

5. Linear Response Theory

5.1 Adiabatic Linear Response Theory

In this chapter we will discuss how an external field F_e , perturbs an N -particle system. We assume that the field is sufficiently weak that only the linear response of the system need be considered. These considerations will lead us to equilibrium fluctuation expressions for mechanical transport coefficients such as the electrical conductivity. These expressions are formally identical to the Green-Kubo formulae that were derived in the last chapter. The difference is that the Green-Kubo formulae pertain to thermal transport processes where boundary conditions perturb the system away from equilibrium - all Navier-Stokes processes fall into this category. Mechanical transport coefficients on the other hand, refer to systems where mechanical fields which appear explicitly in the equations of motion for the system, drive the system away from equilibrium.

As we will see it is no coincidence that there is such a close similarity between the fluctuation expressions for thermal and mechanical transport coefficients. In fact one can often mathematically transform the nonequilibrium boundary conditions for a thermal transport process into a mechanical field. The two representations of the system are then said to be *congruent*.

A major difference between the derivations of the equilibrium fluctuation expressions for the two representations is that in the mechanical case one does not need to invoke Onsager's regression hypothesis. The linear mechanical response of a nonequilibrium system is analysed mathematically with resultant expressions for the response that involve equilibrium time correlation functions. In the thermal case - Chapter 4 - equilibrium fluctuations were studied and after invoking Onsager's hypothesis, the connection with nonequilibrium transport coefficients was made. Given a congruent mechanical representation of a thermal transport process, one can in fact prove the validity of Onsager's hypothesis.

The mechanical field F_e , performs work on the system, preventing relaxation to equilibrium. This work is converted into heat. It is easy to show that the rate at which the field performs work on the system is, for small fields, proportional to F_e^2 . As such this is, at least formally, a nonlinear effect. This is why, in the complete absence of any thermostating mechanism, Kubo (1957) was able to derive correct expressions for the linear response. However in spite of heating being a nonlinear effect, a thermostatted treatment of linear response theory leads to a considerably more satisfying discussion. We will therefore include in this chapter a description of thermostats and isothermal linear response theory.

Consider a system of N atoms suddenly subject, at $t = 0$, to a time dependent external field, F_e . The generalisation of our discussion to vector or tensor fields is straightforward. For simplicity we will assume that the particles move in a three dimensional Cartesian space. For times greater than zero the system is assumed to obey the dynamics given in the equations below,

$$\begin{aligned}\dot{\mathbf{q}}_i &= \frac{\mathbf{p}_i}{m} + \mathbf{C}_i F_e(t) \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i + \mathbf{D}_i F_e(t)\end{aligned}\quad (5.1)$$

The phase variables $C_i(\Gamma)$ and $D_i(\Gamma)$ describe the coupling of the field to the system. We assume that the equations have been written in such a way that at equilibrium in the absence of the external field the canonical kinetic energy K , satisfies the equipartition relation,

$$\frac{3N}{2} k_B T = \left\langle \sum_{i=1}^N \frac{p_i^2}{2m} \right\rangle \equiv \langle K \rangle \quad (5.2)$$

This implies that the canonical momenta give the peculiar velocities of each of the particles and that therefore,

$$\sum_{i=1}^N \mathbf{p}_i = 0 \quad (5.3)$$

In this case H_0 ,

$$H_0(\Gamma) = \sum_{i=1}^N \frac{p_i^2}{2m} + \Phi(\mathbf{q}) \quad (5.4)$$

is the instantaneous expression for the internal energy. We do not assume that a Hamiltonian exists which will generate the field-dependent equations of motion. In the absence of the external field and the thermostat, H_0 is the total energy, and is therefore a constant of the motion. The rate of change of internal energy due to the field is

$$\begin{aligned}\dot{H}_0(\Gamma, t) &= \sum_{i=1}^N \left[\frac{\dot{\mathbf{p}}_i(t) \cdot \mathbf{p}_i}{m} - \dot{\mathbf{q}}_i(t) \cdot \mathbf{F}_i \right] \\ &= - \sum_{i=1}^N \left[- \frac{\mathbf{D}_i \cdot \mathbf{p}_i}{m} + \mathbf{C}_i \cdot \mathbf{F}_i \right] F_e(t) \equiv -J(\Gamma) F_e(t)\end{aligned}\quad (5.5)$$

where $J(\Gamma)$, is called the dissipative flux.

The response of the system to the external field can be assessed by monitoring the average response of an arbitrary phase variable $B(\Gamma)$ at some later time t . The average response of the system is the response that is obtained by perturbing an ensemble of initial phases. It is usual to select the starting states from the equilibrium canonical ensemble, thus

$$f(\Gamma, 0) = f_c(\Gamma) = \frac{\exp[-\beta H_0(\Gamma)]}{\int d\Gamma \exp[-\beta H_0(\Gamma)]} = \frac{e^{-\beta H_0(\Gamma)}}{Z(\beta)} \quad (5.6)$$

The average response $\langle B(t) \rangle$ can be calculated from the expression,

$$\langle B(t) \rangle = \int d\Gamma B(\Gamma) f(\Gamma, t) \quad (5.7)$$

This is the Schrödinger representation for the response of B . The problem of determining the response then reduces to determining the perturbed distribution function $f(t)$. The rate of change in the perturbed distribution function is given by the Liouville equation

$$\frac{\partial}{\partial t} f(\Gamma, t) = -iL f(\Gamma, t) = -\left(\frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma}(t) + \dot{\Gamma}(t) \cdot \frac{\partial}{\partial \Gamma} \right) f(\Gamma, t) \quad (5.8)$$

The $\Gamma(t)$ in these equations is given by the first order form of the equations of motion with the external field evaluated at the current time, t .

If the equations of motion are derivable from a Hamiltonian it is easy to show that $\partial \dot{\Gamma} / \partial \Gamma = 0$, (§3.3). We will assume that even in the case where no Hamiltonian exists which can generate the equations of motion (5.1), that $\partial \dot{\Gamma} / \partial \Gamma = 0$. We refer to this condition as the Adiabatic Incompressibility of Phase Space (AIP). A sufficient, but not necessary, condition for this to hold is that the unthermostatted or adiabatic equations of motion are derivable from a Hamiltonian. It is of course possible to pursue the theory without this condition but in practise it is rarely necessary to do so (the only known exception is discussed: Evans and MacGowan, 1986).

Thus in the adiabatic case if AIP holds, we know that the Liouville operator is Hermitian (see §3.3 & §3.5) and therefore,

$$iLA = \frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma} A = \dot{\Gamma} \cdot \frac{\partial}{\partial \Gamma} A = iLA \quad (5.9)$$

If we denote the Liouvillean for the field free equations of motion as iL_0 , and we break up the total Liouvillean into its field free and field dependent parts, equation (5.8) becomes,

$$\frac{\partial}{\partial t} (f_c + \Delta f(\Gamma, t)) = -(iL_0 + i\Delta L(t))(f_c + \Delta f(\Gamma, t)) \quad (5.10)$$

where the distribution function $f(\Gamma, t)$, is written as $f_c + \Delta f(\Gamma, t)$. Since H_0 is a constant of the motion for the field free adiabatic equations of motion, iL_0 therefore preserves the canonical ensemble,

$$\begin{aligned}
 iL_0 f_c &= \dot{\Gamma} \cdot \frac{\partial}{\partial \Gamma} f_c = \sum_{i=1}^N \left(\dot{\mathbf{q}}_i \cdot \frac{\partial}{\partial \mathbf{q}_i} + \dot{\mathbf{p}}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} \right) \frac{e^{-\beta H_0(\Gamma)}}{Z(\beta)} \\
 &= \frac{e^{-\beta H_0(\Gamma)}}{Z(\beta)} \sum_{i=1}^N \left(\dot{\mathbf{q}}_i \cdot \frac{\partial H_0}{\partial \mathbf{q}_i} + \dot{\mathbf{p}}_i \cdot \frac{\partial H_0}{\partial \mathbf{p}_i} \right) = 0
 \end{aligned} \tag{5.11}$$

Substituting (5.11) into equation (5.10) we see,

$$\frac{\partial}{\partial t} \Delta f(\Gamma, t) + iL_0 \Delta f(\Gamma, t) = -i\Delta L(t) f_c(\Gamma) + O(\Delta^2) \tag{5.12}$$

In (5.12) we are ignoring perturbations to the distribution function which are second order in the field. (The Schrödinger-Heisenberg equivalence (§3.3), proves that these second order terms for the distribution are identical to the second order trajectory perturbations.) In §7.8 we discuss the nature of this linearisation procedure in some detail. To linear order, the solution of equation (5.12) is,

$$\Delta f(\Gamma, t) = - \int_0^t ds \exp[-iL_0(t-s)] i\Delta L(s) f_c(\Gamma) + O(\Delta^2) \tag{5.13}$$

The correctness of this solution can easily be checked by noting that at $t = 0$, (5.13) has the correct initial condition, ($\Delta f(\Gamma, t = 0) = 0$) and that the solution for $\Delta f(\Gamma, t)$ given in (5.13) satisfies (5.12) for all subsequent times.

We will now operate on the canonical distribution function with the operator, $iL(t)$. We again use the fact that iL_0 preserves the canonical distribution function.

$$\begin{aligned}
 i\Delta L(t) f_c(\Gamma) &= iL(t) f_c(\Gamma) = \dot{\Gamma} \cdot \frac{\partial}{\partial \Gamma} \frac{\exp[-\beta H_0(\Gamma)]}{Z(\beta)} \\
 &= -\beta f_c(\Gamma) \dot{\Gamma} \cdot \frac{\partial H_0}{\partial \Gamma} = -\beta \dot{H}_0^{ad} f_c(\Gamma)
 \end{aligned} \tag{5.14}$$

The adiabatic time derivative of H_0 is given by the dissipative flux (5.5), so,

$$i\Delta L(s) f_c(\Gamma) = -\beta \dot{H}_0^{ad}(s) f_c(\Gamma) = \beta J(\Gamma) F_e(s) f_c(\Gamma) \tag{5.15}$$

The time argument associated with $i\Delta L(s)$ is the time argument of the external field.

Substituting (5.15) into (5.13) and in turn into (5.7), the linear response of the phase variable B is given by

$$\begin{aligned}
 \langle B(t) \rangle &= \langle B(0) \rangle + \int d\Gamma B(\Gamma) \Delta f(\Gamma, t) \\
 &= \langle B(0) \rangle - \int_0^t ds \int d\Gamma B(\Gamma) e^{-iL_0(t-s)} \beta J(\Gamma) F_e(s) f_c(\Gamma) \\
 &= \langle B(0) \rangle - \beta \int_0^t ds \int d\Gamma B(\Gamma, t-s) J(\Gamma, 0) f_c(\Gamma) F_e(s)
 \end{aligned} \tag{5.16}$$

In deriving the third line of this equation from the second we have *unrolled* the propagator from the dissipative flux onto the response variable B . Note that the propagator has no effect on either the canonical distribution function (which is preserved by it), or on the external field $F_e(t)$ which is not a phase variable.

It is usual to express the result in terms of a linear susceptibility χ_{BJ} , which is defined in terms of the equilibrium time correlation function of B and J ,

$$\chi_{BJ}(t) \equiv \beta \langle B(t)J(0) \rangle \quad (5.17)$$

To linear order, the canonical ensemble averaged linear response for $B(t)$ is,

$$\langle B(t) \rangle = \langle B(0) \rangle - \lim_{F_e \rightarrow 0} \int_0^t ds \chi_{BJ}(t-s) F_e(s) \quad (5.18)$$

This equation is very similar to the response functions we met in Chapter 4 when we discussed viscoelasticity and constitutive relations for thermal transport coefficients. The equation shows that the linear response is non-Markovian. All systems have memory. All N -body systems remember the field history over the decay time of the relevant time correlation function, $\langle B(t)J(0) \rangle$. Markovian behaviour is only an idealisation brought about a lack of sensitivity in our measurements of the time resolved many-body response.

There are, a number of deficiencies in the derivation we have just given. Suppose that by monitoring $\langle B(t) \rangle$ for a family of external fields F_e , we wish to deduce the susceptibility $\chi(t)$. One cannot blindly use equation (5.18). This is because as the system heats up through the conversion of work into heat, the system temperature will change in time. This effect is quadratic with respect to the magnitude of the external field. If χ increases with temperature, the long time limiting value of $\langle B(t) \rangle$ will be infinite. If χ decreases with increasing temperature the limiting value of $\langle B(t) \rangle$ could well be zero. This is simply a reflection of the fact that in the absence of a thermostat there is no steady state. The linear steady state value for the response can only be obtained if we take the field strength to zero before we let time go to infinity. This procedure will inevitably lead to difficulties in both the experimental and numerical determination of the linear susceptibilities.

Another difficulty with the derivation is that if adiabatic linear response theory is applied to computer simulation, one would prefer not to use canonical averaging. This is because a single Newtonian equilibrium trajectory cannot generate or span the canonical ensemble. A single Newtonian trajectory can at most span a microcanonical subset of the canonical ensemble of states. A canonical evaluation of the susceptibility therefore requires an ensemble of trajectories if one is using Newtonian dynamics. This is inconvenient and very expensive in terms of computer time.

One cannot simply extend this adiabatic theory to the microcanonical ensemble. Kubo (1982) recently showed that if one subjects a cumulative microcanonical ensemble (all states less than a specified energy have the same probability) to a mechanical perturbation, then the linear susceptibility is given by the equilibrium correlation of the test variable B and the dissipative flux J , averaged over the delta microcanonical ensemble (all states with a precisely specified energy have the same probability). When the equilibrium ensemble of starting states is not identical to the equilibrium ensemble used to compute the susceptibilities, we say that the theory is *ergodically inconsistent*. We will now show how both of these difficulties can be resolved.

5.2 Thermostats and Equilibrium Distribution Functions

The Gaussian Isokinetic Thermostat

Thermostats were first introduced as an aid to performing nonequilibrium computer simulations. Only later was it realised that these devices have a fundamental role in the statistical mechanics of many-body systems. The first deterministic method for thermostating molecular dynamics simulations was proposed simultaneously and independently by Hoover and Evans (Hoover, Ladd and Moran, 1982, and Evans, 1983). Their method employs a damping or friction term in the equations of motion. Initially the use of such damping terms had no theoretical justification. Later it was realised (Evans, Hoover, Failor, Moran and Ladd, 1983) that these equations of motion could be derived using Gauss' principle of least constraint (§3.1). This systematised the extension of the method to other constraint functions.

Using Gauss' Principle (Chapter 3), the isokinetic equations of motion for a system subject to an external field can be written as,

$$\begin{aligned}\dot{\mathbf{q}}_i &= \frac{\mathbf{p}_i}{m} + \mathbf{C}_i F_e(t) \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i + \mathbf{D}_i F_e(t) - \alpha \mathbf{p}_i\end{aligned}\tag{5.19}$$

This is the thermostatted generalisation of equation (5.1) where the thermostating term $\alpha \mathbf{p}_i$ has been added. In writing these equations we are assuming:

1. that the equations have been written in a form in which the canonical momenta are peculiar with respect to the streaming velocities of the particles;
2. that $\sum \mathbf{p}_i = 0$;
3. and that H_0 is the phase variable which corresponds to the internal energy.

In order to know that these three conditions are valid, we must know quite a lot about the possible flows induced in the system by the external field. This means that if we are considering shear flow for example, the Reynolds number must be small enough for laminar flow to be stable. Otherwise we cannot specify

the streaming component of a particles motion (\mathbf{C}_i must contain the local hydrodynamic flow field $\mathbf{u}(\mathbf{r}, t)$) and we cannot expect condition (1) to be valid.

The isokinetic expression for the multiplier is easily seen to be ,

$$\alpha = \alpha_0 + \alpha_1 F_e(t) = \frac{\sum_i \frac{\mathbf{F}_i \cdot \mathbf{p}_i}{m_i^2}}{\sum_i \frac{\mathbf{p}_i^2}{m_i}} + \frac{\sum_i \frac{\mathbf{D}_i \cdot \mathbf{p}_i}{m_i^2}}{\sum_i \frac{\mathbf{p}_i^2}{m_i}} F_e(t) \quad (5.20)$$

It is instructive to compare this result with the corresponding field free multiplier given in (3.32). It is important to keep in mind that the expression for the multiplier depends explicitly on the external field and therefore on time. This is why we define the time and field independent phase variables α_0, α_1 .

It is easy to show that if Gauss' Principle is used to fix the internal energy H_0 , then the equations of motion take on exactly the same form (Evans, 1983), except that the multiplier is,

$$\alpha = \frac{\sum_{i=1}^N \mathbf{D}_i \cdot \frac{1}{m} \mathbf{p}_i - \mathbf{C}_i \cdot \mathbf{F}_i}{\sum_{i=1}^N \frac{1}{m} \mathbf{p}_i^2} F_e(t) \quad (5.21)$$

It may seem odd that the form of the field dependent equations of motion is independent of whether we are constraining the kinetic or the total energy. This occurs because the vector character of the constraint force is the same for both forms of constraint (see §3.1). In the isoenergetic case it is clear that the multiplier vanishes when the external field is zero. This is as expected since in the absence of an external field, Newton's equations conserve the total energy.

Gaussian thermostats remove heat from the system at a rate,

$$\dot{Q}(t) = \left(\frac{dH_0}{dt} \right)^{therm} = \alpha(t) \sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i} \quad (5.22)$$

by applying a force of constraint which is parallel to the peculiar velocity of each particle in the system.

We will now discuss the equilibrium properties of Gaussian isokinetic systems in more detail. At equilibrium the Gaussian isokinetic equations become,

$$\begin{aligned} \dot{\mathbf{q}}_i &= \frac{\mathbf{p}_i}{m} \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i - \alpha \mathbf{p}_i \end{aligned} \quad (5.23)$$

with the multiplier given by equation (5.20) with $\mathbf{F}_e = 0$. Clearly the average value of the multiplier is zero at equilibrium with fluctuations in its value being precisely those required to keep the kinetic energy constant. Following our

assumption that the initial value of the total linear momentum is zero, it is trivial to see that like the kinetic energy, it is a constant of the motion.

The ergodically generated equilibrium distribution function $f_T(\Gamma)$, can be obtained by solving the Liouville equation for these equations of motion. It is convenient to consider the total time derivative of f . From the Liouville equation (3.34), we see that,

$$\frac{df}{dt} = -f \frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma} = -f \sum_{i=1}^N \frac{\partial}{\partial \mathbf{p}_i} \cdot \dot{\mathbf{p}}_i = f \sum_{i=1}^N \frac{\partial}{\partial \mathbf{p}_i} \cdot (\alpha \mathbf{p}_i) \quad (5.24)$$

In computing the final derivative in this equation we get $3N$ identical intensive terms from the $3N$ derivatives, $\alpha(\partial/\partial \mathbf{p}_i) \cdot \mathbf{p}_i$. We also get $3N$ terms from $\mathbf{p}_i \cdot \partial \alpha / \partial \mathbf{p}_i$ which sum to give $-\alpha$. Since we are interested in statistical mechanical systems we will ignore terms of relative order $1/N$, in the remaining discussion. It is certainly possible to retain these terms but this would add considerably to the algebraic complexity, without revealing any new physics. This being the case, equation (5.24) above becomes,

$$\frac{df}{dt} = 3N\alpha f + O(1)f \quad (5.25)$$

From (5.24) it can be shown that ,

$$\frac{df}{dt} = -\frac{3N}{2K} f \dot{\Phi} \quad (5.26)$$

or,

$$\frac{d \ln f}{dt} = -\frac{3N}{2K} \frac{d\Phi}{dt} \quad (5.27)$$

Integrating both sides with respect to time enables us to evaluate the time independent equilibrium distribution function,

$$f_T(\Gamma) = \frac{\exp[-\beta \Phi(\Gamma)] \delta(K(\Gamma) - K_0)}{\int d\Gamma \exp[-\beta \Phi(\Gamma)] \delta(K(\Gamma) - K_0)} \quad (5.28)$$

where the constant, $\beta = 3N/2K_0$. We call this distribution function the isokinetic distribution f_T (Evans and Morriss, 1983). It has a very simple form: the kinetic degrees of freedom are distributed microcanonically, and the configurational degrees of freedom are distributed canonically. The thermodynamic temperatures $(\partial E / \partial S)_{N,V} = T$ of these two sub systems are of course identical.

If one retains terms of order $1/N$ in the above derivation, the result is the same except that $\beta = (3N - 4)/2K_0$. Such a result could have been anticipated in advance because in our Gaussian isokinetic system four degrees of freedom are frozen,

one by the kinetic energy constraint, and three because the linear momentum is fixed.

One can check that the isokinetic distribution is an equilibrium solution of the equilibrium Liouville equation. Clearly $df_T/dt \neq 0$. As one follows the streaming motion of an evolving point in phase space $\Gamma(t)$, the streaming derivative of the co-moving local density is,

$$\frac{df_T}{dt} = \frac{3N}{2K(\Gamma)} \dot{\Phi}(\Gamma) f_T(\Gamma) \neq 0 \quad (5.29)$$

This is a direct consequence of the fact that for a Gaussian isokinetic system, phase space is compressible. It is clear however, that in the absence of external fields $\langle df_T/dt \rangle = 0$, because the mean value of $\dot{\Phi}$ must be zero. If we sit at a fixed point in phase space and ask whether, under Gaussian isokinetic dynamics, the isokinetic distribution function changes, then the answer is no. The isokinetic distribution is the equilibrium distribution function. It is preserved by the dynamics. Substitution into the Liouville equation gives,

$$\frac{\partial f_T}{\partial t} = -\dot{\Gamma} \cdot \frac{\partial f_T}{\partial \Gamma} - f_T \frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma} = (\beta \dot{\Phi} + 3N\alpha) f_T = 0 \quad (5.30)$$

The proof that the last two terms sum to zero is easily given using the fact that, $\beta = 3N/2K_0$ and that $K = \sum \mathbf{p}^2/2m$ is a constant of the motion.

$$\beta \dot{\Phi} + 3N\alpha = -\beta \sum_i \mathbf{F}_i \cdot \frac{\mathbf{p}_i}{m_i} + 3N \frac{\sum_i \mathbf{F}_i \cdot \frac{\mathbf{p}_i}{m_i}}{\sum_i \frac{\mathbf{p}_i^2}{m_i}} = 0 \quad (5.31)$$

If the equilibrium isokinetic system is ergodic, a single trajectory in phase space will eventually generate the isokinetic distribution. On the other hand a single isokinetic trajectory cannot ergodically generate a canonical distribution. We can however, ask whether isokinetic dynamics will preserve the canonical distribution. If we integrate the equations of motion for an ensemble of systems which are initially distributed canonically, will that distribution be preserved by isokinetic dynamics? Clearly,

$$\frac{\partial f_c}{\partial t} = f_c \left(3N\alpha + \beta \dot{K} + \beta \dot{\Phi} \right) = f_c \left(\beta - \frac{3N}{2K(\Gamma)} \right) \dot{\Phi}(\Gamma) = f_c \Delta(\beta) \dot{\Phi}(\Gamma) \quad (5.32)$$

is not identically zero. In this expression K is a phase variable and not a constant, and $\dot{\Phi}$ is only equal to zero on average. K would only be a constant if all members of the ensemble had identical kinetic energies. The mean value of $3N/2K$ is of course β .

Consider the time derivative of the canonical average of an arbitrary extensive phase variable, B , where the dynamics is Gaussian isokinetic.

$$\frac{d}{dt}\langle B(t) \rangle = \int d\Gamma B \frac{\partial f_c}{\partial t} = \int d\Gamma B \Delta(\beta) \dot{\Phi} f_c \quad (5.33)$$

The time derivative of the ensemble average is,

$$\frac{d}{dt}\langle B(t) \rangle = \left\langle B \left(\frac{3N}{2K} - \beta \right) \dot{\Phi} \right\rangle = \frac{\beta}{K_0} \langle B \Delta K \dot{\Phi} \rangle + O(\Delta^2) \quad (5.34)$$

where $\Delta K \equiv K - \langle K \rangle = K - K_0$. Equation (5.34) can be written as the time derivative of a product of three extensive, zero-mean variables.

$$\frac{d}{dt}\langle B(t) \rangle = \frac{\beta}{K_0} \left[\langle B \Delta K \dot{\Phi} \rangle + \langle \Delta B \Delta K \dot{\Phi} \rangle \right] = \frac{\beta}{K_0} \langle \Delta B \Delta K \dot{\Phi} \rangle = O(1) \quad (5.35)$$

In deriving these equations we have used the fact that $\langle \Delta K \dot{\Phi} \rangle = 0$, and that the ensemble average of the product of three extensive, zero mean phase variables is of order N , while $K_0 = \langle K \rangle$ is extensive.

The above equation shows that although B is extensive, the change in $\langle B(t) \rangle$ with time, (as the ensemble changes from canonical at $t = 0$, to whatever for the Gaussian isokinetic equations generate as $t \rightarrow \infty$) is of order 1 and therefore can be ignored relative to the average of B itself. In the thermodynamic limit the canonical distribution is *preserved* by Gaussian isokinetic dynamics.

Nosé-Hoover thermostat - canonical ensemble

The Gaussian thermostat generates the isokinetic ensemble by a differential feedback mechanism. The kinetic temperature is constrained precisely by setting its time derivative to be zero. Control theory provides a range of alternative feedback processes. After the Gaussian thermostat was developed, Nosé (1984a,b) utilised an integral feedback mechanism. As we will see the Nosé thermostat, especially after a simplifying reformulation by Hoover (1985), provides a simple and direct way of ergodically generating the canonical ensemble.

The original Nosé method considers an extended system with an additional degree of freedom s , which acts like an external reservoir, interacting with the system of interest by scaling all the velocities of the particles, $\mathbf{v}_i = s \dot{\mathbf{q}}_i$. The new potential energy that Nosé chose to associate with this new degree of freedom was $(g+1)k_B T \ln s$, where g is related to the number of degrees of freedom of the system and T is the desired value of the temperature. It is essentially the choice of the potential for s which leads to dynamics which generate the canonical ensemble.

The equivalent Hoover formulation of the Nosé thermostat uses equations of motion with the same form as the Gaussian equations. The difference being that the thermostating multiplier α , is determined by a time integral of the difference of the actual kinetic temperature from its desired value. All present applications of the Nosé thermostat use the Hoover reformulation rather than the original, somewhat cumbersome approach.

The Nosé Hamiltonian for the extended system is,

$$H_N(\mathbf{q}, \mathbf{p}, s, p_s) = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i s^2} + \Phi(\mathbf{q}) + \frac{p_s^2}{2Q} + (g+1)k_B T \ln s \quad (5.36)$$

where Q is effectively the mass associated with the heat bath (s is dimensionless so the parameter Q does not have the dimensions of mass). The equations of motion generated by this Hamiltonian are

$$\begin{aligned} \dot{\mathbf{q}}_i &= \frac{\mathbf{p}_i}{m_i s^2}, & \dot{\mathbf{p}}_i &= \mathbf{F}_i, \\ \dot{s} &= \frac{p_s}{Q}, & \dot{p}_s &= \sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i s^3} - \frac{(g+1)k_B T}{s} \end{aligned} \quad (5.37)$$

If we eliminate the variable p_s from the equations of motion obtaining instead of the last two equations a single second order differential equation for s ,

$$\frac{d^2 s}{dt^2} = \frac{1}{Q} \left(\sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i s^3} - \frac{(g+1)k_B T}{s} \right) \quad (5.38)$$

If the system is at equilibrium, the average force on the s coordinate must be zero, so that

$$\left\langle \sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i s^3} \right\rangle = \left\langle \sum_{i=1}^N \frac{m_i^2 s^4 \dot{\mathbf{q}}_i^2}{m_i s^3} \right\rangle = (g+1)k_B T \left\langle \frac{1}{s} \right\rangle \quad (5.39)$$

Suppose we interpret the time appearing in (5.37) to be a non-Galilaean fictitious time, and the *real velocities* to be $\mathbf{v}_i = s(d\mathbf{q}_i/dt)$. The instantaneous temperature is related to $\sum_i m_i \mathbf{v}_i^2$, and its time averaged value is equal to $(g+1)k_B T$, where $g+1$ is the number of degrees of freedom. This is consistent with a non-Galilaean time average being given by

$$\langle A \rangle_t = \frac{\int_0^T dt \frac{A(t)}{s}}{\int_0^T dt \frac{1}{s}} \quad (5.40)$$

This is an unusual definition of a time average as it implies that equal intervals non-Galilaean time dt , correspond to unequal intervals in *real time* of dt/s . Large values of s can be understood as corresponding to a rapid progress of fictitious time t . Division by s in the time averages appearing in (5.40) cancels out the

uneven passage of fictitious time restoring the averages to their correct Galilean values.

To calculate the equilibrium distribution function corresponding to the Nosé Hamiltonian we use the fact that for an ergodic system, the equilibrium distribution function for Nosé's extended system is microcanonical. The microcanonical partition function for the extended system is,

$$Z = \frac{1}{N!} \int d\mathbf{q} d\mathbf{p} ds dp_s \delta(H_N(\mathbf{q}, \mathbf{p}, s, p_s) - E) \quad (5.41)$$

$$Z = \frac{1}{N!} \int d\mathbf{q} d\mathbf{p} ds dp_s \delta\left(\sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i s^2} + \Phi(\mathbf{q}) + \frac{p_s^2}{2Q} + (g+1)k_B T \ln s - E\right) \quad (5.42)$$

where \mathbf{q} and \mathbf{p} are $3N$ -dimensional vectors, $\mathbf{q} \equiv (\mathbf{q}_1, \dots, \mathbf{q}_N)$ and $\mathbf{p} \equiv (\mathbf{p}_1, \dots, \mathbf{p}_N)$. If we change variables from \mathbf{p} to \mathbf{p}' , where $\mathbf{p}'_i = \mathbf{p}_i/s$ for all i , then

$$Z = \frac{1}{N!} \int d\mathbf{q} d\mathbf{p}' ds dp_s s^{3N} \delta\left(H'(\mathbf{q}, \mathbf{p}')_0 + \frac{p_s^2}{2Q} + (g+1)k_B T \ln s - E\right) \quad (5.43)$$

where H'_0 is the usual N particle Hamiltonian $\sum_i \frac{1}{2m_i} \mathbf{p}'_i{}^2 + \Phi(\mathbf{q})$, (the prime indicates that H'_0 is a function of \mathbf{p}'). The integral over s can be performed as the only contributions come from the zeros of the argument of the delta function. If $G(s) = H'(\mathbf{q}, \mathbf{p}')_0 + \frac{1}{2Q} p_s^2 + (g+1)k_B T \ln s - E$, then G has only one zero, that is

$$s_0 = \exp\left(-\frac{H'(\mathbf{q}, \mathbf{p}')_0 + \frac{p_s^2}{2Q} - E}{(g+1)k_B T}\right) \quad (5.44)$$

Using the identity $\delta(G(s)) = \delta(s - s_0)/G'(s)$ it is easy to show that performing the integral over s gives

$$Z = \frac{1}{N!} \int d\mathbf{q} d\mathbf{p}' dp_s \frac{1}{(g+1)k_B T} \exp\left(-\frac{3N+1}{(g+1)k_B T} \left(H'(\mathbf{q}, \mathbf{p}')_0 + \frac{p_s^2}{2Q} - E\right)\right) \quad (5.45)$$

The integral over p_s is the infinite integral of a Gaussian and the result is

$$Z = \frac{1}{N!} \left(\frac{2\pi Q}{(g+1)(3N+1)k_B T}\right)^{1/2} \int d\mathbf{q} d\mathbf{p}' \exp\left(-\frac{3N+1}{(g+1)k_B T} (H'(\mathbf{q}, \mathbf{p}')_0 - E)\right) \quad (5.46)$$

If we choose $g = 3N$ then this partition function is simply related to the canonical partition function

$$Z = \frac{1}{(3N+1)} \left(\frac{2\pi Q}{k_B T}\right)^{1/2} \frac{1}{N!} \int d\mathbf{q} d\mathbf{p}' \exp\left(-\frac{H'(\mathbf{q}, \mathbf{p}')_0 - E}{k_B T}\right) \quad (5.47)$$

If the variables $\mathbf{q}, \mathbf{p}, s, p_s$ are distributed microcanonically then variables \mathbf{p}' and \mathbf{q} are canonically distributed. The notion of non-Galilaean time makes this formulation of the Nosé thermostat rather cumbersome to use and difficult to interpret.

The next step in the development of this method was made by Hoover (1985) who realised that if one's interest lies solely in computing averages over \mathbf{q}, \mathbf{p}' in real time then you may as well rewrite the equations of motion in terms of \mathbf{q}, \mathbf{p}' and real time, t' , and eliminate the \mathbf{p}, s, p_s, t variables entirely. He used the time transformation

$$t' = \int_0^t \frac{d\tau}{s} \quad (5.48)$$

so that $dt' = dt/s$, to rewrite the Nosé equations of motion as

$$\begin{aligned} \frac{d\mathbf{q}_i}{dt'} &= \frac{\mathbf{p}'_i}{m_i}, & \frac{d\mathbf{p}'_i}{dt'} &= \mathbf{F}_i - \zeta \mathbf{p}'_i \\ \frac{ds}{dt} &= \zeta s, & \frac{d\zeta}{dt'} &= \frac{1}{Q} \left(\sum_{i=1}^N \frac{\mathbf{p}'_i{}^2}{m_i} - (g+1)k_B T \right) = \frac{1}{\tau^2} \left(\frac{K(\mathbf{p}')}{K_0} - 1 \right) \end{aligned} \quad (5.49)$$

where K_0 is the value of the kinetic energy corresponding to the required value of the temperature $K_0 = (g+1)k_B T/2$, $K(\mathbf{p}')$ is the instantaneous value of the kinetic energy, τ is a relaxation time which is related to the mass of the s degree of freedom ($\tau^2 = Q/2K_0$) and $\zeta = p_s/Q$. The motion of the system of interest can now be determined without reference to s . It is an irrelevant variable which can be ignored. The variable $d\zeta/dt'$ is a function of \mathbf{p}' only, so the complete description of the system can be given in terms of the variables \mathbf{q} and \mathbf{p}' .

An important result, obtained from this time transformation by Evans and Holian (1985), is that time averages in terms of the variables \mathbf{q} , \mathbf{p}' and t' take their usual form, that is

$$\langle A(\mathbf{q}, \mathbf{p}') \rangle_{t'} = \frac{1}{T'} \int_0^{T'} dt' A(\mathbf{q}, \mathbf{p}', t') = \langle A(\mathbf{q}, \mathbf{p}') \rangle_{\text{canonical}} \quad (5.50)$$

To obtain this result we start by considering the Nosé-Hoover phase variable Liouvillean $iL_{NH}(\mathbf{q}, \mathbf{p}', s, p_s; t')$ and relating it to the Nosé Liouvillean $iL_N(\mathbf{q}, \mathbf{p}, s, p_s; t)$.

$$\begin{aligned} iL_N(\mathbf{q}, \mathbf{p}, s, p_s; t) &= \dot{\mathbf{q}} \cdot \frac{\partial}{\partial \mathbf{q}} + \dot{\mathbf{p}} \cdot \frac{\partial}{\partial \mathbf{p}} + \dot{s} \cdot \frac{\partial}{\partial s} + \dot{p}_s \cdot \frac{\partial}{\partial p_s} \\ &= \frac{\mathbf{p}}{ms^2} \cdot \frac{\partial}{\partial \mathbf{q}} + \mathbf{F} \cdot \frac{\partial}{\partial \mathbf{p}} \bigg|_s + \frac{p_s}{Q} \cdot \frac{\partial}{\partial s} \bigg|_{\mathbf{p}} + \left(\sum_{i=1}^N \frac{\mathbf{p}_i^2}{ms^2} - (g+1)k_B T \right) \frac{1}{s} \cdot \frac{\partial}{\partial p_s} \end{aligned} \quad (5.51)$$

Using the results:

$$\left. \frac{\partial}{\partial s} \right|_{\mathbf{p}} = \left. \frac{\partial}{\partial s} \right|_{\mathbf{p}'} - \mathbf{p}' \cdot \left. \frac{\partial}{\partial \mathbf{p}} \right|_s \quad (5.52)$$

and

$$\left. \frac{\partial}{\partial \mathbf{p}} \right|_s = \frac{1}{s} \left. \frac{\partial}{\partial \mathbf{p}'} \right|_s \quad (5.53)$$

equation (5.51) becomes

$$\begin{aligned} iL_N(\mathbf{q}, \mathbf{p}, s, p_s; t) &= \frac{\mathbf{p}}{ms^2} \cdot \left. \frac{\partial}{\partial \mathbf{q}} \right| + \left(\mathbf{F} - \mathbf{p}' \frac{p_s}{Q} \right) \frac{1}{s} \cdot \left. \frac{\partial}{\partial \mathbf{p}'} \right|_s + \frac{p_s}{Q} \cdot \left. \frac{\partial}{\partial s} \right|_{\mathbf{p}'} + \left(\sum_{i=1}^N \frac{\mathbf{p}_i^2}{ms^2} - (g+1)k_B T \right) \frac{1}{s} \cdot \left. \frac{\partial}{\partial p_s} \right| \\ &= \frac{\mathbf{p}'}{ms} \cdot \left. \frac{\partial}{\partial \mathbf{q}} \right| + (\mathbf{F} - \zeta \mathbf{p}') \frac{1}{s} \cdot \left. \frac{\partial}{\partial \mathbf{p}'} \right|_s + \zeta \cdot \left. \frac{\partial}{\partial s} \right|_{\mathbf{p}'} + \left(\sum_{i=1}^N \frac{\mathbf{p}_i'^2}{m} - (g+1)k_B T \right) \frac{1}{s} \cdot \left. \frac{\partial}{\partial p_s} \right| \\ &= \frac{1}{s} \left[\frac{\mathbf{p}'}{m} \cdot \left. \frac{\partial}{\partial \mathbf{q}} \right| + (\mathbf{F} - \zeta \mathbf{p}') \cdot \left. \frac{\partial}{\partial \mathbf{p}'} \right|_s + s \zeta \cdot \left. \frac{\partial}{\partial s} \right|_{\mathbf{p}'} + \left(\sum_{i=1}^N \frac{\mathbf{p}_i'^2}{m} - (g+1)k_B T \right) \cdot \left. \frac{\partial}{\partial p_s} \right| \right] \\ &= \frac{1}{s} iL_{NH}(\mathbf{q}, \mathbf{p}', s, p_s; t') \end{aligned} \quad (5.54)$$

If A is an arbitrary phase variable then the Liouvillean describes the rate of change of A . If we consider A to be a function of \mathbf{q} and \mathbf{p} then the rate of change of A with respect to time t is

$$\frac{d}{dt} A(\mathbf{q}, \mathbf{p}) = iL_N(\mathbf{q}, \mathbf{p}, s, p_s, t) A(\mathbf{q}, \mathbf{p}) \quad (5.55)$$

Since iL_N contains no explicit time dependence, integrating with respect to time gives

$$\begin{aligned} A(\mathbf{q}, \mathbf{p}, t) &= \exp \left[\int_0^t d\tau iL_N(\mathbf{q}, \mathbf{p}, s, p_s) \right] A(\mathbf{q}, \mathbf{p}, 0) \\ &= \exp [iL_N(\mathbf{q}, \mathbf{p}, s, p_s) t] A(\mathbf{q}, \mathbf{p}, 0) \end{aligned} \quad (5.56)$$

In a similar fashion we can consider A to be function of \mathbf{q} and \mathbf{p}' . In that circumstance it is natural to ask for the value of A at t' .

$$A(\mathbf{q}, \mathbf{p}', t') = \exp \left[\int_0^{t'} d\tau' iL_N(\mathbf{q}, \mathbf{p}') \right] A(\mathbf{q}, \mathbf{p}', 0) = \exp [iL_{NH}(\mathbf{q}, \mathbf{p}') t'] A(\mathbf{q}, \mathbf{p}', 0) \quad (5.57)$$

Now A is function of the reduced phase space only, so the dependence on s and p_s can be ignored. These two different representations of the phase variable can be equated. To do this consider the time transformation (5.48). It implies,

$$t' = \int_0^{t'} d\tau' = \int_0^t \frac{d\tau}{s} \quad (5.58)$$

So that $d\tau' = d\tau/s$, and

$$\begin{aligned}
 A(\mathbf{q}, \mathbf{p}, t) &= \exp \left[\int_0^t d\tau iL_N(\mathbf{q}, \mathbf{p}) \right] A(\mathbf{q}, \mathbf{p}, 0) = \exp \left[\int_0^t d\tau \frac{1}{s} iL_{NH}(\mathbf{q}, \mathbf{p}') \right] A(\mathbf{q}, \mathbf{p}', 0) \\
 &= \exp \left[\int_0^{t'} d\tau' iL_{NH}(\mathbf{q}, \mathbf{p}') \right] A(\mathbf{q}, \mathbf{p}', 0) = A(\mathbf{q}, \mathbf{p}', t')
 \end{aligned} \tag{5.59}$$

Using (5.59) and the time transformation (5.48) we find that $T' = \int_0^{t'} dt' = \int_0^t dt/s$ so that we can rewrite the time average in the usual form,

$$\langle A \rangle_t = \frac{\int_0^{t'} dt' A(\mathbf{q}, \mathbf{p}', t')}{\int_0^{t'} dt'} = \frac{\int_0^T dt \frac{A(\mathbf{q}, \mathbf{p}, t)}{s}}{\int_0^T dt \frac{1}{s}} = \langle A \rangle \tag{5.60}$$

So the time average over t is equal to the time average over t' . Using the variables \mathbf{q}, \mathbf{p}' and t' the time average over equal intervals of t' takes the usual form. The time average over \mathbf{q}, \mathbf{p} and t however, involves the scaling variable s , or equivalently a time average over unequal intervals of t .

One can of course dispense with the original form of Nosé's equations entirely. There is now no need to consider the notion of non-Galilaean time. We simply repeat the derivation we gave for the isokinetic distribution based on the Gaussian isokinetic equations of motion, for the Nosé-Hoover equations. Since there is no need to refer to non-Galilaean time we refer to $\mathbf{q}, \mathbf{p}', t'$ simply as, $\mathbf{q}, \mathbf{p}, t$ (dropping the prime). The N particle distribution function $f(\Gamma, \zeta)$ generated by the Nosé-Hoover equations of motion can be obtained by solving the Liouville equation for the equations of motion written in terms of \mathbf{q}, \mathbf{p} and t . It is convenient to consider the total time derivative of $f(\Gamma, \zeta)$ which from the Liouville equation is

$$\frac{df}{dt} = -f \left(\frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma} + \frac{\partial}{\partial \zeta} \dot{\zeta} \right) \tag{5.61}$$

From the equations of motion (5.49), dropping the primes, it is easy to see that $d\zeta/dt$ is a function of \mathbf{q} and \mathbf{p} , and hence independent of ζ . The only nonzero contribution to the right hand side comes from the \mathbf{p} dependence of $d\mathbf{p}/dt$, so that

$$\frac{df}{dt} = 3N\zeta f \tag{5.62}$$

Consider the time derivative of the quantity $H_0 + \frac{1}{2}Q\zeta^2$

$$\begin{aligned}
 \frac{d}{dt} \left(H_0 + \frac{1}{2}Q\zeta^2 \right) &= \dot{H}_0 + Q\zeta\dot{\zeta} = -\zeta \sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i} + \zeta \left(\sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i} - (g+1)k_B T \right) \\
 &= -\zeta (g+1)k_B T
 \end{aligned} \tag{5.63}$$

If we take $g = 3N - 1$ then we find that

$$\frac{d}{dt} \ln f = -\beta \frac{d}{dt} \left(H_0 + \frac{1}{2} Q \zeta^2 \right) \quad (5.64)$$

So that the equilibrium distribution function is the extended canonical distribution f_c ,

$$f_c(\Gamma, \zeta) = \frac{\exp \left[-\beta \left(H_0 + \frac{1}{2} Q \zeta^2 \right) \right]}{\int d\Gamma d\zeta \exp \left[-\beta \left(H_0 + \frac{1}{2} Q \zeta^2 \right) \right]} \quad (5.65)$$

In the Hoover representation of the equations of motion, the scaling variable s has essentially been eliminated so the number of degrees of freedom of the system, changes from $3N + 1$ to $3N$ and g changes from $3N$ to $3N - 1$.

5.3 Isothermal Linear Response Theory

In §5.2 we considered two forms of thermostatted dynamics - the Gaussian isokinetic dynamics and the Nosé-Hoover canonical ensemble dynamics. Both of these thermostatted equations of motion can add or remove energy from the system to control its temperature. It is particularly important to incorporate thermostatted dynamics when the system is perturbed by an external field. This allows the irreversibly produced heat to be removed continuously, and the system maintained in a steady, nonequilibrium state. We now generalise the adiabatic linear response theory of §5.1, to treat perturbed thermostatted systems we have developed in §5.2. We consider (Morris and Evans, 1985) an N -particle system evolving under the Gaussian isokinetic dynamics for $t < 0$, but subject for to an external field F_e , for all times $t > 0$. The equations of motion are given by

$$\begin{aligned} \dot{\mathbf{q}}_i &= \frac{\mathbf{p}_i}{m} + \mathbf{C}_i F_e(t) \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i + \mathbf{D}_i F_e(t) - \alpha \mathbf{p}_i \end{aligned} \quad (5.66)$$

The term $\alpha \mathbf{p}_i$ couples the system to a thermostat and we shall take

$$\alpha = \alpha_0 + \alpha_1 F_e(t) = \frac{\sum_i \frac{\mathbf{F}_i \cdot \mathbf{p}_i}{m_i}}{\sum_i \frac{\mathbf{p}_i^2}{m_i}} + \frac{\sum_i \frac{\mathbf{D}_i \cdot \mathbf{p}_i}{m_i}}{\sum_i \frac{\mathbf{p}_i^2}{m_i}} F_e(t) \quad (5.67)$$

so that the peculiar kinetic energy, $K(\Gamma) = \sum_i p_i^2 / 2m = K_0$, is a constant of the motion. In the absence of the field these equations of motion ergodically generate the isokinetic distribution function, f_T , equation (5.28), with $\beta = 3N/2K_0$. As we have seen, the isokinetic distribution function f_T , is preserved by the field free isokinetic equations of motion and that,

$$\frac{\partial f_T}{\partial t} = -iL_T f_T = 0 \quad (5.68)$$

we use iL_T for the zero field, isokinetic Liouvillean.

To calculate the linear thermostatted response we need to solve the linearised Liouville equation for thermostatted systems. Following the same arguments used in the adiabatic case (equations (5.8-12)), the linearised Liouville equation is,

$$\frac{\partial}{\partial t} \Delta f(\Gamma, t) + iL_T \Delta f(\Gamma, t) = -\Delta iL(t) f_T(\Gamma) + O(\Delta^2) \quad (5.69)$$

where $iL(t)$ is the external field dependent, isokinetic Liouvillean and $\Delta iL(t) = iL(t) - iL_T$. Its solution is the analogue of (5.13), namely

$$\Delta f(\Gamma, t) = -\int_0^t ds \exp(-iL_T(t-s)) \Delta iL(s) f_T(\Gamma) + O(\Delta^2) \quad (5.70)$$

Using equations (5.8), (5.28) and (5.66), and the fact that $\beta = 3N/2K_0$, it is easy to show that

$$\begin{aligned} \Delta iL(t) f_T(\Gamma) &= iL(t) f_T(\Gamma) - iL_T f_T(\Gamma) = iL(t) f_T(\Gamma) \\ &= \left(\dot{\Gamma}(t) \cdot \frac{\partial}{\partial \Gamma} + \left(\frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma}(t) \right) \right) f_T(\Gamma) \\ &= -\beta \Phi f_T(\Gamma) - f_T(\Gamma) \sum_i \frac{\partial}{\partial \mathbf{p}_i} \cdot (\alpha \mathbf{p}_i) \end{aligned} \quad (5.71)$$

There is one subtle point in deriving the last line of (5.71),

$$\begin{aligned} \sum_{i=1}^N \dot{\mathbf{p}}_i \cdot \frac{\partial f_T}{\partial \mathbf{p}_i} &= \sum_{i=1}^N \dot{\mathbf{p}}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} \frac{\delta(K(\mathbf{p}) - K_0) e^{-\beta \Phi(\mathbf{q})}}{Z_T(\beta)} \\ &= \frac{e^{-\beta \Phi(\mathbf{q})}}{Z_T(\beta)} \sum_{i=1}^N \dot{\mathbf{p}}_i \cdot \frac{\partial K(\mathbf{p})}{\partial \mathbf{p}_i} \frac{\partial \delta(K(\mathbf{p}) - K_0)}{\partial K(\mathbf{p})} \\ &= \frac{e^{-\beta \Phi(\mathbf{q})}}{Z_T(\beta)} \dot{K}(\mathbf{p}) \frac{\partial \delta(K(\mathbf{p}) - K_0)}{\partial K(\mathbf{p})} = 0 \end{aligned} \quad (5.72)$$

The last line follows because $K(p)$ is a constant of the motion for the Gaussian isokinetic equations of motion. We have also assumed that the only contribution to the phase space compression factor comes from the thermostating term $\alpha \mathbf{p}_i$. This means that in the absence of a thermostat, that is the adiabatic case, the phase space is incompressible and

$$\frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma}(t)^{ad} = \sum_{i=1}^N \left(\frac{\partial}{\partial \mathbf{q}_i} \cdot \mathbf{C}_i + \frac{\partial}{\partial \mathbf{p}_i} \cdot \mathbf{D}_i \right) = 0 \quad (5.73)$$

This assumption or condition, is known as the *adiabatic incompressibility of phase space* (AII). A sufficient, but not necessary condition for it to hold is that the

adiabatic equations of motion should be derivable from a Hamiltonian. It is important to note that AIF does not imply that the phase space for the thermostatted system should be incompressible. Rather it states that if the thermostat is removed from the field dependent equations of motion, the phase space is incompressible. It is essentially a condition on the external field coupling terms $C_i(\mathbf{q}, \mathbf{p})$ and $D_i(\mathbf{q}, \mathbf{p})$. It is not necessary that C_i be independent of q , and D_i be independent of p . Indeed in §6.3 we find that this is not the case for planar Couette flow, but the combination of partial derivatives in equation (5.73) is zero. It is possible to generalise the theory to treat systems where AIF does not hold but this generalisation has proved to be unnecessary.

Using equation (5.67) for the multiplier α , to first order in N we have

$$\begin{aligned}\Delta iL(t)f_T(\Gamma) &= -(\beta\dot{\Phi}(t) + 3N\alpha)f_T(\Gamma) \\ &= \beta \sum_{i=1}^N \left(\mathbf{C}_i \cdot \mathbf{F}_i - \mathbf{D}_i \cdot \frac{\mathbf{p}_i}{m} \right) F_e(t)f_T(\Gamma) \\ &= \beta J(\Gamma)F_e(t)f_T(\Gamma)\end{aligned}\tag{5.74}$$

This equation shows that $\Delta iL(t)f(\Gamma)$ is independent of thermostating. Equations (5.74) and (5.15) are essentially identical. This is why the dissipative flux J is defined in terms of the adiabatic derivative of the internal energy. Interestingly, the kinetic part of the dissipative flux, $J(\Gamma)$, comes from the multiplier α , while the potential part comes from the time derivative of Φ .

Substituting (5.74) into (5.70), the change in the isokinetic distribution function is given by

$$\Delta f(\Gamma, t) = -\beta \int_0^t ds \exp(-iL(t-s))J(\Gamma)F_e(s)f_T(\Gamma)\tag{5.75}$$

Using this result to calculate the mean value of $B(t)$, the isothermal linear response formula corresponding to equation (5.16), is,

$$\begin{aligned}\langle B(t) \rangle_T - \langle B(0) \rangle_T &= \int d\Gamma B(\Gamma) \Delta f(\Gamma, t) \\ &= -\beta \int_0^t ds \int d\Gamma B(\Gamma) \exp(-iL(t-s))J(\Gamma)F_e(s)f_T(\Gamma) \\ &= -\beta \int_0^t ds \int d\Gamma f_T(\Gamma) J(\Gamma) \exp(iL(t-s))B(\Gamma)F_e(s) \\ &= -\beta \int_0^t ds \int d\Gamma f_T(\Gamma) J(\Gamma) B(t-s)F_e(s) \\ &= -\beta \int_0^t ds \langle B(t-s)J(0) \rangle_{T,0} F_e(s)\end{aligned}\tag{5.76}$$

Equation (5.76) is very similar in form to the adiabatic linear response formula derived in §5.1. The notation $\langle \rangle_{T,0}$ signifies that a field-free (0), isokinetic (T) ensemble average should be taken. Differences from the adiabatic formula are that;

1. the field-free Gaussian isokinetic propagator governs the time evolution in the equilibrium time correlation function $\langle B(t-s)J(0) \rangle_{T,0}$,
2. the ensemble averaging is Gaussian isokinetic rather than canonical,
3. because both the equilibrium and nonequilibrium motions are thermostatted, the long time limit of $\langle B(t) \rangle_T$ on the left hand side of (5.76), is finite,
4. and the formula is ergodically consistent. There is only one ensemble referred to in the expression, the Gaussian isokinetic distribution. The dynamics used to calculate the time evolution of the phase variable B in the equilibrium time correlation function, ergodically generates the ensemble of time zero starting states $f_T(\Gamma)$. We refer to this as *ergodically consistent linear response theory*.

The last point means that time averaging rather than ensemble averaging can be used to generate the time zero starting states for the equilibrium time correlation function on the right hand side of equation (5.76).

It can be useful, especially for theoretical treatments, to use ergodically inconsistent formulations of linear response theory. It may be convenient to employ canonical rather than isokinetic averaging, for example. For the canonical ensemble, assuming AIF, we have in place of equation (5.71),

$$\begin{aligned}
 \Delta iL(t)f_c(\Gamma) &= -(\beta\Delta\Phi + 3N\Delta\alpha)f_c(\Gamma) \\
 &= \left(\beta \sum \mathbf{F}_i \cdot \mathbf{C}_i - \frac{3N}{2K} \sum_m \frac{\mathbf{p}_i}{m} \cdot \mathbf{D}_i \right) F_e f_c(\Gamma) \\
 &= \beta J(\Gamma) F_e f_c(\Gamma) + \beta \frac{\Delta K}{\langle K \rangle_{c,0}} \sum_m \frac{\mathbf{p}_i}{m} \cdot \mathbf{D}_i F_e f_c(\Gamma) + O(\Delta^2)
 \end{aligned} \tag{5.77}$$

where $\Delta d\Phi/dt$ is the difference between the rate of change of Φ with the external field turned on and with the field turned off ($d\Phi(F_e)/dt - d\Phi(F_e=0)/dt$). Similarly $\Delta\alpha = \alpha(F_e) - \alpha(F_e=0) = \alpha_1 F_e$ (see equation 5.67). The response of a phase variable B , is therefore,

$$\begin{aligned}
 \langle B(t) \rangle_c &= \langle B(0) \rangle_c - \beta \int_0^t ds \langle B(t-s)J(0) \rangle_{c,0} F(s) \\
 &\quad - \beta \int_0^t ds \left\langle B(t-s) \frac{\Delta K}{\langle K \rangle_{c,0}} \sum_m \frac{\mathbf{p}_i}{m} \cdot \mathbf{D}_i(0) \right\rangle_{c,0} F(s)
 \end{aligned} \tag{5.78}$$

Using the same methods as those used in deriving equation (5.35), we can show that if B is extensive, the second integral in equation (5.78) is of order 1 and can therefore be ignored.

Thus for a canonical ensemble of starting states and thermostatted Gaussian isokinetic dynamics, the response of an extensive variable B , is given by

$$\langle B(t_T) \rangle_c = \langle B(0) \rangle_c - \beta \int_0^t ds \langle B(t-s)_T J(0) \rangle_{c,0} F(s) \quad (5.79)$$

Like the isokinetic ensemble formula, the response, $\langle B(t_T) \rangle_c$, possesses well defined steady state limit.

It is straightforward to apply the linear response formalism to a wide variety of combinations of statistical mechanical ensembles, and equilibrium dynamics. The resultant susceptibilities are shown in the Table 5.1 below. It is important to appreciate that the dissipative flux $J(\Gamma)$ is determined by both the choice of equilibrium ensemble of starting states and the choice of the equilibrium dynamics.

Table 5.1 Linear Susceptibilities expressed as equilibrium time correlation functions[‡]

Adiabatic response of canonical ensemble	
$\chi = \beta \langle B(t_N) J(0) \rangle_c$	(T.5.1)
Isothermal response of canonical or isothermal ensemble	
$\chi = \beta \langle B(t_T) J(0) \rangle_{c,T}$	(T.5.2)
Isoenergetic response of canonical or microcanonical ensembles (Evans and Morriss, 1984b).	
$\chi(t) = \beta \langle B(t_N) J(0) \rangle_{c,E}$	(T.5.3)
Isoenthalpic response of isoenthalpic ensemble	
$\chi = \beta \langle B(t_I) J(0) \rangle_I$	(T.5.4)
$-JF_e \equiv dl/dt$, isoenthalpic dynamics defined in (Evans and Morriss, 1984b).	
Nosé dynamics of the canonical ensemble	
$\chi = \beta \langle B(t_c) J(0) \rangle_c$	(T.5.5)

[‡] Equilibrium dynamics: t_N , Newtonian; t_T , Gaussian Isokinetic; t_I Gaussian isoenthalpic; t_c Nosé-Hoover. Ensemble averaging:- $\langle \rangle_c$ canonical; $\langle \rangle_T$ isokinetic; $\langle \rangle_E$ microcanonical; $\langle \rangle_I$ isoenthalpic.

§ Proof of (T.5.5) can be found in a paper by Holian and Evans (1983).

5.4 The Equivalence of Thermostatted Linear Responses

We shall now address the important question of how the various linear susceptibilities described in Table 5.1, relate to one another. For simplicity let us assume that the initial unperturbed ensemble is canonical. In this case the only difference between the adiabatic, the isothermal, the isoenergetic and the Nosé susceptibilities is in the respective field free propagators used to generate the equilibrium time correlation functions. We will now discuss the differences between the adiabatic and isothermal responses, however the analysis of the other cases involve similar arguments. Without loss of generality we shall assume that the dissipative flux J and the response phase variable B are both extensive

and have mean values which vanish at equilibrium. The susceptibility is of order N .

The only difference between (T.5.1) and (T.5.2) is in the time propagation of the phase variable B ,

$$B(t_T) = U_T(t)B(\Gamma) = \exp(iL_T t)B(\Gamma) \quad (5.80)$$

and

$$B(t_N) = U_N(t)B(\Gamma) = \exp(iL_N t)B(\Gamma) \quad (5.81)$$

In equations (5.80) and (5.81) the Liouvillean iL_N is the Newtonian Liouvillean, and iL_T is the Gaussian isokinetic Liouvillean obtained from the equations of motion (5.23), with α given by the $F_e \rightarrow 0$ limit of equation (5.20). In both cases there is no explicit time dependence in the Liouvillean. We note that the multiplier α , is intensive.

We can now use the Dyson equation (3.102), to calculate the difference between the isothermal and adiabatic susceptibilities for the canonical ensemble. If \Rightarrow denotes the isothermal propagator and \rightarrow the Newtonian, the difference between the two relevant equilibrium time correlation functions is

$$\langle J \Rightarrow B \rangle - \langle J \rightarrow B \rangle = \langle J \Rightarrow \Delta \rightarrow B \rangle \equiv \delta \langle J \Rightarrow B \rangle \quad (5.82)$$

where we have used the Dyson equation (3.102). Now the difference between the isothermal and Newtonian Liouvillean is

$$\Delta = iL_T - iL_N = \Delta \tilde{\Gamma} \cdot \frac{\partial}{\partial \Gamma} = -\alpha \sum_{i=1}^N \mathbf{p}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} \quad (5.83)$$

Thus

$$\delta \langle J \Rightarrow B \rangle = - \int_0^t ds \left\langle J \exp(iL_N s) \alpha \sum_{i=1}^N \mathbf{p}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} \exp(iL_N(t-s)) B \right\rangle \quad (5.84)$$

where α is the field-free Gaussian multiplier appearing in the isothermal equation of motion. We assume that it is possible to define a new phase variable B' by

$$\exp(iL_N t) B' = \sum_{i=1}^N \mathbf{p}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} \exp(iL_N t) B \quad (5.85)$$

This is a rather unusual definition of a phase variable, but if B is an analytic function of the momenta, then an extensive phase variable B' always exists. First we calculate the average value of $B'(t)$.

$$\begin{aligned}
\langle B'(t_N) \rangle &= \left\langle \sum_{i=1}^N \mathbf{p}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} B(t_N) \right\rangle = \int d\Gamma f_c(\Gamma) \sum_{i=1}^N \mathbf{p}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} B(t_N) \\
&= - \int d\Gamma B(t_N) \sum_{i=1}^N \frac{\partial}{\partial \mathbf{p}_i} \cdot (\mathbf{p}_i f_c(\Gamma)) \\
&= -3N \langle B(t_N) \rangle + 2\beta \langle B(t_N) K(0) \rangle = 2\beta \langle B(t_N) [K(0) - \langle K(0) \rangle] \rangle
\end{aligned} \tag{5.86}$$

Unless B is trivially related to the kinetic energy K , $\langle B'(t_N) \rangle = 0$. Typically B will be a thermodynamic flux such as the heat flux vector or the symmetric traceless part of the pressure tensor. In these cases $\langle B'(t_N) \rangle$ vanishes because of Curie's Principle (§2.3).

Assuming, without loss of generality, that $\langle B(t_N) \rangle = 0$, then we can show ,

$$\begin{aligned}
\delta \langle J \Rightarrow B \rangle &= - \int_0^t ds \langle J \exp(iL_T s) \alpha \exp(iL_N(t-s)) B' \rangle \\
&= - \int_0^t ds \langle J(-s_T) \alpha(0) B'(t_N - s_N) \rangle
\end{aligned} \tag{5.87}$$

This is because $\langle J \rangle = \langle \alpha \rangle = 0$. Because J , B and B' are extensive and α is intensive, equation (5.87) can be expressed as the product of three zero mean extensive quantities divided by N . The average of three local, zero mean quantities is extensive, and thus the quotient is intensive. Therefore, except in the case where B is a scalar function of the kinetic energy, the difference between the susceptibilities computed under Newton's equations and under Gaussian isokinetic equations, is of order $1/N$ compared to the magnitude of the susceptibilities themselves. This means that in the large system limit the adiabatic and isokinetic susceptibilities are equivalent. Similar arguments can be used to show the thermodynamic equivalence of the adiabatic and Nosé susceptibilities. It is pleasing to be able to prove that the mechanical response is independent of the thermostatting mechanism and so only depends upon the thermodynamic state of the system.

Two further comments can be made at this stage: firstly, there is a simple reason why the differences in the respective susceptibilities is significant in the case where B is a scalar function of the kinetic energy. This is simply a reflection of the fact that in this case B , is intimately related to a constant of the motion for Gaussian isokinetic dynamics. One would expect to see a difference in the susceptibilities in this case. Secondly, in particular cases one can use Dyson decomposition techniques, (in particular equation (3.107)), to systematically examine the differences between the adiabatic and isokinetic susceptibilities. Evans and Morriss (1984) used this approach to calculate the differences, evaluated using Newtonian and isokinetic dynamics, between the correlation functions for each of the Navier-Stokes transport coefficients. The results showed

that the equilibrium time correlation functions for the shear viscosity, for the self diffusion coefficient and for the thermal conductivity and independent of thermostatting in the large system limit.

References

- Evans, D.J.,(1983). *J. Chem. Phys.*, **78**, 3297.
- Evans, D.J. and Holian, B.L.,(1985). *J. Chem. Phys.*, **83**, 4069.
- Evans, D.J., Hoover, W.G., Failor, B.H. , Moran, B. and, Ladd, A.J.C.,(1983). *Phys. Rev. A*, **28**, 1016.
- Evans, D.J. and Morriss, G.P., (1983). *Phys. Lett.*, **98A**, 433.
- Evans, D.J. and Morriss, G.P., (1983). *Chem. Phys.*, **77**, 63.
- Evans, D.J. and Morriss, G.P., (1984). *Chem. Phys.*, **87**, 451.
- Evans, D.J. and Morriss, G.P., (1984). *Comput. Phys. Rep.*, **1**, 297.
- Holian, B.L. and Evans, D.J., (1983). *J. Chem. Phys.*, **78**, 5147.
- Hoover, W.G., (1985). *Phys. Rev. A*, **31**, 1695.
- Hoover, W.G., Ladd, A.J.C. and Moran, B.,(1982). *Phys. Rev. Lett.*, **48**, 1818.
- Kubo, R., (1957). *J. Phys. Soc. Japan* **12**, 570.
- Kubo, R., (1982). *Int. J. Quantum Chem.*, **16**, 25.
- MacGowan, D. and Evans, D.J., (1986). *Phys. Lett.*, **117A**, 414.
- Morriss, G.P., and Evans, D.J., (1985). *Mol. Phys.*, **54**, 629.
- Nosé, S., (1984a). *J. Chem. Phys.*, **81**, 511.
- Nosé, S., (1984b). *Mol. Phys.*, **52**, 255.