

9 Steady State Fluctuations

9.1 INTRODUCTION

Nonequilibrium steady states are fascinating systems to study. Although there are many parallels between these states and equilibrium states, a convincing theoretical description of steady states, particularly far from equilibrium, has yet to be found. Close to equilibrium, linear response theory and linear irreversible thermodynamics provide a relatively complete treatment, (§2.1 - 2.3). However, in systems where local thermodynamic equilibrium has broken down, and thermodynamic properties are not the same local functions of thermodynamic state variables that they are at equilibrium, our understanding is very primitive indeed.

In §7.3 we gave a statistical mechanical description of thermostatted, nonequilibrium steady states far from equilibrium - the *transient time correlation function* (TTCF) and *Kawasaki* formalisms. The Transient Time Correlation Function is the nonlinear analogue of the Green-Kubo correlation functions. For linear transport processes the Green-Kubo relations play a role which is analogous to that of the partition function at equilibrium. Like the partition function, Green-Kubo relations are highly nontrivial to evaluate. They do however provide an exact starting point from which one can derive exact interrelations between thermodynamic quantities. The Green-Kubo relations also provide a basis for approximate theoretical treatments as well as being used directly in equilibrium molecular dynamics simulations.

The TTCF and Kawasaki expressions may be used as nonlinear, nonequilibrium partition functions. For example if a particular derivative commutes with the thermostatted, field-dependent propagator then one can formally differentiate the TTCF and Kawasaki expressions for steady state phase averages, yielding fluctuation expressions for the so-called *derived properties*. The key point in such derivations is that the particular derivative should commute with the relevant propagators. If this is not so one cannot derive tractable or useful results.

In order to constrain thermodynamic variables two basic feedback mechanisms can be employed: the integral feedback mechanism employed for example in the Nose-Hoover thermostat, (§5.2) and the differential mechanism employed in the Gaussian thermostat.

A third mechanism, the proportional mechanism has not found much use either in simulations or in theory because it necessarily employs irreversible equations of motion.

In this chapter we will derive fluctuation expressions for the derivatives of steady state phase averages. We will derive expressions for derivatives with respect to temperature, pressure and the mean value of the dissipative flux. Applying these derivatives in turn to averages of the internal energy, the volume and the thermodynamic driving force yields expressions for the specific heats, the compressibility and the inverse Burnett coefficients respectively. In order to ensure the commutivity of the respective derivatives and propagators, we will employ the Gaussian feedback mechanism exclusively. Corresponding derivations using Nose-Hoover feedback are presently unknown.

Rather than giving a general but necessarily formal derivation of the fluctuation formulae, we will instead concentrate on two specific systems: planar Couette flow and colour conductivity. By concentrating on specific systems we hope to make the discussion more concrete and simultaneously illustrate particular applications of the theory of nonequilibrium steady states discussed in Chapter 7.

9.2 THE SPECIFIC HEAT

In this section we illustrate the use of the Kawasaki distribution function and the Transient Time Correlation Function formalism by deriving formally exact expressions for the temperature derivative of nonequilibrium averages. Applying these expressions to the internal energy, we obtain two formulae (Evans and Morriss, 1987), for the isochoric specific heat. One of these shows that the specific heat can be calculated by analysing fluctuations in the steady state. The second formula relates the steady state specific heat to the transient response observed when an ensemble of equilibrium systems is perturbed by the field.

Transient Time Correlation Function Approach

For a system undergoing planar Couette flow the transient correlation function expression for the canonical ensemble average of a phase variable B is,

$$\langle B(t) \rangle = \langle B(0) \rangle - \beta\gamma V \int_0^t ds \langle B(s) P_{xy}(0) \rangle \quad (9.1)$$

This expression relates the nonequilibrium value of a phase variable B at time t , to the integral of a transient time correlation function (the correlation between P_{xy} in the equilibrium starting state, $P_{xy}(0)$, and B at time s after the field is turned on). The temperature implied by the β is the temperature of the initial ensemble. The steady state is *tied* to the initial ensemble by the constraint of constant peculiar kinetic energy. For systems that exhibit mixing, equation (9.1) can therefore be rewritten as,

$$\langle B(t) \rangle = \langle B(0) \rangle - \beta \gamma V \int_0^t ds \langle \Delta B(s) P_{xy}(0) \rangle \quad (9.2)$$

where the difference variable $\Delta B(s)$ is defined as the difference between the phase variable at s and its *average value at s* ,

$$\Delta B(s) = B(s) - \langle B(s) \rangle \quad (9.3)$$

Systems which are not expected to exhibit mixing are turbulent systems or systems which execute quasi-periodic oscillations.

An important property of the Gaussian thermostat is that although it fixes the kinetic energy of a system, the Gaussian isokinetic Liouville operator is **independent** of the temperature of the initial distribution. For each member of the ensemble, the Gaussian thermostat simply constrains the peculiar kinetic energy to be constant. As the Liouvillian, and the propagator in (9.2), are independent of the *value* of the temperature we can calculate the temperature derivative very easily. The result is,

$$\begin{aligned} \frac{\partial}{\partial T} \langle B(t) \rangle &= k_B \beta^2 \langle \Delta(B(0)) \Delta(H_0(0)) \rangle - k_B \beta \langle \langle B(t) \rangle - \langle B(0) \rangle \rangle \\ &\quad - k_B \beta^3 F_e \int_0^t ds \langle \Delta(B(s)) J(0) \Delta(H_0(0)) \rangle \end{aligned} \quad (9.4)$$

The first term on the right hand side of (9.4) is the equilibrium contribution. This is easily seen by setting $t=0$. The second and third terms are nonequilibrium terms. In deriving the second term on the right hand side of (9.4) we use equation (9.3) to simplify a number of terms. It is worth noting that equation (9.4) is not only valid in the steady state limit $t \rightarrow \infty$, but is also correct for all intermediate times t , which correspond to the transients which take the system from the initial equilibrium state to the final nonequilibrium steady state.

If we choose to evaluate the temperature derivative of the internal energy H_0 , we can calculate the specific heat at constant volume and external field, $C_{v,Fe}$. The result is (Evans and Morriss, 1987),

$$C_{v,Fe} = k_B \beta^2 \langle \Delta(H_0(0))^2 \rangle - k_B \beta \langle \langle H_0(t) \rangle - \langle H_0(0) \rangle \rangle - k_B \beta^3 F_e \int_0^t ds \langle \Delta(H_0(s) J(0)) \Delta(H_0(0)) \rangle \quad (9.5)$$

Again the first term on the right hand side is easily recognised as the equilibrium specific heat. The second and third terms are nonlinear nonequilibrium terms. They signal the breakdown of local thermodynamic equilibrium. In the linear regime for which linear response theory is valid, they are of course both zero. The third term takes the form of a transient time correlation function. It measures the correlations of equilibrium energy fluctuations, $\Delta H_0(0)$, with the transient fluctuations in the composite-time variable, $\Delta(H_0(s) J(0))$. The second term can of course be rewritten as the integral of a transient time correlation function using (9.1).

Kawasaki representation.

Consider the Schrödinger form,

$$\langle B(t) \rangle = \int d\Gamma B(\Gamma) f(t) \quad (9.6)$$

The thermostatted Kawasaki form for the N-particle distribution function is,

$$f(t) = \exp \left[-\beta F_e \int_0^t ds J(-s) \right] f(0) \quad (9.7)$$

Since $f(t)$ is a distribution function it must be normalised. We guarantee this by dividing the right hand side of equation (9.7) by its phase integral. If we take the initial ensemble to be **canonical**, we find,

$$f(t) = \frac{\exp \left[-\beta \left(H_0 + F_e \int_0^t ds J(-s) \right) \right]}{\int d\Gamma \exp \left[-\beta \left(H_0 + F_e \int_0^t ds J(-s) \right) \right]} \quad (9.8)$$

The exponents contains a divergences due to the fact that the time average of $J(-s)$ is nonzero. This secular divergence can be removed by multiplying the numerator and the denominator of the explicitly normalised form by $\exp[+\beta F_e \int_0^t ds \langle J(-s) \rangle]$. This has

the effect of changing the dissipative flux that normally appears in the Kawasaki exponent from $J(-s)$ to $\Delta J(-s)$, in both the numerator and denominator. The removal of the secular divergence has **no** effect on the results computed in this chapter and is included here for largely aesthetic reasons.

$$f(t) = \frac{\exp\left[-\beta\left(H_0 + F_e \int_0^t ds \Delta J(-s)\right)\right]}{\int d\Gamma \exp\left[-\beta\left(H_0 + F_e \int_0^t ds \Delta J(-s)\right)\right]} \quad (9.9)$$

The average of an arbitrary phase variable $B(\Gamma)$ in the renormalized Kawasaki representation is,

$$\langle B(t) \rangle = \langle B(0) \rangle + \frac{\int d\Gamma \Delta B \exp\left[-\beta\left(H_0 + F_e \int_0^t ds \Delta J(-s)\right)\right]}{\int d\Gamma \exp\left[-\beta\left(H_0 + F_e \int_0^t ds \Delta J(-s)\right)\right]} \quad (9.10)$$

To obtain the temperature derivative of equation (9.10) we differentiate with respect to β . This gives

$$\begin{aligned} \frac{\partial \langle B(t) \rangle}{\partial \beta} = & - \int d\Gamma B \left(H_0 + F_e \int_0^t ds \Delta J(-s) \right) f(t) \\ & + \left(\int d\Gamma B f(t) \right) \left(\int d\Gamma \left(H_0 + F_e \int_0^t ds \Delta J(-s) \right) f(t) \right) \end{aligned} \quad (9.11)$$

Using the Schrödinger-Heisenberg equivalence we transfer the time dependence from the distribution function to the phase variable in each of the terms in equation (9.11). This gives

$$\frac{\partial \langle B(t) \rangle}{\partial \beta} = - \left\langle \Delta B(t) \Delta \left(H_0(t) + F_e \int_0^t ds \Delta J(t-s) \right) \right\rangle \quad (9.12)$$

Substituting the internal energy for B in equation (9.12) and making a trivial change of variable in the differentiation ($\beta \rightarrow T$) and integration ($t-s \rightarrow s$), we find that the specific heat can be written as,

$$C_{V,F_e}(t) = k_B \beta^2 \left\langle \Delta \left(H_0(t)^2 \right) \right\rangle + k_B \beta^2 F_e \int_0^t ds \left\langle \Delta H_0(t) \Delta J(s) \right\rangle \quad (9.13)$$

The first term gives the steady state energy fluctuations and the second term is a steady state time correlation function. As $t \rightarrow \infty$, the only times s , which contribute to the integral are times within a relaxation time of t , so that in this limit the time correlation function has no memory of the time at which the field was turned on.

These theoretical results for the specific heat of nonequilibrium steady states have been tested in nonequilibrium molecular dynamics simulations of isothermal planar Couette flow (Evans, 1986 and Evans and Morriss, 1987). The system studied was the Lennard-Jones fluid at its triple point, ($k_B T/\epsilon=0.722$, $\rho\sigma^3=0.8442$). 108 particles were employed with a cutoff of 2.5σ .

Table 9.1. Lennard-Jones Specific Heat Data.

Potential: $\Phi(r) = 4\epsilon[(r/\sigma)^{-12} - (r/\sigma)^{-6}]$.

State point: $T^* = 0.722$, $\rho^* = 0.8442$, $\gamma^* = 1.0$, $N = 108$, $r_c^* = 2.5$.

| | |
|---|----------------------|
| Transient Correlation Results: 200K timesteps | |
| $C_{V,\gamma}^*/N$ | 2.662 ± 0.004 |
| $(\langle E_\gamma^* \rangle_{ss} - \langle E_\gamma^* \rangle_{\gamma=0})/NT^*$ | 0.287± 0.0014 |
| $(\gamma^*/T^{*3}\rho^*)\int_0^\infty ds \langle \Delta(H_0^*(s)P_{xy}^*(0))\Delta(H_0^*(0)) \rangle$ | -0.02± 0.05 |
| $C_{V,\gamma}^*/N$ | 2.395± 0.06 |
| Kawasaki Correlation results: 300K timesteps | |
| $\langle \Delta(E)^{*2} \rangle_{ss}/NT^{*2}$ | 3.307±0.02 |
| $(\gamma^*/T^{*2}\rho^*)\int_0^\infty ds \langle \Delta E^*(s)\Delta P_{xy}^*(0) \rangle_{ss}$ | -1.050 ±0.07 |
| $C_{V,\gamma}^*/N$ | 2.257±0.09 |
| Direct NEMD calculation: 100K timesteps | |
| $C_{V,\gamma}^*/N$ | 2.35±0.05 |

Reduced units are denoted by *. Units are reduced to dimensionless form in terms of the Lennard-Jones parameters, m, σ, ϵ . $\tau = \partial u_x / \partial y \sigma (m/\epsilon)^{1/2}$. $\Delta t^* = 0.004$. $\langle \dots \rangle_{ss}$ denotes nonequilibrium steady state average.

The steady state specific heat was calculated in three ways: from the transient correlation function expression equation (9.5), from the Kawasaki expression equation (9.13) and by direct numerical differentiation of the internal energy with respect to the initial temperature. The results are shown in the Table 9.1 below. Although we have been unable to prove the result theoretically, the numerical results suggest that the integral appearing on the right hand side of (9.5) is zero. All of our simulation results, within error bars, are consistent with this. As can be seen in the Table 9.1 the transient correlation expression for the specific heat predicts that it decreases as we go away from equilibrium. The predicted specific heat at a reduced strain rate $(\gamma\sigma(m/\epsilon)^{1/2}) = 1$ is some 11% smaller than the equilibrium value. This behaviour of the specific heat was first observed in 1983 by Evans (Evans, 1983).

Table 9.2. Comparison of Soft Sphere Specific Heats as a function of Strain Rate
Potential: $\Phi(r) = \epsilon(r/\sigma)^{-12}$. State point: $T^* = 1.0877$, $\rho^* = 0.7$, $N = 108$, $r_c^* = 1.5$.

| γ^* | $\frac{E^*}{NT^*}$ | $\frac{C_{v,\gamma}^*}{N}$ direct | $\frac{C_{v,\gamma}^*}{N}$ transient |
|----------------|--------------------|-----------------------------------|--------------------------------------|
| 0.0 | 4.400 | 2.61 | 2.61 |
| 0.4 | 4.441 | 2.56 | 2.57 |
| 0.6 | 4.471 | 2.53 | 2.53 |
| 0.8 | 4.510 | 2.48 | 2.49 |
| 1.0 ± 0.01 | 4.550 ± 0.001 | 2.43 | 2.46 ± 0.002 |

Note: In these calculations, the transient time correlation function integral, (9.5), was assumed to be zero. Data from (Evans, 1983, Evans, 1986, Evans and Morriss, 1987).

The results obtained from the Kawasaki formula show that although the internal energy fluctuations are greater than at equilibrium, the specific heat decreases as the strain rate is increased. The integral of the steady state energy-stress fluctuations more than compensates for increase in internal energy fluctuations. The Kawasaki prediction for the specific heat is in statistical agreement with the transient correlation results. Both sets of results also agree with the specific heat obtained by direct numerical differentiation of the internal energy. Table 9.2 shows a similar set of comparisons based on published data (Evans, 1983). Once again there is good agreement between results predicted on the basis of the transient correlation formalism and the direct NEMD method.

As a final comment of this section we should stress that the specific heat as we have defined it, refers only to the derivative of the internal energy with respect to the temperature of the *initial* ensemble (or equivalently, with respect to the nonequilibrium *kinetic* temperature). Thus far, our derivations say nothing about the thermodynamic temperature ($\equiv \partial E / \partial S$) of the steady state. We will return to this subject in Chapter 10.

9.3 THE COMPRESSIBILITY AND ISOBARIC SPECIFIC HEAT

In this section we calculate formally exact fluctuation expressions for other derived properties including the specific heat at constant pressure and external field, $C_{p,Fe}$, and the compressibility, $\chi_{T,Fe} \equiv -\partial \ln V / \partial p_{T,Fe}$. The expressions are derived using the isothermal Kawasaki representation for the distribution function of an isothermal isobaric steady state.

The results indicate that the compressibility is related to nonequilibrium volume fluctuations in exactly the same way that it is at equilibrium. The isobaric specific heat, $C_{p,Fe}$, on the other hand, is not simply related to the mean square of the enthalpy fluctuations as it is at equilibrium. In a nonequilibrium steady state, these enthalpy fluctuations must be supplemented by the integral of the steady state time cross correlation function of the dissipative flux and the enthalpy.

We begin by considering the isothermal-isobaric equations of motion considered in §6.7. The obvious nonequilibrium generalisation of these equations is,

$$\begin{aligned}\dot{\mathbf{q}}_i &= \frac{\mathbf{p}_i}{m} + \varepsilon \mathbf{q}_i + \mathbf{C}(\Gamma) F_e(t) \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i - \varepsilon \mathbf{p}_i + \mathbf{D}(\Gamma) F_e(t) - \alpha(\Gamma, t) \mathbf{p}_i \\ \frac{dV}{dt} &= 3V\dot{\varepsilon}\end{aligned}\tag{9.14}$$

In the equations $d\varepsilon/dt$ is the dilation rate required to precisely fix the value of the hydrostatic pressure, $p = \sum (\mathbf{p}^2/m + \mathbf{q} \cdot \mathbf{F}) / 3V$. α is the usual Gaussian thermostat multiplier used to fix the peculiar kinetic energy, K . Simultaneous equations must be solved to yield explicit expressions for both multipliers. We do not give these expressions here since they are straightforward generalisations of the field-free ($F_e=0$), equations given in §6.7.

The external field terms are assumed to be such as to satisfy the usual Adiabatic Incompressibility of Phase Space (AIP) condition. We define the dissipative flux, J , as the obvious generalisation of the usual isochoric case.

$$\left(\frac{dI_0}{dt}\right)^{ad} \equiv -J(\Gamma)F_e \quad (9.15)$$

This definition is consistent with the fact that in the field-free adiabatic case the enthalpy $I_0 \equiv H_0 + pV$, is a constant of the equations of motion given in (9.14). It is easy to see that the isothermal isobaric distribution, f_0 , is preserved by the field-free thermostatted equations of motion.

$$f_0 = \frac{e^{-\beta I_0}}{\int_0^\infty dV \int d\Gamma e^{-\beta I_0}} \quad (9.16)$$

It is a straightforward matter to derive the Kawasaki form of the N-particle distribution for the isothermal-isobaric steady state. The normalised version of the distribution function is,

$$f(t) = \frac{\exp\left[-\beta\left(I_0 + \int_0^t ds J(-s)F_e\right)\right]}{\int_0^\infty dV \int d\Gamma \exp\left[-\beta\left(I_0 + \int_0^t ds J(-s)F_e\right)\right]} \quad (9.17)$$

The calculation of derived quantities is a simple matter of differentiation with respect to the variables of interest. As was the case for the isochoric specific heat, the crucial point is that the field-dependent isothermal-isobaric propagator implicit in the notation $f(t)$, is independent of the pressure and the temperature of the entire ensemble. This means that the differential operators $\partial/\partial T$ and $\partial/\partial p_0$ commute with the propagator.

The pressure derivative is easily calculated as,

$$\left(\frac{\partial \langle B(t) \rangle}{\partial p_0}\right)_{T, F_e} = -\beta \langle B(t)V(t) \rangle + \beta \langle B(t) \rangle \langle V(t) \rangle \quad (9.18)$$

If we choose B to be the phase variable corresponding to the volume then the expression for the isothermal, fixed field compressibility takes on a form which is formally identical to its equilibrium counterpart.

$$\chi_{T, F_e} = \lim_{t \rightarrow \infty} -\frac{\beta}{V} \langle \Delta V(t)^2 \rangle \quad (9.19)$$

The limit appearing in (9.19) implies that a steady state average should be taken. This follows from the fact that the external field was 'turned on' at $t=0$.

The isobaric temperature derivative of the average of a phase variable can again be calculated from (9.17).

$$\begin{aligned} \frac{\partial}{\partial \beta} \langle B(t) \rangle &= \int_0^\infty dV \int d\Gamma f(t) B(0) \left(I_0 + \int_0^t ds J(-s) F_e \right) \\ &\quad - \langle I_0(t) \rangle \int_0^\infty dV \int d\Gamma f(t) \left[-\beta \left(I_0 + \int_0^t ds J(-s) F_e \right) \right] \end{aligned} \quad (9.20)$$

In deriving (9.20) we have used the fact that $\int dV \int d\Gamma f(t) B(0) = \langle B(t) \rangle$. Equation (9.20) can clearly be used to derive expressions for the expansion coefficient. However setting the test variable B to be the enthalpy and remembering that

$$C_{p, F_e} = \left(\frac{\partial I_0}{\partial T} \right)_{p, F_e} \quad (9.21)$$

leads to the isobaric specific heat,

$$C_{p, F_e} = \lim_{t \rightarrow \infty} \frac{1}{k_B T^2} \left\{ \langle \Delta I_0(t)^2 \rangle + F_e \int_0^t ds \langle \Delta I_0(t) \Delta J(s) \rangle \right\} \quad (9.22)$$

This expression is of course very similar to the expression derived for the isochoric specific heat in §9.2.

In contrast to the situation for the compressibility, the expressions for the specific heats are not simple generalisations of the corresponding equilibrium fluctuation formulae. Both specific heats also involve integrals of steady state time correlation functions involving cross correlations of the appropriate energy with the dissipative flux. Although the time integrals in (9.13) & (9.22) extend back to $t=0$ when the system was at equilibrium, for systems which exhibit mixing, only the steady state portion of the integral contributes. This is because in such systems, $\lim_{t \rightarrow \infty} \langle \Delta B(t) \Delta J(0) \rangle = \langle \Delta B(t) \rangle \langle \Delta J(0) \rangle = 0$. These correlation functions are therefore comparatively easy to calculate in computer simulations.

9.4 DIFFERENTIAL SUSCEPTIBILITY

In §2.3 we introduced the linear transport coefficients as the first term in an expansion, about equilibrium, of the thermodynamic flux in terms of the driving thermodynamic forces. The nonlinear Burnett coefficients are the coefficients of this Taylor expansion. Before we address the question of the nonlinear Burnett coefficients we will consider the *differential susceptibility* of a nonequilibrium steady state. Suppose we expand the irreversible fluxes in powers of the forces, about a nonequilibrium steady state. The leading term in such an expansion is called the differential susceptibility. As we will see, difficulties with commutation relations force us to work in the Norton rather than the Thévenin ensemble. This means that we will always be considering the variation of the thermodynamic forces which result from possible changes in the thermodynamic fluxes.

Consider an ensemble of N-particle systems satisfying the following equations of motion. For simplicity we assume that each member of the ensemble is electrostatically neutral and consists only of univalent ions of charge, $\pm e = \pm 1$. This system is formally identical to the colour conductivity system which we considered in §6.2.

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m} \equiv \mathbf{v}_i \quad (9.23)$$

$$m\dot{\mathbf{v}}_i = \mathbf{F}_i + \lambda \mathbf{e}_i - \alpha(\mathbf{v}_i - \mathbf{i} \mathbf{e}_i J) \quad (9.24)$$

In these equations, λ and α are Gaussian multipliers chosen so that the x-component of the current per particle, $J = \sum \mathbf{e}_i \mathbf{v}_{xi} / N$ and the temperature $T = \sum m(\mathbf{v}_i - \mathbf{i} \mathbf{e}_i J)^2 / 3Nk_B$ are constants of the motion. This will be the case provided that,

$$\lambda = - \frac{\sum F_{xi} e_i}{N} \quad (9.25)$$

and

$$\alpha = \frac{\sum \mathbf{F}_i \cdot (\mathbf{v}_i - \mathbf{i} \mathbf{e}_i J)}{\sum \mathbf{v}_i \cdot (\mathbf{v}_i - \mathbf{i} \mathbf{e}_i J)} \quad (9.26)$$

In more physical terms λ can be thought of as an external electric/colour field which takes on precisely those values required to ensure that the current J is constant. Because it precisely fixes the current, it is a phase variable. It is clear from (9.4.3) that the form

of the phase variable λ is independent of the value of the current. Of course the ensemble average of λ will depend on the average value of the current. It is also clear that the expression for α is similarly independent of the **average** value of the current for an ensemble of such systems.

These points can be clarified by considering an initial ensemble characterised by the canonical distribution function, $f(0)$,

$$f(0) = \frac{\exp\left[-\beta\left(\sum \frac{m}{2}(\mathbf{v}_i - e_i \mathbf{J}_0)^2 + \Phi\right)\right]}{\int d\Gamma \exp\left[-\beta\left(\sum \frac{m}{2}(\mathbf{v}_i - e_i \mathbf{J}_0)^2 + \Phi\right)\right]} \quad (9.27)$$

In this equation \mathbf{J}_0 is a constant which is equal to the canonical average of the current,

$$\langle \mathbf{J}(0) \rangle = \mathbf{J}_0 = iJ_0 \quad (9.28)$$

If we now subject this ensemble of systems which we will refer to as the J-ensemble, to the equations of motion (9.23 and 9.24), the electrical current and the temperature will remain fixed at their initial values and the mean value of the field multiplier λ , will be determined by the electrical conductivity of the system.

It is relatively straightforward to apply the theory of nonequilibrium steady states to this system. It is easily seen from the equations of motion that the condition known as the Adiabatic Incompressibility of Phase Space (AIF) holds. Using equation (9.23) to (9.27), the adiabatic time derivative of the energy functional is easily seen to be,

$$\dot{H}^{ad} \equiv \left(\frac{d}{dt}\right)^{ad} \left\{ \sum_i \frac{m}{2}(\mathbf{v}_i - e_i \mathbf{J}_0)^2 + \Phi \right\} = N\lambda(\Gamma)J(\Gamma) \quad (9.29)$$

This equation is unusual in that the adiabatic derivative does not factorise into the product of a dissipative flux and the magnitude of a perturbing external field. This is because in the J-ensemble the obvious external field, λ , is in fact a phase variable and the current, J , is a constant of the motion. As we shall see this causes us no particular problems. The last equation that we need for the application of nonlinear response theory is the derivative,

$$\frac{\partial}{\partial \mathbf{J}_0} H = -mN(\mathbf{J} - \mathbf{J}_0) \quad (9.30)$$

Kawasaki Representation

If we use the isothermal generalisation of the Kawasaki expression for the average of an arbitrary phase variable, B , we find,

$$\langle B(t) \rangle = \frac{\left\langle B(0) \exp \left[\beta N \int_0^{-t} ds J(s) \lambda(s) \right] \right\rangle}{\left\langle \exp \left[\beta N \int_0^{-t} ds J(s) \lambda(s) \right] \right\rangle} \quad (9.31)$$

In distinction to the usual case we considered in §7.2, the Kawasaki exponent involves a product of two phase variables J and λ , rather than the usual product of a dissipative flux (ie. a phase variable), and a time-dependent external field. The propagator used in (9.31) is the field-dependent thermostatted propagator implicit in the equations of motion (9.23) to (9.26). The only place that the ensemble averaged current appears in (9.31) is in the initial ensemble averages. We can therefore easily differentiate (9.31) with respect to \mathbf{J}_0 to find that (Evans and Lynden-Bell, 1988),

$$\frac{\partial \langle B(t) \rangle}{\partial \mathbf{J}_0} = \beta m N \langle \Delta B(t) \Delta \mathbf{J}(0) \rangle \quad (9.32)$$

where $\Delta(B(t)) \equiv B(t) - \langle B(t) \rangle$ and $\Delta(\mathbf{J}(t)) \equiv \mathbf{J}(t) - \langle \mathbf{J}(t) \rangle = \mathbf{J}(0) - \mathbf{J}_0$. This is an exact canonical ensemble expression for the \mathbf{J} -derivative of the average of an arbitrary phase variable. If we let t tend toward infinity we obtain a steady state fluctuation formula which complements the ones we derived earlier for the temperature and pressure derivatives. Equation (9.4.10) gives a steady state fluctuation relation for the differential susceptibility of, B .

One can check that this expression is correct by rewriting the right hand side of (9.32) as an integral of responses over a set of Norton ensembles in which the current takes on specific values. Using equation (9.27) we can write the average of $B(t)$ as,

$$\langle B(t) \rangle = \frac{\int dJ \exp \left[-\beta m N \Delta J^2 / 2 \right] \langle B(t); J \rangle}{\int dJ \exp \left[-\beta m N \Delta J^2 / 2 \right]} \quad (9.33)$$

We use the notation $\langle B(t); J \rangle$ to denote that subset of the canonical ensemble, (9.27), in which the current takes on the exact value of J . The probability of the J -ensemble taking on an initial x -current of J is easily calculated from (9.27) to be proportional to,

$\exp[-\beta m N \Delta J^2 / 2]$. Since the current is a constant of the motion we do not need to specify a time at which the current takes on the specified value.

Differentiating (9.33) we can write the derivative with respect to the average current as a superposition of ΔJ -ensemble contributions,

$$\begin{aligned} \frac{\partial \langle B(t) \rangle}{\partial J_0} &= \beta m N \frac{\int dJ \exp[-\beta m N \Delta J^2] \Delta J \langle B(t); J \rangle}{\int dJ \exp[-\beta m N \Delta J^2 / 2]} \\ &= \beta m N \langle \Delta B(t) \Delta J(0) \rangle \end{aligned} \quad (9.34)$$

This expression is of course identical to equation (9.32) which was derived using the Kawasaki distribution. (9.34) was derived however, without the use of perturbative mechanical considerations such as those implicit in the use of the Kawasaki distribution. This second derivation is based on two points: the initial distribution is a normal distribution of currents about \mathbf{J}_0 , and; the dynamics preserves the value of the current for each member of the ensemble. Of course the result is still valid even when \mathbf{J} is not exactly conserved provided that the time-scale over which it changes is much longer than the time-scale for the decay of steady state fluctuations. This derivation provides independent support for the validity of the renormalized Kawasaki distribution function.

We will now derive relations between the \mathbf{J} -derivatives in the \mathbf{J} -ensemble and in the constrained ensemble in which \mathbf{J} takes on a precisely fixed value (the $\Delta \mathbf{J}$ -ensemble). In the thermodynamic limit, the spread of possible values of $\Delta \mathbf{J}$ will become infinitely narrow suggesting that we can write a Taylor expansion of $\langle B(t); \mathbf{J} \rangle$ in powers of $\Delta \mathbf{J}$ about \mathbf{J}_0 .

$$\langle B(t); \mathbf{J} \rangle = \langle B(t); \mathbf{J}_0 \rangle + \Delta J \frac{\partial \langle B(t); \mathbf{J}_0 \rangle}{\partial J} + \frac{\Delta J^2}{2!} \frac{\partial^2 \langle B(t); \mathbf{J}_0 \rangle}{\partial J^2} + \dots \quad (9.35)$$

Substituting (9.35) into (9.34) and performing the Gaussian integrals over \mathbf{J} , we find that,

$$\frac{\partial \langle B(t) \rangle}{\partial J_0} = \frac{\partial \langle B(t); \mathbf{J}_0 \rangle}{\partial J} + \frac{1}{2\beta m N} \frac{\partial \langle B(t); \mathbf{J}_0 \rangle}{\partial J^3} + \dots \quad (9.36)$$

This is a very interesting equation. It shows the relationship between the derivative computed in a canonical ensemble and a $\Delta \mathbf{J}$ -ensemble. It shows that differences between the two ensembles arise from non-linearities in the local variation of the phase variable

with respect to the current. It is clear that these ensemble corrections are of order $1/N$ compared to the leading terms.

9.5 THE INVERSE BURNETT COEFFICIENTS

We will now use the TTCF formalism in the Norton ensemble, to derive expressions for the inverse Burnett coefficients. The Burnett coefficients, L_i , give a Taylor series representation of a nonlinear transport coefficient $L(X)$, defined by a constitutive relation between a thermodynamic force X , and a thermodynamic flux $J(\Gamma)$,

$$\langle J \rangle = L(X)X = L_1 X + \frac{1}{2!} L_2 X^2 + \frac{1}{3!} L_3 X^3 + \quad (9.37)$$

It is clear from this equation the Burnett coefficients are given by the appropriate partial derivatives of $\langle J \rangle$, evaluated at $X=0$. As mentioned in §9.4 we will actually be working in the Norton ensemble in which the thermodynamic force X , is the dependent rather than the independent variable. So we will in fact derive expressions for the inverse Burnett coefficients, L^{-1}

$$\langle X \rangle = L^{-1}(J)J = L_1^{-1} J + \frac{1}{2!} L_2^{-1} J^2 + \frac{1}{3!} L_3^{-1} J^3 + \quad (9.38)$$

The TTCF representation for a steady state phase average for our electrical/colour diffusion problem is easily seen to be.

$$\langle B(t) \rangle = \beta N \int_0^t ds \langle \Delta B(s) \lambda(0) J(0) \rangle \quad (9.39)$$

We expect that the initial values of the current will be clustered about \mathbf{J}_0 . If we write,

$$\langle \Delta B(s) \lambda(0) J(0) \rangle = \langle \Delta B(s) \lambda(0) \rangle J_0 + \langle \Delta B(s) \lambda(0) \Delta J(0) \rangle \quad (9.40)$$

it is easy to see that if B is extensive then the two terms on the right hand side of (9.40) are $O(1)$ and $O(1/N)$ respectively. For large systems we can therefore write,

$$\langle B(t) \rangle = \beta N \int_0^t ds \langle \Delta B(s) \lambda(0) \rangle J_0 \quad (9.41)$$

It is now a simple matter to calculate the appropriate J -derivatives.

$$\begin{aligned}
\frac{\partial \langle B(t) \rangle}{\partial J_0} &= \beta N \int_0^t ds \langle B(s) \lambda(0) \rangle + \beta J_0 N \int_0^t ds \int d\Gamma B(s) \lambda(0) \frac{\partial f(0)}{\partial J_0} \\
&= \beta N \int_0^t ds \langle B(s) \lambda(0) \rangle + \beta^2 J_0 m N^2 \int_0^t ds \langle B(s) \lambda(0) \Delta J(0) \rangle
\end{aligned} \tag{9.42}$$

This equation relates the J-derivative of phase variables to TTCFs. If we apply these formulae to the calculation of the leading Burnett coefficient we of course evaluate the derivatives at $J_0=0$. In this case the TTCFs become equilibrium time correlation functions. The results for the leading Burnett coefficients are (Evans and Lynden-Bell, 1988):

$$\left(\frac{\partial \langle B(t) \rangle}{\partial J_0} \right)_{J_0=0} = \beta N \int_0^t ds \langle B(s) \lambda(0) \rangle_{eq} \tag{9.43}$$

$$\left(\frac{\partial^2 \langle B(t) \rangle}{\partial J_0^2} \right)_{J_0=0} = 2\beta^2 m N^2 \int_0^t ds \langle B(s) \lambda(0) \Delta J(0) \rangle_{eq} \tag{9.44}$$

$$\left(\frac{\partial^3 \langle B(t) \rangle}{\partial J_0^3} \right)_{J_0=0} = 3\beta^3 m^2 N^3 \int_0^t ds \langle B(s) \lambda(0) \{ \Delta^2[J(0)] - \langle \Delta^2[J(0)] \rangle \} \rangle_{eq} \tag{9.45}$$

Surprisingly, the expressions for the Burnett coefficients only involve equilibrium, two-time correlation functions. At long times assuming that the system exhibits mixing they each factor into a triple product $\langle B(s \rightarrow \infty) \rangle \langle \lambda(0) \rangle \langle \text{cum}(J(0)) \rangle$. The terms involving $\lambda(0)$ and the cumulants of $J(0)$ factor because at time zero the distribution function (9.27), factors into kinetic and configurational parts. Of course these results for the Burnett coefficients could have been derived using the ΔJ -ensemble methods discussed in §9.4.

It is apparent that our discussion of the differential susceptibility and the inverse Burnett coefficients has relied heavily on features unique to the colour conductivity problem. It is not obvious how one should carry out the analogous derivations for other transport coefficients. General fluctuation expressions for the inverse Burnett coefficients have recently been derived by Standish and Evans (1989). The general results are of the same form as the corresponding colour conductivity expressions. We refer the reader to the above reference for details.

REFERENCES

Evans, D. J., (1983), *J. Chem. Phys.*, **78**, 3297.

- Evans, D. J., (1986), *Proceedings of the Fourth Australian National Congress on Rheology*, ed Huilgol, R. R. (Australian Society of Rheology), p 23.
- Evans, D. J. and Lynden-Bell, R. M., (1988), *Phys. Rev.*, **A38**, 5249.
- Evans, D. J. and Morriss, G. P., (1987), *Mol. Phys.*, **61**, 1151.
- Standish, R. K. and Evans, D. J., (1989), *Phys. Rev. A* (submitted).