8. Time Dependent Response Theory

8.1 INTRODUCTION

In this chapter we extend the nonlinear response theory discussed in Chapter 7 to describe the response of classical, many-body systems to time dependent external fields. The resulting formalism is applicable to both adiabatic and thermostatted systems. The results are then related to a number of known special cases: time dependent linear response theory, and time independent nonlinear response theory as described by the transient time correlation approach and the Kawasaki response formula.

We begin by developing a formal operator algebra for manipulating distribution functions and mechanical phase variables in a thermostatted system subject to a time dependent applied field. The analysis parallels perturbation treatments of quantum field theory (Raimes, 1972 and Parry, 1973). The mathematical techniques required for the time dependent case are sufficiently different from, and more complex than, those required in the time independent case that we have reserved their discussion until now. One of the main differences between the two types of nonequilibrium system is that time-ordered exponentials are required for the definition of propagators in the time dependent case. New commutivity constraints which have no counterparts in the time independent case, place severe limitations on the mathematical forms allowed to express the nonlinear time dependent response. In the time independent case two forms have already been met in Chapter 7: the Kawasaki and the Transient Time Correlation Function forms. In this chapter we will meet yet another. Of these three forms only **one** is applicable in the time dependent case.

8.2 TIME EVOLUTION OF PHASE VARIABLES

When a system is subject to time dependent external fields the equations of motion for both the distribution function and phase variables, become quite complex. There are two time dependences in such a system. One is associated with the time at which you wish to know the phase position $\mathbf{\Gamma}(t)$ and the other is associated with the explicit time

dependence of the field, $F_e(t)$. In order to deal with this complexity in a convenient way we introduce a more compact notation for the propagator. Apart from some important notational differences the initial development parallels that of Holian and Evans (1985). We define the p-propagator $U_R(0,t)$ to be the operator which advances a function of $\mathbf{\Gamma}$ only, forward in time from 0 to t (the meaning of the subscript will emerge later). That is

$$\mathbf{\Gamma}(t) = U_R(0,t)\mathbf{\Gamma}(0) \tag{8.1}$$

The operator $U_R(0,t)$ operates on all functions of phase located to its right. The equations of motion for the system at time t, which are themselves a function of phase $\mathbf{\Gamma}$, are given by

$$\dot{\mathbf{\Gamma}}(\mathbf{\Gamma}(t),t) = U_R(0,t)\ \dot{\mathbf{\Gamma}}(\mathbf{\Gamma}(0),t) \tag{8.2.2}$$

The notation $d\mathbf{\Gamma}(\mathbf{\Gamma}(t),t)/dt$ implies that the derivative should be calculated on the current phase $\mathbf{\Gamma}(t)$, using the current field $F_e(t)$. On the other hand $d\mathbf{\Gamma}(\mathbf{\Gamma}(0),t)/dt$ implies that the derivative should be calculated on the initial phase $\mathbf{\Gamma}(0)$, using the current field $F_e(t)$. The p-propagator $U_R(0,t)$ has no effect on explicit time. Its only action is to advance the implicit time dependence of the phase, $\mathbf{\Gamma}$.

The total time derivative of a phase function $B(\mathbf{\Gamma})$ with no explicit time dependence (by definition a phase function cannot have an explicit time dependence) is

$$\begin{aligned}
\frac{d}{dt}B(\mathbf{\Gamma}(t)) &= \dot{\mathbf{\Gamma}}[\mathbf{\Gamma}(t),t]\cdot\left.\frac{\partial B(\mathbf{\Gamma})}{\partial\mathbf{\Gamma}}\right|_{\mathbf{\Gamma}=\mathbf{\Gamma}(t)} \\
&= U_R(0,t)\,\dot{\mathbf{\Gamma}}[\mathbf{\Gamma},t]\cdot\left.\frac{\partial}{\partial\mathbf{\Gamma}}B(\mathbf{\Gamma})\right|_{\mathbf{\Gamma}} \\
&= U_R(0,t)\ iL(t)\ B(\mathbf{\Gamma}) \\
&= \frac{\partial}{\partial t}U_R(0,t)\,B(\mathbf{\Gamma})
\end{aligned} \tag{8.2.3}$$

where we have introduced the time dependent p-Liouvillean, $iL(t) \equiv iL(\mathbf{\Gamma},t)$ which acts on functions of the *initial* phase $\mathbf{\Gamma}$, but contains the external field at the *current* time. The partial derivative of B with respect to initial phase $\mathbf{\Gamma}$ is simply another phase function, so that the propagator $U_R(0,t)$ advances this phase function to time t (that is the partial derivative of B with respect to phase evaluated at time t). In writing the last line of (8.2.3) we have used the fact that the p-propagator is an explicit function of time (as well as phase), and that when written in terms of the p-propagator, $dB(\mathbf{\Gamma}(t))/dt$, must

only involve the partial time derivative of the p-propagator. Equation (8.2.3) implies that the p-propagator $U_R(0,t)$ satisfies an operator equation of the form

$$\frac{\partial}{\partial t} U_R(0,t) \;=\; U_R(0,t)\;\; iL(t) \tag{8.2.4}$$

where the order of the two operators on the right-hand side is crucial. As we shall see shortly, $U_R(0,t)$ and $iL(t)$ do not commute since the propagator $U_R(0,t)$ contains sums of products of $iL(s_i)$ at different times s_i, and $iL(s_i)$ and $iL(s_j)$, do not commute unless $s_i = s_j$. The formal solution of this operator equation is

$$U_R(0,t) = \sum_{n=0}^{\infty} \int_0^t ds_1 \int_0^{s_1} ds_2 \,\ldots\, \int_0^{s_{n-1}} ds_n \;\; iL(s_n) \,\ldots\, iL(s_2)\, iL(s_1) \tag{8.2.5}$$

Notice that the p-Liouvilleans are *right ordered* in time (latest time to the right). As Liouvilleans do not commute this time ordering is fixed. The integration limits imply that $t > s_1 > s_2 > .... > s_n$, so that the time arguments of the p-Liouvilleans in the expression for $U_R(0,t)$ increase as we move from the left to the right. It is very important to remember that in generating B(t) from B(0) using (8.2.5), if we write the integrals as say, a trapezoidal approximation it is the Liouvillean at the **latest** time iL(t), which attacks B(0) first. The Liouvilleans attack B in an *anti-causal* order. We will have more to say on this issue in §8.4.

We can check that (8.2.5) is the solution to (8.2.4) by differentiating with respect to time. We see that, $\int_0^{\infty} ds_1$ disappears and the argument $iL(s_1)$, changes to $iL(t)$. This term appears on the right hand side, as it must to satisfy the differential operator equation. It is easy to derive an equation for the incremental p-propagator $U_R(\tau,t)$ which advances a phase function from time τ to t,

$$U_R(\tau,t) \;=\; \sum_{n=0}^{\infty} \int_\tau^t ds_1 \int_\tau^{s_1} ds_2 \,\ldots\, \int_\tau^{s_{n-1}} ds_n \;\; iL(s_n) \,\ldots\, iL(s_2)\, iL(s_1) \tag{8.2.6}$$

Our convention for the time arguments of the U-propagators is that the first argument (in this case τ), is the lower limit of all the integrals. The second argument (in this case t), is the upper limit of the first integral.

8.3 THE INVERSE THEOREM

We will assume that $t > 0$. Intuitively it is obvious that the inverse of $U_R(0,t)$, which we write as $U_R(0,t)^{-1}$, should be the propagator that propagates backwards in time from t to 0. From (8.2.6) we can write down

$$U_R(0,t)^{-1} = \sum_{n=0}^{\infty} \int_t^0 ds_1 \int_t^{s_1} ds_2 \ldots \int_t^{s_{n-1}} ds_n \; iL(s_n) \ldots iL(s_2)\, iL(s_1) \qquad (8.3.1)$$

Before proceeding further we will introduce an identity which is useful for manipulating these types of integrals. Often we will have a pair of integrals which we want to exchange. The limits of the inner most integral depend on the integration variable for the outer integral. The result we shall use is the following, that

$$\int_{t_0}^{t} ds_1 \int_{t_0}^{s_1} ds_2 = \int_{t_0}^{t} ds_2 \int_{s_2}^{t} ds_1 \qquad (8.3.2)$$

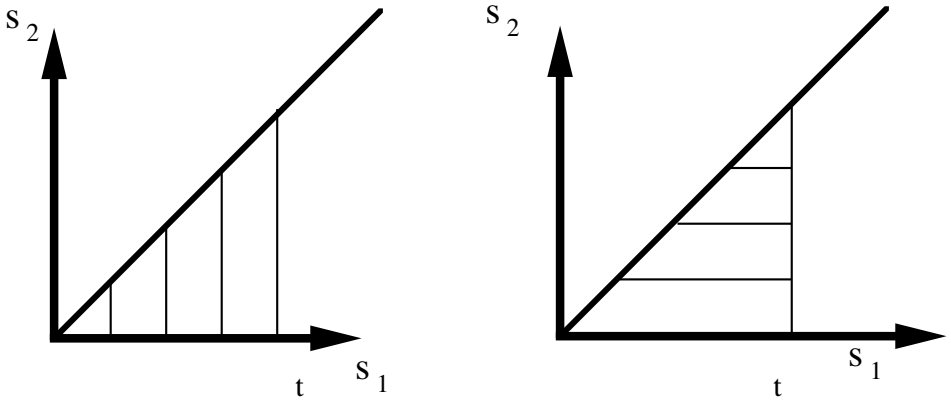

Figure 8.1

As can be seen from Figure 8.1, the range of integration for both integrals is the same. If we approximate the integral as a sum we see that the difference is in the order in which the contributions are summed. As long as the original integral is absolutely convergent the result is true. We will assume that all integrals are absolutely convergent.

It is illustrative to develop other representations of $U_R(0,t)^{-1}$ so we consider the expression (8.3.1) term by term,

$$U_R(0,t)^{-1} = 1 + \int_t^0 ds\, iL(s) + \int_t^0 ds_1 \int_t^{s_1} ds_2\, iL(s_2)\, iL(s_1) + \int_t^0 ds_1 \int_t^{s_1} ds_2 \int_t^{s_2} ds_3\, iL(s_3) iL(s_2) iL(s_1)$$
$$+ \ldots\ldots \qquad (8.3.3)$$

Interchanging the integration limits in every integral gives a factor of minus one for each interchange.

$$U_R(0,t)^{-1} = 1 - \int_0^t ds\, iL(s) + \int_0^t ds_1 \int_{s_1}^t ds_2\, iL(s_2)iL(s_1) - \int_0^t ds_1 \int_{s_1}^t ds_2 \int_{s_2}^t ds_3\, iL(s_3)iL(s_2)iL(s_1) + .. \tag{8.3.4}$$

We can use the integral interchange result (8.3.2) on the third term on the RHS (note that the integrand is unchanged by this operation). In the fourth term we can use the interchange result three times to completely reverse the order of the integrations giving,

$$U_R(0,t)^{-1} = 1 - \int_0^t ds\, iL(s) + \int_0^t ds_2 \int_0^{s_2} ds_1\, iL(s_2)iL(s_1) - \int_0^t ds_3 \int_0^{s_3} ds_2 \int_0^{s_2} ds_1\, iL(s_3)iL(s_2)iL(s_1) + . \tag{8.3.5}$$

The final step is to relabel the dummy integration variables to give

$$U_R(0,t)^{-1} = 1 - \int_0^t ds\, iL(s) + \int_0^t ds_1 \int_0^{s_1} ds_2\, iL(s_1)iL(s_2) - \int_0^t ds_1 \int_0^{s_1} ds_2 \int_0^{s_2} ds_3\, iL(s_1)iL(s_2)iL(s_3) + ..$$

$$U_R(0,t)^{-1} = \sum_{n=0}^{\infty} (-)^n \int_0^t ds_1 \int_0^{s_1} ds_2 \ldots \int_0^{s_{n-1}} ds_n\, iL(s_1)\, iL(s_2) \ldots iL(s_n) \tag{8.3.6}$$

As $t > 0$, an examination of the integration limits reveals that the Liouvilleans in this expression are left-ordered. Comparing this expression with the definition of $U_R(0,t)$ there are two differences, the time ordering **and** the factor of $(-)^n$. We now define the operator $U_L(0,t)$ to be equal to the RHS of (8.3.6), so we have

$$U_L(0,t) \equiv \sum_{n=0}^{\infty} (-)^n \int_0^t ds_1 \int_0^{s_1} ds_2 \ldots \int_0^{s_{n-1}} ds_n\, iL(s_1)\, iL(s_2) \ldots iL(s_n) \tag{8.3.7}$$

and

$$U_R(0,t)^{-1} = U_L(0,t) \tag{8.3.8}$$

From this definition of $U_L(0,t)$, it can be shown that $U_L(0,t)$ satisfies the operator equation

$$\frac{\partial}{\partial t} U_L(0,t) = - iL(t)\, U_L(0,t) \tag{8.3.9}$$

This result can be obtained by differentiating the definition of $U_L(0,t)$, (8.3.7), or by differentiating $U_R(0,t)^{-1}$, (8.3.1), directly. Equation (8.3.9) allows us to verify that $U_L(0,t)$ is the inverse of $U_R(0,t)$ in a new way. First we note that $U_L(0,t)\, U_R(0,t) = 1$ is true for t=0. Then differentiating with respect to time we find that,

$$\frac{\partial}{\partial t}\left[U_R(0,t)\, U_L(0,t)\right] = \left[\frac{\partial}{\partial t}\, U_R(0,t)\right] U_L(0,t) + U_R(0,t)\left[\frac{\partial}{\partial t}\, U_L(0,t)\right]$$

$$= U_R(0,t)\, iL(t)\, U_L(0,t) - U_R(0,t)\, iL(t)\, U_L(0,t)$$

$$= 0, \quad \forall t. \tag{8.3.10}$$

As the result is true at t=0, and the time derivative of each side of the equation is true for all time, the result is true for all time.

8.4 The Associative Law and Composition Theorem

The action of the p-propagator $U_R(0,t)$ is to advance the phase $\mathbf{\Gamma}$, or a phase variable, forward in time from 0 to t. This must be equivalent to advancing time from 0 to s, then advancing time from s to t, whenever $0 < s < t$. This implies that

$$U_R(0,t)\; B(\mathbf{\Gamma}) = U_R(s,t)\left[U_R(0,s)\; B(\mathbf{\Gamma})\right] = U_R(s,t)\, B(s) \tag{8.4.1}$$

The right hand side of (8.4.1) is a physical rather than mathematical statement. It is a statement of causality. If we wish to understand how we can **generate** B(t) from B(0) through an intermediate time s, we find that we will have to attack B first with the operator $U_R(s,t)$ and then attack the resultant expression with $U_R(0,s)$. The operator expression $U_R(s,t)U_R(0,s)B$ cannot be equal to $U_R(0,t)$, because its time arguments are not ordered from left to right. The correct operator equation is

$$U_R(0,t) = U_R(0,s)\; U_R(s,t) \tag{8.4.2}$$

To prove (8.4.2) we consider the product on the right-hand side and show that it is equal to $U_R(0,t)$.

$$U_R(0,s)U_R(s,t) = \Big(\sum_{m=0}^{\infty}\int_0^s ds_1 .. \int_0^{s_{m-1}} ds_m\; iL(s_m)\ldots iL(s_1)\Big)\Big(\sum_{n=0}^{\infty}\int_s^t ds_1' .. \int_s^{s_{n-1}'} ds_n'\; iL(s_n')\ldots iL(s_1')$$

$$= 1 + \int_0^t ds_1\; iL(s_1) + \int_0^s ds_1 \int_0^{s_1} ds_2\; iL(s_2)\, iL(s_1)$$

$$+ \int_0^s ds_1\, iL(s_1) \int_s^t ds_1'\, iL(s_1') + \int_s^t ds_1' \int_s^{s_1'} ds_2'\, iL(s_2')\, iL(s_1') + \ldots\ldots \tag{8.4.3}$$

The first two terms are straightforward so we will consider in detail the three second order terms. In the second of these three terms the integration limits imply that

$$0 < s_1 < s < s_1' < t$$

so that the time arguments of the operator product are correctly ordered, and we relabel them as follows:

$$s_1' \rightarrow s_1 \quad \text{and} \quad s_1 \rightarrow s_2$$

The integration limits are independent, so we can interchange the order of integration, (8.3.2). After dropping the primes in the third term, all three terms have the same integrand so we need only consider the integration limits. The three second order terms are

$$\int_0^s ds_1 \int_0^{s_1} ds_2 + \int_s^t ds_1 \int_0^s ds_2 + \int_s^t ds_1 \int_s^{s_1} ds_2$$

In the second and third terms, the s_1 integrals are the same and the s_2 integrals add together to give

$$\int_0^s ds_1 \int_0^{s_1} ds_2 + \int_s^t ds_1 \int_0^{s_1} ds_2$$

Now the s_2 integrals are identical and the s_1 integrals add together to give the required result

$$\int_0^t ds_1 \int_0^{s_1} ds_2$$

This is exactly the second order term in $U_R(0,t)$. It may seem that we have laboured through the detail of the second order term, but it is now straightforward to apply the same steps to all the higher order terms and see that the result is true to all orders. Indeed it is a useful exercise for the reader to examine the third order term, as there are

four integrals to consider, and after the same relabelling process is applied to the second and third terms, the four integrals obtained collapse from the right-hand side.

Combining equations (8.4.1) and (8.4.2) we see that the p-propagator U_R obeys an anti-causal associative law, (8.4.1). The fundamental reason for its anti-causal form is implicit in the form of the p-propagator itself, U_R. In applying the p-propagator to a phase variable it is, as we have seen, the latest times that attack the phase variable first.

Apart from the present discussion we will always write operators in a form which reflects the mathematical rather than the causal ordering. As we will see any confusion that arises from the anti-causal ordering of p-propagators can always be removed by considering the f-propagator form and then unrolling the operators in sequence to attack the phase variables. The f-propagators are causally ordered.

8.5 TIME EVOLUTION OF THE DISTRIBUTION FUNCTION

The Liouville equation for a system subject to a time dependent external field is given by

$$\frac{\partial}{\partial t} f(t) \;=\; - \frac{\partial}{\partial \mathbf{\Gamma}} \cdot \left[\dot{\mathbf{\Gamma}}(\mathbf{\Gamma},t)\, f(\mathbf{\Gamma},t) \right] \;=\; - iL(t)\, f(t) \tag{8.5.1}$$

where we have defined the time dependent f-Liouvillean, $iL(t)$. This equation tells you that if you sit at a **fixed** point in phase space denoted by the dummy variable $\mathbf{\Gamma}$, the density of phase points near $\mathbf{\Gamma}$, changes with time in accord with (8.5.1). In the derivation of this equation we related the partial derivative of f(t) to various fluxes in phase space at the *same* value of the explicit time.

We define the distribution function propagator $U_R^\dagger(0,t)$ which advances the time dependence of the distribution function from 0 to t, by

$$f(\mathbf{\Gamma},t) \;=\; U_R^\dagger(0,t)\; f(\mathbf{\Gamma},0) \tag{8.5.2}$$

In this equation $U_R^\dagger(0,t)$ is the adjoint of $U_R(0,t)$. It is therefore closely related to $U_L(0,t)$ except that the Liouvilleans appearing in equation (8.3.7) are replaced by their adjoints $iL(s_i)$. Combining equation (8.5.2) with the Liouville equation (8.5.1) we find that $U_R^\dagger(0,t)$ satisfies the following equation of motion

$$\frac{\partial}{\partial t} U_R^\dagger(0,t) \;=\; - iL(\mathbf{\Gamma},t)\; U_R^\dagger(0,t) \tag{8.5.3}$$

The formal solution to this operator equation is

$$U_R^{\dagger}(0,t) = \sum_{n=0}^{\infty} (-)^n \int_0^t ds_1 \int_0^{s_1} ds_2 \ldots \int_0^{s_{n-1}} ds_n \; iL(s_1)\, iL(s_2) \ldots iL(s_n) \tag{8.5.4}$$

In distinction to the propagator for phase variables, the integration limits imply that $t > s_1 > s_2 > .... > s_n$, so that the f-Liouvilleans are *left time ordered*. The time arguments increase as we go from the right to the left. This is opposite to the time ordering in the p-propagator $U_R(0,t)$ but the definition of $U_R^{\dagger}(0,t)$ is consistent with the definition of $U_L(0,t)$.

For the f-propagator $U_R^{\dagger}(0,t)$, the usual associative law is satisfied as the time arguments are ordered right to left,

$$U_R^{\dagger}(0,t)\, f(0) = \left[U_R^{\dagger}(s,t)\, U_R^{\dagger}(0,s) \right] f(0) = U_R^{\dagger}(s,t) \left[U_R^{\dagger}(0,s)\, f(0) \right] \tag{8.5.5}$$

This equation can be verified directly using similar arguments to those used in §8.4.

8.6 TIME ORDERED EXPONENTIALS

A notation which is common in quantum mechanics is to refer to the phase and distribution function propagators as *right* and *left ordered exponentials* ($\exp_R$ and $\exp_L$) respectively. To exploit this notational simplification we introduce the time ordering operators T_R and T_L. The operator T_R simply reorders a product of operators so that the time arguments increase from left to right. In this notation we write the p-propagator $U_R(0,t)$ as

$$U_R(0,t) = \exp_R\left(\int_0^t ds\, iL(s) \right) = T_R \exp\left(\int_0^t ds\, iL(s) \right) \tag{8.6.1}$$

Using the series expansion for the exponential this becomes

$$U_R(0,t) = T_R \sum_{n=0}^{\infty} \frac{1}{n!} \int_0^t ds_1 \int_0^t ds_2 \ldots \int_0^t ds_n \; iL(s_n) \ldots iL(s_2)\, iL(s_1) \tag{8.6.2}$$

Taking this series term by term the first two terms are trivial. We will consider the second order term in some detail.

$$T_R \frac{1}{2!}\int_0^t ds_1 \int_0^t ds_2 \; iL(s_2)\, iL(s_1)$$

$$= \frac{1}{2!} T_R \left\{ \int_0^t ds_1 \int_0^{s_1} ds_2 \; iL(s_2)\, iL(s_1) + \int_0^t ds_1 \int_{s_1}^t ds_2 \; iL(s_2)\, iL(s_1) \right\} \tag{8.6.3}$$

The time arguments in the first integral are time ordered from left to right so the operator will have no effect. In the second integral the order of the integrations can be interchanged to give

$$\int_0^t ds_2 \int_0^{s_2} ds_1 \; iL(s_2)\, iL(s_1) = \int_0^t ds_1 \int_0^{s_1} ds_2 \; iL(s_1)\, iL(s_2) \tag{8.6.4}$$

The second form is obtained by relabelling the dummy variables s_1 and s_2. Now both integrals have the same integration limits, and after the operation of T_R both integrands are the same, so the second order term is

$$\int_0^t ds_2 \int_0^{s_2} ds_1 \; iL(s_2)\, iL(s_1)$$

Using exactly the same steps we can show that each of the higher order terms are the same as those in the original representation of $U_R(0,t)$. After manipulating the integrals to obtain the same range of integration for each term of a particular order, the integrand is the sum of all permutations of the time arguments. At the n^{th} order there are n! permutations, which after the operation of T_R are all identical. This n! then cancels the $(n!)^{-1}$ from the expansion of the exponential, and the result follows. Using the same arguments, the f-propagator $U_R^{\dagger}(0,t)$ also be written in this form

$$U_R^{\dagger}(0,t) = \exp_L\left(-\int_0^t ds\; iL(s) \right) = T_L \exp\left(-\int_0^t ds\; iL(s) \right) \tag{8.6.5}$$

The use of the time ordering operator can realise considerable simplifications in many of the proofs that we have given.

Using time ordered exponentials, the Composition theorem can be derived quite easily.

$$B(t) = T_R \exp[\int_0^t d\tau\, iL(\tau)]\, B$$

$$= T_R \exp[\int_0^s d\tau\, iL(\tau)] \exp[\int_s^t d\tau\, iL(\tau)]\, B \qquad (8.6.6)$$

Because the exponentials are already right ordered we can write them as,

$$B(t) = T_R\{ \exp[\int_0^s d\tau\, iL(\tau)]\}\, T_R\, \{ \exp[\int_s^t d\tau\, iL(\tau)]\}B$$

$$= \exp_R[\int_0^s d\tau\, iL(\tau)]\ \exp_R[\int_s^t d\tau\, iL(\tau)]\, B \qquad (8.6.7)$$

8.7 SCHRÖDINGER AND HEISENBERG REPRESENTATIONS

In this section we will derive some of the more important properties of the Liouville operators. These will lead us naturally to the discussion of the various representations for the properties of classical systems. The first property we shall discuss relates the p-Liouvillean to the f-Liouvillean as follows;

$$\int d\mathbf{\Gamma}\, f(0)\, iL(t)\, B(\mathbf{\Gamma}) = -\int d\mathbf{\Gamma}\, B(\mathbf{\Gamma})\, iL(t)\, f(0) \qquad (8.7.1)$$

The proof is a straightforward application of integration by parts.

$$\int d\mathbf{\Gamma}\, f(0)\, \dot{\mathbf{\Gamma}}(\mathbf{\Gamma}, t).\frac{\partial}{\partial \mathbf{\Gamma}} B\Big|_{\mathbf{\Gamma}}$$

$$= f(0)\ \dot{\mathbf{\Gamma}}(\mathbf{\Gamma}, t)\, B(\mathbf{\Gamma})\Big]_S - \int d\mathbf{\Gamma}\, B(\mathbf{\Gamma}) \frac{\partial}{\partial \mathbf{\Gamma}}.(f(0)\, \dot{\mathbf{\Gamma}}(\mathbf{\Gamma}, t))$$

$$= -\int d\mathbf{\Gamma}\, B(\mathbf{\Gamma}) \left\{ \dot{\mathbf{\Gamma}}(\mathbf{\Gamma}, t).\frac{\partial}{\partial \mathbf{\Gamma}} + \frac{\partial}{\partial \mathbf{\Gamma}}.\dot{\mathbf{\Gamma}}(\mathbf{\Gamma}, t) \right\} f(0)$$

$$= -\int d\mathbf{\Gamma}\, B(\mathbf{\Gamma})\, iL(t)\, f(0) \qquad (8.7.2)$$

Equation (8.7.1) shows that iL(t) and -iL(t) are adjoints.

We can compute the average of a phase variable B at time t by following the value of B(t) as it changes along single trajectories in phase space. The average is taken by summing over the values of B for trajectories starting from each possible initial phase

point $\mathbf{\Gamma}$, but weighting each B(t) with the probability of that **starting** phase. These probabilities are chosen from an initial distribution function f($\mathbf{\Gamma}$,0). This is the so-called Heisenberg picture.

$$< B(t) > \; = \; \int d\mathbf{\Gamma} \;\; B(\mathbf{\Gamma}(t)) \;\; f(\mathbf{\Gamma},0) \;\; = \; \int d\mathbf{\Gamma} \;\; f(\mathbf{\Gamma},0) \;\; U_R(0,t) \;\; B(\mathbf{\Gamma}) \qquad (8.7.3)$$

The Heisenberg picture is exactly analogous to the Lagrangian formulation of fluid mechanics, we can imagine that the phase space *mass point* has a differential box d$\mathbf{\Gamma}$ surrounding it which changes shape (and volume for a compressible fluid) with time as the phase point follows its trajectory. The probability of the differential element, or mass f($\mathbf{\Gamma}$) d$\mathbf{\Gamma}$ remains constant, but the value of the observable changes implicitly in time.

The second view is the Schrödinger, or distribution based picture, where the $\mathbf{\Gamma}$ refers not to the initial value of the phase point, but to a stationary point (fixed for all time) inside a stationary differential box d$\mathbf{\Gamma}$. Just as in the Eulerian formulation of fluid mechanics, the observable takes on a fixed value for all time B($\mathbf{\Gamma}$), while mass points with different probability flow through the box.

$$< B(t) > \; = \; \int d\mathbf{\Gamma} \;\; B(\mathbf{\Gamma}) \;\; f(\mathbf{\Gamma},t) \;\; = \; \int d\mathbf{\Gamma} \; B(\mathbf{\Gamma}) \;\; U_R^{\dagger}(0,t) \;\; f(\mathbf{\Gamma},0) \qquad (8.7.4)$$

The average value of B changes with time as the distribution function changes. The average of B is computed by multiplying the value of B at $\mathbf{\Gamma}$, by the probability of find the phase point $\mathbf{\Gamma}$ at time t, that is f($\mathbf{\Gamma}$,t).

The average value of a phase variable B at time t can be evaluated in the two ways. The mathematical proof of the equivalence of the Schrödinger and Heisenberg pictures can be obtained by successive integrations by parts. Consider

$$\int d\mathbf{\Gamma} \; f(0) \; B(\mathbf{\Gamma}(t)) \;\; = \;\; \int d\mathbf{\Gamma} \;\; f(0) \;\; U_R(0,t) \;\; B(\mathbf{\Gamma})$$

$$= \; \sum_{n=0}^{\infty} \int_0^t ds_1 \; \ldots \int_0^{s_{n-1}} ds_n \; \int d\mathbf{\Gamma} \;\; f(0) \;\; iL(s_n) \; \ldots \; iL(s_1) \; B(\mathbf{\Gamma}) \qquad (8.7.5)$$

One can unroll each Liouvillean in turn from the phase variable onto the distribution function using equation (8.7.1). For the first transfer we consider $iL(s_{n-1})...iL(s_1)B$ to be the composite phase variable, so that the right hand side becomes,

$$= \sum_{n=0}^{\infty} \int_0^t ds_1 \ldots \int_0^{s_{n-1}} ds_n \; (-) \int d\mathbf{\Gamma} \left(iL(s_n)\, f(0) \right) iL(s_{n-1}) \ldots iL(s_1)\, B(\mathbf{\Gamma})$$

We can then repeat this operator unrolling,

$$= \sum_{n=0}^{\infty} \int_0^t ds_1 \ldots \int_0^{s_{n-1}} ds_n \; (-)^2 \int d\mathbf{\Gamma} \; \left(iL(s_{n-1})\, iL(s_n)\, f(0) \right) iL(s_{n-2}) \ldots iL(s_1)\, B(\mathbf{\Gamma})$$

Repeated unrolling leads to

$$= \sum_{n=0}^{\infty} \int_0^t ds_1 \ldots \int_0^{s_{n-1}} ds_n \; (-)^n \int d\mathbf{\Gamma}\, B(\mathbf{\Gamma})\, iL(s_1)\, iL(s_2) \ldots iL(s_n)\, f(0)$$

$$= \int d\mathbf{\Gamma}\, B(\mathbf{\Gamma}) \sum_{n=0}^{\infty} (-)^n \int_0^t ds_1 \ldots \int_0^{s_{n-1}} ds_n \; iL(s_1) \ldots iL(s_n)\, f(0)$$

$$= \int d\mathbf{\Gamma}\; B(\mathbf{\Gamma})\; U_R^{\dagger}(0,t)\; f(0)$$

$$= \int d\mathbf{\Gamma}\; B(\mathbf{\Gamma})\; f(t) \qquad (8.7.6)$$

We have obtained this result where the Liouvilleans explicitly depend on time. The derivation we have used has not made any reference to the details of either the initial distribution function or the first order equations of motion of the system. That means that these results are valid for arbitrary equations of motion, in particular the equations of motion can contain a time dependent external field. The initial distribution function is also arbitrary, the only constraint is that the distribution function at time t must have evolved from the initial distribution function under the influence of the perturbed equations of motion. They are also valid regardless of whether the equations of motion can be derived from a Hamiltonian or whether they satisfy AI$\mathbf{\Gamma}$ (§5.3).

8.8 THE DYSON EQUATION

The Dyson equation is useful for deriving relationships between propagators. We first met a restricted form of this equation in §3.6 when we were dealing with time independent propagators. We will now give a general derivation of the Dyson equation.

For two arbitrary p-Liouvilleans, the most general form of the Dyson equation is

$$U_R(0,t) = U_{R0}(0,t) + \int_0^t ds\ U_R(0,s)\ (iL(s) - iL_0(s))\ U_{R0}(s,t) \qquad (8.8.1)$$

and

$$U_R(0,t) = U_{R0}(0,t) + \int_0^t ds\ U_{R0}(0,s)\ (iL(s) - iL_0(s))\ U_R(s,t) \qquad (8.8.2)$$

Both Liouvilleans iL(t) and iL_0 (t) may be time dependent. One can prove the correctness of these equations by showing that the left and right hand sides of (8.8.1) and (8.8.2) satisfy the same differential equations with identical initial conditions. The corresponding equations for left ordered propagators are:

$$U_R^\dagger(0,t) = U_{R0}^\dagger(0,t) - \int_0^t ds\ U_R^\dagger(s,t)\ (iL(s) - iL_0(s))\ U_{R0}^\dagger(0,s) \qquad (8.8.3)$$

$$U_R^\dagger(0,t) = U_{R0}^\dagger(0,t) - \int_0^t ds\ U_{R0}^\dagger(s,t)\ (iL(s) - iL_0(s))\ U_R^\dagger(0,s) \qquad (8.8.4)$$

We will give a proof for one of these equations, equation (8.8.2). Proofs for the other equations are very similar. If we let LHS denote $U_R(0,t)$, the left hand side of (8.8.2), we know that,

$$\frac{\partial}{\partial t} LHS = U_R(0,t)\ iL(t) = LHS\ iL(t) \qquad (8.8.5)$$

On the other hand we see that,

$$\frac{d}{\partial t} RHS = U_{R0}(0,t)iL_0(t) + U_{R0}(0,t)(iL(t) - iL_0(t)) + \int_0^t ds\ U_{R0}(0,s)(iL(s) - iL_0(s))U_R(s,t)iL(t)$$

$$= RHS\ iL(t) \qquad (8.8.6)$$

Thus since both sides of equation (8.8.1) satisfy the same differential equation with the same initial condition, both sides must be the same for all time.

8.9 RELATION BETWEEN *p*- AND *f*-PROPAGATORS

In order to be able to manipulate propagators for thermostatted systems it is useful to be able to relate p-propagators and f-propagators. The relation we shall derive is a time dependent generalisation of equation (7.2.17). It is a relatively straightforward

application of the Dyson equation. We let $U_R(0,t) = \exp_R \int_0^t iL(s)ds$, be the test propagator and $U_{R0}(0,t) = \exp_R \int_0^t iL(s)\, ds$, be the reference propagator. $iL(s)A(\mathbf{\Gamma}) = \partial(A(\mathbf{\Gamma})\, d\mathbf{\Gamma}/dt)\bullet/\partial\mathbf{\Gamma}$ and $iL(s)A(\mathbf{\Gamma}) = d\mathbf{\Gamma}/dt \bullet \partial(A(\mathbf{\Gamma}))/\partial\mathbf{\Gamma}$.

Substitution into the Dyson equation gives,

$$U_R(0,t) = U_{R0}(0,t) + \int_0^t ds\, U_R(0,s)\, (iL(s) - iL(s))\, U_{R0}(s,t) \tag{8.9.1}$$

We define,

$$iL(s) - iL(s) \equiv \Lambda(\mathbf{\Gamma},s) = [\frac{\partial}{\partial\mathbf{\Gamma}} \bullet \dot{\mathbf{\Gamma}}(s)] \tag{8.9.2}$$

It is important to realise that Λ is a phase variable **not** an operator. Λ is known as the phase space compression factor since $d\ln f(t)/dt = -\Lambda = 3N\alpha(t) + O(1)$ (see (7.2.10)).

One can recursively substitute for U_R in equation (8.9.1) to eliminate U_R from the right hand side. This gives,

$$U_R(0,t) = U_{R0}(0,t) + \int_0^t ds_1\, U_{R0}(0,s_1)\, \Lambda(s_1)\, U_{R0}(s_1,t)$$

$$+ \int_0^t ds_1 \int_0^{s_1} ds_2\; U_{R0}(0,s_2)\, \Lambda(s_2)\, U_{R0}(s_2,s_1)\, \Lambda(s_1)\, U_{R0}(s_1,t) + \ldots\ldots\ldots \tag{8.9.3}$$

Using the fact that Λ is a phase variable rather than an operator we see that,

$$U_R(0,t) = U_{R0}(0,t) + \int_0^t ds_1\, \Lambda(\mathbf{\Gamma}(s_1),s_1)\, U_{R0}(0,t)$$

$$+ \int_0^t ds_1 \int_0^{s_1} ds_2\; \Lambda(\mathbf{\Gamma}(s_2),s_2)\, \Lambda(\mathbf{\Gamma}(s_1),s_1)\, U_{R0}(0,t) + \ldots\ldots\ldots \tag{8.9.4}$$

So that,

$$U_R(0,t) = \exp[\int_0^t ds\; \Lambda(\mathbf{\Gamma}(s),s)\,]\; U_{R0}(0,t) \tag{8.9.5}$$

or,

$$\exp_R[\int_0^t ds\ iL(s)\ ] = \exp[\int_0^t ds\ \Lambda(\mathbf{\Gamma}(s),s)]\ \exp_R[\int_0^t ds\ iL(s)\ ] \qquad (8.9.6)$$

This result is fundamental to our understanding of the dynamic behaviour of thermostatted systems. Its correctness can easily be checked by verifying that the left and right hand sides satisfy the same differential equation with the same initial condition. At zero time both sides are equal to unity. The derivative of the left hand side is,

$$\frac{\partial}{\partial t}\ [\mathrm{LHS}] = \exp_R[\int_0^t ds\ iL(s)]\ iL(t) = \mathrm{LHS}\ iL(t) \qquad (8.9.7)$$

While the derivative of the right hand side is,

$$\frac{\partial}{\partial t}\ \left[\mathrm{RHS}\right] = \exp\ [\int_0^t ds\ \Lambda(\mathbf{\Gamma}(s),s)]\ \Lambda(\mathbf{\Gamma}(t),t)\ \exp_R[\int_0^t ds\ iL(s)]$$

$$+\ \mathrm{RHS}\ iL(\mathbf{\Gamma},t)$$

$$= \left[\ \mathrm{RHS}\ \right]\ \Lambda(\mathbf{\Gamma},t) + \left[\ \mathrm{RHS}\ \right] iL(\mathbf{\Gamma},t) = \mathrm{RHS}\ iL(\mathbf{\Gamma},t) \qquad (8.9.8)$$

Thus the right hand side and the left hand sides are identical.

8.10 TIME DEPENDENT RESPONSE THEORY

Consider an equilibrium ensemble of systems, characterised by a distribution function, f_0, subject at t=0, to an external time dependent field $F_e(t)$. We assume that the equilibrium system (t<0), has evolved under the influence of the Gaussian isokinetic Liouvillean iL_0. This Liouvillean has no explicit time dependence. The equilibrium distribution could be the canonical or the isokinetic distribution. These assumptions are summarised by the equation,

$$\frac{\partial f_0}{\partial t} = -\ iL_0\ f_0 = 0 \qquad (8.10.1)$$

The equations of motion for the system can be written as,

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m} + \mathbf{C}_i(\mathbf{\Gamma})\, F_e(t)$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i + \mathbf{D}_i(\mathbf{\Gamma})\, F_e(t) - \alpha(\mathbf{\Gamma}, t)\, \mathbf{p}_i \qquad (8.10.2)$$

Provided that the temperature can be obtained from the expression, $3Nk_BT/2 = \sum \mathbf{p}_i^2/2m$, the term $\alpha \mathbf{p}_i$ represents the Gaussian thermostat. α is chosen so that $\sum \mathbf{p}_i^2/2m$ is a constant of the motion.

$$\alpha = \frac{\sum \mathbf{p}_i \bullet \mathbf{F}_i + \sum \mathbf{p}_i \bullet \mathbf{D}_i\, F_e}{\sum \mathbf{p}_i^2} \qquad (8.10.3)$$

The terms $\mathbf{C}, \mathbf{D}$ couple the external field $F_e(t)$ to the system. The adiabatic, unthermostatted equations of motion need not be derivable from a Hamiltonian (i.e. $\mathbf{C}, \mathbf{D}$ do not have to be perfect differentials). We assume that the AI$\mathbf{\Gamma}$ holds,

$$\frac{\partial}{\partial \mathbf{\Gamma}} \bullet iL^{ad}(s)\, \mathbf{\Gamma} = 0 \qquad (8.10.4)$$

The dissipative flux is defined in the usual way,

$$iL^{ad}(s)\, H_0 \equiv -J(\mathbf{\Gamma})\, F_e(s) \qquad (8.10.5)$$

where,

$$H_0 = \sum_i \frac{\mathbf{p}_i^2}{2m} + \frac{1}{2} \sum_{i,j} \phi_{ij} \qquad (8.10.6)$$

The response of an arbitrary phase variable $B(\mathbf{\Gamma})$ can obviously be written as,

$$\langle B(t) \rangle = \int d\mathbf{\Gamma}\, f_0\, e_R^{\int_0^t ds\, iL(s)}\, B(\mathbf{\Gamma}) = \int d\mathbf{\Gamma}\, f_0\, U_R(0,t)\, B \qquad (8.10.7)$$

In this equation iL(t) is the p-Liouvillean for the field-dependent Gaussian thermostatted dynamics, t>0. If we use the Dyson decomposition of the field-dependent p-propagator in terms of the equilibrium thermostatted propagator we find that,

$$\langle B(t) \rangle = \langle B(0) \rangle + \int_0^t ds \int d\mathbf{\Gamma}\, f_0\, U_{R0}(0,s)(iL(s) - iL_0) U_R(s,t) B \qquad (8.10.8)$$

By successive integrations we unroll U_{R0} propagator onto the distribution function.

$$< B(t) > = < B(0) > + \int_0^t ds \int d\Gamma\, [U^{\dagger}_{R0}(0,s)\, f_0]\, (iL(s)-iL_0)\, U_R(s,t)\, B \tag{8.10.9}$$

However $U^{\dagger}_{R0}$ is the equilibrium f-propagator and by equation (8.10.1) it has no effect on the equilibrium distribution f_0.

$$< B(t) > = < B(0) > + \int_0^t ds \int d\Gamma\, f_0\, (iL(s)-iL_0)\, U_R(s,t)\, B \tag{8.10.10}$$

We can now unroll the Liouvilleans to attack the distribution function rather than the phase variables. The result is,

$$< B(t) > = < B(0) > - \int_0^t ds \int d\Gamma\, [(iL(s)-iL_0)\, f_0]\, U_R(s,t)\, B \tag{8.10.11}$$

From equation (8.10.1) it is obvious that it is only the operation of the field-dependent Liouvillean which needs to be considered. Provided A$\Pi\Gamma$ is satisfied, we know from (7.3.4., et. seq.) that,

$$iL(s)\, f_0 = \beta f_0 J(\Gamma) F_e(s) \tag{8.10.12}$$

For either the canonical or Gaussian isokinetic ensembles therefore,

$$< B(t) > = < B(0) > - \beta \int_0^t ds \int d\Gamma\, f_0\, J\, F_e(s)\, U_R(s,t)\, B \tag{8.10.13}$$

Thus far the derivation has followed the same procedures used for the time dependent linear response and time independent nonlinear response. The operation of $U_R(s,t)$ on B however, presents certain difficulties. No simple meaning can be attached to $U_R(s,t)$ B. We can now use the Composition and the Inverse theorems to break up the incremental p-propagator $U_R(s,t)$. Using equations (8.4.4),

$$U_R(s,t) = U_R^{-1}(0,s)\, U_R(0,t) \tag{8.10.14}$$

Substituting this result into (8.10.13) we find

$$< B(t) > = < B(0) > - \beta \int_0^t ds \int d\Gamma\, F_e(s)\, f_0 J\, U_R^{-1}(0,s)\, U_R(0,t)\, B \tag{8.10.15}$$

Using the Inverse theorem (8.3.1), and integrating by parts we find,

$$< B(t) > = < B(0) > - \beta \int_0^t ds \int d\mathbf{\Gamma}\, F_e(s)\, B(t)\, \exp_R[\int_0^s ds_1\, iL(s_1)]\, J\, f_0 \qquad (8.10.16)$$

where after unrolling $U_R^{-1}(0,s)$ we attack B with $U_R(0,t)$ giving B(t). As it stands the exponential in this equation has the right time ordering of a p-propagator but the argument of the exponential contains an f-Liouvillean. We obviously have some choices here. We choose to use (8.9.5) to rewrite the exponential in terms of a p-propagator. This equation gives

$$\exp_R[\int_0^s ds_1\, iL(s_1)\,] = \exp[\int_0^s ds_1\, \Lambda(s_1)]\; U_R(0,s) \qquad (8.10.17)$$

where

$$\Lambda(s_1) = -3N\, \alpha(\mathbf{\Gamma}(s_1), s_1) + O(1) \qquad (8.10.18)$$

$\alpha(\mathbf{\Gamma},s)$ is the Gaussian isokinetic multiplier required to maintain a fixed kinetic energy. Substituting these results into equation (8.10.16), using the fact that,

$$iL(s)\, H_0(\mathbf{\Gamma}) = -J(\mathbf{\Gamma})\, F_e(s) - 3Nk_BT\, \alpha(\mathbf{\Gamma}, s) \qquad (8.10.19)$$

gives,

$$< B(t) > = < B(0) > - \beta \int_0^t ds_1 \int d\mathbf{\Gamma}\, f_0\, B(t)\, J(s_1)\, \exp[\int_0^{s_1} ds_2\, \beta J(s_2) F_e(s_2)]\, F_e(s_1) \qquad (8.10.20)$$

or,

$$< B(t) > = < B(0) > - \beta \int_0^t ds_1\, < B(t)\, J(s_1)\, e^{\beta \int_0^{s_1} ds_2\, J(s_2)\, F_e(s_2)} > F_e(s_1) \qquad (8.10.21)$$

This equation is the fundamental result of this chapter. It must be remembered that all time evolution is governed by the field-dependent thermostatted equations of motion implicit in the Liouvillean, iL(t).

8.11 RENORMALISATION

We can apply our fundamental result, equation (8.10.21), to a number of known special cases. In the linear regime our equation obviously becomes,

$$< B(t) > = < B(0) > - \beta \int_0^t ds \; < B(t) J(s) >_0 F_e(s) \qquad (8.11.1)$$

The notation '$< .. >_0$' denotes an equilibrium average over the field-free thermostatted dynamics implicit in the Liouvillean, iL_0. This equation is the well-known result of time dependent linear response theory, (see §5.3).

Another special case that can be examined is the time independent nonlinear response. In this circumstance the Liouvillean iL(t) is independent of time, iL, and the propagator, $U_R(0,t)$ becomes much simpler,

$$U_R(0,t) = e^{iLt} \qquad (8.11.2)$$

One does not need to use time ordered exponentials. In this case the response is,

$$< B(t) > = < B(0) > -\beta F_e \int_0^t ds < B(t) J(s) \; e^{\beta F_e \int_0^s ds_1 J(s_1)} > \qquad (8.11.3)$$

Again all time propagation is generated by the field-dependent thermostatted Liouvillean, iL. This equation is new. As was the case for the Kawasaki form of the nonequilibrium distribution function, explicit normalisation can be easily achieved.

Comparing equation (8.11.3) with the following identity that can be obtained using the equivalence of the Schrödinger and Heisenberg representations, (§8.7),

$$< B(t) > = < B(0) > + \int d\Gamma \; B(t) \; (f(0) - f(-t)) \qquad (8.11.4)$$

implies that,

$$f(0) - f(-t) = -\beta F_e \int_0^t ds \; f(0) J(s) \; e^{\beta \int_0^s ds_1 J(s_1) F_e} \qquad (8.11.5)$$

The integral (0,t), on the right hand side of the equation can be performed yielding,

$$f(-t) = f(0) \; e^{\beta F_e \int_0^t ds \; J(s)} \qquad (8.11.6)$$

The correctness of this equation can easily be checked by differentiation. Furthermore it is clear that this expression is just the unnormalised form of the Kawasaki distribution function (7.2.19).

This equation can be used to renormalize our expression for the time independent nonlinear response. Clearly

$$f(-t) = \frac{f(0)\exp[\beta F_e \int_0^t ds\, J(s)]}{\int d\Gamma\, f(0)\exp[\beta F_e \int_0^t ds\, J(s)]} \tag{8.11.7}$$

is an explicitly normalised distribution function. By differentiating this distribution in time and then reintegrating we find that,

$$f(0) - f(-t) = -\beta F_e \int_0^t ds_1 \left\{ \frac{f(0)\, J(s_1)\exp[\beta F_e \int_0^{s_1} ds_2\, J(s_2)}{<\exp[\beta F_e \int_0^{s_1} ds_2\, J(s_2)]>} \right.$$

$$\left. - \frac{f(0)\exp[\beta F_e \int_0^{s_1} ds_2\, J(s_2)] < J(s_1)\exp[\beta F_e \int_0^{s_1} ds_2\, J(s_2)] >}{<\exp[\beta F_e \int_0^{s_1} ds_2\, J(s_2)>^2} \right\} \tag{8.11.8}$$

To simplify the notation we define the brace $\{\ \}_s$ as

$$\{ B(t) \}_s \equiv \frac{\int d\Gamma\, B(t)\, f(0)\exp[\beta F_e \int_0^s ds_1\, J(s_1)]}{\int d\Gamma\, f(0)\exp[\beta F_e \int_0^s ds_1\, J(s_1)]} \tag{8.11.9}$$

Using this definition our renormalised expression for the response is (Evans and Morriss, 1988)

$$< B(t > = < B(0) > - \beta F_e \int_0^t ds \quad \{[B(t) - \{B(t)\}_s][J(s) - \{J(s)\}_s]\}_s \tag{8.11.10}$$

8.12 DISCUSSION

We have described a consistent formalism for the nonlinear response of many-body systems to time dependent external perturbations. This theory reduces to the standard results of linear response theory in the linear regime and can be used to derive the Kawasaki form of the time-independent nonlinear response. It also is easy to show that our results lead to the transient time correlation function expressions for the time-independent nonlinear case.

If we consider equation (8.10.13) in the time-independent case and remember that,

$$U_R(s,t) = \exp_R \int_s^t ds_1 \, iL(s_1) = \exp[(t\text{-}s)iL] \tag{8.12.1}$$

then we can see immediately,

$$\begin{aligned} < B(t) > &= < B(0) > - \beta F_e \int_0^t ds \int d\Gamma \; f_0 J \, B(t\text{-}s) \\ &= < B(0) > - \beta F_e \int_0^t ds \; < J(0) \, B(s) > \end{aligned} \tag{8.12.2}$$

This is the standard transient time correlation function expression for the nonlinear response, (7.3.8).

It may be thought that we have complete freedom to move between the various forms for the nonlinear response: the Kawasaki form equation (8.11.6), the transient correlation function expression equation (8.12.2) and the new formulation developed in this chapter, equation (8.11.10). These various formulations can be characterised by noting the times at which the test variable B and the dissipative flux J, are evaluated. In the Kawasaki form B is evaluated at time zero, in the transient correlation approach J is evaluated at time zero, and in the new form developed in this paper, B is evaluated at time t. These manipulations are essentially trivial for the linear response.

As we have shown, these forms are all equivalent for the nonlinear response to time-independent external fields. However for the time-dependent nonlinear case only our new form equation (8.11.10), seems to be valid. One can develop a Kawasaki version of

the nonlinear response to time-dependent fields but it is found that the resulting expression is not very useful. It, like the corresponding transient correlation form, involves convolutions of incremental propagators, Liouvilleans and phase variables which have no directly interpretable meaning. None of the operators in the convolution chains commute with one another and the resulting expressions are intractable and formal.

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