NONEQUILIBRIUM STATISTICAL MECHANICS OF INHOMOGENEOUS SYSTEMS

by

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ABSTRACT

The response technique is extended to the nonlinear and inhomogeneous regimes. It is then shown how to obtain the equations governing the macroscopic time evolution. For the correct choice of macroscopic variables, these equations are local in time, but nonlocal in space. A local equilibrium formulation of the macroscopic phenomena is also presented.

For systems in weak external fields it is shown how the nonlocal macroscopic equations may be localized. For simple fluids the resulting local equations differ from those in homogeneous systems in that an additional term, proportional to the external force, appears and the parameters in the equations have a weak spatial dependence. It is shown that the parameters may be related to those in homogeneous systems.

A multipole technique for describing interfacial systems is presented. It is shown how an exact equation of motion can be expanded into a hierarchy making the degrees of structure of the inhomogeneity explicit. By truncating this hierarchy a finite set of equations of motion and boundary conditions is obtained. Possible causes for the truncation are examined.

The equations of motion and boundary conditions are examined in detail when the system is close to equilibrium and the interfacial curvature is small. The resulting linear equations are further simplified by using some mechanical invariances inherent in these systems and by assuming that the macroscopic variables are conserved.

The multipole technique is applied to the hydrodynamics of two phase single component simple fluids. When all interfacial structure is neglected, it is shown that the usual boundary conditions ensue. Equations of motion for surface excess dyanmics are examined in detail for ideal systems.

Thesis Supervisor: Irwin Oppenheim

Title: Professor of Chemistry

To my parents

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Chapter I. Introduction

Many phenomenological theories predict, with good accuracy, the manner in which the macroscopic state of a nonequilibrium system evolves with time[1-4]. The macroscopic state is specified by the instantaneous average values of a relatively small number of variables. These variables have two features in common: they all evolve on a time scale which is much longer than typical molecular times (i.e., 10^{-12} - 10^{-13}sec) and they may be expressed as a sum of terms each involving only the properties of a small number of particles or degrees of freedom.

Recently much work has been devoted to finding relationships between the macroscopic equations and microscopic properties of the system[5-9]. A common feature in this field lies in the fact that the link between the microscopic behavior of the system is established through the use of time correlation functions. One approach has been to predict the evolution of the time correlation functions by using the macroscopic phenomenological equations[10,11]. This is analogous to the inverse problem in scattering theory. The other approaches attempt to derive the macroscopic equations from microscopic considerations.

Many techniques are available for deriving the macroscopic equations. Historically, the first of these methods has been kinetic theory[12-14]. Here one is concerned with generalized Boltzmann equations[15] which take into account the effects of single, double and higher order collisions in the macroscopic behavior of the system. The results of kinetic theory, strictly speaking, are valid only for systems of low to moderate densities, although many of the conclusions obtained by this

method are valid for any density. Kinetic theory has the advantage that for systems at low density it yields a rather complete description (of the available analytic techniques), since a time dependent reduced distribution function is found.

The next approach is the projection operator formalism[16-18]. This is a procedure by which exact equations of motion for the variables of interest are derived from the Liouville equation through the introduction of a projection operator which projects out the relevant parts of the dynamical variables. A generalized Langevin equation results from this technique. After a few simplifying assumptions are made, macroscopic equations with microscopic expressions for the parameters appearing in them are found. These expressions involve time correlation functions which in general cannot be evaluated except at low density or by computer simulation[19]. However, some quantitative statements about the low frequency behavior of the parameters appearing in the expressions sometimes can be made[20,21]. The projection operator techniques can be applied to many problems including Brownian motion[22].

The final method used in obtaining the macroscopic equations of motion is response theory[23,24]. It is this theory which we shall use in this work. The technique consists of solving the Liouville equation for a system which is coupled to some weak time dependent external forces in a perturbation expansion in the external force strength. When the equations of motion for the macroscopic variables are computed using this method, expressions involving equilibrium time correlation functions are also obtained for the parameters appearing in these equations. These expressions can be shown to be equivalent to those obtained using the projection

operator formalism[25] and to those obtained by kinetic theory[26,27]. The response technique has found wide application in hydrodynamic problems[25, 28-30] and is easily extended to systems where macroscopic nonlinearities start becoming important[31,32]. This method may be used to generalize the hydrodynamic equations, thereby extending their range of validity.

The projection operator and response formalisms both give very compact expressions for the parameters appearing in the equations of motion. These expressions are valid at all densities. For example, for homogeneous classical systems one obtains the general result that $L_{\alpha\gamma}$, the linear Onsager coefficient, can be written as

$$L_{\alpha\gamma} = \int \frac{d\bar{r}d\bar{r}'}{V} \int_0^\infty dt_1 \, \langle I_\alpha(\bar{r}, t_1) \, I_\gamma(\bar{r}_1, 0)\rangle \tag{1.1}$$

where $I_\alpha(\bar{r}, t)$ is the dissipative flux associated with the transport of the quantity α, V is the volume and the angular brackets represent an equilibrium avarage. Relations of this type are known as Green-Kubo[33] relations.

While much work has appeared concerning nonequilibrium statistical mechanics of homogeneous systems, relatively little has been done on inhomogeneous ones. Examples of inhomogeneous systems are those in external fields (e.g., gravity), next to walls, and those having more than one phase. Kinetic theory can easily handle the first two of these examples (refs. 34-39). Since multiphase phenomena usually do not persist when the density goes to zero, it is not clear how kinetic theory could be used to describe this case. On the other hand, the response and projection operator formalisms are not subject to density restrictions, and thus can be

used.

Relatively simple phenomenological theories are used to describe these systems. For the case where the system is subject to weak external fields the equations of motion are modified to take the effects of the external force into account[1-4]. Should the system have some surface of discontinuity (e.g., a wall or a phase boundary), then the phenomenological equations appropriate for the homogeneous bulk phases are assumed to be valid right up to the surface of discontinuity. In order to determine the solution to these equations, boundary conditions must be imposed. There is no general understanding of the microscopic origin of these conditions. To illustrate this problem we consider the boundary conditions for the hydrodynamic equations for an isothermal system next to a stationary solid body. They may generally be written as

$$p_n(\bar{r}, t) = 0 \quad , \tag{1.2}$$

$$\bar{p}_{//}(\bar{r}, t) = \phi \frac{\partial \bar{p}_{//}(\bar{r}, t)}{\partial n} \quad , \text{ at the surface,} \tag{1.3}$$

where $\bar{p}(\bar{r}, t)$ is the momentum density for the fluid, n and // indicate the components normal and parallel to the surface, respectively, $\partial/\partial n$ is the normal derivative and ϕ is the slipping length. If ϕ is zero then we have stick boundary conditions, while if ϕ is infinite then slip boundary conditions result. Most experiments indicate that, except at very low densities, the stick condition is appropriate for flow next to macroscopic bodies. Recently some evidence has been presented which suggests that for flow next to small bodies the slip condition yields a more accurate description[40].

It is the aim of this work to find, from microscopic considerations, the forms of the macroscopic equations of motion for inhomogeneous systems and where necessary, the boundary conditions needed to solve these equations. We shall consider classical systems which are relaxing to equilibrium. The hamiltonian of the relaxing system is

$$H(\bar{r}^N, \bar{p}^N) = \sum_{j=1}^{N} [\, \bar{p}_j^{\,2}/2m + \phi_{ext}(\bar{r}_j) + \tfrac{1}{2} \sum_{\substack{j'=1 \\ j' \neq j}}^{N} u_{jj'}(\bar{r}_j - \bar{r}_{j'}) \,], \tag{1.4}$$

where $\bar{r}^N$, $\bar{p}^N$ represent the coordinates and momenta of the particles, $\phi_{ext}(\bar{r})$ is the static external potential and $u_{jj'}$ is the interaction potential for a pair of particles. We have assumed that the particles interact via pairwise additive forces, although most of the results to be given in this work do not depend on this fact.

The macroscopic state of the system is specified by the instantaneous nonequilibrium average of some relatively small set of dynamical variables, $A_\alpha(\bar{r}, t)$. These variables are chosen to include all those whose average rate of change is small. In practice, the choice of the slow variables is not always easy. One must consider the conservation principles, broken symmetries and experiment when picking these variables. For the systems examined here we can always write the dynamical variables as

$$A_\alpha(\bar{r}, t) = \sum_{j=1}^{N} \delta(\bar{r} - \bar{r}_j(t)) \; A_{\alpha_j}(\bar{r}^N(t), \bar{p}^N(t)) \tag{1.5}$$

where δ is the Dirac δ function and where the A_{α_j} may be written as a sum of terms, each of which depends only on the coordinates and momenta of a small number of particles. The quantities A_{α_j} may be interpreted as the

amount of A_α carried by the j^{th} particle. In eq.(1.5) we have written the variables as "densities" by introducing the additional field parameter $\bar{r}$. The essential property of the set of variables is that it includes all the variables whose evolution is on a macroscopic time scale. It is also important that this time scale is separated from the characteristic microscopic relaxation times.

In chapter II the response of an isolated system to an external time dependent perturbation is derived. We compute the average response of the dynamical variables to second order in the external perturbation, for systems which were microcanonically distributed in the infinite past. The response expressions which are obtained contain equilibrium microcanonical time correlation functions and are valid for inhomogeneous systems. We show how to express the microcanonical quantities in terms of canonical or grand canonical correlation functions and find when the average response of a microcanonical ensemble of systems is equivalent to that in other ensembles. In the last part of chapter II we show how the response expression may be used to derive the macroscopic equations of motion. These equations are in general local in time but nonlocal in space. We also show that a local equilibrium distribution function can be introduced which greatly simplifies the forms of the equations of motion. Using the local equilibrium distribution function, it is possible to define the entropy of the system. The entropy production is then shown to be nonnegative. The results of chapter II are valid for systems not too far from equilibrium and to second order in the smallness parameter characterizing the rate of change of the slow variables.

Chapter III applies the response formalism to inhomogeneous systems in which the inhomogeniety is caused by a weak static external field. The field is assumed to cause equilibrium inhomogenieties whose characteristic length is large compared to the correlation length. In a procedure completely analogous to that used in ref. 25 we show how the equations of motion may be approximated by equations which are local in space. The parameters in these macroscopic equations of motion are easily related to those in a homogeneous system whose uniform density equals the equilibrium local density in our system. Further, an additional term appears in the equations of motion which accounts for explicit effects of the external force. These equations are valid to quadratic order in displacements of the macroscopic variables from equilibrium when the length scale of the nonequilibrium phenomena is smaller than that of the equilibrium inhomogeneity and only to linear order if it is not. We also give a detailed discussion of the hydrodynamic equations and local equilibrium formalism for the example of a simple fluid in weak external fields. The nonlinear considerations given in this chapter will be necessary before a molecular understanding of nonequilibrium instabilities can be found. Such an analysis has already been given for the Bénard instability[41].

Even when the correct equations of motion for inhomogeneous or slightly inhomogeneous regions of the system have been found, the problem still remains of what to do in the highly inhomogeneous region surrounding a phase boundary. When the boundary is a gas/solid surface, kinetic theory may be used to compute the correct macroscopic boundary conditions. A well known example of this is the problem of

Kramers[35-38] which computes the slipping length by imposing a microscopic boundary condition on the solution to the Boltzmann equation at the wall. Another approach has been to model the solid surface by an extremely rapidly changing potential field (e.g., an infinite step) and to solve the Boltzmann equation which includes the wall force explicitly[34]. In this case slip boundary conditions are obtained for hydrodynamic problems. Unfortunately these methods cannot be easily extended to dense systems having a fluid/fluid or fluid/vapour interface.

At first sight, it would seem extraordinarily difficult to treat in general the dynamics of two phase systems, due to the complex structure which appears in the interfacial region. This structure is also present at equilibrium and there it is well known that most of the details of the interfacial region can be omitted. The procedure in equilibrium studies is to introduce the Gibbs dividing surface and surface excess quantities[42-44] and then use thermodynamics or equilibrium statistical mechanics in order to describe the equilibrium phenomena.

Recently the phenomenological (nonequilibrium thermodynamic) treatment has been applied to two phase systems[45-48]. Here a local equilibrium assumption as well as the postulate that the surface excess entropy production is nonnegative are made. The equations of motion for the bulk variables, the surface excess densities and the requisite number of boundary conditions are obtained. Unfortunately, the above assumptions are not well understood for the surface region and it would be advantageous to find a molecular method to verify these results.

In chapter IV we present a systematic method for obtaining the appropriate boundary conditions for the bulk equations. The method entails the generalization of the Gibbs dividing surface and surface excess quantities to the nonequilibrium regime. In addition to the usual surface excess quantities, the concept of surface multipoles is introduced. Each of the surface multipoles is defined so as to give more information about the structure of the interfacial region. We derive equations of motion for the surface multipoles and then assume that only a limited amount of surface structure must be included in a problem where the typical bulk length scales are large compared to the interfacial thickness. This allows us to truncate the infinite hierarchy of equations of motion for the surface multipoles, and thus we obtain the boundary conditions for the problem. A further advantage of this method is that all nonequilibrium quantities now are slowly varying in space. This allows us to localize the equations of motion and boundary conditions in a manner similar to that used in the previous chapter. Finally, a set of finite order partial differential equations and boundary conditions are obtained. We then linearize these equations and boundary conditions in displacements of the variables from equilibrium and in the displacement of the surface from its equilibrium position.

In chapter V we examine the linearized equations of motion and boundary conditions obtained in chapter IV. As should be expected, these equations contain a large number of undetermined parameters. In the present chapter we show how invariance principles and conservation laws may be used to reduce the number of unknown parameters. Further, we show how to remove the restriction that the displacement of the surface

be small. In fact, we show that providing the curvature of the surface is not too large the same boundary conditions, as were found earlier, will apply at the true surface position. In this chapter the response theory and the results of the multipole technique are combined to give correlation function expressions for the parameters appearing in the equations of motion and boundary conditions. Finally, the assumptions concerning the truncations performed in obtaining the macroscopic equations and boundary conditions are examined further and it is shown how they may be related to equilibrium considerations.

Chapter VI contains applications of the multipole technique to the problem of two phase, simple fluid hydrodynamics. Two examples are considered. The first is that of an ideal fluid in which the dynamics of the surface excess densities are included explicitly. We show that the correct number of boundary conditions is obtained and that the usual boundary conditions result when all surface structure is neglected. The second example is that of a viscous, heat conducting fluid. We do not consider the effect of surface structure. Here too we find the correct number of boundary conditions and after examining the form of the coefficients appearing in them further, show that they are equivalent to the usual phenomenological ones.

We conclude this work with a discussion in chapter VII.

Chapter II. Nonlinear Response for Inhomogeneous Systems

The equations governing the behavior of macroscopic systems can be obtained by response theory[23,24]. These equations relate the macroscopic behavior to correlation functions containing information about the microscopic fluctuations in the system. Usually one is content with a linearized description. However, recently the response technique has been extended to the nonlinear regime[31]. The nonlinear response equations are necessary in order to examine systems far from equilibrium or any instabilities which might be present[41].

The majority of the work already done on response theory has considered only homogeneous systems. In this chapter, the extension of these results to inhomogeneous systems is presented and some ambiguous points present in earlier works are clarified.

In response theory a system at equilibrium in the infinite past is adiabatically removed from equilibrium by weak time-dependent forces (either real or fictitious) which couple to the pertinent microscopic variables. These variables are those which are slowly varying in time and specify the macroscopic state of the system. The only purpose of the forces is to create an initial nonequilibrium distribution function. At $t = 0$ these forces are suddenly removed and the relaxation begins.

In contrast to the small number of variables needed to specify the macroscopic state of the system, the microscopic state is specified by an immensely greater number. A classical system of N particles confined by walls or other external static fields to some region of space, V, is considered. The complete microscopic state of the system

is given by the phase point

$$X^N(t) \equiv \{ \bar{r}^N(t), \bar{p}^N(t) \} , \tag{2.1}$$

where $\bar{r}^N$ and $\bar{p}^N$ are the system's coordinates and momenta. The time dependence of the phase point is governed by the hamiltonian $H_T(X^N, t)$ via Hamilton's equations. This hamiltonian may be written as

$$\begin{aligned} H_T(X^N, t) &\equiv H(X^N) + H_1(X^N, t) \\ H_1(X^N, t) &\equiv -\underline{A}(\bar{r}, X^N) * \underline{F}(\bar{r}, t) \end{aligned} \tag{2.2}$$

where $H(X^N)$ is the hamiltonian of the unperturbed system, $\underline{A}(\bar{r}, X^N)$ is a column vector whose components are the slow variables, $\underline{F}(\bar{r}, t)$ is a similar column vector of fictitious forces and

$$\underline{A}(\bar{r}, X^N) * \underline{F}(\bar{r}, t) \equiv \int_V d^3\bar{r}\, \underline{A}(\bar{r}, X^N) \cdot \underline{F}(\bar{r}, t). \tag{2.3}$$

For the response experiment described above the forces have the time dependence:

$$\underline{F}(\bar{r}, t) \equiv \left\{ \begin{array}{ll} 0 & t > 0 \\ \underline{F}(\bar{r}) e^{\varepsilon t} & t \leq 0; \varepsilon \to 0^+ \end{array} \right\} . \tag{2.4}$$

Derivation of the Response Equation

The distribution function $f(X^N, t)$ satisfies Liouville's equation

$$\frac{\partial f(X^N, t)}{\partial t} = - iL_T(t)\, f(X^N, t) , \tag{2.5}$$

where the Liouville operator is defined as

$$L_T(t) \equiv L + L_1(t) \ ,$$

$$L \equiv i[H, \ ], \tag{2.6}$$

$$L_1(t) \equiv i[H_1(t), \ ] \ ,$$

the symbol [,] indicating a Poisson bracket. Eq.(2.5) has the formal solution

$$f(X^N, t) = T_+ \exp[-i \int_{-\infty}^{t} dt_1 \ L_T(t_1)] \ f(X^N, -\infty) \tag{2.7}$$

$$\equiv [1 - i \int_{-\infty}^{t} dt_1 \ L_T(t_1) + \int_{-\infty}^{t} dt_1 \ iL_T(t_1) \int_{-\infty}^{t_1} dt_2 \ iL_T(t_2) + \ldots] f(X^N, -\infty) \tag{2.8}$$

where T_+ is a time ordering operator.

We shall assume that the $t = -\infty$ system was at equilibrium, which means

$$iLf(X^N, -\infty) = 0 \ . \tag{2.9}$$

As is well known, eq.(2.9) does not uniquely specify the equilibrium distribution function, as any function of $H(X^N)$ will be a solution. The usual procedure[25,28,31] has been to choose a canonical or grand canonical distribution function for $f(X^N, -\infty)$. Since the Liouville operator $L_T(t)$ governs the evolution of a system isolated from particle or heat reservoirs, eq.(2.7), with a canonical or grand canonical $f(X^N, -\infty)$, gives the average response of isolated systems which were so distributed in the infinite past. This is not the relaxation of a system in contact with reservoirs.

All experiments are performed either on isolated systems or on systems in contact with reservoirs. The former situation requires $f(X^N, -\infty)$ to be a microcanonical distribution function, while the latter requires the inclusion of bath degrees of freedom in $L_T(t)$ [49]. The choice of a canonical distribution function and an isolated Liouville operator[25,28,31] presupposes the equivalence of the relaxation of a canonical ensemble of systems to that of a microcanonical ensemble. As shall soon be shown, this is indeed the case.

In this work only isolated systems are considered and the microcanonical distribution is used:

$$f(X^N, -\infty) \equiv f_0(X^N) \equiv \delta(E - H(X^N)) \,/\, \Omega(E), \tag{2.10}$$

where $\delta(X)$ is the Dirac δ function and

$$\Omega(E) \equiv \int dX^N \, \delta(E - H(X^N)) \tag{2.11}$$

is the microcanonical partition function.

Eq.(2.7) can be rewritten as

$$\begin{aligned} f(X^N, t) &= \{ e^{-iLt} - \int_{-\infty}^{t} dt_1 \, e^{-iL(t-t_1)} \, iL_1(t_1) \, T_+ \exp[-i \int_{-\infty}^{t_1} dt_2 \, L_T(t_2)]\} \\ &\qquad \cdot f(X^N, -\infty) \\ &= f_0(X^N) - \int_{-\infty}^{t} dt_1 \, e^{-iL(t-t_1)} \, iL_1(t_1) \, f(X^N, t_1) \, , \end{aligned} \tag{2.12}$$

where eq.(2.9) has been used. Iterating eq.(2.12) and keeping terms only to second order in the forces results in:

$$f(X^N, t) = f_0(X^N) - \int_{-\infty}^{t} dt_1\, e^{-iL(t-t_1)}\, iL_1(t_1)\, f_0(X^N)$$

$$+ \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2\, e^{-iL(t-t_1)}\, iL_1(t_1)\, e^{-iL(t_1-t_2)}\, iL_1(t_2)\, f_0(X^N) + \ldots$$

$$= f_0(X^N) + \int_{-\infty}^{t} dt_1\, e^{-iL(t-t_1)}\, [f_0(X^N), \underline{A}(\bar{r}_1, X^N)] * \underline{F}(\bar{r}_1, t_1)$$

$$+ \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2\, e^{-iL(t-t_1)} [(e^{-iL(t_1-t_2)} [f_0(X^N), \underline{A}(\bar{r}_2 X^N)]), \underline{A}(\bar{r}_1 X^N)]$$

$$** \underline{F}(\bar{r}_1, t_1)\, \underline{F}(\bar{r}_2, t_2) + \ldots \qquad (2.13)$$

Using the definition of $f_0(X^N)$, eq.(2.10) and the fact that in the unperturbed system

$$\dot{\underline{A}}(\bar{r}, t) \equiv \frac{d\underline{A}(\bar{r}, X^N(t))}{dt} = iL\underline{A}(\bar{r}, t) \qquad (2.14)$$

allows us to rewrite eq.(2.13) as

$$f(X^N, t) = f_0(X^N) + \Omega^{-1}(E) \{ \frac{\partial}{\partial E} (\Omega(E)\, f_0(X^N)) \int_{-\infty}^{t} dt_1\, \dot{\underline{A}}(\bar{r}_1, t_1-t) * \underline{F}(\bar{r}_1, t_1)$$

$$+ \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \, [\frac{\partial^2(\Omega(E)\, f_0(X^N))}{\partial E^2} \dot{\underline{A}}(\bar{r}_2, t_2-t)\, \dot{\underline{A}}(\bar{r}_1, t_1-t) ** \underline{F}(\bar{r}_1, t_1)\, \underline{F}(\bar{r}_2, t_2)$$

$$+ \frac{\partial(\Omega(E)\, f_0(X^N))}{\partial E}\, e^{-iL(t-t_1)} [\dot{\underline{A}}(\bar{r}_1, t_2-t_1), \underline{A}(\bar{r}_2, 0)] ** \underline{F}(\bar{r}_2, t_2)\, \underline{F}(\bar{r}_1, t_1)]$$

$$+ \ldots \} \qquad (2.15)$$

It is well known[50] that perturbation expansions of the above type are unsuitable for the description of the microscopic behavior of many-body systems. For variables A, consisting of a sum of N terms as dis-

cussed in the introduction, the perturbation felt by the distribution function is O(NF) not O(F). However, when the distribution function given by eq.(2.15) is used to compute the average evolution of the dynamical variables, an expansion in powers of F is obtained. Letting

$$\hat{\underline{a}}(\bar{r},\, t) \equiv \underline{a}(\bar{r},\, t) - <\underline{A}(\bar{r})> \equiv \int dX^N [f(X^N,\, t) - f_0(X^N)]\, \underline{A}(\bar{r},\, X^N), \quad (2.16)$$

where the symbols < > and ^ represent an equilibrium microcanonical average and displacement from equilibrium, respectively, and using eq.(2.15) results in

$$\hat{\underline{a}}(\bar{r},\, t) = \Omega^{-1}(E)\, [\int_{-\infty}^{t} dt_1\, \frac{\partial}{\partial E}(\Omega(E) <\underline{A}(\bar{r},\, 0)\, \dot{\underline{A}}(\bar{r}_1, t_1-t)> * \underline{F}\,(\bar{r}_1,\, t_1))$$

$$+ \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2\, \{\frac{\partial^2}{\partial E^2}(\Omega(E) <\underline{A}(\bar{r},\, 0)\, \dot{\underline{A}}(\bar{r}_1,\, t_1-t)\, \dot{\underline{A}}(\bar{r}_2,\, t_2-t)>)$$

$$+ \frac{\partial}{\partial E}(\Omega(E) < \underline{A}(\bar{r}, t-t_1)\, [\dot{\underline{A}}(\bar{r}_1,\, t_2-t_1),\, \underline{A}(\bar{r}_2, 0)]>)\}_{**} \underline{F}(\bar{r}_2, t_2)\, \underline{F}(\bar{r}_1, t_1)\,]$$

$$+ O(F^3). \quad (2.17)$$

We have written

$$\underline{A}(\bar{r},\, t) \equiv \underline{A}(\bar{r},\, X^N(t)) \quad (2.18)$$

in the above equation.

An important difference between this work and earlier ones lies in the assumption that the system is mixing. That is, for the variables $\underline{A}(\bar{r},\, t)$:

$$\lim_{t \to \pm\infty} <\underline{A}(\bar{r},\, t)\, \underline{A}(\bar{r}')> = <\underline{A}(\bar{r})><\underline{A}(\bar{r}')>, \quad (2.19)$$

where we have written $\underline{A}(\bar{r})$ for $\underline{A}(\bar{r},\, 0)$.

As was discussed in refs. 51 and 52, we can expect eq.(2.19) to hold only if the ensemble is constructed such that all normal constants of motion do not fluctuate. Should the system have other conserved quantities (for example total linear or angular momentum), the equilibrium distribution function whose averages will obey the mixing condition must contain additional δ functions pertaining to these additional quantities.

Earlier works[25,28,31] assumed that eq.(2.19) was valid for canonical averages. This assumption is only correct up to terms $O(N^{-1})$. Since these terms are integrated over the volume of the system, an error $O(1)$ was made. This error is responsible for a contradiction inherent in the response expressions of these works, as will be shown below.

In ref. 32 a modified mixing assumption for canonical averages was used to eliminate these problems for homogeneous systems. It was assumed that

$$\lim_{t \to \pm\infty} < [(1-P_0)\, \underline{\hat{A}}(\bar{r}, t)]\, \underline{\hat{A}}(\bar{r}') >_c = 0 \tag{2.20}$$

where $< >_c$ represents a canonical average,

$$P_0 \underline{\hat{A}}(\bar{r}, t) \equiv <\underline{\hat{A}}(\bar{r}, t)\, \underline{\hat{C}}>_c \cdot\ <\underline{\hat{C}}\, \underline{\hat{C}}>_c^{-1} \cdot \underline{\hat{C}}. \tag{2.21}$$

and where $\underline{C}$ denotes a column vector of conserved quantities. The operator P_0 is the projection operator onto the set of conserved variables.

The microcanonical formulation has the advantage that the mixing assumption, eq.(2.19), is well studied within the context of ergodic theory . In fact Sinai[53] has shown that a system consisting of a finite number of hard spheres in a box is mixing. Thus we can expect eq.(2.19) to hold before the thermodynamic limit is taken, a crucial requirement

if finite systems are to be studied.

Returning to the development of the response equations, eq.(2.17) is integrated by parts, keeping only lowest order terms in ε (cf. eq.(2.4)) and using eq.(2.19). This yields for $t \geq 0$:

$$\hat{\underline{a}}(\bar{r}, t) = \Omega^{-1}(E) \left[\frac{\partial}{\partial E} \left(\Omega(E) < \hat{\underline{A}}(\bar{r}, t)\, \hat{\underline{A}}(\bar{r}_1) > * \underline{F}(\bar{r}_1)\right)\right.$$

$$+ \tfrac{1}{2} \frac{\partial^2}{\partial E^2} \left(\Omega(E) < \hat{\underline{A}}(\bar{r}, t)\, \hat{\underline{A}}(\bar{r}_1)\, \hat{\underline{A}}(\bar{r}_2) > \overset{*}{*} \underline{F}(\bar{r}_2)\, \underline{F}(\bar{r}_1)\right)$$

$$\left. - \frac{\partial}{\partial E} \int_{-\infty}^{0} dt_1 \lim_{t_2 \to -\infty} \Omega(E) < \underline{A}(\bar{r}, t-t_1)[\underline{A}(\bar{r}_2, t_2), \underline{A}(\bar{r}_1)] > \overset{*}{*} \underline{F}(\bar{r}_1)\, F(\bar{r}_2)\right]$$

$$+ O(\varepsilon) + O(F^3) \ . \qquad (2.22)$$

Note the fact that for any dynamical variables, Y_1, Y_2, Y_3:

$$< Y_1 [Y_2, Y_3] > = < Y_2 [Y_3, Y_1] > - \Omega^{-1}(E) \frac{\partial}{\partial E} \left(\Omega(E) < \dot{Y}_3\, Y_1\, Y_2 > \right) , \qquad (2.23)$$

which is easily shown by integration by parts. Using this identity and eq.(2.19) allows the last term in eq.(2.22) to be rewritten as:

$$\Omega^{-1}(E) \frac{\partial}{\partial E} \int_{-\infty}^{0} dt_1 \lim_{t \to -\infty} \Omega(E) < \underline{A}(\bar{r}, t-t_1)\, [\underline{A}(\bar{r}_2, t_2), \underline{A}(\bar{r}_1)] > \overset{*}{*} \underline{F}(\bar{r}_1)\, \underline{F}(\bar{r}_2)$$

$$= \Omega^{-1}(E) \frac{\partial}{\partial E} \int_{\infty}^{0} dt_1 \left[-\Omega(E) < [\underline{A}(\bar{r}, t-t_1), \underline{A}(\bar{r}_2)] > <\underline{A}(\bar{r}_1)> \right.$$

$$\left. - \frac{\partial}{\partial E} \left(\Omega(E) < \underline{A}(\bar{r}, t-t_1)\, \dot{\underline{A}}(\bar{r}_2) > <\underline{A}(\bar{r}_1)> \right)\right] \overset{*}{*} \underline{F}(\bar{r}_1)\, \underline{F}(\bar{r}_2)]$$

$$= -\Omega^{-1}(E) \frac{\partial}{\partial E} \left(< \hat{\underline{A}}(\bar{r}, t)\, \hat{\underline{A}}(\bar{r}_2) > \frac{\partial <\underline{A}(\bar{r}_1)>}{\partial E} \right) \overset{*}{*} \underline{F}(\bar{r}_1)\, \underline{F}(\bar{r}_2) \ , \qquad (2.24)$$

where eq.(2.23) was used again in obtaining the last equality. Combining eqs.(2.24) and (2.22) gives

$$\hat{\underline{a}}(\bar{r},\, t) = \Omega^{-1}(E)\, \frac{\partial}{\partial E}\, [\, \Omega(E) < \hat{\underline{A}}(\bar{r},\, t)\, \hat{\underline{A}}(\bar{r}_1) > * \underline{F}(\bar{r}_1)\, \left(1 + \frac{\partial < \underline{A}(\bar{r}_2) > * \underline{F}(\bar{r}_2)}{\partial E}\right)$$

$$+ \tfrac{1}{2}\, \frac{\partial}{\partial E}\, \Omega(E) < \hat{\underline{A}}(\bar{r},\, t)\, \hat{\underline{A}}(\bar{r}_1)\, \hat{\underline{A}}(\bar{r}_2) > \overset{*}{*}\, \underline{F}(\bar{r}_2)\, \underline{F}(\bar{r}_1)\,] + O(F^3) \qquad (2.25)$$

The derivation of eq.(2.25) depends only on the mixing assumption (cf. eq.(2.19)) and on the neglect of the $O(F^3)$ terms. Neither of these restrictions need involve the size of N or E and so eq.(2.25) should also be valid for small systems.

From now on, only large systems are considered. That is, $N \gg 1$ with $E \sim O(N)$. Note that the temperature of a microcanonical ensemble, $T(N, E, V)$, is given by

$$\beta(N, E, V) \equiv (K_B\, T(N, E, V))^{-1} = \left(\frac{\partial\, \ln(\Omega(E))}{\partial E}\right)_{N,V}, \qquad (2.26)$$

where K_B is Boltzmann's constant and where $\Omega(E) \sim O(e^N)$. Since the correlation functions appearing in eq.(2.25) decay to $O(N^{-1})$ whenever any of their arguments are separated beyond some microscopic correlation length, the response expression becomes for large systems:

$$\hat{\underline{a}}(\bar{r},\, t) = \beta < \hat{\underline{A}}(\bar{r},\, t)\, \hat{\underline{A}}(\bar{r}_1) > * \underline{F}(\bar{r}_1)\, \left(1 + \frac{\partial < \underline{A}(\bar{r}\,) > * \underline{F}(\bar{r}\,)}{\partial E}\right)$$

$$+ \tfrac{1}{2}\, \beta^2 < \hat{\underline{A}}(\bar{r},\, t)\, \hat{\underline{A}}(\bar{r}_1)\, \hat{\underline{A}}(\bar{r}_2) > \overset{*}{*}\, \underline{F}(\bar{r}_2)\, \underline{F}(\bar{r}_1) + O(N^{-1}) \,. \qquad (2.27)$$

This last equation gives the response of the system to quadratic order in F. It differs from other nonlinear response equations[31,32] in that

the correlation functions appearing in eq.(2.27) are microcanonical.

The response equation guarantees that the total number of particles and energy of the system are never removed from their $t = -\infty$ values for $t \geq 0$. In contrast to this the response expressions presented in ref. 31 do not have this property. The response equation of ref. 31 (eq.(9)), in our notation, is:

$$\underline{\hat{a}}(\bar{r},t) = \beta < \underline{\hat{A}}(\bar{r},t)\ \underline{\hat{A}}(\bar{r}_1) >_c * \underline{F}(\bar{r}_1) + \tfrac{1}{2}\beta^2 < \underline{\hat{A}}(\bar{r},t)\ \underline{\hat{A}}(\bar{r}_1)\ \underline{\hat{A}}(\bar{r}_2) >_{c**} \underline{F}(\bar{r}_2)\,\underline{F}(\bar{r}_1). \tag{2.28}$$

For this equation it is easily seen that in general the total energy of the system does not necessarily equal its $t = -\infty$ value at $t = 0$. Further, there is no special restriction to the choice of canonical ensemble in these other works. One could equally as well have chosen the initial distribution to be grand canonical. In that case eq.(2.28) would also have been obtained with the modification that the averages are now grand canonical averages. If the displacement from equilibrium of the total number of particles is now computed, one obtains a result which is not necessarily zero. However, the Liouville operators used in the theory are those for systems not in contact with particle reservoirs and thus cannot change the total number of particles. This is in contradiction to the response theory result. The reason for the difference lies in the fact that the mixing assumption, eq.(2.19), is not valid for grand canonical averages. It will be shown below that for homogeneous systems the response expressions of ref. 31 are valid except for infinite wavelength phenomena, for which the mixing assumption fails.

Transformation to Other Ensembles

For many applications and for the sake of comparison it would be advantageous to express eq.(2.27) in terms of correlation functions defined in ensembles other than the microcanonical ensemble. In order to accomplish this, the method of Lebowitz and Percus[54] for finding the aymptotic forms of reduced canonical distribution functions is extended to arbitrary correlation functions.

Two ensembles Γ and Γ' are considered. They differ in the fact that the set of variables $\underline{C}(X^N)$ fluctuate in the latter but not in the former. In addition, it is required that the variables $\underline{C}$ are O(N) in the Γ ensemble and that $\langle \underline{C} \rangle_{\Gamma} = \langle \underline{C} \rangle_{\Gamma'}$. The symbols $\langle \ \rangle_{\Gamma}$ and $\langle \ \rangle_{\Gamma'}$ shall be used to represent averages in the Γ and Γ' ensembles, respectively.

Averages in the two ensembles are related by

$$\langle B\rangle_{\Gamma'} = \int d\underline{C}\ \langle B\rangle_{\Gamma} P(\underline{C}, \underline{\gamma}) \ , \tag{2.29}$$

where

$$P(\underline{C}, \underline{\gamma}) \equiv g(\underline{C})\ \exp[-\underline{\gamma}\cdot\underline{C}] / \Lambda(\underline{\gamma}) \ . \tag{2.30}$$

The γ_i are the variables conjugate to the C_i, $g(\underline{C})$ is a degeracy factor and $\Lambda(\underline{\gamma})$ is a normalization constant.

For large systems at finite temperatures and away from critical points, the function $P(\underline{C}, \underline{\gamma})$ should be sharply peaked near $\underline{C} = \langle\underline{C}\rangle_{\Gamma'}$. This allows us to expand $\langle B\rangle_{\Gamma}$ in eq.(2.29) in a Taylor series in $\underline{C}$ about $\underline{C} = \langle\underline{C}\rangle_{\Gamma'}$ with the result that

$$\langle B\rangle_{\Gamma'} = \langle B\rangle_{\Gamma} + \tfrac{1}{2}\langle\hat{\underline{C}}\hat{\underline{C}}\rangle_{\Gamma'} : \left.\frac{\partial^2\langle B\rangle_{\Gamma}}{\partial\underline{C}\,\partial\underline{C}}\right|_{\underline{C}=\langle\underline{C}\rangle_{\Gamma'}}$$

$$+ \frac{1}{3!}\langle\hat{\underline{C}}\,\hat{\underline{C}}\,\hat{\underline{C}}\rangle_{\Gamma'} \vdots \left.\frac{\partial^3\langle B\rangle_{\Gamma}}{\partial\underline{C}\,\partial\underline{C}\,\partial\underline{C}}\right|_{\underline{C}=\langle\underline{C}\rangle_{\Gamma'}} + O(N^{-3}) \ . \tag{2.31}$$

For the quadratic response theory only terms to $O(N^{-2})$ need be retained. Rearranging this last equation and iterating allows us to write

$$\langle B\rangle_{\Gamma} = \langle B\rangle_{\Gamma'} - \tfrac{1}{2}\langle\hat{\underline{C}}\hat{\underline{C}}\rangle_{\Gamma'} : \frac{\partial^2\langle B\rangle_{\Gamma'}}{\partial\langle\underline{C}\rangle_{\Gamma'}\,\partial\langle\underline{C}\rangle_{\Gamma'}}$$

$$- \frac{1}{3!}\langle\hat{\underline{C}}\hat{\underline{C}}\hat{\underline{C}}\rangle_{\Gamma'} \vdots \frac{\partial^3\langle B\rangle_{\Gamma'}}{\partial\langle\underline{C}\rangle_{\Gamma'}\,\partial\langle\underline{C}\rangle_{\Gamma'}\,\partial\langle\underline{C}\rangle_{\Gamma'}} \tag{2.32}$$

$$+ \tfrac{1}{4}\langle\hat{\underline{C}}\hat{\underline{C}}\rangle_{\Gamma'} : \frac{\partial^2}{\partial\langle\underline{C}\rangle_{\Gamma'}\,\partial\langle\underline{C}\rangle_{\Gamma'}} \left(\langle\hat{\underline{C}}\hat{\underline{C}}\rangle_{\Gamma'} : \frac{\partial^2\langle B\rangle_{\Gamma'}}{\partial\langle\underline{C}\rangle_{\Gamma'}\,\partial\langle\underline{C}\rangle_{\Gamma'}}\right) + O(N^{-3})$$

The correlation functions in eq.(2.27) differ from canonical or grand canonical ones by long range terms of order N^{-1}. This difference when multiplied by the F's and integrated over the volume is not negligible and must be taken into account. In order to accomplish this we first consider some binary correlation function of the form

$$\langle \hat{B}\hat{D} \rangle_{\Gamma} = \langle BD \rangle_{\Gamma} - \langle B \rangle_{\Gamma} \langle D \rangle_{\Gamma} \tag{2.33}$$

where B and D are any dynamical variables. Using eq.(2.32) on each of the averages appearing in eq.(2.33) results in

$$\langle \hat{B}\hat{D} \rangle_{\Gamma} = \langle \hat{B}\hat{D} \rangle_{\Gamma'} - \tfrac{1}{2} \langle \underline{\hat{C}}\,\underline{\hat{C}} \rangle_{\Gamma'} : \frac{\partial^2 \langle \hat{B}\hat{D} \rangle_{\Gamma'}}{\partial \langle \underline{C} \rangle_{\Gamma'} \, \partial \langle \underline{C} \rangle_{\Gamma'}}$$

$$- \langle \underline{\hat{C}}\,\underline{\hat{C}} \rangle : \frac{\partial \langle B \rangle_{\Gamma'}}{\partial \langle \underline{C} \rangle_{\Gamma'}} \frac{\partial \langle D \rangle_{\Gamma'}}{\partial \langle \underline{C} \rangle_{\Gamma'}} + O(N^{-2}) \tag{2.34}$$

where for our purposes it is sufficient to keep only terms to $O(N^{-1})$, since binary correlation functions appear only in the linear term in eq.(2.27) which contains only one volume integration.

By using eq.(2.29) it is easily shown that

$$\frac{\partial \langle C_i \rangle_{\Gamma'}}{\partial \gamma_j} = \langle \hat{C}_i \hat{C}_j \rangle_{\Gamma'}, \tag{2.35}$$

and

$$\frac{\partial \langle \hat{C}_i \hat{C}_j \rangle_{\Gamma'}}{\partial \gamma_k} = \langle \hat{C}_i \hat{C}_j \hat{C}_k \rangle_{\Gamma'} \quad . \tag{2.36}$$

Eq.(2.35) is used to rewrite eq.(2.34) as

$$\langle\hat{B}\hat{D}\rangle_{\Gamma} = \langle\hat{B}(1-P)\hat{D}\rangle_{\Gamma'} - \tfrac{1}{2}\langle\underline{C}\,\underline{C}\rangle_{\Gamma'} : \frac{\partial^2\langle\hat{B}\hat{D}\rangle_{\Gamma}}{\partial\langle C\rangle_{\Gamma'}\,\partial\langle C\rangle_{\Gamma'}} + O(N^{-2}) \tag{2.37}$$

where the operator P is now defined by

$$PB \equiv \langle B\,\underline{C}\rangle_{\Gamma'} \cdot \langle\underline{C}\,\underline{C}\rangle^{-1}_{\Gamma'} \cdot \hat{\underline{C}} \,. \tag{2.38}$$

The operator P is the projection operator onto the fluctuating parts of the variables $\underline{C}$ in the Γ' ensemble.

We also need to know (now to $O(N^{-2})$) how correlation functions of the form $\langle\hat{B}\,\hat{D}\,\hat{E}\rangle_{\Gamma}$ may be expressed in terms of Γ' quantities. This is accomplished by using eq.(2.32) in a rather tedious calculation given in appendix A.

Taking the Γ ensemble to be microcanonical and using eqs.(2.32), (2.37) and (A.7) in eq.(2.27) gives

$$\hat{\underline{a}}(\bar{r},\,t) = \beta\langle\hat{\underline{A}}(\bar{r},\,t)(1-P)\,\hat{\underline{A}}(\bar{r}_1)\rangle_{\Gamma'} * \underline{F}(\bar{r}_1)\left[1 + \frac{\partial\langle\underline{A}(\bar{r}_2)\rangle_{\Gamma'}}{\partial\langle E\rangle_{\Gamma'}} * \underline{F}(\bar{r}_2)\right]$$

$$+ \tfrac{1}{2}\beta^2\Big[\langle\big[(1-P)\,\hat{\underline{A}}(\bar{r},\,t)\big]\hat{\underline{A}}(\bar{r}_1)\,\hat{\underline{A}}(\bar{r}_2)\rangle_{\Gamma'} - \langle\hat{\underline{A}}(\bar{r},\,t)\big[P\,\hat{\underline{A}}(\bar{r}_1)\big]\,\hat{\underline{A}}(\bar{r}_2)\rangle_{\Gamma'}$$

$$- \langle\hat{\underline{A}}(\bar{r},\,t)\,\hat{\underline{A}}(\bar{r}_1)\,[P\,\underline{A}(\bar{r}_2)]\rangle_{\Gamma'} + 2\,\langle\hat{C}_i\,\hat{C}_j\,\hat{C}_k\rangle_{\Gamma'}\,\frac{\partial\langle\underline{A}(\bar{r})\rangle_{\Gamma'}}{\partial\langle C_i\rangle_{\Gamma'}}\,\frac{\partial\langle\underline{A}(\bar{r}_1)\rangle_{\Gamma'}}{\partial\langle C_j\rangle_{\Gamma'}}\,\frac{\partial\langle\underline{A}(\bar{r}_2)\rangle_{\Gamma'}}{\partial\langle C_k\rangle_{\Gamma'}}$$

$$+ \tfrac{1}{2}\,\langle\hat{C}_i\,\hat{C}_j\rangle_{\Gamma'}\,\langle\hat{C}_k\,\hat{C}_\ell\rangle_{\Gamma'}\Big[\frac{\partial^2\langle\underline{A}(\bar{r})\rangle_{\Gamma'}}{\partial\langle C_i\rangle_{\Gamma'}\,\partial\langle C_j\rangle_{\Gamma'}}\,\frac{\partial\langle\underline{A}(\bar{r}_1)\rangle_{\Gamma'}}{\partial\langle C_k\rangle_{\Gamma'}}\,\frac{\partial\langle\underline{A}(\bar{r}_2)\rangle_{\Gamma'}}{\partial\langle C_\ell\rangle_{\Gamma'}}$$

$$+ 4\,\frac{\partial^2\langle\underline{A}(\bar{r})\rangle_{\Gamma'}}{\partial\langle C_i\rangle_{\Gamma'}\,\partial\langle C_k\rangle_{\Gamma'}}\,\frac{\partial\langle\underline{A}(\bar{r})\rangle_{\Gamma'}}{\partial\langle C_j\rangle_{\Gamma'}}\,\frac{\partial\langle\underline{A}(\bar{r}_2)\rangle_{\Gamma'}}{\partial\langle C_\ell\rangle_{\Gamma'}} + 4 \text{ terms obtained by permuting the position of the double derivative in these last two terms}\Big]\Big] * \underline{F}(\bar{r}_2)\,\underline{F}(\bar{r}_1) + O(N^{-1}) \tag{2.39}$$

where repeated indices are to be summed. If the set of variables $\underline{C}$ includes the energy, and the condition

$$\frac{\partial \langle \underline{A}(\bar{r}) \rangle_{\rho'}}{\partial \langle C_i \rangle_{\rho'}} * \underline{F}(\bar{r}) = 0 \text{ for all } i \tag{2.40}$$

is imposed, then eq.(2.39) simplifies to:

$$\underline{a}(\bar{r}, t) = \beta \langle \hat{\underline{A}}(\bar{r}, t)\, \hat{\underline{A}}(\bar{r}_1) \rangle_{\rho'}^{*} \underline{F}(\bar{r}_1)$$

$$+ \tfrac{1}{2} \beta^2 \langle [(1 - P)\, \hat{\underline{A}}(\bar{r}, t)]\, \hat{\underline{A}}(\bar{r}_1)\, \hat{\underline{A}}(\bar{r}_2) \rangle_{\rho'}^{**} \underline{F}(\bar{r}_2)\, \underline{F}(\bar{r}_1) \,. \tag{2.41}$$

Eq.(2.41) is valid to quadratic order in F and lowest order in N^{-1} providing eq.(2.40) holds. By using eq.(2.35) it may be shown that the constraint eq.(2.40), is equivalent to

$$\langle \underline{C}\, \underline{A}(\bar{r}) \rangle_{\rho'} * \underline{F}(\bar{r}) = 0 \,. \tag{2.42}$$

The non-fluctuating quantities in the microcanonical ensemble are the total number of particles and energy, both of which are conserved. Using the response expression eq.(2.41) we find that

$$\int_V d\bar{r}\, \hat{a}_i(\bar{r}, t) = 0 \qquad i = \text{number, energy} \tag{2.43}$$

only if eq.(2.42) holds. Since the actual relaxation ocurrs in an isolated system, the integrals of the densities of the non-fluctuating quantities must never change from their equilibrium values, independent of the choice of ensemble used to express the correlation functions. This is quaranteed by eq.(2.42).

The form of eq.(2.43) is similar to the response equation given in ref. 32. The difference lies in the fact that the projection operator

P in this work does not contain projections onto the total momentum, a quantity which is not conserved in a closed system and fluctuates in the microcanonical ensemble. For the homogeneous systems considered in ref. 32 the momentum is conserved and so the mixing assumption (eq.(2.19)) would not be valid for the microcanonical ensemble, as discussed earlier. Thus eq.(2.41) is valid for inhomogeneous systems, the object of this work. By redefining the projection operator appearing in eq.(2.41) (cf. ref. 32), we may extend its validity to homogeneous systems.

Transport Equations and Local Equilibrium

The relaxation equation (eq.(2.41)) is not very useful in its present form since the time dependence of rather complicated time correlation functions must be known before it can be used. At present this behavior may be found only for low density systems[26] or through rather involved molecular dynamics computations[19]. The way to circumvent this problem is to consider not eq.(2.41), but an equation derived from it for the time derivatives of the $\underline{\hat{a}}(\overline{r}, t)$. Once this is obtained, certain information about the time correlation functions may be inferred[10,11].

The first step in finding these equations is to express the forces, $\underline{F}(\overline{r})$, in terms of the variables $\underline{\hat{a}}(\overline{r}, t)$. This is most easily accomplished when the Γ' ensemble in eq.(2.41) is grand canonical. In this case the correlation functions appearing in eq.(2.41) can be expected to decay rigorously to zero when any of their arguments are separated beyond some microscopic length. Because of this property, we can expect the inverse $\underline{\underline{K}}^{-1}(\overline{r}|\overline{r}', t)$ defined by

$$\underline{\underline{K}}^{-1}(\overline{r}|\overline{r}', t) * \langle \underline{\hat{A}}(\overline{r}', t)\, \underline{\hat{A}}(\overline{r}'') \rangle_{G.C.} \equiv \underline{\underline{I}}\, \delta(\overline{r}-\overline{r}'') \qquad (2.44)$$

to exist. In eq.(2.44) $\underline{\underline{I}}$ is the identity matrix. Henceforth, all averages shall be grand canonical and so the subscript "G.C." will be omitted.

Owing to the form of the variables $\underline{A}(\bar{r}, t)$, cf. eq.(1.5), the correlation function appearing in this last equation can for $t = 0$ be written

$$<\hat{\underline{A}}(\bar{r})\ \hat{\underline{A}}(\bar{r}')> \equiv \delta(\bar{r}-\bar{r}')\ \underline{\underline{R}}(\bar{r}) + \underline{\underline{R}}(\bar{r}) \cdot \underline{\underline{h}}(\bar{r}|\bar{r}') \cdot \underline{\underline{R}}(\bar{r}') \tag{2.45}$$

where

$$\underline{\underline{R}}(\bar{r}) \equiv < \delta(\bar{r}-\bar{r}_1)\ N\underline{A}_1(X^N)\ \underline{A}_1(X^N) > \quad . \tag{2.46}$$

The quantities in $\underline{\underline{h}}(\bar{r}|\bar{r}')$ are generalizations of the Ursell functions[56] and decay to zero when $|\bar{r}-\bar{r}'|$ is larger than some microscopic correlation length. Write

$$\underline{\underline{K}}^{-1}(\bar{r}|\bar{r}') \equiv \delta(\bar{r}-\bar{r}')\ \underline{\underline{\underline{R}}}^{-1}(\bar{r}) - \underline{\underline{C}}(\bar{r}|\bar{r}') \ , \tag{2.47}$$

where omission of the time shall imply $t = 0$. Then by using eqs.(2.44), (2.45) and (2.47) the relation

$$\underline{\underline{h}}(\bar{r}|\bar{r}') = \underline{\underline{C}}(\bar{r}|\bar{r}') + \underline{\underline{C}}(\bar{r}|\bar{r}'')* \underline{\underline{R}}(\bar{r}'')\ \underline{\underline{h}}(\bar{r}''|\bar{r}') \tag{2.48}$$

is obtained. This is an Ornstein-Zernicke equation[57] in which $\underline{\underline{C}}(\bar{r}|\bar{r}')$ plays the role of the direct correlation function, a short ranged function. Thus (cf. eq.(2.47)) $\underline{\underline{K}}^{-1}(\bar{r}|\bar{r}', 0)$ is a short range function.

Returning to the development of the transport equations, we may express the forces $\underline{F}(\bar{r})$ in terms of the $\hat{\underline{a}}(\bar{r}, t)$ by using eqs.(2.44) and (2.41) with the result that

$$\beta \underline{F}(\bar{r}) = \underline{\underline{K}}^{-1}(\bar{r}|\bar{r}_1,\ t) * \{ \hat{\underline{a}}(\bar{r}_1,t) - \tfrac{1}{2} < [(1 - P)\ \hat{\underline{A}}(\bar{r}_1, t)]\ \hat{\underline{A}}(\bar{r}_2)\ \underline{A}(\bar{r}_3) >$$

$$\overset{*}{*}(\underline{\underline{K}}^{-1}(\bar{r}_3|\bar{r}_4,\ t) * \hat{\underline{a}}(\bar{r}_4,\ t))\ \ (\underline{\underline{K}}^{-1}(\bar{r}_2|\bar{r}_5,\ t) * \hat{\underline{a}}(\bar{r}_5,\ t)) \}$$

$$+ O(\hat{a}^3)\ . \tag{2.49}$$

Since for the grand canonical ensemble the variables $\underline{C}$ are the number and energy, both constants of the motion, we find

$$\dot{\underline{a}}(\bar{r},\ t) = <\dot{\hat{\underline{A}}}(\bar{r},\ t)\ \hat{\underline{A}}(\bar{r}_1)> * \beta\, \underline{F}(\bar{r}_1) + \tfrac{1}{2} <\dot{\hat{\underline{A}}}(\bar{r},\ t)\ \hat{\underline{A}}(\bar{r}_1)\ \hat{\underline{A}}(\bar{r}_2)> \overset{*}{*} \beta^2\ \underline{F}(\bar{r}_2)\ \underline{F}(\bar{r}_1), \tag{2.50}$$

which on eliminating the forces (cf. eq.(2.49)) becomes

$$\dot{\hat{\underline{a}}}(\bar{r},\ t) = \underline{\underline{M}}(\bar{r}|\bar{r}_1,\ t) * \hat{\underline{a}}(\bar{r}_1,\ t) + \underline{\underline{W}}(\bar{r}|\bar{r}_1|\bar{r}_2,\ t) \overset{*}{*} \hat{\underline{a}}(\bar{r}_2,\ t)\ \hat{\underline{a}}(\bar{r}_1,\ t)$$

$$+ O(\hat{\underline{a}}^3)\ . \tag{2.51}$$

In this last equation

$$\underline{\underline{M}}(\bar{r}|\bar{r}_1,\ t) \equiv <\dot{\hat{\underline{A}}}(\bar{r},\ t)\ \hat{\underline{A}}(\bar{r}_2)> * \underline{\underline{K}}^{-1}(\bar{r}_2|\bar{r}_1,\ t) \tag{2.52}$$

and

$$\underline{\underline{W}}(\bar{r}|\bar{r}_1|\bar{r}_2,\ t) \equiv [\tfrac{1}{2}<\dot{\underline{A}}(\bar{r},\ t)\ \underline{A}(\bar{r}_3)\ \underline{A}(\bar{r}_4)> - \tfrac{1}{2}<\dot{\underline{A}}(\bar{r},\ t)\ \underline{A}(\bar{r}_5)> * \underline{\underline{K}}^{-1}(\bar{r}_5|\bar{r}_6,\ t)$$

$$* <[\,(1 - P)\ \ \hat{\underline{A}}(\bar{r}_6,\ t)]\ \hat{\underline{A}}(\bar{r}_3)\ \hat{\underline{A}}(\bar{r}_4)\,>] \overset{*}{*} \underline{\underline{K}}^{-1}(\bar{r}_4|\bar{r}_1,\ t)\ \underline{\underline{K}}^{-1}(\bar{r}_3|\bar{r}_2,\ t)\ . \tag{2.53}$$

The number and energy are both conserved quantities whose densities are slowly varying (in this instance the smallness parameter for the time evolution would be the size of the nonequilibrium gradients in the system). As such the number and energy densities must be included in the set of dynamical variables $\underline{A}(\bar{r},\ t)$.

Since from eq.(2.44)

$$\langle \dot{\underline{A}}(\bar{r}, t)\, \hat{\underline{A}}(\bar{r}_1)\rangle * \underline{\underline{K}}^{-1}(\bar{r}_1|\bar{r}', t) = -\langle \hat{\underline{A}}(\bar{r}, t)\, \dot{\hat{\underline{A}}}(\bar{r}_1)\rangle * \underline{\underline{K}}^{-1}(\bar{r}_1|\bar{r}', t), \quad (2.54)$$

this implies that

$$\langle \dot{\underline{A}}(\bar{r}, t)\, \hat{\underline{A}}(\bar{r}_1)\rangle * \underline{\underline{K}}^{-1}(\bar{r}_1|\bar{r}_2, t) * \langle (P\hat{\underline{A}}(\bar{r}_2, t))\, \hat{\underline{A}}(\bar{r}_3)\, \hat{\underline{A}}(\bar{r}_4)\rangle$$

$$= -\langle \hat{\underline{A}}(\bar{r}, t)\, \hat{\underline{A}}(\bar{r}_1)\rangle * \dot{\underline{\underline{K}}}^{-1}(\bar{r}_1|\bar{r}_2, t) * \int d\bar{r}_5 \langle \hat{\underline{A}}(\bar{r}_2, t)\, \hat{\underline{C}}(\bar{r}_5)\rangle \cdot \langle \hat{\underline{C}}\hat{\underline{C}}\rangle^{-1}$$

$$\cdot \langle \hat{\underline{C}}\hat{\underline{A}}(\bar{r}_3)\, \hat{\underline{A}}(\bar{r}_4)\rangle \ , \quad (2.55)$$

where $\underline{C}(\bar{r}, t)$ is the column vector whose components are the number and energy densities, a subset of the variables appearing in $\underline{A}(\bar{r}, t)$. We may use eq.(2.54) to move the time derivative to the right in eq.(2.55) with the result that

$$\dot{\underline{\underline{K}}}^{-1}(\bar{r}_1|\bar{r}_2, t) * \int d\bar{r}_5 \langle \hat{\underline{A}}(\bar{r}_2, t)\, \hat{\underline{C}}(\bar{r}_5)\rangle$$

$$= -\underline{\underline{K}}^{-1}(\bar{r}_1|\bar{r}_2, t) * \langle \dot{\underline{A}}(\bar{r}, t)\, \hat{\underline{C}}\rangle = 0 \ . \quad (2.56)$$

Hence the projection operator appearing in eq.(2.53) may be neglected. The resulting equation for $\dot{\underline{a}}$ is identical to that obtained in ref. 31, providing eq.(2.43) is valid. Since the total number and energy are conserved, eq.(2.43) need only hold at $t = 0$ in order to be valid at all times.

The set of variables $\underline{A}(\bar{r}, t)$ was assumed to be slowly varying. This means that on the average $\dot{A}$ should be "small". In order to exploit this fact we rewrite $\underline{\underline{M}}$ and $\underline{\underline{W}}$ making as many time derivatives of $\underline{A}$ explicit as possible. That is,

$$\underline{\underline{M}}(\bar{r}|\bar{r}',\, t) = \underline{\underline{M}}(\bar{r}|\bar{r}',\, 0) - \int_0^t dt_1 \langle \underline{I}(\bar{r},\, t_1)\ \underline{I}(\bar{r}_1)\rangle * \underline{\underline{K}}^{-1}(\bar{r}_1|\bar{r}',\, t_1) \qquad (2.57)$$

and

$$\underline{\underline{W}}(\bar{r}|\bar{r}'|\bar{r}'',\, t) = \underline{\underline{W}}(\bar{r}|\bar{r}'|\bar{r}'',\, 0) - \tfrac{1}{2}\int_0^t dt_1 [\langle \underline{I}(\bar{r},\, t_1)\ \hat{\underline{A}}(\bar{r}_1)\ \underline{I}(\bar{r}_2)\rangle$$

$$+ \langle \underline{I}(\bar{r},\, t_1)\ \underline{I}(\bar{r}_1)\ \hat{\underline{A}}(\bar{r}_2)\rangle - \langle \underline{I}(\bar{r},\, t_1)\ \underline{I}(\bar{r}_3)\rangle * \underline{\underline{K}}^{-1}(\bar{r}_3|\bar{r}_4,\, t_1)$$

$$* \langle \hat{\underline{A}}(\bar{r}_4,\, t_1)\ \hat{\underline{A}}(\bar{r}_1)\ \hat{\underline{A}}(\bar{r}_2)\rangle] \overset{*}{*} \underline{\underline{K}}^{-1}(\bar{r}_2|\bar{r}',\, t_1)\ \underline{\underline{K}}^{-1}(\bar{r}_1|\bar{r}'',\, t_1) \qquad (2.58)$$

where the dissipative part of $\dot{\underline{A}}$ is defined by

$$\underline{I}(\bar{r},\, t) \equiv \dot{\underline{A}}(\bar{r},\, t) - \underline{\underline{M}}(\bar{r}|\bar{r}_1,\, t) * \hat{\underline{A}}(\bar{r}_1,\, t) \quad . \qquad (2.59)$$

The dissipative parts of $\dot{\underline{A}}$ have the property of being orthogonal to the slow variables in the sense that

$$\langle \underline{I}(\bar{r},\, t)\ \hat{\underline{A}}(\bar{r}')\rangle = 0 \quad . \qquad (2.60)$$

Up to this point the generalized transport equation (eq.(2.51)) is correct, providing the perturbation expansion in $\underline{F}$ is valid, eq.(2.43) holds and the number and energy densities are included in the set of dynamical variables $\underline{A}$. Unfortunately, it is no more useful than the relaxation equation (eq.(2.41)) since the time dependence of the non-local transport coefficients, $\underline{\underline{M}}$ and $\underline{\underline{W}}$, is not known. The transport equations presented above should be compared with the exact ones derived by Tokuyama and Mori[18], the two being very similar.

We shall assume that the set of variables $\underline{A}$ contains all slowly varying dynamical variables. Since $\underline{I}$ is orthogonal to $\underline{A}$ (cf. eq.(2.60)), it does not contain any slow parts, and hence time correlation functions

containing $\underline{I}$ should decay on a moleuclar time scale, τ_m. Thus, to second order in the smallness parameter characterizing the rate of change of the slow variables, we may neglect the time dependence of any of the quantities appearing in eqs.(2.57) and (2.58) not containing $\underline{I}$. That is,

$$\underline{\underline{M}}(\bar{r}|\bar{r}', t) = \underline{\underline{M}}(\bar{r}|\bar{r}', 0) - \int_0^t dt_1 \langle \underline{I}(\bar{r}, t_1)\, \underline{I}(\bar{r}_1) \rangle * \underline{\underline{K}}^{-1}(\bar{r}_1|\bar{r}') \qquad (2.61)$$

and

$$\underline{\underline{W}}(\bar{r}|\bar{r}'|\bar{r}'', t) = \underline{\underline{W}}(\bar{r}|\bar{r}'|\bar{r}'', 0) - \tfrac{1}{2} \int_0^t dt_1 [\langle \underline{I}(\bar{r}, t_1)\, \hat{\underline{A}}(\bar{r}_1)\, \underline{I}(\bar{r}_2) \rangle + \langle I(\bar{r}, t_1)\, \underline{I}(\bar{r}_1)\, \hat{\underline{A}}(\bar{r}_2) \rangle \qquad (2.62)$$

$$- \langle \underline{I}(\bar{r}, t_1)\, \underline{I}(\bar{r}_3) \rangle * \underline{\underline{K}}^{-1}(\bar{r}_3|\bar{r}_4) * \langle \hat{\underline{A}}(\bar{r}_4)\, \hat{\underline{A}}(\bar{r}_1)\, \hat{\underline{A}}(\bar{r}_2) \rangle]^{*}_{*} \underline{\underline{K}}^{-1}(\bar{r}_2|\bar{r}')\, \underline{\underline{K}}^{-1}(\bar{r}_1|\bar{r}'').$$

In addition, we may take

$$\underline{I}(\bar{r}, t) = \dot{\underline{A}}(\bar{r}, t) - \underline{\underline{M}}(\bar{r}|\bar{r}_1, 0) * \hat{\underline{A}}(\bar{r}_1, t) \qquad (2.63)$$

for $\underline{\underline{M}}$ and $\underline{\underline{W}}$ to second order in the smallness parameter.

For $t \gg \tau_m$ the time integrals in eqs.(2.61) and (2.62) do not change and so the limits of integration may be extended to infinity.

The generalized transport equation may be concisely written if we define force-like quantities, $\underline{\Phi}(\bar{r}, t)$, as was done in ref. 32. That is, let

$$\hat{\underline{a}}(\bar{r}, t) \equiv \langle \hat{\underline{A}}(\bar{r})\, \hat{\underline{A}}(\bar{r}_1) \rangle * \beta\, \underline{\Phi}(\bar{r}_1, t) + \tfrac{1}{2} \beta^2 \langle \hat{\underline{A}}(\bar{r})\, \hat{\underline{A}}(\bar{r}_1)\, \hat{\underline{A}}(\bar{r}_2) \rangle ^{*}_{*} \underline{\Phi}(\bar{r}_1, t)\, \underline{\Phi}(\bar{r}_2, t) \qquad (2.64)$$

or, by using eq. (2.44),

$$\beta\underline{\Phi}(\bar{r},t) = \underline{\underline{K}}^{-1}(\bar{r}|\bar{r}_1)*[\underline{\hat{a}}(\bar{r}_1,t) - \tfrac{1}{2}<\underline{\hat{A}}(\bar{r}_1)\,\underline{\hat{A}}(\bar{r}_2)\,\underline{\hat{A}}(\bar{r}_3)>^{*}_{*}(\underline{\underline{K}}^{-1}(\bar{r}_3|\bar{r}_4)*\underline{\hat{a}}(\bar{r}_4,t))$$

$$\times\,(\underline{\underline{K}}^{-1}(\bar{r}_2|\bar{r}_5)*\underline{\hat{a}}(\bar{r}_5,\,t))\,] \;+\; O(\hat{a}^3)\quad . \tag{2.65}$$

Combining eqs. (2.51), (2.61), (2.62) and (2.65) yields

$$\dot{\underline{a}}(\bar{r},t) = <\dot{\underline{A}}(\bar{r})\;\underline{\hat{A}}(\bar{r}_1)>*\beta\underline{\Phi}(\bar{r}_1,t) + \tfrac{1}{2}\beta^2<\dot{\underline{A}}(\bar{r})\;\underline{\hat{A}}(\bar{r}_1)\;\underline{\hat{A}}(\bar{r}_2)>^{*}_{*}\underline{\Phi}(\bar{r}_2,t)\;\underline{\Phi}(\bar{r}_1,t)$$

$$-\int_0^\infty dt_1\,\{<\underline{I}(\bar{r},t)\;\underline{I}(\bar{r}_1)>*\beta\underline{\Phi}(\bar{r}_1,t) + \tfrac{1}{2}\beta^2<\underline{I}(\bar{r},t_1)\;(\underline{\hat{A}}(\bar{r}_1)\,\underline{I}(\bar{r}_2)$$

$$+\,\underline{I}(\bar{r}_1)\;\underline{\hat{A}}(\bar{r}_2))>^{*}_{*}\underline{\Phi}(\bar{r}_2,t)\;\underline{\Phi}(\bar{r}_1,t)\,\}\quad , \tag{2.66}$$

the generalized transport equation. It is valid to second order in both $\underline{\hat{a}}$ and the smallness paramerer characterizing the rate of change of the slow variables and for $t \gg \tau_m$. The form of the equation is identical to that presented in earlier works[31,32]. An important difference between eq.(2.66) and the transport equations derived by others lies in the fact that the force-like quantities $\underline{\Phi}(\bar{r},\,t)$ do not become the fictitious forces at $t = 0$. In fact, using eqs.(2.49) and (2.65) it can be shown that

$$\beta(\underline{\Phi}(\bar{r},0) - \underline{F}(\bar{r})) = -\tfrac{1}{2}\,\underline{\underline{K}}^{-1}(\bar{r}|\bar{r}_1)*<(P\,\underline{\hat{A}}(\bar{r}_1))\;\underline{\hat{A}}(\bar{r}_2)\;\underline{\hat{A}}(\bar{r}_3)>^{*}_{*}(\underline{\underline{K}}^{-1}(\bar{r}_3|\bar{r}_4)*\underline{\hat{a}}(\bar{r}_4,0))$$

$$\times\,(\underline{\underline{K}}^{-1}(\bar{r}_2|\bar{r}_5)*\underline{\hat{a}}(\bar{r}_5,0)) \;+\; O(\hat{a}^3) \tag{2.67}$$

$$= -\tfrac{1}{2}<\underline{\hat{C}}\,\underline{\hat{C}}>^{-1}\cdot<\underline{\hat{C}}\,\underline{\hat{A}}(\bar{r}_1)\;\underline{\hat{A}}(\bar{r}_2)>^{*}_{*}(\underline{\underline{K}}^{-1}(\bar{r}_2|\bar{r}_3)*\underline{\hat{a}}(\bar{r}_3,0))\;(\underline{\underline{K}}^{-1}(\bar{r}_1|\bar{r}_4)*\underline{\hat{a}}(\bar{r}_4,0))$$

$$+\,O(\hat{a}^3)\quad . \tag{2.68}$$

In obtaining the last equality, the fact that the densities of the variables $\underline{C}$ are included in the set of variables and eq.(2.44) were used.

Also using eqs. (2.68), (2.29) and (2.30) we find that

$$\beta(\underline{F}(\bar{r}) - \underline{\Phi}(\bar{r},0))_\alpha = O(\hat{a}^3), \quad \alpha \neq \text{number, energy}$$

$$= \tfrac{1}{2}\left(\frac{\partial \langle \hat{\underline{A}}(\bar{r}_1)\ \hat{\underline{A}}(\bar{r}_2)\rangle}{\partial \langle C_\alpha \rangle}\right)_{\langle \underline{C}\rangle_{\gamma\neq\alpha}} * (\underline{\underline{K}}^{-1}(\bar{r}_2|\bar{r}_3) * \hat{\underline{a}}(\bar{r}_3,0))\ (\underline{\underline{K}}^{-1}(\bar{r}_1|\bar{r}_4) * \hat{\underline{a}}(\bar{r}_4,0))$$

$$+ O(\hat{a}^3) \qquad \alpha = \text{number, energy.} \tag{2.69}$$

From this last equation we see that the difference between $\underline{F}(\bar{r})$ and $\underline{\Phi}(\bar{r}, 0)$ is at most a quantity constant in space.

Bearing these differences in mind, a local equilibrium distribution function, $f_L(X^N, t)$ may be defined in terms of the force-like quantities. That is, let

$$f_L(X^N,t) \equiv \frac{f_{g.c.}(X^N)\ \exp[\beta \underline{A}(\bar{r},X^N) * \underline{\Phi}(\bar{r},t)]}{\sum_{N=0}^{\infty} \int dX^N\ f_{g.c.}(X^N)\ \exp[\beta \underline{A}(\bar{r},X^N) * \underline{\Phi}(\bar{r},t)]} \tag{2.70}$$

where $f_{g.c.}(X^N)$ is the equilibrium grand canonical distribution function:

$$f_{g.c.}(X^N) \equiv \frac{\exp[\beta \mu N - \beta H(X^N)]}{h^{3N} N!\, \Xi}, \tag{2.71}$$

h being Planck's constant, μ the total chemical potential and Ξ the grand partition function.

From eqs.(2.70) and (2.64) it follows that

$$\hat{\underline{a}}(\bar{r},t) = \langle \hat{\underline{A}}(\bar{r})\rangle_L(t) + O(\underline{\Phi}^3), \tag{2.72}$$

while from eq.(2.66)

$$\dot{\underline{a}}(\bar{r},t) = \langle \dot{\underline{A}}(\bar{r})\rangle_L(t) - \beta \int_0^\infty dt_1 \langle \underline{I}(\bar{r},t_1)\ \underline{I}(\bar{r}_1)\rangle_L(t) * \beta \underline{\Phi}(\bar{r}_1,t) + O(\underline{\Phi}^3), \tag{2.73}$$

where the symbol $< >_L(t)$ denotes an average using the distribution function defined by eq.(2.70). From eqs.(2.69) - (2.71) we see that in general

$$f_L(X^N,0) \neq \exp[-\beta H_T(0) + \mu\beta N] \div (h^{3N}N! \sum_{N'=0}^{\infty} \int dX^{N'} \exp[-\beta H_T(0) + \beta\mu N']/h^{3N'}N'!).$$

In order to make contact with the phenomenological theories[2] we define the nonequilibrium entropy by

$$S(t) \equiv -K_B < \ln f_L >_L(t) \tag{2.74}$$

which, using eqs.(2.70) - (2.72), becomes

$$S(t) = -K_B \left[\beta\mu <N>_L(t) - \beta <H>_L(t) + \beta\, \underline{a}(\bar{r}, t) * \underline{\Phi}(\bar{r}, t) - \ln \left(\sum_{N=0}^{\infty} \int dX^N f_{g.c.}(X^N) \exp[\beta \underline{A}(\bar{r}, X^N) * \underline{\Phi}(\bar{r}, t)] \right) \right] . \tag{2.75}$$

Noting that $<N>_L(t) = <N>$ and $<H>_L(t) = <H>$, eq.(2.75) shows that the quantities $\underline{\Phi}(\bar{r}, t)$ correspond to the displacements from equilibrium of the intensive variables conjugate to the $\underline{a}(\bar{r}, t)$. This point shall be made more clear within the context of a specific example, to be presented in the following chapter.

From eq.(2.75) it follows that

$$\dot{S}(t) = -T^{-1} \dot{\hat{\underline{a}}}(\bar{r}, t) * \underline{\Phi}(\bar{r}, t) + O(\underline{\Phi}^4) \quad , \tag{2.76}$$

which is a generalization of the usual form for entropy production. Using eq.(2.66) in eq.(2.76), it is easily shown that

$$\dot{TS}(t) = \beta \int_0^\infty dt_1 \langle \underline{I}(\bar{r},t_1)\ \underline{I}(\bar{r}_1)\rangle \overset{*}{*} \underline{\Phi}(\bar{r}_1,t)\ \underline{\Phi}(\bar{r},t)$$

$$- \frac{\beta^2}{2} \int_0^\infty dt_1 \langle \underline{I}(\bar{r},t)\ [\underline{I}(\bar{r}_1)\ \hat{\underline{A}}(\bar{r}_2) + \hat{\underline{A}}(\bar{r}_1)\ \underline{I}(\bar{r}_2)]\ \overset{*}{*} \underline{\Phi}(\bar{r}_2,t)\ \underline{\Phi}(\bar{r}_1,t)\ \underline{\Phi}(\bar{r},t)$$

$$+ O(\underline{\Phi}^4) \quad . \tag{2.77}$$

$$= \beta \int_0^\infty dt_1 \langle \underline{I}(\bar{r},t_1)\ \underline{I}(\bar{r}_1)\rangle_L(t) \overset{*}{*} \underline{\Phi}(\bar{r}_1,t)\ \underline{\Phi}(\bar{r},t) + O(\Phi^4) \tag{2.78}$$

where the last equality follows from eq.(2.70).

We consider only systems which are invariant under time reversal. This implies[6]

$$\langle I_\alpha(\bar{r},t)\ I_\gamma(\bar{r}_1)\rangle = \langle I_\alpha(\bar{r})\ I_\gamma(\bar{r}_1,-t)\rangle = \varepsilon_\alpha\varepsilon_\gamma \langle I_\gamma(\bar{r}_1,t)\ I_\alpha(\bar{r})\rangle \ , \tag{2.79}$$

where $\varepsilon_\alpha = \pm 1$, is the parity of $I_\alpha(\bar{r},t)$ under time reversal. Thus the leading order terms in the entropy production may be written:

$$\beta \int_0^\infty dt_1 \langle \underline{I}(\bar{r},t_1)\ \underline{I}(\bar{r}_1)\rangle \overset{*}{*} \underline{\Phi}(\bar{r}_1,t)\ \underline{\Phi}(\bar{r},t)$$

$$= \frac{\beta}{2} \int_0^\infty dt_1 \langle I_\alpha(\bar{r},t_1)\ I_\gamma(\bar{r}_1)\rangle (1+\varepsilon_\alpha\varepsilon_\gamma) \overset{*}{*} \Phi_\alpha(\bar{r}_1,t)\ \Phi_\gamma(\bar{r},t) \tag{2.80}$$

where repeated indices are summed. This shows that the leading order entropy production arises only from terms containing Φ's conjugate to variables of the same time reversal parity. This is also the case in the phenomenological theory.

It can be shown that the leading order contribution to the entropy production is non-negative. Consider the quantity

$$Y_n \equiv \sum_{k=1}^{n} Z_k \, \underline{I}(\bar{r}, t_k) * \underline{\Phi}(\bar{r},t) \div [<\underline{I}(\bar{r}) \, \underline{I}(\bar{r}_1)> \overset{*}{*} \underline{\Phi}(\bar{r},t) \, \underline{\Phi}(\bar{r}_1,t)]^{\frac{1}{2}} \qquad (2.81)$$

where the sets of complex numbers, $\{Z_k\}_{k=1}^{n}$ and real times, $\{t_k\}_{k=1}^{n}$, are arbitrary. From this definition it follows that

$$0 \leq <|Y_n|^2> = \sum_{k,\ell=1}^{n} Z_k^* \, Z_\ell \, G_t(t_k - t_\ell) \qquad (2.82)$$

where

$$G_t(t_k - t_\ell) \equiv \frac{<\underline{I}(\bar{r},t_k) \, \underline{I}(\bar{r}_1,t_\ell)> \overset{*}{*} \underline{\Phi}(\bar{r}_1, t) \, \underline{\Phi}(\bar{r},t)}{<\underline{I}(\bar{r}) \, \underline{I}(\bar{r}_1)> \overset{*}{*} \underline{\Phi}(\bar{r}_1,t) \, \underline{\Phi}(\bar{r},t)} \, . \qquad (2.83)$$

Note that $G_t(0) = 1$. According to Bochner's theorem[58], a function satisifying the inequality (2.82) and initially equal to unity has a non-negative Fourier transform. Hence for any ω

$$0 \leq \int_{-\infty}^{\infty} dt_1 \, e^{i\omega t_1} \, G_t(t_1) \, . \qquad (2.84)$$

Combining this result with eqs.(2.79) and (2.80) yields

$$\beta \int_{0}^{\infty} dt_1 <\underline{I}(\bar{r},t_1) \, \underline{I}(\bar{r}_1)> \overset{*}{*} \underline{\Phi}(\bar{r}_1,t)>\underline{\Phi}(\bar{r},t) \geq 0 \, , \qquad (2.85)$$

which is just the statement that the leading order contribution to the entropy production is non-negative. The next term in the expression for entropy production (cf. eq.(2.77)) can be either positive or negative.

In summary, this chapter has dealt with the response theory and transport equations for isolated inhomogeneous systems. We have obtained equations local in time but nonlocal in space. In addition, a local equilibrium formulation of these results was presented and it was shown that for systems close to equilibrium the entropy production was non-

negative. Most importantly, we have shown that the choice of ensemble is immaterial to the transport equations providing certain quantities are never removed from equilibrium. This is analogous to the equivalence of ensembles in equilibrium statistical mechanics.

In the remainder of this work we shall consider methods for localizing the above equations in space. The next chapter will deal with the situations where the spatial gradients in the equilibrium system are small.

Chapter III. Fluids in Weak External Fields

Many important macroscopic phenomena occur in static external fields (e.g., gravity, electric fields, etc.). These fields cause the equilibrium systems to be inhomogeneous. By weak external fields we mean those where the characteristic length of the equilibrium inhomogeneity, Δ, is large compared to the correlation length λ_c. Most experimental situations meet this requirement, except near the critical point. It is also assumed that the external force, $\overline{F}_{ext}(\overline{r})$, is conservative, i.e.,

$$\overline{F}_{ext}(\overline{r}) \equiv -\overline{\nabla} \cdot \phi_{ext}(\overline{r}) \quad , \tag{3.1}$$

where $\phi_{ext}(\overline{r})$ is the external potential.

For the dynamical variables discussed in the introduction it is reasonable to assume that

$$\dot{\underline{A}}(\overline{r}, X^N) \equiv \underline{\underline{\theta}}(\overline{r}) \cdot \underline{A}(\overline{r}, X^N) + \underline{Q}(\overline{r}, X^N) \tag{3.2}$$

where $\underline{\underline{\theta}}(\overline{r})$ is a function only of the external force and $\underline{Q}(\overline{r},X^N)$ is the field-free form of $\dot{\underline{A}}(\overline{r},X^N)$. Eq.(3.2) can usually be made to hold by choosing the variables, $\underline{A}$, such that they do not contain $\overline{F}_{ext}$ or ϕ_{ext} explicitly and/or by neglecting terms of the order σ/Δ, where σ is the range of the intermolecular potential. The function $\underline{\underline{\theta}}(\overline{r})$ vanishes when the external force is not present. It should also be noted that the motion of the phase point in eq.(3.2) implicitly contains the effects of the external field.

Macroscopic Equations and Expansion in Gradients

The macroscopic equations, discussed in the previous chapter, may easily be rewritten for variables satisfying eq.(3.2). In this case the nonlocal transport coefficients (cf. eqs.(2.61) and (2.62)) become, for $t >> \tau_m$,

$$\underline{\underline{M}}(\bar{r}|\bar{r}') = \underline{\underline{\theta}}(\bar{r})\,\delta(\bar{r}-\bar{r}') + \langle\hat{\underline{Q}}(\bar{r})\,\hat{\underline{A}}(\bar{r}_1)\rangle * \underline{\underline{K}}^{-1}(\bar{r}_1|\bar{r}')$$

$$- \int_0^\infty dt_1 \langle \underline{I}(\bar{r}, t_1)\,\underline{I}(\bar{r}_1)\rangle * \underline{\underline{K}}^{-1}(\bar{r}|\bar{r}') \qquad (3.3)$$

$$\equiv \underline{\underline{\theta}}(\bar{r})\,\delta(\bar{r}-\bar{r}') + \underline{\underline{M}}'(\bar{r}|\bar{r}') \qquad (3.4)$$

and

$$\underline{\underline{\underline{W}}}(\bar{r}|\bar{r}'|\bar{r}'') = \tfrac{1}{2}[\langle \underline{I}(\bar{r})\,\hat{\underline{A}}(\bar{r}_1)\,\hat{\underline{A}}(\bar{r}_2)\rangle + \int_0^\infty dt_1 \{\langle \underline{I}(\bar{r}, t_1)\,\underline{I}(\bar{r}_3)\rangle * \underline{\underline{K}}^{-1}(\bar{r}_3|\bar{r}_4)$$

$$*\langle \hat{\underline{A}}(\bar{r}_3)\,\hat{\underline{A}}(\bar{r}_1)\,\hat{\underline{A}}(\bar{r}_2)\rangle - \langle \underline{I}(\bar{r}, t_1)\,(\underline{I}(\bar{r}_1)\,\hat{\underline{A}}(\bar{r}_2) + \hat{\underline{A}}(\bar{r}_1)\,\underline{I}(\bar{r}_2))\rangle\}]$$

$$** \underline{\underline{K}}^{-1}(\bar{r}_2|\bar{r}')\,\underline{\underline{K}}^{-1}(\bar{r}_1|\bar{r}'') \qquad (3.5)$$

where the time variable in the notation for $\underline{\underline{M}}$ and $\underline{\underline{\underline{W}}}$ has been suppressed. In obtaining these last two relations we utilized the fact that

$$\underline{\underline{\theta}}(\bar{r}) \circ \langle \underline{A}(\bar{r})\rangle = -\langle \underline{Q}(\bar{r})\rangle \quad , \qquad (3.6)$$

which follows from eq.(3.2). From eqs.(2.63) and (3.6) we find that

$$\underline{I}(\bar{r}, t) = \hat{\underline{Q}}(\bar{r}, t) - \tilde{\underline{\underline{M}}}(\bar{r}|\bar{r}') * \hat{\underline{A}}(r', t) \quad , \qquad (3.7)$$

with

$$\tilde{\underline{\underline{M}}}(\bar{r}|\bar{r}') \equiv <\hat{\underline{Q}}(\bar{r})\ \hat{\underline{A}}(\bar{r}_1)> * \underline{\underline{K}}^{-1}(\bar{r}_1|\bar{r}') \quad . \tag{3.8}$$

Eqs.(3.3) - (3.8) show that explicit dependence on $\bar{F}_{ext}$ appears only in the first term in $\underline{\underline{M}}$, the linear nonlocal transport coefficient. The remaining terms have the same explicit form as in force free systems, although they contain the effects of the force implicitly. These effects shall be considered below.

For the forms of $\underline{\underline{M}}$ and $\underline{\underline{W}}$ given above, the generalized transport equation, eq.(2.51), becomes:

$$\dot{\hat{\underline{a}}}(\bar{r},\ t) = \underline{\underline{\theta}}(\bar{r})\ \hat{\underline{a}}(\bar{r},\ t) + \underline{\underline{M}}'(\bar{r}|\bar{r}') * \hat{\underline{a}}(\bar{r}',t) + \underline{\underline{\underline{W}}}(\bar{r}|\bar{r}'|\bar{r}'') \overset{*}{*} \hat{\underline{a}}(\bar{r}',t)\ \hat{\underline{a}}(\bar{r}'',t)$$

$$+ O(\hat{\underline{a}}^3) \quad , \tag{3.9}$$

or in terms of the local equilibrium averages and conjugate variables, $\underline{\Phi}(\bar{r},\ t)$, discussed in the preceding chapter,

$$\dot{\hat{\underline{a}}}(\bar{r},\ t) = \underline{\underline{\theta}}(\bar{r})\ \hat{\underline{a}}(\bar{r},\ t) + <\hat{\underline{Q}}(\bar{r})>_L(t) - \beta \int_0^\infty dt_1 <\underline{I}(\bar{r},\ t_1)\ \underline{I}(\bar{r}_1)>_L(t) * \underline{\Phi}(\bar{r}_1,t)$$

$$+ O(\underline{\Phi}^3) \quad . \tag{3.10}$$

It is assumed that the various terms appearing in eqs.(3.3) and (3.5) decay to zero whenever any of their arguments are separated beyond some microscopic length (on the order of λ_c). For this to be true it is essential that the time correlation functions decay on the τ_m time scale. The decay length of a time correlation function increases with time. Thus, if sufficiently long time contributions to the integrals appearing in eqs.(3.3) and (3.5) are important, then the resulting term might be

long ranged. However, as was discussed in chapter two, the time correlation functions should rapidly decay in time, thereby causing $\underline{\underline{M}}$ and $\underline{\underline{W}}$ to be quasi-local in space (i.e., they decay to zero whenever any of their arguments are separated beyond a distance λ_c). On the other hand, the macroscopic variagles $\underline{a}(\bar{r}, t)$ should vary only over distances much greater than λ_c. This suggests that we expand the $\hat{a}$'s appearing in the nonlocal terms in eq.(3.9) into a Taylor series about the point $\bar{r}$, with the result that

$$\dot{\hat{\underline{a}}}(\bar{r},t) = \underline{\underline{\theta}}(\bar{r})\ \hat{\underline{a}}(\bar{r},t) + \sum_{j=0}^{\infty} \underline{\underline{M}}^{(j)}(\bar{r}) \cdot (\cdot)^j\ \bar{\nabla}_r^j\ \hat{\underline{a}}(\bar{r},t)$$

$$+ \sum_{j,k=0}^{\infty} \underline{\underline{\underline{W}}}^{(j,k)}(\bar{r}) :\ (\cdot)^{k+j} (\bar{\nabla}_r^j\ \hat{\underline{a}}(\bar{r},t))\ \ (\bar{\nabla}_r^k\ \hat{\underline{a}}(\bar{r},t)) \tag{3.11}$$

where

$$\underline{\underline{M}}^{(j)}(\bar{r}) \equiv \int \frac{d\bar{r}'}{j!}\ \underline{\underline{M}}'(\bar{r}|\bar{r}')\ (\bar{r}' - \bar{r})^j \tag{3.12}$$

$$\underline{\underline{\underline{W}}}^{(j,k)}(\bar{r}) \equiv \frac{1}{j!\ k!} \int\int d\bar{r}_1 d\bar{r}_2\ \underline{\underline{\underline{W}}}(\bar{r}|\bar{r}_1|\bar{r}_2)\ (\bar{r}_1 - \bar{r})^k\ (\bar{r}_2 - \bar{r})^j \tag{3.13}$$

and where $(\cdot)^k$ denotes a k-fold contraction. The coefficients $\underline{\underline{M}}^{(j)}(\bar{r})$ and $\underline{\underline{\underline{W}}}^{(j,k)}(\bar{r})$ are the generalizations of those presented in refs. 25 and 31 to inhomogeneous systems up to second order in the smallness parameter characterizing the slowness of the variables $\underline{A}$. In fact, we could have performed the above expansion using the "exact" nonlocal transport coefficients given by eqs.(2.57) and (2.58), thereby obtaining time dependent $\underline{\underline{M}}^{(j)}$ and $\underline{\underline{\underline{W}}}^{(j,k)}$, valid for any time scale.

As we saw in the previous chapter, the terms in $\underline{\underline{M}}$ and $\underline{\underline{W}}$ containing the variables $\underline{I}(\bar{r}, t)$ were responsible for the entropy production and thus the dissipation. The other terms must be responsible for the reversible effects. This implies that the coefficients $\underline{\underline{M}}^{(j)}$ and $\underline{\underline{W}}^{(j,k)}$ also will be composed of irreversible and reversible terms. For a given effect (i.e., one of the terms in $\underline{\underline{M}}^{(j)}$ or $\underline{\underline{W}}^{(j,k)}$), terms with increasing j and/or k in eq.(3.11) yield corrections due to nonlocality. They may be ordered, with respect to the lowest non-vanishing contribution, by powers of λ_c/ε, where ε is the macroscopic length scale. The reversible or irreversible effects are ordered with respect to each other by the usual macroscopic similarity parameters[1a] (e.g., Reynolds, Froude, or Prandtl numbers).

In practice one usually neglects all nonlocality effects, thereby obtaining a finite order partial differential equation governing the relaxation, since most of the terms appearing in eq.(3.11) are nonlocality corrections. These considerations will become clearer within the context of an example to be presented later in this chapter.

The Coefficients $\underline{\underline{M}}^{(j)}(\bar{r})$ and $\underline{\underline{W}}^{(j,k)}(\bar{r})$

The coefficients $\underline{\underline{M}}^{(j)}(\bar{r})$ and $\underline{\underline{W}}^{(j,k)}(\bar{r})$ are given terms of equilibrium correlation functions. For systems in weak external fields they will vary on the length scale Δ. They are intensive quantities and for single component systems, may be considered functions of the temperature and functions of the equilibrium density, $n_{eq}(\bar{r})$. Since $\lambda_c/\Delta << 1$, the method of Lebowitz and Percus[59] for finding the functional dependence of thermodynamic quantities on density may be applied to the coefficients,

$\underline{\underline{M}}^{(j)}(\bar{r})$ and $\underline{\underline{W}}^{(j,k)}(\bar{r})$.

Consider $\underline{\underline{M}}^{(j)}(\bar{r})$. From its definition, cf. eqs.(3.4), (3.12), we see that it depends on the equilibrium state of the system only in some small region about the point $\bar{r}$. This suggests that we expand $\underline{\underline{M}}^{(j)}(\bar{r})$ in a functional Taylor series in density about the uniform system with density $n = n_{eq}(\bar{r})$ (the effects of walls are neglected). That is,

$$\underline{\underline{M}}^{(j)}(\bar{r}) = \underline{\underline{M}}^{(j)}_{hom}(T, n_{eq}(\bar{r})) + \int d\bar{r}_1 \left[\frac{\delta \underline{\underline{M}}^{(j)}(\bar{r})}{\delta n(\bar{r}_1)}\right]_{hom} (n_{eq}(\bar{r}_1) - n_{eq}(\bar{r}))$$

$$+ \tfrac{1}{2} \int d\bar{r}_1 d\bar{r}_2 \left[\frac{\delta^2 \underline{\underline{M}}^{(j)}(\bar{r})}{\delta n(\bar{r}_1)\, \delta n(\bar{r}_2)}\right]_{hom} (n_{eq}(\bar{r}_1) - n_{eq}(\bar{r}))\ (n_{eq}(\bar{r}_2) - n_{eq}(\bar{r})) + \ldots \tag{3.14}$$

where the subscript "hom" is used to indicate the function in a homogeneous system with temperature T and density $n = n_{eq}(\bar{r})$. The functional derivatives in the last equation may be calculated by noting that[56]

$$\frac{\delta n(\bar{r})}{\delta(-\beta \phi_{ext}(\bar{r}_1))} * \frac{\delta - \beta \phi_{ext}(\bar{r}_1)}{\partial n(\bar{r}')} \equiv \delta(\bar{r} - \bar{r}') \tag{3.15}$$

where

$$\frac{\delta n(\bar{r})}{\delta(-\beta \phi_{ext}(\bar{r}_1))} = \langle \hat{N}(\bar{r})\ \hat{N}(\bar{r}_1) \rangle \ , \tag{3.16}$$

$$\frac{\delta(-\beta \phi_{ext}(\bar{r}_1))}{\delta n(\bar{r}')} = \delta(\bar{r}_1 - \bar{r}')/n_{eq}(\bar{r}') - c(\bar{r}|\bar{r}') \ , \tag{3.17}$$

and where $c(\bar{r}|\bar{r}')$ is the direct correlation function. Using the func-

tional derivative chain rule[60] and eq.(3.17) gives

$$\left[\frac{\delta \underline{\underline{M}}^{(j)}(\bar{r})}{\delta\, n(\bar{r}_1)}\right]_{hom} = \int d\bar{r}_1 \left[\frac{\delta \underline{\underline{M}}^{(j)}(\bar{r})}{\delta - \beta \phi_{ext}(\bar{r}_2)}\right]_{hom} \left[\frac{\delta(\bar{r}_2 - \bar{r}_1)}{n_{eq}(\bar{r}_1)} - c_{hom}(\bar{r}_2 - \bar{r}_1)\right], \tag{3.18}$$

with similar results for the other derivatives in eq.(3.14). In appendix B we show how the functional derivatives with respect to ϕ_{ext} in eq.(3.18) can be expressed in terms of integrals of correlation functions. The important result of the calculation is that the functional derivatives decay whenever their arguments are separated beyond a distance λ_c. Since the direct correlation function is short ranged, this implies (cf. eq.(3.18)) that the density functional derivatives in eq.(3.14) are quasi-local.

As was done earlier, we expand $n_{eq}(\bar{r}_1)$ into a Taylor series about the point $\bar{r}$ in eq.(3.14), thereby obtaining

$$\underline{\underline{M}}^{(j)}(\bar{r}) = \underline{\underline{M}}^{(j)}_{hom}(T, n_{eq}(\bar{r})) + \int d\bar{r}_1 \left[\frac{\partial \underline{\underline{M}}^{(j)}(\bar{r})}{\partial\, n(\bar{r}_1)}\right]_{hom} (\bar{r}_1 - \bar{r}) : \bar{\nabla}_r\, n_{eq}(\bar{r})$$

$$+ \int \frac{d\bar{r}_1}{2} \left[\frac{\delta \underline{\underline{M}}^{(j)}(\bar{r})}{\delta\, n(\bar{r}_1)}\right]_{hom} (\bar{r}_1 - \bar{r})\,(\bar{r}_1 - \bar{r}) : \bar{\nabla}_r \bar{\nabla}_r\, n_{eq}(\bar{r})$$

$$+ \int \frac{d\bar{r}_1 d\bar{r}_2}{2} \left[\frac{\delta^2 \underline{\underline{M}}^{(j)}(\bar{r})}{\delta\, n(\bar{r}_1)\, \delta\, n(\bar{r}_2)}\right]_{hom} (\bar{r}_1 - \bar{r})\,(\bar{r}_2 - \bar{r}) : (\bar{\nabla}_r\, n_{eq}(\bar{r}))\,(\bar{\nabla}_r\, n_{eq}(\bar{r}))$$

$$+ \ldots \tag{3.19}$$

The expansion parameter in the above series is λ_c/Δ, a very small quantity for the systems under consideration. Keeping only the zero'th order term yields

$$\underline{\underline{M}}^{(j)}(\bar{r}) = \underline{\underline{M}}^{(j)}_{hom}(T, n_{eq}(\bar{r})) + O(\lambda_c/\Delta) \quad , \tag{3.20}$$

which is the relation usually assumed in the phenomenological theories.

The above discussion is also applicable to the coefficients $\underline{\underline{W}}^{(j,k)}$, with the result that

$$\underline{\underline{W}}^{(j)}(\bar{r}) = \underline{\underline{W}}^{(j)}_{hom}(T, n_{eq}(\bar{r})) + O(\lambda_c/\Delta) \quad . \tag{3.21}$$

Strictly speaking, in order to use eq.(3.20) in the nonlinear transport equation, we must require that $\varepsilon/\Delta << 1$. Should this not be the case, some of the linear correction terms to eq.(3.20) (cf. appendix B) can be of the same size as some of the nonlinear terms arising from eq.(3.21). In any case, the linear theory is valid. The homogeneous coefficients have been studied extensively for hydrodynamic problems[31].

In summary, we have shown that the effect of the external force on the generalized transport equations is twofold. First, an additional term proportional to the external field appears and second, the local coefficients are those of a homogeneous system in which the density equals the local density at equilibrium.

Simple Fluids

In order to illustrate some of the points mentioned in this chapter, we consider the generalized transport equation for a simple fluid in an

external field. For example, consider a gravitational field[41] in which

$$\phi_{ext}(\bar{r}) = mg\ z \tag{3.22}$$

where m is the mass of the particles and g is the gravitational acceleration. From considerations of low density systems[80] one finds that the length scale Δ is of the order $K_B T/mg$. For argon at 300^0K, Δ is approximately 6 Km. In dense liquids Δ is somewhat less than its gas value, but nevertheless it is still macroscopic.

For simple fluids in weak external fields, the appropriate variables, $\underline{A}$, are the number, energy and momentum densities:

$$N(\bar{r},X^N) \equiv \sum_{j=1}^{N} \delta(\bar{r} - \bar{r}_j) \ , \tag{3.23}$$

$$\bar{\pi}(\bar{r},X^N) \equiv \sum_{j=1}^{N} \bar{p}_j \delta(\bar{r} - \bar{r}_j) \ , \tag{3.24}$$

and
$$H(\bar{r},X^N) \equiv \sum_{j=1}^{N} [\bar{p}_j^{\,2}/2m + \phi_{ext}(\bar{r}) + \tfrac{1}{2} \sum_{\substack{j'=1 \\ j'\neq j}}^{N} u_{jj'}(\bar{r}_{jj'})] \delta(\bar{r} - \bar{r}_j) . \tag{3.25}$$

Instead of the total energy density it will be more convenient to use the internal energy density,

$$E(\bar{r},X^N) \equiv H(\bar{r},X^N) - \phi_{ext}(\bar{r})\ N(\bar{r},X^N) \tag{3.26}$$

$$= \sum_{j=1}^{N} \delta(\bar{r} - \bar{r}_j) \left[\bar{p}_j^{\,2}/2m + \tfrac{1}{2} \sum_{j'\neq j} u_{jj'}\right] . \tag{3.27}$$

Of course, the set of dynamical variables, $\underline{A}(\bar{r}, X^N)$, contains the same information no matter which energy variable is used.

For the set of variables $\underline{A} = \{ N, E, \bar{\pi} \}$ the microscopic equations of motion are easily shown to be

$$\dot{N}(\bar{r}, X^N) = -\bar{\nabla}_r \cdot \bar{\pi}(\bar{r}, X^N) / m \quad , \tag{3.28}$$

$$\dot{E}(\bar{r}, X^N) = \bar{F}_{ext}(\bar{r}) \cdot \bar{\pi}(\bar{r}, t) / m - \bar{\nabla}_r \cdot \bar{J}_E(\bar{r}, X^N) \, , \tag{3.29}$$

and

$$\dot{\bar{\pi}}(\bar{r}, X^N) = \bar{F}_{ext}(\bar{r}) \; N(\bar{r}, X^N) - \bar{\nabla}_r \cdot \bar{\bar{\tau}}(\bar{r}, X^N) \tag{3.30}$$

where the energy current, J_E, and stress tensor, $\bar{\bar{\tau}}$, have their usual definitions[75]. They are most easily expressed via their Fourier transforms (cf. ref. 25 a):

$$\bar{J}_E(\bar{k}, X^N) \equiv \int d\bar{r} \; e^{i\bar{k}\cdot\bar{r}} \; \bar{J}_E(\bar{r}, X^N)$$

$$= \sum_{j=1}^{N} e^{i\bar{k}\cdot\bar{r}_j} \left[\left(\bar{p}_j^{\,2}/2m + \tfrac{1}{2} \sum_{j' \neq j} u_{jj'} \right) \frac{\bar{p}_j}{m} - \frac{1}{2m} \sum_{j' \neq j}^{N} \bar{r}_{jj'} \bar{\nabla}_{\bar{r}_j} u_{jj'} \cdot \bar{p}_j \right.$$

$$\left. \times \left(\frac{1 - e^{-i\bar{k}\cdot\bar{r}_{jj'}}}{i\bar{k}\cdot\bar{r}_{jj'}} \right) \right] \tag{3.31}$$

and

$$\bar{\bar{\tau}}(\bar{k}, X^N) = \sum_{j=1}^{N} e^{i\bar{k}\cdot\bar{r}_j} \left[\frac{\bar{p}_j \bar{p}_j}{m} - \tfrac{1}{2} \sum_{j \neq j}^{N} \bar{r}_{jj'} \bar{\nabla}_{\bar{r}_j} u_{jj'} \left(\frac{1 - e^{-i\bar{k}\cdot\bar{r}_{jj'}}}{i\bar{k}\cdot\bar{r}_{jj'}} \right) \right] . \tag{3.32}$$

These variables are slow since the external force is weak and since spatial gradients in the system are small. It is well known[20] that these are not the only slow variables in simple fluids. The multilinear variables, $\underline{A}(\bar{r}, X^N) \; \underline{A}(\bar{r}', X^N)$, $\underline{A}(\bar{r}, X^N) \; \underline{A}(\bar{r}', X^N) \; \underline{A}(\bar{r}'', X^N)$, etc.,

will also be slow. It has been shown for homogeneous simple fluids that in three dimensions they may be neglected. We shall neglect them in this work although they may easily be included in the formalism (cf. ref. 31).

The fact that one of the slowness parameters involves the size of the gradients in the system can lead to some confusion. The expansion parameter for the localization procedure also contains these gradients. In refs. 25 and 31 Taylor expansions in the wavevector were performed, thereby not differentiating between the effects associated with the two expansion parameters. Fortunately, this problem only appears at third order for hydrodynamic problems. As was discussed earlier, the way to overcome these difficulties is to first make the effects attributable to different orders in the smallness parameters characterizing the slowness of the variables explicit (cf. eqs.(2.61), (2.62), (3.3) and (3.5)) and then localize (cf. eq.(3.11)).

For the choice of variables given above, eq.(3.2) holds. In fact,

$$\underline{\underline{\theta}}\,(\overline{r}) = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & \overline{F}_{ext}(\overline{r})/m \\ \overline{F}_{ext}(\overline{r}) & 0 & 0 \end{bmatrix} \tag{3.33}$$

and

$$\underline{Q}(\overline{r},X^N) = -\overline{\nabla}_r \cdot \underline{\overline{J}}(\overline{r},X^N) \equiv -\overline{\nabla}_r \cdot [\,\overline{\pi}(\overline{r},X^N)/m,\ \overline{J}_E(\overline{r},X^N),\ \overline{\overline{\tau}}(\overline{r},X^N)\,]^T . \tag{3.34}$$

The notation $\underline{\overline{B}}$ will be used to indicate a supervector of vectors or tensors. From eq.(3.7) it is easily shown that

$$\underline{I}(\overline{r},\,t) = -\overline{\nabla}_r \cdot \underline{\overline{I}}(\overline{r},\,t) \tag{3.35}$$

where the dissipative currents, $\underline{I}$, are defined by

$$\underline{I}(\bar{r},t) \equiv \hat{\underline{J}}(\bar{r},t) - <\hat{\underline{J}}(\bar{r})\ \hat{\underline{A}}(\bar{r}_1)> * \underline{\underline{K}}^{-1}(\bar{r}_1|\bar{r}_2) * \hat{\underline{A}}(\bar{r}_2,t) \tag{3.36}$$

Using the local equilibrium averages (cf. eq.(2.70)) and eq.(2.44) it follows that

$$<\underline{J}(\bar{r})\ \hat{\underline{A}}(\bar{r}_1)> = \left[\frac{\delta <\underline{J}(\bar{r})>_L}{\delta\, \beta\, \underline{\Phi}(\bar{r}_1)}\right]_{\underline{\Phi}(\bar{r},t)=0} \tag{3.37}$$

and that

$$\left[\frac{\delta\, \beta\, \underline{\Phi}(\bar{r})}{\delta\, \underline{a}(\bar{r}_1)}\right]_{\underline{\Phi}=0} = \underline{\underline{K}}^{-1}(\bar{r}|\bar{r}_1)\ . \tag{3.38}$$

Hence using eqs.(3.36) - (3.38) we have

$$\underline{I}(\bar{r},t) = \hat{\underline{J}}(\bar{r},t) - \left[\frac{\delta <\underline{J}(\bar{r})>_L}{\delta\, \underline{a}(\bar{r}_1)}\right]_{\underline{\Phi}=0} * \hat{\underline{A}}(\bar{r}_1,t) \tag{3.39}$$

where the time variable is omitted when it is zero.

The generalized coefficients, cf. eqs.(3.12) and (3.13), become

$$\underline{\underline{M}}^{(j)}(\bar{r}) = -\bar{\nabla}_r \cdot \underline{\underline{M}}^{(j)}(\bar{r}) - \underline{\underline{M}}^{(j-1)}(\bar{r}) \tag{3.40}$$

and

$$\underline{\underline{W}}^{(j,k)}(\bar{r}) = -\bar{\nabla}_r \cdot \underline{\underline{W}}^{(j,k)}(\bar{r}) - \underline{\underline{W}}^{(j,k-1)}(\bar{r}) - \underline{\underline{W}}^{(j-1,k)}(\bar{r})\ , \tag{3.41}$$

where

$$\underline{\underline{M}}^{(j)}(\bar{r}) \equiv \frac{1}{j!} \int d\bar{r}_1 \left[<\underline{J}(\bar{r})\ \hat{\underline{A}}(\bar{r}_2)> - \int_0^\infty dt_1 <\underline{I}(\bar{r},t_1)\ \underline{I}(\bar{r}_2)> \overleftarrow{\nabla}_{\bar{r}_2}\right] \tag{3.42}$$

$$* \underline{\underline{K}}^{-1}(\bar{r}_2|\bar{r}_1)\ (\bar{r}_1 - \bar{r})^j$$

and

$$\underline{\underline{W}}^{(j,k)}(\bar{r}) \equiv \frac{1}{j!\,k!} \int d\bar{r}_1 d\bar{r}_2 \tfrac{1}{2}\Big[<\underline{I}(\bar{r})\ \hat{\underline{A}}(\bar{r}_3)\ \hat{\underline{A}}(\bar{r}_4)> + \int_0^\infty dt_1 \Big\{ <\underline{I}(\bar{r},t_1)\ \underline{I}(\bar{r}_5)> \bar{\nabla}_{\bar{r}_5}$$

$$* \underline{\underline{K}}^{-1}(\bar{r}_5|\bar{r}_6) * <\hat{\underline{A}}(\bar{r}_6)\ \hat{\underline{A}}(\bar{r}_3)\ \hat{\underline{A}}(\bar{r}_4)> - <\underline{I}(\bar{r},t_1)\ (\underline{I}(\bar{r}_3)\ \bar{\nabla}_{\bar{r}_3} \hat{\underline{A}}(\bar{r}_4) + \hat{\underline{A}}(\bar{r}_3)\ \underline{I}(\bar{r}_4)\ \bar{\nabla}_{\bar{r}_4}>\Big\}$$

$$\Big] \overset{*}{*} \underline{\underline{K}}^{-1}(\bar{r}_4|\bar{r}_1)\ \underline{\underline{K}}^{-1}(\bar{r}_3|\bar{r}_2)\ (\bar{r}_1 - \bar{r})^k\ (\bar{r}_2 - \bar{r})^j \ . \qquad (3.43)$$

The coefficients $\underline{\underline{M}}^{(j)}$ and $\underline{\underline{W}}^{(j,k)}$ may be evaluated in terms of quantities defined in homogeneous systems (cf. eqs.(3.30), (3.21)). Neglecting all nonlocality corrections, we find:

$$\underline{\underline{M}}^{(o)}(\bar{r}) = \int d\bar{r}_1 \Big[<\underline{J}(\bar{r})\ \hat{\underline{A}}(\bar{r}_2)> * \underline{\underline{K}}^{-1}(\bar{r}_2|\bar{r}_1) \Big]_{hom} \qquad (3.44)$$

$$\underline{\underline{M}}^{(1)}(\bar{r}) = - \int d\bar{r}_1 \int_0^\infty dt_1 \Big[<\underline{I}(\bar{r},t)\ \underline{I}(\bar{r}_2)> * \underline{\underline{K}}^{-1}(\bar{r}_2|\bar{r}_1) \Big]_{hom} \qquad (3.45)$$

$$\underline{\underline{W}}^{(o,o)}(\bar{r}) = \int d\bar{r}_1 d\bar{r}_2 \tfrac{1}{2}\Big[<\underline{I}(\bar{r})\ \hat{\underline{A}}(\bar{r}_3)\ \hat{\underline{A}}(\bar{r}_4)> \overset{*}{*} \underline{\underline{K}}^{-1}(\bar{r}_3|\bar{r}_2)\ \underline{\underline{K}}^{-1}(\bar{r}_4|\bar{r}_1) \Big]_{hom} \qquad (3.46)$$

$$\underline{\underline{W}}^{(o,1)}(\bar{r}) = \tfrac{1}{2} \int d\bar{r}_1 d\bar{r}_2 \int_0^\infty dt_1 \Big[\Big\{ <\underline{I}(\bar{r},t_1)\ \underline{I}(\bar{r}_3)> * \underline{\underline{K}}^{-1}(\bar{r}_3|\bar{r}_4) * <\hat{\underline{A}}(\bar{r}_4)\ \hat{\underline{A}}(\bar{r}_5)\ \hat{\underline{A}}(\bar{r}_6)>$$

$$- <\underline{I}(\bar{r},t_1)\ \hat{\underline{A}}(\bar{r}_5)\ \hat{\underline{I}}(\bar{r}_6)>\Big\} \overset{*}{*} \underline{\underline{K}}^{-1}(\bar{r}_6|\bar{r}_1)\ \underline{\underline{K}}^{-1}(\bar{r}_5|\bar{r}_2) \Big]_{hom} \qquad (3.47)$$

$$\underline{\underline{W}}^{(1,0)} = \tfrac{1}{2} \int d\bar{r}_1 d\bar{r}_2 \int_0^\infty dt_1 [\{ < \underline{I}(\bar{r},t_1)\ \underline{I}(\bar{r}_3) > * \underline{\underline{K}}^{-1}(\bar{r}_3|\bar{r}_4) * < \hat{\underline{A}}(\bar{r}_4)\ \hat{\underline{A}}(\bar{r}_5)\ \hat{\underline{A}}(\bar{r}_6) >$$

$$- < \underline{I}(\bar{r},t_1)\ \underline{I}(\bar{r}_5)\ \hat{\underline{A}}(\bar{r}_6) > \} * * \underline{\underline{K}}^{-1}(\bar{r}_6|\bar{r}_1)\ \underline{\underline{K}}^{-1}(\bar{r}_5|\bar{r}_2)]_{hom} \cdot \quad (3.48)$$

The higher order coefficients may be neglected, as they are nonlocality corrections (to second order in the smallness parameters characterizing $\underline{A}$). Hence the transport equation, eq.(3.11), becomes

$$\dot{\underline{a}}(\bar{r},t) = \underline{\underline{\theta}}(\bar{r})\ \underline{\hat{a}}(\bar{r},t) - \bar{\nabla}_r \cdot \{ \underline{\underline{M}}^{(0)}_{hom}(\bar{r})\ \underline{\hat{a}}(\bar{r},t) + \underline{\underline{M}}^{(1)}_{hom}(\bar{r}) \cdot \bar{\nabla}_r\ \underline{\hat{a}}(\bar{r},t)$$

$$+ \underline{\underline{W}}^{(0,0)}_{hom}(\bar{r})\ \underline{\hat{a}}(\bar{r})\ \underline{\hat{a}}(\bar{r}) + \underline{\underline{W}}^{(1,0)}_{hom}(\bar{r}) \cdot (\bar{\nabla}_r\ \underline{\hat{a}}(\bar{r},t))\ \underline{\hat{a}}(\bar{r},t)$$

$$+ \underline{\underline{W}}^{(0,1)}_{hom}(\bar{r}) \cdot \underline{\hat{a}}(\bar{r},t)\ \bar{\nabla}_r\ \underline{\hat{a}}(\bar{r},t) \} \quad (3.49)$$

where the coefficients depend on position only through the equilibrium density. We may also neglect gradients of the coefficients appearing in eq.(3.49) when $\varepsilon/\Delta << 1$.

At this point, the symmetries of the homogeneous system as well as the forms of some of the correlation functions appearing in eqs.(3.44) - (3.48) could be used to arrive at the equations of motion for the macroscopic variables. The resulting equations are rather complex and may be expressed in a more concise manner if they are written in terms of the conjugate variables $\underline{\Phi}(\bar{r}, t)$.

This is most easily done by returning to eq.(3.10) and expanding $\underline{\Phi}(\bar{r}, t)$ in a Taylor series as was done in obtaining eq.(3.11). The resulting coefficients are then approximated by their homogeneous values and all nonlocality corrections are dropped. We then obtain (cf.

eq.(2.66))

$$\dot{\hat{\underline{a}}}(\bar{r},t) = \underline{\underline{\theta}}(\bar{r})\ \hat{\underline{a}}(\bar{r},t) - \bar{\nabla}_r \cdot \{ \int d\bar{r}_1 \langle \underline{\bar{J}}(\bar{r})\ \hat{\underline{A}}(\bar{r}_1) \rangle_{hom} \cdot \beta \underline{\Phi}(\bar{r},t)$$

$$+ \tfrac{1}{2} \int d\bar{r}_1 d\bar{r}_2 \langle \hat{\underline{J}}(\bar{r})\ \hat{\underline{A}}(\bar{r}_1)\ \hat{\underline{A}}(\bar{r}_2) \rangle_{hom} : \beta \underline{\Phi}(\bar{r},t)\, \beta \underline{\Phi}(\bar{r},t) - \int_0^\infty dt_1 \int d\bar{r}_1 \langle \underline{\bar{I}}(\bar{r},t)\ \underline{\bar{I}}(\bar{r}_1) \rangle_{hom}$$

$$\cdot \bar{\nabla}_r \beta \underline{\Phi}(\bar{r},t)$$

$$- \int_0^\infty dt_1 \int d\bar{r}_1 d\bar{r}_2 \langle \underline{\bar{I}}(\bar{r},t_1)\ \underline{\bar{I}}(\bar{r}_1)\ \hat{\underline{A}}(\bar{r}_2) \rangle_{hom} \cdot \beta \underline{\Phi}(\bar{r},t)\ \bar{\nabla}_r \beta \underline{\Phi}(\bar{r},t) \} \ . \quad (3.50)$$

Before examining eq.(3.50) for each of the dynamic variables, the quantities $\underline{\Phi}(\bar{r}, t)$ shall be given physical meaning. This is done by introducing a phenomenological local equilibrium distribution function of the form

$$f_L'(X^N,t) = \frac{1}{\Xi_L'(t)\ N!\ h^{3N}} \exp\Big[- \int d^3\bar{r}\ \frac{1}{K_B T(\bar{r},t)} \{ E(\bar{r},X^N) - \bar{v}(\bar{r},t)\cdot\bar{\pi}(\bar{r},X^N)$$

$$- \mu^+(\bar{r},t)\ N(\bar{r},X^N) \} \Big] \quad (3.51)$$

where $\Xi_L'(t)$ is determined from normalization. The quantities $T(\bar{r}, t)$, $\bar{v}(\bar{r}, t)$ and $\mu^+(\bar{r}, t)$ can be interpreted as the nonequilibrium local temperature, velocity and chemical potential (excluding the external field in a coordinate frame moving with velocity $\bar{v}(\bar{r}, t)$), respectively. The chemical potential $\mu^+(\bar{r}, t)$ is related to the total chemical potential, $\mu(\bar{r}, t)$, by

$$\mu^+(\bar{r}, t) \equiv \mu(\bar{r}, t) - \phi_{ext}(\bar{r}) - \tfrac{1}{2} m \bar{v}^2(\bar{r}, t) \ . \quad (3.52)$$

The phenomenological distribution function given above is the generalization to inhomogeneous systems of the one used in refs. 31, 32 and 64. Comparing eqs.(3.52) and (2.70) lets us set

$$\bar{\Phi}_p(\bar{r},t) = \beta(\bar{r},t)\ \bar{v}(\bar{r},t)/\beta\ , \tag{3.53}$$

$$\Phi_E(\bar{r},t) = 1 - \beta(\bar{r},t)/\beta\ , \tag{3.54}$$

and

$$\underline{\Phi}_N(\bar{r},t) = [\ \beta(\bar{r},t)\ \mu^+(\bar{r},t) - \beta(\mu - \phi_{ext}(\bar{r})\ )\ ]/\beta\ , \tag{3.55}$$

where

$$\beta(\bar{r},t) \equiv (K_B T(\bar{r},t)\ )^{-1}\ . \tag{3.56}$$

Thus we see that the variables $\underline{\Phi}$ are related to displacements of intensive quantities from equilibrium. We can now present the equations of motion for the macroscopic variables.

i Number Density

From eqs.(3.39) and (3.28) it follows that

$$\bar{I}_N(\bar{r},\ t) = 0 \tag{3.57}$$

and so only the non-dissipative parts of the equations of motion need be considered for the number equation. Using eqs.(3.11) and (3.44) - (3.48) it is easily shown that

$$\dot{n}(\bar{r},\ t) \equiv \frac{\partial}{\partial t} < N(\bar{r}) >_L (t) = -\bar{\nabla} \cdot \bar{p}(\bar{r},\ t)\ /\ m \tag{3.58}$$

where $\bar{p}(\bar{r},\ t) \equiv < \bar{\pi}(\bar{r},\ t) >_L (t)$. (3.59)

This is the usual equation of continuity for a one component fluid.

ii Energy Density

The homogeneous coefficients appearing in eq.(3.50) have been studied in detail by Weare and Oppenheim[31]. Taking their results for the energy equation yields

$$\frac{\partial e(\bar{r},t)}{\partial t} = \frac{1}{m} \bar{F}_{ext}(\bar{r}) \cdot \bar{p}(\bar{r},t) - \bar{\nabla}\cdot[\; (\; p_h(\bar{r},t) + e(\bar{r},t) \;) \; \bar{v}(\bar{r},t)$$

$$+ L_{ee}(\bar{r},t) \, \bar{\nabla}\beta(\bar{r},t) - \bar{\bar{L}}_{ep}(\bar{r}) \vdots \beta(\bar{r},t) \; \bar{v}(\bar{r},t) \; \bar{\nabla}_r \; \beta(\bar{r},t) \; \bar{v}(\bar{r},t) \;] \tag{3.60}$$

where

$$L_{ee}(\bar{r},t) \equiv [\; 1 + \Phi_N(\bar{r},t) \left(\frac{\partial}{\partial \mu}\right)_\beta + \beta \Phi_E(\bar{r},t) \left(\frac{\partial}{\partial(-\beta)}\right)_{\beta\mu} \;]$$

$$\times \; \frac{1}{3} d\bar{r}_1 \int_0^\infty dt_1 \, < \bar{I}_E(\bar{r},t_1) \cdot \bar{I}_E(\bar{r}_1) >_{hom} \; , \tag{3.61}$$

$$L_{ep}^{(ijk\ell)}(\bar{r}) \equiv (\delta_{ij} \, \delta_{k\ell} + \delta_{ik} \, \delta_{j\ell}) \int d\bar{r}_1 d\bar{r}_2 \int_0^\infty dt_1 < I_E^x(\bar{r},t) \; I_p^{xy}(\bar{r}_1) \; \pi^y(\bar{r}_2) >_{hom}$$

$$\pm \delta_{i\ell} \, \delta_{jk} \int d\bar{r}_1 \, d\bar{r}_2 \int_0^\infty dt_1 < I_E^x(\bar{r},t_1) \; I_p^{yy}(\bar{r}_1) \; \pi^x(\bar{r}_2) >_{hom} \; , \tag{3.62}$$

$$e(\bar{r},t) \equiv < E(\bar{r}) >_L (t) \quad , \tag{3.63}$$

and

$$p_h(\bar{r},t) \equiv p_{h,hom} + \left(\frac{\partial p_h}{\partial \beta\mu}\right)_{\beta,hom} \beta\Phi_N(\bar{r},t) + \left(\frac{\partial p_h}{\partial(-\beta)}\right)_{\beta\mu,hom} \beta\Phi_E(\bar{r},t)$$

$$+ \tfrac{1}{2}\Big[\left(\frac{\partial^2 p_h}{\partial(-\beta)\,\partial(-\beta)}\right)_{hom} (\beta\Phi_E(\bar{r},t))^2 + \left(\frac{\partial^2 p_h}{\partial(\beta\mu)\,\partial(\beta\mu)}\right)_{hom} (\beta\Phi_N(\bar{r},t))^2$$

$$+ 2\left(\frac{\partial^2 p_h}{\partial(\beta\mu)\partial(-\beta)}\right)_{hom} \beta\phi_N(\bar{r},t)\,\beta\Phi_E(\bar{r},t)\Big] . \quad (3.64)$$

The quantity $p_h(\bar{r}, t)$ is thus seen to be the local equilibrium hydrostatic pressure. The Onsager coefficient $L_{ee}(\bar{r}, t)$ is simply the generalization of the linear coefficient to the nonlinear regime. It contains corrections for the fact that the local temperature and chemical potential (cf. eqs.(3.54) and (3.55)) are not at equilibrium. In addition, a new coupling between the energy current and velocity gradients appears via $\overline{\overline{\overline{L}}}_{ep}(\bar{r})$ in the nonlinear theory. As was discussed above, all the coefficients in eq.(3.30) are functions of the equilibrium temperature and of the local density at equilibrium and are evaluated in homogeneous systems.

iii Momentum Density

Proceding as in the energy equation we find for the momentum equation:

$$\frac{\partial \bar{p}(\bar{r},t)}{\partial t} = \bar{F}_{ext}(\bar{r})\,\hat{n}(\bar{r},t) - \bar{\nabla}_r \cdot [\hat{p}_h(\bar{r},t) - \overline{\overline{\overline{L}}}_{pp}(\bar{r},t) : \bar{\nabla}_r\,\beta(\bar{r},t)\,\bar{v}(\bar{r},t)$$

$$+ \overline{\overline{\overline{L}}}_{pe}(\bar{r}) : \beta(\bar{r},t)\,\bar{v}(\bar{r},t)\,\bar{\nabla}_r\,\beta(\bar{r},t)\,] , \quad (3.65)$$

where

$$L_{pp}^{(ijk\ell)}(\bar{r},t) \equiv \{1 + \Phi_N(\bar{r},t)\left(\frac{\partial}{\partial\mu}\right)_\beta + \beta\Phi_E(\bar{r},t)\left(\frac{\partial}{\partial(-\beta)}\right)_{\mu\beta}\}$$

$$\times [\,\delta_{ij}\delta_{k\ell}\int d\bar{r}_1 \int_0^\infty dt_1 < I_p^{xx}(\bar{r},t)\; I_p^{yy}(\bar{r}_1) >_{hom} + (\delta_{ik}\delta_{j\ell} + \delta_{i\ell}\delta_{jk})$$

$$\times \int d\bar{r}_1 \int_0^\infty dt_1 < I_p^{xy}(\bar{r},t)\; I_p^{xy}(\bar{r}_1) >_{hom} \qquad (3.66)$$

and where

$$L_{pe}^{(ijk\ell)}(\bar{r}) \equiv \delta_{ij}\delta_{k\ell}\int d\bar{r}_1 d\bar{r}_2 \int_0^\infty dt_1 < I_p^{xx}(\bar{r},t)\; I_E^{y}(\bar{r}_1)\; \pi^y(r_2) >_{hom}$$

$$+ (\delta_{ik}\delta_{j\ell} + \delta_{i\ell}\delta_{jk}) \int d\bar{r}_1 d\bar{r}_2 \int_0^\infty dt_1 < I_p^{xy}(\bar{r},t_1)\; I_E^{x}(\bar{r}_1)\; \pi^y(\bar{r}_2) >_{hom} .$$

(3.67)

The interpretation of the various terms appearing in the momentum equation is analogous to that for the energy equation.

Since the total momentum is conserved in homogeneous systems, using eqs.(3.62) and (3.66) we find that

$$L_{pe}^{(xxyy)}(\bar{r}) = L_{ep}^{(xyyx)}(\bar{r}) \qquad (3.68)$$

and

$$L_{pe}^{(xyxy)}(\bar{r}) = L_{ep}^{(xxyy)}(\bar{r}) \; . \qquad (3.69)$$

These are nonlinear Onsager reciprocal relations[2] and are due to time reversal invariance.

This concludes our discussion of systems in weak external fields. We have seen that the external field introduces an additional term in the macroscopic equations of motion exactly as in the phenomenological theories. In addition, a weak spatial dependence of the coefficients is present. This dependence is found entirely from considerations of homogeneous systems.* The inhomogeneity does not affect the form of the nonlinear correction terms. These show the central role played by the conjugate variables $\underline{\Phi}(\overline{r},t)$ and their gradients in the hydrodynamic theory. Of course, before the equations involving the $\underline{\Phi}(\overline{r},t)$ can be solved, the constituitive relation linking $\underline{\Phi}(\overline{r},t)$ and $\underline{a}(\overline{r},t)$ must be considered. This will be equivalent to eq.(3.49). The nonlinear macroscopic equations obtained for simple fluids are valid to second order in the slowness parameters characterizing the change of energy, number and momentum densities, to zero'th order in λ_c/Δ and ε/Δ, and to quadratic order in displacements from equilibrium. Should ε/Δ be large, then the equations presented here are valid only to linear order in displacements from equilibrium of the dynamical variables.

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* Similar results have been found by Kim and Oppenheim for Brownian motion theory[65].

Chapter IV. Systems With Large Spatial Gradients: General Theory

The previous chapter dealt with fluid systems where the length scale of the inhomogeneity, Δ, was large compared with the correlation length. For a very important class of problems, those having phase boundaries, Δ is small. The length scale of the inhomogeneity is the thickness of the interfacial region which, away from the critical point, is microscopic.

It is clear that even if the generalized transport equation presented in chapter II is correct, the localization procedure of the last chapter cannot be valid in the region separating the phases. In the interfacial region the dynamical variables have large gradients in the direction normal to the interface and thus any expansion in gradients would be doomed to failure.

On the other hand, the phenomenological theory for the dynamics of multiphase systems is well known[1a, 3, 45-48]. There the usual procedure is to solve macroscopic problems in the bulk of the system and then to connect the bulk solutions through boundary conditions imposed at the interface. The usual arguments leading to these boundary conditions are generally heuristic and there is not always agreement as to which are the correct conditions for a given problem[45-48].

The problems confronting a molecular approach are manyfold. In the first place, what is the interface? What is its initial configuration? How are the large gradients handled? These questions have been examined within the context of thermodynamics[42] and equilibrium statistical mechanics[44, 66]. There the interface is described in terms of surface excess quantities defined with respect to a mathematical dividing

surface. Lately, some progress has been made in obtaining the density profiles in equilibrium fluid-solid and fluid-fluid[66-68] interfacial regions from microscopic considerations. However, the techniques used are not directly applicable to the nonequilibrium problem.

The concept of surface excess quantities has recently been introduced into the framework of nonequilibrium thermodynamics[45-48]. There the assumptions that local equilibrium is valid at the interface and that excess entropy production is positive were needed in order to obtain the equations of motion and boundary conditions. The validity of these assumptions is not well understood.

In this chapter, we shall systematically extend the equilibrium concepts of a dividing surface and surface excess quantities to the nonequilibrium regime. We shall assume that the interfacial region is only a few molecular dimensions in thickness and thus exclude the critical point from our considerations.

Mathematical Preliminaries

Following Morse and Feshbach[69] we introduce a set of orthogonal curvilinear coordinates $\xi_i(\bar{r},t)$, $i = 1, 2, 3$. The time dependent position of the dividing surface shall be determined implicitly by the relation

$$\xi_1(\bar{r}, t) = 0 \quad . \tag{4.1}$$

The unit vectors in the direction of increasing ξ_i are

$$\bar{\alpha}_i = h_i \bar{\nabla}\xi_i = \frac{1}{h_i} \frac{\partial \bar{r}}{\partial \xi_i} \tag{4.2}$$

where

$$h_i \equiv |\bar{\nabla}\xi_i|^{-1} = \left|\frac{\partial \bar{r}}{\partial \xi_i}\right| \quad . \tag{4.3}$$

The second equalities in eqs.(4.2) and (4.3) are a consequence of the coordinates being orthogonal:

$$\bar{\alpha}_i \cdot \bar{\alpha}_j = \delta_{ij} \ . \tag{4.4}$$

In terms of these coordinates the cartesian gradient becomes

$$\bar{\nabla} = \sum_{i=1}^{3} \bar{\alpha}_i \frac{1}{h_i} \frac{\partial}{\partial \xi_i} \tag{4.5}$$

and

$$\frac{\partial}{\partial \xi_i} = h_i \, \bar{\alpha}_i \cdot \bar{\nabla} \ . \tag{4.6}$$

Whenever we write differentials with respect to ξ_i or $\bar{r}$ they are to be taken at constant t.

The velocity field of the coordinate system is defined by

$$\bar{v}(\bar{r},t) \equiv \left(\frac{\partial \bar{r}}{\partial t}\right)_{\bar{\xi}} = -\sum_{i=i}^{3} \bar{\alpha}_i h_i \left(\frac{\partial \xi_i}{\partial t}\right)_{\bar{r}} \ , \tag{4.7}$$

where $\bar{v}(\bar{r}, t)$ is not be be confused with the conjugate momentum variable introduced in chapter III (cf. eq.(3.51)). The time derivative at constant ξ_i, i = i, 2, 3 is related to that at constant $\bar{r}$ by

$$\left(\frac{\partial}{\partial t}\right)_{\bar{\xi}} = \left(\frac{\partial}{\partial t}\right)_{\bar{r}} + \bar{v}(\bar{r},t) \cdot \bar{\nabla} \ . \tag{4.8}$$

Differentiating eq.(4.4) with respect to time at constant ξ one finds

$$\bar{\alpha}_i \, \bar{\alpha}_j : \bar{\nabla} \, \bar{v} = -\bar{\alpha}_j \bar{\alpha}_i : \bar{\nabla} \, \bar{v} \qquad \text{for } i \neq j \ . \tag{4.9}$$

Using eqs.(4.7) - (4.9) it may be shown that

$$\left(\frac{\partial \bar{\alpha}_i}{\partial t}\right)_{\bar{r}} + \bar{v}\cdot\bar{\nabla}\bar{\alpha}_i = (\bar{\bar{1}} - \bar{\alpha}_i\bar{\alpha}_i)\bar{\alpha}_i : \bar{\nabla}\,\bar{v}$$

$$= -(\bar{\bar{1}} - \bar{\alpha}_i\bar{\alpha}_i)\cdot \overline{\bar{\nabla}\,\bar{v}}\cdot\bar{\alpha}_i \ , \tag{4.10}$$

where the $\overline{\quad}$ connecting $\bar{\nabla}$ and $\bar{v}$ indicates that $\bar{\nabla}$ acts only on $\bar{v}$.

In this paper we shall consider certain functions which are nonzero only in a small region near the $\xi_1 = 0$ surface. In order to define a multipole expansion of such functions around $\xi_1 = 0$ we define the following generalized functions

$$\delta^s_{(m)} \equiv (h_2h_3)^{-1}\left(\frac{1}{h_1}\frac{\partial}{\partial\xi_1}\right)^m \frac{h_2h_3}{h_1} \ \delta(\xi_1) \ . \tag{4.11}$$

The $\delta^s_{(m)}$ have the property that for any test function ϕ

$$\int d\bar{r}\ \phi\ \delta^s_{(m)} = (-1)^m \int_{\xi_1=0} dA \left(\frac{\partial^m \phi}{\partial n^m}\right) \ , \tag{4.12}$$

where we have used the fact that the element of volume and the element of surface area are given by

$$d\bar{r} = h_1h_2h_3\ d^3\xi \text{ and } dA = h_2h_3\ d\xi_2\ d\xi_3 \ . \tag{4.13}$$

The normal derivative is defined by

$$\frac{\partial}{\partial n} \equiv \bar{\alpha}_1\cdot\bar{\nabla} = \frac{1}{h_1}\frac{\partial}{\partial\xi_1} \ . \tag{4.14}$$

Eq.(4.11) may be written in the alternative form

$$\delta^s_{(m)} = (\bar{\nabla}\cdot\bar{\alpha}_1)^m\,\delta^s(0) \tag{4.15}$$

which follows in view of the fact that integration with any test-function again leads to eq.(4.12).

A function $b(\bar{r}, t)$ which is nonzero only near the dividing surface can be usefully written in terms of the $\delta^s_{(m)}$ as

$$b(\bar{r},t) = \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} b^s_{(m)}\ (\xi_2,\xi_3,t)\delta^s_{(m)}(\bar{r},t). \tag{4.16}$$

This expression represents a "multipole expansion" of b about the $\xi_1 = 0$ surface which converges in a generalized sense[70]. By eqs.(4.12) and (4.16) it is easily shown that for any test-function ϕ:

$$\int d\bar{r}\ b(\bar{r},t)\phi = \sum_{m=0}^{\infty} \frac{1}{m!} \int_{\xi_1=0} dA\ b^s_{(m)} \left(\frac{\partial^m \phi}{\partial n^m}\right) . \tag{4.17}$$

The distance from the $\xi_1 = 0$ surface along the line ξ_2, ξ_3 constant to the point ξ_1 is given by

$$\lambda \equiv \int_0^{\xi_1} d\xi_1' \left(\frac{\partial \bar{r}}{\partial \xi_1} \cdot \frac{\partial \bar{r}}{\partial \xi_1}\right)^{1/2} = \int_0^{\xi_1} d\xi_1' h_1(\xi_1',\xi_2,\xi_3,t). \tag{4.18}$$

An expression for $b^s_{(m)}$ may now be found by taking

$$\phi = \delta(\xi_2 - \xi_2^o)\ \delta(\xi_3 - \xi_3^o)\ \lambda^m \tag{4.19}$$

in eq.(4.17). This yields the following expression for the "surface multipole densities":

$$b^s_{(m)}(\xi^0_2,\xi^0_3,t) = (h_2h_3)^{-1}_{\xi_1=0}\int d\bar{r}\ \delta(\xi_2-\xi^0_2)\delta(\xi_3-\xi^0_3)\lambda^m b(\bar{r},t)$$

$$= (h_2h_3)^{-1}_{\xi_1=0}\int d\xi_1\ h_1h_2h_3\lambda^m b(\bar{r},t), \tag{4.20}$$

where we have used eq.(4.13).

Using eqs. (4.16) and (4.20) it follows immediately that

$$\sum_{m=0}^{\infty}\frac{(-1)^m}{m!}\, b^s_{(m)}(\xi_2,\xi_3,t)\delta^s_{(m)}(\bar{r},t) = 0, \tag{4.21}$$

if and only if $b^s_{(m)} = 0$. We note that it is essential for the validity of this equation that $b^s_{(m)}$ does not depend on ξ_1. In order to eliminate the ξ_1 dependence in the product of an arbitrary function with $\delta^s_{(m)}$, one may use the following formula which is derived in appendix C:

$$\phi(\bar{r},t)\delta^s_{(m)}(\bar{r},t) = \sum_{j=0}^{m}(-1)^{m-j}\binom{m}{j}\delta^s_{(j)}\left(\frac{\partial^{m-j}\phi}{\partial n^{m-j}}\right)_s \tag{4.22}$$

where the subscript s implies that the corresponding quantity is to be taken at $\xi_1 = 0$

We shall now consider the time dependence of the terms in the multipole expansion, eq.(4.16). The time dependence of $b^s_{(m)}\delta^s_{(m)}$ is caused by two different phenomena. In the first place, $b^s_{(m)}(\xi_2,\xi_3,t)$ will in general depend explicitly on the time. In the second place, the motion of the curvilinear coordinates and in particular the motion of the $\xi_1 = 0$ surface results in an additional time dependence. In appendix C we show that

$$\left(\frac{\partial}{\partial t}\, b^s_{(m)}\, \delta^s_{(m)}\right)_{\bar{r}} = b^s_{(m)} \left(\frac{\partial \delta^s_{(m)}}{\partial t}\right)_{\bar{r}} + \left(\frac{\partial b^s_{(m)}}{\partial t}\right)_{\bar{r}} \delta^s_{(m)}$$

$$= b^s_{(m)} \{ -(C\, v_n)_s\, \delta^s_{(m)} - v_{n,s}\, \delta^s_{(m+1)} + \sum_{j=0}^{m-1} (-1)^{m-j}\, \delta^s_{(j)} [\binom{m}{j-1} \left(\frac{\partial}{\partial n}\right)^{m-j} \left(\frac{\partial \bar{\alpha}_1}{\partial t}\right)_{\bar{r}} \cdot \bar{\nabla}_{/\!/} \lambda$$

$$- \binom{m}{j} \sum_{\ell=2}^{3} (h_2 h_3)^{-1} \frac{\partial}{\partial \xi_\ell} (h_2 h_3 \left(\frac{\partial}{\partial n}\right)^{m-j-1} \frac{\bar{\alpha}_\ell}{h_\ell} \cdot \left(\frac{\partial \bar{\alpha}_1}{\partial t}\right)_{\bar{r}}))] \}$$

$$+ \left(\frac{\partial b^s_{(m)}}{\partial t}\right)_{\bar{r},s} \delta^s_{(m)} - \sum_{j=0}^{m-1} (-1)^{m-j} \binom{m}{j} \delta^s_{(j)} \left[\left(\frac{\partial}{\partial n}\right)^{m-j} \bar{v} \cdot \bar{\nabla}_{/\!/}\, b^s_{(m)} \right]_s \qquad (4.23)$$

where C is the total curvature of the ξ_1 surfaces

$$C \equiv -(\bar{\nabla} \cdot \bar{\alpha}_1) = -\frac{\partial}{\partial n} \ell n\, (h_2 h_3) \quad , \qquad (4.24)$$

$$v_n \equiv \bar{\alpha}_1 \cdot \bar{v} \quad ,$$

and

$$\bar{\nabla}_{/\!/} \equiv (\bar{\bar{1}} - \bar{\alpha}_1 \bar{\alpha}_1) \cdot \bar{\nabla} = \frac{\bar{\alpha}_2}{h_2} \frac{\partial}{\partial \xi_2} + \frac{\bar{\alpha}_3}{h_3} \frac{\partial}{\partial \xi_3} \quad . \qquad (4.25)$$

For m = 0 the sums in eq.(4.23) disappear and one finds

$$\left(\frac{\partial}{\partial t}\, b^s_{(o)}\, \delta^s_{(o)}\right)_{\bar{r}} = \left(\left(\frac{\partial b^s_{(o)}}{\partial t}\right)_{\bar{r},s} - b^s_{(o)}\, C_s\, v_{n,s} \right) \delta^s_{(o)} - b^s_{(o)} v_{n,s} \delta^s_{(i)} \qquad (4.26)$$

which may be shown to be equivalent to the formula used in ref. 47.

Finally, we shall need the time derivatives of the "Heaviside" functions for the + and - region:

$$\theta^{\pm}(\bar{r},\ t) \equiv \theta(\pm\xi_1(\bar{r},\ t)) \quad , \tag{4.27}$$

where θ is the usual Heaviside step function. One finds[47]

$$\left(\frac{\partial\theta^{\pm}}{\partial t}\right)_{\bar{r}} = -\bar{v}\cdot\bar{\nabla}\,\theta^{\pm} = \mp\, v_{n,s}\,\delta^{s}_{(o)} \quad . \tag{4.28}$$

This completes the mathematical framework needed in the rest of this chapter.

The multipole moments defined above are not unique in the sense that they depend on the specific choice of the curvilinear coordinates. In addition, other choices for the surface δ functions could have been made (although eq.(4.12) would not be valid). For the macroscopic quantities of interest, these differences should be negligible providing the radii of curvature of the $\xi_1 = 0$ surface are much larger than the thickness of the interface.

Surface Multipole Expansion of the Equations of Motion

We are interested in the evolution on a macroscopic scale of a set of variables $\underline{a}(\bar{r},\ t)$. In its most general form the equations of motion may be written as

$$\left(\frac{\partial \underline{a}(\bar{r},t)}{\partial t}\right)_{\bar{r}} = \underline{\mathcal{F}}(\bar{r},t\,|\,\underline{a}(\bar{r},t')) \tag{4.29}$$

where $\underline{\mathcal{F}}$ is some, possibly nonlinear, functional of the variables which is causal. For example, $\underline{\mathcal{F}}$ could be given in terms of equilibrium correlation functions as was the case in chapter II. In principle $\underline{\mathcal{F}}$ contains the effects due to external driving forces as well as those due to internal relaxation processes. In the subsequent analysis a number of assump-

tions will be made concerning $\underline{\mathcal{F}}$:

i $\underline{\mathcal{F}}$ is quasilocal in time and in space, i.e., $\underline{\mathcal{F}}$ depends only on $\underline{a}(\bar{r}', t')$ for $|\bar{r} - \bar{r}'| < \lambda_c$ and $|t - t'| < \tau_m$ where λ_c and τ_m are the typical microscopic correlation length and memory time, respectively (cf. chapter II).

ii The explicit $\bar{r}$ dependence of $\underline{\mathcal{F}}$ divides space into three time dependent regions: the +, -, and interfacial regions. In the plus and minus regions the explicit dependence of $\underline{\mathcal{F}}$ on $\bar{r}$ and t is on a macroscopic scale. In fact we assume

$$\underline{\mathcal{F}}(\bar{r},t|\underline{a}(\bar{r}',t')) = \underline{\mathcal{F}}^{\pm}(\bar{r},t|\underline{a}(\bar{r}',t')) \qquad \text{in the } \pm \text{ region,} \tag{4.30}$$

where $\underline{\mathcal{F}}^{\pm}$ describe the evolution in "pure" (i.e., filling all of space) phases. In the interfacial region $\underline{\mathcal{F}}$ changes rapidly from $\underline{\mathcal{F}}^{+}$ to $\underline{\mathcal{F}}^{-}$ over a microscopic distance λ_s. The "motion" and the "curvature" of the interfacial region are both assumed to be on a macroscopic scale. Within the context of this chapter we shall not discuss the microscopic motivation of the above assumptions. The generalized transport equations found in chapter II satisfy condition i and we shall assume they satisfy condition ii sufficiently close to equilibrium. Condition i is just an extension of the usual assumption made in the analysis of the pure phases. From a macroscopic point of view, condition ii simply implies the existence of an interface.

We now choose a time dependent orthogonal curvilinear coordinate system as described above, such that the $\xi_1(\bar{r}, t) = 0$ surface lies in the

interfacial region (cf. condition ii). Furthermore, the coordinate system should be chosen in such a way that its curvature is macroscopic (i.e., large compared to λ_c^{-1} and λ_s^{-1}), as is its time development. Within this context one still has the freedom to choose the coordinate system and hence the $\xi_1 = 0$ surface in many ways. Similar freedom exists in the choice of the equilibrium surface position[42]. We shall return to this point later in this chapter.

As we have already indicated, we are interested only in the evolution of the variables on a macroscopic scale. In principle eq.(4.29) may have solutions with variations on a microscopic scale in space and time, even outside the interfacial region, in spite of the conditions we have imposed on $\mathcal{F}$. In our analysis in this chapter we shall restrict ourselves to "macroscopic solutions" which we define by the following two conditions:

iii The variations of $\underline{a}(\bar{r}, t)$ outside the interfacial region are over distances and times which are much larger than λ_c, λ_s and τ_m, respectively.

iv In the interfacial region only the spatial variations of a parallel to the $\xi_1 = 0$ plane (i.e., as a function of ξ_2 and ξ_3) are required to be over distances much larger than λ_c and λ_s. The variation in time is again over times much larger than τ_m.

In the region of the interface, spatial variations over microscopic distances are allowed normal to the dividing surface $\xi_1 = 0$. In many respects it is precisely this structure normal to the interface which we shall discuss in this chapter.

Any solution $\underline{a}$ of eq.(4.29) will, over a microscopic distance, approach a solution $\underline{a}^{\pm}$ of the equation

$$\left(\frac{\partial \underline{a}^{\pm}(\bar{r},t)}{\partial t}\right)_{\bar{r}} = \underline{\mathcal{F}}^{\pm}(\bar{r},t|\underline{a}^{\pm}(\bar{r}',t')) \tag{4.31}$$

in the + or - regions, respectively. This is a consequence of condition ii. While $\underline{a}^{\pm}$ becomes equal to $\underline{a}$ only in the $\pm$ regions, eq.(4.31) defines them everywhere and in particular in the interfacial region. The solution to eq.(4.31) is just the solution to the bulk problem discussed within the context of the phenomenological approach. In view of the conditions imposed above and the choice of $\underline{a}^{\pm}$, the excess functions

$$\underline{a}^{s}(\bar{\bar{r}},t) \equiv \underline{a}(\bar{\bar{r}},t) - \underline{a}^{-}(\bar{\bar{r}},t)\,\theta^{-}(\bar{\bar{r}},t) - \underline{a}^{+}(\bar{\bar{r}},t)\,\theta^{+}(\bar{\bar{r}},t) \tag{4.32}$$

and

$$\underline{\mathcal{F}}^{s}(\bar{r},t|\,\underline{a}^{s},\,\underline{a}^{\pm}) \equiv \underline{\mathcal{F}}(\bar{r},t|\underline{a}) - \underline{\mathcal{F}}^{-}(\bar{r},t|\underline{a}^{-})\,\theta^{-}(\bar{r},t) - \underline{\mathcal{F}}^{+}(\bar{r},t|\underline{a}^{+})\,\theta^{+}(\bar{r},t) \tag{4.33}$$

are unequal to zero only in a microscopic region around $\xi_1 = 0$. These excess functions may therefore be multipole expanded around the $\xi_1 = 0$ surface in the manner outlined above. This yields the following expressions

$$\underline{a}(\bar{r},t) = \underline{a}^{-}(\bar{r},t)\,\theta^{-}(\bar{r},t) + \underline{a}^{+}(\bar{r},t)\,\theta^{+}(\bar{r},t) + \sum_{m=0}^{\infty} \frac{(-1)^m}{m!}\,\underline{a}^{s}_{(m)}(\bar{r},t)\,\delta^{s}_{(m)}(\bar{r},t) \tag{4.34}$$

and

$$\underline{\mathcal{F}} = \underline{\mathcal{F}}^{-}\,\theta^{-} + \underline{\mathcal{F}}^{+}\,\theta^{+} + \sum_{m=0}^{\infty} \frac{(-1)^m}{m!}\,\underline{\mathcal{F}}^{s}_{(m)}\,\delta^{s}_{(m)} \tag{4.35}$$

where the multipole moments $\underline{a}^{s}_{(m)}$ and $\underline{\mathcal{F}}^{s}_{(m)}$ may be calculated from $\underline{a}^{s}$ and $\underline{\mathcal{F}}^{s}$ using eq.(4.20).

One may now construct equations of motion for the multipole moments $\underline{a}^{s}_{(m)}$ in the following manner. Substituting eqs.(4.34) and (4.35) into eq.(4.29) and using eq.(4.31) one finds

$$\underline{a}^{-}\left(\frac{\partial\theta^{-}}{\partial t}\right)_{\bar{r}} + \underline{a}^{+}\left(\frac{\partial\theta^{+}}{\partial t}\right)_{\bar{r}} + \sum_{m=0}^{\infty} \frac{(-1)^m}{m!}\left(\frac{\partial\,\underline{a}^{s}_{(m)}\,\delta^{s}_{(m)}}{\partial t}\right)_{\bar{r}} \tag{4.36}$$

$$= \sum_{m=0}^{\infty} \frac{(-1)^m}{m!}\,\delta^{s}_{(m)}\,\underline{\mathcal{F}}^{s}_{(m)}\ .$$

Subsequently, we rewrite the time derivatives on the left-hand side using eqs.(4.28) and (4.23). The resulting expression is in a form for which eq.(4.21) holds. One thus obtains

$$\left(\frac{\partial\,\underline{a}^{s}_{(j)}}{\partial t}\right)_{\bar{r},s} = \underline{\mathcal{F}}^{s}_{(j)} + C_s\,v_{n,s}\,\underline{a}^{s}_{(j)} + (\underline{a}^{+}-\underline{a}^{-})_s\,v_{n,s}\,\delta_{j,o}$$

$$- j\,v_{n,s}\,\underline{a}^{s}_{(j-1)} - \sum_{m=j+1}^{\infty} \frac{1}{(m-j)!}\Big\{\underline{a}^{s}_{(m)}\Big[j\,(m-j+1)\left(\frac{\partial}{\partial n}\right)^{m-j}\left(\left(\frac{\partial\bar{\bar{a}}_1}{\partial t}\right)_{\bar{r}}\cdot\bar{\nabla}_{/\!/}\lambda\right)$$

$$- \sum_{\ell=2}^{3} (h_2h_3)^{-1}\,\frac{\partial}{\partial\xi_\ell}\left(h_2h_3\left(\frac{\partial}{\partial n}\right)^{m-j-1}\left(\frac{\bar{\bar{\alpha}}_\ell}{h_\ell}\cdot\left(\frac{\partial\,\bar{\alpha}_1}{\partial t}\right)_{\bar{r}}\right)\right)\Big]_s$$

$$- \Big[\left(\frac{\partial}{\partial n}\right)^{m-j}\bar{v}\cdot\bar{\nabla}_{/\!/}\,\underline{a}^{s}_{(m)}\Big]_s\Big\}\ , \tag{4.37}$$

where eq.(4.10) may be used to eliminate $(\frac{\partial \overline{\alpha_i}}{\partial t})_{\underline{r}}$.

We emphasize that the solution of this infinite hierarchy together with eq.(4.31) is formally equivalent to the solution of the original problem. The free parameters which appear in the bulk equations are determined by the requirement that the higher multipole moments tend to zero. This is needed in order to guarantee the convergence of the multipole series. The terms appearing on the right-hand side of eq.(4.37) may be interpreted as follows. The first term is simply the moment of $\underline{\mathcal{F}}^s$ which couples to the j^{th} multipole. The second is due to the change in surface area for a curved surface by motion in the direction of the normal. The third term describes the amount of $\underline{a}^s_{(0)}$ that is exchanged with the + and - regions due to motion of the surface. The next term is of a similar nature, but for the higher order moments. The terms in the sum represent rather complicated effects related to the evolution of the shape of the surface as well as flow effects inside the interfacial region. The interpretations given above will become more clear in the rest of this work.

Truncation of the Multipole Expansion-Boundary Conditions

The surface multipoles of the variables introduced in the previous section describe the internal structure of the interfacial region. For instance, $\underline{a}^s_{(0)}$ is the excess of the variable $\underline{a}$ defined with respect to the $\xi_1 = 0$ dividing surface. In equilibrium this quantity is the Gibb's surface excess[42]. The higher order multipoles describe details of the distribution of $\underline{a}$ within the interfacial region by giving higher and higher moments of this distribution with respect to the dividing surface.

Similar considerations hold for $\underline{\mathcal{F}}^{s}_{(j)}$.

In view of the fact that the excess functions are nonzero only in the interfacial region, one may give the following crude estimates for the magnitudes of the multipoles:

$$\underline{a}^{s}_{(j)} \propto (\lambda_s)^{j+1} \tag{4.38}$$

From physical considerations it follows that the effect of multipoles on the macroscopic behavior will decrease with increasing order. This leads us to the conjecture that for many purposes one may truncate the multipole expansion such that:

$$\underline{a}^{s}_{(j)} \equiv 0 \quad \text{for } j \geq j_m \,. \tag{4.39}$$

In general j_m will depend on the system, the initial conditions and the desired information concerning the interface. In the next chapter, we shall show how the truncation parameter j_m can arise from considerations of equilibrium quantities. A somewhat weaker requirement would be that the variables $\underline{a}^{s}_{(j)}$, $j \geq j_m$, decay on a molecular time scale and can therefore be neglected when considering macroscopic phenomena. At present it is not known if this is true. Using the truncation, the original problem, eqs.(4.31) and (4.37), reduces to solving the following set of equations:

$$\left(\frac{\partial \underline{a}^{\pm}(\bar{r},t)}{\partial t}\right)_{\bar{r}} = \underline{\mathcal{F}}^{\pm}(\bar{r},t|\underline{a}(\bar{r}',t'))\,, \tag{4.40}$$

$$\left(\frac{\partial \underline{a}^s(j)}{\partial t}\right)_{\bar{r},s} = \underline{\mathcal{F}}^s_{(j)} + C_s\, v_{n,s}\, \underline{a}^s_{(j)} + \delta_{j,o}\, v_{n,s}(\underline{a}^+_s - \underline{a}^-_s)$$

$$-j\, v_{n,s}\, \underline{a}^s_{(j-1)} - \sum_{m=j+1}^{j_m-1} \frac{1}{(m-j)!} \{\underline{a}^s_{(m)}[j(m-j+1)^{-1} \left(\frac{\partial}{\partial n}\right)^{m-j} \left(\left(\frac{\partial \bar{\alpha}_i}{\partial t}\right)_{\bar{r}} \cdot \bar{\nabla}_{/\!/}\lambda\right)$$

$$- \sum_{\ell=2}^{3} (h_2h_3)^{-1} \frac{\partial}{\partial \xi_\ell} \left(h_2h_3 \left(\frac{\partial}{\partial n}\right)^{m-j-1} \left(\frac{\bar{\alpha}_\ell}{h_\ell}\right) \cdot \left(\frac{\partial \bar{\alpha}_1}{\partial t}\right)_{\bar{r}}\right)\Big]_s$$

$$- \left[\left(\frac{\partial}{\partial n}\right)^{m-j} \bar{v} \cdot \bar{\nabla}_{/\!/}\, \underline{a}^s_{(m)}\right]_s\} \quad ,$$

$$j<j_m \quad , \tag{4.41}$$

and

$$0 = \underline{\mathcal{F}}^s_{(j)} + (\underline{a}^+_s - \underline{a}^-_s)\, v_{n,s}\, \delta_{j,o} - j_m\, v_{n,s}\, \underline{a}^s_{(j_m-1)}\, \delta_{j,j_m} \quad , \tag{4.42}$$

$$j \geq j_m \, .$$

We note that the sum in eq.(4.41) contributes only if $j < j_m - 1$. Furthermore, the $\underline{\mathcal{F}}^s_{(j)}$ are evaluated for $\underline{a}^s_{(k)} = 0$, $k \geq j_m$.

Eqs.(4.40) and (4.41) are the equations of motion for the truncated set of variables. Eq.(4.42) is the infinite set of boundary conditions, which follow from the requirement that eq.(4.39) be maintained for all times. The reason that an infinite set of boundary conditions is obtained

is related to the fact that the above equations are nonlocal in space and are therefore equivalent to infinite order partial differential equations. We shall show below that if one approximates these equations by partial differential equations of a finite order, then it is consistent to retain only a finite number of boundary conditions.

We note that, if the condition that the solutions are of a macroscopic nature is dropped, then one may show that the solution of eqs. (4.40) - (4.42) is formally equivalent to the original problem given in eq.(4.29) for any choice of j_m. In fact this formal equivalence simply implies that the "neglected" higher order multipoles reappear as microscopic variations in $\underline{a}^{\pm}$ near the interface. The imposed condition of macroscopic variation of the variables is essential to the localization procedure now to be introduced.

Localization

The quasi-local nature of $\underline{\mathcal{F}}$, condition i, and the macroscopic nature of $\underline{a}$, conditions iii and iv, can be used to approximate eqs.(4.40) and (4.41) by finite order partial differential equations which are local in space. Consistent with this approximation, only a finite number of boundary conditions will result from eqs.(4.42). The macroscopic nature of $\underline{a}$ (in the sense of conditions iii and iv given above) implies that $\underline{a}$ and $\underline{a}^s_{(j)} (j < j_m)$ vary only over macroscopic lengths. The functionals $\underline{\mathcal{F}}^{\pm}(\bar{r}, t|\underline{a}^{\pm})$ involve values of $\underline{a}^{\pm}$ only near the point $\bar{r}$. In addition, quasi-locality implies that the multipole moments $\underline{\mathcal{F}}^s_{(j)}(\bar{r},t|\underline{a}^{\pm}, \underline{a}^s)$ depend only on values of $\underline{a}^{\pm}$ near the interface.

These characteristics may be used to advantage if the $\underline{a}^{\pm}(\bar{r},t)$ and $\underline{a}^s_{(j)}(\bar{r}',t')$ appearing in $\underline{\mathcal{F}}^{\pm}$ and $\underline{\mathcal{F}}^s_{(j)}$ are Taylor expanded about the point $\bar{r}$

$$\underline{\mathcal{F}}^{\pm}(\bar{r},t|\underline{a}^{\pm}(\bar{r}',t')) = \underline{\mathcal{F}}^{\pm}(\bar{r},t|\sum_{k=0}^{\infty}\frac{1}{k!}(\bar{r}'-\bar{r})\ (\cdot)^k\ \bar{\nabla}^k\ \underline{a}^{\pm}(\bar{r},t')) \tag{4.43}$$

and, taking $\bar{r}=\bar{r}_s\equiv\bar{r}(\xi_1=0,\ \xi_2,\ \xi_3,\ t)$,

$$\underline{\mathcal{F}}^{s}_{(j)}\ (\bar{r}_s,t|\underline{a}^{\pm}(\bar{r}',t'),\ \underline{a}^{s}_{(j')}(\bar{r}',t'))$$

$$=\underline{\mathcal{F}}^{s}_{(j)}\ (\bar{r}_s,t|\sum_{k=0}^{\infty}\frac{1}{k!}(\bar{r}'-\bar{r}_s)^k\ (\cdot)^k\ (\bar{\nabla}^k\ \underline{a}^{\pm}(\bar{r},t'))_{\bar{r}_s}\ , \tag{4.44}$$

$$\sum_{k=0}^{\infty}\frac{1}{k!}(\bar{r}'-\bar{r}_s)^k\ (\cdot)^k\ (\bar{\nabla}^k\ \underline{a}^{s}_{(j')}(\bar{r},t'))_{\bar{r}_s})$$

where $(\cdot)^k$ indicates a k-fold contraction.* We now assume in view of the quasi-local nature of $\underline{\mathcal{F}}$ and its specific form, for hydrodynamic problems, for example, that gradients in these Taylor expansions beyond the q^{th} can be ordered by factors of order λ_c. The order of the n^{th} gradient, $n>q$ is $(\lambda_c)^{n-q}$. Terms with more and more gradients therefore become less and less important. Consequently, one usually neglects all terms in the $\underline{\mathcal{F}}$'s containing more than a certain maximum number of gradients, $k_m \geq q$, in eqs.(4.43) and (4.44). This approximation has the advantage that it reduces the integral form of the equations of motion to partial differential equations of a finite order which are much easier to solve. The truncated versions of eqs.(4.43) and (4.44) can be valid only if the bulk solutions

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*Note that we used a three dimensional Taylor expansion of $\underline{a}^{s}_{(j')}(\bar{r}',t')\equiv\underline{a}^{s}_{(j')}(\xi'_2,\ \xi'_3,t')$. One could also use a two dimensional Taylor expansion in curvilinear coordinates. The final results are of course equivalent.

and multipole moments are macroscopic, since otherwise large gradients would appear. This restricts the choice of j_m. In addition, it is quite possible that the numbers of gradients needed in the bulk and surface equations could be different (in fact this appears to be the case, cf. chapter V). Should this be true, k_m should be taken to be the larger of the two choices and the extra terms neglected in either of eqs.(4.43) or (4.44).

Specifically, eq.(4.40) becomes a partial differential equation of the k_m'th order for the solutions in the + and the - regions. Similarly, eq.(4.41) becomes a partial differential equation of the same order for the $\underline{a}^s_{(j)}$, $j < j_m$. The boundary conditions in eq.(4.42) require more discussion. As $\underline{\mathcal{F}}^s_{(j)}$ is a j'th order multipole moment, it has the dimensionality of length to the power $j+1$. We shall therefore assume that

$$\underline{\mathcal{F}}^s_{(j)} \text{ is a sum over terms } \alpha\lambda_s^{j+1-k}\lambda_c^{k-q} \quad q \leq k \leq j+1 \ . \tag{4.45}$$

In view of the truncation of the multipole expansion, one should neglect all contributions for which $j - k \geq j_m$. Similarily, because of the localization one should neglect all contributions for which $k > k_m$. It follows therefore that consistent with our approximations the boundary conditions in eq.(4.42),

$$\underline{\mathcal{F}}^s_{(j)} = 0, \text{ are trivially satisfied for } j \geq j_m + k_m \ . \tag{4.46}$$

Thus, we conclude that eq.(4.42) leads to exactly k_m sets of boundary conditions:

$$0 = \underline{\mathcal{F}}^{s}_{(j)} + (\underline{a}^{+}_{s} - \underline{a}^{-}_{s})\, v_{n,s}\, \delta_{j,0} - j_m\, v_{n,s}\, \underline{a}^{s}_{(j_m-1)}\, \delta_{j,j_m}$$

$$\text{for } j_m \leq j < j_m + k_m \,. \tag{4.47}$$

In the above equation, $\underline{\mathcal{F}}^{s}_{(j)}$ is given by eq.(4.44) (keeping only terms involving up to k_m gradients) and therefore depends on $\underline{a}^{\pm}$ and their derivatives at the interface. For a given problem some of these boundary conditions may not be independent, while others will be used to specify properties of the coordinate velocity field. We shall not attempt to answer the question of whether eq.(4.49) over-determines the general problem. In chapter VI we shall demonstrate these points.

It is important to realize that the length scales λ_s and λ_c are used more to make the amount of surface structure and nonlocality of a particular term explicit than the real order of magnitude. It is very well possible that some of the terms that we take into account are as small as the terms which have been neglected. It is only possible to obtain a more detailed estimate of the size of the various terms within the context of a specific problem. Also, it should be realized that in actual problems more length scales, both for the surface as well as in bulk, will in general appear.

Linearization

Many problems are adequately described by linear equations. In this section we examine the linearized form of the localized equations and boundary conditions discussed in the previous sections. The linearization is performed about equilibrium. We assume that the equilibrium

surface is planar.

Expanding $\underline{\mathcal{F}}$ and $\underline{\mathcal{F}}^{\pm}$ in a functional Taylor series and noting that $\underline{\mathcal{F}}(\bar{r},t|\underline{a})$ and $\underline{\mathcal{F}}^{\pm}(\bar{r},t|\underline{a}^{\pm})$ vanish at equilibrium results in

$$\underline{\mathcal{F}}(\bar{r},t|\underline{a}) = \int d\bar{r}' \int_{-\infty}^{\infty} dt' \, \underline{\underline{M}}(\bar{r},t|\bar{r}',t') \cdot (\underline{a}(\bar{r}',t') - \underline{a}_{eq}(\bar{r}')) \tag{4.48}$$

and

$$\underline{\mathcal{F}}^{\pm}(\bar{r},t|\underline{a}) = \int d\bar{r}' \int_{-\infty}^{\infty} dt' \, \underline{\underline{M}}^{\pm}(\bar{r},t|\bar{r}',t') \cdot (\underline{a}^{\pm}(\bar{r}',t') - \underline{a}^{\pm}_{eq}(\bar{r}')) \tag{4.49}$$

to linear order in displacements from equilibrium. Here $\underline{\underline{M}}$ and $\underline{\underline{M}}^{\pm}$ depend on the properties of the equilibrium system only. The subscript "eq" denotes the value of the functions at equilibrium. Also, causality requires the M's to equal zero for $t' > t$. For example, we could use the $\underline{\underline{M}}$ presented in chapter II, thereby eliminating the non-locality in time.

In addition to the linearization in the variables, we shall linearize in the deviation of the position of the surface from equilibrium. In the next chapter we shall show how this requirement may be removed, providing the curvature is still macroscopic. Since the dividing surface in equilibrium is a plane, we may choose the curvilinear coordinates in equilibrium and the Cartesian coordinates such that

$$\bar{\xi}_{eq} = \bar{r} \, . \tag{4.50}$$

This implies that

$$\theta^{\pm}_{eq}(\bar{r}) = \theta(\pm x), \; \delta^{s}_{(j),eq}(\bar{r}) = \delta^{(j)}(x) \equiv \frac{\partial^{j}}{\partial x^{j}} \delta(x) \tag{4.51}$$

and

$$\bar{\alpha}_{i,eq} = (1,0,0) \equiv \bar{e}_1, \ \bar{\alpha}_{2,eq} = (0,1,0) \equiv \bar{e}_2, \ \bar{\alpha}_{3,eq} = (0,0,1) \equiv \bar{e}_3 . \quad (4.52)$$

Away from equilibrium we write

$$\bar{\xi}(\bar{r}, t) = \bar{r} + \hat{\bar{\xi}}(\bar{r}, t). \quad (4.53)$$

We shall now linearize in $\hat{\bar{\xi}}$. The velocity field of the curvilinear coordinates becomes, cf. eq.(4.7),

$$\bar{v}(\bar{r},t) = - \left(\frac{\partial \hat{\bar{\xi}}(\bar{r},t)}{\partial t}\right)_{\bar{r}} \quad (4.54)$$

to linear order. This equation implies that $\bar{v}$ is of linear order. In appendix D we show that to linear order in $\hat{\xi}_i$,

$$\theta^{\pm}(\bar{r},t) - \theta(\pm x) = \pm \hat{\xi}_1(\bar{r},t) \ \delta(x) \quad (4.55)$$

and

$$\delta^{s}_{(j)}(\bar{r},t) - \delta^{(j)}(x) = \bar{\nabla}_{//} \cdot (\hat{\bar{\xi}}(\bar{r},t) - \hat{\bar{\xi}}(x=0, y, z, t)) \ \delta^{(j)}(x) + \hat{\xi}_1(x=0, y, z, t) \ \delta^{(j+1)}(x) , \quad (4.56)$$

where from now on

$$\bar{\nabla}_{//} = \bar{\nabla}_{//,eq} = (0, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}) . \quad (4.57)$$

We shall now proceed to express $\underline{\mathcal{F}}^{s}_{(j)}$ in terms of $\underline{a}^{\pm}$, $\underline{a}^{s}_{(j)}$ and $\hat{\bar{\xi}}$, to linear order. Using eqs.(4.48) and (4.49) one has

$$\underline{\mathcal{F}}^{s}_{(j)} = \int_{-\infty}^{\infty} dx\, x^{j} \int d\bar{r}' \int_{-\infty}^{t} dt' [\underline{\underline{M}}(\bar{r},t|\bar{r}',t')\cdot(\underline{a}(\bar{r}',t') - \underline{a}_{eq}(\bar{r}'))$$

$$-\theta(x)\underline{\underline{M}}^{+}(\bar{r},t|\bar{r}',t')\cdot(\underline{a}^{+}(\bar{r}',t') - \underline{a}^{+}_{eq}(\bar{r}')) - \theta(-x)\,\underline{\underline{M}}^{-}(\bar{r},t|\bar{r}',t')\cdot(\underline{a}^{-}(\bar{r}',t')$$

$$- \underline{a}^{-}_{eq}(\bar{r}'))] \qquad (4.58)$$

where, in view of the linear nature of the integrand, these multipoles may be calculated around the equilibrium dividing surface. Upon substitution of the multipole expansions of $\underline{a}$ about the nonequilibrium and of $\underline{a}_{eq}$ about the equilibrium dividing surfaces, cf. eq.(4.34), eq.(4.58) becomes to linear order

$$\underline{\mathcal{F}}^{s}_{(j)} = \int_{-\infty}^{\infty} dx\, x^{j} \int d\bar{r}' \int_{-\infty}^{t} dt' \{\underline{\underline{M}}(\bar{r},t|\bar{r}',t')\cdot \sum_{n=0}^{j_m-1} \frac{(-1)^n}{n!} (\delta^{s}_{(n)}\,\underline{a}^{s}_{(n)}$$

$$-\delta^{(n)}(x')\,\underline{a}^{s}_{(n),eq}) + \underline{\underline{M}}(\bar{r},t|\bar{r}',t')\cdot[(\theta^{+} - \theta(x'))\,\underline{a}^{+}_{eq} + (\theta^{-} - \theta(-x'))\,\underline{a}^{-}_{eq}]$$

$$+ \underline{\underline{S}}^{+}(\bar{r},t|\bar{r}',t')\cdot\hat{\underline{a}}^{+} + \underline{\underline{S}}^{-}(\bar{r},t|\bar{r}',t')\cdot\hat{\underline{a}}^{-}\} \,, \qquad (4.59)$$

where

$$\underline{\underline{S}}^{\pm}(\bar{r},t|\bar{r}',t') \equiv \underline{\underline{M}}(\bar{r},t|\bar{r}',t')\,\theta(\pm x') - \theta(\pm x)\,\underline{\underline{M}}^{\pm}(\bar{r},t|\bar{r}',t') \quad . \qquad (4.60)$$

Using the fact that

$$\underline{a}^{s}_{(j)}(\xi_2, \xi_3, t) = \underline{a}^{s}_{(j)}(y, z, t) + \hat{\bar{\xi}}_{//}\cdot\bar{\nabla}_{//}\,\underline{a}^{s}_{(j)}(y, z, t) \qquad (4.61)$$

$$= \hat{\underline{a}}^{s}_{(j)}(\bar{r}_{//},t) + \underline{a}^{s}_{(j),eq}(\bar{r}_{//}) + \hat{\bar{\xi}}_{//}\cdot\bar{\nabla}_{//}\,\underline{a}^{s}_{(j),eq}(\bar{r}_{//})$$

and eqs.(4.55) and (4.56), one obtains from eq.(4.59) to linear order

$$\underset{\sim}{\mathcal{F}}^{s}_{(j)} = \int_{-\infty}^{\infty} dx \int d\bar{r}' \int_{-\infty}^{t} dt' \; x^{j} [\underline{\underline{S}}^{+}(\bar{r},t|\bar{r}',t') \cdot \underline{\hat{a}}^{+}(\bar{r}',t') + \underline{\underline{S}}^{-}(\bar{r},t|\bar{r}',t') \cdot \underline{\hat{a}}^{-}(\bar{r}',t')$$

$$+ \sum_{n=0}^{j_m-1} \frac{(-1)^n}{n!} \underline{\underline{M}}(\bar{r},t|\bar{r}',t') \cdot \{\delta^{(n)}(x') \, (\underline{\hat{a}}_{(n)}(\bar{r}'_{/\!/},t') + \delta_{n,0} (\underline{a}^{+}(\bar{r}') - \underline{a}(\bar{r}'))_{eq} \hat{\xi}_1(\bar{r}',t')$$

$$+ \underline{a}^{s}_{(n),eq}(\bar{r}'_{/\!/}) \, \bar{\nabla}_{/\!/} \cdot (\hat{\bar{\xi}}(\bar{r}',t') - \hat{\bar{\xi}}(\bar{r}',t')_{x'=0}) + \hat{\bar{\xi}}(\bar{r}',t') \cdot \bar{\nabla}_{/\!/} \, \underline{a}^{s}_{(n),eq}(\bar{r}'_{/\!/}))$$

$$+ \delta^{(n+1)}(x') \, \hat{\xi}_1(\bar{r}',t')_{x'=0} \, \underline{a}^{s}_{(n),eq}(\bar{r}'_{/\!/}) \}] \; . \tag{4.62}$$

Since we have made all dependence on $\hat{\bar{\xi}}$ explicit in this equation, the multipoles have become functions of $\bar{r}_{/\!/} \equiv (0, y, z)$.

Eq.(4.62) gives the desired expression, valid to linear order, for $\underset{\sim}{\mathcal{F}}^{s}_{(j)}$. Substituting this expression into eqs.(4.41) and (4.42), linearizing the remaining terms in these equations and carrying out the localization procedure described in the preceding section results in the following set of equations and boundary conditions:

$$\left(\frac{\partial \, \underline{\hat{a}}^{\pm}(\bar{r},t)}{\partial t}\right)_{\bar{r}} = \sum_{k=0}^{k_m} \int_{o}^{t} dt' \; \underline{\underline{M}}^{\pm}_{k}(\bar{r},t|t') \; (\cdot)^{k} \, \bar{\nabla}^{k} \, \underline{\hat{a}}^{\pm}(\bar{r},t') \; , \tag{4.63}$$

$$\left(\frac{\partial \hat{\underline{a}}^{s}(j)}{\partial t}\right)_{\bar{r},s} = (\underline{a}_{s}^{+} - \underline{a}_{s}^{-})_{eq}\, v_x|_{x=0}\, \delta_{j,0} - j\, \underline{a}^{s}_{(j-1),eq}\, v_x|_{x=0}$$

$$+ \bar{\nabla}_{/\!/} \cdot \sum_{n=j+1}^{\min(j_m-1,\, k_m+j-1)} ((n-j)!)^{-1} \left(\frac{\partial^{n-j}\, \bar{v}}{\partial x^{n-j}}\right)_{x=0} \underline{a}^{s}(n),eq$$

$$+ \sum_{k=0}^{k_m} \int_{-\infty}^{t} dt' \{ {}^{j}\underline{\underline{A}}_{k}^{+}(\bar{r}_{/\!/},t|t')\, (\cdot)^{k}\, (\bar{\nabla}^{k} \hat{\underline{a}}^{+}(\bar{r},t'))_{x=0}$$

$$+ {}^{j}\underline{\underline{A}}^{-}(\bar{r}_{/\!/},t|t')\, (\cdot)^{k}\, (\bar{\nabla}^{k}\, \hat{\underline{a}}^{-}(\bar{r},t))_{x=0} + \sum_{j'=0}^{j_m-1} {}^{j}\underline{\underline{A}}_{k}^{j'}(\bar{r}_{/\!/},t|t')\, (\cdot)^{k}\, \bar{\nabla}_{/\!/}^{k}\, \hat{\underline{a}}^{s}_{(j')}(\bar{r}_{/\!/},t')$$

$$+ {}^{j}\underline{B}_{k}(\bar{r}_{/\!/},t|t')\, (\cdot)^{k+1}\, (\bar{\nabla}\, \hat{\bar{\xi}}(\bar{r},t'))_{x=0}\}$$

$$j < j_m\ ,$$

(4.64)

and

$$0 = (\underline{a}_{s}^{+} - \underline{a}_{s}^{-})_{eq}\, v_x|_{x=0}\, \delta_{j,0} - j_m\, a^{s}_{(j_m-1),eq}\, v_x|_{x=0}\, \delta_{j,j_m}$$

$$+ \sum_{k=0}^{k_m} \int_{-\infty}^{t} dt' \{ {}^{j}\underline{\underline{A}}_{k}^{+}(\bar{r}_{/\!/},t|t')\, (\cdot)^{k}\, (\bar{\nabla}^{k}\, \hat{\underline{a}}^{+}(\bar{r},t'))_{x=0}$$

$$+ {}^{j}\underline{\underline{A}}^{-}(\bar{r}_{/\!/},t|t')\, (\cdot)^{k}\, (\bar{\nabla}^{k} \hat{\underline{a}}^{-}(\bar{r},t'))_{x=0}$$

$$+ \sum_{j'=0}^{j_m-1} {}^{j}\underline{\underline{A}}_{k}^{j'}(\bar{r}_{//},t|t')\ (\cdot)^{k}\ \bar{\nabla}_{//}^{k}\ \underline{\hat{a}}_{(j')}^{s}(\bar{r}_{//},t')$$

$$+ {}^{j}\underline{B}_{k}(\bar{r}_{//},t|t')\ (\cdot)^{k+1}(\bar{\nabla}^{k}\hat{\xi}(\bar{r},t'))_{x=0}\}\ ,$$

$$\text{for } j_m \leq j < j_m + k_m\ , \qquad (4.65)$$

where the coefficients are defined by

$$\underline{\underline{M}}_{k}^{\pm}(\bar{r},t|t') \equiv \frac{1}{k!}\int d\bar{r}'\ \underline{\underline{M}}^{\pm}(\bar{r},t|\bar{r}',t')\ (\bar{r}'-\bar{r})^{k}\ , \qquad (4.66)$$

$${}^{j}\underline{\underline{A}}_{k}^{\pm}(\bar{r}_{//},t|t') \equiv (k!)^{-1}\int_{-\infty}^{\infty} dx \int d\bar{r}'\ x^{j}\ \underline{\underline{S}}^{\pm}(\bar{r},t|\bar{r}',t')\ (\bar{r}'-\bar{r}_{//})^{k}\ , \qquad (4.67)$$

$${}^{j}\underline{\underline{A}}_{k}^{j'}(\bar{r}_{//},t|t') \equiv (-1)^{j'}(k!j'!)^{-1}\int_{-\infty}^{\infty} dx \int d\bar{r}'\ x^{j}\ \underline{\underline{M}}(\bar{r},t|\bar{r}',t')\ \delta^{(j')}(x)(\bar{r}_{//}'-\bar{r}_{//})^{k}, \qquad (4.68)$$

and

$${}^{j}\underline{B}_{k}(\bar{r}_{//},t|t') \equiv \int_{-\infty}^{\infty} dx \int d\bar{r}'\ \frac{x^{j}}{k!}\underline{\underline{M}}(\bar{r},t|\bar{r}',t')\cdot\sum_{n=0}^{j_m-1}\frac{(-1)^{n}}{n!}\{\delta^{(n)}(x')[(\delta_{n,0}(\underline{a}^{+}(\bar{r}')$$

$$-\underline{a}^{-}(\bar{r}'))_{eq}\bar{e}_1 - \overline{\nabla_{//}\ \underline{a}_{(n),eq}^{s}(\bar{r}_{//}')})\ (\bar{r}'-\bar{r}_{//})^{k} + k\ \underline{a}_{(n),eq}^{s}(\bar{r}_{//}')\ (\bar{e}_2\bar{e}_2+\bar{e}_3\bar{e}_3)((\bar{r}'-\bar{r}_{//})^{k-1}$$

$$-(\bar{r}_{//}'-\bar{r}_{//})^{k-1})] + \delta^{(n+1)}(x')\ \underline{a}_{(n),eq}^{s}(\bar{r}_{//}')\bar{e}_1(\bar{r}_{//}'-\bar{r}_{//})^{k}\}\ . \qquad (4.69)$$

If $j_m = 0$ then only the term involving $(\underline{a}^{+}(\bar{r}') - \underline{a}^{-}(\bar{r}'))_{eq}$ will appear in eq.(4.69).

Eq.(4.63) gives a linear partial differential equation describing the evolution of the variables in the bulk phases. These equations are the same as those usually found in the description of single phase systems, as is easily seen from the discussions in the preceding chapters.

Eq.(4.64) is the linearized equation of motion for the surface multipole densities, and contains, in addition to convective terms, coupling to the bulk and surface variables. Eq.(4.65) gives the linearized boundary conditions necessary to match the solutions at the dividing surface. In addition, one needs the equation of motion, eq.(4.54), for the orthogonal curvilinear coordinate system. In general one will find that only certain aspects of the coordinate system and its motion couple to the variables. Eqs.(4.66) - (4.69) give explicit expressions for the coefficients appearing in the equations of motion and the boundary conditions in terms of the original integral kernels and the equilibrium densities. These relations will yield the generalized Green-Kubo (or fluctuation-dissipation) relations for the constitutive coefficients, in particular those for the coefficients appearing in the boundary conditions and in the expressions for surface kinetics.

Eqs.(4.63) - (4.69) in their general form are of course rather complicated. For a given problem, symmetry considerations usually cause many of the coefficients to vanish and thereby greatly simplify the equations. In particular, many systems will be homogeneous in the bulk phases and along the surface in equilibrium and stationary in time. Also for many systems the nonlocality in time may be neglected, as was shown earlier. The formulae have been presented for general values of k_m and j_m. In practice, one usually stops after the first significant term and consequently k_m and j_m are small. In chapter VI we shall explore the effects of changing j_m and/or k_m on the bulk equations. Before this is done some unfinished aspects of the multipole technique, as well as its relation to response theory, are examined.

Chapter V. Systems with Large Spatial Gradients: Additional Considerations

At the end of the last chapter, the linearized equations of motion and boundary conditions for the bulk and multipole variables were presented. In this chapter the connections between the multipole expansion and equations of motion given by the response theory of chapter II shall be examined.

We consider a two phase single component system which is translationally invariant and isotropic everywhere, except near the interface. The interface is planar at equilibrium and has both translational and rotational invariances in the plane.

In order to describe mathematically such a system we must consider the limiting behavior of finite systems. It is well known[9] that a weak external field must be imposed in order to orient the interface. Once the interface has been oriented we allow the system to become infinite ($V\to\infty$ with β, μ constant) and then allow the orienting field to vanish. The interface should remain unchanged. The Hamiltonian now has full rotational and translational invariances, whereas the macroscopic system does not. Such systems are said to possess a broken symmetry[9,72].

We shall assume that the linearized macroscopic behavior is given by the generalized transport equation (cf. eq.(2.51)) using

$$\underline{\underline{M}}(\bar{r}|\bar{r}', t) \equiv \lim_{g\to 0} \lim_{\substack{V\to\infty \\ \beta,\mu \text{ constant}}} \underline{\underline{M}}(\bar{r}|\bar{r}', t)_{V,g} \quad , \tag{5.1}$$

where $\underline{\underline{M}}(\bar{r}|\bar{r}', t)_{V,g}$ is the nonlocal linear transport coefficient for a finite system in an external field characterized by g, the strength parameter of the orienting field, and volume V.

Since the generalized transport equation, eq.(2.51), is local in time, all time nonlocality effects in the linearized equations of motion and definitions of the coefficients (cf. eqs.(4.63-4.69))disappear. For $t >> \tau_m$ all references to time in the definitions of the coefficients shall be dropped.

Invariances

The systems under consideration possess a number of invariances other than limited rotational and translational invariances consistent with the position and orientation of the interface.

Some of these additional invariances are present as a result of the limit (cf. eq.(5.1)) under which the system is examined. For example, should the entire equilibrium system suffer a uniform displacement or rotation, then the result is also an equilibrium system. For these changes, $\hat{\underline{a}}^{\pm}$ and $\hat{\underline{a}}^{s}_{(j)}$, $j = 0, 1, \ldots$, are zero while we may take

$$\hat{\overline{\xi}}(\overline{r}, t) = \left\{ \begin{array}{l} \Delta\overline{\xi}_o \text{, any constant vector, for a displacement} \\ \\ \overline{r} \wedge \delta\overline{\Omega} \text{, where } \delta\overline{\Omega} \text{ is any vector characterizing an infinitesimal rotation.} \end{array} \right\} \tag{5.2}$$

Substituting eq.(5.2) into eqs.(4.64) and (4.65) we immediately find that

$$\underline{j\overline{B}}_o = 0 \text{ and } \underline{j\overline{\overline{B}}}_1 = \underline{j\overline{\overline{B}}}^T_1, \quad j = 0, 1, \ldots, \tag{5.3}$$

where the symbol T indicates the transpose of a matrix and where the spatial dependence of the coefficients has been omitted since they are constant in systems with translational invariance in the y and z directions.

We also have Galilean invariance. This means that setting the system into steady motion yields a solution to eqs.(4.63) - (4.64). Thus, assuming the momentum density is included in the set of variables, we should find that for any $\bar{w}$:

$$\bar{v}(\bar{r},\ t) = \bar{w} \tag{5.4 a}$$

$$\hat{a}^{\pm}_{\alpha}(\bar{r},\ t) = 0,\ \hat{a}^{s}_{(j),\alpha} = 0 \quad j = 0,\ 1,\ \ldots,\ \alpha \neq \bar{p} \tag{5.4 b}$$

$$\bar{p}^{\pm}(\bar{r},\ t) = m\, n^{\pm}_{eq}\, \bar{w} \tag{5.5}$$

and

$$\bar{p}^{s}_{(j)}(\bar{r}_{//},\ t) = m\, n^{s}_{(j)_{eq}}\, \bar{w} \tag{5.6}$$

solves the multipole hierarchy to linear order in $\bar{w}$. This can be true (cf. eqs.(4.63) - (4.64)) only if

$$M^{\pm}_{o,\alpha\bar{p}} = 0\ , \tag{5.7}$$

$$(a^{+}_{\alpha,eq} - a^{-}_{\alpha,eq})\ \delta_{j,0} - j\, a^{s}_{(j-1),\alpha,eq} + {}^{j}A^{+}_{o,\alpha p_x}\, m\, n^{+}_{eq} + {}^{j}A^{-}_{o,\alpha p_x}\, m\, n^{-}_{eq}$$

$$+ \sum_{j'=0}^{j_m-1} {}^{j}A^{j'}_{o,\alpha p_x}\, m\, n^{s}_{(j'),eq} = 0\ , \tag{5.8}$$

and

$${}^{j}A^{+}_{o,\alpha\bar{p}_{//}}\, m\, n^{+}_{eq} + {}^{j}A^{-}_{o,\alpha\bar{p}_{//}}\, m\, n^{-}_{eq} + \sum_{j'=0}^{j_m-1} {}^{j}A^{j'}_{o,\alpha\bar{p}_{//}}\, m\, n^{s}_{(j'),eq} = 0\ . \tag{5.9}$$

In obtaining eqs.(5.7) - (5.9) we also assumed that the variables A_{α}, $\alpha \neq \bar{p}$ are even functions of the momenta. Should this not be the case, eq.(5.4 b)

will not be correct and thus eqs.(5.7) - (5.9) will not hold, but may easily be generalized to include these situations.

A different sort of invariance is that associated with displacing the mathematical dividing surface. The resulting system must be in equilibrium. Letting $\xi_1(\bar{r}, t) = x + \Delta x$, $\xi_2 = y$, and $\xi_3 = z$ in eq.(4.20) yields

$$\hat{\underline{a}}^s_{(j)} = \int dx(x+\Delta x)^j \left[\underline{a}_{eq}(x) - \theta(x+\Delta x)\, \underline{a}^+_{eq} - \theta(-x-\Delta x)\, \underline{a}^-_{eq}\right] - \underline{a}^s_{(j),eq}$$

$$= -\left[\delta_{j,0}(\underline{a}^+_{eq} - \underline{a}^-_{eq}) - j\, \underline{a}^s_{(j-1),eq}\right] \Delta x + O(\Delta x^2) \quad . \tag{5.10}$$

In addition,

$$\hat{\underline{a}}^{\pm}(\bar{r}, t) = 0 \text{ and } \bar{v}(\bar{r}, t) = 0 \quad , \tag{5.11}$$

for the displacement described above. Substituting eqs.(5.10) and (5.11) into the multipole hierarchy, eqs.(4.63) - (4.65), we find that an equilibrium system can result from a displacement of the mathematical dividing surface only if

$$\sum_{j'=0}^{j_m} {}^{j}\underline{A}^{j'}_{=(o)} \cdot \left[\delta_{j',o}(\underline{a}^+_{eq} - \underline{a}^-_{eq}) - j'\, \underline{a}^s_{(j'-1),eq}\right] = 0 \quad . \tag{5.12}$$

In addition to the conditions on the coefficients presented above, there will also be constraints imposed by time reversal invariance. This invariance is better handled within the context of a specific example, to be given in the next chapter.

Generalization to Large $\hat{\xi}_1$

The equations of motion and boundary conditions presented at the end of the last chapter were obtained for small ξ_1. For large ξ_1 it is not obvious that the linear generalized transport equation, eq.(2.50), is applicable, as there will be a non-negligible region near the interface where $\underline{\hat{a}}(\bar{r}, t) \sim \underline{a}^{+}_{eq} - \underline{a}^{-}_{eq}$. Even in this case, the quantities $\underline{\hat{a}}^{\pm}$ and $\underline{\hat{a}}^{s}_{(j)}$ should be small.

We shall now show that, providing that the surface curvature is not large, the equations of motion and boundary conditions presented at the end of the last chapter may be applied to this situation as well, with the modification that they are applied at the true surface position, not at $x = 0$. The coefficients appearing in the equations are unchanged.

In addition to the requirement that the curvature be small, we shall assume that gradients of $\hat{\bar{\xi}}$ are also small. That is, the surface normal is not displaced too much. As will be shown below this last restriction can be relaxed. In this case, using eqs.(4.18) and (D.3), we find that

$$\lambda = \xi_1 + 0(\bar{\nabla}\hat{\bar{\xi}}) \ . \tag{5.13}$$

Further, in view of the invariance with respect to uniform displacements we find

$$\underline{\tilde{\mathcal{F}}}(\bar{r}, t \mid \underline{a}_0(\bar{r}', \Delta\xi_1)) = 0 \tag{5.14}$$

where

$$\begin{aligned} \underline{a}_0(\bar{r}, \Delta\xi_1) \equiv\ & \theta(x + \Delta\xi_1)\ \underline{a}^{+}_{eq} + \theta(-x - \Delta\xi_1)\ \underline{a}^{-}_{eq} \\ & + \sum_j \frac{(-1)^j}{j!}\ \delta^{(j)}(x + \Delta\xi_1)\ \underline{a}^{s}_{(j),eq} \ . \end{aligned} \tag{5.15}$$

The quantities $\underline{a}_0(\bar{r}, \Delta\xi)$ are just the values of the densities in the displaced system, characterized by the displacement $\Delta\xi_1$. We now expand the integrand in the definition of $\underline{\mathcal{F}}^s_{(j)}$ into a functional Taylor series in the displacements of the bulk and multipole densities from equilibrium as well as in $\hat{\bar{\nabla}}\hat{\bar{\xi}}$. Using eqs.(4.20), (4.35), (5.14) and (5.15) we find that

$$\underline{\mathcal{F}}^s_{(j)} = \int d\xi_1 \xi_1^j \{ \left[\frac{\delta \underline{\mathcal{F}}(\bar{r},t|\underline{a})}{\delta \underline{a}(\bar{r}_1,t)}\right]_{\underline{a}=\underline{a}_0, \hat{\bar{\nabla}}\hat{\bar{\xi}}=0} * [\theta(x_1 + \Delta\xi_1(\bar{r}_{//},t))\hat{\underline{a}}^+(\bar{r}_1,t)$$

$$+ \theta(-x_1 - \Delta\xi_1(\bar{r}_{//},t))\hat{\underline{a}}^-(\bar{r}_1,t) + \sum_j \frac{(-1)^j}{j!} \delta^{(j)}(x + \Delta\xi_1(\bar{r}_{//},t))\hat{\underline{a}}^s_{(j)}(\bar{r}_{1,//},t)]$$

$$+ \left[\frac{\delta \underline{\mathcal{F}}(\bar{r},t \mid \underline{a})}{\delta \hat{\bar{\nabla}}\hat{\bar{\xi}}(\bar{r}_1,t)}\right]_{\underline{a}=\underline{a}_0, \hat{\bar{\nabla}}\hat{\bar{\xi}}=0} * \hat{\bar{\nabla}}\hat{\bar{\xi}}(\bar{r}_1,t) - \theta(x + \Delta\xi_1(\bar{r}_{//},t)) \left[\frac{\delta \underline{\mathcal{F}}^+(\bar{r}\,t \mid \underline{a}^+)}{\delta \underline{a}^+(\bar{r}_1,\, t)}\right]_{\hat{\underline{a}}^+=0}$$

$$* \hat{\underline{a}}^+(\bar{r}_1,t) - \theta(-x - \Delta\xi(\bar{r}_{//},t)) \left[\frac{\delta \underline{\mathcal{F}}^-(\bar{r}\,t \mid \underline{a}^-)}{\delta \underline{a}^-(\bar{r}_1,t)}\right]_{\hat{\underline{a}}^-=0} * \hat{\underline{a}}^-(\bar{r}_1,t)\} \,, \tag{5.16}$$

to linear order. The quantity $-\Delta\xi_1(\bar{r}_{//},t)$ is the displacement of the surface from equilibrium at the point $\bar{r}_{//}$ in the y, z plane. In addition, eq.(5.16) neglects all time nonlocality. Thus the functional derivatives appearing in eq.(5.16) are evaluated for an equilibrium system with a flat interface at the actual interface position and parallel to the x = 0 plane.

Since the quantities appearing in eq.(5.16) are quasi-local in space, it is easily seen that values of $\hat{\underline{a}}^{\pm}$, $\hat{\underline{a}}^s_{(j)}$ and $\hat{\bar{\nabla}}\hat{\bar{\xi}}$ only near the

actual interface contribute to $\underline{\mathcal{F}}^s_{(j)}$. We may Taylor expand these quantities about the point

$$\bar{r} = \bar{r}_s \equiv (-\Delta\xi_1(\bar{r}_{//}, t), \bar{r}_{//}) \quad , \tag{5.17}$$

as was described in the previous chapter (cf. eq.(4.44)). In view of the invariance to uniform displacements, the coefficients in the Taylor expansion will be independent of $\Delta\xi_1(\bar{r}_{//}, t)$ and will equal those presented at the end of the last chapter. Hence we have for large surface displacements:

$$\underline{\mathcal{F}}^s_{(j)} = \sum_{k=0}^{\infty} {}^{j}\underline{\underline{A}}^{+}_{k} (\cdot)^k (\bar{\nabla}^k \hat{\underline{a}}^{+})_s + {}^{j}\underline{\underline{A}}^{-}_{k} (\cdot)^k (\bar{\nabla}^k \hat{\underline{a}}^{-})_s$$

$$+ \sum_{j'=0}^{\infty} {}^{j}\underline{\underline{A}}^{j'}_{k} (\cdot)^k (\nabla^k_{//} \underline{\hat{a}}^s_{(j')})_s + {}^{j}\underline{B}_k (\cdot)^{k+1} (\bar{\nabla}^k \hat{\xi})_s \tag{5.18}$$

where it should be noted that ${}^{j}\underline{B}_0 = 0$ (cf. eq.(5.3)).

On linearizing the remaining terms in eqs.(4.41) and (4.42) and combining them with eq.(5.18), we find that equations similar to eqs.(4.64) and (4.65) are obtained. The only difference between the new equations and eqs.(4.64) and (4.65) lies in the fact that all derivatives in the former are to be taken at the true surface position.

In the above discussion, it was assumed that the surface normal does not deviate too much from its equilibrium direction (i.e., $\bar{\nabla}\hat{\xi}$ is small). Should this not be the case, the invariance to uniform rotations may be used, as uniform translations were used above, to relate the coefficients in the equations of motion and boundary conditions to those given by eqs.(4.67) - (4.69). The resulting equations of motion and boundary conditions are simply those which would be obtained from eqs.

(4.64) - (4.65) on rotating and translating the system such that the true surface is tangent to the plane $x = 0$ locally.

Conserved Variables

For many applications, one finds that the only slow variables in the system are the densities of conserved variables. In this case, cf. chapters II and III,

$$\dot{\underline{A}}(\bar{r},X^N) = -\bar{\nabla}\cdot\underline{J}(\bar{r},X^N) \quad , \tag{5.19}$$

and for $t >> \tau_m$:

$$\underline{\underline{M}}(\bar{r}|\bar{r}') = -\bar{\nabla}_r \cdot \underline{\underline{M}}(x|\bar{r}-\bar{r}') \tag{5.20}$$

where

$$\underline{\underline{M}}(x|\bar{r}-\bar{r}') \equiv [<\hat{\underline{J}}(\bar{r})\ \hat{\underline{A}}(\bar{r}_1)> - \int_0^\infty dt_1 <\underline{I}(\bar{r},t_1)\ \underline{I}(\bar{r}_1)> \bar{\nabla}_{\bar{r}_1}]*\underline{\underline{K}}^{-1}(\bar{r}_1|\bar{r}'). \tag{5.21}$$

The function $\underline{\underline{M}}(x|\bar{y})$ is a rapidly decaying function of $\bar{y}$ (with characteristic length λ_c) and depends on x only near $x = 0$ (i.e., for $|x| \lesssim \lambda_s$), where it rapidly changes from its + to - bulk values. Using eq.(5.20) in eqs.(4.66) - (4.68) gives

$$\underline{\underline{M}}_k^{\pm} = -\underline{\underline{M}}^{(k-1)\pm} \tag{5.22}$$

$$\underline{\underline{{}^jA_k^{\pm}}} = \mp\,\delta_{j,0}\,\underline{\underline{\dot{M}}}^{(k)\pm}\cdot\bar{e}_1 + \int \frac{dx}{k!}\underline{\underline{S}}^{\pm}(x|\bar{r}-\bar{r}')*[jx^{j-1}\,\bar{e}_1(\bar{r}'-\bar{r}_{//})^k - kx^j\,\underline{\underline{I}}_{//}(\bar{r}'-\bar{r}_{//})^{k-1}] \tag{5.23}$$

and

$$\underline{\underline{{}^jA_k^{j'}}} = \frac{(-1)^{j'}}{k!\,j'!}\int dx\ \underline{\underline{M}}(x|\bar{r}-\bar{r}')*\delta^{(j')}(x')\,[j\bar{e}_1x^{j-1}(\bar{r}'_{//}-\bar{r}_{//})^k - k\underline{\underline{I}}_{//}x^j(\bar{r}'_{//}-\bar{r}_{//})^{k-1}], \tag{5.24}$$

where $\underline{\underline{M}}^{(k)^{\pm}}$ is given by eq.(3.42) in the $\pm$ phase,

$$\underline{\underline{I}}_{//} \equiv \bar{e}_2\,\bar{e}_2 + \bar{e}_3\,\bar{e}_3, \tag{5.25}$$

and

$$\underline{\underline{S}}^{\pm}(x|\bar{r}-\bar{r}') \equiv \underline{\underline{M}}(x|\bar{r}-\bar{r}')\;\theta(\pm x') - \theta(\pm x)\;\underline{\underline{M}}^{\pm}(\bar{r}-\bar{r}')\ . \tag{5.26}$$

Note that the integrals in eqs.(5.23) and (5.24) vanish when $j = k = 0$.

The coefficients ${}^{j}\underline{B}_{k}$ require more discussion. From eq.(4.69) we see that

$${}^{j}\underline{B}_{k} = \int \frac{dx}{k!}\, x^{j}\underline{\underline{M}}(\bar{r}|\bar{r}')*\{\frac{\partial \underline{a}_{eq}}{\partial x'}(x')\;\bar{e}\;(\bar{r}'_{//}-\bar{r}_{//})^{k}$$

$$+ k\underline{a}^{s}_{eq}(x')\;\underline{\underline{I}}_{//}\;[(\bar{r}'-\bar{r}_{//})^{k-1} - (\bar{r}'_{//}-\bar{r}_{//})^{k-1}]\}\ , \tag{5.27}$$

which follows from the fact that $\underline{a}^{s}_{(j)_{eq}} = 0$ for $j \geq j_m$.

By using eq.(5.20) in eq.(5.27), the latter becomes

$${}^{j}\underline{B}_{k} = \int \frac{dx}{k!}\,\underline{\underline{M}}(x|\bar{r}-\bar{r}')*\{jx^{j-1}\bar{e}_1(\frac{\partial\,\underline{a}_{eq}(x')}{\partial\,x'}\;\bar{e}_1(\bar{r}'_{//}-\bar{r}_{//})^{k}$$

$$+ k\;\underline{a}^{s}_{eq}(x')\underline{\underline{I}}_{//}[(\bar{r}'-\bar{r}_{//})^{k-1} - (\bar{r}'_{//}-\bar{r}_{//})^{k-1}]) - kx^{j}(\frac{\partial\,\underline{a}_{eq}(x')}{\partial\,x'}\;[\bar{e}_2\bar{e}_1\bar{e}_2+\bar{e}_3\bar{e}_1\bar{e}_3]$$

$$\times\ (\bar{r}'_{//}-\bar{r}_{//})^{k-1} + (k-1)\;\underline{a}^{s}_{eq}(x')(\bar{e}_2\underline{\underline{I}}_{//}\;\bar{e}_2 + \bar{e}_3\underline{\underline{I}}_{//}\;\bar{e}_3)\,[(\bar{r}'-\bar{r}_{//})^{k-2} - (\bar{r}'_{//}-\bar{r}_{//})^{k-2}])\}. \tag{5.28}$$

From this last expresion we see that ${}^{j}\underline{B}_{k} = 0$ when $j = k = 0$, an explicit example of eq.(5.3). In addition, eq.(5.27) shows that ${}^{j}\underline{\underline{B}}_{1}$ gives couplings only to $\bar{\nabla}_{//}\hat{\xi}_1$ in the multipole hierarchy. Using this fact and

eq.(5.3) gives

$$\underline{\underline{j}}_{\underline{B}_1} = 0 \cdot \tag{5.29}$$

This will have important consequences for applications of the multipole technique (cf. chapter VI).

Relationships Between j_m, k_m and Equilibrium Considerations

The truncation parameters j_m and k_m for the multipole equation were introduced in a somewhat heuristic manner in chapter IV. We would like to examine more closely the relationship between the truncation parameters and properties of the equilibrium system.

In order to accomplish this we formally expand $\underline{\underline{M}}(x|\bar{r}-\bar{r}')$ into a series which makes the quasi-locality explicit. That is, write

$$\underline{\underline{M}}(x|\bar{r}-\bar{r}') = \sum_{\ell=0}^{\infty} \underline{\underline{M}}^{(\ell)}(x)\ (\cdot)^{\ell}\ \bar{\nabla}_r^{\ell}\ \delta(\bar{r}-\bar{r}')\ , \tag{5.30}$$

where the coefficients $\underline{\underline{M}}^{(\ell)}(x)$ are defined as for systems in weak external fields (cf. eq.(3.42)). This expansion is analogous to the expansion in powers of the wavevector performed in homogeneous systems[25]. In fact in regions of space where there are no large equilibrium gradients, the $\underline{\underline{M}}^{(\ell)}(x)$ become the quantities discussed in chapter III. As we saw there, the various $\underline{\underline{M}}^{(\ell)}(x)$ were responsible for reversible (flow), irreversible (dissipative) and nonlocality effects. This will also be the case in the bulk regions.

In the interfacial region, the $\underline{\underline{M}}^{(\ell)}(x)$ change rapidly in space. Further, eq.(5.30) cannot be used directly in the equations of motion for the densities $\underline{a}(\bar{r}, t)$ (cf. eq.(3.11)), since in the interfacial region

they also change rapidly in space, thereby having large gradients. On the other hand, the coefficients ${}^{j}\underline{\underline{A}}_{k}^{\pm}$ and ${}^{j}\underline{\underline{A}}_{k}^{j'}$ do not contain the densities, $\underline{a}(\bar{r}, t)$, explicitly and thus it may be possible to use eq.(5.30) in calculating them. Using eqs.(5.23), (5.24) and (5.30) gives

$$ {}^{j}\underline{\underline{A}}_{k}^{\pm} = \mp\, \bar{e}_1 \cdot \underline{\underline{M}}^{(k)^{\pm}} \; \delta_{j,0} + \sum_{\ell=0}^{\infty} \Big[\int_{-\infty}^{\infty} dx\; \theta(\pm x)\; (\underline{\underline{M}}^{(\ell)}(x) - \underline{\underline{M}}^{(\ell)^{\pm}})\; x^{j+k-\ell+1} $$

$$ (\cdot)^{\ell+1} \Big(\frac{{}^{j}\underline{\underline{I}}\,\bar{e}_1^{\ell}\,\bar{e}_1^{k-\ell+1}}{(k-\ell)!} - \frac{\underline{\underline{I}}^{\ell}\,\bar{e}_1^{k-1-\ell}}{(k-1-\ell)!} \Big) \mp \frac{1}{(\ell-j-k)!} \Big(\frac{\partial^{\ell-j-k}\underline{\underline{M}}^{(\ell)}(x)}{\partial x^{\ell-j-k}} \Big)_{x=0} (\cdot)^{\ell+1}\, T_{j,k,\ell} \Big] \tag{5.31} $$

and

$$ {}^{j}\underline{\underline{A}}_{k}^{j'} = \sum_{\ell=0}^{\infty} \gamma(j,j',k,\ell) \Big(\frac{\partial^{j'+\ell-k+1-j}\underline{\underline{M}}^{(\ell)}(x)}{\partial x^{j'+\ell-k+1-j}} \Big)_{x=0} (\cdot)^{\ell+1}\, \bar{e}_1^{\ell-k+1}\, \underline{\underline{I}}_{/\!/}^{k}\,, \tag{5.32} $$

where

$$ \gamma(j,j',k,\ell) \equiv (-1)^{\ell-k}\, \frac{j!}{j!} \Big[\binom{\ell}{\ell-k} \binom{j'+\ell-k}{j-1} + \binom{\ell}{\ell-k+1} \binom{j'+\ell+1-k}{j} \Big]\,, \tag{5.33} $$

and where

$$ T_{j,k,\ell} \equiv \begin{cases} 0 & \ell = 0, \\ \sum_{n=1}^{\ell} (-1)^{n} (n-1)! \Big[\dfrac{{}^{j}\bar{e}_1^{\ell}\, \underline{\underline{I}}^{\ell-n}\, \bar{e}_1^{k-\ell+n+1}}{(k-\ell+n)!} - \dfrac{\underline{\underline{I}}^{\ell-n}\, \bar{e}_1^{n}\, \underline{\underline{I}}_{/\!/}\, \bar{e}_1^{k-1+n-\ell}}{(k-1+n-\ell)!} \Big], & \ell \neq 0. \end{cases} \tag{5.34} $$

In eqs.(5.31) and (5.32) we contract only with the first index of any rank two tensor and $\underline{\underline{I}}$ is the unit tensor. From eq.(5.38) we find

$$ \gamma(j,\, j',\, k,\, \ell) = 0, \text{ when } \ell < k-1 \text{ or } j'+\ell-k-j+1 < 0\,. \tag{5.35} $$

It is rather unlikely that we may use eq.(5.30) directly in calculating

the $\underline{\underline{B}}_k^j$, since more and more gradients of the equilibrium densities would result.

Writing the coefficients in this manner shows some interesting features. From eq.(5.32) we see that the $\underline{\underline{A}}_k^{jj'}$ is made up solely of derivatives of the $\underline{\underline{\bar{M}}}^{(\ell)}(x)$ at $x = 0$. The coefficients $\underline{\underline{A}}_k^{j\pm}$ contain three types of terms: bulk coefficients, moments of $(\underline{\underline{\bar{M}}}^{(\ell)}(x) - \underline{\underline{\bar{M}}}^{(\ell)\pm})\,\theta(\pm x)$ and derivatives of $\underline{\underline{\bar{M}}}^{(\ell)}(x)$ at $x = 0$.

We assume that even in the interfacial region the $\underline{\underline{\bar{M}}}^{(\ell)}(x)$, for $\ell \geq k_m'$, give only nonlocality corrections to the coefficients. It should also be the case that the number of $\underline{\underline{\bar{M}}}^{(\ell)}$'s which are needed in the interface is greater than or equal to the number required in the bulk. More specifically, we assume that

$$\underline{\underline{\bar{M}}}^{(\ell)}(x) = 0, \text{ for } \ell \geq k_m' . \tag{5.36}$$

In addition to eq.(5.36) we shall assume that any equilibrium surface multipole of order $j \geq j_m'$ vanishes. This is a statement about the equilibrium surface structure and is equivalent to the assumption that only a limited amount of equilibrium structure is important in the calculation of long wavelength nonequilibrium phenomena. There are many examples of systems where this is indeed the case (e.g., boundaries in electromagnetic problems).

It is our aim to find the connections between j_m' and k_m' and the truncation parameters j_m and k_m introduced in the previous chapter. We would also like to remark that there are examples for which eq.(5.36) is exactly satisfied, as is shown in the next chapter. Further, Peralta-Fabi[34] has shown that reasonable boundary conditions can be obtained from

finite order local equations with coefficients which vary rapidly in the boundary region.

Using the above two assumptions, we find using eqs.(5.31) - (5.35) that

$$\underline{\underline{M}}^{\pm}_{k} = 0 \qquad \text{when } k > k_m' , \tag{5.37}$$

$$^{j}\underline{\underline{A}}^{\pm}_{k} = 0 \qquad \text{when } j + k \geq j_m' + k_m' , \tag{5.38}$$

and

$$^{j}\underline{\underline{A}}^{j'}_{k} = 0 \qquad \text{when } k > k_m' \text{ or } j' < j + k - k_m' . \tag{5.39}$$

If in addition, we naively used eqs.(5.36), (5.30), (5.28) and (5.3) we would find that

$$^{j}\underline{B}_{k} = 0 \qquad \text{when } j + k > j_m' + k_m' \text{ or } j = j_m' + k_m' . \tag{5.40}$$

In view of the discussion concerning the expansion given in eq.(5.30), it is somewhat questionable whether eq.(5.40) is correct. We shall assume that it is.

If we now use eqs.(5.37) - (5.40) in the linearized multipole hierarchy, eqs.(4.63) - (4.65), before it is truncated (i.e., let $j_m = \infty$, $k_m = \infty$), we find that

$$\left(\frac{\partial\, \hat{\underline{a}}^{s}(j)}{\partial t}\right)_{\bar{r},s} = \sum_{k=0}^{k_m'} \sum_{j'=j+k-k_m'}^{\infty} {}^{j}\underline{\underline{A}}^{j'}_{k} (\cdot)^{k} \left(\bar{\nabla}^{k}_{/\!/}\, \hat{\underline{a}}^{s}(j')\right)_{s} , \quad j \geq j_m' + k_m' . \tag{5.41}$$

This shows that the evolution in time of the multipoles, $\hat{\underline{a}}^{s}_{(j)}$, of order $j \geq j_m' + k_m'$, depends only on the multipoles for which $j' \geq j_m'$. Hence if we impose the condition

$$\underline{\hat{a}}^{s}_{(j)}\ (\overline{r}_{/\!/},\ t) = 0, \qquad j_m' \le j < j_m' + k_m' \tag{5.42}$$

and the initial condition

$$\underline{\hat{a}}^{s}_{(j)}\ (\overline{r}_{/\!/},\ 0) = 0, \qquad j \ge j_m' + k_m' \ , \tag{5.43}$$

then eq.(5.41) shows that the $\underline{\hat{a}}^{s}_{(j)}$, $j \ge j_m' + k_m'$ remain zero, thereby yielding a solution to a truncated hierarchy. When eqs.(5.42) and (5.43) hold, the equations of motion and boundary conditions in the untruncated hierarchy (i.e., $j_m = k_m = \infty$ in eqs.(4.63) - (4.64) become using eqs. (5.37)-(5.40)) :

$$\left(\frac{\partial\, \underline{\hat{a}}^{\pm}(\overline{r},t)}{\partial\, t}\right)_{\overline{r}} = \sum_{k=0}^{k_m'} \underline{\underline{M}}^{\pm}_{k}(\cdot)^{k}\ \ \overline{\nabla}^{k}_{\overline{r}}\ \underline{\hat{a}}^{\pm}(\overline{r},t) \tag{5.44}$$

$$\begin{aligned}\left(\frac{\partial\, \underline{\hat{a}}^{s}_{(j)}}{\partial\, t}\right)_{\overline{r},s} &= (\underline{a}^{+}_{eq} - \underline{a}^{-}_{eq})\ v_{n,s}\ \delta_{j,0} - j\ \underline{a}^{s}_{(j-1),eq}\ v_{n,s} + \overline{\nabla}_{/\!/} \cdot \sum_{j'=j+1}^{j_m'-1} \frac{\underline{a}^{s}_{(j'),eq}}{(j'-j)!}\left(\frac{\partial^{j'-j}\overline{v}}{\partial\, x^{j'-j}}\right)_{s} \\ &+ \sum_{k=0}^{j_m'+k_m'-j-1} \left({}^{j}\underline{\underline{A}}^{+}_{k}\ (\cdot)^{k}(\overline{\nabla}^{k}\ \underline{\hat{a}}^{+})_{s} + {}^{j}\underline{\underline{A}}^{-}_{k}\ (\cdot)^{k}\ (\overline{\nabla}^{k}\ \underline{\hat{a}}^{-})_{s}\right) \\ &+ \sum_{k=0}^{k_m'} \sum_{j'=\max(0,j+k-k_m')}^{j_m'-1} {}^{j}\underline{\underline{A}}^{j'}_{k}\ (\cdot)^{k}\ (\overline{\nabla}^{k}_{/\!/}\ \underline{\hat{a}}^{s}_{(j')})_{s} + \sum_{k=2}^{j_m'+k_m'-j} {}^{j}\underline{\underline{B}}_{k}(\cdot)^{k+1}(\overline{\nabla}^{k}\hat{\xi})_{s,j<j_m'}\ ,\end{aligned} \tag{5.45}$$

and

$$0 = (\underline{a}^{+}_{eq} - \underline{a}^{-}_{eq})\, v_{n,s}\, \delta_{j,0} - j_m'\, \underline{a}^{s}_{(j_m'-1),eq}\, \delta_{j,j_m'}$$

$$+ \sum_{k=0}^{j_m'+k_m'-j-1} {}^{j}\underline{A}^{+}_{k}(\cdot)^{k}\, (\overline{\nabla}^{k}\, \hat{\underline{a}}^{+})_s + {}^{j}\underline{A}^{-}_{k}\, (\cdot)^{k}\, (\overline{\nabla}^{k}\, \hat{\underline{a}}^{-})_s$$

$$+ \sum_{k=0}^{k_m'} \sum_{j'=\max(0,\, j+k-k_m')}^{j_m'-1} {}^{j\,j'}\underline{A}_{k}\, (\cdot)^{k}\, (\overline{\nabla}_{//}^{k}\, \hat{\underline{a}}^{s}_{(j')})_s + \sum_{k=2}^{j_m'+k_m'-j} {}^{j}\underline{B}_{k}(\cdot)^{k+1}(\overline{\nabla}^{k}\hat{\xi})_s$$

$$j_m' \le j < j_m'+k_m' \quad . \tag{5.46}$$

In the above equations, only sums where the lower index does not exceed the upper one are to be included.

In summary then, providing eqs.(5.37) - (5.40) are valid, we have shown that the solution to eqs.(5.44) - (5.46) combined with eqs.(5.42) and (5.43) (at $t = 0$) is a solution to the infinite hierarchy. This will be of the same form as eqs.(4.63) - (4.65) if we choose

$$j_m = j_m' \tag{5.47}$$

and

$$k_m = j_m' + k_m' \quad , \tag{5.48}$$

and note that many of the coefficients are zero (cf. eqs.(5.37) - (5.40)).

It is not known whether or not the solution to the truncated hierarchy is a stable solution. By a stable solution, we mean that even if eq.(5.43) does not hold for all the higher order multipoles, the solution to the infinite hierarchy would soon approach a solution to the truncated hierarchy. Thus the higher order variables could then be regarded as "fast" variables, by decaying on a short time scale.

In addition, it is not clear how the initial condition, eq.(5.48), comes about. Presumably the mechanism which causes the equilibrium multipoles to be unimportant above a certain order will also operate in the initial local equilibrium system (cf. eq.(2.72)), thereby giving eq.(5.43). Just what this mechanism is, is not known. In the following chapter the multipole formalism is applied to simple fluid hydrodynamics.

Chapter VI. Applications: Simple Fluids

The considerations of the previous chapters have been rather formal in nature. In this chapter we shall apply the multipole technique to the problem of linearized hydrodynamics of single component, two phase simple fluids. As mentioned at the beginning of the last chapter, we restrict ourselves to considerations of systems of infinite size and in the limit of vanishing external fields (cf. eq.(5.1)). The coordinate system is chosen such that the plane $x=0$ coincides with the equilibrium dividing surface. Nonlinear effects are not considered and we further limit ourselves to the situation where the deviation of the surface normal from its equilibrium direction is small. For these systems, the invariance considerations of the last chapter are valid. Our starting equations are eqs. (5.44) - (5.46) in which we use the forms of the coefficients given by eqs.(5.22) - (5.28).

In the study of these systems we shall assume that the set of variables $\underline{A}(\overline{r}, t)$ may be chosen as in chapter III. That is, $\underline{A}(\overline{r}, t) \equiv \{N(\overline{r}, t), E(\overline{r}, t), \overline{\pi}(\overline{r}, t)\}$, the densities of the conserved variables. As discussed in chapter III, this choice neglects the multilinear variables. This neglect has been justified for real homogeneous systems up to Navier-Stokes order[62,63] (i.e., for equations of motion containing at most two gradients). Whether it is justified for the surface equations and boundary conditions is not known. In fact a recent mode-mode coupling calculation by Wolynes[73] has shown that, under a certain set of assumptions, the slipping length parameter appearing in the boundary condition for flow next to a surface diverges in a rather strange fashion. This is

contrary to results of most kinetic theories[35]. Further, Wolynes indicates that the divergence should be relatively unimportant except for very small wavevector phenomena. We do not consider this point further and do not include multilinear variables.

The equations to be given below contain couplings between variables of different tensorial rank. The coefficients responsible for this coupling will also be tensorial quantities, and must therefore be consistent with the rotational symmetries inherent in the equilibrium system. The examples we are about to consider all have cylindrical symmetry about the $\bar{e}_1$ direction and involve only polar tensors[69]. In this case the tensorial coupling coefficients must be made up of the following tensors[74]:

$$\bar{e}_1 \qquad \text{for rank 1,} \tag{6.1}$$

$$\bar{e}_1\bar{e}_1 \text{ and } \bar{I}_{//} \qquad \text{for rank 2,} \tag{6.2}$$

$$\bar{e}_1\bar{e}_1\bar{e}_1,\ \bar{e}_1\overline{\overline{I}}_{//},\ \overline{\overline{I}}_{//}\bar{e}_1 \text{ and } \overline{\overline{\overline{T}}}_1 \qquad \text{for rank 3} \tag{6.3}$$

and

$$\bar{e}_1\bar{e}_1\bar{e}_1\bar{e}_1,\ \bar{e}_1\bar{e}_1\overline{\overline{I}}_{//},\ \overline{\overline{I}}_{//}\bar{e}_1\bar{e}_1,\ \bar{e}_1\overline{\overline{I}}_{//}\bar{e}_1,\ \bar{e}_1\overline{\overline{\overline{T}}}_1,\ \overline{\overline{\overline{T}}}_1\bar{e}_1,$$

$$(\bar{e}_2\bar{e}_1\bar{e}_1\bar{e}_2 + \bar{e}_3\bar{e}_1\bar{e}_1\bar{e}_3),\ \overline{\overline{I}}_{//}\overline{\overline{I}}_{//},\ (\bar{e}_2\bar{e}_2\bar{e}_2\bar{e}_2 + \bar{e}_3\bar{e}_3\bar{e}_3\bar{e}_3 + \bar{e}_2\bar{e}_3\bar{e}_2\bar{e}_3 + \bar{e}_3\bar{e}_2\bar{e}_3\bar{e}_2)$$

$$\text{and } (\bar{e}_2\bar{e}_2\bar{e}_2\bar{e}_2 + \bar{e}_3\bar{e}_3\bar{e}_3\bar{e}_3 + \bar{e}_3\bar{e}_2\bar{e}_2\bar{e}_3 + \bar{e}_2\bar{e}_3\bar{e}_3\bar{e}_2) \text{ for rank 4, etc.,} \tag{6.4}$$

where

$$\overline{\overline{\overline{T}}}_1 \equiv \bar{e}_2\bar{e}_1\bar{e}_2 + \bar{e}_3\bar{e}_1\bar{e}_3 \ . \tag{6.5}$$

A polar tensor independent of y and z, with rank ≤ 4, and defined in

terms of equilibrium quantities can always be written as a linear combination of the tensors given in eqs.(6.1) - (6.4). This is known as the Curie principle[2] and greatly reduces the number of independent coefficients which appear in the equations of motion and boundary conditions. In the bulk region, we have full rotational invariance, and this further limits the number of coefficients.

Euler Equations

As a first example we consider a two phase simple fluid for which all dissipation may be neglected. Thus we may omit (cf. eq.(2.77)) the parts of $\underline{\underline{M}}(x|\bar{r}-\bar{r}')$ (defined by eq.(5.21)) which contain the dissipative currents. This gives

$$\underline{\underline{M}}(x|\bar{r}-\bar{r}') = \langle \hat{\underline{J}}(\bar{r})\ \hat{\underline{A}}(\bar{r}_1)\rangle * \underline{\underline{K}}^{-1}(\bar{r}|\bar{r}') = \left[\frac{\delta \langle \underline{J}(\bar{r})\rangle_L}{\delta\, \underline{a}(\bar{r}')}\right]_{\underline{\underline{\Phi}}=0} \tag{6.6}$$

For the set of variables described above we find:

$$\underline{\underline{M}}(x|\bar{r}-\bar{r}') = \begin{bmatrix} 0 & 0 & m^{-1}\underline{\underline{I}}\,\delta(\bar{r}-\bar{r}') \\ 0 & 0 & \underline{\underline{h}}(x)/mn_{eq}(x)\delta(\bar{r}-\bar{r}') \\ \left(\frac{\delta\langle\underline{\underline{\tau}}(\bar{r})\rangle_L}{\delta\, n(\bar{r}')}\right)_{\underline{\underline{\Phi}}=0} & \left(\frac{\delta\langle\underline{\underline{\tau}}(\bar{r})\rangle_L}{\delta\, e(\bar{r}')}\right)_{\underline{\underline{\Phi}}=0} & 0 \end{bmatrix} \tag{6.7}$$

where $\langle\underline{\underline{\tau}}(x)\rangle = \bar{e}_1\bar{e}_1 p_{h,eq} + \underline{\underline{I}}_{//}\langle\tau_{//}(x)\rangle$, (6.8)

and

$$\underline{\underline{h}}(x) \equiv \underline{\underline{I}}\, e(x)_{eq} + \langle\underline{\underline{\tau}}(x)\rangle \equiv h_{\perp}(x)\ \bar{e}_1\bar{e}_1 + \underline{\underline{I}}_{//}\, h_{//}(x)\ . \tag{6.8a}$$

The symbols $\perp$ and $//$ shall be used to denote the $\bar{e}_1\bar{e}_1$ and $\overline{\overline{I}}_{//}$ components of any second rank tensor, which for the systems under consideration have only two independent components. In obtaining eq.(6.7) use was made of the fact that

$$\underline{\underline{K}}^{-1}_{p\gamma}(\bar{r}|\bar{r}') = \underline{\underline{K}}^{-1}_{\gamma p}(\bar{r}|\bar{r}') = \delta\gamma\bar{p}\,\overline{\overline{I}}[m K_B T n_{eq}(x)]^{-1} \tag{6.9}$$

which may easily be shown using eq.(2.44) and time reversal invariance. The quantity $<\tau_{//}(x)>$ equals p_h in the bulk regions but differs from it in the interface.

The couplings in the number and energy equations, as shown by eq.(6.7), are exactly of the form given by eq.(5.30) with $k_m' = 1$. In chapter III it was shown that in the bulk, terms arising from eq.(6.6) containing more than one gradient were nonlocality corrections. We shall take $k_m' = 1$ for this problem.

Using eqs.(6.7) and (3.42) we find

$$\underline{\underline{M}}^{(o)}(x) = \begin{bmatrix} 0 & 0 & m^{-1}\overline{\overline{I}} \\ 0 & 0 & \overline{\overline{h}}(x)/(m n_{eq}(x)) \\ \overline{\overline{\chi}}_n(x) & \overline{\overline{\chi}}_e(x) & 0 \end{bmatrix} \tag{6.10}$$

where

$$\overline{\overline{\chi}}_\gamma(x) \equiv \int d\bar{r}' \left(\frac{\delta <\overline{\overline{\tau}}(\bar{r})>_L}{\delta a_\gamma(\bar{r}')}\right)_{\underline{\Phi}=0} = \chi_{\perp,\gamma}(x)\bar{e}_1\bar{e}_1 + \chi_{//,\gamma}(x)\,\overline{\overline{I}}_{//}, \gamma = n, e. \tag{6.11}$$

In the bulk phases, using the full rotational and translational invariances, we find

$$\overline{\overline{M}}^{(o)\pm} = \begin{bmatrix} 0 & 0 & m^{-1}\overline{\overline{I}} \\ 0 & 0 & h^{\pm}/m n^{\pm}_{eq}\overline{\overline{I}} \\ \left(\frac{\partial p_h}{\partial n}\right)_e \overline{\overline{I}} & \left(\frac{\partial p_h}{\partial e}\right)_n \overline{\overline{I}} & 0 \end{bmatrix} \tag{6.12}$$

where $h^{\pm} \equiv e^{\pm}_{eq} + p_{h,eq}$ is the equilibrium enthalpy density.

For our discussion of the Euler equations, we shall take $j_m' = 1$. That is, we include the dynamics of the surface excess densities. This should yield some corrections to the usual boundary conditions used in the phenomenological theories and should give an indication of when surface structure is important. Recently, some attempts at generalizing the hydrodynamic equations to include the dynamics of surface excesses have been made[45-48]. We would like to examine this from the point of view of response theory and the multipole technique.

Eqs.(6.6) - (6.12) may now be used in calculating the coefficients appearing in eqs.(5.44) - (5.46), thereby obtaining the equations of motion and boundary conditions for an ideal two phase, single component fluid.

Number Equations

Since the exact number equation is completely local, we may use eqs.(5.31) and (5.32) without making any error. In addition, note that

$$\overline{M}^{(o)}_{n,\gamma}(x) - \overline{M}^{(o)\pm}_{n,\gamma} = 0 \tag{6.13}$$

and

$$j_{B_{k,n}} = 0 \ , \tag{6.14}$$

which are consequences of the fact that the equilibrium momentum vanishes and of eqs.(6.10) and (6.12). When eq.(6.13) is used in eqs. (5.31) and (5.32), the results then being used in eqs.(5.44) - (5.46), we obtain

$$\dot{n}^{\pm}(\bar{r}, t) = -\bar{\nabla} \cdot \bar{p}^{\pm}(\bar{r}, t) \ / \ m \ , \tag{6.15}$$

$$\dot{n}^{s}_{(o)} = (n^{+} - n^{-})_{eq} \ v_n(\bar{r}, t)_s - m^{-1}(\bar{p}^{+}(\bar{r}, t) - \bar{p}^{-}(\bar{r}, t))_s \cdot \bar{e}_i$$

$$- \bar{\nabla}_{//} \cdot \bar{p}^{s}_{(o)}(\bar{r}_s, t)/m \tag{6.16}$$

and

$$0 = m n^{s}_{(o),eq} \ v_{n,s}(\bar{r}, t)_s - \bar{e}_1 \cdot \bar{p}^{s}_{(o)}(\bar{r}_s, t) \ . \tag{6.17}$$

No other equations appear for the number densities for j_m' and $k_m' = 1$.

Eq.(6.15) is just the usual continuity equation for simple fluids. The next equation gives the evolution of the excess number density in time. It contains terms due to the motion of the interface, the number flux onto the surface from either side and transport along the interface. As will be shown below, eq.(6.17) may be used to specify the normal surface velocity. As mentioned earlier, these equations do not contain couplings to $\hat{\bar{\xi}}$ since $\bar{p}(\bar{r}, t)$ vanishes at equilibrium.

Energy Equations

We may proceed in the same manner as above for the energy equation. The multipole hierarchy becomes, on using eqs.(6.10) and (6.12),

$$\dot{e}^{\pm}(\bar{r}, t) = -\bar{\nabla} \cdot \bar{j}_e^{\pm}(\bar{r}, t) \quad , \tag{6.18}$$

where

$$\bar{j}_e^{\pm}(\bar{r}, t) \equiv \frac{h^{\pm}}{m n_{eq}^{\pm}} \bar{p}^{\pm}(\bar{r}, t) \quad . \tag{6.19}$$

Eq.(6.18) is the usual energy equation of motion for ideal homogeneous systems. For the excess energy density, we find from eq.(5.45) that

$$\dot{e}^{s}_{(o)} = (e^{+} - e^{-})_{eq} \, v_{n,s} - \bar{e}_1 \cdot (\bar{j}_e^{+} - \bar{j}_e^{-})_s - \bar{\nabla}_{//} \cdot \bar{j}_e^{s} \tag{6.20}$$

where

$$\bar{j}_e^{s}(\bar{r}_{//}, t) \equiv \left. \frac{\overline{\overline{h}}(x)}{m n_{eq}(x)} \right|_{x=0} \cdot \bar{p}^{s}_{(o)}(\bar{r}_{//}, t) + \overline{\overline{\alpha}}^{+} \cdot \bar{p}^{+}(\bar{r}, t)_s + \overline{\overline{\alpha}}^{-} \cdot \bar{p}(\bar{r}, t)_s \, , \tag{6.21}$$

and

$$\overline{\overline{\alpha}}^{\pm} \equiv \int_{-\infty}^{\infty} dx \; \theta(\pm x) \left\{ \frac{\overline{\overline{h}}(x)}{m n_{eq}(x)} - \frac{h^{\pm}}{m n^{\pm}} \overline{\overline{I}} \right\} = \alpha_{\perp} \bar{e}_1 \bar{e}_1 + \overline{\overline{I}}_{//} \alpha_{//} \quad . \tag{6.22}$$

The only other equation which comes from the hierarchy for the energy density is

$$0 = e^{s}_{(o),eq} \, v_{n,s} - \bar{e}_1 \cdot \bar{j}_e^{s} \, , \tag{6.23}$$

which follows from eq.(5.46).

The quantities $\overline{\overline{\alpha}}^{\pm}$, defined by eq.(6.22), are generalized excess enthalpies per unit mass and $\bar{j}_e^{s}$ is the excess surface energy current. The couplings caused by $\overline{\overline{\alpha}}^{\pm}$ in eqs. (6.21) do not appear in the phenomenological theories which include an excess energy density.

We note that all the tensors appearing in the definition for the excess energy current may be resolved into only two components by using eq.(6.2). Further, by using Galilean invariance (cf. eqs.(5.8) and (5.9)) and the fact that

$$p^{+}_{h,eq} = p^{-}_{h,eq} \ , \tag{6.24}$$

we find that

$$\alpha^{+}_{\perp} m n^{+}_{eq} + \alpha^{-}_{\perp} m n^{-}_{eq} + \left[\frac{h_{\perp}(o)}{n(o)_{eq}}\right] n^{s}_{(o),eq} - e^{s}_{(o),eq} = 0 \ . \tag{6.25}$$

We can also obtain this relationship from the definitions of the coefficients. Eq.(6.24) is a consequence of thermodynamic stability or of the fact that

$$\frac{\partial < \tau^{xx}(x) >}{\partial x} = 0 \ , \tag{6.26}$$

which is the hydrodynamic stability requirement. From eq.(5.31) we see that the higher order equations in the multipole hierarchy involve the quantities

$$\int dx\ \theta(\pm x)\ \left[\frac{\overline{\overline{h}}(x)}{m n_{eq}(x)} - \frac{h^{\pm}\overline{\overline{I}}}{m n^{\pm}_{eq}}\right] x^{j} \qquad j > 0 \ . \tag{6.27}$$

These higher order multipoles are neglected in a $j_m' = 1$ theory as was discussed in the last chapter.

Eq.(6.20) is the conservation equation for the energy going into and out of a small area of the interface. Aside from the terms involving the surface motion and bulk energy fluxes at the surface, eq.(6.20) also contains explicit couplings to the bulk momenta at the surface (via the $\overline{\overline{\alpha}}^{\pm}$) as well as a contribution from the surface excess momentum. In the

phenomenological theories to date only the second of the two effects is included, this being a consequence of the local equilibrium assumption made in these works.

Introducing the + or - velocities, $\bar{v}^{\pm}(\bar{r}, t)$, by

$$\bar{v}^{\pm}(\bar{r}, t) \equiv \bar{p}^{\pm}(\bar{r}, t)/m n^{\pm}_{eq} , \tag{6.28}$$

and using eqs.(6.25) and (6.17) allows us to write the energy boundary condition, eq.(6.23), as

$$0 = n^{+}_{eq}\, \underline{\alpha}^{+}_{1}\, (v^{+}_{x,s} - v_{x,s}) + n^{-}_{eq}\, \underline{\alpha}^{-}_{1} (v^{-}_{x,s} - v_{x,s}) . \tag{6.29}$$

Momentum Equations

The momentum equations are somewhat different from the previous ones in that couplings to $\hat{\bar{\xi}}$ now appear. In addition, the expansion given in eq.(5.30) does not terminate exactly, as it did in the case of the number and energy densities.

From eqs.(5.45) and (5.46) we see that only ${}^{o}B_{2,\vec{p}}$ is needed from all of the ${}^{j}B_{k,\bar{p}}$ coefficients, when $j_m' = k_m' = 1$. For this case eq.(5.28) gives

$${}^{o}B_{2,\bar{p}} = - \int dx\, d\bar{r}' \left(\frac{\delta < \bar{\bar{\tau}}(\bar{r}) >_L}{\delta\, a_\gamma(\bar{r}')}\right)_{\underline{\Phi}=0} \cdot \frac{\partial\, a_{\gamma,eq}(x')}{\partial\, x'} \cdot \bar{\bar{T}}_1(\bar{r}'_{//} - \bar{r}_{//}) , \tag{6.30}$$

where we sum repeated indices and where we have also used eqs.(6.5) and (6.7). By resolving the integral into its tensorial components (cf. eq.(6.3)) and noting that $\bar{\bar{\tau}}$ is symmetric, we find

$${}^{o}B_{2,\bar{p}} = - \int dx\, d\bar{r}' \left(\frac{\delta < \tau^{xy}(\bar{r}) >_L}{\delta\, a_\gamma(\bar{r}')}\right)_{\underline{\Phi}=0} \frac{\partial\, a_{\gamma,eq}(x')}{\partial\, x'} \, (y' - y)\, \bar{e}_1 \bar{e}_1 \bar{\bar{I}}_{//} . \tag{6.31}$$

An alternate expression for ${}^{0}B_{2,\bar{p}}$ can be obtained from the fact that ${}^{j}\underline{B}_{1}$ vanishes (cf. eq.(5.29)). Using eq.(5.28) yields

$$ {}^{1}B_{1,\bar{p}} = \int dx\, d\bar{r}' \left(\frac{\delta < \bar{\bar{\tau}}(\bar{r}) >_{L}}{\delta a_{\gamma}(\bar{r}')}\right)_{\underline{\Phi}=0} \frac{\partial a_{\gamma,eq}(x')}{\partial x'} \cdot [\, \bar{e}_1\bar{e}_1(\bar{r}'_{//} - \bar{r}_{//}) - x\bar{\bar{T}}_1 \,] = 0 \,, \tag{6.32} $$

which, on using the rotational symmetries, is equivalent to

$$ \int dx\, d\bar{r}' \left(\frac{\delta < \tau^{xy}(\bar{r}) >_{L}}{\delta a_{\gamma}(\bar{r}')}\right)_{\underline{\Phi}=0} \frac{\partial a_{\gamma,eq}(x')}{\partial x'} (y' - y) = \int dx\, d\bar{r}' \; x \left(\frac{\delta < \tau^{yy}(\bar{r}) >_{L}}{\delta a_{\gamma}(\bar{r}')}\right)_{\underline{\Phi}=0} \cdot \frac{\partial a_{\gamma,eq}(x')}{\partial x'} \,. \tag{6.33} $$

By using the functional derivative chain rule, it is easily shown that

$$ \int d\bar{r}' \left(\frac{\delta < \bar{\bar{\tau}}(\bar{r}) >_{L}}{\delta a_{\gamma}(\bar{r}')}\right)_{\underline{\Phi}=0} \frac{\partial a_{\gamma,eq}(x')}{\partial x'} = \frac{\partial < \bar{\tau}(x) >}{\partial x} \,. \tag{6.34} $$

Using this result in eq.(6.33), noting that

$$ < \bar{\bar{\tau}}(x) > \;\to\; \bar{\bar{I}}\, p_{h,eq} \text{ away from the interface,} \tag{6.35} $$

and integrating by parts gives

$$ \int dx\, d\bar{r}' \left(\frac{\delta < \tau^{xy}(\bar{r}) >}{\delta a_{\gamma}(\bar{r}')}\right)_{\underline{\Phi}=0} \frac{\partial a_{\gamma,eq}(x')}{\partial x'} (y' - y) = \int_{-\infty}^{\infty} dx \, [p_h - < \tau^{yy}(x) >] \equiv \sigma \,. \tag{6.36} $$

The quantity σ is the surface tension as found by Kirkwood and Buff[44] using equilibrium statistical mechanics. Combining eqs.(6.36) and (6.31) gives

$$ {}^{o}B_{2,\bar{p}} = -\sigma\, \bar{e}_1 \bar{e}_1 \cdot \bar{\bar{I}}_{//} \,. \tag{6.37} $$

The remaining coefficients are calculated using eqs.(5.23), (5.24), (6.7) and (6.12). We thus find

$$ {}^{o}A^{\pm}_{i,\bar{p}\gamma} = -\bar{\bar{\Delta}}^{\pm}_{\gamma} \cdot \bar{\bar{I}}_{//} = \Delta^{\pm}_{//,\gamma}\, \bar{\bar{I}}_{//} \,, \tag{6.38} $$

$$ {}^{1}A^{\pm}_{o,\bar{p}\gamma} = \bar{\bar{\Delta}}^{\pm}_{\gamma} \cdot \bar{e}_1 = \Delta^{\pm}_{\perp,\gamma}\, \bar{e}_1 \,, \tag{6.39} $$

$$ {}^{o}A^{o}_{i,\bar{p}\gamma} = -\bar{\bar{\Delta}}^{s}_{\gamma} \cdot \bar{\bar{I}}_{//} = -\Delta^{s}_{//,\gamma}\, \bar{\bar{I}}_{//} \,, \tag{6.40} $$

and

$$ {}^{1}A^{o}_{o,\bar{p}\gamma} = \bar{\bar{\Delta}}^{s}_{\gamma} \cdot \bar{e}_1 = \Delta^{s}_{\perp,\gamma}\, \bar{e}_1 \,, \quad \gamma = n, e \,, \tag{6.41} $$

where eq.(6.2) was used to resolve the tensors and where

$$ \bar{\bar{\Delta}}^{\pm}_{\gamma} \equiv \int dx\, d\bar{r}' \left\{ \left[\frac{\delta < \bar{\bar{\tau}}(\bar{r}) >_L}{\delta\, a_\gamma(\bar{r}')} \right]_{\underline{\Phi}=0} \theta(\pm x') - \theta(\pm x) \left[\frac{\delta < \bar{\bar{\tau}}(\bar{r}) >_L}{\delta\, a_\gamma(\bar{r}')} \right]^{\pm}_{\underline{\Phi}=0} \right\} \,, \tag{6.42} $$

and

$$ \bar{\bar{\Delta}}^{s}_{\gamma} \equiv \int dx\, d\bar{r}' \left[\frac{\delta < \bar{\bar{\tau}}(\bar{r}) >_L}{\delta\, a_\gamma(\bar{r}')} \right]_{\underline{\Phi}=0} \delta(x') \,. \tag{6.43} $$

From eq.(6.42) it may easily be shown that

$$ \bar{\bar{\Delta}}^{\pm}_{\gamma} = \int dx\, d\bar{r}' \left\{ \left[\frac{\delta < \bar{\bar{\tau}}(\bar{r}) >_L}{\delta\, a_\gamma(\bar{r}')} \right]_{\underline{\Phi}=0} - \delta(\bar{r} - \bar{r}')\, \bar{\bar{I}} \left(\frac{\partial p_h}{\partial a_\gamma} \right)^{\pm}_{a_{\gamma' \neq \gamma}} \right\} \theta(\pm x') \tag{6.44} $$

This last expression shows that $\bar{\bar{\Delta}}^{\pm}_{\gamma}$ plays the role of an excess pressure susceptibility.

Using eqs.(6.37) - (6.38) and (6.12) in eqs.(5.44) - (5.46) gives the following equations for the momentum variables:

$$\dot{\bar{p}}^{\pm}(\bar{r}, t) = -\bar{\nabla} \cdot \hat{p}_h^{\pm}(\bar{r}, t) \ , \tag{6.45}$$

$$\dot{\bar{p}}^{s}_{(o)} = -\bar{e}_1(\hat{p}_h^{+} - \hat{p}_h^{-})_s - \bar{\nabla}_{//} \cdot \bar{\bar{P}}^{s} \ , \tag{6.46}$$

and

$$0 = \bar{e}_1 \cdot \bar{\bar{P}}^{s} - \sigma(\bar{\nabla}_{//} \hat{\xi}_1)_s \ . \tag{6.47}$$

In the above equations,

$$\hat{p}_h^{\pm}(\bar{r}, t) \equiv \left(\frac{\partial p_h}{\partial n}\right)^{\pm}_{e} \hat{n}^{\pm}(\bar{r}, t) + \left(\frac{\partial p_h}{\partial e}\right)^{\pm}_{n} \hat{e}^{\pm}(\bar{r}, t) \ , \tag{6.48}$$

and

$$\begin{aligned} \bar{\bar{P}}^{s}(\bar{r}_{//}, t) \equiv{}& \bar{\bar{\Delta}}_n^{+} \hat{n}_s^{+} + \bar{\bar{\Delta}}_e^{+} \hat{e}_s^{+} + \bar{\bar{\Delta}}_n^{s} \hat{n}^{s}_{(o)} + \bar{\bar{\Delta}}_e^{s} \hat{e}^{s}_{(o)} \\ &+ \bar{\bar{\Delta}}_n^{-} \hat{n}_s^{-} + \bar{\bar{\Delta}}_e^{-} \hat{e}_s^{-} + \sigma(\bar{\nabla}_{//} \bar{e}_i + \bar{e}_1 \bar{\nabla}_{//}) \hat{\xi}_{1,s} \ . \end{aligned} \tag{6.49}$$

The quantities $\hat{p}_h^{\pm}(\bar{r}, t)$ are simply the displacements of the local pressure from equilibrium (cf. chapter III). Eq.(6.45) is the usual equation of motion obtained in the phenomenological Euler equations. The tensor $\bar{\bar{P}}^{s}$ may be interpreted as the displacement of the surface excess stress from equilibrium. It contains two parts. The first contains the terms which correspond to the changes in the equilibrium stress excess caused by changes in the surface excess densities. The second term contains the effects due to changes in curvature. In fact, using eqs.(6.46) and

(6.47) we have

$$\dot{p}^{s}_{(o),x} = -(\hat{p}^{+}_{h} - \hat{p}^{-}_{h})_{s} - \sigma \nabla^{2}_{/\!/} \hat{\xi}_{1,s} \quad . \tag{6.50}$$

Noting that for small curvature, the total surface curvature (cf. eqs. (4.24) and (D.3)) may be written as

$$C_{s} = -\nabla^{2}_{/\!/} \hat{\xi}_{1,s} \quad . \tag{6.51}$$

This allows us to write eq.(6.50) as

$$\dot{p}^{s}_{(o),x} = -(\hat{p}^{+}_{h} - \hat{p}^{-}_{h}) + \sigma C_{s} \quad , \tag{6.52}$$

which is a generalization of Laplace's formula[76] to the nonequilibrium regime. It will describe, among other things, capillary waves. In fact, should $\dot{p}^{s}_{(o),x}$ vanish, then eq.(6.52) is Laplace's expression which relates the difference in pressure on either side of the interface to its shape.

Using eqs.(6.47) and (6.49), we may rewrite the boundary condition arising from the momentum equation as

$$0 = \Delta^{+}_{\perp,n} \hat{n}^{+}_{s} + \Delta^{+}_{\perp,e} \hat{e}^{+}_{s} + \Delta^{s}_{\perp,n} \hat{n}^{s}_{(o)} + \Delta^{s}_{\perp,e} \hat{e}^{s}_{(o)} + \Delta^{-}_{\perp,n} \hat{n}^{-}_{s} + \Delta^{-}_{\perp,e} \hat{e}^{-}_{s} \quad . \tag{6.53}$$

In addition to the equations of motion and boundary conditions presented above, we need the equation of motion for $\hat{\xi}_{1}$, which is given by eq.(4.54). We have found three boundary conditions. One of them is used to link the surface velocity to the mechanical variables (cf. eq.(6.17)). The remaining two exactly determine the bulk solutions at the interface (together with the boundary conditions at $x = \pm\infty$). They are different in form from those used in the phenomenological theories which neglect

dynamical surface structure.

The boundary conditions specify the normal parts of the surface excess fluxes. In the phenomenological theories which include surface excesses[45-48] these boundary conditions were assumed to be consequences of the local equilibrium assumption (and would therefore be automatically satisfied) in the Euler theory (i.e., they assume $\Delta^{\pm}_{\perp,\gamma} = 0$, $\alpha^{\pm}_{\perp,\gamma} = 0$, $\bar{\bar{\Delta}}^{s}_{\perp,\gamma} = 0$). They obtain their boundary conditions from considerations of the dissipative parts of the equations, or by examining only cases where $\dot{p}^{s}_{(o),x}$ vanishes[45,46]. This is not consistent with our point of view. It may be the case that the additional terms which will appear in eqs. (6.29) and (6.53) when dissipative effects are included are more important in some cases, although it is not clear whether or not this should be true.

An additional degree of freedom lies in the choice of the position of the equilibrium dividing surface. This freedom may be used to cause one of the excess coefficients (excluding σ) appearing in the equations of motion and boundary conditions to vanish or be otherwise determined (e.g., we could take $e^{s}_{(o),eq} = 0$). Of course, this should not seriously affect the resulting bulk phenomena. For example, in an acoustic scattering experiment only an additional phase factor should result from choosing a different equilibrium dividing surface. Further, it is quite possible that the equilibrium surface position is largely determined by j'_{m}, since some of the higher equilibrium multipoles may be negligible only when the equilibrium surface position is chosen correctly. A well known example of this is Laplace's formula. It has been shown[42,43] that this equation is strictly true only if the equilibrium dividing surface

is the surface of tension. Thus the plane $x = 0$ should be chosen such that

$$(\overline{\overline{\tau}}^{s}_{(1);eq})^{yy} = \int_{-\infty}^{\infty} dx\, x[<\tau^{yy}(x)> - p_{h,eq}] = 0 \tag{6.54}$$

for the systems with a flat interface. In practice the physical differences introduced in the equilibrium theories by choosing another dividing surface are neglegible for reasonable choices of the surface position[76].

Before leaving the Euler equations we shall show how the boundary conditions used in the phenomenological equations for bulk phenomena result from our equations. If we were to use the multipole formalism for $j_m' = 0$ (i.e., neglect all surface structure), we would find the usual bulk equations and the boundary conditions

$$0 = (n^+ - n^-)_{eq}\, v_{x,s} - (n^+_{eq}\, v_x^+ - n^-_{eq}\, v_x^-)_s \quad , \tag{6.55}$$

$$0 = (e^+ - e^-)_{eq}\, v_{x,s} - (h^+\, v_x^+ - h^-\, v_x^-)_s \tag{6.56}$$

and

$$0 = \hat{p}^+_{h,s} - \hat{p}^-_{h,s} \quad . \tag{6.57}$$

This is easily seen to be the case simply by using eqs. (6.16), (6.20) and (6.46), dropping all surface multipoles. Eq.(6.28) was used to make the dependence on $\overline{v}^{\pm}$ explicit in eqs.(6.55) and (6.56). Using the fact that $h^{\pm} = e^{\pm}_{eq} + p_h$ shows that eqs.(6.55) and (6.56) are equivalent to the conditions

$$v_{x,s} = v^+_{x,s} = v^-_{x,s} \quad . \tag{6.58}$$

The relations given in eqs.(6.57) and (6.58) are the usual boundary conditions used in the phenomenological theories when capillarity is neglected (cf. ref. 1 a, chapter VIII).

Thus we have shown that the multipole technique allows us to consistently obtain the equations of motion and boundary conditions for situations where some amount of surface information is desired. The significance of the new equations of motion and boundary conditions found above is currently under investigation.

Navier-Stokes Equations

Of somewhat more practical interest than the Euler equations are the equations of motion and boundary conditions for systems where dissipation is taken into account. In the bulk this is usually accomplished by introducing viscosity and thermal conduction. As was discussed in chapter III, this requires the inclusion of terms containing up to two gradients. This is known as Navier-Stokes order.

Since the number of gradients appearing in the bulk equations has changed, so does the number of boundary conditions required to match the bulk solutions at the interface. Eight conditions at the surface are required for the Navier-Stokes equations when both the energy and number densities can change in either phase. There is not complete agreement as to what all these boundary conditions should be[3,45-48].

We shall examine the Navier-Stokes equations and their boundary conditions when all surface structure can be neglected (i.e., $j_m' = 0$). The choice $j_m' = 0$ includes many situations of real importance. For most engineering problems, dynamic surface structure is not included, although some static structure occasionally is incorporated in the calculations.

Reasonable descriptions of real systems arise from these approaches. Further, we shall assume that $k_m' = 2$ is sufficient to describe the surface equations. Since the equations are linear, we may consider the terms arising from the dissipative parts of $\overline{\overline{M}}(x|\bar{r}-\bar{r}')$ separately and then add them to the appropriate equations already found within the context of the Euler equations.

The dissipative contributions to the coefficients in the multipole hierarchy involve

$$\overline{\overline{M}}_D(x|\bar{r}-\bar{r}') \equiv -\int_0^\infty dt_1 \langle \underline{I}(\bar{r}, t_1)\, \underline{I}(\bar{r}_1) \rangle * \bar{\nabla}_{\bar{r}_1} \overline{\overline{K}}^{-1}(\bar{r}_1|\bar{r}') \ . \quad (6.59)$$

The subscript "D" shall be used to indicate the part of any coefficient arising from $\overline{\overline{M}}_D(x|\bar{r}-\bar{r}')$. For terms involving the momentum, using eq.(6.9) yields

$$\overline{\overline{M}}_{D,\gamma\bar{p}}(x|\bar{r}-\bar{r}') = -\int_0^\infty dt_1 \langle \underline{I}_\gamma(\bar{r},t_1)\, \overline{\overline{I}}_p(\bar{r}_1) \rangle * \bar{\nabla}_{\bar{r}_1} \frac{\delta(\bar{r}_1-\bar{r}')}{m\, n_{eq}(\bar{r}')K_B T} \ . \quad (6.60)$$

This last result will be useful in simplifying some of the expressions which are presented below. Note that $\overline{\overline{I}}_p$ is symmetric. Finally, we find that in the bulk regions the dissipative parts to the coefficients are given by (cf. eqs.(5.22) and (3.12)) :

$$[\overline{\overline{M}}_k^{\pm}]_D = \frac{1}{(k-2)!} \int d\bar{r}' \int_0^\infty dt_1 \ [\langle \underline{I}(\bar{r},t_1)\, \underline{I}(\bar{r}_1) \rangle * \overline{\overline{K}}^{-1}(\bar{r}_1-\bar{r}')]^{\pm} (\bar{r}'-\bar{r})^{k-2} \ . \quad (6.61)$$

With these preliminary remarks, we shall now proceed to give the equations of motion and boundary conditions for the Navier-Stokes fluid.

Since $\overline{M}_{D,N\gamma} = 0$ (cf. eq.(3.58)), the number equation and boundary conditions are just those found for the Euler equations when $j_m' = 0$, that is eqs.(6.15) and (6.55).

Energy Equations

The additional terms in the bulk energy equations are easily found using eqs.(6.61) and the facts that the bulk phases are translationally invariant and isotropic locally. Thus

$$\dot{e}^{\pm}(\overline{r},t) = -\overline{\nabla}_r \cdot \overline{j}_T^{\pm}(\overline{r},t) \ , \tag{6.62}$$

where

$$\overline{j}_T^{\pm}(\overline{r},t) \equiv \overline{j}_e^{\pm}(\overline{r},t) - (\lambda_{en}^{\pm} \overline{\nabla}_r \hat{n}^{\pm}(\overline{r},t) + \lambda_{ee}^{\pm} \overline{\nabla}_r \hat{e}^{\pm}(\overline{r},t)) \ , \tag{6.63}$$

and

$$\lambda_{e,\gamma}^{\pm} \equiv \frac{1}{3} \int d\overline{r}' \int_0^{\infty} dt_1 < \overline{I}_E(\overline{r},t_1) \cdot \overline{I}_E(\overline{r}_1) >^{\pm} * K_{e,\gamma}^{-1\pm}(\overline{r}_1 - \overline{r}') \ . \tag{6.64}$$

It can be shown[28] that

$$\lambda_{e,\gamma}^{\pm} = + \lambda_q^{\pm} \left(\frac{\partial T}{\partial a_\gamma}\right)^{\pm}_{a_{\gamma'}=\gamma} \tag{6.65}$$

where the thermal conductivity, $\lambda_q^{\pm}$, is defined as

$$\lambda_q^{\pm} \equiv \frac{1}{3K_B T^2} \int d\overline{r}_1 \int_0^{\infty} dt_1 < \overline{I}_E(\overline{r},t_1) \cdot \overline{I}_E(\overline{r}_1) >^{\pm} \ . \tag{6.66}$$

Equation (6.62) is equivalent to the linearized form of eq.(3.61).

The discussion at the end of chapter V indicates that when $j_m' = 0$ and $k_m' = 2$, the terms involving ${}^{0}\underline{\underline{A}}_{=0}^{\pm}$, ${}^{0}\underline{\underline{A}}_{=1}^{\pm}$, ${}^{1}\underline{\underline{A}}_{=0}^{\pm}$ and ${}^{0}\underline{B}_2$ should be included

in the hierarchy. This is partly due to the additional gradient which is contained in $\underline{\underline{M}}_D$. From eq.(5.28) we have

$$[{}^0\underline{B}_2]_D = - \int dx\ \underline{\underline{M}}_D(x|\bar{r}-\bar{r}') * \frac{\partial \underline{a}_{eq}}{\partial x'}(x')\ \bar{\bar{\bar{T}}}_1(\bar{r}'_{//} - \bar{r}_{//}) \ , \tag{6.67}$$

which becomes, on using eqs.(6.59), (6.60), and (3.57) and the fact that the equilibrium momentum vanishes,

$$[{}^0\underline{B}_2]_D = \int dx\ d\bar{r}' \int_0^\infty dt_1 < \underline{I}(\bar{r},t_1)\ \bar{I}_E(\bar{r}_1)> * \bar{\nabla}_{\bar{r}_1} K^{-1}_{e\gamma}(\bar{r}_1|\bar{r}')$$

$$\cdot \bar{\bar{\bar{T}}}_1 \frac{\partial a_{\gamma,eq}}{\partial x'}(x')\ (\bar{r}_{//} - \bar{r}_{//}) \ . \tag{6.68}$$

In the last equation repeated indices are summed. Using eqs.(6.68) and (6.3) for the energy equation gives

$$[{}^0B_2]_{D,e} = \sigma_e\ \bar{e}_1 \bar{\bar{I}}_{//} \tag{6.69}$$

where

$$\sigma_e \equiv \int dx\, d\bar{r}' \int_0^\infty dt_1 < I_E^y(\bar{r},t_1)\ \bar{I}_E(\bar{r}_1) >* \bar{\nabla}_{\bar{r}_1} K^{-1}_{e\gamma}(\bar{r}_1|\bar{r}')\ \frac{\partial a_{\gamma,eq}}{\partial x'}(x')\ (y' - y). \tag{6.70}$$

We may re-express σ_e by using the property that the functions appearing in eq.(6.70) are translationally invariant along the equilibrium surface. This gives

$$\sigma_e = \int dx\, d\bar{r}' \int_0^\infty dt_1 \{ < I_E^y(\bar{r},t_1)\ I_E^y(\bar{r}_1) >* K^{-1}_{e\gamma}(\bar{r}_1|\bar{r}')\ \frac{\partial a_{\gamma,eq}}{\partial x'}(x')$$

$$+ < I_E^y(\bar{r},t_1)\ I_E^x(\bar{r}_1) > (y_1 - y) * \frac{\partial}{\partial x_i} K^{-1}_{e\gamma}(\bar{r}_1|\bar{r}')\ \frac{\partial a_{\gamma,eq}}{\partial x'}(x') \} , \tag{6.71}$$

where in eq.(6.71) we have used the fact that

$$\int d\bar{r}'\ K^{-1}_{e\gamma}(\bar{r}_1|\bar{r}')\ \frac{\partial a_{\gamma,eq}(x')}{\partial x'}\ (y'-y_1) = 0\ ,$$

as required by eq.(6.1).

Using eqs.(5.23), (6.59), (6.60) and the rotational symmetries discussed at the beginning of this chapter gives

$$\left[{}^{o}A^{\pm}_{1,e\gamma}\right]_D = \begin{cases} 0 & \gamma = n,e \\ -\zeta^{\pm}_{/\!/,p}\ \overline{\overline{I}}_{/\!/} & \gamma = p \end{cases} \mp e_1 \cdot \bar{M}^{(1)\pm}_{D,e\gamma}\ , \qquad (6.72)$$

and

$$\left[{}^{1}A^{\pm}_{o,e\gamma}\right]_D = \begin{cases} \zeta^{\pm}_{\gamma} & \gamma = n,e \\ \zeta^{\pm}_{\perp,p}\ \bar{e}_1 & \gamma = p \end{cases}\ , \qquad (6.73)$$

where

$$\zeta^{\pm}_{\gamma} \equiv -\int dx\, d\bar{r}' \left\{ \int_0^{\infty} dt_1 < I^x_E(\bar{r},t_1)\ I^x_E(\bar{r}_1) > * \frac{\partial}{\partial x_1}\ K^{-1}_{e\gamma}(\bar{r}_1|\bar{r}')\ \theta(\pm x') \right\}, \qquad (6.74)$$

and

$$\bar{\bar{\zeta}}^{\pm}_{p} \equiv \zeta^{\pm}_{\perp,p}\ \bar{e}_1\bar{e}_1 + \zeta^{\pm}_{/\!/,p}\ \overline{\overline{I}}_{/\!/} = -\int dx\, d\bar{r}'\ \int_0^{\infty} dt_1 < \bar{I}_E(\bar{r},t_1)\ \bar{\bar{I}}_p(\bar{r}') > \cdot\ \bar{e}_1\ \frac{\partial}{\partial x'}\left[\frac{\theta(\pm x')}{mK_B T n_{eq}(x')}\right] \qquad (6.75)$$

Using eqs.(6.73), (6.72), (6.69), (6.63) and the results for the Euler equations, in the multipole hierarchary for $j'_m = 0$, $k'_m = 1$ gives

$$0 = (e^{+}_{eq} - e^{-}_{eq})\ v_{x,s} - \bar{e}_1 \cdot (\bar{j}^{+}_T - \bar{j}^{-}_T)_s - \bar{\nabla}_{/\!/} \cdot \left[\zeta^{+}_{/\!/,p}\ \bar{p}^{+} + \zeta^{-}_{/\!/,p}\ \bar{p}^{-}\right]_s + \sigma_e\ \nabla^2_{/\!/}\ \hat{\zeta}_{i,s} \qquad (6.76)$$

and

$$0 = \zeta_n^+ \hat{n}_s^+ + \zeta_e^+ \hat{e}_s^+ + \zeta_n^- \hat{n}_s^- + \zeta_e^- \hat{e}_s^- + (\zeta_{\perp}^+ p_x^+ + \zeta_{\perp}^- p_x^-)_s \tag{6.77}$$

The last equation may be rewritten in terms of the bulk velocities. Using eqs.(5.8) and (6.28) in eq.(6.77) yields

$$0 = \zeta_n^+ \hat{n}_s^+ + \zeta_e^+ \hat{e}_s^+ + \zeta_n^- \hat{n}_s^- + \zeta_e^- \hat{e}_s^- + \zeta_{\perp}^+ m n_{eq}^+ (v_x^+ - v_x^-)_s \ . \tag{6.78}$$

Neither of the boundary conditions given by eqs.(6.76) or (6.78) appear to correspond to any of the usual ones found in the phenomenological theories. Before interpreting these conditions we shall examine the boundary conditions arising from the momentum equation.

Momentum Equation

The momentum equations for the bulk phases follow from eqs.(6.61) (6.48) and (6.49). Taking isotropy into consideration gives

$$\dot{\bar{p}}^{\pm}(\bar{r},t) = -\bar{\nabla} \cdot \bar{\bar{P}}^{\pm}(\bar{r},t) \tag{6.79}$$

where

$$\bar{\bar{P}}^{\pm}(\bar{r},t) \equiv \hat{p}_h^{\pm}(\bar{r},t)\, \bar{\bar{I}} - \eta^{\pm}(\vec{\nabla}\bar{v}^{\pm} + \bar{v}^{\pm}\overleftarrow{\nabla} - \tfrac{2}{3}\bar{\bar{I}}\,\bar{\nabla}\cdot\bar{v}^{\pm}) - \zeta_B^{\pm}\bar{\bar{I}}\,\bar{\nabla}\cdot\bar{v}^{\pm} \ , \tag{6.80}$$

$$\eta^{\pm} \equiv \frac{1}{K_B T} \int d\bar{r}_1 \int_0^{\infty} dt_1 \, < I_p^{xy}(\bar{r},t_1)\ I_p^{xy}(\bar{r}_1) >^{\pm} \ . \tag{6.81}$$

and

$$\frac{4}{3}\eta^{\pm} + \zeta_B^{\pm} \equiv \frac{1}{K_B T} \int d\bar{r}_1 \int_0^{\infty} dt_1 \, < I_p^{xx}(\bar{r},t_1)\ I_p^{xx}(\bar{r}_1) >^{\pm} \ . \tag{6.82}$$

Eq.(6.80) is the usual form of the macroscopic stress tensor for a vis-

cous fluid. The coefficients $\eta^{\pm}$ and $\zeta_B^{\pm}$ are the dynamic and bulk viscosities, respectively. It is easily shown that eq.(6.79) is equivalent to the linearized form of eq.(3.65) in homogeneous phases.

Proceeding as in the energy equation (cf.(eq.(6.68)), we find that

$$[{}^{0}B_{2,p}]_D = \int dx\, d\bar{r}' \int_0^{\infty} dt_1 < \bar{\bar{I}}_p(\bar{r},t_1)\ \bar{I}_E(\bar{r}_1) > * \bar{\nabla}_{\bar{r}_1} K_{e\gamma}^{-1}(\bar{r}_1|\bar{r}')\ \frac{\partial a_{\gamma,eq}(x')}{\partial x'} \cdot \bar{\bar{\bar{T}}}_1(\bar{r}'_{//} - \bar{r}_{//}) \ , \tag{6.83}$$

which by using eq.(6.3) becomes

$$[{}^{0}B_{2,p}]_D = \sigma_p\, \bar{e}_1\bar{e}_1\, \bar{\bar{I}}_{//} \ , \tag{6.84}$$

where

$$\sigma_p \equiv \int dx\, d\bar{r}' \int_0^{\infty} dt_1 < I_p^{xy}(\bar{r},t_1)\ \bar{I}_E(\bar{r}_1) > * \bar{\nabla}_{r_1} K_{e\gamma}^{-1}(\bar{r}_1|\bar{r}')\ \frac{\partial a_{\gamma,eq}(x')}{\partial x'}(y'-y) . \tag{6.85}$$

An alternate expression for σ_p can be obtained by noting that for $j_m' = 0$ the Euler parts of ${}^{1}B_{1,p}$ (i.e., the surface tension) should be neglected. Therefore, using eq.(5.3) gives

$$[{}^{1}B_{1,p}]_D = 0 \ . \tag{6.86}$$

From eq.(6.86), in exactly the same procedure that led to eq.(6.33), it follows that

$$\sigma_p = \int dx\, d\bar{r}' \int_0^{\infty} dt_1\ x < I_p^{yy}(\bar{r},t_1)\ I_E^{x}(\bar{r}_1) > * \frac{\partial K_{e\gamma}^{-1}(\bar{r}_1|\bar{r}')}{\partial x_1}\ \frac{\partial a_{\gamma,eq}(x')}{\partial x'} \ . \tag{6.87}$$

The remaining coefficients needed for the hierarchy are obtained using eqs.(5.23), (6.59), (6.60) and the rotational symmetries. We thus find

$$\left[{}^{o}A^{\pm}_{1,p\gamma}\right]_D = \left\{ \begin{array}{ll} -\kappa^{\pm}_{/\!/,\gamma}\,\overline{\overline{I}}_{/\!/}\,, & \gamma = n,e \\ -\kappa^{\pm}_{1,p}\,\bar{e}_1\,\overline{\overline{I}}_{/\!/} - \kappa^{\pm}_{2,p}\,\overline{\overline{\overline{T}}}_1\,, & \gamma = p \end{array} \right\} \mp \bar{e}_1 \cdot M^{(1)\pm}_{D,p\gamma} \tag{6.88}$$

and

$$\left[{}^{1}A^{\pm}_{o,p\gamma}\right]_D = \left\{ \begin{array}{ll} \kappa^{\pm}_{\perp,\gamma}\,\bar{e}_1 & \gamma = n,e \\ \kappa^{\pm}_{3,p}\,\bar{e}_1\bar{e}_1 + \kappa^{\pm}_{1,p}\,\overline{\overline{I}}_{/\!/} & \gamma = p \end{array} \right\}, \tag{6.89}$$

where

$$\overline{\overline{\kappa}}^{\pm}_{\gamma} \equiv \kappa^{\pm}_{\perp,\gamma}\,\bar{e}_1\bar{e}_1 + \kappa^{\pm}_{/\!/,\gamma}\,\overline{\overline{I}}_{/\!/} \equiv -\int dx\, d\bar{r}' \int_0^\infty dt_1 \,\langle \overline{\overline{I}}_p(\bar{r},t_1)\; I^x_E(\bar{r}_1)\rangle * \frac{\partial K^{-1}_{e\gamma}(\bar{r}_1|\bar{r}')}{\partial x_1}\,\theta(\pm x'), \tag{6.90}$$

$$\kappa^{\pm}_{1,p} \equiv -\int dx\, d\bar{r}' \int_0^\infty dt_1 \,\langle I^{xy}_p(\bar{r},t_1)\; I^{xy}_p(\bar{r}')\rangle \frac{\partial}{\partial x'}\left(\frac{\theta(\pm x')}{m K_B T n_{eq}(x')}\right), \tag{6.91}$$

$$\kappa^{\pm}_{2,p} \equiv -\int dx\, d\bar{r}' \int_0^\infty dt_1 \,\langle I^{yy}_p(\bar{r},t_1)\; I^{xx}_p(\bar{r}')\rangle \frac{\partial}{\partial x'}\left(\frac{\theta(\pm x')}{m K_B T n_{eq}(x')}\right), \tag{6.92}$$

and

$$\kappa^{\pm}_{3,p} \equiv -\int dx\, d\bar{r}' \int_0^\infty dt_1 \,\langle I^{xx}_p(\bar{r},t_1)\; I^{xx}_p(\bar{r}')\rangle \frac{\partial}{\partial x'}\left(\frac{\theta(\pm x')}{m K_B T n_{eq}(x')}\right). \tag{6.93}$$

The boundary conditions for the momentum equation may now be written out by using eqs.(6.89), (6.88), (6.85) and the Euler coefficients in the multipole hierarchy, eq.(5.46) . Thus

$$0 = -\bar{e}_1 \cdot (\bar{\bar{P}}^+ - \bar{\bar{P}}^-)_s - \bar{\nabla}_{/\!/} \cdot [\kappa^+_{/\!/,n}\, \hat{n}^+ + \kappa^+_{/\!/,e}\, \hat{e}^+ + \kappa^-_{/\!/,n}\, \hat{n}^- + \kappa^-_{/\!/,e}\, e^-$$

$$+ \kappa^+_{2,p}\, p^+_x + \kappa^-_{2,p}\, p^-_x]_s + \bar{e}_1\, \bar{\nabla}_{/\!/} \cdot [\sigma_p\, \bar{\nabla}_{/\!/}\, \hat{\xi}_1 - \kappa^+_{1,p}\, \bar{p}^+ - \kappa^-_{1,p}\, \bar{p}^-]_s \quad (6.94)$$

and

$$0 = \bar{e}_1[\kappa^+_{\perp,n}\, \hat{n}^+ + \kappa^+_{\perp,e}\, \hat{e}^+ + \kappa^-_{\perp,n}\, \hat{n}^- + \kappa^-_{\perp,e}\, \hat{e}^- + \kappa^+_{3,p}\, p^+_x + \kappa^-_{3,p}\, p^-_x]_s$$

$$+ \bar{\bar{I}}_{/\!/} \cdot [\kappa^+_{1,p}\, \bar{p}^+ + \kappa^-_{1,p}\, \bar{p}^-]_s \,. \quad (6.95)$$

Using eqs.(5.8) and (6.28) in the above equations yields

$$0 = (\bar{v}^+_{/\!/,s} - \bar{v}^-_{/\!/,s}) \quad \text{(providing } \kappa^+_{1,p} \neq 0) \quad (6.96)$$

and

$$0 = \kappa^+_{\perp,n}\, \hat{n}^+_s + \kappa^+_{\perp,e}\, \hat{e}^+_s + \kappa^-_{\perp,n}\, \hat{n}^-_s + \kappa^-_{\perp,e}\, \hat{e}^-_s + \kappa^+_{3,p}\, m n^+_{eq} (v^+_{x,s} - v^-_{x,s}) \quad (6.97)$$

$$0 = -\bar{e}_1\bar{e}_1 : (\bar{\bar{P}}^+ - \bar{\bar{P}}^-)_s + \sigma_p\, \nabla^2_{/\!/}\, \hat{\xi}_{1,s} \quad (6.98)$$

$$0 = -e_1 \cdot (\bar{\bar{P}}^+ - \bar{\bar{P}}^-)_s \cdot \bar{\bar{I}}_{/\!/} - \bar{\nabla}_{/\!/} [\kappa^+_{/\!/,n}\, \hat{n}^+_s + \kappa^+_{/\!/,e}\, \hat{e}^+_s + \kappa^-_{/\!/,n}\, \hat{n}^-_s + \kappa^-_{/\!/,e}\, \hat{e}^-_s] \quad (6.99)$$

where we have decomposed the conditions into normal and transverse components.

Of the above equations, only eq.(6.96) is one of the usual boundary conditions. From eqs.(6.96) - (6.99), (6.76), (6.78) and (6.55) we see that in all, nine independent conditions have been obtained. One of them is used to specify the surface velocity, while the others match the bulk

solutions at the interface. Although we obtain the correct number of boundary conditions, it is not immediately obvious how they are related to those used in the usual phenomenological theories.

In order to make some connection with the phenomenological theories, we note that the $\zeta_\gamma^\pm$ and $\kappa_\gamma^\pm$ coefficients (cf. (6.90) - (6.93), (6.74) and (6.75)) are all various components of

$$\bar{\bar{\Lambda}} \equiv - \int dx\, d\bar{r}' \int_0^\infty dt_1 \langle \bar{\bar{I}}(\bar{r},t_1)\ \bar{\bar{I}}(\bar{r}_1)\rangle^* \cdot \bar{e}_1 \frac{\partial}{\partial x_1} \bar{\bar{K}}^{-1}(\bar{r}_1|\bar{r}')\ \theta(\pm x'), \tag{6.100}$$

$$= \mp \bar{\bar{L}}(0) \cdot \bar{e}_1 \int d\bar{r}_1 (\bar{\bar{K}}^{-1}(\bar{r}_1))^\pm + \bar{\bar{\Omega}}^\pm \quad , \tag{6.101}$$

where

$$\bar{\bar{L}}(x_1) \equiv \int d\bar{r} \int_0^\infty dt_1 \langle \bar{\bar{I}}(\bar{r},t_1)\ \bar{\bar{I}}(\bar{r}_1)\rangle \quad , \tag{6.102}$$

and

$$\bar{\bar{\Omega}}^\pm \equiv - \int dx_1\, \bar{\bar{L}}(x_1) \cdot \bar{e}_1 \frac{\partial}{\partial x_1} \int d\bar{r}' \left[\bar{\bar{K}}^{-1}(\bar{r}_1|\bar{r}')\ \theta(\pm x') - \theta(\pm x_1)\ \bar{\bar{K}}^{-1\pm}(\bar{r}_1-\bar{r})\right]. \tag{6.103}$$

The quantity $\bar{\bar{L}}(x_1)$ is a position dependent version of the generalized Onsager coefficients introduced in chapter III. Further, with the assumption that all surface multipoles vanish ($j_m' = 0$), we see from (6.103) that $\bar{\bar{\Omega}}^\pm = 0$, since $\int d\bar{r}' [\bar{\bar{K}}^{-1}(\bar{r}_1|\bar{r}')\ \theta(\pm x') - \bar{\bar{K}}^{-1\pm}(\bar{r}_1-\bar{r}')\ \theta(\pm x_1)]$ is non-zero only near $x_1 = 0$. That is, it contains no bulk terms in a multipole expansion. In addition, it can be shown[28] that

$$\int d\bar{r}_1\ K_{e\gamma}^{-1\pm}(\bar{r} - \bar{r}_1) = \frac{1}{K_B T^2} \left(\frac{\partial T}{\partial a_\gamma}\right)_{a_{\gamma'\neq\gamma}} . \tag{6.104}$$

Thus using eqs.(6.104) and (6.101) in the $\zeta_\gamma^\pm$ and $\kappa_\gamma^\pm$ parameters in eqs.(6.96) - (6.99), (6.76), (6.78) and (6.55) give the following set of boundary conditions:

$$0 = n_{eq}^{+}(v_{x,s}^{+}-v_{x,s}) - n_{eq}^{-}(v_{x,s}^{-}-v_{x,s}) \ , \tag{6.105 a}$$

$$0 = (e_{eq}^{+} - e_{eq}^{-})\, v_{n,s} - \bar{e}_1 \cdot (\bar{j}_T^{+} - \bar{j}_T^{-})_s + \sigma_e \nabla_{/\!/}^2 \hat{\xi}_{1,s} \ , \tag{6.105 b}$$

$$0 = \frac{L_{ee(o)}^{xx}}{K_B T^2} (\hat{T}^{+} - \hat{T}^{-})_s + \frac{L_{ep(o)}^{xxx}}{K_B T} (v_x^{+} - v_x^{-}) \ , \tag{6.105 c}$$

$$0 = \bar{v}_{/\!/,s}^{+} - \bar{v}_{/\!/,s}^{-} \ , \tag{6.105 d}$$

$$0 = \frac{L_{pe(o)}^{xxx}}{K_B T^2} (\hat{T}^{+} - \hat{T}^{-})_s + L_{pp(o)}^{xxxx} (v_{x,s}^{+} - v_{x,s}^{-})/K_B T \ , \tag{6.105 e}$$

$$0 = -\bar{e}_1 \bar{e}_1 : (\bar{\bar{P}}_s^{+} - \bar{\bar{P}}_s^{-}) + \sigma_p \nabla_{/\!/}^2 \hat{\xi}_{1,s} \ , \tag{6.105 f}$$

and

$$0 = -\bar{e}_1 \cdot (\bar{\bar{P}}_s^{+} - \bar{\bar{P}}_s^{-}) \cdot \bar{\bar{I}}_{/\!/} + \nabla_{/\!/} L_{pe(o)}^{yyx} (\hat{T}^{+} - \hat{T}^{-})_s / K_B T^2 \ , \tag{6.105 g}$$

where the displacement of the temperature from equilibrium is given by

$$\hat{T}^{\pm}(\bar{r},t) \equiv \left(\frac{\partial T}{\partial n}\right)_e^{\pm} \hat{n}^{\pm}(\bar{r},t) + \left(\frac{\partial T}{\partial e}\right)_n^{\pm} \hat{e}^{\pm}(\bar{r},t) \ . \tag{6.106}$$

Eqs.(6.105 a) - (6.105 g) are equivalent to the conditions:

$$\bar{v}_s^{+} = \bar{v}_s^{-} \ , \ v_{x,s} = v_{x,s}^{+} \ , \tag{6.107 a}$$

$$\hat{T}_s^+ = \hat{T}_s^- \quad , \tag{6.107 b}$$

$$0 = -\bar{e}_1 \cdot (\bar{j}_q^+ - \bar{j}_q^-)_s + \sigma_e \bar{\nabla}_{//}^2 \hat{\xi}_{1,s} \quad , \tag{6.107 c}$$

and

$$0 = -\bar{e}_1 \cdot (\bar{\bar{P}}^+ - \bar{\bar{P}}^-)_s + \bar{e}_1 \sigma_p \nabla_{//}^2 \hat{\xi}_{1,s} \quad , \tag{6.107 d}$$

where the heat current is defined as

$$\bar{j}_q^{\pm}(\bar{r},t) \equiv -\lambda_q^{\pm} \bar{\nabla} \hat{T}^{\pm}(\bar{r},t) \quad . \tag{6.108}$$

If σ_e and σ_p vanish, then eqs.(6.107 a) - (6.107 d) are the usual boundary conditions imposed at a free surface[1a] when surface excess quantities (e.g., surface tension) are neglected. That σ_e and σ_p do indeed vanish, may be seen from the equality:

$$\int dr' \, K_{e\gamma}^{-1}(\bar{r}|\bar{r}') \frac{\partial a_{\gamma,eq}(r')}{\partial x'} = -\left[\frac{\partial \beta(\bar{r},0)}{\partial x}\right]_{\Phi=0} = 0 \tag{6.109}$$

where we have used eqs.(3.38) and (3.54), the functional derivative chain rule, and the fact that the equilibrium temperature is constant. Using eq.(6.109) in eqs.(6.87) and (6.71) shows that σ_e and σ_p vanish, providing orders of integration can be interchanged. For the integrands in these expressions this seems reasonable, although some other expressions might contain long range correlation functions as a consequence of the broken symmetry[9]. Wertheim[77] has given some arguments for the existence of long range correlations in the interfacial region. When considering correlations in systems with a broken symmetry, it is usually assumed that the dissipative current correlation functions are of short range[9], and this

allows us to interchange the orders of integration.

The boundary conditions, eqs.(6.107 a) - (6.107 b), for $j_m' = 0$ are now seen to be those used in many macroscopic calculations. They require velocity and temperature, the normal stress, and the heat current to be continuous across the interface.

In this chapter we have shown how to apply the multipole technique to problems concerning single component two phase hydrodynamics. We have shown that the usual phenomenological boundary conditions result when all surface structure is neglected. In addition, we have found the equations of motion for perfect fluids when excess densities (both dynamic and static) are included. Equations of motion for viscous fluids including surface structure can be obtained by considering the additional coefficients that are now needed. Since about 50 new parameters must be introduced, we do not present these equations here.

Chapter VII. Concluding Remarks

In the last chapter we examined the equations of motion and boundary conditions arising from the multipole hierarchy for two phase, single component, simple fluids. In the two cases considered, Navier-Stokes and ideal fluids, the usual boundary conditions were obtained when all surface structure was neglected.

We have also given the equations of motion and boundary conditions for ideal systems when the dynamic surface excesses (zero'th multipoles) are included. These equations and boundary conditions are currently being studied. Preliminary results indicate that the effect of the surface excesses on the bulk solutions is small. A possible exception to this may occur in acoustic scattering off of interfaces. It is well known[1a] that if the usual boundary conditions are imposed, then there will exist a scattering angle for which the reflected sound wave vanishes (this is analogous to the Brewster angle in optics). However, if surface structure is included, it can be shown that at this angle only the leading contribution to the reflection coefficient vanishes. The remainder contains surface specific information. It may therefore be possible to use an acoustic experiment to study interfacial structure.

It is clear that many problems may be approached using the multipole technique. A very important one is that of hydrodynamics next to a real solid. In a crude version of the multipole technique we have shown that if all surface structure is neglected, then for flow next to a flat hard wall slip boundary conditions should be imposed[80]. The fact that stick conditions are usually found experimentally implies that surface structure, surface roughness, or inelastic processes at the sur-

face are extremely important. In fact, Richardson[81] has shown that stick-like flow can result using the macroscopic hydrodynamic equations and slip boundary conditions on a rough surface. The multipole technique can be used to examine all these questions from a somewhat more fundamental point of view.

As was shown in chapter VI, there can be no relative velocity of the two phases at a fluid/fluid interface (cf. eq.(6.10a). This arises from the fact that momentum can freely be transferred across the interface. It seems likely that if inelastic processes occur at a solid surface, then a similar boundary condition should be found. The multipole method may also find use in interpreting the results of optical-acoustic spectroscopy[82] and in reactions which occur at electrodes or other surfaces. In addition to the effect of the surface structure on the bulk phenomena, the multipole hierarchy can be used to study dynamical surface modes[78] and show how these may be measured by techniques such as light scattering from interfaces[83].

In conclusion then, we have shown that it is possible to obtain the macroscopic equations of motion using response theory in inhomogeneous systems. We have shown how the usual equations of motion arise when the inhomogeneity is weak. A general scheme was developed for systems with strong equilibrium inhomogeneities. This yielded boundary conditions for the macroscopic equations. Finally, we have applied the multipole technique to fluid systems and have shown how the usual boundary conditions are caused. We have also given equations which will yield corrections due to surface structure in the case of the Euler equations. Some of the additional applications discussed in this chapter are currently under investigation.

Appendix A: Transformation of Triple Correlation Functions

In this appendix we shall show how triple correlation functions of the form $\langle\hat{B}\hat{D}\hat{E}\rangle_{\Gamma}$, transform to the Γ' ensemble. For our purposes only corrections to $O(N^{-2})$ need be retained. Eq. (2.31) may be rewritten as

$$\langle B\rangle_{\Gamma} = \langle B\rangle_{\Gamma'} + I^{(2)}_{ij}\frac{\partial^2\langle B\rangle_{\Gamma'}}{\partial\langle C_i\rangle_{\Gamma'}\partial\langle C_j\rangle_{\Gamma'}} + I^{(3)}_{ijk}\frac{\partial^3\langle B\rangle_{\Gamma'}}{\partial\langle C_i\rangle_{\Gamma'}\partial\langle C_j\rangle_{\Gamma'}\partial\langle C_k\rangle_{\Gamma'}} + I^{(4)}_{ijkl}\frac{\partial^4\langle B\rangle_{\Gamma'}}{\partial\langle C_i\rangle_{\Gamma'}\partial\langle C_j\rangle_{\Gamma'}\partial\langle C_k\rangle_{\Gamma'}\partial\langle C_l\rangle_{\Gamma'}} + \mathcal{O}(N^{-3}), \tag{A.1}$$

where repeated indices are summed,

$$I^{(2)}_{ij} \equiv -\tfrac{1}{2}\langle\hat{C}_i\hat{C}_j\rangle_{\Gamma'} + \tfrac{1}{4}\langle\hat{C}_k\hat{C}_l\rangle_{\Gamma'}\frac{\partial^2\langle\hat{C}_i\hat{C}_j\rangle_{\Gamma'}}{\partial\langle C_k\rangle_{\Gamma'}\partial\langle C_l\rangle_{\Gamma'}}, \tag{A.2}$$

$$I^{(3)}_{ijk} \equiv \tfrac{1}{2}\langle\hat{C}_k\hat{C}_l\rangle_{\Gamma'}\frac{\partial\langle\hat{C}_i\hat{C}_j\rangle_{\Gamma'}}{\partial\langle C_l\rangle_{\Gamma'}} - \frac{1}{3!}\langle\hat{C}_i\hat{C}_j\hat{C}_k\rangle_{\Gamma'} \tag{A.3}$$

and

$$I^{(4)}_{ijkl} \equiv \tfrac{1}{4}\langle\hat{C}_i\hat{C}_j\rangle_{\Gamma'}\langle\hat{C}_k\hat{C}_l\rangle_{\Gamma'}. \tag{A.4}$$

By using eqs. (2.35), (2.36) and (A.3) it is easily shown that

$$I^{(3)}_{ijk} = \tfrac{1}{3}\langle\hat{C}_i\hat{C}_j\hat{C}_k\rangle_{\Gamma'}. \tag{A.5}$$

Note that

$$\langle\hat{B}\hat{D}\hat{E}\rangle_{\Gamma} = \langle BDE\rangle_{\Gamma} - \langle B\rangle_{\Gamma}\langle DE\rangle_{\Gamma} - \cdots + 2\langle B\rangle_{\Gamma}\langle D\rangle_{\Gamma}\langle E\rangle_{\Gamma}, \tag{A.6}$$

where the symbol ... represents the other two permutations of the variables B, D. E. By using eq.(A.1) in each of the averages in (A.6) and retaining terms to $O(N^{-2})$, we obtain after some lengthy manipulations

$$
\begin{aligned}
\langle \hat{B}\hat{D}\hat{E}\rangle_{\Gamma} = {} & \langle \hat{B}\hat{D}\hat{E}\rangle_{\Gamma'} + I^{(2)}_{ij}\left[\frac{\partial^2\langle \hat{B}\hat{D}\hat{E}\rangle_{\Gamma'}}{\partial\langle C_i\rangle_{\Gamma'}\partial\langle C_j\rangle_{\Gamma'}} + 2\,\frac{\partial\langle B\rangle_{\Gamma'}}{\partial\langle C_i\rangle_{\Gamma'}}\frac{\partial\langle \hat{D}\hat{E}\rangle_{\Gamma'}}{\partial\langle C_j\rangle_{\Gamma'}} + \cdots\right] \\
& + I^{(3)}_{ijk}\left[\frac{\partial^3\langle \hat{B}\hat{D}\hat{E}\rangle_{\Gamma'}}{\partial\langle C_i\rangle_{\Gamma'}\partial\langle C_j\rangle_{\Gamma'}\partial\langle C_k\rangle_{\Gamma'}} + 3\,\frac{\partial^2\langle B\rangle_{\Gamma'}}{\partial\langle C_i\rangle_{\Gamma'}\partial\langle C_j\rangle_{\Gamma'}}\frac{\partial\langle \hat{D}\hat{E}\rangle_{\Gamma'}}{\partial\langle C_k\rangle_{\Gamma'}} + \cdots\right. \\
& \left. + 3\,\frac{\partial\langle B\rangle_{\Gamma'}}{\partial\langle C_i\rangle_{\Gamma'}}\frac{\partial^2\langle \hat{D}\hat{E}\rangle_{\Gamma'}}{\partial\langle C_j\rangle_{\Gamma'}\partial\langle C_k\rangle_{\Gamma'}} + \cdots + 6\,\frac{\partial\langle B\rangle_{\Gamma'}}{\partial\langle C_i\rangle_{\Gamma'}}\frac{\partial\langle D\rangle_{\Gamma'}}{\partial\langle C_j\rangle_{\Gamma'}}\frac{\partial\langle E\rangle_{\Gamma'}}{\partial\langle C_k\rangle_{\Gamma'}}\right] \\
& + I^{(4)}_{ijkl}\left[\frac{\partial^4\langle \hat{B}\hat{D}\hat{E}\rangle_{\Gamma'}}{\partial\langle C_i\rangle_{\Gamma'}\partial\langle C_j\rangle_{\Gamma'}\partial\langle C_k\rangle_{\Gamma'}\partial\langle C_l\rangle_{\Gamma'}} + 4\,\frac{\partial\langle B\rangle_{\Gamma'}}{\partial\langle C_i\rangle_{\Gamma'}}\frac{\partial^3\langle \hat{D}\hat{E}\rangle_{\Gamma'}}{\partial\langle C_j\rangle_{\Gamma'}\partial\langle C_k\rangle_{\Gamma'}\partial\langle C_l\rangle_{\Gamma'}} + \cdots\right. \\
& + 4\,\frac{\partial^3\langle B\rangle_{\Gamma'}}{\partial\langle C_i\rangle_{\Gamma'}\partial\langle C_j\rangle_{\Gamma'}\partial\langle C_k\rangle_{\Gamma'}}\frac{\partial\langle \hat{D}\hat{E}\rangle_{\Gamma'}}{\partial\langle C_l\rangle_{\Gamma'}} + \cdots \\
& + \frac{\partial^2\langle B\rangle_{\Gamma'}}{\partial\langle C_i\rangle_{\Gamma'}\partial\langle C_j\rangle_{\Gamma'}}\frac{\partial^2\langle \hat{D}\hat{E}\rangle_{\Gamma'}}{\partial\langle C_k\rangle_{\Gamma'}\partial\langle C_l\rangle_{\Gamma'}} + \cdots \\
& + 4\,\frac{\partial^2\langle B\rangle_{\Gamma'}}{\partial\langle C_i\rangle_{\Gamma'}\partial\langle C_k\rangle_{\Gamma'}}\frac{\partial^2\langle \hat{D}\hat{E}\rangle_{\Gamma'}}{\partial\langle C_j\rangle_{\Gamma'}\partial\langle C_l\rangle_{\Gamma'}} + \cdots + 2\,\frac{\partial^2\langle B\rangle_{\Gamma'}}{\partial\langle C_i\rangle_{\Gamma'}\partial\langle C_j\rangle_{\Gamma'}}\frac{\partial\langle D\rangle_{\Gamma'}}{\partial\langle C_k\rangle_{\Gamma'}}\frac{\partial\langle E\rangle_{\Gamma'}}{\partial\langle C_l\rangle_{\Gamma'}} \\
& \left. + \cdots + 8\,\frac{\partial^2\langle B\rangle_{\Gamma'}}{\partial\langle C_i\rangle_{\Gamma'}\partial\langle C_k\rangle_{\Gamma'}}\frac{\partial\langle D\rangle_{\Gamma'}}{\partial\langle C_j\rangle_{\Gamma'}}\frac{\partial\langle E\rangle_{\Gamma'}}{\partial\langle C_l\rangle_{\Gamma'}} + \cdots\right] + \mathcal{O}(N^{-3}),
\end{aligned}
\tag{A.7}
$$

which is the desired result.

Appendix B: Evaluation of Functional Derivatives with Respect to $\phi_{ext}(\bar{r})$

In Chapter III we needed functional derivatives of $\underline{\underline{M}}^{(j)}$ (cf. eq. (3.18)) with respect to $\phi_{ext}(\bar{r})$. Since $\underline{\underline{M}}^{(j)}(\bar{r})$ is made up of two types of quantities, static and time correlation functions, we shall first consider

$$\left[\frac{\delta < \hat{B}_1(\bar{r},t)\ \hat{B}_2(\bar{r}') >}{\delta(-\beta\ \phi_{ext}(\bar{r}''))}\right]_{\phi_{ext}=0} \tag{B.1}$$

where $B_i(\bar{r},t)$ $i = 1,2$ are dynamical variables which do not contain the external potential or force explicitly; otherwise they are arbitrary.

The contributions to the functional derivative, eq.(B.1), arise from two sources: the explicit ϕ_{ext} dependence of the distribution function and the implicit dependence contained in the motion of the phase point. Using the identity

$$e^{iLt} = \exp[i\ L_o\ t] + \int_o^t dt_1\ e^{i L_o (t-t_1)}\ i\ L_{ext}\ e^{i L\ t_1}\ , \tag{B.2}$$

where L_o is the Liouville operator in the absence of the external field and where

$$i\ L_{ext} \equiv [\ ,\ \sum_j \phi_{ext}(\bar{r}_j)] = -\sum_j \frac{\partial \phi_{ext}(\bar{r}_j)}{\partial \bar{r}_j} \cdot \frac{\partial}{\partial \bar{p}_j} \tag{B.3}$$

and using eq.(B.2), it is easily shown that

$$< \hat{B}_1(\bar{r},t)\ \hat{B}_2(\bar{r}') > = < \hat{B}_1(\bar{r},t)\ \hat{B}_2(\bar{r}') >_o - \beta < \sum_j \phi_{ext}(\bar{r}_j)\ \hat{B}_1(\bar{r},t)\ \hat{B}_2(\bar{r}') >_o$$
$$+ \int_o^t dt_1 < (\ i L_{ext} \hat{B}_1(\bar{r},t_1))\ \hat{B}_2(\bar{r}',t_1-t) >_o + O(\phi_{ext}^2)\ , \tag{B.4}$$

where the subscript "o" implies that the average and motion of the phase point are to be taken in a force free system. Using eq.(B.4) the functional derivative, eq.(B.1), is now seen to be

$$\left(\frac{\delta < \hat{B}_1(\bar{r},t)\ \hat{B}_2(\bar{r}') >}{\delta\,(-\beta\,\phi_{ext}(\bar{r}''))}\right)_{\phi_{ext}=0} = < \hat{B}_1(\bar{r},t)\ \hat{B}_2(\bar{r}')\ \hat{N}(\bar{r}'') >_o$$

$$- \int_o^t dt_1\ K_B T \frac{\partial}{\partial \bar{r}''} < \sum_j \delta(\bar{r}''-\bar{r}_j)\ \frac{\partial \hat{B}_1(\bar{r},t_1)}{\partial \bar{p}_j}\ \hat{B}_2(\bar{r}',t_1-t) >_o \ . \tag{B.5}$$

This will be a quasi-local quantity if the time correlation functions decay quickly enough. Equation (B.5) is an exact relation and is valid for any ensemble. In particular, it is valid for the ensemble where the density is homogeneous and equals the local density, $n_{eq}(\bar{r})$, in the inhomogeneous system.

In chapter II, functional derivatives of $\underline{\underline{M}}^{(j)}$ were required. Using eqs.(3.12), (3.3), (3.7), (3.8) and (B.5) we have

$$\left(\frac{\delta\, \underline{\underline{M}}^{(j)}(\bar{r})}{\delta\,\beta\,\phi_{ext}(\bar{r}')}\right)_{hom} = \int \frac{d\bar{r}_1}{j!} \Big[< \underline{I}(\bar{r})\ \underline{\hat{A}}(\bar{r}_2)\ \hat{N}(\bar{r}') >_{hom}$$

$$- \int_o^\infty dt_1 \Big(< \underline{I}(\bar{r},t_1)\ \underline{I}(\bar{r}_2)\ \hat{N}(\bar{r}'') >_{hom} - < \underline{I}(\bar{r},t_1)\ \underline{I}(\bar{r}_3) >_{hom} * \underline{\underline{K}}^{-1}(\bar{r}_3|\bar{r}_4)_{hom}$$

$$* < \underline{\hat{A}}(\bar{r}_4)\ \underline{\hat{A}}(\bar{r}_2)\ \hat{N}(\bar{r}'') >_{hom} - K_B T \int_o^t dt_2 \frac{\partial}{\partial \bar{r}''} < \sum_j \delta(\bar{r}''-\bar{r}_j)\ \frac{\partial}{\partial \bar{p}_j} \underline{I}(\bar{r},t_2)$$

$$\cdot\ \underline{I}(\bar{r}_2,t_2-t_1) >_{hom} \Big) \Big] * \underline{\underline{K}}^{-1}(\bar{r}_2|\bar{r}_1)_{hom}\ (\bar{r}_1-\bar{r})^j \ , \tag{B.6}$$

to second order in the smallness parameter characterizing $\dot{A}$.

Since we have assumed that the dissipative variables $I(\bar{r},t)$ decay on a molecular time scale, this implies that only short times contribute to the integrals appearing in eq.(B.6). As a direct consequence of this, the functional derivative will be short ranged in space.

It is interesting to note the similarity between some of the terms appearing in $\underline{\underline{M}}^{(j)}$ (cf. eq.(3.19)) and in $\underline{\underline{W}}^{(\ell,k)}(\bar{r})_{hom}$. For example, using eqs.(3.18), (3.19) and (B.6) we have

$$\underline{\underline{M}}^{(j)}(\bar{r}) = \underline{\underline{M}}^{(j)}_{hom}(\bar{r}) + \frac{1}{j!}\int d\bar{r}_1 d\bar{r}_4 < \underline{I}(\bar{r})\ \underline{\hat{A}}(\bar{r}_2)\ \hat{N}(\bar{r}_3) >_{hom} * (\delta(\bar{r}_3 - \bar{r}_4)/n_{eq}(\bar{r}) - c_{hom}(\bar{r}_3 - \bar{r}_4))\ \underline{\underline{K}}^{-1}(\bar{r}_2|\bar{r}_1)_{hom}(\bar{r}_2 - \bar{r})^j\ (\bar{r}_4 - \bar{r})\cdot\bar{\nabla}_r\, n_{eq}(\bar{r}) + \ldots \quad . \tag{B.7}$$

This should be compared with

$$\frac{1}{k!}\int d\bar{r}_1 d\bar{r}_4 < \underline{I}(\bar{r})\ \underline{\hat{A}}(\bar{r}_2)\ \hat{N}(\bar{r}_3) >_{hom} * K^{-1}_{NN}(\bar{r}_3|\bar{r}_4)_{hom}\underline{\underline{K}}^{-1}(\bar{r}_2|\bar{r}_1)_{hom}(\bar{r}_1-\bar{r})^k(\bar{r}_4-\bar{r}) \tag{B.8}$$

which appears in the expression for $\underline{\underline{W}}^{(\ell,k)}_{hom}(\bar{r})$ coupling to $\bar{\nabla}\hat{n}(\bar{r},t)$. This does not equal the corresponding term in $\underline{\underline{M}}^{j}$ as $\underline{\underline{K}}^{-1}_{NN}(\bar{r}|\bar{r}')_{hom}$ and $\delta(\bar{r}-\bar{r}')/n_{eq}(\bar{r}) - c_{hom}(\bar{r}-\bar{r}')$ are not identical. However, they are similar enough to indicate that the relations (3.20) and (3.21) will only be correct, as far as the nonlinear equations of motion are concerned, when $\varepsilon/\Delta \ll 1$. Should this not be the case, then only the linear equations resulting from eq. (3.20) are valid.

Appendix C: Proofs of Equations (4.22) and (4.23)

In this appendix the proofs of eqs.(4.22) and (4.23) are presented.

i) Proof of eq.(4.22)

Eqs. (4.16) and (4.20) allow us to write

$$\phi(\bar{r},t)\ \delta^s_{(m)}\ (\bar{r},t) = \sum_{j=0}^{\infty} \frac{(-1)^j}{j!}\ \delta^s_{(j)}\ [h_2h_3]_s^{-1} \int d\xi_1 (h_1h_2h_3\lambda^j\ \phi\ \delta^s_{(m)}) \ . \tag{C.1}$$

Substituting the definition of the $\delta^s_{(m)}$, eq.(4.11), into eq.(C.1) and integrating by parts m times gives

$$\phi(\bar{r},t)\ \delta^s_{(m)}\ (\bar{r},t) = \sum_{j=0}^{\infty} \frac{(-1)^{j+m}}{j!}\ \delta^s_{(j)}\ \left[\left(\frac{1}{h_1}\frac{\partial}{\partial\xi_1}\right)^m\ \lambda^j\ \phi \right]_s \ . \tag{C.2}$$

Since by definition, cf. eq.(4.18),

$$\lambda = 0 \text{ for } \xi_1 = 0 \text{ and } \frac{\partial \lambda}{\partial n} = 1 \ , \tag{C.3}$$

eq.(C.2) immediately reduces to

$$\phi(\bar{r},t)\ \delta^s_{(m)}(\bar{r},t) = \sum_{j=0}^{m} (-1)^{j+m}\ \delta^s_{(j)}\ \binom{m}{j}\ \left(\frac{\partial^{m-j}\phi}{\partial n^{m-j}}\right)_s \tag{C.4}$$

which is eq.(4.22).

ii) Proof of eq.(4.23)

Eqs.(4.8) and (4.15) imply

$$\left(\frac{\partial\, b^s_{(m)}\ \delta^s_{(m)}}{\partial t}\right)_{\bar{r}} = \left(\frac{\partial\, b^s_{(m)}}{\partial t}\right)_{\bar{\xi}} \delta^s_{(m)} - (\bar{v}\cdot\bar{\nabla} b^s_{(m)})\ \delta^s_{(m)} + b^s_{(m)} (\bar{\nabla}\cdot\bar{\alpha}_1)^m \left(\frac{\partial\, \delta^s_{(0)}}{\partial t}\right)_{\bar{r}}$$

$$+ b^s_{(m)} \sum_{k=0}^{m-1} (\bar{\nabla}\cdot\bar{\alpha}_1)^k \, \bar{\nabla}\cdot\left(\frac{\partial \bar{\alpha}_1}{\partial t}\right)_{\bar{r}} (\bar{\nabla}\cdot\bar{\alpha}_1)^{m-1-k} \, \delta^s_{(o)} \,. \tag{C.5}$$

The RHS of eq.(C.5) may now be multipole expanded. Using eq.(C.4) for the first two terms and eqs.(4.16) and (4.20) for the remaining ones, eq.(C.5) is rewritten as

$$\left(\frac{\partial\, b^s_{(m)}\, \delta^s_{(m)}}{\partial t}\right)_{\bar{r}} = \sum_{j=0}^{m} (-1)^{m-j} \binom{m}{j} \delta^s_{(j)} \left[\frac{\partial^{m-j}}{\partial n^{m-j}} \left(\left(\frac{\partial\, b^s_{(m)}}{\partial t}\right)_{\bar{\xi}} - \bar{v}\cdot\bar{\nabla}\, b^s_{(m)} \right) \right]_s$$

$$+ \sum_{j=0}^{\infty} \frac{(-1)^j}{j!} \delta^s_{(j)}\, b^s_{(m)} \, [h_2 h_3]_s^{-1} \int d\bar{r}' \, \delta(\xi_2 - \xi_2^o)\, \delta(\xi_3 - \xi_3^o)\, \lambda^j \{ (\bar{\nabla}\cdot\bar{\alpha}_1)^m \left(\frac{\partial\, \delta^s_{(o)}}{\partial t}\right)_{\bar{r}}$$

$$+ \sum_{k=0}^{m-1} (\bar{\nabla}\cdot\bar{\alpha}_1)^k \, \bar{\nabla}\cdot\left(\frac{\partial \bar{\alpha}_i}{\partial t}\right)_{\bar{r}} (\bar{\nabla}\cdot\bar{\alpha}_1)^{m-1-k} \, \delta^s_{(o)} \} \,. \tag{C.6}$$

Since $b^s_{(m)}$ does not depend on ξ_1, eq.(C.6) becomes

$$\left(\frac{\partial\, b^s_{(m)}\, \delta^s_{(m)}}{\partial t}\right)_{\bar{r}} = \delta^s_{(m)} \left(\frac{\partial\, b^s_{(m)}}{\partial t}\right)_{\bar{r},s} - \sum_{j=0}^{m-1} (-1)^{m-j} \binom{m}{j} \delta^s_{(j)} \left[\frac{\partial^{m-j}}{\partial n^{m-j}} (\bar{v}\cdot\bar{\nabla}_{/\!/} b^s_{(m)})\right]_s$$

$$+ \sum_{j=0}^{\infty} (-1)^{j-m} \delta^s_{(j)}\, b^s_{(m)} [h_2 h_3]_s^{-1} \int d\bar{r}' \, \{ \left(\frac{\partial\, \delta^s_{(o)}}{\partial t}\right)_{\bar{r}'} \frac{\lambda^{j-m}\, \delta(\xi_2 - \xi_2^o)\, \delta(\xi_3 - \xi_3^o)}{(j-m)!}$$

$$+ \sum_{k=0}^{m-1} \delta^s_{(o)} \frac{\partial^{m-1-k}}{\partial n^{m-1-k}} \left(\sum_{\ell=2}^{3} \left(\frac{\partial \bar{\alpha}_i}{\partial t}\right)_{\bar{r}} \cdot \frac{\partial}{\partial \xi_\ell} \left(\frac{\bar{\alpha}_\ell}{h_\ell} \frac{\lambda^{j-k}}{(j-k)!} \delta(\xi_2 - \xi_2^o)\, \delta(\xi_3 - \xi_3^o)\right) \right) \} \,, \tag{C.7}$$

where we have also integrated eq.(C.6) by parts m times and used eqs. (4.8), (4.10) and (C.3). It is easily shown by eqs.(4.8), (4.3) and (4.7) that

$$\left(\frac{\partial\, \delta^s_{(o)}}{\partial t}\right)_{\bar{r}} = -\left(\frac{\partial \ln h_i}{\partial t}\right)_{\bar{\xi}} \delta^s_{(o)} - \bar{v}\cdot\bar{\nabla}\,\delta^s_{(s)}$$

$$= -\bar{\alpha}_1\bar{\alpha}_1 : \overline{\overline{\nabla}\,\bar{v}}\;\delta^s_{(o)} - \bar{v}\cdot\bar{\nabla}\,\delta^s_{(o)}\,. \qquad (C.8)$$

Eq.(C.8) may be used to show that

$$(-1)^{j-m}[h_2h_3]_s^{-1}\int d\bar{r}\,\frac{\lambda^{j-m}}{(j-m)!}\,\delta(\xi_2-\xi_2^o)\,\delta(\xi_3-\xi_3^o)\left(\frac{\partial\, \delta^s_{(o)}}{\partial t}\right)_{\bar{r}} = -[\delta_{m,j+1}v_n + \delta_{m,j}v_n C]_s, \qquad (C.9)$$

where C is defined by eq.(4.24) and where eq.(1.3.6) of ref. 71 was used.

Inserting eq.(C.9) into eq.(C.7), performing the differentiation w.r.t ξ_ℓ, and again integrating by parts yields

$$\left(\frac{\partial\, b^s_{(m)}\,\delta^s_{(m)}}{\partial t}\right)_{\bar{r}} = \delta^s_{(m)}\left(\frac{\partial\, b^s_{(m)}}{\partial t}\right)_{\bar{r},s} - \sum_{j=0}^{m-1}(-1)^{m-j}\binom{m}{j}\,\delta^s_{(j)}\left[\frac{\partial^{m-j}}{\partial n^{m-j}}\left(\bar{v}\cdot\bar{\nabla}_{/\!/}\, b^s_{(m)}\right)\right]_s$$

$$+ b^s_{(m)}\{-\delta^s_{(m)}(C\,v_n)_s - \delta^s_{(m+1)}\,v_{n,s}$$

$$+ \sum_{j=0}^{\infty}\sum_{k=0}^{m-1}(-1)^{j-m}\,\delta^s_{(j)}\left[\binom{m-1-k}{j-k-1}\left[\frac{\partial^{m-j}}{\partial n^{m-j}}\left(\left(\frac{\partial\bar{\alpha}_1}{\partial t}\right)_{\bar{r}}\cdot\bar{\nabla}_{/\!/}\lambda\right)\right]_s\right.$$

$$\left. - \binom{m-1-k}{j-k}\sum_{\ell=2}^{3}[h_2h_3]_s^{-1}\frac{\partial}{\partial\xi_\ell}\left[h_2h_3\,\frac{\partial^{m-j-1}}{\partial n^{m-j-1}}\left(\frac{\bar{\alpha}_\ell}{h_\ell}\cdot\left(\frac{\partial\bar{\alpha}_1}{\partial t}\right)_{\bar{r}}\right)\right]_s\right]\} \qquad (C.10)$$

where eq.(C.2) was also used. Finally, by performing the sum over k in eq.(C.10) and using the identity[71]

$$\sum_{k=0}^{m} \binom{n+k}{n} = \binom{m+n+1}{n+1} , \qquad (C.11)$$

eq.(4.23) is obtained.

Appendix D: Proofs of Equations (4.55) and (4.56)

i) Proof of eq.(4.55)

From eqs.(4.27) and (4.53) it follows that

$$\theta^{\pm}(\bar{r},t) - \theta(\pm x) = \theta(\pm(x + \hat{\xi}_1(\bar{r},t))) - \theta(\pm x) . \tag{D.1}$$

Expanding the RHS of eq.(D.1) in a Taylor series in $\hat{\xi}_1$ about $\xi_1 = 0$ and retaining only terms to linear order yields

$$\theta^{\pm}(\bar{r},t) - \theta(\pm x) = \pm\, \hat{\xi}_1 \delta(x) \tag{D.2}$$

which is eq.(4.55).

Before eq.(4.56) can be derived, we require the forms of h_i and $\bar{\alpha}_i$ for small $\hat{\bar{\xi}}(\bar{r},t)$. These are obtained by expanding eqs.(4.3) and (4.2) to linear order in $\hat{\bar{\xi}}$. Thus, after a simple calculation we find that

$$h_i(\bar{r},t) = 1 - \frac{\partial \hat{\xi}_i}{\partial x_i}(\bar{r},t) \tag{D.3}$$

and

$$\bar{\alpha}_i(\bar{r},t) = \bar{e}_i + (\bar{\nabla} - \bar{e}_i \frac{\partial}{\partial x_i})\, \hat{\xi}_i(\bar{r},t) \tag{D.4}$$

to linear order in $\hat{\bar{\xi}}$.

Similarly, the orthogonality condition, eq.(4.4) and eq.(4.53) imply

$$\frac{\partial \hat{\xi}_i}{\partial x_j} + \frac{\partial \hat{\xi}_j}{\partial x_i} = 0 \qquad i \neq j \text{ (to linear order in } \hat{\bar{\xi}}). \tag{D.5}$$

ii) Proof of eq.(4.56)

By using eqs.(4.11), (4.15) and (4.53) it is easily shown that

$$\delta^{S}_{(j)}(\bar{r},t) - \delta^{(j)}(x) = (\bar{\nabla}\cdot\bar{\alpha}_i)^j \; (h_i^{-1}\; \delta(x+\hat{\xi}_i)) \; - \delta^{(j)}(x) \; . \qquad (D.6)$$

Expanding the RHS of eq.(D.6) to linear order in $\hat{\xi}_i$ (cf. eqs.(D.3) - (D.5)) gives

$$\delta^{S}_{(j)}(\bar{r},t) - \delta^{(j)}(x) = \frac{\partial^j}{\partial x^j}\left\{\left(\frac{\partial \hat{\xi}_i}{\partial x}\right)\delta(x) + \hat{\xi}_1\,\delta'(x)\right\}$$

$$+ \sum_{k=0}^{j-1} \frac{\partial^k}{\partial x^k}\left\{\bar{\nabla}\cdot\overline{\nabla_{//}}\;\hat{\xi}_1\;\left(\frac{\partial^{j-1-k}\,\delta(x)}{\partial\, x^{j-1-k}}\right)\right\} \qquad (D.7)$$

$$= \hat{\xi}_i\Big|_{x=0}\,\delta^{(j+1)}(x) + \bar{\nabla}_{//}\cdot\sum_{k=0}^{j-1}\sum_{\ell=0}^{k}\binom{k}{\ell}\left(\frac{\partial^{\ell}\,\bar{\nabla}_{//}\,\hat{\xi}_i}{\partial\, x^{\ell}}\right)\delta^{(j-1-\ell)}(x) \qquad (D.8)$$

Interchanging the summation order in eq.(D.8) and using eq.(D.5) and the identity eq.(C.11) allows us to write

$$\delta^{S}_{(j)} - \delta^{(j)}(x) = \hat{\xi}_1\Big|_{x=0}\,\delta^{(j+1)}(x) - \bar{\nabla}_{//}\sum_{\ell=0}^{j-1}\binom{j}{\ell+1}\left(\frac{\partial^{\ell+1}\,\hat{\xi}_{//}}{\partial\, x^{\ell+1}}\right)\delta^{(j-\ell-1)}(x) \qquad (D.9)$$

$$= \hat{\xi}_1\Big|_{x=0}\,\delta^{(j+1)}(x) + \bar{\nabla}_{//}\cdot\left(\hat{\xi} - \hat{\xi}\Big|_{x=0}\right)\delta^{(j)}(x) \qquad (D.10)$$

to linear order in $\hat{\xi}_i$. This is the required result.

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