctuations in the phase space density are the objects of interest in kinetic theory and will be analyzed in detail in Chapter IV.

The expressions given in Eqs.(2.29-31) for the averages and the correlation functions of a general set of observables in terms of the reduced distribution functions are obtained by carrying out a partial ensemble average over a reduced number of particles. They provide a connection between macroscopic observables and kinetic theory and a formal reduction of the many-body problem to an effective one-, two-, ... s-body problem. The reduced distribution function method is particularly useful when dealing with gases at low or moderate density. In this limit closed kinetic equations for the lower order distribution functions can be derived.

II.3 Generating Functional for Nonequilibrium

Averages and Fluctuations

To describe the dynamics of a nonequilibrium system it is convenient to introduce a generating functional G , from which averages and correlation functions of any order can be generated through appropriate functional differentiation.

The same idea has already been used by Dufty⁵⁸ to derive kinetic equations for equilibrium multitime correlation functions. The advantage of this formalism is mainly that once a single set of equations for the first functional derivatives of G has been derived, the equations for the correlation functions are simply obtained by functional differentiation.

If $\{\hat{A}_\alpha\}$ is the set of dynamical variables chosen to describe the system, the corresponding generating functional is defined as

$$G[\{\lambda_\alpha\}] = \ln \langle U[\{\lambda_\alpha\}] \rangle, \quad (2.35)$$

where

$$U[\{\lambda_\alpha\}] = \exp \int_{-\infty}^{+\infty} dt \hat{A}_\alpha(\Gamma, t) \lambda_\alpha(t), \quad (2.36)$$

and summation over the index α is understood. The test functions $\{\lambda_\alpha\}$ in Eq.(2.36) have no physical interpretation. The only requirement imposed at this point is that they are sufficiently localized in time for the integrals in Eq.(2.36) to exist.

The first functional derivative of the generating functional is given by

$$A_{\alpha}(t|\lambda) = \frac{\langle \hat{A}_{\alpha}(\Gamma, t) U[\lambda] \rangle}{\langle U[\lambda] \rangle} . \quad (2.37)$$

When evaluated at $\lambda_{\alpha}=0$, Eq.(2.37) reduces to the nonequilibrium average of \hat{A}_{α} ,

$$A_{\alpha}(t|\lambda=0) = A_{\alpha}(t) . \quad (2.38)$$

Similarly, by successive functional differentiation,

$$M_{\alpha\beta}(t_1, t_2) = \frac{\delta^{(2)} G[\lambda]}{\delta \lambda_{\alpha}(t_1) \delta \lambda_{\beta}(t_2)} \Big|_{\{\lambda_{\alpha}=0\}} , \quad (2.39)$$

and in general,

$$M_{\alpha_1 \dots \alpha_k}(t_1, \dots, t_k) = \frac{\delta^{(k)} G[\lambda]}{\delta \lambda_{\alpha_1}(t_1) \dots \delta \lambda_{\alpha_k}(t_k)} \Big|_{\{\lambda_{\alpha}=0\}} . \quad (2.40)$$

Here and in the following the times are chosen to be ordered according to $t_1 \geq t_2 \geq \dots \geq t_s$. This implies no loss in generality since the dynamical variables commute in classical mechanics. As desired, averages and correlation functions of any order can be generated from G . The objective is now to derive a set of equations for the time evolution of the functionals $\{A_{\alpha}(t|\lambda)\}$. When evaluated at $\lambda=0$, these should reduce to the macroscopic regression laws for the system considered. Furthermore equations for the correlation functions of any order can be obtained by functional differentiation. In this sense the generating functional method provides a unified description of the system, since all information can be derived from one single set of equations.

The set of macroscopic regression laws describing, at long times, the nonequilibrium state of a many-particle system (such as the Boltzmann equation and the nonlinear Navier-Stokes equations which apply at the kinetic and hydrodynamic level respectively) can be derived by averaging the microscopic equations of motion, at least in the case of low density gases. The nonlinear Boltzmann equation for the one-particle distribution function is obtained by performing a low density closure of the BBGKY hierarchy. The Chapman-Enskog expansion provides then a systematic method for deriving the hydrodynamic equations. Alternatively, the nonlinear hydrodynamic equations can be obtained directly by averaging the microscopic conservation laws over a nonequilibrium ensemble which is a formal solution of the Liouville equation and by evaluating the constitutive equations expressing the irreversible part of the fluxes as functionals of the thermodynamic gradients.

The same well established methods can be applied to the generating functional to derive a set of equations for the λ -dependent functionals $\{A_\alpha(t|\lambda)\}$. Furthermore the derivation preserves the properties of the generating functional, in the sense that the set of equations so obtained may be differentiated to derive equations for the correlation functions. This program is carried out explicitly in Chapter III and Chapter IV for the hydrodynamic and kinetic limit respectively. The theory of nonequilibrium fluctuations so derived is justified in the same well understood limits leading to the macroscopic description.

The convenience of introducing a generating functional or characteristic function to describe fluctuations has often been recognized in the literature.⁵⁹ In particular Martin, Rose and Siggia⁶⁰ defined a

time ordered generating functional, involving both the dynamical variables of the system and a set of conjugated operators describing the effect of small perturbation in the variables. Also, in Eq.(52) of Ref. 31, Onuki defines a characteristic function analogous to the one proposed here, from which equal time correlation functions of phase space fluctuations can be generated. The definition given in Eqs. (2.35-36) is however more general and it can be applied to a larger class of statistical mechanical systems.

The next two chapters will be dedicated to the explicit derivation of equations for the averages and the correlation functions describing the properties of a fluid at the hydrodynamic and kinetic level. However, before carrying out this program in detail, it is instructive to present the results. The macroscopic description of the dynamic properties of a many-particle system have the same structure at both levels of description (kinetic and hydrodynamic).

The relaxation of the macroscopic variables $\{A_\alpha\}$ is described by nonlinear equations of first order in time (to be identified with the nonlinear Navier-Stokes equations for the average densities and the nonlinear Boltzmann equation for the one-particle distribution function),

$$\frac{\partial}{\partial t} A_\alpha(t) + N_\alpha[\{A(t)\}] = 0 , \quad (2.41)$$

where N_α represents a general nonlinear functional of the $\{A_\alpha\}$. The set of Eqs. (2.41) has to be solved with the appropriate initial and boundary conditions, constituting an experimentally appropriate definition of the macroscopic nonequilibrium state considered.

The dynamics of the correlations of fluctuations around the non-equilibrium state is described by a set of linear homogeneous equations,

$$\frac{\partial}{\partial t_1} M_{\alpha\beta}(t_1, t_2) + L_{\alpha\gamma}[\{A(t_1)\}] M_{\gamma\beta}(t_1, t_2) = 0, \quad (2.42)$$

where

$$L_{\alpha\beta}(t_1) = \frac{\delta N_{\alpha}[\{A(t_1)\}]}{\delta A_{\beta}(t_1)}. \quad (2.43)$$

Equation (2.42) applies as long as the separation $t_1 - t_2$ is large compared to an appropriate microscopic time, t_m , of the order of the lifetime of the transient before the adopted macroscopic description of the system applies. Specifically, $t_m \approx \tau_c$, the duration of an interparticle collision, for a kinetic description, and $t_m \approx t_f$, the mean time between collisions, for a hydrodynamic description. The linear functional $L_{\alpha\beta}$ in Eq. (2.42) depends on the solution of the nonlinear equations, Eqs.(2.41). In this sense the dynamic evolution of the two-time fluctuations is entirely determined by the macroscopic nonequilibrium state.

The correlations of fluctuations at the same time, needed as initial conditions for the set of Eqs.(2.42), are the solutions of a set of bilinear inhomogeneous equations,

$$\frac{\partial}{\partial t} M_{\alpha\beta}(t) + L_{\alpha\gamma}[\{A(t)\}] M_{\gamma\beta}(t) + L_{\gamma\beta}[\{A(t)\}] M_{\alpha\gamma}(t) = \Gamma_{\alpha\beta}[\{A(t)\}]. \quad (2.44)$$

The specific form of the inhomogeneity $\Gamma_{\alpha\beta}$ depends on the problem considered. To interpret these equations, it is instructive to compare

them with the corresponding equilibrium results. In this case Onsager-Machlup's hypothesis applies and the decay of the mean values and of the fluctuations is governed by the same set of linear equations, obtained from Eqs.(2.42) by evaluating $L_{\alpha\beta}$ at equilibrium,

$$\frac{\partial}{\partial t_1} \left\{ \begin{array}{c} A_{\alpha}^0(t_1) \\ M_{\alpha\beta}^0(t_1-t_2) \end{array} \right\} + L_{\alpha\gamma}^0 \left\{ \begin{array}{c} A_{\gamma}^0(t_1) \\ M_{\gamma\beta}^0(t_1-t_2) \end{array} \right\} = 0, \quad (2.45)$$

where the superscript "zero" indicates the equilibrium value or that the average has to be understood as an equilibrium average. Also the fact that in equilibrium, in virtue of time translation invariance, the two-time correlation function depends only on the time difference has been indicated. The equal time fluctuations are given by equilibrium statistical mechanics as a property of the ensemble. Equations (2.44) become then identities: the inhomogeneous term is identified with the amplitude of the noise in the system (this appears evident by using a Langevin description). The inhomogeneity in Eqs.(2.44) can then be interpreted as the noise term. Indeed it originates from microscopic excitations in the system whose lifetime is short compared to the time scale of interest.

CHAPTER III HYDRODYNAMICS

III.1 Generating Functional for Hydrodynamics and Nonlinear Navier-Stokes Equations

In this chapter the generating functional formalism outlined in Section II.3 is applied to derive a set of equations describing macroscopic properties and fluctuations at the hydrodynamic level. For simplicity, attention is limited to the case of a simple fluid whose nonequilibrium state is adequately described by the nonlinear Navier-Stokes equations. The method used here is easily extended to more general systems and other nonequilibrium situations, as will be seen in the next chapter.

In general a hydrodynamic process is one which is adequately described in terms of the averages of the locally conserved quantities in a many-particle system.⁷ This contracted description applies to time scales large compared to a characteristic microscopic time scale, the mean free time between collisions. The hydrodynamic equations are derived by averaging the microscopic conservation laws and by closing the macroscopic equations so obtained with constitutive relations for the irreversible part of the fluxes. This procedure can be carried out in detail by applying, for example, the methods of the response theory and provides a precise statement of the validity of the hydrodynamic description for processes varying on space and time scales large compared to some microscopic space and time scales characteristic of the system.^{6,10}

The microscopic conserved densities for a simple fluid are the microscopic mass density $\hat{\rho}$, the total energy density $\hat{\varepsilon}$, and the three components of the momentum density \hat{g}_i , respectively given by

$$\begin{aligned}\hat{\rho}(\vec{r}) &= \sum_{n=1}^N m \delta(\vec{r}-\vec{q}_n) , \\ \hat{\varepsilon}(\vec{r}) &= \sum_{n=1}^N \varepsilon_n \delta(\vec{r}-\vec{q}_n) , \\ \hat{g}_i(\vec{r}) &= \sum_{n=1}^N p_{ni} \delta(\vec{r}-\vec{q}_n) .\end{aligned}\tag{3.1}$$

Here N is the total number of particles in a volume V and m is the mass of the particles; \vec{r} represents a point in the fluid. The function ε_n is the energy of the n -th particle: for a central pairwise additive interaction potential, $V(q_{nn'})$, with $q_{nn'} = |\vec{q}_n - \vec{q}_{n'}|$, ε_n is given by,

$$\varepsilon_n = \frac{p_n^2}{2m} + \frac{1}{2} \sum_{\substack{n'=1 \\ n' \neq n}}^N V(q_{nn'}) .\tag{3.2}$$

In the following, for convenience, the set of five conserved densities will be indicated as

$$\{\hat{\psi}_\alpha(\vec{r})\} = (\hat{\rho}(\vec{r}), \hat{\varepsilon}(\vec{r}), \hat{g}_i(\vec{r})) ,\tag{3.3}$$

or

$$\hat{\psi}_\alpha(\vec{r}) = \sum_{n=1}^N \hat{a}_\alpha(x_n) \delta(\vec{r}-\vec{q}_n) ,\tag{3.4}$$

with

$$\{\hat{a}_\alpha(x_n)\} = (m, \varepsilon_n, p_{ni}) . \quad (3.5)$$

Also, here and in the following, the indices n, n', \dots are used to label particles and the indices i, j, k, l, \dots are used to label the components of vectors and tensors. Greek indices, α, β, \dots , run from 1 to 5 and label sets of hydrodynamic variables.

The microscopic conservation of mass, energy and momentum is expressed by the set of five conservation laws,

$$\frac{\partial}{\partial t} \hat{\psi}_\alpha(\vec{r}, t) + \frac{\partial}{\partial r_i} \hat{\gamma}_{\alpha i}(\vec{r}, t) = 0 . \quad (3.6)$$

The set of Eqs.(3.6) constitutes the definition of the microscopic fluxes $\hat{\gamma}_{\alpha i}$, explicitly given by

$$\{\hat{\gamma}_{\alpha i}(\vec{r})\} = (\hat{g}_i(\vec{r}), \hat{s}_i(\vec{r}), \hat{t}_{ij}(\vec{r})) , \quad (3.7)$$

where \hat{s}_i is the energy flux and \hat{t}_{ij} is the momentum flux. Explicit expressions for the microscopic fluxes can be found for example in Ref. 7, Eqs.(4.6). It should be noted that in writing Eqs.(3.6) no external sources have been taken into account, even if a general nonequilibrium system in interaction with its surroundings is considered here. The adequacy of Eqs.(3.6) as the starting point to describe properties in the interior of the system and the possibility of incorporating the effect of the boundaries entirely through the thermodynamic parameters is discussed in Appendix A.

The macroscopic quantities of interest are the nonequilibrium averages of the $\{\hat{\psi}_\alpha\}$,

$$\psi_{\alpha}(\vec{r}, t) = \langle \hat{\psi}_{\alpha}(\vec{r}); t \rangle , \quad (3.8)$$

and the correlation functions of their fluctuations around the average,

$$M_{\alpha_1 \dots \alpha_k}(\vec{r}_1, t_1; \dots; \vec{r}_k, t_k) = \langle \delta \hat{\psi}_{\alpha_1}(\vec{r}_1, t_1) \dots \delta \hat{\psi}_{\alpha_k}(\vec{r}_k, t_k) \rangle , \quad (3.9)$$

where

$$\delta \hat{\psi}_{\alpha}(\vec{r}, t) = \hat{\psi}_{\alpha}(\vec{r}, t) - \langle \hat{\psi}_{\alpha}(\vec{r}); t \rangle . \quad (3.10)$$

For a one-component fluid the average densities are explicitly given by

$$\{\psi_{\alpha}(\vec{r}, t)\} = (\rho(\vec{r}, t), \varepsilon(\vec{r}, t), \rho(\vec{r}, t) \vec{v}_i(\vec{r}, t)) , \quad (3.11)$$

where ρ , ε and \vec{v} are the average mass and total energy density and the macroscopic flow velocity, respectively.

The macroscopic conservation laws are obtained by averaging Eqs.(3.6) over the nonequilibrium ensemble,¹⁹ with the result,

$$\frac{\partial}{\partial t} \langle \hat{\psi}_{\alpha}(\vec{r}); t \rangle + \frac{\partial}{\partial r_i} \langle \hat{\gamma}_{\alpha i}(\vec{r}); t \rangle = 0 . \quad (3.12)$$

The hydrodynamic equations are obtained from Eqs.(3.12) when these are supplemented by an equation of state, relating the thermodynamic variables, and by constitutive equations for the macroscopic fluxes as functionals of the average densities.

The intensive thermodynamic variables, $\{y_{\alpha}(\vec{r}, t)\}$, such as temperature, pressure, etc., are defined in the nonequilibrium state by requiring that the nonequilibrium average densities are the same

functionals of temperature, pressure and flow velocity as they are in equilibrium.⁶ This is obtained by choosing

$$\langle \hat{\psi}_\alpha(\vec{r}); t \rangle = \langle \hat{\psi}_\alpha(\vec{r}); t \rangle_L, \quad (3.13)$$

where $\langle \dots; t \rangle_L$ indicates the average over a local equilibrium ensemble at time t ,

$$\langle A; t \rangle_L = \sum_{N=0}^{\infty} \int d\Gamma A(\Gamma) \rho_L(t). \quad (3.14)$$

The local equilibrium ensemble for a one-component fluid is given by

$$\rho_L(t) = \exp\{-q_L(t) - \int d\vec{r} y_\alpha(\vec{r}, t) \hat{\psi}_\alpha(\vec{r})\}, \quad (3.15)$$

where $q_L(t)$ is a constant determined by the requirement that $\rho_L(t)$ is normalized to one. The right hand side of Eq.(3.13) is an explicit functional of the $\{y_\alpha\}$: this equation constitutes the definition of the local thermodynamic variables conjugated to the $\{\hat{\psi}_\alpha\}$. Explicitly,

$$\{y_\alpha(\vec{r}, t)\} = (-v + \frac{1}{2} \beta v^2, \beta, -\beta v_i), \quad (3.16)$$

where $v\beta^{-1}$ is the chemical potential per unit mass and $\beta = 1/k_B T$, where T is the Kelvin temperature and k_B is Boltzmann's constant. Equations (3.13) do not imply a limitation to states near equilibrium or local equilibrium. Other definitions are possible and sometimes desirable. However, the present definition has the advantage that the functional relationships of all nonequilibrium thermodynamic parameters are the same as in equilibrium.

The main problem in closing the hydrodynamic equations is the specification of the irreversible part of the fluxes,

$$\gamma_{\alpha i}^*(\vec{r}, t) \equiv \langle \hat{\gamma}_{\alpha i}(\vec{r}); t \rangle - \langle \hat{\gamma}_{\alpha i}(\vec{r}); t \rangle_L, \quad (3.17)$$

as functionals of the thermodynamic gradients. These expressions can be evaluated to first order in the gradients by using the linear response theory, with the result,⁶

$$\gamma_{\alpha i}^*(\vec{r}, t) = L_{\alpha\beta}^{ij}(\vec{r}, t | \{\psi\}) \frac{\partial y_{\beta}(\vec{r}, t)}{\partial r_j}, \quad (3.18)$$

where $L_{\alpha\beta}^{ij}$ is the Onsager's matrix of transport coefficients. For times large compared to the mean free time between collisions, after the initial transient describing the complicated behavior of the system before hydrodynamics applies, the time evolution of the macroscopic state is then described by the set of nonlinear Navier-Stokes equations, given by

$$\frac{\partial}{\partial t} \phi_{\alpha}(\vec{r}, t) + \frac{\partial}{\partial r_i} \left\{ E_{\alpha}^i(\vec{r}, t; \{\psi\}) + L_{\alpha\beta}^{ij}(\vec{r}, t; \{\psi\}) \frac{\partial y_{\beta}(\vec{r}, t)}{\partial r_j} \right\} = 0, \quad (3.19)$$

where E_{α}^i represents the contribution from the nonlinear Euler equation. Explicitly, the nonlinear Navier-Stokes equations are

$$\frac{\partial}{\partial t} \rho + \vec{\nabla} \cdot (\rho \vec{v}) = 0 \quad (3.20a)$$

$$\left(\frac{\partial}{\partial t} + \vec{v} \cdot \vec{\nabla} \right) u + h \vec{\nabla} \cdot \vec{v} = -\vec{\nabla} \cdot \vec{q}^* - \tau_{ij}^* \frac{\partial v_i}{\partial r_j} \quad (3.20b)$$

$$\left(\frac{\partial}{\partial t} + \vec{v} \cdot \vec{\nabla}\right) v_i = -\frac{1}{\rho} \left(\frac{\partial p}{\partial r_i} + \frac{\partial t_{ij}^*}{\partial r_j}\right), \quad (3.20c)$$

where u is the average internal energy density, $u = \epsilon - \frac{1}{2} \rho v^2$, h is the enthalpy density, $h = u + p$, and p the pressure. To Navier-Stokes order the irreversible parts of the heat flux, q_i^* , and the stress tensor, t_{ij}^* , are given by the usual Fourier and Newton laws as

$$q_i^*(\vec{r}, t) = -\kappa(\rho, u) \frac{\partial T}{\partial r_i} \quad (3.21)$$

$$t_{ij}^*(\vec{r}, t) = -\left\{ \eta(\rho, u) \Delta_{ijkl} + \zeta(\rho, u) \delta_{ij} \delta_{kl} \right\} \frac{\partial v_k}{\partial r_l}, \quad (3.22)$$

where $\Delta_{ijkl} = \delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} - \frac{2}{3} \delta_{ij} \delta_{kl}$. The coefficients of thermal conductivity, κ , and of shear and bulk viscosity, η and ζ , respectively, are in general functions of the thermodynamic variables, as indicated. The generating functional G for hydrodynamic averages and fluctuations is given by Eq.(2.35), with

$$U[\{\lambda_\alpha\}] = \exp \int_{-\infty}^{+\infty} dt \int d\vec{r} \hat{\phi}_\alpha(\vec{r}, t) \lambda_\alpha(\vec{r}, t). \quad (3.23)$$

The first functional derivatives of G are

$$\begin{aligned} \phi_\alpha(\vec{r}, t | \lambda) &\equiv \frac{\delta G[\lambda]}{\delta \lambda_\alpha(\vec{r}, t)} \\ &= \frac{\langle \hat{\phi}_\alpha(\vec{r}, t) U[\lambda] \rangle}{\langle U[\lambda] \rangle}, \end{aligned} \quad (3.24)$$

where λ often will be used to indicate the set of five test functions, $\{\lambda_\alpha\}$. When evaluated at $\lambda=0$, Eq.(3.24) reproduces the average densities

given by Eq.(3.8). Similarly, higher order functional derivatives generate the correlation functions (3.9), as shown in Eq.(2.40).

The explicit form of Eq.(3.24),

$$\begin{aligned} \phi_{\alpha}(\vec{r}, t | \lambda) &= \sum_{N=0}^{\infty} \int d\Gamma \hat{\phi}_{\alpha}(\vec{r}) e^{-Lt} \frac{U[\lambda]}{\langle U[\lambda] \rangle} \rho_N^{(0)} \\ &\equiv \langle \hat{\phi}_{\alpha}(\vec{r}); t \rangle_{\lambda}, \end{aligned} \quad (3.25)$$

where L is the Liouville operator of the isolated system (Eq. (2.4)) and the time evolution operator is defined in Appendix A (Eq. (A.51)), suggests that the same statistical mechanical methods used to derive the hydrodynamic equations from the macroscopic conservation laws can be applied to describe the time evolution of the set of functionals $\{\phi_{\alpha}(\vec{r}, t | \lambda)\}$. In fact, the time evolution operator is the same in both cases and the difference in the equations can be incorporated as a modification of the initial condition for the nonequilibrium ensemble. The initial condition becomes dependent on the test functions λ_{α} through the functional U . This program is carried out explicitly in Appendix A, where the methods of nonlinear response theory are applied to derive a set of equations for the functionals $\{\phi_{\alpha}(\vec{r}, t | \lambda)\}$. The derivation is identical to the derivation of the nonlinear Navier-Stokes equations and preserves the properties of the generating functional.

In particular, a set of λ -dependent thermodynamic variables, $\{y_{\alpha}(\vec{r}, t | \lambda)\}$, is defined in analogy with Eq. (3.13) by requiring,

$$\langle \hat{\phi}_{\alpha}(\vec{r}); t \rangle_{\lambda} = \langle \hat{\phi}_{\alpha}(\vec{r}); t \rangle_{\lambda L}, \quad (3.26)$$

where $\langle \dots; t \rangle_{\lambda L}$ indicates the average over a λ -dependent local equilibrium distribution functional $\rho_L(t|\lambda)$, given by

$$\rho_L(t|\lambda) = \exp\{-q_L(t|\lambda) - \int d\vec{r} y_\alpha(\vec{r}, t|\lambda) \hat{\psi}_\alpha(\vec{r})\} . \quad (3.27)$$

The constant $q_L(t|\lambda)$ assures the normalization to one of the distribution functional (Eq. (A.7)). The functional dependence of $\rho_L(t|\lambda)$ on the set $\{y_\alpha(\vec{r}, t|\lambda)\}$ is the same as indicated in Eq. (3.13) for the case $\lambda=0$. The form of the thermodynamic equations relating $\{\psi_\alpha(\vec{r}, t|\lambda)\}$ and $\{y_\alpha(\vec{r}, t|\lambda)\}$ is therefore preserved and is again the same as in the equilibrium case. The comments made when imposing the equality (3.13) apply here. The thermodynamic variables $\{y_\alpha(\vec{r}, t|\lambda)\}$ depend on the $\{\lambda_\alpha\}$ only through the λ -dependent densities, $\{\psi_\alpha(\vec{r}, t|\lambda)\}$.

The set of generalized Navier-Stokes equations for the five functionals $\{\psi_\alpha[\lambda]\}$ derived in Appendix A are formally identical to the usual nonlinear Navier-Stokes equations. In a matrix form they are given by

$$\begin{aligned} \frac{\partial}{\partial t} \psi_\alpha(\vec{r}, t|\lambda) + \frac{\partial}{\partial r_i} \{E_\alpha^i(\vec{r}, t; \{\psi[\lambda]\}) \\ + L_{\alpha\beta}^{ij}(\vec{r}, t; \{\psi[\lambda]\}) \frac{\partial y_\beta(\vec{r}, t|\lambda)}{\partial r_j}\} = - \frac{\partial}{\partial r_i} \gamma_{\alpha i}^{**}(\vec{r}, t|\lambda)_{NS}, \end{aligned} \quad (3.28)$$

where the Euler matrix, E_α^i , and the matrix of the transport coefficients, $L_{\alpha\beta}^{ij}$, are respectively defined as

$$E_\alpha^i(\vec{r}, t; \{\psi[\lambda]\}) \equiv \langle \hat{\gamma}_{\alpha i}(\vec{r}); t \rangle_{\lambda L} , \quad (3.29)$$

and

$$L_{\alpha\beta}^{ij}(\vec{r}, t; \{\psi[\lambda]\}) = \lim_{t \gg t_f} \int_0^t dt \langle \{e^{L(t-\tau)} \hat{\gamma}_{\alpha i}(\vec{r})\} \hat{\Phi}_{\beta j}[\lambda] \rangle_{0\lambda}, \quad (3.30)$$

where $\hat{\Phi}_{\beta j}[\lambda]$ is the total (volume integrated) projected flux defined in Eqs. (A.23) and (A.57), and the average in Eq. (3.30) is over the λ -dependent equilibrium ensemble with local thermodynamic variables, defined in Eq. (A.54). Both E_{α}^i and $L_{\alpha\beta}^{ij}$ are nonlinear functionals of the densities $\{\psi_{\alpha}(\vec{r}, t|\lambda)\}$ and depend on the test functions $\{\lambda_{\alpha}\}$ only through the $\{\psi_{\alpha}\}$ themselves.

Additional contributions to the irreversible fluxes, not present in the Navier-Stokes equations, appear in Eqs. (3.28). They originate from the λ -dependence of the initial condition for the nonequilibrium distribution functional. The subscript NS to $\gamma_{\alpha i}^{**}$ indicates that the right hand side of Eqs. (3.28) has to be evaluated to Navier-Stokes order in the thermodynamic gradients and in the limit of time t long compared to the mean free time t_f , i.e.

$$\frac{\partial}{\partial r_i} \gamma_{\alpha i}^{**}(\vec{r}, t|\lambda)_{NS} \equiv \lim_{t \gg t_f} \left[\frac{\partial}{\partial r_i} \gamma_{\alpha i}^{**}(\vec{r}, t|\lambda) \right]_{NS}, \quad (3.31)$$

where $[A]_{NS}$ indicates the result of an expansion of the function A to second order in the gradients of the thermodynamic variables. The explicit form of $\gamma_{\alpha i}^{**}$ is derived in Appendix A, with the result,

$$\gamma_{\alpha i}^{**}(\vec{r}, t|\lambda) = \langle \hat{\gamma}_{\alpha i}(\vec{r}) [e^{D(t|\lambda)} - e^{D'(t|\lambda)}]; t \rangle_{\lambda L}. \quad (3.32)$$

Here the nonequilibrium distribution functional has been written

$$\rho_N(t|\lambda) = \rho_L(t|\lambda) e^{D(t|\lambda)}, \quad (3.33)$$

with

$$D(t|\lambda) = e^{-Lt} D_0(\lambda) + D'(t|\lambda), \quad (3.34)$$

and

$$D'(t|\lambda) = \int_0^t d\tau \int d\vec{r} e^{-L(t-\tau)} \left\{ \frac{\partial y_\alpha(\vec{r}, \tau|\lambda)}{\partial r_i} \hat{\phi}_{\alpha i}(\vec{r}|\lambda) + \frac{\partial \gamma_{\alpha i}^*(\vec{r}, \tau|\lambda)}{\partial r_i} \hat{\xi}_\alpha(\vec{r}|\lambda) \right\}, \quad (3.35)$$

$$D_0(\lambda) \equiv D(0|\lambda)$$

$$= \ln \frac{U[\lambda]}{\langle U[\lambda] \rangle_{\lambda L}} \frac{\rho_L(0)}{\rho_L(0|\lambda)}, \quad (3.36)$$

where $\hat{\phi}_{\alpha i}$ and $\hat{\xi}_\alpha$ are the projected fluxes and the normalized densities given by Eqs. (A.23) and (A.21), respectively, when the local equilibrium average is substituted with an average over $\rho_L(t|\lambda)$. When evaluated at $\lambda=0$, the additional contributions to the irreversible fluxes vanish identically, since $D_0(\lambda=0) = 0$, and Eqs. (3.28) reduce to the nonlinear Navier-Stokes equations (3.19). However, when the generalized equations for the functionals $\{\psi_\alpha(\vec{r}, t|\lambda)\}$ are considered, these extra contributions have to be kept and will be shown to be directly related to the strength of the noise in the system.

The Navier-Stokes limit indicated in Eq. (3.31) is consistent with the approximations introduced in the left hand side of Eqs. (3.28), but can only be taken after functionally differentiating $\gamma_{\alpha i}^{**}$ and evaluating the result at $\lambda=0$. The evaluation of this term will be needed when

deriving the equations for the correlation functions, and is carried out explicitly in Appendix B.

The only assumption introduced in the derivation of Eqs. (3.28) regards the form of the initial state, which has been chosen to be local equilibrium. This choice does not imply any serious restriction, because the deviations from initial local equilibrium are expected to decay in a time of the order of the mean free time, τ_f , in states leading to hydrodynamics.^{3,10} These deviations are only responsible for the initial short lived transient in the system.

Using the same notation for the functionals and the corresponding average densities, the λ -dependent Navier-Stokes equations are explicitly given by

$$\frac{\partial}{\partial t} \rho[\lambda] + \vec{\nabla} \cdot (\rho[\lambda] \vec{v}[\lambda]) = 0, \quad (3.37a)$$

$$\left(\frac{\partial}{\partial t} + \vec{v}[\lambda] \cdot \vec{\nabla} \right) u[\lambda] + h[\lambda] \vec{\nabla} \cdot \vec{v}[\lambda] = -\vec{\nabla} \cdot \vec{q}^*[\lambda] - t_{ij}^*[\lambda] \frac{\partial v_i[\lambda]}{\partial r_j}, \quad (3.37b)$$

$$\left(\frac{\partial}{\partial t} + \vec{v}[\lambda] \cdot \vec{\nabla} \right) v_i[\lambda] = -\frac{1}{\rho[\lambda]} \left(\frac{\partial p[\lambda]}{\partial r_i} + \frac{\partial t_{ij}^*[\lambda]}{\partial r_j} \right), \quad (3.37c)$$

where the dependence on \vec{r} and t of the functionals has been omitted to simplify the notation. The irreversible parts of the heat flux and the stress tensor are now given by

$$q_i^*[\lambda] = -\kappa[\lambda] \frac{\partial T[\lambda]}{\partial r_i} + q_i^{**}[\lambda]_{NS}, \quad (3.38)$$

$$t_{ij}^*[\lambda] = -\left\{ \eta[\lambda] \Delta_{ijkl} + \zeta[\lambda] \delta_{ij} \delta_{kl} \right\} \frac{\partial v_k[\lambda]}{\partial r_l} + t_{ij}^{**}[\lambda]_{NS}. \quad (3.39)$$

The transport coefficients in Eqs.(3.38-39) are functionals of λ through the λ -dependent densities, $\{\phi_\alpha(\vec{r}, t|\lambda)\}$. The additional contributions to the irreversible fluxes are defined as

$$q_i^{**}(\vec{r}, t|\lambda) = \langle \hat{q}_i(\vec{r}) [e^{D(t|\lambda)} - e^{D'(t|\lambda)}]; t \rangle_{\lambda L}, \quad (3.40)$$

$$t_{ij}^{**}(\vec{r}, t|\lambda) = \langle \hat{t}_{ij}(\vec{r}) [e^{D(t|\lambda)} - e^{D'(t|\lambda)}]; t \rangle_{\lambda L}, \quad (3.41)$$

where $\hat{q}_i(\vec{r})$ is the microscopic heat flux, $\hat{q}_i(\vec{r}) = \hat{s}_i(\vec{r}) - v_j \hat{t}_{ij}(\vec{r})$.

Finally it should be stressed that although the extra contribution to the irreversible fluxes may seem similar to the ones suggested by Landau and Lifschitz⁴⁷ to construct hydrodynamic Langevin equations (and in effect their physical origin is analogous), there is a basic difference in the present formulation. All the equations here are equations for averaged variables, not stochastic equations. In this way the description obtained is directly related to the experimental situation.

III.2 Correlation of Fluctuations

The fluctuations of interest are those of the set of microscopic densities, $\{\hat{\phi}_\alpha(\vec{r}, t)\}$. In particular the second order correlation functions are defined as

$$M_{\alpha\beta}(\vec{r}_1, t_1; \vec{r}_2, t_2) = \langle \delta\hat{\phi}_\alpha(\vec{r}_1, t_1) \delta\hat{\phi}_\beta(\vec{r}_2, t_2) \rangle. \quad (3.42)$$

Using Eqs. (3.23-25), such correlation functions can also be expressed as the first functional derivatives of the λ -dependent densities,

$$M_{\alpha\beta}(\vec{r}_1, t_1; \vec{r}_2, t_2) = \left[\frac{\delta \langle \hat{\phi}_\alpha(\vec{r}_1); t_1 \rangle_\lambda}{\delta \lambda_\beta(\vec{r}_2, t_2)} \right]_{\{\lambda_\alpha=0\}} . \quad (3.43)$$

A set of equations for the two-time correlation functions can then be obtained by functionally differentiating the generalized Navier-Stokes equations, derived in the preceding section, Eqs. (3.28). In a general nonequilibrium state no symmetry properties relating the different correlation functions can be identified a priori. The equations for the set of twenty-five functions $M_{\alpha\beta}$ (for $\alpha=1, \dots, 5$ and $\beta=1, \dots, 5$) are in general all coupled together.

By functionally differentiating Eqs. (3.28) and remembering that the λ -dependence occurs in these equations only through the $\{\phi_\alpha(\vec{r}, t|\lambda)\}$ (or, equivalently, the thermodynamic variables $\{y_\alpha(\vec{r}; t|\lambda)\}$) and through the additional terms in the irreversible fluxes, $\gamma_{\alpha i}^{**}$, the following set of equations for the correlation functions is obtained

$$\begin{aligned} \frac{\partial}{\partial t_1} M_{\alpha\beta}(\vec{r}_1, t_1; \vec{r}_2, t_2) + \mathcal{L}_{\alpha\sigma}(\vec{r}_1, t_1; \{\phi_\alpha\}) M_{\sigma\beta}(\vec{r}_1, t_1; \vec{r}_2, t_2) \\ = I_{\alpha\beta}(\vec{r}_1, t_1; \vec{r}_2, t_2) , \end{aligned} \quad (3.44)$$

where

$$\begin{aligned} \mathcal{L}_{\alpha\beta}(\vec{r}, t; \{\phi_\alpha\}) = \frac{\partial}{\partial r_i} \left\{ \frac{\partial E_\alpha^i(\vec{r}, t; \{\phi\})}{\partial \phi_\beta(\vec{r}, t)} + \frac{\partial L_{\alpha\sigma}^{ij}(\vec{r}, t; \{\phi\})}{\partial \phi_\beta(\vec{r}, t)} \frac{\partial y_\sigma(\vec{r}, t)}{\partial r_j} \right. \\ \left. + L_{\alpha\sigma}^{ij}(\vec{r}, t; \{\phi\}) \frac{\partial}{\partial r_j} \frac{\partial y_\sigma(\vec{r}, t)}{\partial \phi_\beta(\vec{r}, t)} \right\} , \end{aligned} \quad (3.45)$$

and

$$I_{\alpha\beta}(\vec{r}_1, t_1; \vec{r}_2, t_2) = - \lim_{t_1 \gg t_f} \left[\frac{\partial}{\partial r_{1i}} \frac{\delta \gamma_{\alpha i}^{**}(\vec{r}_1, t_1|\lambda)}{\delta \lambda_\beta(\vec{r}_2, t_2)} \right]_{\lambda=0} \text{NS} . \quad (3.46)$$

The fluxes $\gamma_{\alpha i}^{**}$ are defined in Eq. (3.32) and $[\Lambda]_{NS}$ indicates, as in Section III.1, the Navier-Stokes limit of the function A. The differential operators in $\mathcal{L}_{\alpha\beta}$ operate on everything to their right, including the operand of $\mathcal{L}_{\alpha\beta}$ itself. In deriving the set of Eqs. (3.44) the assumption that the local equilibrium correlation functions appearing in the operator $\mathcal{L}_{\alpha\beta}$ are localized in space has been introduced. Therefore these equations apply only if the system is away from critical points. In the general case the operator $\mathcal{L}_{\alpha\beta}$ is nonlocal and the derivatives in Eq. (3.45) have to be substituted with functional derivatives.

The inhomogeneous term on the right hand side of Eqs. (3.44) is evaluated in Appendix B. For $t_1 - t_2 \gg t_f$, it is given by

$$I_{\alpha\beta}(\vec{r}_1, t_1; \vec{r}_2, t_2) = - \lim_{t_1 \gg t_f} \int_0^{t_2} d\tau \langle [e^{L(t_1 - t_2 + \tau)} \hat{\gamma}_{\alpha i}(\vec{r}_1)] \tilde{\Phi}_{\sigma j} \rangle_0 \\ \times \frac{\partial}{\partial r_{ij}} G_{\beta\sigma}^H(\vec{r}_2, \tau; \vec{r}_1, 0) , \quad (3.47)$$

where $\langle \dots \rangle_0$ indicates an average over a reference equilibrium ensemble with local thermodynamic variables evaluated at the point (\vec{r}_1, t_1) (the definition is given by Eq. (A.54), evaluated at $\lambda=0$), and $\tilde{\Phi}_{\sigma j}$ is the volume integrated flux, defined by Eq. (A.57), at $\lambda=0$. Also, $G_{\beta\sigma}^H(\vec{r}_2, \tau; \vec{r}_1, 0)$ is the Green's function for the Navier-Stokes equations, defined in Eq. (B.17).

The time correlation function in Eq. (3.47) is the correlation function appearing in the matrix of the transport coefficients, given by Eq. (3.30) at $\lambda=0$. Its lifetime is of the order of the mean free time t_f , and therefore much shorter than the macroscopic time scales of interest in hydrodynamics. Consequently the term $I_{\alpha\beta}$ does not contribute to the

hydrodynamic equations for the two-time correlation functions if

$$t_1 \gg t_f ,$$

$$t_1 - t_2 \gg t_f . \quad (3.48)$$

In this limit Eq. (3.44) becomes

$$\frac{\partial}{\partial t} M_{\alpha\beta}(\vec{r}_1, t_1; \vec{r}_2, t_2) + \mathcal{L}_{\alpha\sigma}(\vec{r}_1, t_1; \{\psi\}) M_{\sigma\beta}(\vec{r}_1, t_1; \vec{r}_2, t_2) = 0 . \quad (3.49)$$

This set of coupled equations describes correlations over time scales large compared to a mean free time, as desired in a hydrodynamic description. The equations for the correlation of fluctuations at different times are linear, although coupled to the solution of the nonlinear Navier-Stokes equations through the dependence of $\mathcal{L}_{\alpha\beta}$ on the $\{\psi_\alpha\}$. The linear character of the equations is a general result and does not restrict their applicability to small fluctuations around the nonequilibrium state.

For the case of small fluctuations around a nonequilibrium steady state, Eqs. (3.49) agree with the results of others.^{26,39-42,46} The equations derived here represent therefore a generalization of these results: they provide a hydrodynamic description of fluctuations, valid to Navier-Stokes order in the gradients, for nonstationary states and fluctuations of arbitrary amplitude. A detailed comparison with previous work will be presented in Section III.4.

For the special case of equilibrium fluctuations, the operator $\mathcal{L}_{\alpha\beta}$ reduces to that of the linearized Navier-Stokes equations. The

equations for the fluctuations at different times are then exactly those suggested by Onsager's assumption: the fluctuations decay according to the macroscopic linearized regression laws governing the dynamics of a nonequilibrium system near equilibrium.

The explicit form of Eqs. (3.49) for a one-component fluid is conveniently written in terms of the correlation functions

$$\begin{aligned}
 M_{\rho\beta}(\vec{r}_1, t_1; \vec{r}_2, t_2) &= \langle \delta\hat{\rho}(\vec{r}_1, t_1) \delta\hat{\psi}_\beta(\vec{r}_2, t_2) \rangle , \\
 M_{u\beta}(\vec{r}_1, t_1; \vec{r}_2, t_2) &= \langle \delta\hat{u}(\vec{r}_1, t_1) \delta\hat{\psi}_\beta(\vec{r}_2, t_2) \rangle , \\
 M_{g_i\beta}(\vec{r}_1, t_1; \vec{r}_2, t_2) &= \langle \delta\hat{g}_i(\vec{r}_1, t_1) \delta\hat{\psi}_\beta(\vec{r}_2, t_2) \rangle , \tag{3.50}
 \end{aligned}$$

$\beta=1,2,\dots,5$. It is convenient to write the hydrodynamic equations in terms of the correlation functions $M_{u\beta}$ instead of $M_{\varepsilon\beta}$, where \hat{u} is defined by

$$\hat{u}(\vec{r}) = \sum_{n=1}^N \varepsilon_n (\vec{p}_n - m\vec{v}(\vec{q}_n)) \delta(\vec{r} - \vec{q}_n) . \tag{3.51}$$

The two correlation functions are related by

$$\begin{aligned}
 M_{u\beta}(\vec{r}_1, t_1; \vec{r}_2, t_2) &= M_{\varepsilon\beta}(\vec{r}_1, t_1; \vec{r}_2, t_2) - v_i(\vec{r}_1, t_1) M_{g_i\beta}(\vec{r}_1, t_1; \vec{r}_2, t_2) \\
 &\quad + \frac{1}{2} [v(\vec{r}_1, t_1)]^2 M_{\rho\beta}(\vec{r}_1, t_1; \vec{r}_2, t_2) . \tag{3.52}
 \end{aligned}$$

A coupled set of equations for the correlation functions (3.50) is obtained from Eqs. (3.49) by respectively setting $\alpha=\rho, u, g_i$,

$$\frac{\partial}{\partial t_1} M_{\rho\beta} + \frac{\partial}{\partial r_{li}} M_{g_i\beta} = 0, \quad (3.53)$$

$$\begin{aligned} & \left(\frac{\partial}{\partial t_1} + v_i \frac{\partial}{\partial r_{li}} \right) M_{u\beta} + h \frac{\partial}{\partial r_{li}} M_{v_i\beta} + M_{v_i\beta} \frac{\partial u}{\partial r_{li}} + \left(\frac{\partial v_i}{\partial r_{li}} \right) (h_\rho M_{\rho\beta} + h_u M_{u\beta}) \\ & - \frac{\partial}{\partial r_{li}} \left\{ \kappa \frac{\partial}{\partial r_{li}} (T_\rho M_{\rho\beta} + T_u M_{u\beta}) + (\kappa_\rho M_{\rho\beta} + \kappa_u M_{u\beta}) \frac{\partial T}{\partial r_{li}} \right\} \\ & - \frac{\partial v_i}{\partial r_{lj}} \frac{\partial v_k}{\partial r_{lm}} \left\{ (\eta_\rho \Delta_{ijkm} + \zeta_\rho \delta_{ij} \delta_{km}) M_{\rho\beta} + (\eta_u \Delta_{ijkm} + \zeta_u \delta_{ij} \delta_{km}) M_{u\beta} \right\} \\ & - 2 \left\{ \eta \Delta_{ijkm} + \zeta \delta_{ij} \delta_{km} \right\} \frac{\partial v_k}{\partial r_{lm}} \frac{\partial}{\partial r_{li}} M_{v_i\beta} = 0, \quad (3.54) \end{aligned}$$

$$\begin{aligned} & \frac{\partial}{\partial t_1} M_{g_i\beta} + \frac{\partial}{\partial r_{lj}} (v_j M_{g_i\beta} + \rho v_i M_{v_j\beta}) \\ & + \frac{\partial}{\partial r_{li}} (p_\rho M_{\rho\beta} + p_u M_{u\beta}) + \frac{\partial}{\partial r_{lj}} \left\{ (\eta \Delta_{ijkm} + \zeta \delta_{ij} \delta_{km}) \frac{\partial}{\partial r_{lm}} M_{v_k\beta} \right\} \\ & + \frac{\partial}{\partial r_{lj}} \left\{ \frac{\partial v_k}{\partial r_{lm}} \left[(\eta_\rho \Delta_{ijkm} + \zeta_\rho \delta_{ij} \delta_{km}) M_{\rho\beta} \right. \right. \\ & \left. \left. + (\eta_u \Delta_{ijkm} + \zeta_u \delta_{ij} \delta_{km}) M_{u\beta} \right] \right\} = 0, \quad (3.55) \end{aligned}$$

where

$$\begin{aligned} \rho(\vec{r}_1, t_1) M_{v_i\beta}(\vec{r}_1, t_1; \vec{r}_2, t_2) & \equiv M_{g_i\beta}(\vec{r}_1, t_1; \vec{r}_2, t_2) \\ & - v_i(\vec{r}_1, t_1) M_{\rho\beta}(\vec{r}_1, t_1; \vec{r}_2, t_2). \quad (3.56) \end{aligned}$$

The space and time arguments of the correlation functions and the hydrodynamic variables have been omitted in Eqs. (3.53-55) to simplify the notation. The dependence of the correlation functions is the same indicated in Eqs. (3.50) and the hydrodynamic variables are evaluated at

the point (\vec{r}_1, t_1) . Also, the thermodynamic derivatives of a function $A = A(\rho, u)$ have been indicated as

$$\begin{aligned} A_\rho &\equiv \left[\frac{\partial A(\rho, u)}{\partial \rho} \right]_u, \\ A_u &\equiv \left[\frac{\partial A(\rho, u)}{\partial u} \right]_\rho. \end{aligned} \quad (3.57)$$

By comparing Eqs. (3.49) with Eqs. (3.53-5), the matrix $f_{\alpha\beta}(\vec{r}, t)$ is identified as

$$f_{\alpha\beta}(\vec{r}, t) = \begin{pmatrix} 0 & 0 & f_{\rho g_i} \\ f_{u\rho} & f_{uu} & f_{u g_i} \\ f_{g_i\rho} & f_{g_i u} & f_{g_i g_j} \end{pmatrix}, \quad (3.58)$$

where

$$\begin{aligned} f_{\rho g_i} &= \frac{\partial}{\partial r_i}, \\ f_{u\rho} &= -h \frac{\partial}{\partial r_i} \frac{v_i}{\rho} - \left(\frac{\partial u}{\partial r_i} \right) \frac{v_i}{\rho} + h_\rho D \\ &\quad - \frac{\partial}{\partial r_i} \left[\kappa \frac{\partial}{\partial r_i} T_\rho + \left(\frac{\partial T}{\partial r_i} \right) \kappa_\rho \right] - \frac{1}{2} D_{ij} \left[2\eta D_{ij} + \left(\zeta - \frac{2}{3}\eta \right) D\delta_{ij} \right] \\ &\quad + 2 \left[2\eta D_{ij} + \left(\zeta - \frac{2}{3}\eta \right) D\delta_{ij} \right] \frac{\partial}{\partial r_j} \frac{v_i}{\rho}, \\ f_{uu} &= v_i \frac{\partial}{\partial r_i} + h_u D - \frac{\partial}{\partial r_i} \left[\kappa \frac{\partial}{\partial r_i} T_u + \left(\frac{\partial T}{\partial r_i} \right) \kappa_u \right] \\ &\quad - \frac{1}{2} D_{ij} \left[2\eta D_{ij} + \left(\zeta - \frac{2}{3}\eta \right) D\delta_{ij} \right], \end{aligned}$$

$$\begin{aligned}
\mathcal{L}_{u g_i} &= h \frac{\partial}{\partial r_i} \frac{1}{\rho} + \frac{1}{\rho} \left(\frac{\partial u}{\partial r_i} \right) - 2[2\eta D_{ij} + (\zeta - \frac{2}{3}\eta) D \delta_{ij}] \frac{\partial}{\partial r_i} \frac{1}{\rho}, \\
\mathcal{L}_{g_i \rho} &= \frac{\partial}{\partial r_i} p_\rho + 2 \frac{\partial}{\partial r_j} \eta_\rho D_{ij} + \frac{\partial}{\partial r_i} (\zeta_\rho - \frac{2}{3}\eta_\rho) D \\
&\quad - \frac{\partial}{\partial r_j} v_i v_j - \frac{\partial}{\partial r_j} (\eta \Delta_{ijkm} + \zeta \delta_{ij} \delta_{km}) \frac{\partial}{\partial r_m} \frac{v_k}{\rho}, \\
\mathcal{L}_{g_i u} &= \frac{\partial}{\partial r_i} p_u + 2 \frac{\partial}{\partial r_j} \eta_u D_{ij} + \frac{\partial}{\partial r_i} (\zeta_u - \frac{2}{3} \eta_u) D, \\
\mathcal{L}_{g_i g_j} &= \delta_{ij} \frac{\partial}{\partial r_k} v_k + \frac{\partial}{\partial r_j} v_i + \frac{\partial}{\partial r_k} (\eta \Delta_{ijkm} + \zeta \delta_{ik} \delta_{jm}) \frac{\partial}{\partial r_m} \frac{1}{\rho},
\end{aligned} \tag{3.59}$$

where

$$D_{ij} = \frac{1}{2} \left(\frac{\partial v_i}{\partial r_j} + \frac{\partial v_j}{\partial r_i} \right), \tag{3.60}$$

and

$$D \equiv D_{ii} = \vec{\nabla} \cdot \vec{v}. \tag{3.61}$$

The differential operators in Eqs. (3.59) act on everything to their right, unless otherwise indicated by the presence of a parenthesis.

III.3 Equal time fluctuations

Second order equal time correlation functions, defined by setting $t_1=t_2$ in Eq. (3.42), i.e.

$$M_{\alpha\beta}(\vec{r}_1, t; \vec{r}_2, t) = \langle \delta \hat{\psi}_\alpha(\vec{r}_1, t) \delta \hat{\psi}_\beta(\vec{r}_2, t) \rangle, \tag{3.62}$$

are needed as initial conditions for the solution of Eqs. (3.49). However, equations for the equal time correlation functions cannot be obtained directly by functional differentiation of the equations for $\{\langle \hat{\psi}_\alpha(\vec{r}_1); t \rangle_\lambda\}$, as was done for the equations for the correlation of fluctuations at different times, because the functional differentiation does not commute with the time derivative. Instead, they can be determined from the limit,

$$\frac{\partial}{\partial t} M_{\alpha\beta}(\vec{r}_1, t; \vec{r}_2, t) = \left[\lim_{\varepsilon \rightarrow 0^+} (1 + P_{12} P_{\alpha\beta}) \frac{\partial}{\partial \varepsilon} \frac{\delta \langle \hat{\psi}_\alpha(\vec{r}_1); t + \varepsilon \rangle_\lambda}{\delta \lambda_\beta(\vec{r}_2, t)} \right]_{\lambda=0}, \quad (3.63)$$

where the operators P_{12} and $P_{\alpha\beta}$ permute \vec{r}_1, \vec{r}_2 and α, β , respectively. By using the results of the preceding section, (Eq. 3.44), and observing that the $\varepsilon \rightarrow 0^+$ limit can be taken immediately on the left hand side of the equation, an equation for $M_{\alpha\beta}$ is obtained in the form

$$\begin{aligned} \frac{\partial}{\partial t} M_{\alpha\beta}(\vec{r}_1, t; \vec{r}_2, t) + (1 + P_{12} P_{\alpha\beta}) \mathcal{L}_{\alpha\sigma}(\vec{r}_1, t; \{\psi\}) M_{\sigma\beta}(\vec{r}_1, t; \vec{r}_2, t) \\ = \Gamma_{\alpha\beta}(\vec{r}_1, \vec{r}_2; t), \end{aligned} \quad (3.64)$$

where the operator $\mathcal{L}_{\alpha\sigma}$ is defined in Eq. (3.45), and

$$\Gamma_{\alpha\beta}(\vec{r}_1, \vec{r}_2; t) = \lim_{\varepsilon \rightarrow 0^+} (1 + P_{12} P_{\alpha\beta}) I_{\alpha\beta}(\vec{r}_1, t + \varepsilon; \vec{r}_2, t). \quad (3.65)$$

The inhomogeneous term $\Gamma_{\alpha\beta}$ is evaluated in Appendix B, with the result

$$\Gamma_{\alpha\beta}(\vec{r}_1, \vec{r}_2; t) = (1 + P_{12} P_{\alpha\beta}) \frac{\partial}{\partial r_{1i}} L_{\alpha\beta}^{ij}(\vec{r}_1, t; \{\psi\}) \frac{\partial}{\partial r_{2j}} \delta(\vec{r}_1 - \vec{r}_2), \quad (3.66)$$

where $L_{\alpha\beta}^{ij}$ is the Onsager's matrix of transport coefficients.

Equations (3.64), together with the set of Eqs. (3.19) and the equations for the two time correlation functions, give a closed description of transport and fluctuations (up to second order correlations) in a hydrodynamic system whose macroscopic state is described in terms of the nonlinear Navier-Stokes equations.

Again, the interpretation of Eq. (3.64) is clarified by comparing with the case of fluctuations around the equilibrium state. Onsager's assumption applies then and, as seen in the preceding section, the time evolution of the two-time correlations is governed by the linearized hydrodynamic equations. Similarly, Eq. (3.64), evaluated at equilibrium, becomes

$$\begin{aligned} & (1 + P_{12} P_{\alpha\beta}) \mathcal{L}_{\alpha\sigma}^0(\vec{r}_1, \{\psi^0\}) M_{\alpha\beta}^0(\vec{r}_1; \vec{r}_2) \\ & = (1 + P_{12} P_{\alpha\beta}) L_{\alpha\beta}^{ij}(\{\psi^0\}) \frac{\partial^2}{\partial r_{1i} \partial r_{2j}} \delta(\vec{r}_1 - \vec{r}_2), \end{aligned} \quad (3.67)$$

where the superscript zero indicates the equilibrium value and $\mathcal{L}_{\alpha\beta}^0$ now depends on \vec{r}_1 only through the differential operators. Equation (3.67) is an identity or, equivalently, constitutes a statement of the fluctuation-dissipation theorem relating equilibrium fluctuations and transport coefficients.

The description of nonequilibrium fluctuations derived here indicates clearly how Onsager's assumption should be modified for systems out of equilibrium. First, it is no longer true that the

regression laws for the fluctuations are the same as those for the average values. They are instead linear equations, whose coefficients depend on the solution of the nonlinear regression laws (they can be interpreted as a linearization about the nonequilibrium macroscopic state, $\{\psi_\alpha(\vec{r}, t)\}$, at each instant t). In this sense knowledge of the average dynamics still allows determination of the dynamics of fluctuations. The two sets of equations form a bilinear set that must be solved simultaneously. Secondly, the fluctuation-dissipation theorem must be abandoned in favor of Eqs. (3.64) and (3.66) which, for nonstationary states, indicate that even the equal time fluctuations are dynamical variables.

In equilibrium, $\Gamma_{\alpha\beta}$ is determined by the left hand side of Eq. (3.67), since the equal time fluctuations can be calculated directly in the Gibbs ensemble. In the nonequilibrium case, however, $\Gamma_{\alpha\beta}$ must be provided independently. Its calculation requires the analysis of the initial transients due to microscopic degrees of freedom not incorporated in the Navier-Stokes equations. In this sense the source function $\Gamma_{\alpha\beta}$ can be interpreted as a noise amplitude.

The explicit form of Eqs. (3.64) for a one-component fluid can be obtained by using Eqs. (3.58-59) for the elements of the matrix $\mathcal{L}_{\alpha\beta}$. The inhomogeneous term $\Gamma_{\alpha\beta}(\vec{r}_1, \vec{r}_2; t)$ is diagonal in the labels α and β for α and $\beta = \rho, u, g_i$. Its explicit form is given by Eq. (3.66), with

$$L_{\rho\rho}^{ij}(\vec{r}, t) = 0,$$

$$L_{uu}^{ij}(\vec{r}, t) = \lim_{t \gg t_f} \int_0^t dt \langle [e^{L\tau} \hat{s}_i^j(\vec{r})] \hat{S}_j \rangle_0,$$

$$L_{g_k g_l}^{ij}(\vec{r}, t) = \lim_{t \gg t_f} \int_0^t d\tau \langle [e^{L\tau} \hat{t}_{ik}'(\vec{r})] \hat{T}_{jl} \rangle_0, \quad (3.68)$$

where $\hat{s}_i'(\vec{r})$ and $\hat{t}_{ij}'(\vec{r})$ are the projected energy and momentum fluxes, given by

$$\hat{s}_i'(\vec{r}) = \hat{s}_i(\vec{r}) - \frac{h(\vec{r}, t)}{\rho(\vec{r}, t)} \hat{g}_i(\vec{r}), \quad (3.69)$$

and

$$\hat{t}_{ij}'(\vec{r}) = \hat{t}_{ij}(\vec{r}) - \delta_{ij} \left[p(\vec{r}, t) + \left(\frac{\partial p}{\partial u} \right)_\rho \hat{u}(\vec{r}) + \left(\frac{\partial p}{\partial \rho} \right)_u \hat{\rho}(\vec{r}) \right]. \quad (3.70)$$

Equations (3.68) are the Green-Kubo expressions for the transport coefficients, or

$$L_{uu}^{ij}(\vec{r}, t) = \delta_{ij} K_B T^2(\vec{r}, t) \kappa(\rho, u), \quad (3.71)$$

$$L_{g_k g_l}^{ij}(\vec{r}, t) = K_B T(\vec{r}, t) \left[\eta(\rho, u) \Delta_{ijkl} + \zeta(\rho, u) \delta_{ij} \delta_{kl} \right]. \quad (3.72)$$

The transport coefficients depend on \vec{r} and t through the average mass and internal energy density.

III.4 Discussion

Several authors^{26,27,39-46} have recently formulated a description of fluctuations in nonequilibrium hydrodynamic steady states which are adequately described by the nonlinear Navier-Stokes equations. It seems therefore appropriate to compare these approaches with the one used here and to discuss differences and similarities.

Tremblay, Arai and Siggia²⁶ have proposed a Langevin theory of fluctuations in nonequilibrium steady states. They assumed that the Landau-Lifschitz theory of hydrodynamic fluctuations can be applied not

only for equilibrium fluctuations (in a regime where the macroscopic regressions laws are linear), but also for small fluctuations around the nonequilibrium state. The equations governing the time evolution of the fluctuations are obtained by linearizing the nonlinear macroscopic regression laws around the nonequilibrium state. The correlations of the random forces are assumed to have the same form as in equilibrium, with local thermodynamic variables. This description is supported by the work of Keizer.³⁰ It is however phenomenological in character and restricted to small fluctuations around the nonequilibrium state. The results of the present formulation basically confirm the Langevin hypothesis. There are however some important differences. First, the equations for the fluctuations are always linear, independent of the size of the fluctuations. Secondly, the form of the noise spectrum is derived here on the basis of a microscopic description, that clearly places the source of the fluctuations in the transients present in the system before the macroscopic description applies. Furthermore the approach used here is not stochastic, but describes the system entirely in terms of macroscopic variables (averages and correlation functions), as required to make a precise and immediate connection with experiments.

Microscopic or semi-microscopic formulations of the description of fluctuations in nonequilibrium steady states, similar in spirit and content to the present one, have been developed by Kirkpatrick, Cohen and Dorfman (KCD),^{45,46} and by an MIT collaboration,³⁹⁻⁴² as indicated in Chapter I. The results of KCD agree with the ones obtained here, when the latter are specialized to the case of nonequilibrium steady states. The inhomogeneous term in their equation for the equal time correlation functions has apparently a different form from the one in Eq. (3.66). The correlation of interest in Ref. 46 is the deviation of

the equal time correlation function from its local equilibrium value. The noise term there originates from the action of the Euler part of the hydrodynamic equation over the local equilibrium correlation function, as it is shown in Ref. 41. The form given in Ref. 46 and the one derived here, Eq. (3.66), are however equivalent. The hydrodynamic equations obtained by Kirkpatrick, Cohen and Dorfman are therefore identical to the ones derived here.

Instead, the results obtained by the MIT group (and, it seems, also the Langevin theory) differ from those obtained through the generating functional approach because the second term in the evolution matrix $f_{\alpha\beta}$ [see Eq. (3.45)], containing the thermodynamic derivatives of the transport coefficients, is neglected there.⁴¹ This term is often small, but is still of first order in the fluctuations around the nonequilibrium state, and therefore cannot be neglected even when fluctuations of small amplitude are considered.

CHAPTER IV KINETIC THEORY

IV.1 Generating Functional for Phase Space Fluctuations

The hydrodynamic description of nonequilibrium fluctuations developed in the previous chapter is restricted to states adequately described in terms of the nonlinear Navier-Stokes equations and rests on an estimate of the lifetime of certain correlations functions.

Within the framework of kinetic theory, it is possible, at least in the limit of low density (where a small expansion parameter is available), to derive an exact description of nonequilibrium fluctuations. Furthermore the kinetic description is more general than hydrodynamics. It describes macroscopic processes varying on shorter space and time scales (of the order of or smaller than the mean free path and the mean free time between collisions) and it incorporates the hydrodynamic limit.^{3,8} Also, as shown in Section II.2, the averages and the correlation functions of the dynamical variables of interest in the study of a large class of systems are simply related to the reduced distribution functions and to the correlations of phase space fluctuations.

The generating functional method is applied here to describe phase space nonequilibrium fluctuations. No restrictions are imposed on the nonequilibrium state or on its stability other than the well understood assumptions entering in the derivation of the Boltzmann equation.^{4,5,57} The description of fluctuations obtained is justified in the same limits

which apply to the macroscopic description of the state. In particular no extra assumptions are introduced to evaluate the amplitude of the "noise" in the system, which contributes to the equations for the equal time fluctuations. Finally, in the last section, the hydrodynamic limit is recovered. Again, the results are restricted to nonequilibrium states in low density gases. However all of the known qualitative dynamics of fluids in general are also exhibited by gases. In particular, the nonlinear hydrodynamic behavior is identical.^{8,9}

The system considered is the classical system of N interacting point particles in a volume V introduced in Chapter II. Since the internal degrees of freedom of the molecules are neglected, the discussion is limited to monoatomic gases.

The time evolution of the distribution function of the system is governed by the Liouville equation for a system in interaction with its surroundings, as given in Eq.(2.2). For pairwise additive central interatomic forces the Liouville operator of the isolated system has the form

$$L(x_1, \dots, x_N) = \sum_{i=1}^N L_0(x_i) - \sum_{i < j=1}^N \theta(x_i, x_j), \quad (4.1)$$

with

$$L_0(x_i) = \frac{\vec{p}_i \cdot \vec{\nabla}_{\vec{q}_i}}{m}, \quad (4.2)$$

and

$$\theta(x_i, x_j) = \left[\vec{\nabla}_{\vec{q}_i} V(q_{ij}) \right] \cdot \left(\vec{\nabla}_{\vec{p}_i} - \vec{\nabla}_{\vec{p}_j} \right). \quad (4.3)$$

Equation (4.3) applies for continuous interatomic potentials, $V(q_{ij})$, with $q_{ij} = |\vec{q}_i - \vec{q}_j|$. The potential V is also assumed to be short ranged (of range σ) and purely repulsive. The first term in Eq.(4.1) represents the free streaming of the particles and the second term contains the effects of the collisions.

Kinetic theory describes phenomena whose space and time variations occur over scales large compared to the force range, σ , and the duration of a collision, τ_c . The derivation of the kinetic theory from the microscopic N -particle dynamics rests on the assumption that, for a particular class of nonequilibrium states, a contraction of the description takes place over a time of the order of τ_c . For times large compared to τ_c all the properties of the system depend on time only through the one-particle distribution function. This is the idea proposed by Bogoliubov to derive the Boltzmann equation from the Liouville equation.⁴ The special states to which this macroscopic description applies are identified through the requirement that the initial correlations decay on times of the order of the time required for a collision.⁵ The kinetic theory of nonequilibrium fluctuations derived here will be restricted to the same class of states.

As mentioned, the macroscopic variable of interest is the one-particle distribution function, $f_1(x,t)$, defined in Eq.(2.27) as the nonequilibrium average of the phase space density, $\hat{f}_1(x,t)$. The corresponding generating functional is given by Eq.(2.35), with

$$U[\lambda] \equiv U_N[\lambda] = \exp \int_{-\infty}^{+\infty} dt \int dx \hat{f}_1(x,t) \lambda(x,t) . \quad (4.4)$$

The first functional derivative of G is then given by

$$\frac{\delta G[\lambda]}{\delta \lambda(\mathbf{x}, t)} = \frac{\langle \hat{f}_1(\mathbf{x}, t) U[\lambda] \rangle}{\langle U[\lambda] \rangle}, \quad (4.5)$$

and reduces to the one particle distribution function when evaluated at $\lambda=0$,

$$\left[\frac{\delta G[\lambda]}{\delta \lambda(\mathbf{x}, t)} \right]_{\lambda=0} = f_1(\mathbf{x}, t). \quad (4.6)$$

To obtain a kinetic equation, it is convenient to define the functional $f_1(\mathbf{x}, t | \lambda)$ as*

$$n f_1(\mathbf{x}, t | \lambda) \equiv \frac{\langle \hat{f}_1(\mathbf{x}, t) U[\lambda] \rangle}{\langle U[\lambda] \rangle}, \quad \text{for } t > t_0, \quad (4.7)$$

where t_0 is an arbitrary parameter introduced to assist in ordering the times obtained on functional differentiation. Again, evaluating Eq. (4.7) at $\lambda=0$ and choosing $t_0=0$, the functional $f_1[\lambda]$ reduces, at all times $t > 0$, to the one-particle distribution function, as in Eq. (4.6). The dependence on the parameter t_0 can be introduced explicitly by choosing the tests functions to be nonzero only for $t \leq t_0$, i.e.

$$\lambda(\mathbf{x}, t) = \lambda'(\mathbf{x}, t) \theta(t_0 - t), \quad (4.8)$$

where θ is the unit step function. In this way only time correlation functions involving time arguments smaller than t can be generated. The ordering chosen in Eq. (2.40) can be obtained by appropriate choice of t_0 . The correlation functions of phase space fluctuations, defined in

*A similar approach has been used in Ref. 58 to derive kinetic equations for multitime equilibrium fluctuations.

Eqs.(2.32) and (2.34), are then immediately obtained as higher functional derivatives of G , as shown in Eqs.(2.40). In the following the dependence on the parameter t_0 will be indicated explicitly only when needed.

As already done at the hydrodynamic level, it can be argued that the detailed form of the external forces and of their interaction with the particles of the system should not appear in the equations governing the time evolution of the reduced distribution functions (or functionals).^{6,57} The dependence on the surroundings can be entirely incorporated through appropriate boundary conditions to be used when solving the kinetic equations. This is a consequence of the fact that the lower order reduced distribution functions are localized quantities describing properties at a particular point in the gas. Therefore, as long as properties in the interior of the system are considered, at a distance from the boundaries large compared to the force range, the Liouville equation for the isolated system can be used to describe the time evolution of the dynamical variables. Equation (4.5) can then be rewritten as

$$n f_1(x, t | \lambda) = \sum_{N \geq 1}^{\infty} N \int dx_1 \dots dx_N e^{-Lt} \frac{U[\lambda]}{\langle U[\lambda] \rangle} \rho_N(0) . \quad (4.9)$$

This form suggests that $f_1(x, t | \lambda)$ can be identified as the first member of a set of functionals defined by

$$n^s f_s(x_1, \dots, x_s, t | \lambda) = \sum_{N \geq s} \frac{N!}{(N-s)!} \int dx_{s+1} \dots dx_N e^{-Lt} \frac{U[\lambda]}{\langle U[\lambda] \rangle} \rho_N(0) . \quad (4.10)$$

When evaluated at $\lambda=0$, $f_s(x_1, \dots, x_s, t|\lambda)$ reduces to the s -particle distribution function defined in Eq.(2.25). The operator governing the time evolution of the set of functionals $\{f_s[\lambda]\}$ is the Liouville operator of the system and does not depend on the test function λ . This dependence only enters through the initial condition. By differentiating Eq.(4.10) with respect to time it can then be shown that the functionals $f_s[\lambda]$ satisfy the BBGKY hierarchy. In particular, for $s=1$,

$$\left\{ \frac{\partial}{\partial t} + L_0(x_1) \right\} f_1(x_1, t|\lambda) = n \int dx_2 \theta(x_1, x_2) f_2(x_1, x_2, t|\lambda) . \quad (4.11)$$

Again, as done in the hydrodynamic case, the standard methods of statistical mechanics which allow closure of the hierarchy and derivation of a kinetic equation for the one-particle distribution function⁵ can be applied to the λ -dependent functionals. By assuming that the functional relationship between $f_1[\lambda]$ and λ , as defined in Eq.(4.7), may be inverted, it is possible to express, at least formally, $f_2[\lambda]$ as a functional of $f_1[\lambda]$. A formally closed equation for $f_1[\lambda]$ is then obtained,

$$\left\{ \frac{\partial}{\partial t} + L_0(x_1) \right\} f_1(x_1, t|\lambda) = n \int dx_2 \theta(x_1, x_2) H(x_1, x_2, t|f_1[\lambda]) . \quad (4.12)$$

The functional H is highly nonlinear but it simplifies considerably when evaluated at $\lambda=0$. However, in order to preserve the properties of the generating functional, the evaluation of H at nonvanishing λ has to be attempted. This evaluation is carried out in the next section in the limit of low density.

IV.2 Low Density Limit and Boltzmann Equation

A systematic evaluation of the functional H defined in Eq.(4.12) is possible in the limit of low density, by using the nonequilibrium cluster expansion developed by Cohen⁵ as a generalization of the technique proposed by Mayer for equilibrium systems. In this way the two-particle distribution function for a dilute gas can be expressed in terms of the one-particle distribution as a power series in the reduced density $n\sigma^3$. When this result is substituted in the first equation of the BBGKY hierarchy, an expression for the rate of change of the single particle distribution function in the form of a density expansion is obtained. The terms in the expansion depend successively on the dynamics of clusters of two, three, etc., isolated particles. To lowest order in the expansion parameter, corresponding to the Boltzmann limit, only binary collisions are retained.

The cluster expansion for the functionals $f_s[\lambda]$ is formally identical to the one for the distribution functions and is outlined in Appendix C. To lowest order in the density, the result is

$$f_2(x_1, x_2, t | \lambda) = \quad {}_t(x_1, x_2) f_1(x_1, t | \lambda) f_1(x_2, t | \lambda) \\ + R(x_1, x_2, t | f_1[\lambda]) , \quad (4.13)$$

where the streaming operator ${}_t$ is defined as

$${}_t(x_1, x_2) = S_{-t}(x_1, x_2) S_t(x_1) S_t(x_2) \quad (4.14)$$

and $S_t(x_1, \dots, x_s)$ is the operator governing the time evolution of a

dynamical variable in a system of s isolated particles. It is given by

$$S_t(x_1, \dots, x_s) = e^{tL(x_1, \dots, x_s)}, \quad (4.15)$$

where $L(x_1, \dots, x_s)$ is the s -particle Liouville operator (see Eqs.(4.1)). In other words $S_t(x_1, \dots, x_s)$ describes the dynamics of an isolated cluster of s particles. Finally, $R(x_1, x_2, t | f_1[\lambda])$ is a nonlinear functional of $f_1[\lambda]$, depending on the initial correlations in the system. Its explicit form is given in Appendix C. For times long compared to a collision time the streaming operator \mathfrak{S}_t reaches a time independent value,⁵⁷

$$\mathfrak{S}_\infty(x_1, x_2) = \lim_{t \gg \tau_c} \mathfrak{S}_t(x_1, x_2). \quad (4.16)$$

Furthermore it is shown in Appendix C that if attention is restricted to the time evolution of initial states of the system where the particles have only short-range correlations (i.e. the s -particle distribution function factorizes for interparticle distances large compared to the force range), a part of the contribution to Eq.(4.12) from the functional $R(x_1, x_2, t | f_1[\lambda])$ vanishes for times long compared to the collision time.

By inserting Eq.(4.13) into Eq.(4.11) and by making use of the above results, an equation describing the time evolution of the one-particle functional $f_1(x_1, t | \lambda)$ is obtained. The equation only describes variations over time scales large compared to τ_c and is given by

$$\left\{ \frac{\partial}{\partial t} + L_o(x_1) \right\} f_1(x, t | \lambda) = n \bar{J}[f_1[\lambda], f_1[\lambda]] + W(x_1, t | f_1[\lambda]), \quad (4.17)$$

for $t > t_0$, where

$$\overline{J}[A,B] = \int dx_2 \overline{K}(x_1, x_2) A(x_1) B(x_2) \quad (4.18)$$

and

$$\overline{K}(x_1, x_2) = \theta(x_1, x_2) \mathfrak{S}_\infty(x_1, x_2) . \quad (4.19)$$

The second term on the right hand side of Eq.(4.17) is given by

$$\begin{aligned} W(x_1, t | f_1[\lambda]) &= \lim_{t \gg \tau_c} n \int dx_2 \theta(x_1, x_2) S_{-t}(x_1, x_2) \\ &\times \{ U_2^0[x_1, x_2 | \lambda] U_1^{0-1}[x_1 | \lambda] U_1^{0-1}[x_2 | \lambda]^{-1} \} \\ &\times S_t(x_1) S_t(x_2) f_1(x_1, t | \lambda) f_1(x_2, t | \lambda), \end{aligned} \quad (4.20)$$

where $U_s^0[x_1, \dots, x_s | \lambda]$ is the low density limit of the s -particle functional analogous to the N -particle functional defined in Eq.(4.4).

It is given by

$$\begin{aligned} U_s^0[x_1, \dots, x_s | \lambda] &= \exp \int_{-\infty}^{+\infty} dt S_t(x_1, \dots, x_s) \sum_{i=1}^s \lambda(x_i, t) \\ &= \exp \left\{ \sum_{i=1}^s \int_{-\infty}^{+\infty} dt \lambda(x_i^s(t), t) \right\}, \end{aligned} \quad (4.21)$$

where

$$x_i^s(t) = S_t(x_1, \dots, x_s) x_i(0) . \quad (4.22)$$

A precise justification of the use of Eq.(4.21) as the low density form of U_s is given in Appendix C.

By evaluating Eq.(4.17) at $\lambda=0$ and observing that $U_s[x_1, \dots, x_s | \lambda=0] = 1$ for all values of s , it follows that

$$W(x_1, t | f_1[\lambda=0]) = 0, \quad (4.23)$$

identically. Choosing $t_0 = 0$, a homogeneous equation for the one-particle distribution function is obtained,

$$\left\{ \frac{\partial}{\partial t} + L_0(x_1) \right\} f_1(x_1, t) = n \bar{J}[f_1, f_1]. \quad (4.24)$$

The right hand side of Eq.(4.24) is a nonlinear functional of the one-particle distribution function. When the further approximation of neglecting the difference in position of the colliding pair is introduced (this implies that the resulting equation will only describe space variations over distances large compared to the force range), the operator \bar{J} assumes the familiar form of the nonlinear Boltzmann operator, given by

$$\begin{aligned} J[A, B] = & \int d\vec{p}_2 \int_0^\infty db b \int_0^{2\pi} d\phi \frac{|\vec{p}_1 - \vec{p}_2|}{m} \{ A(\vec{q}_1, \vec{p}'_1) B(\vec{q}_1, \vec{p}'_2) \\ & - A(\vec{q}_1, \vec{p}_1) B(\vec{q}_1, \vec{p}_2) \}, \end{aligned} \quad (4.25)$$

where b is the impact parameter for the binary collision and ϕ is the azimuthal angle measuring the orientation of the scattering plane. The prime over the momenta indicates their values after the collision. The nonlinear Boltzmann equation for the one-particle distribution function is then recovered. In the following both the operators J and \bar{J} will be referred to as the nonlinear Boltzmann operator.

Equation (4.17) has therefore the form of a generalized Boltzmann equation. The extra term on the right hand side of the equation is a complicated functional of λ and its behavior at long times cannot be analyzed before setting $\lambda=0$. As just shown, it does not contribute to the dynamics of the macroscopic variables of the system. However it has to be retained in the equation for the functional $f_1(x,t|\lambda)$ for the purpose of deriving equations for the correlation functions.

Equations for the correlations of phase space fluctuations are derived in the next two sections. As in the hydrodynamic limit, the contribution from W to the equation for the multitime correlation functions vanishes on a time scale of the order of τ_c . However, when correlations of equal time fluctuations are considered, this term does not vanish, but is responsible for the appearance of an inhomogeneous part in the equations.

IV.3 Correlation of Fluctuations

The multitime correlation functions of phase space fluctuations defined in Eq.(2.34) are obtained by functional differentiation of $G[\lambda]$, as indicated in Eq.(2.40), or, equivalently,

$$\begin{aligned}
 C_s(x_1, t_1; \dots; x_s, t_s) &\equiv \langle \prod_{k=1}^s \hat{\delta} f_1(x_k, t_k) \rangle \\
 &= \left[\frac{\delta^{(s-1)} f_1(x_1, t_1 | \lambda)}{\delta \lambda(x_2, t_2) \dots \delta \lambda(x_s, t_s)} \right]_{t_0=t_2, \lambda=0}, \quad (4.26)
 \end{aligned}$$

with the time ordering $t_1 \geq t_2 \geq \dots \geq t_s$. Equations for the time evolution of C_s are then obtained by functionally differentiating Eq.(4.17) and evaluating the resulting equation at $\lambda=0$.

It is shown in Appendix C that the inhomogeneous term $W(x_1, t_1 | \lambda)$ vanishes at long times ($t_1 \gg \tau_c$) if t_0 is chosen to satisfy $t - t_0 > \tau_c$. This choice corresponds to the one needed to generate multitime correlation functions in a Boltzmann description. In this sense it immediately appears that W does not contribute to the equation for the two-time correlation function, as long as $t_1 - t_2 > \tau_c$. Here this result is also explicitly shown to follow from the analysis of the functional derivative of W . This will make evident the difference between the unequal and the equal time cases.

The equation for the two-time correlation function ($s=2$) is

$$\left\{ \frac{\partial}{\partial t_1} + L(x_1, t_1 | f_1) \right\} C_2(x_1, t_1; x_2, t_2) = \left[\frac{\delta W(x_1, t_1 | f_1[\lambda])}{\delta \lambda(x_2, t_2)} \right]_{t_0=t_2, \lambda=0}, \quad (4.27)$$

where

$$L(x_1, t_1 | f_1) = L_0(x_1) - n \Lambda(x_1, t_1 | f_1) \quad (4.28)$$

and

$$\Lambda(x_1, t_1 | f_1) = \int dx_3 \theta(x_1, x_3) \omega(x_1, x_3) (1 + P_{13}) f_1(x_3, t_1). \quad (4.29)$$

By functionally differentiating Eq.(C.26), the term on the right hand side of Eq.(4.27) can be evaluated explicitly as a functional of the one-particle distribution, with the result,

$$\begin{aligned} \left[\frac{\delta W(x_1, t_1 | \lambda)}{\delta \lambda(x_2, t_2)} \right]_{\lambda=0} &= n \int dx_3 \theta(x_1, x_3) S_{-t_1}(x_1, x_3) \{ [S_{t_2}(x_1, x_3) \\ &\quad - S_{t_2}(x_1) S_{t_2}(x_3)] [\delta(x_1 - x_2) + \delta(x_3 - x_2)] \} \\ &\quad \times S_{t_1}(x_1) S_{t_1}(x_3) f_1(x_1, t_1) f_1(x_3, t_1) \end{aligned} \quad (4.30)$$

or,

$$\begin{aligned}
 \left[\frac{\delta W(x_1, t_1 | \lambda)}{\delta \lambda(x_2, t_2)} \right]_{\lambda=0} &= n \int dx_3 \theta(x_1, x_3) \{ [\mathbb{S}_{t_1-t_2}(x_1, x_3) - \mathbb{S}_{t_1}(x_1, x_3)] \\
 &\quad \times \mathbb{S}_{t_2-t_1}(x_1) \mathbb{S}_{t_2-t_1}(x_3) [\delta(x_1-x_2) + \delta(x_3-x_2)] \} \\
 &\quad \times \mathbb{S}_{t_1}(x_1, x_3) f_1(x_1, t_1) f_1(x_3, t_1) , \quad (4.31)
 \end{aligned}$$

where the choice $t_0 = t_2$ is understood. The streaming operator \mathbb{S}_t reaches a time independent limit for $t \gg \tau_c$, as shown in Eq.(4.16). Therefore the difference between the two streaming operators in Eq.(4.31) vanishes if

$$t_1 \gg \tau_c ,$$

$$t_1 - t_2 \gg \tau_c . \quad (4.32)$$

In the above limit the right hand side of Eq.(4.26) vanishes,

$$\lim_{\substack{t_1 \gg \tau_c \\ t_1 - t_2 \gg \tau_c}} \left[\frac{\delta W(x_1, t_1 | \lambda)}{\delta \lambda(x_2, t_2)} \right]_{t_0=t_2, \lambda=0} = 0 , \quad (4.33)$$

and the time evolution of the two-time correlation function is governed by a homogeneous equation given by

$$\left\{ \frac{\partial}{\partial t_1} + L(x_1, t_1 | f_1) \right\} C_2(x_1, t_1; x_2, t_2) = 0 . \quad (4.34)$$

The conditions imposed in Eqs.(4.32) imply that Eq.(4.34) can only be applied to describe correlations over time scales large compared to a collision time. Not only the times t_1 and t_2 have to be large compared to τ_c , but also their difference. This is the natural outcome of considering the Boltzmann limit.

As in the preceding section, when the difference in position of the colliding pair of particles is neglected, Eq.(4.34) becomes

$$\left\{ \frac{\partial}{\partial t_1} + L_B(x_1, t_1 | f_1) \right\} C_2(x_1, t_1; x_2, t_2) = 0, \quad (4.35)$$

where,

$$L_B(x_1, t_1 | f_1) = L_0(x_1) - nI(x_1, t_1 | f_1), \quad (4.36)$$

and

$$\begin{aligned} I(x_1, t_1 | f_1) A(x_1) = & \int d\vec{p}_3 \int_0^\infty db \int_0^{2\pi} d\phi \frac{|\vec{p}_1 - \vec{p}_3|}{m} [1 + P(\vec{p}_1, \vec{p}_3)] \\ & \times \{ f_1(\vec{q}_1, \vec{p}'_3, t_1) A(\vec{q}_1, \vec{p}'_1) - f_1(\vec{q}_1, \vec{p}_3, t_1) A(\vec{q}_1, \vec{p}_1) \}. \end{aligned} \quad (4.37)$$

The permutation operator $P(\vec{p}_1, \vec{p}_3)$ interchanges only the momenta of the two particles. When the one-particle distribution function in Eq.(4.37) is evaluated at equilibrium (i.e. coincides with a Maxwell-Boltzmann distribution), the operator I reduces to the linearized Boltzmann operator.⁸

The equation for the correlation function is linear. This is an exact result (in the Boltzmann limit considered here), not the outcome of a linearization around the state. No restrictions have been imposed

on the size of the fluctuations. The operator $L(x,t|f_1)$ depends on the nonequilibrium state of the system, characterized by the distribution function $f_1(x,t)$, which is given by the solution of the nonlinear Boltzmann equation. In this sense the dynamics of the fluctuations is entirely determined by the macroscopic nonequilibrium state of the system.

To solve Eq.(4.34) specification of the initial condition, represented by the equal time correlation function $C_2(x_1,t;x_2,t)$, is also needed. The derivation of an equation for the equal time correlation is the subject of the next section.

Finally, the method described here can be extended to evaluate higher order multitime correlation functions. In particular the equation for the three-time correlation function is given by

$$\begin{aligned} & \left\{ \frac{\partial}{\partial t_1} + L(x_1, t_1 | f_1) \right\} C_3(x_1, t_1; x_2, t_2; x_3, t_3) \\ & = n \int dx_4 \bar{K}(x_1, x_4) (1 + P_{14}) C_2(x_1, t_1; x_2, t_2) C_2(x_4, t_1; x_3, t_3) , \quad (4.38) \end{aligned}$$

where the operator $\bar{K}(x_1, x_4)$ has been defined in Eq.(4.19). The equation for the three time correlation function is again linear, but is coupled to the lower order correlations through the inhomogeneous term on the right hand side of Eq.(4.38).

In general, the equation for the s-time correlation function is a linear inhomogeneous equation. The homogeneous part has, at any order, the form given in Eq.(4.34) and depends therefore on the nonequilibrium distribution function. The inhomogeneous part couples the s-th order equation to all the lower order ones. As s increases, the equations become therefore very complicated, but always conserve linearity.

Furthermore the solution of the equation for the s-th order multi-time correlation function requires the knowledge of all the correlation functions obtained by progressively setting $t_1=t_2$, $t_1=t_2=t_3$, ..., $t_1=t_2=...=t_s$, in Eq.(4.26). Equations describing the time evolution of such correlation functions can be obtained by applying an appropriate limiting procedure on the equations obtained by functional differentiation of Eq.(4.17). The second term on the right hand side of Eq.(4.17) will only contribute when at least two of the time arguments in the correlation function are equal, as will be shown in the next section.

IV.4 Equal Time Fluctuations

In order to derive equations for the correlation functions of equal time fluctuations, defined in Eq.(2.32), a limiting procedure on the equations for the unequal time correlation has to be used. In this way it is possible to circumvent the problem arising from the fact that the time derivative and the functional derivative can only be interchanged when involving different time arguments. As in the previous section, the calculation will be carried out explicitly for the second order correlation function. The rate of change of $C_2(x_1, t; x_2, t)$ can be written in the form,

$$\frac{\partial}{\partial t} C_2(x_1, t; x_2, t) = \lim_{\epsilon \rightarrow 0^+} \left\{ \frac{\partial}{\partial \epsilon} C_2(x_1, t+\epsilon; x_2, t) + \frac{\partial}{\partial \epsilon} C_2(x_2, t+\epsilon; x_1, t) \right\} . \quad (4.39)$$

An equation for the equal time correlation can then be obtained from the equations for the unequal time correlations, Eq.(4.27), with the result,

$$\left\{ \frac{\partial}{\partial t} + (1 + P_{12})L(x_1, t | f_1) \right\} C_2(x_1, t; x_2, t) \\ = \lim_{\varepsilon \rightarrow 0^+} \left\{ \left[\frac{\delta W(x_1, t + \varepsilon | \lambda)}{\delta \lambda(x_2, t)} \right]_{t_0 = t, \lambda = 0} + \left[\frac{\delta W(x_2, t + \varepsilon | \lambda)}{\delta \lambda(x_1, t)} \right]_{t_0 = t, \lambda = 0} \right\} . \quad (4.40)$$

On the left hand side of the equation the limit $\varepsilon \rightarrow 0^+$ has been taken. The operator $L(x, t | f_1)$ has been defined in Eqs.(4.28-29). By using Eq.(4.31) the right hand side of the equation can be written,

$$\Gamma(x_1, x_2, t) \equiv \lim_{\varepsilon \rightarrow 0^+} \left\{ \left[\frac{\delta W(x_1, t + \varepsilon | \lambda)}{\delta \lambda(x_2, t)} \right]_{t_0 = t, \lambda = 0} + \left[\frac{\delta W(x_2, t + \varepsilon | \lambda)}{\delta \lambda(x_1, t)} \right]_{t_0 = t, \lambda = 0} \right\} \\ = \lim_{\varepsilon \rightarrow 0^+} (1 + P_{12})^n \int dx_3 \theta(x_1, x_3) S_{\varepsilon}(x_1, x_3) [1 - S_t(x_1, x_3)] \\ \times S_{-\varepsilon}(x_1) S_{-\varepsilon}(x_3) [\delta(x_1 - x_2) + \delta(x_2 - x_3)] \\ \times S_{t+\varepsilon}(x_1, x_3) f_1(x_1, t + \varepsilon) f_1(x_3, t + \varepsilon) , \quad (4.41)$$

or, taking the limit,

$$\Gamma(x_1, x_2, t) \doteq (1 + P_{12})^n \int dx_3 \theta(x_1, x_3) \{ [\delta(x_1 - x_2) + \delta(x_3 - x_2)] S_t(x_1, x_3) \\ - S_t(x_1, x_2) [\delta(x_1 - x_2) + \delta(x_2 - x_3)] \} f_1(x_1, t) f_1(x_3, t) . \quad (4.42)$$

By using the form (4.3) of the interaction operator $\theta(x_1, x_3)$, it can easily be shown that, for an arbitrary function $F(x_1, x_3)$, the following identities hold:

$$(1 + P_{12}) \int dx_3 \theta(x_1, x_3) \delta(x_2 - x_3) F(x_1, x_3) = \theta(x_1, x_2) F(x_1, x_2) \quad (4.43)$$

and

$$\begin{aligned} (1 + P_{12}) \int dx_3 \theta(x_1, x_3) \delta(x_1 - x_2) F(x_1, x_3) \\ = \delta(x_1 - x_2) \int dx_3 \theta(x_1, x_3) F(x_1, x_3) . \end{aligned} \quad (4.44)$$

By introducing the above identities and considering the limit $t \gg \tau_c$, Eq.(4.42) can be written in the form,

$$\begin{aligned} \Gamma(x_1, x_2, t) = n \theta(x_1, x_2) \mathfrak{S}_\infty(x_1, x_2) f_1(x_1, t) f_1(x_2, t) \\ + \delta(x_1 - x_2) n \int dx_3 \theta(x_1, x_3) \mathfrak{S}_\infty(x_1, x_3) f_1(x_1, t) f_1(x_3, t) \\ - n [\Lambda(x_1, t | f_1) + \Lambda(x_2, t | f_1)] \delta(x_1 - x_2) f_1(x_1, t) , \end{aligned} \quad (4.45)$$

or, from Eqs.(4.18) and (4.19),

$$\begin{aligned} \Gamma(x_1, x_2, t) = n \bar{K}(x_1, x_2) f_1(x_1, t) f_1(x_2, t) + n \delta(x_1 - x_2) \bar{J}[f_1, f_1] \\ - n [\Lambda(x_1, t | f_1) + \Lambda(x_2, t | f_1)] \delta(x_1 - x_2) f_1(x_1, t) . \end{aligned} \quad (4.46)$$

The equation for the equal time correlation function is then given by

$$\left\{ \frac{\partial}{\partial t} + (1 + P_{12}) L(x_1, t | f_1) \right\} C_2(x_1, t; x_2, t) = \Gamma(x_1, x_2, t) . \quad (4.47)$$

By neglecting again the difference in position of the colliding pair, the various terms in Eq.(4.46) can be identified with Boltzmann-like

operators, as defined in Eqs.(4.25) and (4.37). In this limit, the inhomogeneity Γ is given by

$$\begin{aligned} \Gamma_B(x_1, x_2, t) = & n \delta(\vec{q}_1 - \vec{q}_2) K(\vec{p}_1, \vec{p}_2) f_1(x_1, t) f_1(x_2, t) \\ & + n \delta(x_1 - x_2) J[f_1, f_1] \\ & - n [I(x_1, t | f_1) + I(x_2, t | f_1)] \delta(x_1 - x_2) f_1(x_1, t) , \end{aligned} \quad (4.48)$$

where $K(\vec{p}_1, \vec{p}_2)$ is the kernel of the nonlinear Boltzmann operator, defined by

$$\int d\vec{p}_2 K(\vec{p}_1, \vec{p}_2) f_1(x_1, t) f_1(x_2, t) = J[f_1, f_1] . \quad (4.49)$$

The dynamics of the equal time correlation function is determined by the same operator that governs the time evolution of the two-time correlation and again depends on the solution of the nonlinear macroscopic problem. The linear equation for the equal time correlation function however has now a inhomogeneous term, which is also a function of $f_1(x_1, t)$, i.e. of the state of the system.

The inhomogeneity in Eq.(4.47) assumes a familiar form when the equilibrium case is considered for comparison. Equation (4.47) reduces then to an identity, given by

$$(1 + P_{12}) n [I_0(\vec{p}_1) + I_0(\vec{p}_2)] G_2^{(0)}(x_1; x_2) = \Gamma_0(x_1, x_2) , \quad (4.50)$$

with

$$\Gamma_o(x_1, x_2) = n[I_o(\vec{p}_1) + I_o(\vec{p}_2)]\delta(x_1 - x_2)\phi(p_1) , \quad (4.51)$$

where $\phi(p)$ is the Maxwell-Boltzmann distribution and $I_o(\vec{p})$ is the usual linearized Boltzmann operator. An identity equivalent to Eq. (4.50) is obtained when equilibrium fluctuations are described through a linearized Boltzmann-Langevin equation.⁵³ The right hand side of the equation is then identified with the amplitude of the noise in the system. In a similar way the right hand side of Eq. (4.47) can be interpreted as a measure of the noise in the system. It is a complicated function of the nonequilibrium state through the one-particle distribution function. This is a reflection of the new sources of fluctuations, besides the thermal one, present in the nonequilibrium state. As the random force in a Langevin description, the inhomogeneous term Γ originates from microscopic excitations whose lifetime is shorter than τ_c , which sets the time scale of the macroscopic description.

An alternative, and perhaps more popular, approach to the study of phase space fluctuations in low density gases is based on a hierarchy method analogous to the one used to derive the Boltzmann equation. Sets of equal time and multitime distribution functions are defined as the nonequilibrium averages of phase space densities.³⁷ Hierarchies of coupled equations for these distribution functions, formally identical to the BBGKY hierarchy, are then derived from the Liouville equation. The correlation of phase space fluctuations of equal and different time argument are simply related to these distribution functions. A properly reduced density can then be used as the expansion parameter to close the hierarchies and derive kinetic equations for the correlation functions.

This approach has been used by several authors.³⁴⁻³⁷ In particular Ernst and Cohen³⁷ have derived kinetic equations for the nonequilibrium correlation functions in a gas of hard spheres at low density by performing an expansion in the parameter $n\sigma^3$ and by retaining, to each order in the density, only terms involving collisions among a limited number of particles. The results derived in Ref. 37 agree with the ones obtained here by using the generating functional method, but the identification of terms of different order in the density is certainly not transparent for space scales greater than σ . The reason for this lies in the choice of the expansion parameter. Ernst and Cohen applied the method used when deriving a kinetic equation for the one-particle distribution function. To close the first equation of the hierarchy information on the two-particle distribution function, $f_2(x_1, x_2, t)$, over distances smaller than or of the order of the force range σ is needed in this case. An expansion of f_2 in powers of $n\sigma^3$ is therefore appropriate. The cluster expansion in fact gives information on the variation of the distribution functions over space and time scales of the order of the force range σ and the collision time τ_c respectively. In low density gases, however, second or higher order correlations among particles vary appreciably also over distances and times of the order of the mean free path λ and the mean free time t_f , both much larger than σ and τ_c . A different and more systematic method of expansion of the hierarchy can then be developed by better analyzing the role of the various length and time scales in the problem. If the s -th equation of the hierarchy is scaled according to the two characteristic lengths over which a variation of the correlation functions is expected, λ and t_f , the expansion parameter $\alpha = (n\lambda^3)^{-1}$ naturally

appears in the equation. The terms of an expansion of the s -th order distribution function in powers of α can then be systematically evaluated. The condition $\alpha \ll 1$ corresponds to a gas at low density in the usual sense (i.e. $n\sigma^3 \ll 1$, since $\alpha \approx (n\sigma^3)^2$), but with a large number of particles in a volume of the linear size of a mean free path. This is exactly the condition under which the effect of collisions will be important over the space and time scale considered and will be responsible for higher order correlations. The scaling of the BBGKY hierarchy and the evaluation of correlation functions to zeroth and first order in α is carried out in Appendix D for a gas of hard spheres. Again the results agree with Ref. 37 and with those obtained by using the generating functional method.

IV.5 Hydrodynamic Limit

In the low density limit, the average conserved densities in a fluid are defined as

$$\phi_\alpha(\vec{r}, t) = \int d\vec{p} \hat{a}_\alpha(\vec{p}) n f_1(x, t) , \quad (4.52)$$

where $\{\hat{a}_\alpha(\vec{p})\}$ are the one-particle conserved quantities, defined in Eq. (3.5). In this section, in order to simplify the notation, x is used to indicate also the set of variables (\vec{r}, \vec{p}) , where \vec{r} represents a point in the fluid and \vec{p} is the canonical momentum. The hydrodynamic equations are then obtained by averaging the microscopic conservation laws, Eqs. (3.6), over the nonequilibrium one-particle distribution function and by supplementing the equations so obtained with constitutive equations for the macroscopic fluxes as functionals of the average densities.

A set of λ -dependent average densities can be defined as

$$\phi_{\alpha}(\vec{r}, t | \lambda) = \int d\vec{p} \hat{a}_{\alpha}(\vec{p}) n f_1(x, t | \lambda) \quad (4.53)$$

where $f_1[\lambda]$ is the one-particle functional defined in Eq. (4.7). When evaluated at $\lambda=0$ (and for $t_0=0$), Eqs. (4.53) reduce, at all times, to the usual average densities, defined in Eq. (4.52). The functionals $\{\phi_{\alpha}(\vec{r}, t | \lambda)\}$ are the low density limit of the ones defined in Chapter III.

Again, intensive λ -dependent thermodynamic variables $\{y_{\alpha}(\vec{r}, t | \lambda)\}$ are defined by requiring

$$\phi_{\alpha}(\vec{r}, t | \lambda) = \int d\vec{p} \hat{a}_{\alpha}(\vec{p}) f_L(x, t | \lambda) , \quad (4.54)$$

where f_L is a one-particle local equilibrium functional, given by

$$f_L(x, t | \lambda) = \exp\{-y_{\alpha}(\vec{r}, t | \lambda) \hat{a}_{\alpha}(\vec{p})\} . \quad (4.55)$$

The local equilibrium distribution is normalized as follows,

$$\int dx f_L(x, t | \lambda) = N,$$

where N is total number of particles in the system. The thermodynamic variables $\{y_{\alpha}(\vec{r}, t)\}$ are given explicitly in Eq. (3.16). The comments made in Chapter III, when requiring the equality (3.13), apply here.

Hydrodynamic equations for the functionals $\{\phi_{\alpha}(\vec{r}, t | \lambda)\}$ are simply obtained by projecting Eq. (4.17) for $f_1[\lambda]$ over the five conserved densities $\{\hat{a}_{\alpha}(\vec{p})\}$. By writing

$$f_1(x, t | \lambda) = f_L(x, t | \lambda) + \Delta(x, t | \lambda) \quad (4.56)$$

and substituting in Eq. (4.17), an equation for Δ is obtained

$$\begin{aligned} & \left\{ \frac{\partial}{\partial t} + L_0(x) - n \Lambda_L(x, t | f_L) \right\} \Delta(x, t | \lambda) \\ & = - \left[\frac{\partial}{\partial t} + L_0(x_1) \right] f_L(x, t | \lambda) + W(x, t | \lambda) , \end{aligned} \quad (4.57)$$

where, for consistency with the purpose of deriving equations to Navier-Stokes order, only terms linear in Δ have been retained. The operator Λ_L in Eq. (4.57) is the local equilibrium form of the operator defined in Eq. (4.29), i.e.

$$\Lambda_L(x_1, t | f_L) = \int dx_2 \theta(x_1, x_2) \mathfrak{S}_\infty(x_1, x_2) (1 + P_{13}) f_L(x_1, t | \lambda) . \quad (4.58)$$

The solution of Eq. (4.57) is given by

$$\begin{aligned} \Delta(x, t | \lambda) & = T(x; t, 0) \Delta(x, 0 | \lambda) + \int_0^t dt T(x; t, \tau) W(x, \tau | \lambda) \\ & - \int_0^t d\tau T(x; t, \tau) \left[\frac{\partial}{\partial \tau} + L_0(x) \right] f_L(x, \tau | \lambda) , \end{aligned} \quad (4.59)$$

where the time evolution operator T is λ -dependent and is defined as the solution of the equation,

$$\left\{ \frac{\partial}{\partial t} + L_0(x) - n \Lambda_L(x, t | f_L) \right\} T(x; t, \tau) = 0 , \quad (4.50)$$

with initial condition $T(x; t, t) = 1$. Also, the initial deviation from

the local equilibrium distribution functional is given by

$$\Delta(x,0|\lambda) = \frac{\langle \hat{f}_1(x)U[\lambda] \rangle}{\langle U[\lambda] \rangle} - f_L(x,0|\lambda) . \quad (4.61)$$

By projecting now the equation for $f_1[\lambda]$ over the conserved densities $\{\hat{a}_\alpha\}$ and making use of Eq. (4.54), the following set of equations for the $\{\psi_\alpha[\lambda]\}$ is obtained

$$\begin{aligned} \frac{\partial}{\partial t} \psi_\alpha(\vec{r},t|\lambda) + \frac{\partial}{\partial r_i} \int d\vec{p} \cdot v_i \hat{a}_\alpha(\vec{p}) f_L(x,t|\lambda) + \frac{\partial}{\partial r_i} \int d\vec{p} \cdot v_i \hat{a}_\alpha(\vec{p}) \Delta(x,t|\lambda) \\ = \int d\vec{p} \hat{a}_\alpha(\vec{p}) W(x,t|\lambda) . \end{aligned} \quad (4.62)$$

The term on the right hand side of Eq. (4.62) can be neglected. In fact it contains the potential part of the momentum and energy fluxes which are of higher order in the density and therefore negligible in the Boltzmann limit. By inserting Eq. (4.59) for Δ , the set of Eqs. (4.62) becomes

$$\begin{aligned} \frac{\partial}{\partial t} \psi_\alpha(\vec{r},t|\lambda) + \frac{\partial}{\partial r_i} E_\alpha^i(\vec{r},t;\{\psi[\lambda]\}) \\ - \frac{\partial}{\partial r_i} \int_0^t d\tau \int d\vec{p} v_i \hat{a}_\alpha(\vec{p}) T(x;t,\tau) \left[\frac{\partial}{\partial \tau} + \vec{v} \cdot \vec{\nabla}_{\vec{r}} \right] f_L(x,\tau|\lambda) \\ = - \frac{\partial}{\partial r_i} \int d\vec{p} v_i \hat{a}_\alpha(\vec{p}) T(x;t,0) \Delta(x,0|\lambda) \\ - \frac{\partial}{\partial r_i} \int_0^t d\tau \int d\vec{p} v_i \hat{a}_\alpha(\vec{p}) T(x;t,\tau) W(x,\tau|\lambda) , \end{aligned} \quad (4.63)$$

where the Euler matrix E_α^i has been defined as

$$E_{\alpha}^i(\vec{r}, t; \{\phi[\lambda]\}) \equiv \int d\vec{p} v_i \hat{a}_{\alpha}(\vec{p}) f_L(x, t | \lambda) . \quad (4.64)$$

Furthermore, to lowest order in the gradients,

$$\left[\frac{\partial}{\partial \tau} + \vec{v} \cdot \vec{\nabla}_{\vec{r}} \right] f_L(x, \tau | \lambda) = - f_L(x, \tau | \lambda) \frac{\partial y_{\beta}(\vec{r}, \tau | \lambda)}{\partial r_j} \hat{\phi}_{\beta j}(\vec{p}) , \quad (4.65)$$

where

$$\hat{\phi}_{\beta j}(\vec{p}) = (i - P_o^{(1)}) v_j \hat{a}_{\beta}(\vec{p}) . \quad (4.66)$$

Here $P_t^{(1)}$ is the low density form of the local equilibrium projection operator defined in Eq. (B.9) and it is given by

$$P_t^{(1)} A(\vec{p}) = \hat{a}_{\alpha}(\vec{p}) g_{\alpha\beta}^{-1}(\vec{r}) \int d\vec{p}' f_L(\vec{r}, \vec{p}', t | \lambda) \hat{a}_{\beta}(\vec{p}') A(\vec{p}') , \quad (4.67)$$

where

$$g_{\alpha\beta}(\vec{r}) = \int d\vec{p} f_L(x, t | \lambda) \hat{a}_{\alpha}(\vec{p}) \hat{a}_{\beta}(\vec{p}) , \quad (4.68)$$

and $g_{\alpha\beta}^{-1}$ is the $(\alpha\beta)$ element of the inverse matrix. The thermodynamic variables $\{y_{\alpha}\}$ and their gradients appearing in Eq. (4.65) can also be expanded in a functional Taylor series around the point $t=\tau$. To Navier-Stokes order only the first terms in these expansions have to be retained. Substituting Eq. (4.65) into (4.63), the latter becomes

$$\begin{aligned} \frac{\partial}{\partial t} \psi_{\alpha}(\vec{r}, t | \lambda) + \frac{\partial}{\partial r_i} \left\{ E_{\alpha}^i(\vec{r}, t; \{\psi\}) + L_{\alpha\beta}^{ij}(\vec{r}, t; \{\psi\}) \frac{\partial y_{\beta}(\vec{r}, t | \lambda)}{\partial r_j} \right\} \\ = W_{\alpha}(\vec{r}, t | \lambda) , \end{aligned} \quad (4.69)$$

where $L_{\alpha\beta}^{ij}$ is the matrix of the transport coefficients for a low density gas, given by

$$L_{\alpha\beta}^{ij}(\vec{r}, t; \{\psi\}) = \lim_{t \gg t_f} \int_0^t dt \int dx f_L(x, t | \lambda) [T^\dagger(x; t, \tau) v_i \hat{a}_\alpha(\vec{p}) \delta(\vec{r} - \vec{q})] \hat{\phi}_{\beta j}(\vec{p}) , \quad (4.70)$$

For convenience, the same notation that was adopted to indicate the matrix of transport coefficient for a dense fluid is used here for the case of a low density gas. The two differ because the coefficient of bulk viscosity vanishes at low density. The operator T^\dagger in Eq. (4.70) is the adjoint of the operator T and is defined by

$$\int dx \hat{a}(x) T(x; t, \tau) \hat{b}(x) f_1(x, \tau) = \int dx f_1(x, \tau) \hat{b}(x) T^\dagger(x; t, \tau) \hat{a}(x) , \quad (4.71)$$

for any pair of one-particle phase functions, \hat{a} and \hat{b} . Equation (4.70) can be put in a more familiar form by observing that, to Navier-Stokes order, the hydrodynamic variables $\{y_\alpha(\vec{r}, t)\}$ in the operator T^\dagger can be evaluated at $\tau=t$. The time evolution operator is then given by

$$T^\dagger(x; t, \tau) = \exp\{[\vec{v} \cdot \vec{\nabla}_q - nI_L(x, t)](t - \tau)\} , \quad (4.72)$$

where

$$nI_L(x, t) = f_L^{-1}(x, t | \lambda) n \Lambda_L(x, t | f_L) f_L(x, t | \lambda) . \quad (4.73)$$

The time integral in Eq. (4.70) can then be performed with the result,

$$L_{\alpha\beta}^{ij}(\vec{r}, t; \{\psi\}) = - \int dx f_L(x, t | \lambda) \hat{\phi}_{\beta j}(\vec{p}) [\vec{v} \cdot \vec{\nabla}_{\vec{q}} - n I_L(x, t)]^{-1} \\ \times v_i \hat{a}_{\alpha}(\vec{p}) \delta(\vec{r} - \vec{q}) . \quad (4.74)$$

The action of the derivative operator in Eq. (4.74) on the operator $I_L(\vec{q}, \vec{p}, t)$ or on $f_L(x, t | \lambda)$ generates gradients of the thermodynamic variables $\{y_{\alpha}\}$. To lowest order these terms can be neglected and Eq. (4.74) can be written as

$$L_{\alpha\beta}^{ij}(\vec{r}, t; \{\psi\}) = - \int d\vec{q} d\vec{p} f_L(\vec{r}, \vec{p} | \lambda) \hat{\phi}_{\beta j}(\vec{p}) [\vec{v} \cdot \vec{\nabla}_{\vec{q}} - n I_L(\vec{r}, \vec{p}, t)]^{-1} \\ \times v_i \hat{a}_{\alpha}(\vec{p}) \delta(\vec{r} - \vec{q}) , \quad (4.75)$$

or

$$L_{\alpha\beta}^{ij}(\vec{r}, t; \{\psi\}) = \int d\vec{p} f_L(\vec{r}, \vec{p} | \lambda) \hat{\phi}_{\beta j}(\vec{p}) [n I_L(\vec{r}, \vec{p}, t)]^{-1} v_i \hat{a}_{\alpha}(\vec{p}) , \quad (4.76)$$

which is the familiar expression for the transport coefficients in the Boltzmann limit, derived, for example, by using the Chapman-Enskog expansion.⁸ The inhomogeneous term on the right hand side of Eq. (4.69) is

$$W_{\alpha}(\vec{r}, t | \lambda) = - \frac{\partial}{\partial r_i} \int d\vec{p} v_i \hat{a}_{\alpha}(\vec{p}) T(x; t, 0) \Delta(x, 0 | \lambda) \\ - \frac{\partial}{\partial r_i} \int_0^t d\tau \int d\vec{p} v_i \hat{a}_{\alpha}(\vec{p}) T(x; t, \tau) W(x, \tau | \lambda) . \quad (4.77)$$

When evaluated at $\lambda=0$, the right hand side of Eq. (4.69) vanishes identically and the left hand side reduces to the nonlinear hydrodynamic equations for a low density gas.

The correlation functions of the fluctuations of the conserved densities around their average value are given by

$$M_{\alpha\beta}(\vec{r}_1, t_1; \vec{r}_2, t_2) = \int d\vec{p}_2 \hat{a}_\beta(\vec{p}_2) \left[\frac{\delta\psi_\alpha(\vec{r}_1, t_1 | \lambda)}{\delta\lambda(x_2, t_2)} \right]_{\lambda=0} . \quad (4.78)$$

Equations for the correlation functions are then obtained by functionally differentiating Eq. (4.69) and projecting the resulting equation over the conserved densities. The case of correlation of fluctuations at different time is first considered, with the result

$$\begin{aligned} \frac{\partial}{\partial t_1} M_{\alpha\beta}(\vec{r}_1, t_1; \vec{r}_2, t_2) + \mathcal{L}_{\alpha\sigma}(\vec{r}_1, t_1; \{\psi_\alpha\}) M_{\sigma\beta}(\vec{r}_1, t_1; \vec{r}_2, t_2) \\ = I_{\alpha\beta}(\vec{r}_1, t_1; \vec{r}_2, t_2) , \end{aligned} \quad (4.79)$$

where

$$I_{\alpha\beta}(\vec{r}_1, t_1; \vec{r}_2, t_2) = \lim_{t_1 \gg t_f} \int d\vec{p}_2 \hat{a}_\beta(\vec{p}_2) \left[\frac{\delta W_\alpha(\vec{r}_1, t_1 | \lambda)}{\delta\lambda(x_2, t_2)} \right]_{\lambda=0} . \quad (4.80)$$

The operator $\mathcal{L}_{\alpha\beta}$ is given in Eq. (3.45) and depends on the state of the system through the solution of the nonlinear hydrodynamic equations. In the low density limit considered here, the terms containing the bulk viscosity and the derivative of the pressure or of the enthalpy density with respect to the density vanish, and do not appear in $\mathcal{L}_{\alpha\beta}$.

The inhomogeneous term on the right hand side of Eq. (4.79) is analyzed in Appendix E. The contribution from the second term on the right hand side of Eq. (4.77) is shown to vanish on a time scale of the order of the collision time, τ_c . Therefore, it does not contribute to the hydrodynamic equations for the correlation functions, which describe

variations over time scales large compared to the mean free time, t_f . The functional derivative of the first term in Eq. (4.77) vanishes in the limit

$$\lim_{\substack{t_1 > t_f \\ t_1 - t_2 > t_f}} I_{\alpha\beta}(\vec{r}_1, t_1; \vec{r}_2, t_2) \longrightarrow 0, \quad (4.81)$$

and gives no contribution to the equation for the unequal time correlation functions, which reduces to the same linear homogeneous equation obtained in Section III.2, Eq. (3.49).

An equation for the equal time correlation functions can be obtained by using the same limiting procedure applied for example in Section III.3 (see Eq. (3.63)). The resulting equation is

$$\begin{aligned} \frac{\partial}{\partial t} M_{\alpha\beta}(\vec{r}_1, t; \vec{r}_2, t) + (1 + P_{12} P_{\alpha\beta}) \mathcal{L}_{\alpha\sigma}(\vec{r}_1, t; \{\psi\}) M_{\sigma\beta}(\vec{r}_1, t; \vec{r}_2, t) \\ = \Gamma_{\alpha\beta}(\vec{r}_1, \vec{r}_2; t), \end{aligned} \quad (4.82)$$

where

$$\Gamma_{\alpha\beta}(\vec{r}_1, \vec{r}_2; t) = \lim_{\epsilon \rightarrow 0^+} (1 + P_{12} P_{\alpha\beta}) I_{\alpha\beta}(\vec{r}_1, t + \epsilon; \vec{r}_2, t). \quad (4.83)$$

Only the contribution to $I_{\alpha\beta}$ from the first term on the right hand side of Eq. (4.77) survives on the time scale of interest, leading to the result,

$$\Gamma_{\alpha\beta}(\vec{r}_1, \vec{r}_2; t) = (1 + P_{12} P_{\alpha\beta}) \frac{\partial}{\partial r_{1i}} L_{\alpha\beta}^{ij}(\vec{r}_1, t; \{\psi\}) \frac{\partial}{\partial r_{2j}} \delta(\vec{r}_1 - \vec{r}_2), \quad (4.84)$$

where $L_{\alpha\beta}^{ij}$ is given by Eq. (4.76).

The set of hydrodynamic equations derived here to describe the time evolution of averages and fluctuations strictly applies only to a low density gas. With this restriction in mind, they are identical to the equations obtained in Chapter III for a dense fluid.

CHAPTER V
TAGGED-PARTICLE FLUCTUATIONS IN SHEAR FLOW

V.1 Definition of the Problem

To illustrate the application of the formalism developed in the previous chapters, the problem of steady shearing flow is considered. Substantial simplifications occur as the result of three conditions: (1) low density, (2) Maxwell molecules, and (3) uniform shear flow. In fact for Maxwell molecules* the irreversible momentum flux can be determined exactly from the nonlinear Boltzmann equation, as a nonlinear function of the shear rate. The macroscopic conservation laws can then be closed and solved exactly for the situation of uniform shear. All the information on the macroscopic state of the system, which is needed in the equations for the correlation functions, can be evaluated for arbitrarily large shear rate, as has been shown elsewhere.^{19,20,22-24} In particular the velocity-velocity autocorrelation function of a tagged particle in the fluid is evaluated here. For the particular system chosen, this correlation function can be calculated without any approximation. Due to the presence of the shear on the system, equal time correlations which are zero in equilibrium are now nonvanishing, and their amplitude increases with the shear rate.

*Maxwell (or Maxwellian) molecules are monoatomic molecules interacting through a weakly repulsive potential of the form $V(r) = \epsilon_0 (\sigma/r)^4$, where r is the interparticle distance.

The steady shear flow corresponds physically to a fluid between two parallel plates at a fixed distance apart and in relative motion. The flow field, $\vec{U}(\vec{r})^*$, is expected to vary linearly between the plates (except near the surfaces) and be of the form,

$$U_i(\vec{r}, t) = U_{oi} + a_{ij} r_j . \quad (5.1)$$

The constant vector U_{oi} and the constant tensor a_{ij} are the velocity of the lower plate and the shear rate tensor, respectively. In the following U_{oi} will be set equal to zero without loss of generality. For the geometry considered, the tensor a_{ij} has the following properties:

$$a_{ii} = 0, \quad (5.2)$$

where no summation is intended in Eq. (5.2), and

$$a_{ij} a_{jk} = 0 . \quad (5.3)$$

It is also assumed that the externally imposed shear flow represents the only inhomogeneity in the system, and

$$\begin{aligned} \rho(\vec{r}, t) &= \rho(t), & q_i^*(\vec{r}, t) &= q_i^*(t) , \\ u(\vec{r}, t) &= u(t), & t_{ij}^*(\vec{r}, t) &= t_{ij}^*(t) . \end{aligned} \quad (5.4)$$

*In this chapter the macroscopic flow velocity of the fluid is indicated with $\vec{U}(\vec{r}, t)$, instead of $\vec{v}(\vec{r}, t)$, as was done in Ch. III.

Therefore, the walls of the system are not maintained at a constant temperature (the extraction of heat from the system would create an inhomogeneity in the temperature field). Heat is produced in the system through viscous friction and the temperature grows in time. The state considered is therefore nonstationary.

By inserting Eqs. (5.1-4) into the hydrodynamic equations for a simple fluid, Eqs. (3.20), these reduce to

$$\frac{\partial \rho(t)}{\partial t} = 0 , \quad (5.5)$$

$$\frac{\partial u(t)}{\partial t} = - a_{ij} t_{ij}^*(t) . \quad (5.6)$$

The mass density ρ is therefore constant,

$$\rho(t) = \rho_0 . \quad (5.7)$$

The internal energy density u can be considered a function of ρ and of the temperature T (or the pressure p). The hydrodynamic equations reduce then to one single equation, given by

$$\frac{\partial T(t)}{\partial t} = - a_{ij} \alpha(t) t_{ij}^*(t) , \quad (5.8)$$

where $\alpha(t) = \left(\frac{\partial T}{\partial u}\right)_\rho$. In the case of a low density gas, the ideal gas equation of state can be used, to obtain $\alpha = \frac{2}{3} (nK_B)^{-1}$, where $n = \rho_0/m$ is the constant number density. The temperature equation becomes then

$$\frac{\partial T(t)}{\partial t} = -\frac{2}{3} (nK_B)^{-1} a_{ij} t_{ij}^*(t) . \quad (5.9)$$

The system is prepared at $t=0$ in a state of local equilibrium with a temperature $T(0) = T_0$ and a uniform flow field of the form given in Eq. (5.1). External forces will also be present at $t>0$ to maintain the desired flow field. Consequently $t_{ij}^*(t=0) = 0$, and the initial state of the system is described by the local equilibrium ensemble,

$$\rho_L(0) = \exp\{-q_L(0) + v(0)N - \beta(0)H'\} , \quad (5.10)$$

where $q_L(0)$ is the normalization constant defined in Eq. (A.7), and

$$H' = H(\{\vec{p}_n - m\vec{U}(\vec{q}_n)\}) , \quad (5.11)$$

where H is the Hamiltonian of the system. The choice of initial local equilibrium is equivalent to the assumption that the effect of the external forces can be incorporated entirely through boundary conditions on the thermodynamic variables.

At low density, the state of the fluid (or bath) is described entirely in terms of the one-particle distribution function, $f_b(x_b, t)$, whose time evolution is governed by the nonlinear Boltzmann equation,

$$\left\{ \frac{\partial}{\partial t} + \vec{v}_b \cdot \vec{\nabla}_{\vec{q}_b} \right\} f_b(x_b, t) = n J[f_b, f_b] , \quad (5.12)$$

where J is the nonlinear Boltzmann operator defined in Eq. (4.21). The suffix b is used to distinguish the variables of the bath from the variables of the tagged particle. Consistent with the preparation of

the system described above, the initial condition for Eq. (5.12) is

$$\begin{aligned} n f_b(x_b, 0) &= f_L(x_b, 0) \\ &= \phi(\beta_0, \vec{v}'_b) \end{aligned} \quad (5.13)$$

where $\phi(\beta_0, \vec{v}'_b)$ is a Maxwell Boltzmann distribution at the initial temperature $T_0 = (K_B \beta_0)^{-1}$, as a function of $\vec{v}'_b = \vec{v}_b - \vec{U}(\vec{q}_b)$, i.e.

$$\phi(\beta_0, \vec{v}'_b) = n \left(\frac{m \beta_0}{2\pi} \right)^{3/2} \exp \left[- \frac{1}{2} m \beta_0 (\vec{v}_b - \vec{U}(\vec{q}_b))^2 \right] . \quad (5.14)$$

The distribution function for a tagged particle in the fluid can be defined as*

$$f_T(x, t) = \langle \delta(x - x_T(t)) \rangle , \quad (5.15)$$

where the average is over the initial ensemble of the system. The time evolution of f_T is governed by a linear equation,

$$\left\{ \frac{\partial}{\partial t} + \vec{v} \cdot \vec{\nabla}_{\vec{q}} - n I_{BL} [f_b] \right\} f_T(x, t) = 0 , \quad (5.16)$$

where

$$\begin{aligned} I_{BL} [f_b] f_T(x, t) &= \int d\vec{v}_b \int_0^\infty db \int_0^{2\pi} d\phi |\vec{v} - \vec{v}_b| \{ f_b(\vec{q}, \vec{v}'_b, t) f_T(\vec{q}, \vec{v}'_b, t) \\ &\quad - f_b(\vec{q}, \vec{v}_b, t) f_T(\vec{q}, \vec{v}, t) \} . \end{aligned} \quad (5.17)$$

*In this chapter the velocity of the particle, instead of its momentum is used as a phase space variable, i.e. $x = (\vec{q}, \vec{v})$.

The operator defined in Eq. (5.16) reduces to the Boltzmann-Lorentz operator when f_b is a Maxwell-Boltzmann distribution. Here the operator I_{BL} will be referred to as the nonequilibrium Boltzmann-Lorentz operator. The tagged particle is assumed to be initially in local equilibrium, and localized at the origin, i.e.

$$f_T(x,0) = \frac{1}{n} \delta(\vec{q}) \phi(\beta_0, \vec{v}') , \quad (5.18)$$

where $\vec{v}' = \vec{v} - \vec{U}(\vec{q})$.

The correlation function of interest here is the velocity-velocity correlation function of the tagged particle, defined as ($t \geq 0$)

$$G_{ij}^{VV}(t,\tau) = \langle v_i(t+\tau) [v_j(\tau) - \langle v_j(\tau) \rangle] \rangle . \quad (5.19)$$

As shown in Section II.2, $G_{ij}(t,\tau)$ can be written in terms of the correlation function of the fluctuations of the tagged particle phase space density,

$$G_{ij}^{VV}(t,\tau) = \int dx_1 dx_2 v_{1i} v_{2j} C_2^T(x_1, t+\tau; x_2, \tau) , \quad (5.20)$$

where

$$C_2^T(x_1, t+\tau; x_2, \tau) = \langle \delta(x_1 - x_T(t+\tau)) [\delta(x_2 - x_T(\tau)) - \langle \delta(x_2 - x_T(\tau)) \rangle] \rangle . \quad (5.21)$$

As shown in Section IV.3, the time evolution of C_2^T is governed by a linear equation, given by

$$\left\{ \frac{\partial}{\partial t} + \vec{v}_1 \cdot \vec{\nabla}_{\vec{q}_1} - nI_{BL} [f_b] \right\} C_2^T(x_1, t+\tau; x_2, \tau) = 0, \quad (5.22)$$

with initial condition

$$C_2^T(x_1, \tau; x_2, \tau) = \delta(x_1 - x_2) f_T(x_1, \tau) - f_T(x_1, \tau) f_T(x_2, \tau), \quad (5.23)$$

since the equal time two-point correlation is zero by definition for a tagged particle.

The dynamics of the average properties and the fluctuations of the tagged particle is described by the set of three coupled equations (5.12), (5.16) and (5.22), to be solved with the initial conditions (5.13), (5.18) and (5.23), respectively.

V.2 Transformation to the Rest Frame

The form of the initial distribution functions for the bath and the tagged particle, Eqs. (5.13) and (5.18), indicates that the dependence on the externally imposed flow field can be transposed from the initial conditions into the kinetic equations by introducing a pseudo-Galilean transformation (or transformation to the rest frame), defined by

$$\begin{aligned} q_i' &= q_i - a_{ij} q_j t \equiv \Lambda_{ij}(t) q_j, \\ v_i' &= v_i - a_{ij} q_j, \end{aligned} \quad (5.24)$$

where the time-dependent tensor $\Lambda_{ij}(t)$ is

$$\Lambda_{ij}(t) = \delta_{ij} - a_{ij} t. \quad (5.25)$$

For a flow field satisfying the properties (5.2-3), this transformation is easily inverted, since

$$[\Lambda^{-1}(t)]_{ij} = \Lambda_{ij}(-t) , \quad (5.26)$$

with the result

$$\begin{aligned} q_i &= q'_i + a_{ij} q'_j t = \Lambda_{ij}(-t) q'_j , \\ v_i &= v'_i + a_{ij} q'_j . \end{aligned} \quad (5.27)$$

A function F , which depends on the phase variables \vec{q} and \vec{v} , $F = F(\vec{q}, \vec{v})$, transforms as follows

$$\begin{aligned} F(\vec{q}, \vec{v}) &= F(\{\Lambda_{ij}(-t) q'_j\}, \{v'_i + a_{ij} q'_j\}) \\ &\equiv F'(\vec{q}', \vec{v}') . \end{aligned} \quad (5.28)$$

It can immediately be seen that this change of variables does not change the form of the binary collision operators in the kinetic equations obtained in the previous sections. The transformed equations are then given by: (1) for the bath distribution function,

$$\left\{ \frac{\partial}{\partial t} + v_{bi} \Lambda_{ji}(t) \frac{\partial}{\partial q_{bj}} - v_{bi} a_{ji} \frac{\partial}{\partial v_{bj}} \right\} f'_b(x_b, t) = nJ[f'_b, f'_b] , \quad (5.29)$$

(2) for the tagged particle distribution function,

$$\left\{ \frac{\partial}{\partial t} + v_i \Lambda_{ji}(t) \frac{\partial}{\partial q_j} - v_i a_{ji} \frac{\partial}{\partial v_j} - n I_{BL} [f'_b] \right\} f'_T(x, t) = 0, \quad (5.30)$$

(3) for the phase space correlation function,

$$\left\{ \frac{\partial}{\partial t} + v_{li} \Lambda_{ji}(t) \frac{\partial}{\partial q_{lj}} - v_{li} a_{ji} \frac{\partial}{\partial v_{lj}} - n I_{BL} [f'_b] \right\} C_2^T(x_1, t+\tau; x_2, \tau) = 0. \quad (5.31)$$

The prime on the transformed variables has been suppressed to simplify the notation. The initial conditions for Eqs. (5.29-31) are now

$$f'_b(\vec{v}_b, 0) = \phi(\beta_0, v_b), \quad (5.32)$$

$$f'_T(x, 0) = \frac{1}{n} \delta'(\vec{q}) \phi(\beta_0, v), \quad (5.33)$$

$$C_2^T(x_1, \tau; x_2, \tau) = \delta(x_1 - x_2) f'_T(x_1, \tau) - f'_T(x_1, \tau) f'_T(x_2, \tau). \quad (5.34)$$

Some information on the behavior of the bath distribution function can immediately be extracted by inspection of Eqs. (5.29) and (5.32). The transformed initial condition, $f'_b(x_b, 0)$, is independent on position. Furthermore, Eq. (5.29) is a homogeneous equation with respect to the variable \vec{q} . The bath distribution function in the rest frame will then be independent of position at all times.

Also, the subtracted part of the velocity autocorrelation function, as in Eq. (5.19), vanishes for the initial condition (5.33) and will then be omitted.

It is useful for the following to rewrite the velocity-velocity autocorrelation function in terms of the phase space correlation functions in the rest frame,

$$G_{ij}^{vv}(t, \tau) = \int dx_1 dx_2 (v_{1i} + a_{ik} q_{1k})(v_{2j} + a_{j1} q_{21}) C_2^T(x_1, t+\tau; x_2, \tau) , \quad (5.35)$$

or

$$G_{ij}^{vv}(t, \tau) = R_{ij}^{vv}(t, \tau) + a_{ik} R_{kj}^{qv}(t, \tau) + a_{j1} R_{i1}^{vq}(t, \tau) \\ + a_{ik} a_{j1} R_{k1}^{qq}(t, \tau) , \quad (5.36)$$

where $R_{ij}^{\alpha\beta}$ (for α and $\beta = q, v$) are the position and velocity correlations in the rest frame, defined as

$$R_{ij}^{\alpha\beta}(t, \tau) = \int dx_1 dx_2 \alpha_{1i} \beta_{2j} C_2^T(x_1, t+\tau; x_2, \tau) . \quad (5.37)$$

The velocity autocorrelation function will be evaluated in the next two sections by solving a set of equations for the $R_{ij}^{\alpha\beta}$.

V.3 Two-time Velocity Autocorrelation Function

The asymptotic (t large compared to a microscopic collision time) behavior of the two-time velocity autocorrelation function $G_{ij}^{vv}(t, \tau)$, defined in Eq. (5.19), can be analyzed immediately, before evaluating G_{ij}^{vv} itself for all times. In fact, it is expected that, at large t , the velocity of the tagged particle will be equal to the velocity of the fluid at the position of the particle, i.e.

$$\lim_{t \rightarrow \infty} \langle v_i(t+\tau) v_j(\tau) \rangle = \lim_{t \rightarrow \infty} a_{ik} \langle q_k(t+\tau) v_j(\tau) \rangle . \quad (5.38)$$

By using,

$$q_k(t+\tau) = q_k(\tau) + \int_0^t ds v_k(s+\tau) , \quad (5.39)$$

the long t limit of the correlation function is given by,

$$\begin{aligned} G_{ij}^{vv}(\infty, \tau) &\equiv \lim_{t \rightarrow \infty} G_{ij}^{vv}(t, \tau) \\ &= a_{ik} G_{kj}^{qv}(0, \tau) + \int_0^\infty ds a_{ik} G_{kj}^{vv}(s+\tau, \tau) . \end{aligned} \quad (5.40)$$

Therefore, the velocity autocorrelation function does not decay to zero at long times. This is a result of the presence of the shear in the system and of the nonstationary nature of the state considered. At large t , G_{ij}^{vv} reaches an asymptotic limit, which depends on correlations between position and velocity of the particle that are created by the presence of the shear.

For the purpose of evaluating the velocity correlation function at all times t and τ it is not necessary to solve the kinetic equations themselves. Instead, it is more convenient to project the kinetic equations over the one-particle dynamical variables of interest (the components of \vec{q} and \vec{v}), and obtain equations for the correlation function. In this way the Maxwellian form of the interparticle potential will lead to substantial simplifications.

A set of equations for the two-time correlation functions in the rest frame, $R_{ij}^{\alpha\beta}(t, \tau)$, is immediately obtained by projecting Eq. (5.31) onto v_i and q_i . For Maxwell molecules the velocity moments of the Boltzmann-Lorentz operator can be calculated exactly (see Appendix F) and simply generate eigenvalues of the operator itself. The resulting equations are

$$\left(\frac{\partial}{\partial t} + \nu_1\right) R_{ij}^{v\alpha}(t, \tau) + a_{ik} R_{kj}^{v\alpha}(t, \tau) = 0, \quad (5.41)$$

and

$$\frac{\partial}{\partial t} R_{ij}^{q\alpha}(t, \tau) - \Lambda_{ik}(t) R_{kj}^{v\alpha}(t, \tau) = 0, \quad (5.42)$$

for $\alpha = q, v$, where ν_1 is the collision frequency given in Eqs.

(F.10-11). Equations (5.41-42) can be integrated immediately, with the result

$$R_{ij}^{vv}(t, \tau) = e^{-\nu_1 t} \Lambda_{ik}(t) R_{kj}^{v\alpha}(0, \tau), \quad (5.43)$$

and

$$R_{ij}^{q\alpha}(t, \tau) = R_{ij}^{q\alpha}(0, \tau) + \frac{1}{\nu_1} [\delta_{ik} - T_{ik}(t)] R_{kj}^{v\alpha}(0, \tau), \quad (5.44)$$

where

$$T_{ij}(t) = \delta_{ij} e^{-\nu_1 t} + \frac{a_{ij}}{\nu_1} [1 - (1 + \nu_1 t) e^{-\nu_1 t}]. \quad (5.45)$$

Substituting Eqs. (5.43-44) into Eq. (5.36), the velocity auto-correlation function is then given by

$$\begin{aligned} G_{ij}^{vv}(t, \tau) = & T_{ik}(t) [R_{kj}^{vv}(0, \tau) + a_{jl} R_{kl}^{vq}(0, \tau)] \\ & + a_{ik} R_{jk}^{vq}(0, \tau) + a_{ik} a_{jl} R_{kl}^{qq}(0, \tau). \end{aligned} \quad (5.46)$$

It can easily be shown that the asymptotic value $G_{ij}^{vv}(\infty, \tau)$ given in Eq. (5.40) is identical to the one obtained by taking the limit $\nu_1 t \gg 1$ in Eq. (5.46).

In principle, all four equal time correlation functions $R_{ij}^{\alpha\beta}(0, \tau)$, for $\alpha = v, q$ and $\beta = v, q$, have to be evaluated. However, it is shown in the next section that Eq. (5.46) can be reexpressed entirely in terms of the velocity autocorrelation function in the rest frame, $R_{ij}^{vv}(0, \tau)$.

V.4 Equal Time Velocity Fluctuations

The equal time ($t=0$) velocity autocorrelation function is given by

$$\begin{aligned} G_{ij}^{vv}(0, \tau) &= \langle v_i(\tau) v_j(\tau) \rangle \\ &= \int dx v_i v_j f_T(x, \tau) . \end{aligned} \quad (5.47)$$

Equations for the equal time correlation functions in the rest frame are then obtained by projecting Eq. (5.30) for f_T^i over the components of \vec{v} and \vec{q} . Again, the collision integrals can be evaluated in the case of Maxwell molecules (Appendix F), and the resulting equations are

$$\frac{\partial}{\partial \tau} R_{ij}^{qq}(0, \tau) - \Lambda_{ik}(\tau) R_{kj}^{vq}(0, \tau) - \Lambda_{jk}(\tau) R_{ki}^{vq}(0, \tau) = 0, \quad (5.48)$$

$$\left(\frac{\partial}{\partial \tau} + v_1 \right) R_{ij}^{vq}(0, \tau) - \Lambda_{jk}(\tau) R_{ki}^{vv}(0, \tau) + a_{ik} R_{kj}^{vq}(0, \tau) = 0, \quad (5.49)$$

$$\begin{aligned} &\left(\frac{\partial}{\partial \tau} + v_1 + v_2 \right) R_{ij}^{vv}(0, \tau) + a_{ik} R_{kj}^{vv}(0, \tau) + a_{jk} R_{ki}^{vv}(0, \tau) \\ &- \frac{1}{3} v_2 \delta_{ij} R_{kk}^{vv}(0, \tau) = I_{ij}(\tau), \end{aligned} \quad (5.50)$$

where R_{kk}^{vv} is the trace of the tensor R_{ij}^{vv} , and

$$I_{ij}(\tau) = \frac{v_1 - v_2}{\rho} t_{ij}^*(\tau) + \delta_{ij} \frac{v_1}{\rho} p(\tau). \quad (5.51)$$

The correlation functions R_{ij}^{vq} and R_{ij}^{qq} enter Eq. (5.46) only in combination with the shear rate tensor. Making use of the properties (5.2-3) and of Eqs. (5.48) and (5.49) it is then shown that $G_{ij}^{vv}(t, \tau)$ can

be expressed entirely in terms of the single equal time correlation function $R_{ij}^{vv}(0, \tau)$, with the result,

$$G_{ij}^{vv}(t, \tau) = T_{ik}(t)R_{kj}^{vv}(0, \tau) + \int_0^\tau ds [a_{ik}T_{jl}(\tau-s) + a_{jl}T_{ik}(\tau-s)]R_{kl}^{vv}(0, s) \\ + a_{jl}[T_{ik}(t) - \delta_{ik}] \int_0^\tau ds e^{-v_1(\tau-s)} \Lambda_{kn}(\tau-s)R_{nl}^{vv}(0, s) . \quad (5.52)$$

The problem is now reduced to the one of solving Eq. (5.50). The inhomogeneous term $I_{ij}(\tau)$ on the right hand side of Eq. (5.50) depends on the hydrodynamic state of the fluid through the pressure (or temperature, $T(\tau) = (nK_B)^{-1}p(\tau)$) and the irreversible stress tensor. For the case of Maxwell molecules a closed equation for t_{ij}^* has been obtained elsewhere,^{19*} with the result,

$$\left(\frac{\partial}{\partial t} + 2v_2\right)t_{ij}^* + a_{ik}t_{jk}^* + a_{jk}t_{ik}^* + nK_B T(a_{ij} + a_{ji}) \\ - \frac{2}{3} \delta_{ij} a_{kl} t_{kl}^* = 0 . \quad (5.53)$$

Equations (5.50) and (5.53), together with the heating equation (5.9), are a closed set of equations that can be solved exactly** for a

The equation for t_{ij}^ is also immediately obtained by projecting the nonlinear Boltzmann equation for f_b' over $v_i v_j$.^{22,54}

**In Refs. 19 and 20 the nonlinear viscosity η and the viscometric functions have been calculated as nonlinear functions of the shear rate. Also, the rate of increase of the temperature in the system has been evaluated.

specified flow field. The solution is carried out in the second part of Appendix F. The results are presented in the next section.

V.5 Results and Discussion

The coupled set of Eqs. (5.9), (5.50) and (5.53) is solved in the second part of Appendix F for the following choice of the flow field,

$$a_{ij} = a \delta_{ix} \delta_{jy} . \quad (5.54)$$

The Laplace transforms of the temperature field and of the equal time correlation functions (see Eq. (F.21)) have three poles in the complex z -plane, one real and two complex conjugate, corresponding to excitations with different lifetimes. The real part of the complex poles is always negative, for either the temperature or the correlation functions. These poles are responsible for contributions that decay exponentially in a time of the order of v_1^{-1} or v_2^{-1} (both v_1 and v_2 are of the order of the mean free time, t_f), and should therefore be considered as initial transients in the system. Here only the properties of the system at times well separated from the initial time are considered ($\tau \gg t_f$). Such terms are therefore neglected.

The real pole of the temperature field is positive and corresponds to a contribution which grows exponentially in time at a rate that increases with the shear rate. Explicitly, in terms of the reduced quantities introduced in Appendix F, i.e.

$$T^*(t^*) = T(v_1^{-1} t^*)/T_0 , \quad (5.55)$$

with $t^* = t/v_1$, the temperature field at $t^* \gg 1$ is given by

$$T^*(t^*) = H(x) \exp[t^* 2v^* \lambda^*(x/2)] , \quad (5.56)$$

where $v^* = v_2/v_1$, $x = a^*/v^* = a/v_2$, with $a^* = a/v_1$, and

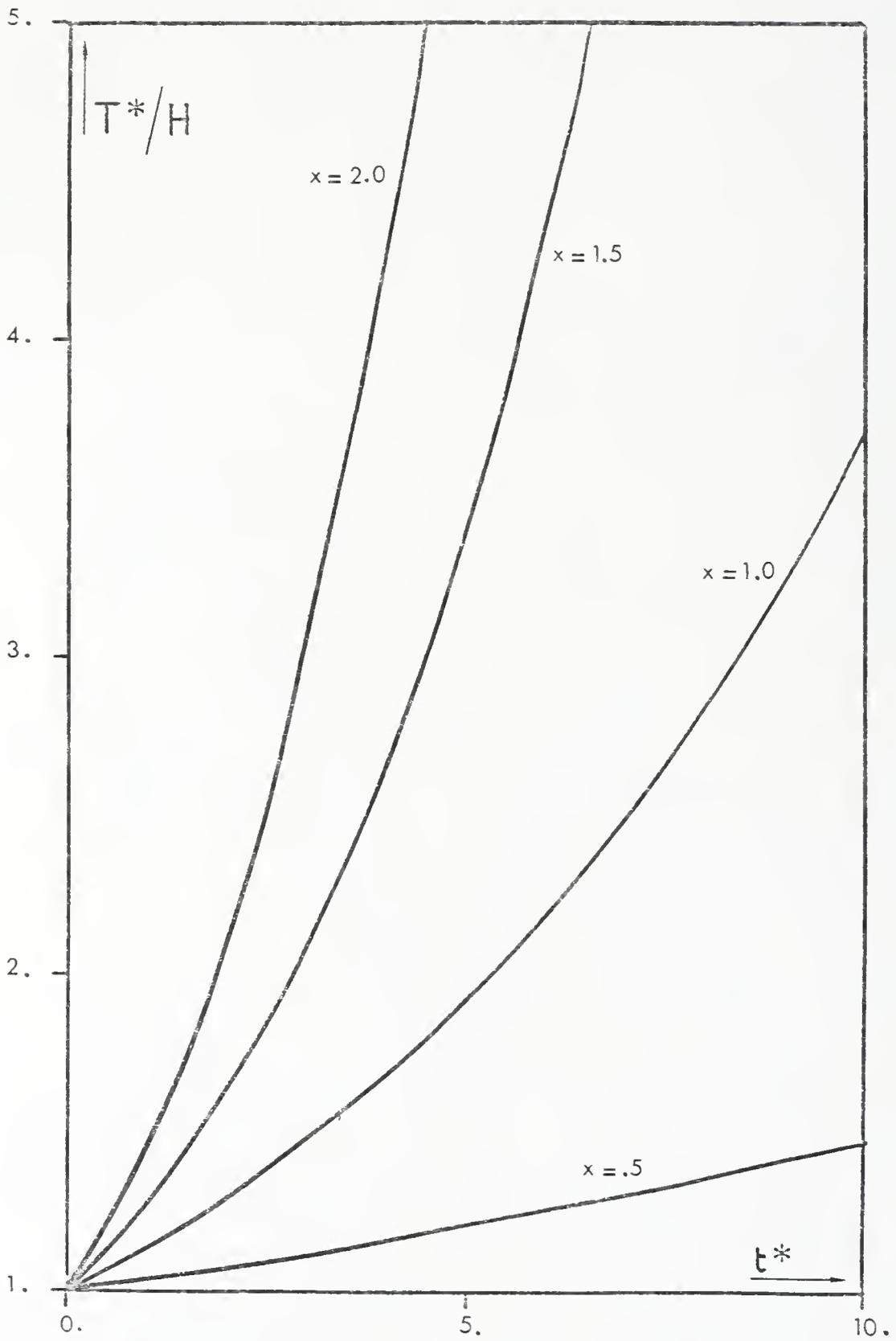
$$H(x) = \frac{[1 + \lambda^*(x/2)]^2 + x^2/6}{1 + 4\lambda^*(x/2) + 3\lambda^{*2}(x/2)} . \quad (5.57)$$

The function $\lambda^*(x)$ is defined in Eq. (F.37). It is a highly nonlinear and monotonically increasing function of x . The temperature as a function of time is shown in Fig. 1 for several values of the shear rate. The expression (5.56) applies with no restrictions on the size of the shear rate.

In contrast, the real pole of the equal time correlation functions changes sign as a function of the shear rate. As discussed in Appendix F, for $\tau^* \gg 1$ its contribution is important only at very large shear rate, i.e. $x \gtrsim 3.3$, when the pole is positive and leads to a term which grows in time in the correlation functions. For shear rate such that $x \lesssim 3.3$ this term decays to zero in a time of the order of the mean free time. The time dependence of the equal time correlation functions for $\tau^* \gg 1$ is therefore the same as that of the temperature, given in Eq. (5.56), and can be scaled out by simply normalizing the correlations with the temperature at the time considered. These normalized correlation functions are then constants, independent of time. The form of these constants is indicated in eqs. (F.44-45): they are highly nonlinear functions of the shear rate.

At nonzero values of t , another effect entirely due to the presence of the shear in the system arises. The tensor $G_{ij}^{VV}(t, \tau)$ is no longer

Fig. 1 Reduced temperature $T^*(t^*)/H(x)$ as a function of $t^* = v_1 t$, for $x = .5, 1.0, 1.5, 2.0$ (Eq. (5.56)).



symmetric in i and j . The asymmetries depend on time and are complicated functions of the shear rate. Their amplitude increases with the shear rate. As an example, define,

$$\Delta_{xy}(t, \tau) \equiv G_{xy}^{vv}(t, \tau) - G_{yx}^{vv}(t, \tau) . \quad (5.58)$$

From Eq. (5.52), with the flow field chosen in Eq. (5.54),

$$\begin{aligned} \Delta_{xy}(t, \tau) = & a(1 - e^{-v_1 t}) \int_0^\tau ds e^{-v_1(\tau-s)} R_{yy}^{vv}(0, s) \\ & + \frac{a}{\lambda_1} [1 - (1 + v_1 t)e^{-v_1 t}] R_{yy}^{vv}(0, \tau) . \end{aligned} \quad (5.59)$$

As discussed before, for $v_1^{-1} \tau \gg 1$ and $x \lesssim 3.3$ the time evolution of the equal time correlation function is entirely governed by the same growing exponential as controls the heating in the system, i.e. by the second term of Eq. (F.42). By inserting this expression in the right hand side of Eq. (5.59), the time integration can be performed, with the result,

$$\begin{aligned} \Delta_{xy}(t, \tau) = & \left\{ 2a^* (1 - e^{-v_1 t}) \frac{1 + v^* \lambda^*(x/2)}{1 + 2v^* \lambda^*(x/2)} \right. \\ & \left. - a^* v_1 t e^{-v_1 t} \right\} R_{yy}^{vv}(0, \tau) , \end{aligned} \quad (5.60)$$

or, defining the corresponding reduced quantity,

$$\Delta_{xy}^*(t^*) \equiv \frac{\Delta_{xy}(v_1^{-1} t^*, v_1^{-1} \tau^*)}{K_B T(\tau)/m} , \quad (5.61)$$

the asymmetry in the xy components is given by

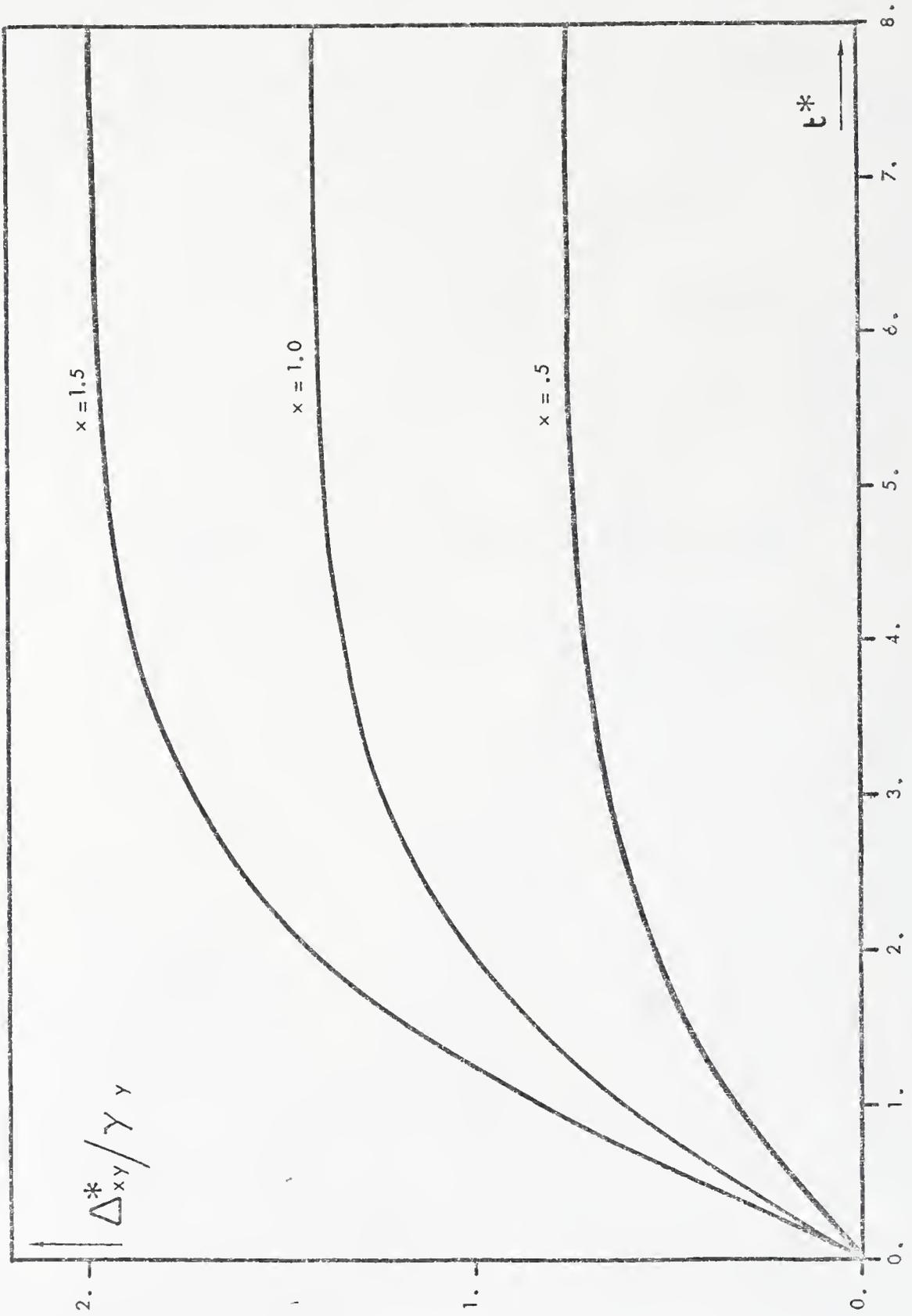
$$\Delta_{xy}^*(t^*) = \gamma_{yy}(x, v^*) \left\{ 2a^* (1 - e^{-t^*}) \frac{1 + v^* \lambda^*(x/2)}{1 + 2v^* \lambda^*(x/2)} - a^* t^* e^{-t^*} \right\}, \quad (5.62)$$

where $t^* = t/v_1$, and γ_{yy} is given in Eq. (F.46). The expression (5.62) applies at all times t^* , with the restriction $\tau^* \gg 1$ and $a^* \lesssim 3.3$. The behavior of $\Delta_{xy}^*/\gamma_{yy}$ as a function of t^* is shown in Fig. 2 for several values of the shear rate.

Fig. 2 Difference between the xy and yx components of the velocity autocorrelation function,

$$\frac{\Delta_{xy}^*(t^*)}{\gamma_{yy}^*(x, v)} = \frac{G_{xy}^{vv}(t, \tau) - G_{yx}^{vv}(t, \tau)}{R_{yy}^{vv}(0, \tau)},$$

as a function of $t^* = v_1 t$, for $x = .5, 1.0, 1.5$ (Eq. (5.62)).



CHAPTER VI DISCUSSION

A unified description of transport and fluctuations in systems macroscopically displaced from thermal equilibrium has been formulated. The general structure of the theory obtained has been identified in Section II.3 and only a brief summary is given here.

The class of nonequilibrium states considered is quite general. It includes situations where the important variations occur on both kinetic and hydrodynamic length and time scales, for either stationary or nonstationary conditions. No limitations on the stability of the solution of the nonlinear macroscopic regression laws (hydrodynamic equations or Boltzmann equation) are imposed. In summary, it is shown that a complete theory of the dynamical behavior of a nonequilibrium fluid requires three coupled sets of equations: (1) equations for the average values, which are in general nonlinear, (2) equations for the correlation of the fluctuations around the average values at different times, (3) equations for the correlation of fluctuations at the same time. The generating functional method used here allows the derivation of these three sets of equations from one single equation and states a precise connection between the dynamics of the macroscopic observables and that of the correlation functions (see Eqs. (2.42-43)). The description of nonequilibrium fluctuations so obtained is macroscopic in character and applies under the same conditions that set the adequacy of the macroscopic regression laws. This, together with the generality of

the nonequilibrium state considered, mostly differentiates the present formulation from others with similar objectives.

Another important result is the linearity of the equations for the correlation functions. No restrictions are imposed in the present work on the size of the nonequilibrium fluctuations. The linearity of the equations is therefore an exact result, not the outcome of a linearization around the nonequilibrium state.

The point of view adopted here is to describe the state of the system entirely in terms of macroscopic quantities, either observables or correlation functions. The information on the nonequilibrium state enters in two ways. First, they are introduced as boundary conditions on the macroscopic observables when solving the nonlinear regression laws: these are the quantities that are controlled in an experiment. Secondly, they are contained in the noise term, which constitutes the inhomogeneous part of the equations for the equal time correlation functions (see Eq. (2.44)). The evaluation of this term requires a microscopic analysis of the transients present in the system at times shorter than those at which the macroscopic description applies. The details of the analysis depend on the time scale of interest, and no general prescription for the calculation of the noise has been identified.

Here only equations for the correlation functions have been considered. No attempt has been made to construct the full probability distribution of fluctuations or a closed form of the nonequilibrium ensemble of the system. This is in agreement with the spirit of the present discussion, whose objective is to present a theoretical description that can be put in direct correlation with the experimental

one. However, it would be very useful to derive a prescription to determine the noise spectrum in a nonequilibrium system, analogous to the relationship between the equal time fluctuations and the entropy in a system in equilibrium. The work of Grabert, Graham and Green²⁷ constitutes an attempt in this direction. However, their results rest entirely on the assumption that the macroscopic deterministic regression laws of the system correspond to a minimum of a properly defined time-dependent action functional. The justification of such an assumption is not clear.

A limitation of the present work regards the class of hydrodynamic nonequilibrium states considered. In fact, while the kinetic theory of fluctuations is quite general (it imposes no restrictions on the size of the displacement of the system from equilibrium), the hydrodynamic theory is limited to macroscopic states which are adequately described by the nonlinear Navier-Stokes equations. In other words the nonequilibrium state is one which is close to local equilibrium, in the sense that only terms to second order in the gradients of the thermodynamic variables are retained. The description of systems with large thermodynamic gradients is an open problem, even at the level of deriving the macroscopic regression laws. It requires in fact the evaluation of the constitutive equations for nonlinear transport, expressing the irreversible fluxes in a fluid as nonlinear functionals of the thermodynamic forces. It is straightforward to calculate the first corrections to the Navier-Stokes result^{18,20} (Burnett coefficients), but the solution of the general problem represents a very difficult task. An example of a model system where the evaluation of the nonlinear irreversible fluxes is possible²³ is the low density gas of Maxwell molecules studied in Chapter V.

Another problem which has not been addressed here is the determination of the boundary conditions for the correlation functions which are needed when solving the equations. Such boundary conditions could be formulated on a macroscopic scale and then checked at low density through kinetic theory calculations. Out of equilibrium the walls can play an important role since the system is prepared or maintained in the desired state through the application of external forces at the boundary. Finite size effects have for example been identified as responsible for a large part of the discrepancies between the theoretical calculations* and the experimental measurements⁶¹ of the asymmetry in the Brillouin scattering from a fluid with an applied temperature gradient.

The application of the present formalism to a concrete problem is in general a difficult computational task. It requires first of all the solution of the nonlinear equations describing the macroscopic state considered with specified initial and/or boundary conditions. Even this is possible only in a few cases.

There are very few experiments to check the description of nonequilibrium fluctuations. Primarily these have been Brillouin scattering experiments from mechanically or thermally driven fluids, where the presence in the system of long range correlations that vanish in equilibrium has been identified. There is a need for proposing new situations where nonequilibrium fluctuations could be probed and that are still simple enough for a theoretical description.

*Several different methods have been applied to this problem.
See Refs. 26, 28, 33, 38, 40, 43-46, 49, 50.

Finally, as discussed in Chapter I, nonequilibrium fluctuations can be very important in hydrodynamic flows near an instability or a bifurcation point, since they are a possible mechanism to amplify the spontaneous thermal fluctuations and determine the transition of the system to a new branch.²⁵ Another class of related phenomena where fluctuations play an important role is constituted by nonequilibrium phase transitions. The three sets of hydrodynamic equations obtained in Chapter III are local in space, as a result of an expansion of the local equilibrium distribution function around a reference equilibrium ensemble (Eq. (A.53)) and of the assumption that some local equilibrium correlation functions are short ranged. Consequently, they do not apply in this form for fluids near critical points or instabilities. However, the same procedure can be followed to derive a nonlocal form of the three sets of hydrodynamic equations, suitable to describe nonequilibrium effects in systems near a phase transition.

APPENDIX A
DERIVATION OF THE λ -DEPENDENT NONLINEAR NAVIER-STOKES EQUATIONS

The methods of nonlinear response theory⁶ are applied here to the first functional derivatives of the generating functional for hydrodynamic fluctuations to derive the set of generalized Navier-Stokes equations given in Section III.1, Eqs. (3.28). The derivation is essentially identical to the derivation of the nonlinear Navier-Stokes equations, except for the treatment of the initial conditions and the definition of the parameters in the local equilibrium ensemble.

As described in Section II.1, the system considered is prepared and maintained in a general nonequilibrium state through the action of external particle, energy and momentum reservoirs, whose thermodynamic parameters are controllable. The time evolution of the distribution function and of the dynamical variables of the system is then governed by Eqs. (2.2) and (2.9) respectively.

The first functional derivatives of the generating functional G , defined by Eqs. (2.35) and (3.23), are then explicitly given by

$$\begin{aligned} \psi_{\alpha}(\vec{r}, t | \lambda) &= \sum_{N=0}^{\infty} \int d\Gamma [T(t, 0) \hat{\psi}_{\alpha}(\vec{r})] \frac{U[\lambda]}{\langle U[\lambda] \rangle} \rho_N(0) \\ &= \sum_{N=0}^{\infty} \int d\Gamma \hat{\psi}_{\alpha}(\vec{r}) T^{\dagger}(t, 0) \frac{U[\lambda]}{\langle U[\lambda] \rangle} \rho_N(0) , \end{aligned} \quad (\text{A.1})$$

where the time evolution operator $T(t, t')$ has been defined in Eq.(2.11) and $T^{\dagger}(t, t')$ is the solution of the equation,

$$\left(\frac{d}{dt} + \frac{\partial \vec{F}_n}{\partial \vec{p}_n}\right) T^\dagger(t, t') = 0, \quad (\text{A.2})$$

with $\frac{d}{dt} = \frac{\partial}{\partial t} + \mathcal{L}$, and initial condition $T^\dagger(t, t') = 1$. In other words, $T^\dagger(t, t')$ is the operator that governs the time evolution of the nonequilibrium distribution function; $\rho_N(0)$ is the initial nonequilibrium ensemble of the system.

Equation (A.1) can be reinterpreted as the average of $\hat{\phi}_\alpha(\vec{r})$ over a λ -dependent nonequilibrium distribution functional, defined as

$$\psi_\alpha(\vec{r}, t | \lambda) = \sum_{N=0}^{\infty} \int d\Gamma \hat{\phi}_\alpha(\vec{r}) \rho_N(t | \lambda) \equiv \langle \hat{\phi}_\alpha(\vec{r}); t \rangle_\lambda. \quad (\text{A.3})$$

The time evolution of $\rho_N(t | \lambda)$ is governed by the same equation describing the time evolution of the distribution function,

$$\rho_N(t | \lambda) = T^\dagger(t, t') \rho_N(0 | \lambda). \quad (\text{A.4})$$

The λ -dependence of the functional $\rho_N(t | \lambda)$ is entirely placed in the special initial condition to be used when solving Eq. (A.4),

$$\rho_N(0 | \lambda) = \frac{U[\lambda]}{\langle U[\lambda] \rangle} \rho_N(0). \quad (\text{A.5})$$

The system considered is contained in a finite volume V . The external nonconservative forces are localized at the boundaries and short ranged. The objective here is to derive a set of hydrodynamic equations describing the behavior of the conserved densities in the interior of the system, where the effect of the external forces does not depend on the details of the interaction. The resulting description

will therefore apply in a subvolume Ω , differing from the volume V of the system by a boundary layer whose width is determined by the range of the external forces.

Since the aim here is to obtain a hydrodynamic description, it is convenient to represent the solution, Eq.(A.4), in terms of the deviation from a local equilibrium functional, $\rho_L(t|\lambda)$, defined as

$$\rho_L(t|\lambda) = \exp\{-q_L(t|\lambda) - \int_{\Omega} d\vec{r} y_{\alpha}(\vec{r},t|\lambda)\hat{\psi}_{\alpha}(\vec{r})\} , \quad (\text{A.6})$$

where $q_L(t|\lambda)$ is the normalization constant determined by the condition

$$\sum_{N=0}^{\infty} \int d\Gamma \rho_L(t|\lambda) = 1 . \quad (\text{A.7})$$

The parameters $\{y_{\alpha}[\lambda]\}$ are defined by requiring the equality (3.26), rewritten here for completeness,

$$\langle \hat{\psi}_{\alpha}(\vec{r}); t \rangle_{\lambda} = \langle \hat{\psi}_{\alpha}(\vec{r}); t \rangle_{\lambda L} , \quad (\text{A.8})$$

where $\langle \dots; t \rangle_{\lambda L}$ indicates an average over the local equilibrium functional,

$$\langle \hat{A}; t \rangle_{\lambda L} = \sum_{N=0}^{\infty} \int d\Gamma \hat{A}(\Gamma) \rho_L(t|\lambda) . \quad (\text{A.9})$$

Therefore the $\{y_{\alpha}[\lambda]\}$ in Eq. (A.6) depend on the $\{\lambda_{\alpha}\}$ through the set of functionals $\{\psi_{\alpha}(\vec{r},t|\lambda)\}$. The form of the functional relationship between the $\{y_{\alpha}(\vec{r},t|\lambda)\}$ and the $\{\psi_{\alpha}(\vec{r},t|\lambda)\}$ is the same as the one defined in Eq. (3.13) for the thermodynamic variables, which is recovered by setting $\{\lambda_{\alpha} = 0\}$.

The microscopic fluxes associated with the conserved densities $\hat{\psi}_\alpha(\vec{r})$ are defined by

$$L\hat{\psi}_\alpha(\vec{r}) = -\frac{\partial}{\partial r_i} \hat{\gamma}_{\alpha i}(\vec{r}) , \quad (\text{A.10})$$

where L is the Liouville operator for the isolated system.

Since the λ dependence enters only through the initial condition, as indicated in Eq.(A.5), and through the thermodynamic variables, in the sense specified in Eqs. (A.6-8), the derivation of a formal solution (A.4), suitable for obtaining the hydrodynamic equations, is essentially identical to the case of $\lambda=0$ more usually considered. Therefore the λ dependence will be suppressed in the following to simplify the notation and will be introduced only at the end of the derivation.

Setting,

$$\rho_N(t) = \rho_L(t)e^{D(t)} \quad (\text{A.11})$$

in Eq. (A.4), an equation for $D(t)$ is obtained, given by

$$\frac{d}{dt} D(t) = -\frac{d}{dt} \ln \rho_L(t) - \frac{\partial \vec{F}_n}{\partial \vec{p}_n} , \quad (\text{A.12})$$

where

$$-\frac{d}{dt} \ln \rho_L(t) = \frac{d}{dt} q_L(t) + \int_{\Omega} d\vec{r} \frac{d}{dt} (y_\alpha(\vec{r}, t) \hat{\psi}_\alpha(\vec{r})) . \quad (\text{A.13})$$

Making use of the requirement that $\rho_L(t)$ be normalized to one and letting a tilde over a phase function denote its deviation from the local equilibrium average,

$$\hat{A}(\vec{r};t) = \hat{A}(\vec{r}) - \langle \hat{A}(\vec{r});t \rangle_L, \quad (\text{A.14})$$

Eq. (A.13) can be rewritten in the form

$$-\frac{d}{dt} \ln \rho_L(t) = \int_{\Omega} d\vec{r} \left\{ \frac{\partial y_{\alpha}(\vec{r},t)}{\partial t} \hat{\psi}_{\alpha}(\vec{r};t) + y_{\alpha}(\vec{r},t) [L\hat{\psi}_{\alpha}(\vec{r}) + \vec{F}_n \cdot \vec{\nabla}_{\vec{p}_n} \hat{\psi}_{\alpha}(\vec{r})] \right\}. \quad (\text{A.15})$$

The time dependence on the left hand side of Eq. (A.14) will sometimes be left implicit to simplify the notation. Using Eqs. (A.10) and integrating by parts this becomes

$$-\frac{d}{dt} \ln \rho_L(t) = \int_{\Omega} d\vec{r} \left\{ \frac{\partial y_{\alpha}(\vec{r},t)}{\partial t} \hat{\psi}_{\alpha}(\vec{r};t) + \frac{\partial y_{\alpha}(\vec{r},t)}{\partial r_i} \hat{\gamma}_{\alpha i}(\vec{r}) \right\} - \int_{S_{\Omega}} dS_i y_{\alpha}(\vec{r},t) \hat{\gamma}_{\alpha i}(\vec{r}) + \int_{\Omega} d\vec{r} y_{\alpha}(\vec{r},t) \vec{F}_n \cdot \vec{\nabla}_{\vec{p}_n} \hat{\psi}_{\alpha}(\vec{r}), \quad (\text{A.16})$$

where S_{Ω} is the boundary surface of the volume Ω considered.

To proceed it is convenient to eliminate the time derivative of y_{α} in favor of its spatial gradients. This can be done by using the definition of the $\{y_{\alpha}\}$ and the macroscopic conservation laws, obtained by averaging the microscopic conservation laws. In the volume Ω , the latter are given by

$$\frac{\partial \hat{\psi}_{\alpha}}{\partial t} + \frac{\partial \hat{\gamma}_{\alpha i}}{\partial r_i} = 0, \quad (\text{A.17})$$

since no external sources are present inside Ω . The macroscopic laws

may then be written

$$\frac{\partial}{\partial t} \langle \hat{\psi}_\alpha(\vec{r}); t \rangle_L + \frac{\partial}{\partial r_i} \langle \hat{\gamma}_{\alpha i}(\vec{r}); t \rangle_L = - \frac{\partial}{\partial r_i} \gamma_{\alpha i}^*(\vec{r}, t), \quad (\text{A.18})$$

where use has been made of Eqs.(3.13); $\gamma_{\alpha i}^*$ are the irreversible fluxes, defined as

$$\gamma_{\alpha i}^*(\vec{r}, t) = \langle \hat{\gamma}_{\alpha i}(\vec{r}); t \rangle - \langle \hat{\gamma}_{\alpha i}(\vec{r}); t \rangle_L. \quad (\text{A.19})$$

Since $\langle \hat{\psi}_\alpha; t \rangle_L$ and $\langle \hat{\gamma}_{\alpha i}; t \rangle_L$ are specified functionals of the $\{y_\alpha\}$, these macroscopic laws can also be expressed as equations for the $\{y_\alpha\}$ (see for example Ref. 18) with the result,

$$\begin{aligned} \frac{\partial}{\partial t} y_\alpha(\vec{r}, t) + \int_\Omega d\vec{r}' K_{\alpha\beta}^i(\vec{r}, \vec{r}') \frac{\partial y_\beta(\vec{r}', t)}{\partial r_i'} \\ = \int_\Omega d\vec{r}' g_{\alpha\beta}^{-1}(\vec{r}, \vec{r}') \frac{\partial \gamma_{\beta i}^*(\vec{r}', t)}{\partial r_i'}, \end{aligned} \quad (\text{A.20})$$

where

$$g_{\alpha\beta}(\vec{r}, \vec{r}') \equiv \langle \hat{\psi}_\alpha(\vec{r}) \hat{\psi}_\beta(\vec{r}'); t \rangle_L,$$

$$K_{\alpha\beta}^i(\vec{r}, \vec{r}') = \langle \hat{\xi}_\alpha(\vec{r}) \hat{\gamma}_{\beta i}(\vec{r}'); t \rangle_L,$$

$$\hat{\xi}_\alpha(\vec{r}) = \int_\Omega d\vec{r}' g_{\alpha\beta}^{-1}(\vec{r}, \vec{r}') \hat{\psi}_\beta(\vec{r}'), \quad (\text{A.21})$$

and $g_{\alpha\beta}^{-1}$ indicates the $(\alpha\beta)$ element of the inverse matrix. The time dependence of g and K has been left implicit. Also surface terms have been neglected for points far from the boundary in the manipulations

leading to Eq. (A.20), due to the short range character of the correlation functions in Eqs. (A.21). In Appendix D of Ref. 18 the explicit form of Eqs. (A.20-21) for the case of a one-component fluid is also given. Substitution of Eq. (A.20) into Eq. (A.16) gives

$$\begin{aligned}
 -\frac{d}{dt} \ln \rho_L(t) = & \int_{\Omega} d\vec{r} \left\{ \frac{\partial y_{\alpha}(\vec{r}, t)}{\partial r_i} \hat{\phi}_{\alpha i}(\vec{r}; t) + \frac{\partial \gamma_{\alpha i}^*(\vec{r}, t)}{\partial r_i} \hat{\xi}_{\alpha}(\vec{r}; t) \right\} \\
 & - \int_{S_{\Omega}} dS_i y_{\alpha}(\vec{r}, t) \hat{\gamma}_{\alpha i}(\vec{r}) + \int_{\Omega} d\vec{r} y_{\alpha}(\vec{r}, t) \vec{F}_n \cdot \vec{\nabla}_{\vec{p}_n} \hat{\phi}_{\alpha}(\vec{r}) ,
 \end{aligned} \tag{A.22}$$

with

$$\hat{\phi}_{\alpha i}(\vec{r}; t) = \hat{\gamma}_{\alpha i}(\vec{r}; t) - \int d\vec{r}' \hat{\psi}_{\beta}(\vec{r}'; t) K_{\beta\alpha}^i(\vec{r}', \vec{r}) . \tag{A.23}$$

Because of the short range character of the forces \vec{F}_n and the definition of the volume Ω , the integrand of the last term on the right hand side of Eq. (A.22) is zero over the region of integration. This term can therefore be neglected and Eq. (A.12) becomes

$$\frac{d}{dt} D(t) = \int_{\Omega} d\vec{r} \left\{ \frac{\partial y_{\alpha}(\vec{r}, t)}{\partial r_i} \hat{\phi}_{\alpha i}(\vec{r}; t) + \frac{\partial \gamma_{\alpha i}^*(\vec{r}, t)}{\partial r_i} \hat{\xi}_{\alpha}(\vec{r}; t) \right\} - S(t) , \tag{A.24}$$

where

$$S(t) = \vec{\nabla}_{\vec{p}_n} \cdot \vec{F}_n + \int_{S_{\Omega}} dS_i y_{\alpha}(\vec{r}, t) \hat{\gamma}_{\alpha i}(\vec{r}) . \tag{A.25}$$

The boundary values of the thermodynamic variables y_{α} appearing in the second term on the right hand side of Eq.(A.25) are at this point arbitrary. They can be specified to satisfy $S(t) = 0$, or,

$$\vec{\nabla}_{\vec{p}_n} \cdot \vec{F}_n = - \int_{S_\Omega} dS_i y_\alpha(\vec{r}, t) \hat{\gamma}_{\alpha i}(\vec{r}) . \quad (\text{A.26})$$

In this way the effect of the external forces is entirely incorporated through the boundary conditions on the thermodynamic variables, as desired for a macroscopic description of the nonequilibrium state. The same result can be obtained by following the argument proposed by McLennan in Ref. 6. In order for the Liouville equation to admit a solution representing equilibrium between the system and the reservoirs, the forces must satisfy the condition $S=0$ in equilibrium. It is therefore sufficient to require that this condition holds for the nonequilibrium state as well to recover the result given in Eq. (A.26). This choice does not represent the most general situation, but is consistent with the experimentally interesting case in which the interaction is entirely specified through the y_α . Equation (A.24) for $D(t)$ becomes then

$$\frac{d}{dt} D(t) = \int_{\Omega} d\vec{r} \left\{ \frac{\partial y_\alpha(\vec{r}, t)}{\partial r_i} \hat{\phi}_{\alpha i}(\vec{r}; t) + \frac{\partial \gamma_{\alpha i}^*(\vec{r}, t)}{\partial r_i} \hat{\xi}_\alpha(\vec{r}; t) \right\} , \quad (\text{A.27})$$

whose solution is given by,

$$\begin{aligned} D(t) = & T^\dagger(t, t_0) D(t_0) + \int_{t_0}^t d\tau T^\dagger(t, \tau) \int_{\Omega} d\vec{r} \left\{ \frac{\partial y_\alpha(\vec{r}, \tau)}{\partial r_i} \hat{\phi}_{\alpha i}(\vec{r}; \tau) \right. \\ & \left. + \frac{\partial \gamma_{\alpha i}^*(\vec{r}, \tau)}{\partial r_i} \hat{\xi}_\alpha(\vec{r}; \tau) \right\} . \end{aligned} \quad (\text{A.28})$$

Here $D(t_0)$ represents the initial deviation from local equilibrium and will be important when deriving the generalized hydrodynamic equations for the functionals $\phi_\alpha(\vec{r}, t | \lambda)$. The time evolution operator,

$T^\dagger(t, t')$, has been defined in Eq. (A.2). By substituting Eq. (A.28) into Eq. (A.11), the formal solution of Liouville equation is obtained in the form,

$$\rho_N(t) = \rho_L(t) \exp \left\{ T^\dagger(t, t_0) D(t_0) + \int_{t_0}^t d\tau T^\dagger(t, \tau) \int_{\Omega} d\vec{r} \left[\frac{\partial y_\alpha(\vec{r}, \tau)}{\partial r_i} \hat{\phi}_{\alpha i}(\vec{r}; \tau) + \frac{\partial \gamma_{\alpha i}^*(\vec{r}, \tau)}{\partial r_i} \hat{\xi}_\alpha(\vec{r}; \tau) \right] \right\} . \quad (\text{A.29})$$

An important class of nonequilibrium states is constituted by nonequilibrium stationary states. A stationary solution is defined by

$$\lim_{t-t_0 \rightarrow \infty} \frac{\partial}{\partial t} \rho_N(t) = 0 . \quad (\text{A.30})$$

The limit may be implicitly incorporated by imposing the initial condition in the infinite past. The solution given in Eq. (A.28) becomes then

$$D(t) = \lim_{t_0 \rightarrow -\infty} T^\dagger(t, t_0) D(t_0) + \int_{-\infty}^t d\tau T^\dagger(t, \tau) \int_{\Omega} d\vec{r} \left\{ \frac{\partial y_\alpha(\vec{r}, \tau)}{\partial r_i} \hat{\phi}_{\alpha i}(\vec{r}; \tau) + \frac{\partial \gamma_{\alpha i}^*(\vec{r}, \tau)}{\partial r_i} \hat{\xi}_\alpha(\vec{r}; \tau) \right\} . \quad (\text{A.31})$$

For initial equilibrium, the first term on the right hand side of Eq. (A.31) vanishes. This choice of the initial condition restricts the applicability of the stationary solution to the case $\{\lambda_\alpha = 0\}$ (the initial condition given in Eq. (A.5) cannot be used). In fact when deriving equations describing fluctuations in nonequilibrium steady states by using the generating functional method, the condition of stationarity

has to be imposed only after functionally differentiating the generalized (λ -dependent) Navier-Stokes equations and evaluating the resulting equations at $\{\lambda_\alpha = 0\}$. In order to lead to a stationary solution, the external forces must be asymptotically constant, or,

$$\vec{F}_N(t) = \vec{F}_N \quad \text{for } t \text{ finite,}$$

and, consequently,

$$T^\dagger(t, \tau) = T^\dagger(t - \tau) \quad \text{for } t - \tau \text{ finite.}$$

The stationary solution is then given by

$$\rho_N = \rho_L e^D, \quad (\text{A.32})$$

with

$$D = \int_{-\infty}^0 d\tau T^\dagger(\tau) \int_{\Omega} d\vec{r} \left\{ \frac{\partial y_\alpha(\vec{r})}{\partial r_i} \tilde{\phi}_{\alpha i}(\vec{r}) + \frac{\partial \gamma_{\alpha i}^*(\vec{r})}{\partial r_i} \tilde{\xi}_\alpha(\vec{r}) \right\}. \quad (\text{A.33})$$

A comment on the stationary solution may be made regarding the treatment of $\frac{\partial y_\alpha}{\partial t}$ in Eq. (A.16). In the derivation of the stationary solution of the Liouville equation presented here, the time derivative of y_α was first eliminated in terms of the space derivatives, and then it was assumed that the $\{y_\alpha\}$ are independent of t , at large t . A different result would have been obtained if $\frac{\partial y_\alpha}{\partial t}$ had been set equal to zero at the beginning, in Eq. (A.16). The first procedure is the correct one, because the y_α in the solution are integrated over an infinite time interval and in general, for finite τ , $y_\alpha(\vec{r}, \tau) - y_\alpha(\vec{r}, -\infty)$ is finite.

The time dependence of the $\{y_\alpha\}$ may therefore be neglected only if the phase functions in the integrand vanish sufficiently rapidly as $\tau \rightarrow -\infty$. This is not the case for the phase functions $\hat{\gamma}_{\alpha i}(\vec{r})$ and $\hat{\psi}_\alpha(\vec{r})$, appearing in Eq.(A.16). However the term $T^\dagger(t, \tau)\hat{\phi}_{\alpha i}(\vec{r})$ may be expected to vanish rapidly as $\tau \rightarrow -\infty$ because the $\hat{\phi}_{\alpha i}$ are orthogonal to the conserved densities $\{\hat{\psi}_\alpha\}$,

$$\langle \hat{\phi}_{\alpha i}(\vec{r})\hat{\psi}_\beta(\vec{r}'); t \rangle_L = 0 . \quad (\text{A.34})$$

The term containing $T^\dagger(t, \tau)\hat{\xi}_\alpha(\vec{r})$ causes no problem, because it may be accounted for as a modification of the time development operator on $\hat{\phi}_{\alpha i}$ to represent the dynamics in the subspace orthogonal to the $\{\hat{\psi}_\alpha\}$, as shown in Ref. 18 (see Eqs.(2.29) and (2.30) of Ref. 18).

The above evaluation of the formal solution (A.29) also applies for the special initial condition (A.5). Furthermore, the definitions (A.6) and (A.8) imply that the λ -dependence of $\rho_N(t|\lambda)$ occurs only through the initial condition and the hydrodynamic variables $\{y_\alpha(\vec{r}, t|\lambda)\}$. Making this λ -dependence explicit, Eqs. (A.11) and (A.28) become

$$\rho_N(t|\lambda) = \rho_L(t|\lambda)e^{D(t|\lambda)} , \quad (\text{A.35})$$

and

$$D(t|\lambda) = T^\dagger(t, 0)D_0(\lambda) + D'(t|\lambda) , \quad (\text{A.36})$$

with

$$\begin{aligned}
D'(t|\lambda) = \int_0^t d\tau T^\dagger(t, \tau) \int_\Omega d\vec{r} \left\{ \frac{\partial y_\alpha(\vec{r}, \tau|\lambda)}{\partial r_i} \hat{\phi}_{\alpha i}(\vec{r}; \tau|\lambda) \right. \\
\left. + \frac{\partial \gamma_{\alpha i}^*(\vec{r}, \tau|\lambda)}{\partial r_i} \tilde{\xi}_\alpha(\vec{r}; \tau|\lambda) \right\} , \tag{A.37}
\end{aligned}$$

and

$$\begin{aligned}
D_0(\lambda) &\equiv D(0|\lambda) \\
&= \ln \frac{U[\lambda]}{\langle U[\lambda] \rangle} \frac{\rho_N(0)}{\rho_L(0|\lambda)} . \tag{A.38}
\end{aligned}$$

The initial time has been chosen at $t_0=0$. The densities $\tilde{\xi}_\alpha(\vec{r}; t|\lambda)$ and the fluxes $\hat{\phi}_{\alpha i}(\vec{r}; t|\lambda)$ are identical to the ones defined in Eqs. (A.21) and (A.23), when the local equilibrium average is substituted with an average over the functional $\rho_L(t|\lambda)$. The irreversible fluxes $\gamma_{\alpha i}^*(\vec{r}, t|\lambda)$ are given by

$$\gamma_{\alpha i}^*(\vec{r}, t|\lambda) = \langle \hat{\gamma}_{\alpha i}(\vec{r}); t \rangle_\lambda - \langle \hat{\gamma}_{\alpha i}(\vec{r}); t \rangle_{\lambda L} . \tag{A.39}$$

When evaluated at $\lambda=0$, Eq. (A.35) reduces to Eq. (A.29). In this case the initial condition term $D_0(\lambda=0)$ represents the deviation of the initial state from local equilibrium, and is usually neglected when deriving hydrodynamics, at $\lambda=0$, because it is expected to decay on a time scale of the order of a mean free time for states leading to hydrodynamic behavior. This deviation is only responsible for the initial transients in the system, occurring before hydrodynamics applies. This is not the case for the λ -dependent functional, $D_0(\lambda)$. However the same restriction can still be imposed on the class of initial states considered, by choosing

$$\rho_N(0) = \rho_L(0) . \quad (\text{A.40})$$

The initial condition $D_o(\lambda)$, becomes then

$$D_o(\lambda) = \ln \frac{U[\lambda]}{\langle U[\lambda] \rangle_L} \frac{\rho_L(0)}{\rho_L(0|\lambda)} , \quad (\text{A.41})$$

and vanishes identically when evaluated at $\lambda=0$.

The generalized (λ -dependent) hydrodynamic equations are obtained by averaging the microscopic conservation laws, Eqs. (A.17), over the nonequilibrium ensemble given by Eqs. (A.35-38), i.e.

$$\frac{\partial}{\partial t} \langle \hat{\phi}_\alpha(\vec{r}); t \rangle_{\lambda L} + \frac{\partial}{\partial r_i} \langle \hat{\gamma}_{\alpha i}(\vec{r}); t \rangle_{\lambda L} = - \frac{\partial}{\partial r_i} \gamma_{\alpha i}^*(\vec{r}, t | \lambda), \quad (\text{A.42})$$

and then closing Eqs. (A.42) with constitutive equations for the irreversible fluxes.

The local equilibrium averages on the left hand side of Eq. (A.42) can be evaluated explicitly. From the definition of the local equilibrium functional, $\rho_L(t|\lambda)$, it follows that the functional relationship between the λ -dependent fluxes, $\langle \hat{\gamma}_{\alpha i}(\vec{r}); t \rangle_{\lambda L}$, and the λ -dependent densities, $\langle \hat{\phi}_\alpha(\vec{r}); t \rangle_{\lambda L}$, is the same as in the case $\lambda=0$. In particular for a simple fluid the local equilibrium averages are found to be

$$\{ \langle \hat{\phi}_\alpha(\vec{r}); t \rangle_{\lambda L} \} = \{ \rho[\lambda], \varepsilon[\lambda], \rho[\lambda] v_i[\lambda] \} \quad (\text{A.43})$$

$$\{ \langle \hat{\gamma}_{\alpha i}(\vec{r}); t \rangle_{\lambda L} \} = \{ \rho[\lambda] v_i[\lambda], (h[\lambda] + \frac{1}{2} \rho[\lambda] v^2[\lambda]) v_i[\lambda],$$

$$p[\lambda] \delta_{ij} + \rho[\lambda] v_i[\lambda] v_j[\lambda] \} . \quad (\text{A.44})$$

The \vec{r} and t dependence of the functionals has been omitted to simplify the notation. When evaluated at $\lambda=0$, the functionals on the right hand side of Eqs. (A.43-44) are identified with the thermodynamic variables: ρ , ε and h are the mass, energy and enthalpy density, respectively, \vec{v} is the macroscopic flow velocity and p is the pressure. The functional relationship between the λ -dependent thermodynamic variables $\{y_\alpha(\vec{r}, t|\lambda)\}$, defined in Eq.(A.8), and the λ -dependent densities, $\{\psi_\alpha(\vec{r}, t|\lambda)\}$, is the same as in equilibrium. This is merely a convenient definition and does not imply any restriction on the nonequilibrium state considered. The second term on the left hand side of Eq. (A.42) is then written

$$\frac{\partial}{\partial r_i} \langle \hat{\gamma}_{\alpha i}(\vec{r}); t \rangle_{\lambda L} \equiv \frac{\partial}{\partial r_i} E_\alpha^i(\vec{r}, t | \{\psi[\lambda]\}) , \quad (\text{A.45})$$

where the matrix $E_{\alpha\beta}^i$ is the Euler part of the nonlinear hydrodynamic equations. It depends on λ only through the λ -dependent densities, $\psi_\alpha(\vec{r}, t|\lambda)$; its explicit form for the case of a simple fluid is given in Section III.1.

When deriving the usual hydrodynamic equations ($\lambda=0$), the irreversible fluxes are entirely determined by $D'(t|0)$ (Eqs. (A.35-36)). In order to represent the effect of the λ -dependent initial condition, $D_0(\lambda)$, in the form of additional contributions to the fluxes it is convenient to define

$$\gamma_{\alpha i}^*(\vec{r}, t|\lambda) = \gamma_{\alpha i}^*(\vec{r}, t|\lambda)_H + \gamma_{\alpha i}^{**}(\vec{r}, t|\lambda) , \quad (\text{A.46})$$

where

$$\gamma_{\alpha i}^*(\vec{r}, t | \lambda)_H = \langle \hat{\gamma}_{\alpha i}(\vec{r}) [e^{D'(t|\lambda)} - 1]; t \rangle_{\lambda L}, \quad (\text{A.47})$$

and

$$\gamma_{\alpha i}^{**}(\vec{r}, t | \lambda) = \langle \hat{\gamma}_{\alpha i}(\vec{r}) [e^{D(t|\lambda)} - e^{D'(t|\lambda)}]; t \rangle_L. \quad (\text{A.48})$$

When Eq.(A.46) is evaluated at $\lambda=0$, the additional contributions $\gamma_{\alpha i}^{**}$ vanish identically, since $D(t|0) = D'(t|0)$, and the usual formal expression for the irreversible fluxes in a nonequilibrium fluid is recovered,

$$\gamma_{\alpha i}^*(\vec{r}, t) = \langle \hat{\gamma}_{\alpha i}(\vec{r}) [e^{D'(t)} - 1]; t \rangle_L \quad (\text{A.49})$$

where $D'(t) \equiv D'(t|0)$ (see for example Ref. 17, Eq. (54)). The additional contributions are entirely due to the λ -dependence of the initial condition of the nonequilibrium distribution functional and have to be kept when deriving equations for the λ -dependent densities, $\{\psi_{\alpha}(\vec{r}, t | \lambda)\}$.

For simplicity, only the case of a nonequilibrium system whose macroscopic state is completely described in terms of the nonlinear Navier-Stokes equations is considered here. The two terms in Eq. (A.46) need then to be evaluated only to second order in the gradients of the hydrodynamic variables. However, the additional fluxes $\gamma_{\alpha i}^{**}$ can be evaluated to Navier-Stokes order only after performing the functional differentiation and evaluating the result at $\lambda=0$. The Navier-Stokes part of the first term on the right hand side of Eq. (A.46) is evaluated here. It appears from Eq. (A.37) that $D'(t|\lambda)$ is already at least of first order in the gradients. Therefore, to second order in the

gradients,

$$\gamma_{\alpha i}^*(\vec{r}, t | \lambda)_H = \int_0^t d\tau \int d\vec{r}' \langle [T(t, \tau) \hat{\gamma}_{\alpha i}(\vec{r})] \hat{\phi}_{\beta j}(\vec{r}' | \lambda); t \rangle_{\lambda L} \frac{\partial y_{\beta}(\vec{r}', \tau)}{\partial r'_j} \quad (\text{A.50})$$

where the operator $T(t, \tau)$, adjoint of $T^\dagger(t, \tau)$ has been defined in Eq. (2.11).

Before proceeding further, it is useful to point out that the dynamics of average quantities inside the volume Ω should be independent on the external short ranged forces. For the purpose of evaluating properties away from the boundaries, it can therefore be assumed that the time evolution of a dynamical variable \hat{A} is described by the Liouville operator for the isolated system,

$$\hat{A}(\Gamma, t) = e^{Lt} \hat{A}(\Gamma) . \quad (\text{A.51})$$

The adjoint of the evolution operator e^{Lt} , in the sense defined in Eq. (A.1), is simply $(e^{Lt})^\dagger = e^{-Lt}$. Equation (A.50) can then be written,

$$\gamma_{\alpha i}^*(\vec{r}, t | \lambda)_H = \int_0^t d\tau \int_{\Omega} d\vec{r}' \frac{\partial y_{\beta}(\vec{r}', \tau | \lambda)}{\partial r'_j} \langle [e^{L(t-\tau)} \hat{\gamma}_{\alpha i}(\vec{r})] \hat{\phi}_{\beta j}(\vec{r}' | \lambda); t \rangle_{\lambda L} . \quad (\text{A.52})$$

The irreversible fluxes $\gamma_{\alpha i}^*(\vec{r}, t | \lambda)_H$ are then evaluated to Navier-Stokes order by expanding the thermodynamic variables, y_{α} , in a Taylor series around the reference point (\vec{r}, t) . To first order in the gradients, the local equilibrium distribution functional can be written

$$\rho_L(t | \lambda) = \rho_{\text{eq}}(\vec{r}, t | \lambda) \left\{ 1 - \frac{\partial y_{\alpha}(\vec{r}, t | \lambda)}{\partial r_i} \int_{\Omega} d\vec{r}' (r_i - r'_i) \hat{\phi}_a(\vec{r}' | \lambda) \right\}, \quad (\text{A.53})$$

where

$$\rho_{\text{eq}}(\vec{r}, t | \lambda) = \exp\{-q_{\text{eq}}(\vec{r}, t | \lambda) - y_{\alpha}(\vec{r}, t | \lambda) \hat{\Psi}_{\alpha}\}, \quad (\text{A.54})$$

and $\hat{\Psi}_{\alpha}$ are the total (volume integrated) densities,

$$\hat{\Psi}_{\alpha} = \int_{\Omega} d\vec{r} \hat{\psi}_{\alpha}(\vec{r}). \quad (\text{A.55})$$

The constant $q_{\text{eq}}(\vec{r}, t | \lambda)$ takes account of the normalization to unity of the distribution functional. When evaluated at $\lambda=0$ the distribution function defined in Eq. (A.54) reduces to a reference equilibrium ensemble with local thermodynamic parameters. To Navier-Stokes order, only the first term in the expansion (A.53) has to be kept, with the result

$$\gamma_{\alpha i}^*(\vec{r}, t | \lambda)_{\text{H}} = \frac{\partial y_{\beta}(\vec{r}, t | \lambda)}{\partial r_i} \int_0^t d\tau \langle \{e^{L(t-\tau)} \hat{\gamma}_{\alpha i}(\vec{r})\} \hat{\Phi}_{\beta j}[\lambda] \rangle_{0\lambda}, \quad (\text{A.56})$$

where

$$\hat{\Phi}_{\beta j}[\lambda] = \int_{\Omega} d\vec{r} \hat{\phi}_{\beta j}(\vec{r} | \lambda). \quad (\text{A.57})$$

Here $\langle \dots \rangle_{0\lambda}$ indicates an average over the equilibrium ensemble defined in Eq. (A.54),

$$\langle \hat{A} \rangle_{0\lambda} = \sum_{N=0}^{\infty} \int d\Gamma \hat{A} \rho_{\text{eq}}(\vec{r}, t | \lambda). \quad (\text{A.58})$$

The \vec{r} and t dependence of the averaged quantity through the thermodynamic variables has been left implicit to simplify the notation. Finally, hydrodynamics describes variations over time scales large

compared to the mean free time $t_f = \lambda/v_0$ (where λ is the mean free path and v_0 the thermal velocity of the particles). In this limit, Eq. (A.46) can be written as

$$\gamma_{\alpha i}^*(\vec{r}, t|\lambda) = \gamma_{\alpha i}^{**}(\vec{r}, t|\lambda)_{NS} + L_{\alpha\beta}^{ij}(\vec{r}, t; \{\psi[\lambda]\}) \frac{\partial}{\partial r_j} y_{\beta}(\vec{r}, t|\lambda), \quad (\text{A.59})$$

where $L_{\alpha\beta}^{ij}$ is the matrix of the transport coefficients, defined as

$$L_{\alpha\beta}^{ij}(\vec{r}, t; \{\psi[\lambda]\}) = \lim_{t \gg t_f} \int_0^t d\tau \langle [e^{L(t-\tau)} \hat{\gamma}_{\alpha i}(\vec{r})] \hat{\Phi}_{\beta j}[\lambda] \rangle_{0\lambda}, \quad (\text{A.60})$$

and the additional fluxes $\gamma_{\alpha i}^{**}(\vec{r}, t|\lambda)_{NS}$ are defined as

$$\frac{\partial}{\partial r_i} \gamma_{\alpha i}^{**}(\vec{r}, t|\lambda)_{NS} \equiv \lim_{t \gg t_f} \left[\frac{\partial}{\partial r_i} \gamma_{\alpha i}^{**}(\vec{r}, t|\lambda) \right]_{NS}. \quad (\text{A.61})$$

Here $[A]_{NS}$ indicates the result of an expansion of the function A to second order in the gradients of the thermodynamic variables. The generalized Navier-Stokes equations for the set of functionals $\{\psi_{\alpha}(\vec{r}, t|\lambda)\}$ are then given by

$$\begin{aligned} \frac{\partial}{\partial t} \psi_{\alpha}(\vec{r}, t|\lambda) + \frac{\partial}{\partial r_i} E_{\alpha}^i(\vec{r}, t; \{\psi[\lambda]\}) \\ + \frac{\partial}{\partial r_i} L_{\alpha\beta}^{ij}(\vec{r}, t; \{\psi[\lambda]\}) \frac{\partial}{\partial r_j} y_{\beta}(\vec{r}, t|\lambda) = - \frac{\partial}{\partial r_i} \gamma_{\alpha i}^{**}(\vec{r}, t|\lambda)_{NS}. \end{aligned} \quad (\text{A.62})$$

Both the Euler matrix and the matrix of transport coefficients in Eq.(A.62) are functions of \vec{r} and t and functionals of the $\{\lambda_{\alpha}\}$ only through the average λ -dependent densities, $\{\psi_{\alpha}(\vec{r}, t|\lambda)\}$. The explicit

form of Eqs. (A.62) for a one-component fluid is given in Section III.1. When evaluated at $\lambda=0$, the right hand side of Eqs. (A.62) vanishes identically, since $\gamma_{\alpha i}^{**}(\vec{r}, t|0) = 0$, and the Navier-Stokes equations for the conserved densities are recovered.

The additional contributions $\gamma_{\alpha i}^{**}(\vec{r}, t|\lambda)$ will be evaluated to Navier-Stokes order only after performing the functional differentiation and evaluating the result at $\lambda=0$. A detailed analysis of these terms is given in Appendix B, where they are shown to determine the amplitude of the noise in the system.

APPENDIX B
EVALUATION OF THE SOURCE TERM FOR HYDRODYNAMIC FLUCTUATIONS

The λ -dependent densities, $\{\psi_\alpha(\vec{r}, t|\lambda)\}$, defined in Eq. (3.24), have been shown to satisfy the set of nonlinear hydrodynamic equations (3.28). These equations differ from the usual nonlinear Navier-Stokes equations only by the presence of additional contributions to the irreversible fluxes, given by the Navier-Stokes limit of

$$\gamma_{\alpha i}^{**}(\vec{r}, t|\lambda) = \langle \hat{\gamma}_{\alpha i}(\vec{r}) [e^{D(t|\lambda)} - e^{D'(t|\lambda)}]; t \rangle_{\lambda L}, \quad (\text{B.1})$$

where $D(t|\lambda)$ and $D'(t|\lambda)$ are defined in Eqs. (A.36-38). These terms vanish at $\lambda=0$, when the nonlinear Navier-Stokes equations are recovered. However, their functional derivative contributes to the equations for the correlation functions through the inhomogeneous term $I_{\alpha\beta}$ (see Eq. (3.44) and Eq. (3.64-65)), given by

$$I_{\alpha\beta}(\vec{r}_1, t_1; \vec{r}_2, t_2) = -\lim_{t_1 \gg t_f} \left[\frac{\partial}{\partial r_{1i}} \frac{\delta \gamma_{\alpha i}^{**}(\vec{r}_1, t_1|\lambda)}{\delta \lambda_\beta(\vec{r}_2, t_2)} \Big|_{\lambda=0} \right]_{\text{NS}}. \quad (\text{B.2})$$

As indicated in Sections III.2 and III.3, the right hand side of Eq. (B.2) has to be evaluated to Navier-Stokes order for consistency with the approximations introduced in the left hand side of Eqs. (3.44) and (3.64).

The objective here is to evaluate $I_{\alpha\beta}$ and to show that it only gives a nonvanishing contribution to the equation for the equal time correlation functions, on the time scale of interest.

By carrying out the functional differentiation and making use of the fact that $D(t|0) = D'(t|0) \equiv D'(t)$,

$$\left. \frac{\delta \gamma_{\alpha i}^{**}(\vec{r}_1, t_1 | \lambda)}{\delta \lambda_{\beta}(\vec{r}_2, t_2)} \right|_{\lambda=0} = \langle \hat{\gamma}_{\alpha i}(\vec{r}_1) e^{D'(t_1)} T^{\dagger}(t_1, 0) \left[\frac{\delta D_0(\lambda)}{\delta \lambda_{\beta}(\vec{r}_2, t_2)} \right]_{\lambda=0}; t_1 \rangle_L . \quad (\text{B.3})$$

The nonequilibrium distribution function at time t_1 is given by Eqs. (A.4) and (A.28) for initial local equilibrium, or

$$\begin{aligned} \rho_N(t_1) &= T^{\dagger}(t_1, 0) \rho_L(0) \\ &= \rho_L(t_1) e^{D'(t_1)} . \end{aligned} \quad (\text{B.4})$$

Making use of the properties of T^{\dagger} , which acts as a point operator,* i.e.

$$[T^{\dagger}(t, \tau) \hat{A}] [T^{\dagger}(t, \tau) \hat{B}] = T^{\dagger}(t, \tau) \hat{A} \hat{B} , \quad (\text{B.5})$$

and of Eq. (A.38) for $D_0(\lambda)$, $I_{\alpha\beta}$ can be written as

$$\left. \frac{\delta \gamma_{\alpha i}^{**}(\vec{r}_1, t_1 | \lambda)}{\delta \lambda_{\beta}(\vec{r}_2, t_2)} \right|_{\lambda=0} = \langle [T(t_1, 0) \hat{\gamma}_{\alpha i}(\vec{r}_1)] \left[\frac{\delta}{\delta \lambda_{\beta}(\vec{r}_2, t_2)} \frac{\rho_N(0|\lambda)}{\rho_L(0|\lambda)} \right]_{\lambda=0}; 0 \rangle_L , \quad (\text{B.6})$$

where

$$\rho_N(0|\lambda) = \frac{U[\lambda]}{\langle U[\lambda] \rangle_{\lambda L}} \rho_L(0) . \quad (\text{B.7})$$

*This property follows from the fact that the exponential of T^{\dagger} is a linear combination of differential operators.

Also, in writing Eq. (B.6), the definition of $T(t, \tau)$ as the adjoint of $T^\dagger(t, \tau)$, as given in Eq. (A.1), has been used.

The functional differentiation in Eq. (B.6) can be carried out explicitly. Using the fact that the local equilibrium functional $\rho_L(t|\lambda)$ depends on λ only through the densities $\{\phi_\alpha(\vec{r}, t|\lambda)\}$, the result is

$$\left[\frac{\delta}{\delta \lambda_\beta(\vec{r}_2, t_2)} \frac{\rho_N(0|\lambda)}{\rho_L(0|\lambda)} \right]_{\lambda=0} = \hat{\psi}_\beta(\vec{r}_2, t_2) - \int d\vec{r} \hat{\xi}_\sigma(\vec{r}; 0) \langle \hat{\psi}_\sigma(\vec{r}; 0) \hat{\psi}_\beta(\vec{r}_2, t_2); 0 \rangle_L, \quad (\text{B.8})$$

where the normalized densities $\hat{\xi}_\sigma(\vec{r})$ are defined in Eq. (A.21). It is convenient to define the time dependent local equilibrium projection operator onto the set $\{1, \hat{\psi}_\alpha\}$, given by

$$P_t \hat{A} = 1 \cdot \langle \hat{A}; t \rangle_L + \int d\vec{r} \hat{\xi}_\alpha(\vec{r}; t) \langle \hat{\psi}_\alpha(\vec{r}; t) \hat{A}; t \rangle_L. \quad (\text{B.9})$$

This definition agrees with the one used, for example, by Kawasaki and Gunton in Ref. 2. Inserting Eq. (B.8) into Eq. (B.7) and using the definition of P_t , Eq. (B.6) becomes

$$\left. \frac{\delta \gamma_{\alpha i}^{**}(\vec{r}_1, t_1|\lambda)}{\delta \lambda_\beta(\vec{r}_2, t_2)} \right|_{\lambda=0} = \langle [T(t_1, 0) \hat{\gamma}_{\alpha i}(\vec{r}_1)] Q_0 \hat{\psi}_\beta(\vec{r}_2, t_2); 0 \rangle_L, \quad (\text{B.10})$$

where $Q_t \equiv 1 - P_t$.

As done in Appendix A, it can now be argued that the dynamics of average quantities at points in the interior of the system is independent from the boundary forces. The evolution operator $T(t_1, 0)$

can then be replaced with the corresponding evolution operator for the isolated system (see Eq. (A.51)), with the result,

$$\frac{\delta \gamma_{\alpha i}^{**}(\vec{r}_1, t_1 | \lambda)}{\delta \lambda_{\beta}(\vec{r}_2, t_2)} \Big|_{\lambda=0} = \langle [e^{Lt_1} \hat{\gamma}_{\alpha i}(\vec{r}_1)] Q_0 \hat{\psi}_{\beta}(\vec{r}_2, t_2); 0 \rangle_L . \quad (\text{B.11})$$

The time evolution of the dynamical variable $\hat{\psi}_{\beta}(\vec{r}, t)$ is governed by the equation,

$$\frac{\partial}{\partial t} \hat{\psi}_{\beta}(\vec{r}, t) - L \hat{\psi}_{\beta}(\vec{r}, t) = 0 . \quad (\text{B.12})$$

By applying the projection operator Q_0 on the left of Eq. (B.12), an inhomogeneous equation for $Q_0 \hat{\psi}_{\beta}(\vec{r}, t)$ is obtained,

$$\left\{ \frac{\partial}{\partial t} - Q_0 L \right\} Q_0 \hat{\psi}_{\beta}(\vec{r}, t) = Q_0 L P_0 \hat{\psi}_{\beta}(\vec{r}, t) , \quad (\text{B.13})$$

whose solution is

$$Q_0 \hat{\psi}_{\beta}(\vec{r}, t) = \int_0^t d\tau e^{Q_0 L(t-\tau)} Q_0 L P_0 \hat{\psi}_{\beta}(\vec{r}, \tau) , \quad (\text{B.14})$$

since $Q_0 \hat{\psi}_{\beta}(\vec{r}, 0) = 0$ by definition. Substituting into Eq. (B.11), $I_{\alpha\beta}$ can be written as

$$I_{\alpha\beta}(\vec{r}_1, t_1; \vec{r}_2, t_2) = - \lim_{t_1 \gg t_f} \left[\frac{\partial}{\partial r_{1i}} \int_0^{t_2} d\tau \int d\vec{r}' \langle \{ e^{Lt_1} \hat{\gamma}_{\alpha i}(\vec{r}_1) \} \right. \\ \left. \times e^{Q_0 L(t_2-\tau)} \hat{\psi}_{\sigma j}(\vec{r}'; 0); 0 \rangle_L \frac{\partial}{\partial r'_j} \frac{\delta \langle \hat{\psi}_{\beta}(\vec{r}_2); \tau \rangle_L}{\delta \langle \hat{\psi}_{\sigma}(\vec{r}'); 0 \rangle_L} \right]_{NS} , \quad (\text{B.15})$$

where

$$\begin{aligned}\hat{\phi}_{\sigma j}(\vec{r};0) &\equiv Q_0 \hat{\gamma}_{\sigma j}(\vec{r}) \\ &= \hat{\gamma}_{\sigma j}(\vec{r};0) - \int d\vec{r}' \hat{\xi}_{\alpha}(\vec{r}';0) \langle \hat{\psi}_{\alpha}(\vec{r}';0) \hat{\gamma}_{\sigma j}(\vec{r});0 \rangle_L, \quad (\text{B.16})\end{aligned}$$

i.e. $\hat{\phi}_{\sigma j}$ is the flux already defined in Eq. (A.23), now projected at $t=0$.

No approximations have been introduced at this point. To evaluate $I_{\alpha\beta}$, the right hand side of Eq. (B.15) now has to be expanded to second order in the gradients. The correlation function on the right hand side of Eq. (B.15) is peaked at $\tau = t_1 - t_2$: the functional derivative in the integrand can then be evaluated at this value of the time argument. If the difference $t_1 - t_2$ is large compared to a mean free path, t_f , the functional derivative is identified with the Green's function of the hydrodynamic equations, defined by

$$\delta \langle \hat{\psi}_{\alpha}(\vec{r});t \rangle = \int d\vec{r}' G_{\alpha\beta}^H(\vec{r},t;\vec{r}',0) \delta \langle \hat{\psi}_{\beta}(\vec{r}');0 \rangle, \quad (\text{B.17})$$

with the result

$$\begin{aligned}I_{\alpha\beta}(\vec{r}_1,t_1;\vec{r}_2,t_2) &= - \lim_{t_1 \gg t_f} \left[\frac{\partial}{\partial r_{1i}} \int_0^{t_2} d\tau \int d\vec{r}' \langle [e^{Lt} \hat{\gamma}_{\alpha i}(\vec{r}_1)] \right. \\ &\quad \times e^{Q_0 L(t_2 - \tau)} \hat{\phi}_{\sigma j}(\vec{r}';0);0 \rangle_L \left. \frac{\partial}{\partial r'_j} G_{\beta\sigma}^H(\vec{r}_2,\tau;\vec{r}',0) \right]_{NS}. \quad (\text{B.18})\end{aligned}$$

The Green's function $G_{\alpha\beta}^H$ can be expanded in a Taylor series in the gradients around the point $\vec{r}' = \vec{r}_2$. To lowest order Eq. (B.18) becomes

$$I_{\alpha\beta}(\vec{r}_1, t_1; \vec{r}_2, t_2) = - \lim_{t_1 \gg t_f} \frac{\partial}{\partial r_{1i}} \int_0^{t_2} d\tau \langle e^{L(t_1 - t_2 + \tau)} \hat{\gamma}_{\alpha i}(\vec{r}_1) \hat{\Phi}_{\sigma j} \rangle_0 \times \frac{\partial}{\partial r_{1j}} G_{\beta\sigma}^H(\vec{r}_2, t_1 - t_2; \vec{r}_1, 0) . \quad (\text{B.19})$$

The identity

$$e^{Q_0 L t} = e^{L t} - \int_0^t d\tau e^{L(t-\tau)} P_0 L e^{Q_0 L \tau} \quad (\text{B.20})$$

has been used to show that, to lowest order in the gradients, the projected evolution operator on the right hand side of Eq. (B.18) can be substituted with the usual evolution operator. Also, the local equilibrium ensemble in Eq. (B.18) has been expanded around the reference equilibrium ensemble $\rho_{\text{eq}}(\vec{r}_1, t_1)$, defined by Eq. (A.54), at $\lambda=0$, as required to Navier-Stokes order.

The correlation function on the right hand side of Eq. (B.19) is the correlation function entering the expression for the transport coefficients, Eq. (3.30). Its lifetime is of the order of the mean free time, t_f .² The inhomogeneous term $I_{\alpha\beta}$ therefore vanishes if

$$t_1 \gg t_f,$$

$$t_1 - t_2 \gg t_f, \quad (\text{B.21})$$

or, explicitly,

$$\lim_{\substack{t_1 \gg t_f \\ t_1 - t_2 \gg t_f}} I_{\alpha\beta}(\vec{r}_1, t_1; \vec{r}_2, t_2) = 0, \quad (\text{B.22})$$

and does not contribute to the equations for the unequal time correlation functions.

The contribution from the inhomogeneity $I_{\alpha\beta}$ to the equations for the equal time correlation functions is given by

$$\Gamma_{\alpha\beta}(\vec{r}_1, \vec{r}_2; t) = \lim_{\epsilon \rightarrow 0^+} (1 + P_{12} P_{\alpha\beta}) I_{\alpha\beta}(\vec{r}_1, t + \epsilon; \vec{r}_2, t), \quad (\text{B.23})$$

where

$$\begin{aligned} \lim_{\epsilon \rightarrow 0^+} I_{\alpha\beta}(\vec{r}_1, t + \epsilon; \vec{r}_2, t) = & - \lim_{t \gg t_f} \left[\frac{\partial}{\partial r_{1i}} \int_0^t d\tau \int d\vec{r}' \langle \{ e^{Lt} \hat{\gamma}_{\alpha i}(\vec{r}) \} \right. \\ & \times e^{Q_0 L(t-\tau)} \hat{\phi}_{\sigma j}(\vec{r}'; 0); 0 \rangle_L \left. \frac{\partial}{\partial r'_j} \frac{\delta \langle \hat{\psi}_{\beta}(\vec{r}_2); \tau \rangle_L}{\delta \langle \hat{\psi}_{\sigma}(\vec{r}'); 0 \rangle_L} \right]_{NS}. \end{aligned} \quad (\text{B.24})$$

The correlation function on the right hand side of Eq. (B.24) is now peaked at $\tau=0$. The functional derivative can then be evaluated at $\tau=0$ and reduces to a spatial δ -function, with the result,

$$\begin{aligned} \Gamma_{\alpha\beta}(\vec{r}_1, \vec{r}_2; t) = & (1 + P_{12} P_{\alpha\beta}) \left[\frac{\partial^2}{\partial r_{1i} \partial r_{2j}} \int_0^t d\tau \langle \{ e^{Lt} \hat{\gamma}_{\alpha i}(\vec{r}_1) \} \right. \\ & \times e^{Q_0 L(t-\tau)} \hat{\phi}_{\beta j}(\vec{r}_2; 0); 0 \rangle_L \left. \right]_{NS}. \end{aligned} \quad (\text{B.25})$$

To proceed, it should be observed that, in the solution of the hydrodynamic equations for the correlation functions, $\Gamma_{\alpha\beta}$ will always appear in the combination,

$$\int d\vec{r}'_1 d\vec{r}'_2 K_{\alpha\sigma}^H(\vec{r}_1, \vec{r}'_1, t; \vec{r}_2, \vec{r}'_2, \tau) \Gamma_{\alpha\beta}(\vec{r}'_1, \vec{r}'_2; \tau), \quad (\text{B.26})$$

where $K_{\alpha\sigma}^H$ is the two-point hydrodynamic Green's function for the equation considered. By integrating by parts twice, the double derivative in Eq. (B.25) can be moved over the Green's function. The latter can be expanded in a Taylor series in the gradients around the points \vec{r}_1 and \vec{r}_2 . To Navier-Stokes order the result is

$$\left[\frac{\partial^2}{\partial r_{1i} \partial r_{2j}} K_{\alpha\sigma}^H \right] \lim_{t \gg t_f} (1+P_{12} P_{\alpha\beta}) \int_0^t d\tau \langle [e^{L\tau} \hat{\Gamma}_{\alpha i}] \hat{\Phi}_{\beta j} \rangle_0, \quad (\text{B.27})$$

where, to the desired order in the gradients, the local equilibrium average has been substituted with an average over the reference equilibrium ensemble $\rho_{\text{eq}}(\vec{r}_1, t)$. Also, Eq. (B.20) has been used to show that the difference between the projected and the usual evolution operator generates terms of higher order in the gradients. Finally, in Eq. (B.27) $\hat{\Gamma}_{\alpha i}$ is the volume integrated flux. A convenient form of $\Gamma_{\alpha\beta}$, which leads to the result indicated in Eq. (B.27), is then given by

$$\Gamma_{\alpha\beta}(\vec{r}_1, \vec{r}_2; t) = \lim_{t \gg t_f} (1+P_{12} P_{\alpha\beta}) \frac{\partial^2}{\partial r_{1i} \partial r_{2i}} \delta(\vec{r}_1 - \vec{r}_2) \int_0^t d\tau \langle [e^{L\tau} \hat{\gamma}_{\alpha i}(\vec{r}_1)] \hat{\Phi}_{\beta j} \rangle_0, \quad (\text{B.28})$$

or,

$$\Gamma_{\alpha\beta}(\vec{r}_1, \vec{r}_2; t) = (1+P_{12} P_{\alpha\beta}) \frac{\partial^2}{\partial r_{1i} \partial r_{2j}} \delta(\vec{r}_1 - \vec{r}_2) L_{\alpha\beta}^{ij}(\vec{r}_1, t; \{\psi\}), \quad (\text{B.29})$$

where $L_{\alpha\beta}^{ij}$ is the matrix of the transport coefficients, given by Eq. (3.30) for $\lambda=0$.

APPENDIX C
DERIVATION OF THE λ -DEPENDENT BOLTZMANN EQUATION

The objective here is to evaluate the functional $H(x_1, x_2, t | \lambda)$, defined in Eq.(4.12), to lowest order in the density, deriving a closed kinetic equation for the one-particle reduced distribution functional $f_1(x, t | \lambda)$.

From the definition of the reduced distribution functionals, Eq.(4.10), it appears that the λ -dependence can be incorporated entirely in the initial condition, while the time evolution operator is the same as that appearing in the definition of the usual reduced distribution functions. A nonequilibrium cluster expansion, analogous to the one used by Cohen in deriving the nonlinear Boltzmann equation,⁵ can then be performed to express $f_2[\lambda]$ as a power series in the density in terms of $f_1[\lambda]$. This is done by eliminating the test function λ between the two functionals.

To simplify the notation, the s -particle functional $f_2[\lambda]$ is written as

$$n^2 f_s(x_1, \dots, x_s, t | \lambda) = \sum_{N \geq s} \frac{N!}{(N-s)!} \frac{1}{N!Q} \int dx_{s+1} \dots dx_N F_N(x_1, \dots, x_N, t | \lambda), \quad (C.1)$$

for $t > t_0$, where

$$F_N(x_1, \dots, x_N, t | \lambda) = S_{-t}(x_1, \dots, x_N) U_N[\lambda] \hat{\rho}_N(0), \quad (C.2)$$

and $\hat{\rho}_N(0)$ is the initial distribution function for the system of N particles, without normalization in the grand canonical ensemble. The normalization constant Q is defined by requiring,

$$\sum_{N=0}^{\infty} \frac{1}{N!Q} \int dx_1 \dots dx_N F_N(x_1, \dots, x_N, t | \lambda) = 1. \quad (C.3)$$

The reduced distribution functionals are normalized as follows,

$$\int dx_1 \dots dx_s f_s(x_1, \dots, x_s, t | \lambda) = V^s, \quad (C.4)$$

where V is the volume of the system.

In order to define the cluster expansion, the set of functions $F_k(x_1, \dots, x_k, t | \lambda)$, for $k = 1, 2, \dots, N$, is chosen as the set of basic functions in terms of which the distribution functions of the system will be expressed. The dynamics of F_k is the dynamics of a cluster of k isolated particles.

To derive an expansion for the one- and two-particle distribution functions, two sets of cluster functions, $\chi(x_1 | x_2, \dots, x_k | \lambda)$ and $\chi(x_1, x_2 | x_3, \dots, x_k | \lambda)$ have to be introduced (the time dependence of the cluster functions has been left implicit). They are defined by

$$\begin{aligned} F_k(x_1, \dots, x_k, t | \lambda) &= \chi(x_1 | \lambda) F_{k-1}(x_2, \dots, x_k, t | \lambda) \\ &+ \sum_{i=2}^k \chi(x_1 | x_i | \lambda) F_{k-2}(x_2, \dots, x_{i-1}, x_{i+1}, \dots, x_k, t | \lambda) \\ &+ \sum_{i < j=2}^k \sum \chi(x_1 | x_i, x_j | \lambda) F_{k-3}(x_2, \dots, x_{i-1}, x_{i+1}, \dots, x_{j-1}, x_{j+1}, \dots, x_k; t | \lambda) \\ &+ \dots, \end{aligned} \quad (C.5)$$

and

$$\begin{aligned}
 F_k(x_1, \dots, x_k, t | \lambda) &= \chi(x_1, x_2 | \lambda) F_{k-2}(x_3, \dots, x_k, t | \lambda) \\
 &+ \sum_{i=3}^k \chi(x_1, x_2 | x_i | \lambda) F_{k-3}(x_3, \dots, x_{i-1}, x_{i+1}, \dots, x_k, t | \lambda) \\
 &+ \dots \quad .
 \end{aligned}
 \tag{C.6}$$

The functions χ can be expressed in terms of the F_s by writing explicitly Eqs.(C.5-6) for $s=1,2,\dots,N$ and then inverting them, with the result,

$$\begin{aligned}
 \chi(x_1 | \lambda) &= F_1(x_1, t | \lambda) \quad , \\
 \chi(x_1 | x_2 | \lambda) &= F_2(x_1, x_2, t | \lambda) - F_1(x_1, t | \lambda) F_1(x_2, t | \lambda) \quad , \\
 \text{etc.} \quad , &
 \end{aligned}
 \tag{C.7}$$

and

$$\begin{aligned}
 \chi(x_1, x_2 | \lambda) &= F_2(x_1, x_2, t | \lambda) \quad , \\
 \chi(x_1, x_2 | x_3 | \lambda) &= F_3(x_1, x_2, x_3, t | \lambda) - F_2(x_1, x_2, t | \lambda) F_1(x_3, t | \lambda) \quad , \\
 \text{etc.} \quad . &
 \end{aligned}
 \tag{C.8}$$

It appears from Eqs.(C.7-8) that the functions χ have cluster properties, i.e. vanish when the F_k factorize to a product of lower order functions. They are associated with the motion of isolated groups of molecules in phase space. The cluster expansion provides a means for

systematically treating the distribution functions of a many-particle system in terms of those of small groups of isolated particles. As the density of the system considered increases, correlations among a larger number of particles will become important. Substitution of Eqs.(C.5) and (C.6), for $k=N$, in Eq.(C.1) for $s=1$ and $s=2$, respectively, gives

$$n f_1(x_1, t | \lambda) = \chi(x_1 | \lambda) + \sum_{\ell=2}^{\infty} \frac{1}{(\ell-1)!} \int dx_2 \dots dx_{\ell} \chi(x_1 | x_2, \dots, x_{\ell} | \lambda), \quad (\text{C.9})$$

and

$$n^2 f_2(x_1, x_2, t | \lambda) = \chi(x_1, x_2 | \lambda) + \sum_{\ell=3}^{\infty} \frac{1}{(\ell-2)!} \int dx_3 \dots dx_{\ell} \chi(x_1, x_2 | x_3, \dots, x_{\ell} | \lambda) . \quad (\text{C.10})$$

In this way the one- and two-particle functionals have been written as expansions in terms of clusters of an increasing number of particles. This is therefore an expansion in the density. The cluster functions χ depend on the test function λ through the initial condition for the functions F_k .

The functional relationship between λ and $f_1[\lambda]$ is given by Eq.(C.1) for $s=1$ or, equivalently, by Eq.(C.9). The latter expression can be used to invert the relationship in the limit of low density. Eq.(C.9) has to be solved for λ in terms of $f_1[\lambda]$ and this relationship is then used in Eq.(C.10) to eliminate λ in favor of $f_1[\lambda]$. However, since the distribution functions always depend on λ only through the operator $U_N[\lambda]$, it will be sufficient to invert Eq.(C.9) in terms of such an operator.

To lowest order in the density only clusters involving the smallest number of particles contribute. In this limit the desired functional relationship is given by

$$n f_1(x_1, t | \lambda) = S_{-t}(x_1) U_1^0[x_1 | \lambda] n f_1(x_1, 0) , \quad (\text{C.11})$$

where a subscript or superscript zero indicates, here and in the rest of this Appendix, the low density limit. $U_s[x_1, \dots, x_s | \lambda]$ is an s -particle version of the operator $U_N[\lambda]$, defined in Eq.(4.4), and it is given by

$$U_s[x_1, \dots, x_s | \lambda] = \exp \int_{-\infty}^{+\infty} dt \int dx \lambda(x, t) S_t(x_1, \dots, x_s) \prod_{i=1}^s \delta(x-x_i), \quad (\text{C.12})$$

where the test function λ has the form chosen in Eq.(4.8). The low density limit U_s^0 is formally given by

$$U_s^0[x_1, \dots, x_s | \lambda] = U_s[x_1, \dots, x_s | \lambda_0] , \quad (\text{C.13})$$

where λ_0 denotes the first term in the expansion,

$$\lambda[n, f_1(x_1, t | \lambda)] = \lambda[0, f_1] + O(n) . \quad (\text{C.14})$$

Use of Eq.(C.11) in Eq.(C.10) gives the low density expression for the functional H in terms of $f_1[\lambda]$,

$$H_0(x_1, x_2, t | \lambda) = \mathfrak{S}_t(x_1, x_2) f_1(x_1, t | \lambda) f_1(x_2, t | \lambda) + R(x_1, x_2, t | \lambda), \quad (\text{C.15})$$

where $\mathfrak{S}_t(x_1, x_2)$ is the two-particle streaming operator defined in

Eq.(4.14) and

$$R(x_1, x_2, t | \lambda) = S_{-t}(x_1, x_2) \{ U_2^0[x_1, x_2 | \lambda] f_2(x_1, x_2, 0) - U_1^0[x_1 | \lambda] U_1^0[x_2 | \lambda] f_1(x_1, 0) f_1(x_2, 0) \} . \quad (C.16)$$

The first term on the right hand side of Eq.(C.15) has the form desired to obtain the Boltzmann expression for the rate of change of the one-particle distribution function due to collisions. The second term is a highly nonlinear functional of $f_1[\lambda]$ through the solution, λ_0 , of Eq.(C.11) and depends on the initial correlations in the system. To analyze this term, the case corresponding to $\lambda=0$ is first considered. By setting $\lambda=0$ in Eq.(C.16), R becomes

$$R(x_1, x_2, t | 0) = S_{-t}(x_1, x_2) \{ f_2(x_1, x_2, 0) - f_1(x_1, 0) f_1(x_2, 0) \} . \quad (C.17)$$

This term has to be inserted in the integral on the right hand side of the first equation of the BBGKY hierarchy, Eq.(4.11), where it is premultiplied by $\theta(x_1, x_2)$, which restricts the range of integration to interparticle distances smaller than or of the order of the force range. For purely repulsive, short ranged potentials the operator $S_{-t}(x_1, x_2)$ brings two particles initially closed together far apart (i.e. to relative distances larger than the force range) in a time of the order of τ_c . Therefore the contribution from $R(x_1, x_2, t | 0)$ vanishes in a time of the order of τ_c for all the initial nonequilibrium states where the s -particle distribution function factorizes for interparticle separations large compared to the force range. This is the restriction

usually imposed on the class of initial states when deriving the Boltzmann equation. Explicitly, for initial conditions leading to a state that is adequately described by the Boltzmann equation, the vanishing of the contribution from initial correlations is expressed by

$$\lim_{t \gg \tau_c} \int dx_2 \theta(x_1, x_2) R(x_1, x_2, t | 0) = 0 . \quad (\text{C.18})$$

For nonzero values of λ , however, R is a complicated functional of the initial condition and will contribute to the kinetic equation for $f_1[\lambda]$. It is convenient to rewrite Eq.(C.16) as the sum of two terms,

$$\begin{aligned} R(x_1, x_2, t | \lambda) &= S_{-t}(x_1, x_2) U_2^0[x_1, x_2 | \lambda] \{f_2(x_1, x_2, 0) - f_1(x_1, 0) f_1(x_2, 0)\} \\ &+ S_{-t}(x_1, x_2) \{U_2^0[x_1, x_2 | \lambda] U_1^{0-1}[x_1 | \lambda] U_1^{0-1}[x_2 | \lambda] - 1\} \\ &\times U_1^0[x_1 | \lambda] U_1^0[x_2 | \lambda] f_1(x_1, 0) f_1(x_2, 0) . \end{aligned} \quad (\text{C.19})$$

By applying the group properties of the streaming operator, the first term on the right hand side of Eq.(C.19) can be written in the form,

$$\{S_{-t}(x_1, x_2) U_2^0[x_1, x_2 | \lambda]\} S_{-t}(x_1, x_2) [f_2(x_1, x_2, 0) - f_1(x_1, 0) f_1(x_2, 0)] . \quad (\text{C.20})$$

When substituted in the first equation of the hierarchy this term gives no contribution in the limit $t \gg \tau_c$ for the same class of initial states leading to Eq.(C.18). The long time contribution of $R(x_1, x_2, t | \lambda)$ is then given by

$$\lim_{t \gg \tau_c} R(x_1, x_2, t | \lambda) = \lim_{t \gg \tau_c} S_{-t}(x_1, x_2) \{ U_2^0[x_1, x_2 | \lambda] U_1^{0-1}[x_1 | \lambda] U_1^{0-1}[x_2 | \lambda] - 1 \} \\ \times U_1^0[x_1 | \lambda] U_1^0[x_2 | \lambda] f_1(x_1, 0) f_1(x_2, 0) . \quad (C.21)$$

Using the properties of the streaming operators and Eqs. (C.12-13) for the low density U_s operators, Eq. (C.21) can be rewritten as

$$\lim_{t \gg \tau_c} R(x_1, x_2, t | \lambda) = \lim_{t \gg \tau_c} \left(\exp \left\{ \int_{-\infty}^t d\tau [\mathfrak{S}_{t-\tau}(x_1, x_2) - \mathfrak{S}_{\tau}(x_1, x_2)] \right. \right. \\ \left. \left. \times [\hat{\lambda}(x_1, \tau; t) + \hat{\lambda}(x_2, \tau; t)] \right\} - 1 \right) \\ \times S_{-t}(x_1, x_2) U_1^0[x_1 | \lambda] U_1^0[x_2 | \lambda] f_1(x_1, 0) f_1(x_2, 0) , \quad (C.22)$$

where the choice (4.8) of the test function has been inserted explicitly (t_0 is a parameter to be chosen when functionally differentiating such that $t \geq t_0$) and

$$\hat{\lambda}(x_i, \tau; t) \equiv S_{\tau-t}(x_i) \lambda'(x_i, \tau) . \quad (C.23)$$

It has previously been pointed out (Eq. (4.16)) that the streaming operator $\mathfrak{S}_t(x_1, x_2)$ reaches a time-independent asymptotic limit for $t > \tau_c$. Therefore the argument of the exponential in Eq. (C.22) vanishes if the parameter t_0 is chosen to satisfy $t - t_0 > \tau_c$. As seen in Section IV.3 this choice is appropriate when deriving equations for unequal time correlation functions. For consistency with the Boltzmann limit considered here, the appropriate multitime correlation functions are in fact those whose time arguments are separated by at least a

collision time. Therefore, it already appears from the present analysis that the inhomogeneous term $R(x_1, x_2, t | \lambda)$ will give no contribution to the equations for the unequal time correlation functions. The same result is restated in Section IV.3 by showing explicitly that the functional derivative of R generates terms that vanish in this case.

However, when deriving equations for the equal time correlation function, the parameter t_0 has to be chosen arbitrarily close to t , and the difference between the two streaming operators in Eq. (C.22) does not vanish. The asymptotic form of Eq. (C.22) can only be evaluated after functionally differentiating and setting $\lambda=0$. In Section IV.4 this term is shown to contribute to the equations for the equal time correlation functions. In general, it has to be kept when deriving a kinetic equation for $f_1[\lambda]$ to be used to generate equations for the correlation functions.

Finally, substituting these results into Eq.(4.12), an equation describing the time evolution of the functional $f_1(x_1, t | \lambda)$ for time-variations large compared to τ_c and $t \geq t_0$ is obtained,

$$\begin{aligned}
 & \left\{ \frac{\partial}{\partial t} + L_0(x_1) \right\} f_1(x_1, t | \lambda) \\
 & = n \int dx_2 \theta(x_1, x_2) \xi_\omega(x_1, x_2) f_1(x_1, t | \lambda) f_1(x_2, t | \lambda) \\
 & + W(x_1, t | f_1[\lambda]) , \qquad \qquad \qquad (C.24)
 \end{aligned}$$

with

$$\begin{aligned}
& W(x_1, t | f_1[\lambda]) \\
&= \lim_{t \gg \tau_c} \int dx_2 \theta(x_1, x_2) S_{-t}(x_1, x_2) \{ (U_2^0[x_1, x_2 | \lambda] U_1^{o-1}[x_1 | \lambda] U_1^{o-1}[x_2 | \lambda] - 1) \\
&\quad \times U_1^0[x_1 | \lambda] U_1^0[x_2 | \lambda] f_1(x_1, 0) f_1(x_2, 0) \} . \tag{C.25}
\end{aligned}$$

Again, the dependence of Eqs. (C.24-25) on t_0 has been left implicit. Equation (C.25) can also be rewritten in a form that will be useful in the following, given by

$$\begin{aligned}
& W(x_1, t | f_1[\lambda]) \\
&= \lim_{t \gg \tau_c} \int dx_2 \theta(x_1, x_2) S_{-t}(x_1, x_2) \{ U_2^0[x_1, x_2 | \lambda] U_1^{o-1}[x_1 | \lambda] U_1^{o-1}[x_2 | \lambda] - 1 \} \\
&\quad \times S_t(x_1) S_t(x_2) f_1(x_1, t | \lambda) f_1(x_2, t | \lambda) . \tag{C.26}
\end{aligned}$$

APPENDIX D
SCALING METHOD FOR A LOW DENSITY CLOSURE
OF THE HARD SPHERES BBGKY HIERARCHY

Introduction

An alternative approach to the study of the kinetic theory of fluctuations in low density gases is based on the derivation of hierarchies of equations for equal time and multitime reduced distribution functions. These equations are obtained from the Liouville equation and are formally identical to the equations of the BBGKY hierarchy. The availability of the density as an expansion parameter provides then the possibility of performing controlled approximations to obtain closed equations for the correlation functions.

Several authors³⁴⁻³⁷ have adopted this approach to formulate a description of nonequilibrium phase space fluctuations. In particular Ernst and Cohen³⁷ have treated the case of a gas of hard spheres by using the method of the nonequilibrium cluster expansion to derive kinetic equations for multitime and equal time correlation functions. This amounts to performing an expansion in powers of $n\sigma^3$ (where n is the number density and σ is the force range), selecting, at each order, only collisions involving a limited number of particles. The lower order terms in a cluster expansion describe correlations over distances of the order of the force range, σ . This constitutes an adequate approximation for the two-particle distribution function when closing the first equation of the hierarchy,⁵ since the presence of the force on the right hand side of the equation restricts the integration to interparticle

distances smaller than the force range. The resulting kinetic equation describes the behavior of the one-particle distribution function over space and time scales as small as σ and the collision time τ_c^* , respectively.

However the higher order distribution functions are expected to present appreciable variations also over scales of the order of the mean free path λ and the mean free time t_f between collisions, in a low density gas much larger than σ and τ_c . In other words additional correlations among the particles in the gas are important after the particles have undergone an appreciable number of collisions. The mean free path and the mean free time are the two characteristic scales in the problem. The kinetic equations for higher order distribution functions of interest here describe variations over lengths larger than or of the order of λ and t_f .

In particular, the BBGKY hierarchy for a gas of hard spheres is considered here. The choice of the hard sphere potential simplifies the treatment, because the collision time is zero. At the end of this Appendix it will be indicated how the results for a continuous potential can be recovered by identifying the appropriate collision operator.

When the s -th equation of the hard spheres hierarchy is scaled according to the two characteristic lengths of the problem, λ and t_f , the natural expansion parameter in the equation is identified with $\alpha = (n\lambda^3)^{-1}$. The condition $\alpha \ll 1$ represents a gas at low density in the usual sense (i.e. with $n\sigma^3 \ll 1$, since $\alpha \approx (n\sigma^3)^2$), but with a large

*The collision time τ_c is defined as $\tau_c = \sigma/v_0$, where v_0 is the thermal speed. For continuous-potential it represents the duration of a collision, or interaction time. In the case of the hard sphere potential this identification is not possible, since the interaction time is zero, but the definition of τ_c used here is still meaningful.

number of particles in a volume of the linear size of a mean free path. Only when the latter condition is satisfied, will the collisions have the effect of correlating different particles over distances of the order of λ . By expanding in powers of α the s -th equation of the hierarchy, a systematic approximation for the s -particle distribution function in terms of one-, two-, ..., etc. particle distribution functions is obtained. By imposing the requirement that this approximated form constitutes, to each order in α , a solution to the entire hierarchy, kinetic equations for the lower order correlation functions are obtained.

In particular kinetic equations for the second order two-time and equal time correlation functions are explicitly derived here and are found to be in agreement with those obtained in Ref. 37 by the cluster expansion method. However, the present formulation clarifies the approximations introduced and provides a systematic prescription to derive kinetic equations for higher order correlations.

Finally, the results also agree with those derived in Chapter IV by applying the generating functional method. The advantage of the latter method is evident, since there all the desired information can be derived by a single kinetic equation.

BBGKY Hierarchy for Hard Spheres

The dynamics of a system of particles interacting via a discontinuous potential is difficult to describe, e.g. in terms of Newton's equations of motion, since the force is infinite at the points of discontinuity of the potential. To circumvent this problem a formulation

of the dynamics which avoids explicit dependence on the force is required.

Let $\hat{A}(x_1, \dots, x_N)$ be an arbitrary N-particle phase function. The time development operator is defined by

$$\begin{aligned} \hat{A}(x_1, \dots, x_N, \pm t) &\equiv \hat{A}(x_1(\pm t), \dots, x_N(\pm t)) \\ &\equiv e^{\pm t L} \hat{A}(x_1, \dots, x_N) , \end{aligned} \quad (D.1)$$

where $t > 0$. The Liouville operator L is the generator of time translations. For continuous potentials it is given by Eqs. (4.1-3), rewritten here for convenience,

$$L = \sum_{i=1}^N L_0(x_i) - \sum_{i < j=1}^N \theta(x_i, x_j) , \quad (D.2)$$

where

$$L_0(x_i) = \frac{\vec{p}_i \cdot \vec{\nabla}_{\vec{q}_i}}{m} , \quad (D.3)$$

and

$$\theta(x_i, x_j) = - \vec{F}_{ij} \cdot \left(\vec{\nabla}_{\vec{p}_i} - \vec{\nabla}_{\vec{p}_j} \right) . \quad (D.4)$$

Here \vec{F}_{ij} is the force on the i -th particle due to the interaction with the j -th particle, $\vec{F}_{ij} = -\vec{\nabla}_{\vec{q}_i} V(r_{ij})$, where $V(r_{ij})$, with $r_{ij} \equiv |\vec{q}_i - \vec{q}_j|$, is the corresponding potential. To find the form of L when the potential has discontinuities, the hard sphere potential is considered as the limit of a piecewise continuous potential, defined as

$$V_{\varepsilon}(r_{ij}, V_0) = \begin{cases} V_0 & \text{for } r_{ij} < \sigma - \frac{\varepsilon}{2} \\ \frac{V_0}{\varepsilon} (\sigma + \frac{\varepsilon}{2} - r_{ij}) & \text{for } \sigma - \frac{\varepsilon}{2} \leq r_{ij} \leq \sigma + \frac{\varepsilon}{2} \\ 0 & \text{for } r_{ij} > \sigma + \frac{\varepsilon}{2} \end{cases} \quad (\text{D.5})$$

From Eq. (D.5) it follows that

$$V_{\text{HS}}(r_{ij}) = \lim_{V_0 \rightarrow \infty} \lim_{\varepsilon \rightarrow 0} V_{\varepsilon}(r_{ij}, V_0), \quad (\text{D.6})$$

where the limits have to be taken in the order indicated. In the following, to simplify the notation, the dependence on the parameter V_0 in the potential defined in Eq. (D.5) will be omitted.

The generator of time translations for discontinuous potentials, L_{\pm} (the + and - sign refers respectively to forward and backward streaming), may be defined from Eq. (D.1) as

$$\begin{aligned} L_{\pm} \hat{A}(x_1, \dots, x_N) &= \pm \lim_{t \rightarrow 0^+} \lim_{\substack{\varepsilon \rightarrow 0 \\ V_0 \rightarrow \infty}} \frac{\partial}{\partial t} \hat{A}(x_1, \dots, x_N, \pm t) \\ &= \lim_{t \rightarrow 0^+} \lim_{\substack{\varepsilon \rightarrow 0 \\ V_0 \rightarrow \infty}} L(x_1, \dots, x_N) e^{\pm t L(x_1, \dots, x_N)} \hat{A}(x_1, \dots, x_N), \end{aligned} \quad (\text{D.7})$$

or, formally,

$$L_{\pm} = \lim_{t \rightarrow 0^+} \lim_{\substack{\varepsilon \rightarrow 0 \\ V_0 \rightarrow \infty}} L(\varepsilon) e^{\pm t L(\varepsilon)}. \quad (\text{D.8})$$

The ε -dependence enters in the Liouville operator through the potential defined in Eq. (D.5) and has been indicated explicitly in Eq. (D.8).

The limits in Eq. (D.8) have to be taken in the order indicated, i.e. the exponential cannot be simply set equal to one because the $\varepsilon \rightarrow 0^+$ limit generates singularities in $L(\varepsilon)$.

The time evolution of a dynamical variable is then given by

$$\hat{A}(x_1, \dots, x_N, \pm t) = S_{\pm t}^{\pm}(x_1, \dots, x_N) \hat{A}(x_1, \dots, x_N) , \quad (\text{D.9})$$

where the N-particle streaming operator $S_{\pm t}^{\pm}$ has been defined as

$$S_{\pm t}^{\pm}(x_1, \dots, x_N) = \exp\{\pm t L_{\pm}(x_1, \dots, x_N)\} . \quad (\text{D.10})$$

The scalar product of two N-particle phase variables \hat{A} and \hat{B} is defined as their equilibrium average,

$$\langle \hat{A} \hat{B} \rangle_0 = \int d\Gamma \rho_0(\Gamma) \hat{A}(\Gamma) \hat{B}(\Gamma) , \quad (\text{D.11})$$

where $\rho_0(\Gamma)$ is the N-particle equilibrium distribution function. The adjoint, K^\dagger , of an operator K is defined by

$$\int d\Gamma \rho_0(\Gamma) \hat{B}(\Gamma) [K \hat{A}(\Gamma)] = \int d\Gamma [K^\dagger \rho_0(\Gamma) \hat{B}(\Gamma)] \hat{A}(\Gamma) . \quad (\text{D.12})$$

In particular, setting

$$L_{\pm}^\dagger = -\overline{L_{\mp}} , \quad (\text{D.13})$$

the adjoints of the streaming operators are

$$[s_t^+]^\dagger = \bar{s}_{-t}^-, \quad 161$$

$$[s_{-t}^-]^\dagger = \bar{s}_t^+, \quad (D.14)$$

where

$$\bar{s}_{\pm t}^\pm(x_1, \dots, x_N) = \exp\{\pm t \bar{L}_\pm(x_1, \dots, x_N)\} . \quad (D.15)$$

The barred streaming operators are explicitly defined by

$$\int d\Gamma \rho_0(\Gamma) \hat{B}(\Gamma) [s_{\pm t}^\pm \hat{A}(\Gamma)] = \int d\Gamma [\bar{s}_{\pm t}^\mp \rho_0(\Gamma) \hat{B}(\Gamma)] \hat{A}(\Gamma) . \quad (D.16)$$

They translate in time a phase space point according to

$$\bar{s}_{\pm t}^\mp x_i = x_i(\pm t) .$$

The definition of the adjoint given in Eq. (D.12) is the convenient one for the purpose of the present calculation. However it implies that an operator and its adjoint have different domains and it requires special attention when dealing with the streaming operators for hard spheres. As extensively discussed in Ref. 62, hard sphere molecules are not allowed to overlap and the streaming operator is not defined for overlapping configurations. The distribution function $\rho_0(\Gamma)$ gives a vanishing weight to initially overlapping configurations, but the combination $\bar{s}_{\pm t}^\mp \rho_0$ is not well defined. The derivation presented here, however, deals with a potential with a finite height V_0 , and therefore does not present this problem. Care will be required when the limit $V_0 \rightarrow \infty$ is taken. The barred pseudo-Liouville operators \bar{L}_\pm are formally

defined in a way analogous to Eq. (D.8) as

$$\bar{L}_{\mp} = \lim_{t \rightarrow 0^+} \lim_{\substack{\varepsilon \rightarrow 0 \\ V_0 \rightarrow \infty}} L(\varepsilon) e^{\mp t L(\varepsilon)}, \quad (D.17)$$

where the operator in Eq. (D.17) is understood to act on the distribution function, as in Eq. (D.12).

By using Eq. (D.2), Eq. (D.17) can be rewritten explicitly as

$$\bar{L}_{\mp} = \lim_{t \rightarrow 0^+} \lim_{\substack{\varepsilon \rightarrow 0 \\ V_0 \rightarrow \infty}} \left\{ \sum_{i=1}^N L_0(x_i) e^{\mp t L(\varepsilon)} - \sum_{i < j=1}^N \theta(x_i, x_j; \varepsilon) e^{\mp t L(\varepsilon)} \right\}. \quad (D.18)$$

In the limit $\varepsilon \rightarrow 0$ the streaming operator $e^{\mp t L(\varepsilon)}$ generates a discontinuous function of the momenta of the particles, but a continuous function of their positions. The limits can therefore be taken immediately in the first term on the right hand side of Eq. (D.18), since the operator $L_0(x)$ only contains derivatives with respect to the space variables. The second term, however, involves gradients with respect to the momenta and generates singularities in the regions common to both \vec{F}_{ij} and $\exp[\mp t L(\varepsilon)]$. Equation (D.18) becomes then

$$\begin{aligned} \bar{L}_{\mp} &= \left\{ \sum_{i=1}^N L_0(x_i) - \lim_{t \rightarrow 0^+} \lim_{\substack{\varepsilon \rightarrow 0 \\ V_0 \rightarrow \infty}} \theta(x_i, x_j; \varepsilon) e^{\mp t L(x_i, x_j; \varepsilon)} \right\} \\ &\equiv \left\{ \sum_{i=1}^N L_0(x_i) \mp \sum_{i < j=1}^N \bar{T}_{\mp}(x_i, x_j) \right\}, \end{aligned} \quad (D.19)$$

where,

$$\bar{T}_{\mp}(x_i, x_j) = \pm \lim_{t \rightarrow 0^+} \lim_{\substack{\varepsilon \rightarrow 0 \\ V_0 \rightarrow \infty}} \theta(x_i, x_j; \varepsilon) e^{\mp t L(x_i, x_j; \varepsilon)}, \quad (D.20)$$

and $L(x_i, x_j)$ is the two-particle Liouville operator. Therefore the effective interactions for discontinuous potentials are still pairwise additive. This conclusion can be reached by performing a binary collision expansion of the corresponding N -particle scattering matrix.

In order to determine the specific form of the collision operator defined in Eq. (D.20) a simple two-particle problem can therefore be considered. The scalar product of two real phase functions $\hat{A}(x_1, x_2)$ and $\hat{B}(x_1, x_2)$ (assumed for later convenience to be continuous functions of $|\vec{r}_{12}|$) in the two-particle phase space is defined, in analogy with Eq. (D.11), as

$$\langle \hat{A} | \hat{B} \rangle_2 \equiv \int dx_1 dx_2 \rho_0(x_1, x_2) \hat{A}(x_1, x_2) \hat{B}(x_1, x_2) , \quad (\text{D.21})$$

where

$$\rho_0(x_1, x_2) = f_0(p_1) f_0(p_2) e^{-\beta V(r)} . \quad (\text{D.22})$$

Here $f_0(p)$ is the Maxwell-Boltzmann distribution and $r \equiv r_{12} = |\vec{q}_1 - \vec{q}_2|$.

The operators \overline{T}_\mp are defined by their action on the combination $\rho_0 \hat{B}$, i.e.

$$\begin{aligned} & \int dx_1 dx_2 \hat{A} \overline{T}_\mp \hat{B} \rho_0(x_1, x_2) \\ &= \pm \lim_{t \rightarrow 0^+} \lim_{\varepsilon \rightarrow 0} \int dx_1 dx_2 \hat{A}(x_1, x_2) \theta(x_1, x_2; \varepsilon) e^{\mp t L(x_1, x_2; \varepsilon)} \hat{B}(x_1, x_2) \\ & \quad \quad \quad V_0 \rightarrow \infty . \\ & \equiv \pm \lim_{t \rightarrow 0^+} \lim_{\varepsilon \rightarrow 0} M_\mp(t, \varepsilon) . \end{aligned} \quad (\text{D.23})$$

To evaluate the matrix element defined in Eq. (D.23), the case of back-

ward streaming will be considered explicitly. By introducing center of mass and relative coordinates and momenta,

$$\begin{aligned}\vec{r} &= \vec{q}_1 - \vec{q}_2 & \vec{g} &= \vec{p}_1 - \vec{p}_2 \\ \vec{R} &= \frac{\vec{q}_1 + \vec{q}_2}{2} & \vec{G} &= \frac{\vec{p}_1 + \vec{p}_2}{2}\end{aligned}$$

the matrix element M_- can be written as

$$\begin{aligned}M_-(t, \varepsilon) &= \int d\vec{R}d\vec{r} \int d\vec{G}d\vec{g} \hat{A}(x_1, x_2) [\vec{\nabla}_{\vec{r}} V_{\varepsilon}(r)] \cdot \vec{\nabla}_{\vec{g}} e^{-tL(x_1, x_2; \varepsilon)} \\ &\quad \times \rho_0(x_1, x_2; \varepsilon) \hat{B}(x_1, x_2),\end{aligned}\tag{D.24}$$

where the two-particle Liouville operator is intended as a function of relative and center of mass coordinates,

$$L(x_1, x_2; \varepsilon) = \frac{\vec{G} \cdot \vec{\nabla}_{\vec{R}}}{m} + \frac{\vec{g} \cdot \vec{\nabla}_{\vec{r}}}{m} - [\vec{\nabla}_{\vec{r}} V_{\varepsilon}(r)] \cdot \vec{\nabla}_{\vec{g}}.\tag{D.25}$$

The gradient of the potential V_{ε} is nonzero only in a small spherical region $\sum_{\varepsilon} = \{\sigma - \varepsilon < r < \sigma + \varepsilon\}$. The \vec{r} -integration in Eq. (D.24) can therefore be restricted to this region. Furthermore using the identity,

$$\theta(x_1, x_2) e^{-tL(x_1, x_2)} = \left(\frac{\partial}{\partial t} + L_0(x_1) + L_0(x_2) \right) e^{-tL(x_1, x_2)},\tag{D.26}$$

Eq. (D.24) can be rewritten as

$$M_-(t, \varepsilon) = \int d\vec{R} d\vec{G} d\vec{g} f_o(p_1) f_o(p_2) \int_{\Sigma_\varepsilon} d\vec{r} \hat{A}(x_1, x_2) \left\{ \left[\frac{\partial}{\partial t} + L_o(x_1) + L_o(x_2) \right] \right. \\ \left. \times e^{-tL(x_1, x_2; \varepsilon)} e^{-\beta V_\varepsilon(r)} \hat{B}(x_1, x_2) \right\} . \quad (D.27)$$

Let \hat{r} be a unit vector in the direction of \vec{r} and $d\Omega = \sin\theta d\theta d\phi$ denote the angular part of the \vec{r} -integration. Since $r^2 A$ is a continuous function of r , Eq. (D.27) can be approximated by

$$M_-(t, \varepsilon) = \int d\vec{R} d\vec{G} d\vec{g} f_o(p_1) f_o(p_2) \int d\Omega \sigma^2 \hat{A}(\vec{R}, \sigma\hat{r}; \vec{G}, \vec{g}) \\ \times \left\{ \int_{\sigma-\varepsilon}^{\sigma+\varepsilon} dr \frac{\vec{g} \cdot \hat{r}}{m} \frac{d}{dr} \left[e^{-tL(x_1, x_2; \varepsilon)} e^{-\beta V_\varepsilon(r)} \hat{B}(x_1, x_2) \right] \right. \\ \left. + \left[\frac{\partial}{\partial t} + \frac{\vec{G} \cdot \vec{V}_{\vec{R}}}{m} \right] \int_{\sigma-\varepsilon}^{\sigma+\varepsilon} dr e^{-tL(x_1, x_2; \varepsilon)} e^{-\beta V_\varepsilon(r)} \hat{B}(x_1, x_2) \right\} , \quad (D.28)$$

where \vec{g} has been chosen in the z direction. The last term in Eq. (D.28) vanishes in the limit $\varepsilon \rightarrow 0$ because the integrand in the r -integration is finite. The other term on the right hand side will in general give a nonzero contribution because singularities may arise from the derivative of the discontinuous potential. Carrying out the r -integration, Eq. (D.28) becomes then

$$\lim M_-(t, \varepsilon) = \int d\vec{R} d\vec{G} d\vec{g} f_o(p_1) f_o(p_2) \int d\Omega \sigma^2 \hat{A}(\vec{R}, \sigma\hat{r}; \vec{G}, \vec{g}) \frac{\hat{r} \cdot \vec{g}}{m} \\ \times \left\{ \lim_{\sigma \rightarrow 0^+} \left[e^{-\beta V_\varepsilon} e^{-tL} \hat{B} \right]_{\sigma+\varepsilon} - \lim_{\sigma \rightarrow 0^-} \left[e^{-\beta V_\varepsilon} e^{-tL} \hat{B} \right]_{\sigma-\varepsilon} \right\} , \quad (D.29)$$

where "lim" indicates the three limits, as in Eq. (D.23), and

$[f]_{\sigma \pm \epsilon} \equiv f(r=\sigma \pm \epsilon)$. The second term on the right hand side of Eq. (D.29) vanishes in the limits indicated, since $\lim_{\sigma-\epsilon} [e^{-\beta V_{\epsilon}}] = 0$. The scattered momenta for collisions originated at $\sigma + \epsilon$ can be evaluated explicitly by distinguishing the cases of particle initially on the positive ($\hat{r} \cdot \vec{g} > 0$) or negative ($\hat{r} \cdot \vec{g} < 0$) hemisphere, with the result,

$$\lim_{\sigma+\epsilon} [e^{-\beta V_{\epsilon}} e^{-tL} \hat{B}]_{(\hat{\sigma} \cdot \vec{g}) > 0} = e^{-\beta V_{HS}(\sigma_+)} \hat{B}(\vec{R}, \hat{\sigma}; \vec{G}, \vec{g}'), \quad (D.30)$$

$$\lim_{\sigma+\epsilon} [e^{-\beta V_{\epsilon}} e^{-tL} \hat{B}]_{(\hat{\sigma} \cdot \vec{g}) < 0} = e^{-\beta V_{HS}(\sigma_+)} \hat{B}(\vec{R}, \hat{\sigma}; \vec{G}, \vec{g}), \quad (D.31)$$

where \vec{g}' is the scattered relative velocity in a binary hard spheres collision,

$$\begin{aligned} \vec{g}' &= \vec{g} - 2\hat{r}(\hat{r} \cdot \vec{g}) \\ &\equiv \hat{b}_{12} \vec{g}. \end{aligned} \quad (D.32)$$

By inserting these results into Eq. (D.29) and noting that $\exp[-\beta V_{HS}(\sigma_+)] = 1$, Eq. (D.29) becomes

$$\begin{aligned} \lim M_-(t, \epsilon) &= \int d\vec{R} d\vec{G} d\vec{g} \int d\Omega \hat{A}(\vec{R}, \vec{G}; \hat{\sigma}, \vec{g}) \sigma^2 \frac{\hat{r} \cdot \vec{g}}{m} [\theta(\hat{r} \cdot \vec{g}) \hat{b}_{12} \\ &\quad - \theta(-\hat{r} \cdot \vec{g})] \rho_0^{HS}(x_1, x_2) \hat{B}(\vec{R}, \vec{G}; \hat{\sigma}, \vec{g}), \end{aligned} \quad (D.33)$$

where $\theta(x)$ is the Heaviside step function. Finally, by performing a change of variable in the angular integration over the negative hemisphere and reinserting the r -integration through the introduction of

δ -functions, Eq. (D.33) can be written

$$\begin{aligned} \lim M_-(t, \varepsilon) = & \int dx_1 dx_2 \hat{A}(x_1, x_2) \left\{ \sigma^2 \frac{\hat{r} \cdot \hat{g}}{m} \theta(\hat{r} \cdot \hat{g}) [\delta(r-\sigma) \hat{b}_{12} \right. \\ & \left. - \delta(r+\sigma)] \rho_o^{\text{HS}}(x_1, x_2) \hat{B}(x_1, x_2) \right\} . \end{aligned} \quad (\text{D.34})$$

Comparison with Eq. (D.23) gives

$$\begin{aligned} \bar{T}_-(x_1, x_2) = & \sigma^2 \frac{\hat{r} \cdot \hat{g}}{m} \theta(\hat{r} \cdot \hat{g}) [\delta(r-\sigma) \hat{b}_{12} - \delta(r+\sigma)] \\ = & \sigma^2 \int_{(\hat{\sigma} \cdot \hat{g}) > 0} d\hat{\sigma} \frac{\hat{\sigma} \cdot \hat{g}}{m} [\delta(\vec{r} - \sigma \hat{\sigma}) \hat{b}_{12} - \delta(\vec{r} + \sigma \hat{\sigma})] . \end{aligned} \quad (\text{D.35})$$

Here $d\hat{\sigma} = \sin\theta d\theta d\phi$, where θ is the scattering angle in the binary collision and ϕ is the azimuthal angle which determines the plane of the scattering. The spatial δ -functions in Eq. (D.35) take account of the fact that a collision takes place only where the particles are at contact.

A similar derivation can be carried out for the operator \bar{T}_+ , with the result,

$$\bar{T}_+(x_1, x_2) = - \int_{(\hat{\sigma} \cdot \hat{g}) < 0} d\hat{\sigma} \frac{\hat{\sigma} \cdot \hat{g}}{m} [\delta(\vec{r} - \sigma \hat{\sigma}) \hat{b}_{12} - \delta(\vec{r} + \sigma \hat{\sigma})] . \quad (\text{D.36})$$

The barred N-particle pseudo-Liouville operators are then given by Eq. (D.19) with the form (D.35) or (D.36) for the binary collision operators.

An expression for the unbarred pseudo-Liouville operators defined in Eq. (D.8) can now be obtained by using the definition (D.13). It is

immediately shown that

$$[L_0(x_1) + L_0(x_2)]^\dagger = -[L_0(x_1) + L_0(x_2)] . \quad (\text{D.37})$$

Furthermore, making use of the invariance of the scattering cross section for direct and restituting collisions, the adjoints of the collision operators are found to be

$$[\overline{T}_\mp]^\dagger \equiv T_\pm , \quad (\text{D.38})$$

where

$$T_\pm(x_i, x_j) = \mp \sigma^2 \int d\hat{\sigma} \theta(\mp \hat{\sigma} \cdot \vec{g}_{ij}) \frac{\hat{\sigma} \cdot \vec{g}_{ij}}{m} \delta(\vec{r}_{ij} - \sigma \hat{\sigma}) [\hat{b}_{ij} - 1] , \quad (\text{D.39})$$

and $\vec{g}_{ij} = \vec{p}_i - \vec{p}_j$. The operators L_\pm are then given by

$$L_\pm(x_1, \dots, x_N) = \sum_{i=1}^N L_0(x_i) \pm \sum_{i < j=1}^N T_\pm(x_i, x_j) . \quad (\text{D.40})$$

An alternative definition of the adjoint of an operator K with respect to the scalar product defined in Eq. (D.11), more appropriate when dealing with hard spheres, is given by

$$\int d\Gamma \rho_0(\Gamma) \hat{B}(\Gamma) [K \hat{A}(\Gamma)] \equiv \int d\Gamma \rho_0(\Gamma) [K^\ddagger \hat{B}(\Gamma)] \hat{A}(\Gamma) , \quad (\text{D.41})$$

or,

$$\langle \hat{B} | K \hat{A} \rangle_0 = \langle [K^\ddagger \hat{B}] | \hat{A} \rangle_0 . \quad (\text{D.42})$$

Since the collision operators do not act on the spatial variables and

the kinetic energy of a pair is conserved in a binary collision, it immediately follows that

$$(\bar{T}_+)^{\ddagger} = (\bar{T}_+)^{\dagger} = T_{\pm} . \quad (\text{D.43})$$

The adjoint of the free streaming part however is now given by

$$[L_0(x_i) + L_0(x_j)]^{\ddagger} = -[L_0(x_i) + L_0(x_j)] - \frac{\hat{r}_{ij} \cdot \hat{g}_{ij}}{m} \delta(r_{ij} - \sigma) . \quad (\text{D.44})$$

By combining these results it immediately follows that

$$(L_+)^{\ddagger} = -L_- , \quad (\text{D.45})$$

and consequently, for $t > 0$,

$$(S_t^+)^{\ddagger} = S_{-t}^- . \quad (\text{D.46})$$

The last property implies the time reversal invariance of the equilibrium average, since

$$\langle \hat{A} [S_t^+ \hat{B}] \rangle_0 = \langle [S_{-t}^- \hat{A}] \hat{B} \rangle_0 . \quad (\text{D.47})$$

From the definition of the barred streaming operators it follows that they govern the time evolution of the distribution function of the system. The Liouville equation for the nonequilibrium distribution function, $\rho_N(x_1, \dots, x_N, t)$ of a hard sphere gas is then given by

$$\left\{ \frac{\partial}{\partial t} + \bar{L}_{\pm}(x_1, \dots, x_N) \right\} \rho_N(x_1, \dots, x_N, t) = 0, \quad (\text{D.48})$$

where the - or + sign has to be chosen depending on whether $t > 0$ or $t < 0$, respectively.

A hierarchy of equations for the one-time reduced distribution functions, defined in Eqs. (2.25), can be derived by performing successive partial averages over the Liouville equation (D.48). However, when considering a gas of hard spheres, a more convenient method consists of first deriving a hierarchy of equations for the phase space densities \hat{f}_s , defined in Eqs. (2.24). The derivation presented here follows closely Ref. 37. Equations for the nonequilibrium distribution functions, given by

$$n^s f_s(x_1, \dots, x_s, t) = \langle \hat{f}_s(x_1, \dots, x_s, t) \rangle, \quad (\text{D.49})$$

are then obtained by averaging this set of microscopic equations. Here, as in Section II.2, the same notation is used for both the phase space coordinates and the field coordinates.

The time evolution of the phase-space densities is governed by the pseudo-streaming operator defined in Eq. (D.10), i.e.,

$$\hat{f}_s(x_1, \dots, x_s, t) = e^{tL_{\pm}} \hat{f}_s(x_1, \dots, x_s), \quad (\text{D.50})$$

where the + or - sign has to be chosen depending on whether $t > 0$ or $t < 0$. By differentiating Eq. (D.50) with respect to time for $s=1,2,\dots$, a hierarchy of equations for the functions \hat{f}_s is obtained. The s -th equation of the hierarchy is given by

$$\begin{aligned}
& \left\{ \frac{\partial}{\partial t} + \overline{T}_{\mp}(x_1, \dots, x_s) \right\} \hat{f}_s(x_1, \dots, x_s, t) = \\
& = \pm \sum_{i=1}^s \int dx_{s+1} \overline{T}_{\mp}(x_i, x_{s+1}) \hat{f}_{s+1}(x_1, \dots, x_{s+1}, t) , \quad (D.51)
\end{aligned}$$

where the upper and lower sign has to be chosen for $t > 0$ and $t < 0$ respectively. To derive Eq. (D.51) the presence of δ -functions in the definition of the phase space densities has been used, together with the property of the collision operators given in Eq. (D.43), to transform the operators in the equation to operators acting on the field variables instead of the phase space variables. The hierarchy given by Eq.(D.51) for $s=1,2,3,\dots$ is known as the Klimontovich hierarchy. In particular, since

$$\hat{f}_2(x_1, x_2, t) = \hat{f}_1(x_1, t) \hat{f}_1(x_2, t) - \delta(x_1 - x_2) \hat{f}_1(x_1, t) , \quad (D.52)$$

the first equation of the hierarchy can be written as a closed nonlinear equation for the one-particle phase space density, the Klimontovich equation, given by

$$\begin{aligned}
\left\{ \frac{\partial}{\partial t} + L_0(x_1) \right\} \hat{f}_1(x_1, t) = \pm \int dx_2 \overline{T}_{\mp}(x_1, x_2) [\hat{f}_1(x_1, t) \hat{f}_1(x_2, t) \\
- \delta(x_1 - x_2) \hat{f}_1(x_1, t)] . \quad (D.53)
\end{aligned}$$

The BBGKY hierarchy for the one-time reduced distribution functions f_s is immediately obtained by averaging Eq. (D.51) over the initial non-equilibrium ensemble and by using Eq. (D.49). The s -th equation of the BBGKY hierarchy for hard spheres is given by

$$\begin{aligned} & \left\{ \frac{\partial}{\partial t} + \bar{L}_+(x_1, \dots, x_s) \right\} f_s(x_1, \dots, x_s, t) \\ &= \pm n \sum_{i=1}^s \int dx_{s+1} \bar{T}_+(x_i, x_{s+1}) f_{s+1}(x_1, \dots, x_{s+1}, t), \end{aligned} \quad (D.54)$$

where the sign has to be chosen as indicated before.

The introduction of the phase space densities allows the definition of a set of multitime distribution functions as

$$n^s f(x_1, t_1 | \dots | x_s, t_s) = \langle \prod_{k=1}^s \hat{f}_1(x_k, t_k) \rangle. \quad (D.55)$$

Hierarchies of equations for the multitime distribution functions can again be obtained from the Klimontovich hierarchy. In particular the case of the two-time distribution is considered. For $s=2$ Eq. (D.55) can be rewritten explicitly in the form,

$$n^2 f_{1,1}(x_1, t | x'_1, t') = \sum_{N=0}^{\infty} \int d\Gamma \rho_N(0) e^{t'L_{\pm}} \hat{f}_1(x'_1, 0) e^{(t-t')L_{\pm}} \hat{f}_1(x_1, 0), \quad (D.56)$$

where the + or - sign has to be chosen in L_{\pm} depending on whether the corresponding time difference is positive or negative.

A hierarchy of equations for the two-time distribution functions is then obtained by the Klimontovich hierarchy for $t \rightarrow t-t'$, with the result,

$$\begin{aligned} & \left\{ \frac{\partial}{\partial t} + \bar{L}_-(x_1, \dots, x_s) \right\} f_{s,1}(x_1, \dots, x_s, t | x'_1, t') \\ &= \pm n \sum_{i=1}^s \int dx_{s+1} \bar{T}_-(x_i, x_{s+1}) f_{s+1,1}(x_1, \dots, x_{s+1}, t | x'_1, t'), \end{aligned} \quad (D.57)$$

for $s = 1, 2, 3, \dots$, where

$$n^{s+1} f_{s,1}^{s+1}(x_1, \dots, x_s, t | x'_1, t') = \langle \hat{f}_s(x_1, \dots, x_s, t) \hat{f}_1(x'_1, t') \rangle, \quad (\text{D.58})$$

and the upper or lower sign refers to $t > t'$ or $t < t'$ respectively.

Hierarchies for three or more times distribution functions are derived in a similar way.

Low Density Expansion

In the preceding section the dynamics of phase space fluctuations in a nonequilibrium gas is described in terms of infinite hierarchies of coupled equations. In the limit of low density approximate closed equations can be derived for the lower order correlation functions by performing an expansion in powers of a properly chosen reduced density.

A standard way of identifying the appropriate expansion parameter consists of scaling the equations according to the length and time scales characteristic of the problem. The one-time BBGKY hierarchy is first considered, as given by Eq. (D.54) for $s = 1, 2, \dots$. For simplicity, the case of forward streaming ($t > 0$) is analyzed. Reduced variables, scaled according to the characteristic length and time scales of the problem r_0 and t_0 , are defined as

$$r^* = r/r_0, \quad t^* = t/t_0, \quad p^* = p/mv_0, \quad (\text{D.59})$$

where v_0 is the thermal velocity of the particles and $t_0 = r_0/v_0$. A dimensionless form of the binary collision operator is also introduced,

$$\bar{T}_{-}^{*}(x_i, x_j) = \frac{r_o^3}{\sigma^2 v_o \pi \sqrt{2}} \bar{T}_{-}(x_i, x_j) , \quad (D.60)$$

where

$$\bar{T}_{-}^{*}(x_i, x_j) = \frac{1}{\pi \sqrt{2}} \int_{(\sigma \cdot \vec{g}_{ij}) < 0} \left(\frac{\hat{\sigma} \cdot \vec{g}_{ij}}{m} \right) [\delta(\vec{r}_{ij}^{*} - \hat{\sigma} K) \hat{b}_{ij}^{*} - \delta(\vec{r}_{ij}^{*} + \hat{\sigma} K)] . \quad (D.61)$$

The operator \hat{b}_{ij}^{*} acts on the reduced momenta and $K = \sigma/r_o$. With the chosen normalization, the distribution function f_s has the dimension of $(mv_o)^{-3s}$. A dimensionless distribution function can therefore be defined as

$$f_s^{*}(x_1^{*}, \dots, x_s^{*}, t^{*}) \equiv (mv_o)^{3s} f_s(r_o \vec{q}_1^{*}, mv_o \vec{p}_1^{*}, \dots, r_o \vec{q}_s^{*}, mv_o \vec{p}_s^{*}, t_o t^{*}) , \quad (D.62)$$

where $x_i^{*} = (\vec{q}_i^{*}, \vec{p}_i^{*})$.

By introducing the above definitions in Eq. (D.54) the following scaled form of the s-th equation of the hierarchy is obtained

$$\begin{aligned} \left\{ \frac{\partial}{\partial t} + \sum_{i=1}^s L_o(x_i) \right\} f_s^{*}(x_1, \dots, x_s, t) - \alpha \sum_{i < j=1}^s \bar{T}_{-}^{*}(x_i, x_j) f_s^{*}(x_1, \dots, x_s, t) \\ = \beta \sum_{i=1}^s \int dx_{s+1} \bar{T}_{-}^{*}(x_i, x_{s+1}) f_{s+1}^{*}(x_1, \dots, x_{s+1}, t) , \quad (D.63) \end{aligned}$$

where, to simplify the notation, the stars indicating the reduced variables have been omitted. The parameters α and β are defined as

$$\alpha = \pi \sqrt{2} \left(\frac{\sigma}{r_o} \right)^2 , \quad (D.64)$$

$$\beta = \pi\sqrt{2} n\sigma^2 r_0 . \quad (\text{D.65})$$

The chosen scaling parameters r_0 and t_0 must be of the order of the lengths over which the properties to be described have appreciable variations. For $r_0 = \sigma$ and $t_0 = \tau_c$, the parameters α and β become

$$\alpha = \pi\sqrt{2} , \quad \beta = \pi\sqrt{2}(n\sigma^3) . \quad (\text{D.66})$$

The reduced density $n\sigma^3$ is the appropriate expansion parameter when deriving kinetic equations to describe variations over space and time scales of the order of σ and τ_c . However, as discussed in the introduction, the interest here is not in two-particle or higher order correlation functions that change appreciably over such short scales. By choosing instead $r_0 = \lambda$ and $t_0 = t_f = \lambda/v_0$, where the mean free path λ is given by

$$\lambda = [\pi\sqrt{2} n\sigma^2]^{-1} , \quad (\text{D.67})$$

the parameters α and β become

$$\alpha = (n\lambda^3)^{-1} , \quad \beta = 1 . \quad (\text{D.68})$$

This choice is appropriate to derive kinetic equations describing the desired space and time correlations in a low density gas. The condition $\alpha \ll 1$ represents a low density gas outside of the Knudsen regime (the parameter K in (D.61) is now given by $K = \sigma/\lambda$, i.e. is identified with the Knudsen number).⁸ In this limit the particles

undergo several collisions over a length ℓ and a time t_f , resulting in nonvanishing correlations over such ranges. Kinetic equations for the two-particle and higher order correlation functions are then obtained by a perturbative solution of the s -th equation of the hierarchy, using α as the expansion parameter.

The s -particle distribution function is expanded in powers of α ,

$$f_s^*(x_1, \dots, x_s, t) = \sum_{n=0}^{\infty} \alpha^n f_s^{(n)}(x_1, \dots, x_s, t) . \quad (D.69)$$

By substituting Eq. (D.69) into Eq. (D.63) (with the choice of the parameters given in Eq. (D.68)), a set of coupled equations for $f_s^{(n)}$ is obtained. To zeroth order in α , the equation is given by

$$\left\{ \frac{\partial}{\partial t} + \sum_{i=1}^s L_0(x_i) \right\} f_s^{(0)}(x_1, \dots, x_s, t) - \sum_{i=1}^s \int dx_{s+1} \bar{T}_{-}^*(x_i, x_{s+1}) f_{s+1}^{(0)}(x_1, \dots, x_{s+1}, t) = 0 , \quad (D.70)$$

and to k -th order in α , with $k \geq 1$,

$$\begin{aligned} & \left\{ \frac{\partial}{\partial t} + \sum_{i=1}^s L_0(x_i) \right\} f_s^{(k)}(x_1, \dots, x_s, t) \\ & - \sum_{i=1}^s \int dx_{s+1} \bar{T}_{-}^*(x_i, x_{s+1}) f_{s+1}^{(k)}(x_1, \dots, x_{s+1}, t) \\ & = \sum_{i < j=1}^s \bar{T}_{-}^*(x_i, x_j) f_s^{(k-1)}(x_1, \dots, x_s, t) . \end{aligned} \quad (D.71)$$

The operators in the homogeneous equation for $f_s^{(0)}$ are sums of single particle operators. This suggests a solution in a factorized form,

$$f_s^{(0)}(x_1, \dots, x_s, t) = \prod_{i=1}^s f_1^{(0)}(x_i, t) . \quad (D.72)$$

Substitution of Eq. (D.72) in Eq. (D.70) shows that this form provides a solution to the entire hierarchy, to zeroth order in α , if $f_1^{(0)}(x, t)$ satisfies the equation,

$$\left\{ \frac{\partial}{\partial t} + L_0(x_1) \right\} f_1^{(0)}(x_1, t) = \int dx_2 \bar{T}_-^*(x_1, x_2) f_1^{(0)}(x_1, t) f_1^{(0)}(x_2, t) . \quad (D.73)$$

By translating Eq. (D.73) back into the original variables and by observing that, since the distances of interest are large compared to the force range, the difference in the positions of the colliding particles can be neglected and the binary collision operator can be approximated by a point operator,

$$\begin{aligned} \bar{T}_-(x_1, x_2) &\approx \delta(\vec{q}_1 - \vec{q}_2) T(\vec{p}_1, \vec{p}_2) \\ &= \delta(\vec{r}_{12}) \sigma^2 \int_{(\hat{\sigma} \cdot \vec{g}_{12}) > 0} d\hat{\sigma} \left(\frac{\hat{\sigma} \cdot \vec{g}_{12}}{m} \right) [\hat{b}_{12} - 1] , \end{aligned} \quad (D.74)$$

Eq. (D.73) is immediately recognized as the nonlinear Boltzmann equation for hard spheres.

The equation for the first order correction of f_s is obtained by setting $k=1$ in Eq. (D.71) and substituting the zeroth order solution in the right hand side, with the result,

$$\begin{aligned} &\left\{ \frac{\partial}{\partial t} + \sum_{i=1}^s L_0(x_i) \right\} f_s^{(1)}(x_1, \dots, x_s, t) \\ &- \sum_{i=1}^s \int dx_{s+1} \bar{T}_-^*(x_i, x_{s+1}) f_{s+1}^{(1)}(x_1, \dots, x_{s+1}, t) \\ &= \sum_{i < j=1}^s \left\{ \prod_{\substack{k=1 \\ k \neq i, j}}^s f_1^{(0)}(x_k, t) \right\} \bar{T}_-^*(x_i, x_j) f_1^{(0)}(x_i, t) f_1^{(0)}(x_j, t) . \end{aligned} \quad (D.75)$$

The form of Eq. (D.75) suggests the solution,

$$f_s^{(1)}(x_1, \dots, x_s, t) = \sum_{i=1}^s \prod_{\substack{j=1 \\ j \neq i}}^s f_1^{(0)}(x_j, t) f_1^{(1)}(x_i, t) \\ + \sum_{i < j=1}^s \prod_{\substack{k=1 \\ k \neq i, j}}^s f_1^{(0)}(x_k, t) g_2^{(1)}(x_i, x_j, t) . \quad (D.76)$$

Again, substitution of Eq. (D.76) in Eq. (D.75) shows that the trial form for $f_s^{(1)}$ is a solution of the entire hierarchy, to first order in α , if $f_1^{(0)}$ satisfies Eq. (D.73) and $f_1^{(1)}$ and $g_2^{(1)}$ are the solutions of the two coupled equations,

$$\left\{ \frac{\partial}{\partial t} + L^*(x_1, t) \right\} f_1^{(1)}(x_1, t) = \int dx_2 \bar{T}_-^*(x_1, x_2) g_2^{(1)}(x_1, x_2, t) \quad (D.77)$$

and

$$\left\{ \frac{\partial}{\partial t} + (1 + P_{12}) L^*(x_1, t) \right\} g_2^{(1)}(x_1, x_2, t) = \bar{T}_-^*(x_1, x_2) f_1^{(0)}(x_1, t) f_1^{(0)}(x_2, t), \quad (D.78)$$

where P_{ij} is a permutation operator which interchanges coordinates and momenta of the particles i and j . The operator $L^*(x_1, t)$ is defined as

$$L^*(x_1, t) = L_0(x_1) - \Lambda^*(x_1, t) , \quad (D.79)$$

with

$$\Lambda^*(x_1, t) = \int dx_3 \bar{T}_-^*(x_1, x_3) (1 + P_{13}) f_1^{(0)}(x_3, t) . \quad (D.80)$$

The two-particle function $g_2^{(1)}(x_1, x_2, t)$ can be identified with the first

order term in an expansion in powers of α of the two-particle cluster function,

$$g_2(x_1, x_2, t) = f_2(x_1, x_2, t) - f_1(x_1, t)f_1(x_2, t) . \quad (D.81)$$

In analogy with Eq. (D.62) a dimensionless form of the cluster function is introduced,

$$g_2^*(x_1^*, x_2^*, t^*) = (mv_0)^{-6s} g_2(r_0 mv_0 x_1^*, r_0 mv_0 x_2^*, t_0 t^*) . \quad (D.82)$$

The expansion of g_2^* in powers of α is then given by

$$g_2^*(x_1, x_2, t) = \sum_{n=0}^{\infty} \alpha^n g^{(n)}(x_1, x_2, t) . \quad (D.83)$$

From the definition, Eq. (D.81), and from Eq. (D.72) for $s=1$ and $s=2$, follows that

$$g_2^{(0)}(x_1, x_2, t) = 0 . \quad (D.84)$$

Furthermore $g_2^{(1)}(x_1, x_2)$ is by definition the two-particle function introduced in Eq. (D.76), whose time evolution is governed by Eq. (D.78). Having made this connection, it is easily shown that, when the reduced variables are eliminated in Eq. (D.78) in favor of the original ones and the approximation given in Eq. (D.74) for the binary collision operator is used, the equation for $g_2^{(1)}(x_1, x_2, t)$, the first nonvanishing contribution to the two-particle cluster function, agrees with Eq. (3.3) of Ref. 37.

The procedure outlined here can be easily carried further to evaluate the next term in the expansion of f_s . This will involve three-particle correlations together with corrections to the one- and two-particle distribution functions. In this way, kinetic equations for progressively higher order correlations are consistently obtained.

Correlation Functions

In order to directly compare the results derived here with those of Ref. 37 and of Chapter IV, it is convenient to consider the multi-time and equal time correlation functions as defined in Eqs. (2.34) and (2.32), instead of the corresponding distribution functions. In analogy with eq. (D.62), a dimensionless form of the correlation functions is defined as

$$C_s^*(x_1^*, t_1^*; \dots; x_s^*, t_s^*) \equiv \left(\frac{mv_0}{n}\right)^s C_s(r_{0\,mv_0} x_1^*, t_0 t_1^*; \dots; r_{0\,mv_0} x_s^*, t_0 t_s^*) , \quad (D.85)$$

where this definition applies to both the cases of equal and different time arguments.

An expansion of the correlation function in powers of α is then written as

$$C_s^*(x_1, t_1; \dots; x_s, t_s) = \sum_{n=0}^{\infty} \alpha_n C_s^{(n)}(x_1, t_1; \dots; x_s, t_s) . \quad (D.86)$$

In this section equations for the time evolution of the lowest order terms in the expansion of the second order correlation functions are obtained.

The equal time second order cumulant is first considered. By definition it can be written as

$$C_2^*(x_1, t; x_2, t) = g_2^*(x_1, x_2, t) + \alpha \delta(x_1 - x_2) f_1^*(x_1, t) . \quad (D.87)$$

An equation for C_2^* is therefore immediately obtained from the equations for the one-time reduced distribution functions derived in the previous section. Since the two-particle cluster function vanishes to zeroth order in α , Eq. (D.87) shows explicitly that

$$C_2^{(0)}(x_1, t; x_2, t) = 0 , \quad (D.88)$$

and in nonequilibrium situations both terms on the right hand side of Eq. (D.87) contribute to the lowest order in the expansion parameter. This point has caused confusion in the literature since some authors have argued that only the second term had to be kept to lowest order in the density.³⁴ Ernst and Cohen³⁷ correctly estimated the relative order of the two terms. The present scaling method, however, provides a more explicit statement of the result.

By using Eqs. (D.73), (D.78), and (D.87), the kinetic equation for the lowest order nonvanishing term in the expansion of C_2^* is immediately obtained,

$$\left\{ \frac{\partial}{\partial t} + (1 + P_{12}) L^*(x_1, t) \right\} C_2^{(1)}(x_1, t; x_2, t) = \Gamma^*(x_1, x_2, t) , \quad (D.89)$$

with

$$\begin{aligned}
\Gamma^*(x_1, x_2, t) = & - [\Lambda^*(x_2, t) + \bar{\Lambda}^*(x_2, t)] \delta(x_1 - x_2) f_1^{(0)}(x_1, t) \\
& + \delta(x_1 - x_2) \int dx_3 \bar{T}_-(x_1, x_3) f_1^{(0)}(x_1, t) f_1^{(0)}(x_3, t) \\
& + \bar{T}_-(x_1, x_2) f_1^{(0)}(x_1, t) f_1^{(0)}(x_2, t) \quad . \quad (D.90)
\end{aligned}$$

Again, reexpressing Eq. (D.90) in terms of the original unscaled variables and functions, the low density equation for the second order equal time correlation is found to be

$$\left\{ \frac{\partial}{\partial t} + (1+P_{12})\bar{L}(x_1, t) \right\} C_2(x_1, t; x_2, t) = \Gamma(x_1, x_2, t) \quad , \quad (D.91)$$

with

$$\bar{L}(x_1, t) = L_0(x_1) - n\bar{\Lambda}(x_1, t) \quad , \quad (D.92)$$

and

$$\begin{aligned}
\bar{\Gamma}(x_1, x_2, t) = & -n[\bar{\Lambda}(x_1, t) + \bar{\Lambda}(x_2, t)] \delta(x_1 - x_2) f_1(x, t) \\
& + \delta(x_1 - x_2) \int dx_3 \bar{T}_-(x_1, x_3) f_1(x_1, t) f_1(x_3, t) \\
& + \bar{T}_-(x_1, x_2) f_1(x_1, t) f_1(x_2, t) \quad . \quad (D.93)
\end{aligned}$$

Here, $\bar{\Lambda}(x_1, t)$ is simply given by $\Lambda^*(x_1, t)$ with \bar{T}_- replaced by \bar{T}_- . The one particle distribution function is the solution of the nonlinear Boltzmann equation,

$$\left\{ \frac{\partial}{\partial t} + L_0(x_1) \right\} f_1(x_1, t) = n \int dx_2 \bar{T}_-(x_1, x_2) f_1(x_1, t) f_1(x_2, t) \quad . \quad (D.94)$$

Equation (D.91) agrees with Eq. (3.5a) of Ref. 37 (the factors of n in Eq. (D.91) are due to the different normalization of the distribution functions).

The unequal time correlation functions are directly related to the multitime distribution functions defined in the previous section, Eq. (D.55). In particular, for $s=2$ this relationship is simply given by

$$C_2^*(x_1, t; x_1', t') = f_{1,1}^*(x_1, t | x_1', t') - f_1^*(x_1, t) f_1^*(x_1', t'), \quad (D.95)$$

where the dimensionless form of the distribution functions $f_{s,1}$ is defined as in Eq. (D.62) (a factor of $(mv_0)^{3(s+1)}$ is needed to scale $f_{s,1}$).

The hierarchy of equations for the two-time distribution functions, as given by Eq. (D.57), for $s=1,2,3,\dots$, therefore has to be analyzed. This can be done in the same way described in the previous section, by scaling Eq. (D.57) with $r_0 = \lambda$ and $t_0 = t_f$, with the result,

$$\begin{aligned} & \left\{ \frac{\partial}{\partial t} + \sum_{i=1}^s L_0(x_i) \right\} f_{s,1}^*(x_1, \dots, x_s, t | x_1', t') \\ & - \alpha \sum_{i < j=1}^s \overline{T}_{-}^*(x_i, x_j) f_{s,1}^*(x_1, \dots, x_s, t | x_1', t') \\ & = \sum_{i=1}^s \int dx_{s+1} \overline{T}_{-}^*(x_i, x_{s+1}) f_{s+1,1}^*(x_1, \dots, x_{s+1}, t | x_1', t') . \quad (D.96) \end{aligned}$$

Again the distribution functions are written as a power series in α ,

$$f_{s,1}^*(x_1, \dots, x_s, t | x_1', t') = \sum_{n=0}^{\infty} \alpha^n f_{s,1}^{(n)}(x_1, \dots, x_s, t | x_1', t'). \quad (D.97)$$

By proceeding as before the lowest order terms in the expansion of $f_{s,1}^*$ can be easily evaluated. To zeroth order in α the result is given by

$$f_{s,1}^{(0)}(x_1, \dots, x_s, t | x'_1, t') = f_1^{(0)}(x'_1, t') \prod_{i=1}^s f_1^{(0)}(x_i, t), \quad (\text{D.98})$$

and, to first order,

$$\begin{aligned} f_{s,1}^{(1)}(x_1, \dots, x_s, t | x'_1, t') &= f_1^{(1)}(x'_1, t') \prod_{i=1}^s f_1^{(0)}(x_i, t) \\ &+ \sum_{i=1}^s f_1^{(0)}(x'_1, t') \prod_{\substack{j=1 \\ j \neq i}}^s f_1^{(0)}(x_j, t) f_1^{(1)}(x_i, t) \\ &+ \sum_{i=1}^s \prod_{\substack{j=1 \\ j \neq i}}^s f_1^{(0)}(x_j, t) C_2^{(1)}(x_i, t; x'_1, t') \\ &+ \sum_{\substack{i < j=1 \\ k \neq i, j}}^s \prod_{k=1}^s f_1^{(0)}(x_k, t) f_1^{(0)}(x'_1, t') g_2^{(1)}(x_i, x_j, t), \end{aligned} \quad (\text{D.99})$$

where $f_1^{(0)}$, $f_1^{(1)}$ and $g_2^{(1)}$ are the solutions of the nonlinear Boltzmann equation, Eq. (D.73), and of Eq. (D.77) and Eq. (D.78) respectively.

The requirement that Eq. (D.99) is a solution of the entire hierarchy, to first order in α , implies that the coefficient of α^1 in the expansion of the two-time correlation function satisfies the following equation,

$$\left\{ \frac{\partial}{\partial t} + L^*(x_1, t) \right\} C_2^{(1)}(x_1, t; x'_1, t') = 0, \quad (\text{D.100})$$

where the operator $L^*(x, t)$ has been defined in Eqs. (D.79-80). The zeroth order term, $C_2^{(0)}(x_1, t; x'_1, t')$, vanishes, as follows immediately from Eqs. (D.95) and (D.98). Again, Eq. (D.100), when transformed to

the original unscaled variables and functions (the result of this transformation is simply the substitution of the operator $L^*(x,t)$ with the operator $\bar{L}(x,t)$ as given in Eq. (D.92)) reduces to Eq. (3.9) of Ref. 37 and to the equation derived in Chapter IV by using the generating functional method, Eq. (4.34).

The derivation presented here has the advantage of interpreting the physical meaning of the appropriate expansion parameter and of the approximation introduced. As a consequence of the scaling of the hierarchy, a clear identification of the order of the various terms in every equation follows. Therefore, the method outlined provides a systematic and controlled way of obtaining kinetic equations for higher order correlations. However, it is easy to see that the lowest order nonvanishing term in the expansion (D.86) of the s -th order equal time correlation function is the coefficient of $\alpha^{(s-1)}$. This implies that every time the lowest order approximation for the next order cumulant is desired, it is necessary to derive an extra term in the expansion of the solution of the hierarchy. Therefore, the method, even though straightforward in principle, becomes quite lengthy when third or higher order correlations are desired.

The advantage of the formalism developed in Chapter IV, based on the introduction of a generating functional for phase space fluctuations, is then evident. There all the information desired can be derived from a single kinetic equation, Eq. (4.17). The analysis presented in Chapter IV also applies to systems with continuous purely repulsive interparticle potentials. The results here are however identical if the following correspondence between binary collision operators is made,

$$\bar{T}_-(x_i, x_j) \leftrightarrow \theta(x_i, x_j) \mathfrak{S}_\infty(x_i, x_j) . \quad (\text{D.101})$$

The fact that the right hand side of Eq. (D.101) represents the long time (compared to a collision time) limit of the binary collision operator for continuous potentials can be derived as a rigorous result.⁶²

APPENDIX E
HYDRODYNAMIC "NOISE" FROM KINETIC THEORY

The contribution to the equations for the hydrodynamic correlation functions arising from functional differentiation of the inhomogeneous term $W_\alpha(\vec{r}, t | \lambda)$ in Eq. (4.77) is analyzed here.

For convenience, W_α is rewritten as the sum of two parts,

$$W_\alpha(\vec{r}, t | \lambda) = W_\alpha^{(1)}(\vec{r}, t | \lambda) + W_\alpha^{(2)}(\vec{r}, t | \lambda) , \quad (\text{E.1})$$

with

$$W_\alpha^{(1)}(\vec{r}, t | \lambda) = - \frac{\partial}{\partial r_i} \int d\vec{p} v_i \hat{a}_\alpha(\vec{p}) T(x; t, 0) \Delta(x, 0 | \lambda) , \quad (\text{E.2})$$

and

$$W_\alpha^{(2)}(\vec{r}, t | \lambda) = - \frac{\partial}{\partial r_i} \int_0^t d\tau \int d\vec{p} v_i \hat{a}_\alpha(\vec{p}) T(x; t, \tau) W(x, \tau | \lambda) . \quad (\text{E.3})$$

The functional derivative of the second term on the right hand side of Eq. (E.1) will be shown to vanish on a time scale of the order of the collision time, τ_c . Consequently it does not contribute to the hydrodynamic equations for equal nor unequal time correlation functions. The first term, $W_\alpha^{(1)}$, is instead responsible for the inhomogeneous part in the equations for the equal time correlation functions.

The contribution from the term $W_\alpha^{(2)}$ is first considered. Its functional derivative is given by

$$\begin{aligned}
\left[\frac{\delta W_{\alpha}^{(2)}(\vec{r}_1, t_1 | \lambda)}{\delta \lambda(x_2, t_2)} \right]_{\lambda=0} &= - \frac{\partial}{\partial r_{1i}} \int_0^{t_1} d\tau \theta(\tau - t_0) \theta(t_0 - t_2) \int d\vec{p}_1 dx_3 v_{li} \hat{a}_{\alpha}(\vec{p}_1) \\
&\times T(x_1; t_1, \tau) \theta(x_1, x_2) \{ [\mathfrak{S}_{\tau-t_2}(x_1, x_3) - \mathfrak{S}_{\tau}(x_1, x_3)] S_{t_2-\tau}^0(x_1, x_3) \\
&\times [\delta(x_1 - x_2) + \delta(x_3 - x_2)] \} \mathfrak{S}_{\tau}(x_1, x_3) f_1(x_1, \tau) f_1(x_3, \tau) , \quad (E.4)
\end{aligned}$$

where $S_t^0(x_1, x_2) \equiv S_t(x_1) S_t(x_2)$, and the parameter t_0 has to be chosen to assure the proper order of the times. Since $t_1 \geq \tau \geq t_0 \geq t_2$, and only the case when $t_1 - t_2 > \tau_c$ is considered here, the appropriate choice is the one that restricts the integration to $t_1 \geq \tau \geq t_2 + \tau_c$. Both the streaming operators in square brackets can then be replaced with their asymptotic limit, \mathfrak{S}_{∞} , since $\tau > \tau_c$ and $\tau - t_2 > \tau_c$ over the entire range of integration, and the integrand in Eq. (E.4) vanishes.

Similarly, the contribution from $W_{\alpha}^{(2)}$ to the equation for the equal time correlation function is given by

$$\lim_{\varepsilon \rightarrow 0^+} (1 + P_{12} P_{\alpha\beta}) \int d\vec{p}_2 \hat{a}_{\beta}(\vec{p}_2) \left[\frac{\delta W_{\alpha}^{(2)}(\vec{r}_1, t + \varepsilon | \lambda)}{\delta \lambda(x_2, t)} \right]_{\lambda=0} , \quad (E.5)$$

where P_{12} interchanges \vec{r}_1 and \vec{r}_2 and

$$\begin{aligned}
\left[\frac{\delta W_{\alpha}^{(2)}(\vec{r}_1, t + \varepsilon | \lambda)}{\delta \lambda(x_2, t)} \right]_{\lambda=0} &= - \frac{\partial}{\partial r_{1i}} \int_0^{t+\varepsilon} d\tau \theta(\tau - t_0) \theta(t_0 - t) \int d\vec{p}_1 dx_3 v_{li} \hat{a}_{\alpha}(\vec{p}_1) \\
&\times T(x_1; t + \varepsilon, \tau) \theta(x_1, x_3) \{ [\mathfrak{S}_{\tau-t}(x_1, x_3) - \mathfrak{S}_{\tau}(x_1, x_3)] S_{t-\tau}^0(x_1, x_3) \\
&\times [\delta(x_1 - x_2) + \delta(x_3 - x_2)] \} \mathfrak{S}_{\tau}(x_1, x_3) f_1(x_1, \tau) f_1(x_3, \tau) . \quad (E.6)
\end{aligned}$$

An appropriate choice of the parameter t_0 is now $t_0 = t$. The range of the

time integration in Eq. (E.6) is then restricted to $t+\varepsilon > \tau > t$, i.e. vanishes when the limit $\varepsilon \rightarrow 0^+$ is taken. Since the integrand is well behaved over the time interval of interest, $w_\alpha^{(2)}$ gives no contribution to the equations for the equal time correlation functions.

The contribution from the first term in Eq. (E.1) is given by

$$\int d\vec{p}_2 \hat{a}_\beta(\vec{p}_2) \left[\frac{\delta w_\alpha^{(1)}(\vec{r}_1, t_1 | \lambda)}{\delta \lambda(x_2, t_2)} \right]_{\lambda=0} = - \frac{\partial}{\partial r_{1i}} \int d\vec{p}_1 d\vec{p}_2 v_{1i} \hat{a}_\alpha(\vec{p}_1) \hat{a}_\beta(\vec{p}_2) T(x_1; t_1, 0) \\ \times \{ C_2(x_1, 0; x_2, t_2) - f_L(x_1, 0) \hat{a}_\sigma(\vec{p}_1) g_{\sigma\varepsilon}^{-1}(\vec{r}_1) \\ \times \int d\vec{p}' \hat{a}_\varepsilon(\vec{p}') C_2(\vec{r}_1, \vec{p}', 0; x_2, t_2) \} , \quad (E.7)$$

where C_2 is the two-time correlation function of phase space fluctuations, defined by Eq. (4.26) for $s=2$. Its time evolution is governed by Eq. (4.34) for the variable x_2 (since $t_2 > 0$), whose solution is

$$C_2(x_1, 0; x_2, t_2) = T(x_2; t_2, 0) C_2(x_1, 0; x_2, 0) , \quad (E.8)$$

with

$$C_2(x_1, 0; x_2, 0) = \delta(x_1 - x_2) f_L(x_1, 0) . \quad (E.9)$$

In writing Eq. (E.9) use has been made of the fact that only states such that the initial correlations in the system factorize in products of one-particle distribution functions are considered. Furthermore, the system has been assumed to be in local equilibrium at $t=0$. Substituting, Eqs. (E.8-9) into (E.7), this becomes

$$\int d\vec{p}_2 \hat{a}_\beta(\vec{p}_2) \left[\frac{\delta W_\alpha^{(1)}(\vec{r}_1, t_1 | \lambda)}{\delta \lambda(x_2, t_2)} \right]_{\lambda=0} = - \frac{\partial}{\partial r_{1i}} \int dx f_L(x, 0) [T^\dagger(x; t_1, 0) \times \delta(\vec{r}_1 - \vec{q}) v_{1\alpha} \hat{a}_\alpha(\vec{p})] (1 - P_0^{(1)}) [T^\dagger(x; t_2, 0) \delta(\vec{r}_2 - \vec{q}) \hat{a}_\beta(\vec{p})] , \quad (\text{E.10})$$

where T^\dagger is the adjoint of the operator T , as defined in Eq. (4.71).

The hydrodynamic part, up to Navier-Stokes order, now has to be extracted from Eq. (E.10). This can be done by following closely the method used in Appendix B. The same result is then obtained, i.e.

$$\lim_{\substack{t_1 \gg t_f \\ t_1 - t_2 \gg t_f}} \int d\vec{p}_2 \hat{a}_\beta(\vec{p}_2) \left[\frac{\delta W_\alpha^{(1)}(\vec{r}_1, t_1 | \lambda)}{\delta \lambda(x_2, t_2)} \right]_{\lambda=0} \rightarrow 0 , \quad (\text{E.11})$$

and

$$\begin{aligned} \lim_{t \gg t_f} \lim_{\varepsilon \rightarrow 0^+} (1 + P_{12} P_{\alpha\beta}) \int d\vec{p}_2 \hat{a}_\beta(\vec{p}_2) \left[\frac{\delta W_\alpha^{(1)}(\vec{r}_1, t + \varepsilon | \lambda)}{\delta \lambda(x_2, t)} \right]_{\lambda=0} \\ = (1 + P_{12} P_{\alpha\beta}) \frac{\partial}{\partial r_{1i}} L_{\alpha\beta}^{ij}(\vec{r}_1, t; \{\psi\}) \frac{\partial}{\partial r_{2j}} \delta(\vec{r}_1 - \vec{r}_2) \end{aligned} \quad (\text{E.12})$$

where $L_{\alpha\beta}^{ij}$ is the matrix of transport coefficients for low a density gas, defined in Eq. (4.76).

APPENDIX F
DETERMINATION OF $R_{ij}^{\alpha\beta}$ FOR MAXWELL MOLECULES

Equations for the Rest Frame Correlation Functions

In the first part of this Appendix Eqs. (5.41-42) and Eqs. (5.48-50) are obtained. Consider first $R_{ij}^{v\alpha}(t, \tau)$, defined by Eq. (5.37) for the case $\alpha=v$, and in general given by

$$R_{ij}^{v\alpha}(t, \tau) = \int dx_1 dx_2 v_{li} \alpha_{2j} C_2^T(x_1, t+\tau; x_2, \tau), \quad (F.1)$$

where $\alpha_{2j} = q_{2j}$, v_{2j} , and C_2^T satisfies the equation

$$\left\{ \frac{\partial}{\partial t} + v_{li} \Lambda_{ji}(t) \frac{\partial}{\partial q_{lj}} - v_{li} a_{ji} \frac{\partial}{\partial q_{li}} - n I_{BL}[f'_b] \right\} C_2^T(x_1, t+\tau; x_2, \tau) = 0, \quad (F.2)$$

with $I_{BL}[f'_b]$ given by Eq. (5.17). By projecting Eq. (F.2) onto v_{li} and α_{2j} , an equation for $R_{ij}^{v\alpha}$ follows

$$\frac{\partial}{\partial t} R_{ij}^{v\alpha}(t, \tau) + a_{ik} R_{kj}^{v\alpha}(t, \tau) = n \int dx_1 dx_2 v_{li} \alpha_{2j} I_{BL}[f'_b] C_2^T(x_1, t+\tau; x_2, \tau). \quad (F.3)$$

In general, Eq. (F.3) is not a closed equation for $R_{ij}^{v\alpha}$ because of the term on the right hand side. However, for Maxwell molecules the right hand side can be evaluated, with the result,

$$n \int dx_1 dx_2 v_{li} \alpha_{2j} I_{BL}[f'_b] C_2^T(x_1, t+\tau; x_2, \tau) = -v_{li} R_{ij}^{v\alpha}(t, \tau). \quad (F.4)$$

The proof of Eq. (F.4) follows closely the one presented in Ref. 19.

The symmetry properties of the collision operator can be used to write

$$\begin{aligned}
 & n \int dx_1 dx_2 v_{1i} \alpha_{2j} I_{BL} [f'_b] C_2^T(x_1, t+\tau; x_2, \tau) \\
 &= n \int dx_2 \alpha_{2j} \int dx_1 d\vec{v}_b C_2^T(x_1, t+\tau; x_2, \tau) f'_b(\vec{v}_b, t) \\
 & \times \int_0^\infty db b |\vec{v}_1 - \vec{v}_b| \int_0^{2\pi} d\phi [\hat{v}_{1i} - v_{1i}] , \tag{F.5}
 \end{aligned}$$

where \hat{v}_i denotes the velocity after the collision. Defining the center of mass and the relative velocities,

$$\vec{G} = \frac{1}{2}(\vec{v}_1 + \vec{v}_b) \quad \vec{g} = \vec{v}_1 - \vec{v}_b, \tag{F.6}$$

Eq. (F.5) becomes

$$\begin{aligned}
 & n \int dx_1 dx_2 v_{1i} \alpha_{2j} I_{BL} [f'_b] C_2^T(x_1, t+\tau; x_2, \tau) \\
 &= n \int dx_2 \alpha_{2j} \int dx_1 d\vec{v}_b C_2^T(x_1, t+\tau; x_2, \tau) f'_b(\vec{v}_b, t) \\
 & \times \int_0^\infty db b g \int_0^{2\pi} d\phi \frac{1}{2} [\hat{g}_i - g_i] . \tag{F.7}
 \end{aligned}$$

Now let $\hat{g}_i = g_i \cos\theta - \hat{a}_i g \sin\theta$, where \hat{a} is a unit vector orthogonal to \vec{g} . Then, since $\int_0^{2\pi} d\phi \hat{a}_i = 0$,

$$\begin{aligned}
& n \int dx_1 dx_2 v_{1i} \alpha_{2j} I_{BL} [f'_b] C_2^T(x_1, t+\tau; x_2, \tau) \\
& = n \int dx_2 \alpha_{2j} \int dx_1 d\vec{v}_b C_2^T(x_1, t+\tau; x_2, \tau) f'_b(\vec{v}_b, t) \\
& \quad \times \pi g_i \int_0^\infty db b g(\cos\theta-1) . \tag{F.8}
\end{aligned}$$

For Maxwell molecules, $\int_0^\infty db b g h(\theta)$ is independent of the velocity, for an arbitrary function h . Thus

$$\begin{aligned}
& n \int dx_1 dx_2 v_{1i} \alpha_{2j} I_{BL} [f'_b] C_2^T(x_1, t+\tau; x_2, \tau) \\
& = -v_1 \int dx_1 dx_2 d\vec{v}_b (v_{1i} - v_{bi}) \alpha_{2j} f'_b(\vec{v}_b, t) C_2^T(x_1, t+\tau; x_2, \tau) \\
& = -v_1 R_{ij}^{\nu\alpha}(t, \tau) , \tag{F.9}
\end{aligned}$$

where

$$v_1 = n\pi \int_0^\infty db b g(1-\cos\theta) , \tag{F.10}$$

or

$$v_1 = \pi n \sigma^2 (\epsilon_0 / m)^{1/2} 1.19 . \tag{F.11}$$

The equation (5.42) for $R_{ij}^{q\alpha}(t, \tau)$ can be derived immediately in a similar way, by observing that 1 is an eigenfunction of the Boltzmann-Lorentz operator with zero eigenvalue.

The equations (5.48-50) for the equal time correlation functions,

$$\begin{aligned}
R_{ij}^{\alpha\beta}(t) & \equiv R_{ij}^{\alpha\beta}(0, t) \\
& = \int dx \alpha_i \beta_j f'_T(x, t) , \tag{F.12}
\end{aligned}$$

where f'_T satisfies the same equation as C_2^T , are obtained in a similar way. In particular, the equation for $R_{ij}^{VV}(t)$ is

$$\frac{\partial}{\partial t} R_{ij}^{VV}(t) + a_{ik} R_{kj}^{VV}(t) + a_{jk} R_{ki}^{VV}(t) = n \int dx v_i v_j I_{BL}[f'_b] f'_T(x,t) . \quad (F.13)$$

For Maxwell molecules, the right hand side of Eq. (F.13) can be evaluated as shown before. Using $\int_0^{2\pi} d\phi a_i a_j = \pi(\delta_{ij} - g_i g_j / g^2)$, it becomes

$$\begin{aligned} n \int dx v_i v_j I_{BL}[f'_b] f'_T(x,t) &= n \int dx d\vec{v}_b f'_b f'_T \{ [g_i G_j + g_j G_i] \\ &\times \int_0^\infty db b g \pi (\cos\theta - 1) - \frac{3}{4} (g_i g_j - \frac{1}{3} \delta_{ij} g^2) \int_0^\infty db b g \pi \sin^2\theta \} , \end{aligned} \quad (F.14)$$

or

$$\begin{aligned} n \int dx v_i v_j I_{BL}[f'_b] f'_T(x,t) &= -v_1 \int dx d\vec{v}_b f'_b f'_T [v_i v_j - v_{bi} v_{bj}] \\ &- v_2 \int dx d\vec{v}_b f'_b f'_T [v_i v_j + v_{bi} v_{bj} - v_i v_{bj} - v_{bi} v_j \\ &- \frac{1}{3} \delta_{ij} (v^2 + v_b^2 - 2\vec{v} \cdot \vec{v}_b)] . \end{aligned} \quad (F.15)$$

where v_1 is defined in Eq. (F.10) and

$$v_2 = \frac{3}{4} \pi n \int_0^\infty db b g \sin^2\theta , \quad (F.16)$$

or

$$v_2 = \frac{3}{4} \pi n \sigma^2 (\epsilon_0 / m)^{1/2} \quad 1.23 \quad . \quad (F.17)$$

The cross terms in Eq. (F.15) vanish, and

$$n \int dx v_i v_j I_{BL} [f'_b] f'_T(x, t) = - (v_1 + v_2) R_{ij}^{vv}(t) + \frac{v_2}{3} \delta_{ij} R_{kk}^{vv}(t) \\ + \frac{v_1 - v_2}{\rho} t_{ij}^*(t) + \frac{v_1}{\rho} \delta_{ij} p(t) \quad , \quad (F.18)$$

where the pressure tensor of the fluid is defined as

$$P_{ij}^* = \int dx_b^m v_{bi} v_{bj} f'_b(\vec{v}_b, t) \\ = t_{ij}^* + \delta_{ij} p \quad . \quad (F.19)$$

Substituting Eq. (F.18) in the right hand side of Eq. (F.13), Eq. (5.50) is immediately obtained.

Evaluation of $R_{ij}^{vv}(0, t)$

The second part of this Appendix is dedicated to the solution of Eq. (5.50) for the following choice of flow field,

$$a_{ij} = a \delta_{ix} \delta_{jy} \quad . \quad (F.20)$$

The Laplace transform of a function $A(t)$ is defined

$$\tilde{A}(z) = \int_0^\infty dt e^{-zt} A(t) \quad . \quad (F.21)$$

In terms of the transformed quantities the set of Eqs. (5.50) is then given by

$$(z + v_1 + v_2)\widehat{R}_{xx}(z) + 2a\widehat{R}_{yx}(z) - \frac{1}{3}v_2\widehat{R}_{kk}(z) = \widehat{I}_{xx}(z) + \frac{K_B T_0}{m} ,$$

$$(z + v_1 + v_2)\widehat{R}_{xy}(z) + a\widehat{R}_{yy}(z) = \widehat{I}_{xy}(z) ,$$

$$(z + v_1 + v_2)\widehat{R}_{xz}(z) + a\widehat{R}_{yz}(z) = \widehat{I}_{xz}(z) ,$$

$$(z + v_1 + v_2)\widehat{R}_{yy}(z) - \frac{1}{3}v_2\widehat{R}_{kk}(z) = \widehat{I}_{yy}(z) + \frac{K_B T_0}{m} ,$$

$$(z + v_1 + v_2)\widehat{R}_{yz}(z) = \widehat{I}_{yz}(z) ,$$

$$(z + v_1 + v_2)\widehat{R}_{zz}(z) - \frac{1}{3}v_2\widehat{R}_{kk}(z) = \widehat{I}_{zz}(z) + \frac{K_B T_0}{m} , \quad (F.22)$$

and

$$(z + v_1)\widehat{R}_{kk}(z) + 2a\widehat{R}_{yx}(z) = \frac{3K_B}{m} (v_1\widehat{T}(z) + T_0) , \quad (F.23)$$

where T_0 is the initial temperature of the fluid, and

$$R_{ij}(t) \equiv R_{ij}^{vv}(0,t) = R_{ji}(t) . \quad (F.24)$$

These equations have to be supplemented with equations for the components of the stress tensor,

$$(z + 2v_2)\hat{t}_{xx}^* = -\frac{4}{3} a\hat{t}_{xy}^* ,$$

$$(z + 2v_2)\hat{t}_{yy}^* = (z + 2v_2)\hat{t}_{xx}^* = \frac{2}{3} a\hat{t}_{xy}^* ,$$

$$(z + 2v_2)\hat{t}_{xy}^* = -a\hat{t}_{yy}^* - anK_B\hat{T}(z) ,$$

$$t_{xz}^* = t_{yz}^* = 0 , \quad (F.25)$$

and the heating equation,

$$znK_B\hat{T}(z) = nk_B T_0 - \frac{2}{3} a\hat{t}_{xy}^*(z) . \quad (F.26)$$

The components R_{xz} and R_{yz} do not have any interesting behavior. The other components are given by

$$\begin{aligned} \hat{R}_{xx}(z) = & D \frac{K_B}{m} \{ [(z+v_1+v_2)^2 + 2a^2](v_1\hat{T}(z) + T_0) \\ & + \left[\frac{3}{2}(z+v_1) + v_2 - 2 \frac{a^2 - (z+v_1)(z+v_1+v_2)}{z+2v_2} \right] (v_1 - v_2)(z\hat{T}(z) - T_0) \} , \end{aligned}$$

$$\begin{aligned} \hat{R}_{xy}(z) = & D \frac{K_B}{m} \{ -(z+v_1+v_2)^2(v_1\hat{T}(z) + T_0) + \left[\frac{a}{z+2v_2} \right. \\ & \left. - \frac{3}{2a}(z+v_1+v_2) \right] (z+v_1)(v_1 - v_2)(z\hat{T}(z) - T_0) \} , \end{aligned}$$

$$\begin{aligned} \hat{R}_{yy}(z) = & D \frac{K_B}{m} \{ (z+v_1+v_2)^2(v_1\hat{T}(z) + T_0) + \left[v_2 - \frac{(z+v_1)(z+v_1+v_2)}{z+2v_2} \right] \\ & \times (v_1 - v_2)(z\hat{T}(z) - T_0) \} , \end{aligned}$$

$$\begin{aligned} \widehat{R}_{kk}(z) = D \frac{K_B}{m} \{ & [3(z+v_1+v_2)^2 + 2a^2](v_1 \widehat{T}(z) + T_0) \\ & + [\frac{1}{3}(z+v_1+v_2) - \frac{2a^2}{z+2v_2}](v_1-v_2)(z \widehat{T}(z) - T_0) \} , \end{aligned}$$

$$\widehat{R}_{zz}(z) = \widehat{R}_{yy}(z) , \quad (F.27)$$

where

$$D = [(z+v_1)(z+v_1+v_2)^2 - \frac{2}{3} a^2 v_2]^{-1} . \quad (F.28)$$

The set of Eqs. (F.25) and (F.26) can be solved in terms of the temperature, with the result

$$\widehat{T}(z) = T_0 \frac{(z+2v_2)^2 + 2a^2/3}{z(z+2v_2)^2 - \frac{2}{3} a^2 (2v_2)} . \quad (F.29)$$

The correlation functions and the temperature field have three poles, corresponding to the roots of their denominators. The roots of the third order polynomial D, defined in Eq. (F.28), are

$$\begin{aligned} z_1(a, v_1, v_2) &= \lambda(a, v_2) - v_1 , \\ z_2(a, v_1, v_2) &= -[\frac{1}{2} \lambda(a, v_2) + v_2 + v_1] + i \frac{v_2}{\sqrt{3}} \sinh[\frac{1}{3} \alpha(\frac{a}{v_2})] , \\ z_3(a, v_1, v_2) &= z_2^\dagger(a, v_1, v_2) , \end{aligned} \quad (F.30)$$

where the dagger indicates here the complex conjugate, and

$$\lambda(a, v_2) = \frac{4}{3} v_2 \sinh^2[\frac{1}{6} \alpha(\frac{a}{v_2})] , \quad (F.31)$$

with

$$\alpha\left(\frac{a}{v_2}\right) = 1 + 9 \frac{a^2}{v_2^2} . \quad (\text{F.32})$$

Similarly the poles of the temperature field are given by

$$z_i^T(a, v_2) = z_i(a, 0, 2v_2) , \quad (\text{F.33})$$

for $i=1,2,3$. The real part of the two complex conjugate roots (for both the correlation functions and the temperature) is always negative, and leads to an exponential decay of the function characterized by a lifetime shorter than v_1^{-1} (or v_2^{-1}). The relaxation times v_1^{-1} and v_2^{-1} are of the order of the mean free time between collision of the particles in the system. This exponentially decaying behavior represents therefore an initial transient in the system and can be neglected if the time τ in the two-time correlation function, $G_{ij}^{VV}(t, \tau)$, is chosen to satisfy $\tau \gg t_f$.

The real pole of the temperature field, z_1^T , is always positive and leads to an exponential growth of the temperature in time, with a rate which increases with the shear: this is the manifestation of the viscous heating in the system.

The real pole of the correlation functions, z_1 , changes sign as a function of the shear rate. For $0 \leq a/v_2 \leq 3.3$ it is negative and therefore contributes only to the initial transients in the system. At larger values of the shear rate it becomes positive and it has to be retained. Therefore, as long as the shear rate is not too large ($a/v_2 \lesssim 3.3$), all the time dependence of the equal time correlation functions is determined by that of the temperature field.

It is convenient to define reduced quantities as

$$T^*(t^*) = T(v_1^{-1} t^*) / T_0, \quad (\text{F.34})$$

$$z_i^*(a^*, v^*) = z_i(a, v_1, v_2) / v_1, \quad (\text{F.35})$$

with,

$$a^* = a / v_1, \quad v^* = v_2 / v_1,$$

$$t^* = v_1 t, \quad x = a^* / v^* = a / v_2.$$

The real pole z_1^* is then written as

$$z_1^*(a^*, v^*) = v^* \lambda^*(x) - 1, \quad (\text{F.36})$$

where

$$\lambda^*(x) = \frac{4}{3} \sinh^2 \left[\frac{\alpha(x)}{6} \right]. \quad (\text{F.37})$$

At long times ($t^* \gg 1$), the reduced temperature field is then given by

$$T^*(t^*) = H(x, v^*) \exp \left[t^* (z_1^*(2v^*) + 1) \right], \quad (\text{F.38})$$

where $H(x, v^*)$ is the residue of the right hand side of Eq. (F.29) at the pole z_1^T , i.e.,

$$H(x, v^*) = \frac{[z_1^*(2v^*) + 1 + 2v^*]^2 + 2a^{*2}/3}{[z_1^*(2v^*) - z_2^*(2v^*)][z_1^*(2v^*) - z_2^{T*}(2v^*)]}. \quad (\text{F.39})$$

The a^* dependence of the poles in Eq. (F.39) has not been indicated to simplify the notation. Similarly, reduced correlation functions are defined as

$$R_{ij}^*(\tau^*) = \frac{R_{ij}^{vv}(0, \tau)}{(K_B T_0 / m)}. \quad (\text{F.40})$$

By neglecting the contribution from the two complex poles, which only survive at very short times, at all shear rates, the reduced correlation functions are given by

$$\begin{aligned} R_{ij}^*(\tau^*) = & \left[v^* \lambda^*(x) A_{ij}(x, v^*) + B_{ij}(x, v^*) \right] \int_0^{\tau^*} ds e^{z_1^*(a^*, v^*)(\tau^* - s)} T^*(s) \\ & + A_{ij}(x, v^*) T^*(\tau) + e^{z_1^*(a^*, v^*)} B_{ij}(x, v^*). \end{aligned} \quad (\text{F.41})$$

The coefficients A_{ij} and B_{ij} are linear combinations of the residues of the functions on the right hand side of Eqs. (F.27) at the pole $z = z_1$. Their explicit form is not given here.

By inserting Eq. (F.38) into Eq. (F.36), the time integration can be carried out, with the result

$$R_{ij}^*(\tau^*) = b_{ij}^{(1)}(x, v^*) e^{\tau^* [v^* \lambda^*(x) - 1]} + b_{ij}^{(2)}(x, v^*) e^{\tau^* 2v^* \lambda^*(x/2)}, \quad (\text{F.42})$$

where

$$\begin{aligned} b_{ij}^{(1)}(x, v^*) &= B_{ij} - H \frac{B_{ij} + v^* \lambda^*(x) A_{ij}}{1 + z_1^*(2v^*) - z_1^*(v^*)}, \\ b_{ij}^{(2)}(x, v^*) &= H \left\{ A_{ij} + \frac{B_{ij} + v^* \lambda^*(x) A_{ij}}{1 + z_1^*(2v^*) - z_1^*(v^*)} \right\}. \end{aligned} \quad (\text{F.43})$$

The expression (F.42) applies for $\tau^* \gg 1$ and all values of the shear rate. If only shear rates such that $\alpha^* \lesssim 3.3$ are considered, the exponent in the first term on the right hand side of the equation is negative and this term can be neglected for $\tau^* \gg 1$. In this case the time dependence of the correlation function is the same as that of the temperature and can be scaled out by normalizing the correlation function with the temperature, i.e.

$$\frac{R_{ij}^*(\tau^*)}{T^*(\tau^*)} = \gamma_{ij}(x, v^*) , \quad \text{for } \tau^* \gg 1, \alpha^* \lesssim 3.3 . \quad (\text{F.44})$$

where

$$\gamma_{ij}(x, v^*) = A_{ij} + \frac{B_{ij} + v^* \lambda^*(x) A_{ij}}{1 + z_1^*(2v^*) - z_1^*(v^*)} . \quad (\text{F.45})$$

In particular the explicit form of γ_{yy} is needed in Section V.5. This is given by

$$\begin{aligned} \gamma_{yy}(x, v^*) = & \left\{ [1 + \lambda^*(x)]^2 + 2(1-v^*)\lambda^*(x/2) \left[1 - \frac{v^* \lambda^*(x)(1+\lambda^*(x))}{v^* \lambda^*(x) + 2v^* - 1} \right] \right\} \\ & \times \left\{ [1 + 4\lambda^*(x) + 3\lambda^{*2}(x)] [1 + 2v^* \lambda^*(x/2) - v^* \lambda^*(x)] \right\}^{-1} . \end{aligned} \quad (\text{F.46})$$

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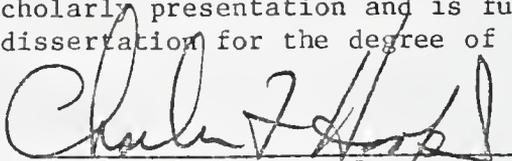
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