CHAPTER 6

Nonequilibrium Steady States

"The number of molecules being finite, it is clear that small finite deviations from absolute precision in the reversal we have supposed would not obviate the resulting disequalisation of the distribution of energy. But the greater the number of molecules, the shorter will be the time during which the disequalising will continue; and it is only when we regard the number of molecules as practically infinite that we can regard spontaneous disequalisation as practically impossible¹." William Thomson, *Nature*, April 9, 1874, pp. 441-444.

6.1 THE PHYSICALLY ERGODIC NONEQUILIBRIUM STEADY STATE

Definition

A nonequilibrium system is *stationary* if it is subject to a thermostatting mechanism and a dissipative field such that for smooth phase functions $B(\Gamma)$

$$\lim_{\tau \to \infty} \lim_{t \to \infty} \int_0^\tau ds \, \frac{B(S^{t+s}\Gamma)}{\tau} = const(\Gamma), \ \forall \Gamma \in D.$$
(6.1.1)

¹ In modern terminology, Thomson is saying that, other things being equal, the largest Lyapunov exponent increases with the number of particles, so that its reciprocal (the reversal time) becomes microscopic for macroscopic systems.

Stationarity simply means that such systems have time independent averages for physical properties at sufficiently long times. The time independent value that these time averages take on could be dependent on the initial phase, Γ .

Definition

A *physically ergodic nonequilibrium steady state* (*peNESS*) satisfies the equation:

$$\lim_{\tau \to \infty} \lim_{t \to \infty} \int_0^\tau ds \, \frac{B(S^{t+s}\Gamma)}{\tau} = \lim_{t \to \infty} \left\langle B(S^t\Gamma) \right\rangle_0 = const \,\,\forall \Gamma \in D \tag{6.1.2}$$

where the subscript zero on the ensemble average denotes an ensemble average over the initial time zero ensemble, $f(\Gamma;0)$ and $B(\Gamma)$ is a smooth phase function. Ddenotes the ostensible phase space domain over which the initial ensemble density is nonzero. For almost initial phase Γ , the *time average* on the left hand side of (6.1.2) equals the right hand *late-time ensemble average* taken with respect to the initial distribution $f(\Gamma;0)$ in D. At late times we say that the steady state is ergodic with respect to ensemble averages of physical properties, over the initial distribution, D.

When we speak of physical ergodicity, we say that *almost* any initial phase leads, at long times, to time averages that are equal to the long time, ensemble average because there are sets of initial phase points, whose measure is zero, but for which the long time, averaged properties are very different from the properties of the steady state. Consider almost any $\Gamma \in D$ if we form the time reversal mapping of the set of late-time phase vectors, $S'\Gamma$, then the set of phases $\{M^TS'\Gamma\}$ has very strange properties. Advancing time for a short while $\tau \ll t$ generates antisteady state properties. They are overwhelmingly likely to convert heat into work. However for sufficiently large *t* the probability of observing these "repeller" phases becomes incredibly small – going to zero in the limit $t \to \infty$.

Equation (6.1.2) implies that the long time averages could be averaged over almost any initial distribution of those initial phases $f(\Gamma; 0)$ so that for a NESS,

$$\lim_{t \to \infty} \left\langle B(S^{t} \Gamma) \right\rangle_{0} = \lim_{t \to \infty} \int_{\Gamma \in D} d\Gamma \ B(S^{t} \Gamma) f(\Gamma; 0) = \lim_{t \to \infty} \left\langle B(S^{t} \Gamma) \right\rangle \quad \forall f(\Gamma; 0), \forall \Gamma \in D \quad (6.1.3)$$

Equation (6.1.3) shows that physically ergodic nonequilibrium steady states are physically ergodic with respect to almost *any* initial distribution of phases, $f(\Gamma;0)$ in the phase space domain *D*. Time averages of physical variables are equal to ensemble averages and in the nonequilibrium steady state the late-time ensemble average is independent of the initial distribution. This coincides with the commonplace observation that for example in shearing laminar flows with fixed boundary conditions of shear rate, boundary temperatures and pressure etc, the nonequilibrium steady state so produced is, at long times, independent of the details of the initial state from which it was produced and a single long time, time average will give the same result for a physical measurement that we would obtain from a late-time ensemble average of repeated experiments.

Later in this chapter we will examine in more detail the mathematical conditions that are required in order to generate a physically ergodic nonequilibrium steady state.

While our physical experience is that physically ergodic NESS do exist, we also know from experience that this is not always the case. For example in Rayleigh-Bernard instability we know that for a fixed geometry and set of boundary conditions systems my form into 2 rolls or 4 rolls *etc* with these number of rolls fixed and persisting indefinitely. Clearly the physical properties on the 2-roll system are different from those of a 4-roll system. These types of system do not satisfy (6.1.2) (*.ie.* they do not form a nonequilibrium steady state).

If we could define the phase space subdomain D_2 over which only 2 rolls form at late times, then over the subdomain D_2 , the system would form a nonequilibrium steady state, while over D it would not. However in such cases it may be practically impossible to actually discover the topology of this phase space subdomain D_2 . If this is the case then from a practical point of view such systems are best viewed as not forming a NESS.

6.2 ENTROPY AND ENTROPY PRODUCTION IN NONEQUILIBRIUM STEADY STATES

In §2.6 we showed that the time derivative of the Gibbs entropy for autonomous Hamiltonian systems satisfies the equation $\dot{S}_G(t) = 0$ and for driven nonequilibrium isokinetic, steady state systems even far from equilibrium – see (2.6.2),

$$\begin{split} \dot{S}_{G}(t) &= -(D_{C}(N_{W}-1)-1)k_{B}\left\langle \alpha(t)\right\rangle \\ &= k_{B}\left\langle \Lambda(t)\right\rangle \xrightarrow{t\to\infty} const < 0 \end{split} \tag{6.2.2}$$

In (6.2.2) D_c is the number of Cartesian dimensions N_w is the number of isokinetically thermostatted wall particles and we assume that 3 Cartesian components of linear momentum are also conserved. The fact that the average value of the thermostat multiplier becomes constant follows from the Dissipation Theorem and the assumption of T-mixing. The fact that this constant is negative comes from applying the Second Law Inequality. At the late times ensemble average of the Gibbs entropy is not constant but rather decreases at a constant rate towards negative infinity!

From our knowledge of thermostats we know that for nonequilibrium steady states (NESS)

$$\lim_{t \to \infty} \dot{S}_G(t) = -\lim_{t \to \infty} \frac{\left\langle \dot{Q}_{th}(t) \right\rangle_{ss}}{T}$$
(6.2.3)

This equation is obtained by noting that $\dot{H}_0(t) = -2K_{th}(t)\alpha(t) = -2K_{th}\alpha(t) = -Q_{th}(t)$ for isokinetically thermostatted systems.

This equation is exactly what one would expect from applying classical thermodynamics to a quasistatic system in which case $2K_{th} = (D_C(N_W - 1) - 1)k_BT$ and *T* is the equilibrium thermodynamic temperature. However (6.2.3) is valid even far from equilibrium in which case *T* can be taken to be the underlying equilibrium temperature, the entire system would relax to, should the dissipative field be removed from the system at time *t*, and it be allowed to relax to that equilibrium. In the latter case the reservoir need not be large nor at equilibrium.

If the reservoir is sufficiently large (to be regarded as being quasistatic then the right hand side is exactly the negative of the rate of change of entropy for the thermostat so we discover in this case:

$$\lim_{t \to \infty} [\dot{S}_G(t) + \dot{S}_{th}(t)] = 0$$
(6.2.3)

This equation shows that the time derivative of the Gibbs entropy of the system of interest (defined using phase space distributions) does equate in magnitude to the macroscopic calorimetric entropy change in the thermostat.

If we define the "universe" to be the union of the system of interest and the thermostat, equation (6.2.3) shows that the entropy of the universe does not increase but rather the entropy of the "universe" is simply constant. This is related to the constancy of the Gibbs entropy in autonomous Hamiltonian (*i.e.* unthermostatted) systems.

In a NESS the distribution function collapses onto a zero volume strange attractor. In most of the phase space, D, the density goes to zero whereas from almost any initial phase in this phase space the density at the streamed phase becomes infinite, $\lim_{t\to\infty} f(S'\Gamma;t) \to +\infty$. The Gibbs entropy can be decomposed into components where the phase space density (defined with respect to the ostensible phase space domain) either goes to zero or diverges to negative infinity, $\lim_{t\to\infty} S_G(t) \to -\infty$ [3]. The logarithm appearing in Gibbs definition of the entropy is a singular function. The Gibbs entropy can only yield satisfactory values if the distribution function is smooth – as it is at equilibrium. It is only for equilibrium systems that the dimension of the space preserved by the dynamics, is known with any accuracy. In a NESS the distribution function defined over the ostensible phase space is singular and the Gibbs entropy is of little use.

In the Appendix we illustrate the relationship between the dissipation, thermodynamic entropy and Gibbs entropy for a simple model system. The system is thermostatted and initially in a canonical equilibrium state. Its temperature is decreased then increased back to the initial state via a nonequilibrium pathway, and finally allowed to relax back to equilibrium. Calculation of the change in the Gibbs entropy throughout this process indicates that the Gibbs entropy will decrease towards $-\infty$ as the system approaches equilibrium. The phase space probability distribution will become a fractal with dimension less than that of the ostensible phase space. However the equilibrium entropy of the state that is approached in the long time limit will be the same as that of the initial state. The physical properties determined using the evolved distribution will become indistinguishable from those of the true equilibrium state, but the fine-grained density will always differ. This demonstrates

that the Gibbs entropy does not describe the physical properties of the system, but rather gives a description of the underlying phase space density.

6.3 DISSIPATION IN NONEQUILIBRIUM STEADY STATES (NESSs)

We will now discuss nonequilibrium steady states in terms of dissipation rather than entropy or so-called entropy production. We begin by considering a system of *N* particles subject to the following equations of motion [20]:

$$\dot{\mathbf{q}}_i = \mathbf{p}_i / m + C_i \mathbf{F}_e, \quad \dot{\mathbf{p}}_i = \mathbf{F}_i + D_i \mathbf{F}_e - S_i \alpha_{IK} \mathbf{p}_i + S_i \mathbf{F}_{th}$$
(6.3.1)

In these equations \mathbf{F}_e is an external dissipative field (*e.g.* an electric field applied to a molten salt), the scalars C_i and D_i couple the system to the field. The system can easily be generalized to tensor coupling parameters if required. If we denote a set of thermostatted particles as belonging to the set *th*, we choose $S_i = 0, i \notin th$; $= 1, i \in th$ is a switch to determine whether particle *i* is a member of the set, *th*, of N_{th} thermostatted particles. α_{IK} is the thermostat multiplier [20] chosen to fix the kinetic energy of the thermostatted particles at the value K_{th} and \mathbf{F}_{th} is a fluctuating force to fix the total momentum of the thermostatted particles, which is selected to have a value of zero. We assume the interatomic forces \mathbf{F}_i ; i = 1, N are smooth functions of the interparticle separation. We also assume that the interatomic forces are short ranged so that there are no convergence problems in the large N limit.

We assume that in the absence of the thermostatting and momentum zeroing forces, the equations of motion preserve phase space volumes $(\partial/\partial\Gamma \cdot \dot{\Gamma}^{ad} \equiv \Lambda(\Gamma) = 0)$ where $\Gamma \equiv (\mathbf{q}_1,...\mathbf{p}_N)$ is the phase space vector and *ad* denotes the fact that the time derivative is calculated with the thermostatting and momentum zeroing forces turned

off. This condition is known as the adiabatic incompressibility of phase space condition or AI Γ for short. [20]

We assume the system of particles is subject to infinite checkerboard boundary conditions [20] – at least in the direction of the force. This means that angular momentum is not a constant of the motion. It also means that dissipation can go on forever without the system relaxing to equilibrium. Currents can flow in the direction of the force forever. The thermostatted particles may be taken to form solid walls parallel to the field, so that they can absorb or liberate heat that may be required to generate a NESS characterized by a fixed value for the kinetic energy of the thermostatted particles.

In contrast, if the system is finite, mixing, and has an autonomous Hamiltonian, even when subject to a *dissipative* external force, it will eventually relax towards microcanonical equilibrium [§5.3]. If these same systems are thermostatted as in (6.3.1) above, they will eventually relax towards canonical equilibrium [§5.4]. For example a finite cell containing charged particles subject to a fixed external field, whether thermostatted or not, will eventually, after dissipative transients, relax towards equilibrium. The charges will be separated by the external field and eventually produce an internal field (space charge) that cancels the externally applied field.

However, although NESSs which persist for an infinite amount of time do not exist in Nature, on accessible timescales they can be approached arbitrarily closely by a judicious choice of large but finite heat reservoirs and managing the magnitude of dissipation in relation to the size of those reservoirs and the nonequilibrium system of interest. If the time taken to relax towards equilibrium is much longer than the time taken to relax towards a (transient) nonequilibrium

"steady" state, averages of smooth phases functions in those transient dissipative states can be approximated as stationary averages.

In the present chapter we consider only those particles that are initially located in the unit cell at time zero. The equations of motion given in (6.3.1), now do not need to refer to the periodic boundaries or re-imaging processes because we follow the coordinates on this initial set of particles indefinitely no matter how far they may diffuse or stream from the initial unit cell. No matter where one of the original particles is located at later times, the force on that particle due to any one of the infinite periodic array of other particles close enough to exert a force on this original particle is computed correctly. This is done by exploiting the infinite checkerboard convention. At long times the nearest neighbours of one of the original unit cell particles are not necessary members of the original unit cell. This is the socalled infinite checkerboard convention commonly used in molecular dynamics and Monte-Carlo computer simulation [20].

The initial distribution is taken to be the equilibrium distribution for this system (see below). It takes the form of a canonical phase space distribution function, $f_c(\mathbf{\Gamma})$, augmented with the necessary delta functions (5.3.4):

$$f(\mathbf{\Gamma},0) = f_c(\mathbf{\Gamma}) = \frac{\exp[-\beta_{th}H_0(\mathbf{\Gamma})]\delta(\mathbf{P}_{th})\delta(K_{th}(\mathbf{\Gamma}) - K_{\beta,th})}{\int d\mathbf{\Gamma} \exp[-\beta_{th}H_0(\mathbf{\Gamma})]\delta(\mathbf{P}_{th})\delta(K_{th}(\mathbf{\Gamma}) - K_{\beta,th})}, \qquad (6.3.2)$$

where $\mathbf{P}_{th} = \sum_{i=1}^{N} S_i \mathbf{p}_i$ is the total momentum of the thermostatted particles and

 $K_{th}(\Gamma) = K_{th}(p) = \sum S_i p_i^2 / 2m_i$ is the kinetic energy of the thermostatted particles

and $K_{\beta,th} = (3N_{th} - 4)\beta_{th}^{-1}/2$ (we assume the system has 3 Cartesian dimensions) is the fixed *value* of the kinetic energy of the thermostatted particles. The number of particles in a unit cell is N. The kinetic energy of the thermostatted particles is fixed using the Gaussian multiplier α_{IK} in the equations of motion. Here $\beta_{Ih} = 1/k_B T_{Ih}$ where k_B is Boltzmann's constant and for isokinetic systems T_{th} is the so-called kinetic temperature of the thermostatted particles. For Nosé-Hoover thermostatted systems [20] it is the reciprocal of the target temperature of the Nosé-Hoover feedback mechanism. In the Nosé-Hoover thermostatted case there is an O(1) change in the equipartition relation between the thermostat kinetic energy and the kinetic temperature of the thermostat [4, 20]. The (only) common feature of all thermostatted systems is that β_{th} is the reciprocal of the equilibrium thermodynamic temperature that the entire driven system would relax towards, if the system is T-mixing (5.3.2), the driving force is set to zero and the whole system is allowed time to relax towards thermodynamic equilibrium [§5]. We call this temperature, the equilibrium thermodynamic temperature of the *underlying* equilibrium state. The internal energy of the *N*-particles in the unit cell is the average of $H_0(\Gamma) = K(\mathbf{p}) + \Phi(\mathbf{q})$ where K, Φ are respectively the peculiar kinetic energy and the potential energy of all the particles in the original unit cell.

To be more mathematically correct we should specify the ostensible phase space domain that is not referred to explicitly in (6.3.2). In principle the particle momenta are unbounded. Clearly the delta functions in (6.3.2) place 4 constraints on the momenta of (some) particles in the system. The initial coordinates of the particles will each range over some finite range $\pm L$ within the unit cell of the periodic system. Because of the infinite periodicity, any particle and its environment are identical to any periodic image of that particle. Particles can always be "re-imaged" back into the

original unit cell [20]. However calculating certain quantities may have spurious discontinuities if this is done. Thermodynamic quantities like pressure, internal energy etc. are all continuous in time, independent of whether particles are "imaged" in the unit cell. Throughout most of the remainder of this paper we will not refer explicitly to this ostensible phase space domain.

The thermostatting region that is unnatural can be made arbitrarily remote from the natural system of interest. The thermostatting particles may be buried far inside realistic walls that contain the nonequilibrium system of interest. This means that there is no way that the particles in the system of interest can "know" how heat is ultimately being removed from the system. The thermostats are important as a bookkeeping device to track the evolution of phase space volume in a deterministic but open system.

The time integral of the dissipation function evaluated at an initial phase, ${\bf \Gamma}$, is formally defined as 7

$$\Omega_{t}(\Gamma) \equiv \ln \left[\frac{f(\Gamma; 0) \exp\left(-\int_{0}^{t} ds \Lambda(S^{s}\Gamma)\right)}{f(M^{T}S'\Gamma; 0)} \right]$$
(6.3.3)

where M^T is the time reversal map, $M^T \Gamma \equiv (\mathbf{q}_1, \dots, \mathbf{q}_N, -\mathbf{p}_1, \dots, -\mathbf{p}_N)$ and S' is the time evolution operator for a time *t*. A key point in the definition of dissipation is that Γ and $M^T S' \Gamma$ are the origin phases for a trajectory and its conjugate antitrajectory respectively. This places constraints on the propagator, S'. Any time dependent driving fields, $\mathbf{F}_e(t)$, *must* have a definite parity under time reversal over the interval (0,t). For a system satisfying (6.3.1) and satisfying the AI Γ condition and having an initially equilibrium distribution of states (6.3.2), it is easy to show that the instantaneous dissipation function (6.3.3) can be written as,

$$\Omega(\mathbf{\Gamma}) \equiv -\beta_{th} J(\mathbf{\Gamma}) V F_e = \beta_{th} \sum_i [\mathbf{p}_i D_i / m - \mathbf{F}_i C_i] \cdot \mathbf{F}_e$$
(6.3.4)

where $J(\Gamma)$ is the so-called dissipative flux and V is the unit cell volume. For example, for electrical conductivity where $C_i = 0$, $\forall i$ and $D_i = c_i$ is the electric charge of particle *i*, and an electric field is applied in the x-direction, $\mathbf{F}_e = (F_e, 0, 0)$, it is easy to see that $-JV = \sum c_i \dot{x}_i$, the electric current in the x-direction.

Such a dissipation function is called a *primary dissipation function* - §4.3. When the field is zero the system remains in equilibrium and there is no dissipation.

From the Dissipation Theorem⁸ [§4] we know that if the system is initially at equilibrium, we can write the nonlinear response of an arbitrary integrable phase function $B(\Gamma)$ as

$$\left\langle B(t)\right\rangle_{F_{e},0} = \left\langle B(0)\right\rangle_{0} - \beta_{th} V \int_{0}^{t} ds \left\langle \mathbf{J}(0)B(s)\right\rangle_{F_{e},0} \cdot \mathbf{F}_{e}$$
(6.3.5)

where $\langle B(t) \rangle_{F_{e},0}$ denotes the ensemble average of the phase function $B(\Gamma)$ evaluated at the propagated phase $S'\Gamma$ with the initial distribution (t = 0) being given by (6.3.2). The first subscript on the ensemble averages F_{e} , indicates that the propagator S^{t} is given by the full field-dependent, thermostatted dynamics of equations (6.3.1), and the second subscript which is zero in this case, indicates that the average is with respect to initial, equilibrium distribution function. In (6.3.5) $B(s) \equiv B(S^{s}\Gamma)$ is also evaluated with the full field-dependent, thermostatted dynamics.

From (6.3.5) we also see that if the driving field is zero then the ensemble averages of *all* integrable phase functions are time independent and thus if the system starts with the equilibrium distribution (6.3.2) the distribution is preserved by the field free, thermostatted dynamics.

Although (6.3.5) only refers directly to the *N* particles in the unit cell, the coordinates and momenta of all periodic image particles follow by symmetry.

This expression (6.3.5) is exact, arbitrarily near or far from equilibrium and also for systems of arbitrary size. If the system is T-mixing, then by *definition* (5.3.2) if $B(\Gamma)$ is a sufficiently smooth, real valued phase function,

$$\lim_{t \to \infty} \left| \left\langle B(t) \right\rangle_{F_{\varepsilon}, 0} \right| = L_0 \in \mathbf{R}$$
(6.3.6)

So the infinite time-integral of the transient time correlation function in (6.3.5) converges to a finite value for an arbitrarily strong, or weak, dissipative field. Physically this corresponds to the relaxation to a nonequilibrium steady state (NESS) at sufficiently long times. The T-mixing property also means that the steady state distribution is physically ergodic and does not break down into non-mixing subspaces that have different values for the steady state averages of smooth phase functions.

If the phase space did break down into subdomains with distinct, time invariant sets of averages of these smooth phase functions, these distinct values could be used to define new constants of the motion. These constants of the motion would lead to nonconvergent integrals for the relevant time correlation functions with the zero time dissipation (6.3.5) and thereby violate the T-mixing assumption. Any initial correlations between the dissipation function and the phase variables which are constants of the motion, would be preserved for all time resulting in divergences in (6.3.5) and (6.3.6).

[As in §4.3 we expressly exclude the case where the system possesses constants of the motion but the TTCF appearing in (6.3.5) vanishes for all times because of perfect cancelation. Unlike the case for quantum systems, in real classical systems there can never be *perfect* cancellation. For example, consider a system that splits its phase space into two perfectly symmetrical domains and suppose that once in either of these domains the system stays in the particular domain forever. Suppose also that the dissipation function at time zero is *perfectly* uncorrelated with the domain occupation. Such a system will possess constants of the motion but the TTCF of $\Omega(0)$ with $S(S'\Gamma) = +1, S'\Gamma \in D_1; = -1, S'\Gamma \in D_2$ namely $\langle \Omega(0)S'\Gamma \rangle = 0, \forall t$. If the lack of correlation is not exact or the average $\langle S(\Gamma) \rangle$ is not *exactly* zero the TTCF integral will diverge and the systems. There will always be some perhaps small physical imperfection that breaks the perfect symmetry.]

Thus steady state time averages must equal ensemble averages over the steady state attractor even though its topology is fractal and its geometry is generally unknown. So the T-mixing condition implies the late-time stationary nonequilibrium states are in fact Nonequilibrium Steady States (NESS) that are physically ergodic over the initial phase space domain.

We do know that the dimension of the steady state attractor is less than that of the ostensible phase space and generally decreases as the dissipation increases (NB it is not known whether the Kaplan-Yorke dimension is in general a monotonic decreasing function of the dissipative field. In the weak field, linear response regime the Kaplan-Yorke dimension is a monotonic decreasing function of the dissipative field⁶.).

Although the long time averages appearing on the left hand side of (6.3.5,6) are finite, these averages could be divergent in the limit of large system sizes. For finite dissipative fields the large system limit is usually problematic. For example for a fixed shear rate in say Couette flow, as the system size increases so does the Reynolds Number for the flow. As the system size increases we know that there will be a transition from laminar to (eventually) highly turbulent flow. Such large systems (*e.g.* Raleigh-Bernard flows) may not be T-mixing.

In the weak field limit this equation (6.3.5) reduces (essentially) to the wellknown Green-Kubo expression⁴ for the linear response

$$\lim_{F_e \to 0} \left\langle B(t) \right\rangle_{F_e,0} = \left\langle B(0) \right\rangle_{F_e=0,0} - \beta_{th} V \int_0^t ds \left\langle \mathbf{J}(0) B(s) \right\rangle_{F_e=0,0} \cdot \mathbf{F}_e, \qquad (6.3.7)$$

where the right hand side is given by the integral of an *equilibrium* (*i.e.* $\mathbf{F}_e = \mathbf{0}$) time correlation function. The initial ensemble for the terms on the right hand side is the equilibrium ensemble (6.3.2), and the dynamics inherent in the equilibrium time correlation function is generated at zero field but with the thermostat on. The field

only appears in the nonequilibrium average on the left hand side of (6.3.7) and as an explicit factor multiplying the correlation function on the right hand side of (6.3.7).

In the linear response regime the T-mixing condition implies that $\lim_{t\to\infty} \langle J(0)B(t) \rangle_{f_c} = 0, i.e. \text{ there is no correlation between } J(0) \text{ and } \lim_{t\to\infty} B(t) \text{ so that}$ $\lim_{t\to\infty} \langle J(0)B(t) \rangle_{f_c} = \langle J(0) \rangle_{f_c} \langle B \rangle_{f_c} = 0 \text{ and the zero field system is$ *mixing*. If correlations were non-zero in the long time limit the integral (6.3.7) could not converge and the system would not be T-mixing. The mixing condition assumes that (5.2.1),

$$\lim_{t \to \infty} \left| \left\langle A(\Gamma(0)) B(\Gamma(t)) \right] \right\rangle_{f_c(\Gamma)} - \left\langle A(\Gamma) \right\rangle_{f_c(\Gamma)} \left\langle B(\Gamma) \right\rangle_{f_c(\Gamma)} \right| = 0$$
(6.3.8)

where $f_c(\Gamma)$ is the equilibrium distribution (6.3.2). In equation (6.3.5) the T-mixing condition for the equilibrium time correlation function implies the system is mixing over the invariant equilibrium distribution (6.3.2).

However mixing does not imply T-mixing. In a T-mixing system the correlation function must go to zero sufficiently rapidly for the integral to converge so that, $\lim_{t\to\infty} |\langle B(\Gamma(t)) \rangle_{F_{e},0}|$ is time independent and *finite*. Having equilibrium time correlation functions going to zero at long times is insufficient to ensure T-mixing.

If the decorrelations in the equilibrium time correlation function scale like 1/t or slower at long times, the system will be mixing but not T-mixing. For example if the equilibrium time correlation function goes to zero as 1/t at long times, $\lim_{t\to\infty}\lim_{F_c\to 0} \langle B(t) \rangle_{F_c} - \langle B(0) \rangle = O(\ln(t)) \text{ and the system will never have a time independent}$ average value for the phase variable even arbitrarily close to equilibrium. Thus we have an example system that is mixing over the equilibrium time correlation function but does not relax to nonequilibrium steady states in the linear response regime close to equilibrium. This is quite different to the ergodic theory result for finite autonomous Hamiltonian systems where mixing does indeed imply relaxation towards the time independent microcanonical equilibrium distribution!

To put this into a more physical context, in two dimensions in the large system limit (*i.e.* the number of particles in the unit cell, *N*, goes to infinity), equilibrium time correlation functions for the macroscopic Navier-Stokes transport coefficients are each thought to have t^{-1} long time tails. In this limit, the Fourier series in our infinitely periodic system become continuous Fourier transforms. Thus macroscopic equilibrium systems in two dimensions may be mixing but would not be T-mixing. Again this does not violate the ergodic theory proof of relaxation to microcanonical equilibrium because that proof only applies to finite systems.

If we turn briefly to the *transient* time correlation function expressions for the nonlinear response (6.3.5), the mixing condition is simply not relevant. The transient time correlation function on the right hand side is not stationary. The measure evolves from the initial equilibrium distribution (6.3.2) and through a set of transient measures (over which the transient integral is computed) till at long times, if the system is T-mixing we have a steady state with stationary averages for physical observables. The mixing condition (6.3.8) can never prove relaxation to a steady state because the condition *already* assumes in its definition (6.3.8), stationarity with respect to time!

We say that equation (6.3.7) is *essentially* the same as the Green-Kubo^{10,11} relations because there are some subtle differences. Kubo's results were for the

linearized adiabatic response (*i.e.* no thermostats) of a canonical ensemble of systems. We derived equation (6.3.7) for isokinetic dynamics where the kinetic energy of the thermostatted particles is fixed and the distribution for the system of interest is canonical – equation (6.3.2). Thus the equilibrium time correlation function appearing in (6.3.7) is for field free isokinetic dynamics. This is not the same as the case considered by Kubo¹⁰. Kubo's time correlation functions involved canonical distributions but field free, constant energy, Newtonian trajectories. Kubo's system was obviously not ergodic (because states of different energies never mix) whereas our results (6.3.7) are ergodic (because the system is T-mixing).

Evans and Sarman have proved¹² that to leading order in the number of degrees of freedom in the system (= O(N)), adiabatic and thermostatted equilibrium correlation functions are identical. Of course if the dissipative field only couples to particles in the system of interest and the thermostat region is large and remote, the fluctuations in the dissipation function (which is local to the system of interest) will hardly be affected by the presence or absence of thermostatting terms in the large remote thermostatting region.

Because the thermostat is unphysical, we only thermostat a small subset of particles. If we only thermostat a small number of particles that are remote from the natural system of interest (still within the unit cell), we can always appeal to the gedanken experiment that if we make the thermostatting region ever more remote from the system of interest there is just no way that the physical system of interest can "know" how the remote thermostatting is actually occurring. If the external fields are set to zero and the T-mixing system is allowed to relax to equilibrium we know the thermodynamic temperature of that underlying equilibrium system. That is the temperature that appears in the equations given above.

In fact Evans and Sarman also proved that at the same state point, transient time correlation functions computed for homogeneously isokinetic, isoenergetic or Nosé-Hoover, dynamics are identical to leading order in N. To define a common state point they fixed N, V, F_e and the average steady state dissipation. So even the nonlinear response is robust with respect to thermostatting mechanism.

There is yet another interesting observation we can make regarding Kubo's^{10,11} system. If you consider viscous flow in a dilute gas then as is known from kinetic theory, the viscosity of a gas increases with temperature. This means that for any finite field, no matter how small, the shear stress of an adiabatic shearing gas must increase with time. This means that a shearing unthermostatted gas can never be T-mixing! In a physical sense for such a system, time correlations never decay – at least not rapidly enough for T-mixing.

You can see how this memory effect occurs. If among the initial ensemble members, one encounters a fluctuation that increases the gas viscosity, that fluctuation will cause slightly more heating of the gas. In this slightly heated gas the viscosity will be slightly higher than on average, increasing the likelihood of further fluctuations that in turn increase the viscosity. This is a run-away process that prevents the decay of correlations required for the T-mixing condition.

6.4 FOR T-MIXING SYSTEMS THE NONEQUILIBRIUM STEADY STATE IS INDEPENDENT OF THE INITIAL EQUILIBRIUM DISTRIBUTION

We have already argued that for T-mixing systems the steady state properties must be independent of the initial distribution. In this section we give an explicit proof of this point.

The dissipation function defined in (6.3.3) is a functional of *both* the dynamics and the initial distribution. The exact transient Evans-Searles Fluctuation Theorem^{13,14} refers to this exact dissipation function. How does the influence of the nonequilibrium initial distribution disappear? We consider an initial distribution that is *not* the equilibrium distribution for the zero-field system but is some deviation from it:

$$f_{g}(\Gamma,0) = \frac{\exp[-\beta_{th}H_{0}(\Gamma) - \lambda g(\Gamma)]\delta(\mathbf{P}_{th})\delta(K_{th}(\Gamma) - K_{\beta,th})}{\int d\Gamma \exp[-\beta_{th}H_{0}(\Gamma) - \lambda g(\Gamma)]\delta(\mathbf{P}_{th})\delta(K_{th}(\Gamma) - K_{\beta,th})}$$
(6.4.1)

We assume the deviation function $g(\Gamma)$ is even in the momenta, is nonsingular, real and integrable. The positive real parameter λ is a simple scaling parameter that allows us to easily scale the magnitude of the deviation from the equilibrium distribution. The dissipation function is easily seen to be

$$\Omega_{\lambda}(\Gamma) = -\beta_{th} \mathbf{J}(\Gamma) V \cdot \mathbf{F}_{e} - \lambda \dot{g}(\Gamma)$$
(6.4.2)

Substituting into the dissipation theorem gives,

$$\left\langle g(t) \right\rangle_{\mathbf{F}_{e},\lambda} = \left\langle g(0) \right\rangle_{\mathbf{F}_{e},\lambda} - \int_{0}^{t} ds \left\langle \left[\beta_{th} \mathbf{J}(0) V \cdot \mathbf{F}_{e} + \lambda \dot{g}(0) \right] g(s) \right] \right\rangle_{\mathbf{F}_{e},\lambda}$$
(6.4.3)

and recalling that g(t) is even in the momenta we have $\langle \dot{g}(0) \rangle_{\mathbf{F}_{c},\lambda} = \langle \mathbf{J}(0) \rangle_{\mathbf{F}_{c},\lambda} = 0$. So if the system is T-mixing then at sufficiently long times the value of the left hand side becomes time independent which means that the part of the average dissipation function due specifically to the deviation function (6.4.3), is zero at long times:

$$\lim_{t \to \infty} \left\langle \dot{g}(t) \right\rangle_{\mathbf{F}_{e}, \lambda} = 0.$$
(6.4.4)

For T-mixing systems we can give a formal proof that at long times the dissipation becomes independent of the deviation function. We write the average dissipation for the deviated system as:

$$\begin{split} \lim_{t \to \infty} \left\langle \Omega_{\lambda}(t) \right\rangle_{\mathbf{F}_{e},\lambda} &= -\lim_{t \to \infty} \left\langle \beta_{th} \mathbf{J}(t) V \cdot \mathbf{F}_{e} + \lambda \dot{g}(t) \right\rangle_{\mathbf{F}_{e},\lambda} \\ &= -\lim_{t \to \infty} \left\langle \beta_{th} \mathbf{J}(t) V \cdot \mathbf{F}_{e} \right\rangle_{\mathbf{F}_{e},\lambda} \\ &= -\lim_{t \to \infty} \frac{\left\langle \beta_{th} \mathbf{J}(t) V \cdot \mathbf{F}_{e} e^{-\lambda g(0)} \right\rangle_{\mathbf{F}_{e},\lambda=0}}{\left\langle e^{-\lambda g(0)} \right\rangle_{\mathbf{F}_{e},\lambda=0}} \\ &= -\lim_{t \to \infty} \frac{\left\langle \beta_{th} \mathbf{J}(t) V \cdot \mathbf{F}_{e} \right\rangle_{F_{e},\lambda=0}}{\left\langle e^{-\lambda g(0)} \right\rangle_{\mathbf{F}_{e},\lambda=0}} \\ &= -\lim_{t \to \infty} \left\langle \beta_{th} \mathbf{J}(t) V \cdot \mathbf{F}_{e} \right\rangle_{\mathbf{F}_{e},\lambda=0} = \lim_{t \to \infty} \left\langle \Omega_{\lambda=0}(t) \right\rangle_{\mathbf{F}_{e},\lambda=0} \end{split}$$

In going from the first to the second line we use (6.4.5). Going from the third line to the fourth we use the fact that at long times the system becomes stationary and the T-mixing transient system must also be weak T-mixing – see (5.3.3). (Note: T-mixing implies weak T-mixing but weak T-mixing does not imply T-mixing.)

An interesting example of a deviation function would be to choose it so that the initial distribution was just a delta function centred on almost any initial phase Γ_0 . One could also – at least in principle choose the deviation function so that the initial distribution of phases corresponded (to arbitrary accuracy) to the steady state attractor traced out by a single phase space trajectory! This reduces the long time *ensemble averages* to simple *time averages* taken along a single exceedingly long trajectory. Equation (6.4.5) holds in each of these cases and in the latter case the results correspond to those obtained from a single dynamical system rather than an ensemble average of dynamical systems.

6.5 IN THE LINEAR RESPONSE REGIME, THE DISSIPATION IS MINIMAL WITH RESPECT TO VARIATIONS OF THE INITIAL DISTRIBUTION

In the linear response regime (where fluxes are linear in \mathbf{F}_{e}, λ), where the average dissipation function is quadratic in \mathbf{F}_{e}, λ , for finite times we have

$$\lim_{\mathbf{F}_{e},\lambda\to0,}\int_{0}^{t}ds\left\langle\Omega_{g}(s)\right\rangle_{\mathbf{F}_{e},\lambda} = -\int_{0}^{t}ds\left[\beta_{th}V\mathbf{F}_{e}\cdot\lim_{\mathbf{F}_{e}\to0,}\left\langle\mathbf{J}(s)\right\rangle_{\mathbf{F}_{e},\lambda=0} + \lambda\lim_{\lambda\to0,}\left\langle\dot{g}(s)\right\rangle_{\mathbf{F}_{e}=\mathbf{0},\lambda}\right]$$
$$> -\lim_{t\to\infty}\int_{0}^{t}ds\;\beta_{th}V\mathbf{F}_{e}\cdot\lim_{\mathbf{F}_{e}\to0,}\left\langle\mathbf{J}(s)\right\rangle_{\mathbf{F}_{e},\lambda=0} = O(F_{e}^{2}) \tag{6.5.1}$$
$$>0, \quad \forall t$$

It is easy to show that any cross terms $\lambda \mathbf{F}_e \cdot \langle \mathbf{J}(0)\dot{g}(t) \rangle_{\mathbf{F}_e=0,\lambda=0}$ vanish by symmetry in the linear response regime and in any case are of higher order $O(F_e^2\lambda^2)$. The second line in this equation follows from applying the Second Law Inequality to the (weak) dissipation due solely to the deviation function: $-\lim_{t\to\infty} \int_0^t ds \left[\lim_{t\to\infty} \langle \dot{g}(s) \rangle_{\mathbf{F}_e=0,\lambda}\right] > 0, \quad \forall t$. So in the linear response regime the average primary dissipation is less than any other dissipation due to variations in the initial distribution away from equilibrium. In the nonlinear regime it is not known whether the average primary dissipation is minimal.

Equation (6.5.1) shows that at sufficiently long times, in T-mixing, driven systems the dissipation always relaxes towards the average of the primary dissipation

function. If the driven system is T-mixing all other forms of dissipation diminish towards zero leaving only the primary dissipation in the limit of infinite time.

This proof that in the linear response regime the primary dissipation is minimal with respect to variations in the initial distribution function gives a proof for T-mixing systems, of Prigogine's principle of minimum entropy production in the linear response regime close to equilibrium. He states¹⁵: "In the linear regime, the total entropy production in a systems subject to [a] flow of energy and matter, $d_iS/dt = \int \sigma \, dV$, reaches a minimum value at the nonequilibrium stationary state. This is because the unconstrained forces adjust themselves to make their conjugate fluxes go to zero." We have already noted that in the linear regime the average dissipation is equal to the so-called entropy production¹⁶. In our system there is no nett mass flow into or out of the unit cell. In our case all we have to do is to construct a second "force" $F_{e,2}$ that is capable of generating the flux \dot{g} . This unconstrained force adjusts itself so that its conjugate flux namely \dot{g} averages to zero in the steady state. To find this "force" and its equations of motion is a trivial exercise. If the equations of motion take the same form as (6.3.1) but with coupling parameters C_{2i} , D_{2i} and a "force" \mathbf{F}_{2e} we see that we merely have to find the coupling

parameters such that $\lambda \dot{g} = \mathbf{F}_{2,e} \cdot \sum_{i=1}^{N} [\mathbf{P}_{i} / \mathbf{D}_{2,i} - \mathbf{F}_{i} C_{2,i}]$, a trivial exercise.

6.6 SUM RULES FOR DISSIPATION IN STEADY STATES

Using (6.4.3) and the T-mixing property we have the following relaxation sum rule

$$\lim_{t \to \infty} \langle \dot{g}(t) \rangle_{F_{e},\lambda} = -\int_{0}^{\infty} ds \left\langle [\beta_{th} \mathbf{J}(0) V \cdot \mathbf{F}_{e} + \lambda \dot{g}(0)] \dot{g}(s)] \right\rangle_{F_{e},\lambda}$$
$$= \frac{-\int_{0}^{\infty} ds \left\langle [\beta_{th} \mathbf{J}(0) V \cdot \mathbf{F}_{e} + \lambda \dot{g}(0)] \dot{g}(s) e^{-\lambda g(0)}] \right\rangle_{F_{e},\lambda=0}}{\left\langle e^{-\lambda g(0)} \right\rangle_{F_{e},\lambda=0}} \tag{6.6.1}$$

This is analogous to the corresponding sum rule for the fluxes of nonconserved quantities in systems relaxing to equilibrium. In the present case the sum rule is for fluxes of nonconserved quantities relaxing to a steady state – the heat death equation (5.4.19). In the heat death case $F_e = 0$ and the first term on the right hand side of the first line of (6.6.1) is simply absent. So for nonequilibrium steady states in the long time, *t*, limit, instead of autocorrelation functions of fluxes of nonconserved quantities integrating to zero, they behave as,

$$\lambda \int_0^t ds \left\langle \dot{g}(0) \dot{g}(s) \right\rangle_{F_e,\lambda} \xrightarrow{\lim(t \to \infty)} - \int_0^t ds \left\langle \beta_{th} \mathbf{J}(0) V \cdot \mathbf{F}_e \dot{g}(s) \right\rangle_{F_e,\lambda}.$$

The fact that in regard to forming averages of smooth phase functions, Tmixing systems forget about their initial distributions is completely consistent with our earlier proof that the steady state is ergodic and consists of a single connected phase space domain - at least as can be ascertained from averages of suitably smooth phase functions. We eventually arrive arbitrarily close to this same domain even if the initial t = 0, distribution differs from the equilibrium distribution for the zero field system. Indeed if we start a single trajectory at time zero in the long time limit the steady state attractor traced out by this single trajectory must explore *essentially* the same attractor as that generated at some arbitrarily long time, from an arbitrary initial distribution of states.

Of course if we examine phase space at extreme resolution (say with a very singular phase function (for example $\ln[f(\Gamma;t)]$), the deterministic phase space never "forgets" its original initial conditions; these can always be retrieved by applying a time reversal map to return to the original distribution of states. However when "observed" by computing averages of smooth phase functions for thermophysical properties like pressure, stress or energy, these very fine structures in phase space cannot be resolved and the knowledge of initial conditions is effectively lost. The measurement of thermophysical properties is the only way we can characterize these macroscopic states. The measurement of the fine-grained phase space density is simply not possible – at least at the resolution required to generate the initial distribution after a long relaxation to the steady state.

Another way to describe these steady state strange attractors is that starting from different initial phase space points we may generate slightly different steady state attractors. These different attractors must, in T-mixing systems, be so tightly interwoven that when we measure steady state averages we cannot observe differences in the long time averages. This is what is implied by the T-mixing condition and equation (6.4.5) for example. This happens despite the fact that these attractors are of lower dimension than the ostensible phase space because there is an

enormous amount of phase space for them to fill differently, leading to different average values even for smooth phase functions.

For all temperatures, densities and external fields the average long time dissipation is identical to that generated from the equilibrium distribution for the system. This means that the nonlinear transport coefficient, $L(F_e)$ defined in terms of the steady state dissipation

$$L(F_e;\lambda) \equiv \lim_{t \to \infty} \frac{\left\langle \Omega_{\lambda}(t) \right\rangle_{\lambda}}{\beta_{th} V F_e^2} = \lim_{t \to \infty} \frac{\left\langle \Omega_{\lambda=0}(t) \right\rangle_{\lambda=0}}{\beta_{th} V F_e^2} = L(F_e;\lambda=0), \qquad (6.6.2)$$

is independent of whether the initial system was in its equilibrium distribution or any deviation from it – so long as the kinetic temperature of the reservoir particles has a fixed value so that the temperature of the underlying equilibrium state is fixed.

Equation (6.6.2) is in accord with our knowledge of the thermosphysical properties of fluids etc. For example the viscosity of argon is history *independent*. It only depends of the temperature, density and strain rate. The initial preparation of the system is irrelevant to the viscous properties of the system in the steady state inside the viscometer. In T-mixing systems the nonlinear and linear transport coefficients are in fact state functions.

6.7 POSITIVITY OF NONLINEAR TRANSPORT COEFFICIENTS

In chapter 4 we gave a derivation of the Dissipation Theorem for an exceedingly general set of time reversible equations of motion and for quite general initial distributions $f(\Gamma; 0)$. If one substitutes Ω for *B* in equation (6.3.5) and then combines the resulting equation with the strong form of the strong Second Law Inequality¹⁴, one knows that time integrals of ensemble averages of the dissipation must be positive: $\int_0^t ds \langle \Omega(s) \rangle > 0$, $\forall t$. Since at long times for T-mixing systems the average dissipation is time independent one can only conclude that in nonequilibrium steady states the ensemble average dissipation must be positive. If this were not the case the Second Law Inequality would be violated for sufficiently large times. Therefore the dissipation in *driven* T-mixing systems,

$$\lim_{t \to \infty} \left\langle \Omega(t) \right\rangle_{F_e, f(\mathbf{\Gamma}; 0)} = \int_0^\infty ds \, \left\langle \Omega(0) \Omega(s) \right\rangle_{F_e, f(\mathbf{\Gamma}; 0)} > 0, \qquad \forall F_e, f(\mathbf{\Gamma}; 0). \tag{6.7.1}$$

So, for driven systems not only does the dissipation autocorrelation function start with a positive value $(\langle \Omega(0)^2 \rangle_{F_e,f(\Gamma;0)} > 0, \forall F_e, f(\Gamma;0) \rangle)$, but for all normalizable initial distributions and for any well defined dynamics with an arbitrarily strong external field (if any) any negative tails in the ensemble averaged dissipation function must disappear before the system enters the necessarily positive dissipation of the final steady state.

If we consider a driven isokinetic system we observe from (6.3.5) that:

$$-\lim_{t \to \infty} \langle J(t) \rangle_{F_{e,c}} = -\langle J(0) \rangle_{c} + \beta_{th} V \int_{0}^{\infty} ds \langle J(0)J(s) \rangle_{F_{e,c}} F_{e}$$
$$= \beta_{th} V \int_{0}^{\infty} ds \langle J(0)J(s) \rangle_{F_{e,c}} F_{e}$$
$$= L(F_{e}) F_{e} > 0, \forall F_{e}$$
(6.7.2)

We have assumed the dissipative flux and force are scalars and we have used the fact that $\beta_{th} \equiv 1/k_B T_{th}$ where T_{th} is the equilibrium thermodynamic temperature that the system will relax to if the driving force is set to zero and the system is allowed to relax to equilibrium. We have also used the fact that for driven systems $\langle J(0) \rangle_c = 0$.

The T-mixing property guarantees that the $t \to \infty$ limit is finite and therefore so too is the nonlinear transport coefficient at the specified value of the driving field, $L(F_e)$. The T-mixing condition further guarantees that the nonequilibrium steady state is ergodic over the specified phase space domain.

The Second Law Inequality means that the conventionally defined average dissipative flux will be negative when the dissipative field is positive. If we consider planar Couette flow as an example, the following mapping applies:

 $F_e \rightarrow \frac{\partial u_x}{\partial y} = \dot{\gamma} ; J \rightarrow P_{xy}; L(F_e) \rightarrow \eta(\dot{\gamma})$ where the variables are in turn: the strain rate $\dot{\gamma}$; the xy-element of the pressure tensor P_{xy} and lastly the nonlinear strain rate dependent shear viscosity $\eta(\dot{\gamma})$ defined in the *nonlinear constitutive relation* for shear viscosity. Equation (6.7.2) gives a *nonlinear constitutive relation* between the dissipative flux and the dissipative field for a finite, driven, thermostatted system that is T-mixing.

The Second Law Inequality guarantees that the nonlinear transport coefficients, $L(F_e), \eta(\dot{\gamma})$ appearing in the nonlinear constitutive relation for finite sized, T-mixing systems is finite and must be positive:

$$\infty > L(F_e) > 0, \quad \forall F_e. \tag{6.7.3}$$

If we look again at (6.7.2) we see that the Second Law Inequality implies that $\int_0^t ds \langle J(s) \rangle_{F_e, f_e(\Gamma, 0)} < 0, \forall t$. However the approach to the steady state may not be monotonic. The ensemble averaged instantaneous current may be positive at intermediate times. In fact in the nonlinear regime, this is a common situation.

6.8 LINEAR CONSTITUTIVE RELATIONS FOR T-MIXING CANONICAL SYSTEMS

Each of these results also includes the linear response regime as a special case in the limit of weak fields.

$$\begin{split} &\lim_{F_{e}\to 0}\lim_{t\to\infty}\frac{-\partial\langle J(t)\rangle_{F_{e},c}}{\partial F_{e}} \\ &= \lim_{F_{e}\to 0}\beta_{th}V\int_{0}^{\infty}ds \left\langle J(0)\frac{\partial J(s)}{\partial F_{e}}\right\rangle_{F_{e},c}F_{e} + \beta_{th}V\int_{0}^{\infty}ds \left\langle J(0)J(s)\right\rangle_{F_{e}=0,c} \\ &= \lim_{F_{e}\to 0}\beta_{th}V\int_{0}^{\infty}ds \left\langle J(0)J'(s)\right\rangle_{F_{e},c}F_{e} + \beta_{th}V\int_{0}^{\infty}ds \left\langle J(0)J(s)\right\rangle_{F_{e}=0,c} \\ &= \beta_{th}V\int_{0}^{\infty}ds \left\langle J(0)J(s)\right\rangle_{F_{e}=0,c} \end{split}$$
(6.8.1)

In equation (6.8.1) there are two places where the field dependence is manifest. One is in the explicit factor, F_e . The second place is in the implicit time dependence of J(s). In going from the first to the second line of (6.8.1) we expect that if J(s) is a smooth function of time, phase Γ and F_e , $J'(\Gamma(s)) \equiv \partial J(\Gamma(s)) / \partial F_e$ will also be smooth. We assume the equations of motion do not contain singularities. We do not cover the case of hard particles or even systems with a piecewise continuous potential. We note that $J'(\Gamma(0)) = \partial J(\Gamma(0)) / \partial F_e = 0$, so that it takes time for the nonlinearities to "grow" into the response. The proof of equation (6.8.1) gives a proof that finite systems that are: thermostatted, driven, satisfy AI Γ , with smooth intermolecular forces and are Tmixing, have finite linear constitutive relations in the weak field limit. Further, the transport coefficient appearing in this linear constitutive relation is positive. For electrical conductivity we therefore have subject to the conditions above, a proof of Ohms "Law" in the limit of weak fields or using the SLLOD equations for shear flow, a proof of Newton's constitutive relation for weak shear flow – at least as they apply to finite systems. There is nothing in the proof given above to prevent the possible divergence of the extrapolated linear transport coefficient as the system size is increased.

6.9 GAUSSIAN STATISTICS FOR T-MIXING NESS

In 2000, we showed¹⁷ that by combining the asymptotic steady state ESFT (proved in the next section) with the Central Limit Theorem, you could prove Green-Kubo relations in driven systems, for transport coefficients in the weak field limit. That derivation required a careful double limit ($t \rightarrow \infty, F_e \rightarrow 0$) that could not be extended to higher field strengths. It also required the *assumption* that for long averaging times the time averaged dissipative flux satisfies the conditions for the Central Limit Theorem to be valid. The Dissipation Theorem⁸ obviates this discussion and shows how both the nonlinear and the linear response can be obtained directly and exactly in terms of integrals of time correlation functions involving the dissipation function directly.

However if the system is T-mixing (or mixing) then for sufficiently long averaging times the time averaged dissipative flux *must* satisfy the Central Limit Theorem with Gaussian statistics close to the mean of the distribution. As we will see in the next section, this fact is essential in order to prove observability of the asymptotic steady state fluctuation relation.

For driven systems, the dissipation function is quite simply related to the dissipative flux and the dissipative force. The Green-Kubo equilibrium time correlation function involves fluctuations in the dissipative flux. This flux is *not* identically zero at equilibrium whereas the dissipation function is. For driven systems satisfying AI Γ , the dissipative force and not the flux is zero at equilibrium.

6.10 THE NONEQUILIBRIUM STEADY STATE FLUCTUATION RELATION

We now consider fluctuation relations for the dissipation in a nonequilibrium steady state – or at least as we approach nonequilibrium steady states. We have already seen (§6.4) that if the initial distribution is not the equilibrium distribution for the zero field dynamics, the influence of the deviation function disappears in time (6.4.5). This means by definition, that any steady state fluctuation relation can only refer to the primary dissipation function for the system.

In the first instance we treat the simple case where there is no serial correlation in the time series data for the instantaneous dissipation. From §3.5, we may approach the steady state by asking what is the probability that the covariant dissipation integrated for a time τ , but starting not at time zero but rather at time, *t*, equals a value *A* compared to -A. As *t* becomes ever larger the time integrated dissipation approaches that of a true nonequilibrium steady state. So using (3.5.4) and (3.6.4) we can write down the following exact Evans-Searles transient fluctuation relation:

$$\frac{p(\Omega_{t,t+\tau} = A)}{p(\overline{\Omega}_{t,t+\tau} = -A)} = \left\langle \exp(-\Omega_{0,2t+\tau}) \right\rangle_{\Omega_{t,t+\tau} = A\tau}^{-1}$$

$$= \exp(A\tau) \left\langle \exp(-\Omega_{0,t+\tau} - \Omega_{t+\tau,2t+\tau}) \right\rangle_{\Omega_{t,t+\tau} = A\tau}^{-1}$$
(6.10.1)

If the time series data for $\Omega(t)$ has no serial correlation we can see that the condition for the ensemble average has no influence on the time integrals inside the ensemble average on the second line of (6.10.1) and so in this case we obtain the following exact relation

$$\frac{p(\overline{\Omega}_{t,t+\tau} = A)}{p(\overline{\Omega}_{t,t+\tau} = -A)} = \exp(A\tau) \left\langle \exp(-\Omega_{0,t+\tau} - \Omega_{t+\tau,2t+\tau}) \right\rangle^{-1}$$
$$= \exp(A\tau) \left\langle \exp(-\Omega_{0,t+\tau}) \right\rangle^{-1} \left\langle \exp(-\Omega_{t+\tau,2t+\tau}) \right\rangle^{-1} \qquad (6.10.2)$$
$$= \exp(A\tau) \left\langle \exp(-\Omega_{t+\tau,2t+\tau}) \right\rangle^{-1}$$

where we have used the nonequilibrium partition identity (3.3.1), to go from line 2 to line 3. If we break up the integral in the nonequilibrium partition identity (3.3.1) into two parts we see that

$$\langle \exp(-\Omega_{0,a+b}) \rangle = \langle \exp(-\Omega_{0,a}) \rangle \langle \exp(-\Omega_{a,b}) \rangle = 1$$

$$= 1 \langle \exp(-\Omega_{a,b}) \rangle = 1$$

$$\Rightarrow \langle \exp(-\Omega_{a,b}) \rangle = 1$$

$$(6.10.3)$$

where again we have assumed there is no serial correlation in the time series data.

If we apply this result to equation (6.10.2) we arrive at an exact steady state fluctuation relation for systems with *no* serial correlation in the time series data for $\Omega(t)$:

$$\lim_{t \to \infty} \frac{p(\overline{\Omega}_{t,t+\tau} = A)}{p(\overline{\Omega}_{t,t+\tau} = -A)} = \exp(A\tau)$$
(6.10.4)

Now of course in any real dynamical system there must be serial correlation in the time series data so (6.10.4) cannot be exact for real dynamical systems. When the serial correlation is allowed for (6.10.4) becomes an asymptotic result that is only valid in the limit $\tau/\tau_M \rightarrow \infty$ where τ_M is the Maxwell time describing the correlation time of the dissipation function:

$$\lim_{\tau/\tau_{M}\to\infty}\lim_{t\to\infty}\frac{p(\Omega_{t,t+\tau}=A)}{p(\overline{\Omega}_{t,t+\tau}=-A)} = \lim_{\tau/\tau_{M}\to\infty}\frac{p(\Omega_{ss,\tau}=A)}{p(\overline{\Omega}_{ss,\tau}=-A)}$$

$$= \exp(A\tau)$$
(6.10.5)

where the subscript "ss" denotes that the integral over τ should only be done when, to your desired level of accuracy, the system has relaxed to its unique nonequilibrium steady state and the dissipation function is the primary dissipation function for the dynamics - independent of the initial distribution of states. We will now derive this result.

Consider (6.10.1) again. We make the worst possible assumption for correlation. We assume that for a Maxwell time before t and after $t + \tau$ the average dissipation is equal to its mean value over the interval $t,t + \tau$ namely A. This worst case analysis assumes *no* decay of correlations until after a Maxwell time. Thus (6.10.1) becomes

$$\frac{p(\overline{\Omega}_{t,t+\tau} = A)}{p(\overline{\Omega}_{t,t+\tau} = -A)} = \left\langle \exp(-\Omega_{0,2t+\tau}) \right\rangle_{\Omega_{t,t+\tau} = A\tau}^{-1}$$

$$= \exp(A\tau) \left\langle \exp(-\Omega_{0,t+\tau-\tau_{M}} - \Omega_{t+\tau+\tau_{M},2t+\tau}) \right\rangle_{\Omega_{t,t+\tau} = A\tau}^{-1} \left\langle \exp(-2A\tau_{M} \right\rangle$$

$$= \exp(A\tau) \left\langle \exp(-\Omega_{0,t+\tau-\tau_{M}} - \Omega_{t+\tau+\tau_{M},2t+\tau}) \right\rangle^{-1} \left\langle \exp(-2A\tau_{M} \right\rangle$$

$$= \exp(A\tau - 2A\tau_{M})$$
(6.10.6)

Thus in this worst case analysis

$$\lim_{\tau/\tau_{M}\to\infty}\lim_{t\to\infty}\frac{1}{\tau}\ln\frac{p(\bar{\Omega}_{t,t+\tau}=A)}{p(\bar{\Omega}_{t,t+\tau}=-A)} = A - O\left(\frac{A\tau_{M}}{\tau}\right)$$

$$= A = O(\tau^{-1/2})$$
(6.10.7)

As we have seen in §6.9, for T-mixing steady states the distribution of average values of dissipation will become Gaussian about the mean. Since the average dissipation is positive the value that is most difficult to observe is minus one times the mean value of the dissipation. Using Gaussian statistics we see that, $-A = O(\tau^{-1/2})$. Taking more and more samples enables us to observe fluctuations further and further from the mean value for Ω - which is positive.

Definition

So the asymptotic steady state fluctuation relation (6.10.7) is *observable* because the error term $O(A\tau_M / \tau) = O(\tau_M / \tau^{3/2})$ vanishes faster than the (negative) fluctuations themselves (= $O(1 / \tau^{1/2})$).

For T-mixing systems the steady state is physically ergodic and independent of the initial distribution of states. If we take the initial distribution to be a delta function at a particular point in phase space our asymptotic steady state fluctuation relation applies to late time averages along a single, phase space trajectory. In this case (6.10.7) is an asymptotic result for an individual dynamical system over arbitrarily long times.

6.11 GALLAVOTTI-COHEN STEADY STATE FLUCTUATION THEOREM

An alternative Steady State Fluctuation Relation to (6.10.5), has been proposed by Gallavotti, Cohen and co-workers [79-81]. The Gallavotti-Cohen Fluctuation Theorem has been *proven* for Anosov and so-called Axiom A, systems [82] but the resulting relationship was anticipated to apply to a wider range of systems.

Anosov systems are hyperbolic everywhere in the specified phase space domain. This is a rather special type of dynamics. For example Anosov systems have equal numbers of positive and negative Lyapunov exponents.

The Gallavotti-CohenFR can be written:

$$\lim_{t \to \infty} \frac{1}{t} \ln \left[\frac{p[\overline{\Lambda}_t = B]}{p[\overline{\Lambda}_t = -B]} \right] = -B \quad \text{for } |B| \le B^*$$
(6.11.1)

where $\Lambda \equiv \partial_0 \Gamma \cdot \dot{\Gamma}$ is the phase space expansion rate, and B^* is some bound (generally unknown) [83]. Equation (6.11.1) refers to results observed along a single, exceedingly long, phase space trajectory.

Equation (6.11.1) has as we have said, be proven for Anosov systems but Gallavotti and Cohen proposed the equation may be valid for sufficiently chaotic non-Anosov systems. This proposal is termed the Chaotic Hypothesis. At the present time there is no test independent of the Gallavotti-CohenFR, to test whether the Chaotic Hypothesis will apply to a given non-Anosov system. Presumably a precondition for the chaotic hypothesis to hold is that the dynamical system does in fact relax to a steady state because (6.1.1) would make no sense for non-steady state systems (*e.g.* adiabatic systems that heat up without bound).

Gallavotti has also proposed a possible modification to (6.11.1) for systems with an unbalanced number of positive and negative exponents in non-Anosov systems. However, numerical tests seem to show no evidence of a discontinuity in (6.11.1) when the number of positive and negative exponents change (*e.g.* by increasing the dissipative field). Such a change would be necessarily discontinuous.

For isoenergetic systems $\Lambda = -\Omega$, and therefore the relations (6.10.5) and (6.11.1) become identical for ergodic, isoenergetic, steady states, implying for this circumstance that $B^* = \infty$.

Application of the Gallavotti-Cohen Fluctuation Relation to systems that are not isoenergetic has recently been discussed [81,84], and it has found that there are serious limitations to its practical utility. For instance for systems driven by a dissipative field F_e , and satisfying AI Γ the bounds in (6.11.1) go to zero as equilibrium is approached: $B^* = O(F_e^2) \rightarrow 0$ as $F_e \rightarrow 0$. This means that the range of applicability of the GCFR shrinks to zero as equilibrium is approached. In fact it is easy to see why this must be the case. At equilibrium, the GCFR for thermostatted systems would predict an asymmetry in the probability of time-averaged values of the phase space expansion factor. This is obviously not possible! By contrast, at equilibrium the Evans Searles FR's simply state that fluctuations in the time integrated dissipation is symmetric about zero – see §6.10.

Perhaps even more difficult is the fact that for thermostatted systems, the time required for convergence of the Gallavotti-CohenFR diverges to infinity as $O(F_e^{-2})$ (*i.e.* the asymptotic limit in (6.11.1) should be written as $\tau/F_e^2 \rightarrow \infty$). Since much of the interest in fluctuation relations arises from the fact that they are exact arbitrarily far from equilibrium, the bound on the range of fluctuations means that the Gallavotti-CohenFR is of limited use in large deviation theory. On the other hand close to equilibrium the shrinking bounds on the range of the argument and the divergence of the convergence time also lead to problems.

One can easily see why this divergence of convergence times occurs close to equilibrium. The phase space expansion factor for thermostatted systems close to equilibrium contains a sum of two terms. One is the dissipation function (times -1) but the other component is just (to leading order close to equilibrium) the equilibrium fluctuations in the phase space expansion factor. The equilibrium fluctuations become independent of the external field close to equilibrium, and they are of course symmetric about zero and therefore cannot satisfy any fluctuation relation. In the long time limit in steady states of thermostatted systems: $\lim_{t\to\infty} (\bar{\Lambda}_t + \bar{\Omega}_t) = 0$ but as the field becomes ever smaller the relative magnitude of the symmetric equilibrium fluctuations becomes ever larger, swamping the dissipation. Thus as the field becomes

smaller it takes longer and longer for the average $\overline{\Lambda}_t$ to become equal to $-\overline{\Omega}_t$. We will discuss an example of the convergence difficulties for the Gallavotti-CohenFR in §7.4 – especially contrasting (7.4.19,20) and (7.4.21).

6.12 SUMMARY

One often sees references in the literature to the supposition that in nonequilibrium steady states the "entropy production" (*i.e.* average dissipation) is a maximum (or sometimes a minimum!) subject to the known constraints. The fact that when a dissipative field is suddenly applied to an equilibrium system the dissipation increases from zero means that in a steady state the dissipation can hardly be an absolute minimum. The fact that the dissipation very frequently overshoots its steady state value means that in general the steady state dissipation cannot be a maximum either. In the present chapter we have shown that in the linear response regime the primary dissipation is minimal with respect to all possible variations of the initial distribution away from the natural equilibrium distribution.

There is a way of rederiving¹⁹ the Dissipation Theorem for driven systems as an extremum principle but the final result is identical to the Dissipation Theorem⁸ and it involves an *infinite* set of constraints. The choice of which constraints should be used in these derivations is best made *after* you already know the correct answer because *a priori* there seems to be no criteria for selecting these constraints.

One of the interesting things our work has revealed is that in T-mixing systems the nonequilibrium steady state is physically ergodic and independent of the initial distribution. This independence with respect to the initial distribution means that there is only one steady state fluctuation relation for a given dynamical system.

The positivity of transport coefficients is a direct result of the fact that the time integral of the average dissipation is positive. It also means that on average, work is converted into heat rather than the reverse. For a driven T-mixing system, that satisfies AI Γ and is isokinetic we have

$$\beta_{th}\dot{H}_{0}(t) = -\beta_{th}VJ(t)F_{e} - 2\beta_{th}K_{th}\alpha(t)$$

$$= -\beta_{th}VJ(t)F_{e} - (3N - 4)\alpha(t)$$
(6.12.1)

If we take long time averages for a steady state,

$$\lim_{t \to \infty} \overline{H}_{0,t} = \lim_{t \to \infty} [-\beta_{th} \overline{J}_t V F_e - (3N - 4) \overline{\alpha}_t]$$
$$= \beta_{th} V L(F_e) F_e^2 - (3N - 4) \lim_{t \to \infty} \overline{\alpha}_t$$
(6.12.2)
$$= 0$$

where $\overline{...}$ denotes a time average of duration *t*. We note that it is the stationary property of the T-mixing steady state that implies the long time average rate of change of the energy goes to zero. Since β_{th} , $L(F_e)$, V, F_e^2 are each strictly positive, so too must the long time average of the thermostat multiplier. This means that when averaged over long times in a nonequilibrium steady state, heat must, on average, be removed from the system by the thermostat. Thus the work performed on the system by the dissipative field, $-\overline{J}VF_e$, is on average, positive and by (6.12.2) this work is *dissipated* into the form of heat and then removed from the system by the (physically remote) thermostat. This gives a mathematical proof of one of the postulated statements of the Second Law of Thermodynamics given in William Thomson's 1852 paper¹⁸ On the universal Tendency in Nature to the Dissipation of Mechanical Energy as follows "Although mechanical energy is indestructible, there is a universal tendency to its dissipation, which produces throughout the system a gradual augmentation and diffusion of heat, cessation of motion and exhaustion of the potential energy of the material Universe".

A6 APPENDIX

ß

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 τ_{1}

Here we consider a system subject to a cyclic change in temperature to demonstrate the behaviour and relationship between the dissipation, and the thermodynamic and Gibbs entropies. Consider a thermostatted system at equilibrium max tat T_1 , which is monitored for a period τ_1 , then is decreased in temperature to T_2 over a period τ_2 , maintained that temperature for a period τ_3 , then warmed back to T_1 over a period τ_2 , and maintained at that temperature for a period τ_1 (see figure 1).

In order to determine the dissipation function, we need to look at a timesymmetric protocol. For simplicity, we make the changes in T such that β varies linearly in time. To ensure ergodic consistency, we consider a Nosé-Hoover thermostatted system. This example can then be used to consider thermodynamically reversible or irreversible changes.



Figure 1. Schematic diagram of the protocol used for change of temperature in the example considered.

The equations of motion are:

$$\dot{\mathbf{q}}_{i} = \mathbf{p}_{i} / m$$

$$\dot{\mathbf{p}}_{i} = \mathbf{F}_{i} - \alpha \mathbf{p}_{i}$$

$$\dot{\alpha} = \frac{1}{\tau_{th}^{2}} \left(\frac{2\mathbf{p}_{i} \cdot \mathbf{p}_{i}}{3NkT(t)m} - 1 \right)$$
(A6.1)

and the initial distribution function is:

$$f(\mathbf{\Gamma}, \alpha) = \frac{e^{-\beta_1 E(\mathbf{\Gamma}) - \frac{3}{2}N\tau_{th}^2 \alpha^2}}{Z_1}$$
(A6.2)

This becomes a cyclic process if the time period τ_1 becomes long enough that, for averages of smooth phase functions, the system approaches equilibrium. We will consider both possibilities here (cyclic and not).

The dissipation function for this process is [31]:

$$\Omega_{\tau_{\max}} = \beta_1 E(\tau_{\max}) - \beta_1 E(0) + \frac{3}{2} N \tau_{th}^2 (\alpha(\tau_{\max})^2 - \alpha(0)^2) + 3N \int_0^{\tau_{\max}} \alpha(t) dt$$
(A.3)

Noting,

$$\frac{d}{dt} \left[\frac{3}{2} N \tau_{th}^2 \alpha(t)^2 \right] = 3N \tau_{th}^2 \alpha(t) \dot{\alpha}(t) = \frac{2K(t)\alpha(t)}{kT(t)} - 3N\alpha(t)$$
(A6.4)

so,

$$\frac{3}{2}N\tau_{th}^{2}(\alpha(\tau_{\max})^{2} - \alpha(0)^{2}) = \int_{0}^{\tau_{\max}} \left(\frac{2K(t)\alpha(t)}{k_{B}T(t)} - 3N\alpha(t)\right) dt$$
(A6.5)

and substituting into (A.3) gives,

$$\Omega_{\tau_{\max}} = \beta_1 E(\tau_{\max}) - \beta_1 E(0) + \int_0^{\tau_{\max}} \frac{2K(t)\alpha(t)}{k_B T(t)} dt$$
(A6.6)

Furthermore, $\dot{E}(t) = -2K(t)\alpha(t) = \dot{Q}(t)$ where $\dot{Q}(t)$ is the rate at which heat is

transferred to the system, since no work is being done on the system. So,

$$\Omega_{\tau_{\max}} = \beta_1 E(\tau_{\max}) - \beta_1 E(0) - \int_0^{\tau_{\max}} \frac{Q(t)}{k_B T(t)} dt$$
(A6.7)

Now consider some special cases:

(i) When $\lim(\tau_2 \to \infty)$ we have a reversible process. Then,

$$\int_{\tau_1}^{\tau_1+\tau_2} \frac{\langle \dot{Q}(t) \rangle}{k_B T(t)} dt = -\int_{\tau_1+\tau_2+\tau_3}^{\tau_1+2\tau_2+\tau_3} \frac{\langle \dot{Q}(t) \rangle}{k_B T(t)} dt \text{ and } \langle E(\tau_{\max}) \rangle = \langle E(0) \rangle \text{ so from (A.7)},$$
$$\left\langle \Omega_{\tau_{\max}} \right\rangle = -\int_{0}^{\tau_{\max}} \frac{\langle \dot{Q}(t) \rangle}{k_B T(t)} dt = 0.$$
(A6.8)

(ii) Now consider the irreversible process with finite τ_2 but with $\lim(\tau_1 \to \infty)$.

With respect to averages of smooth phase functions the system will be arbitrarily close to equilibrium at τ_{\max} , so $\lim_{\tau_{\max}\to\infty} \langle E(\tau_{\max}) \rangle = \langle E(0) \rangle$. Then, from (A.7):

$$\left\langle \Omega_{\tau_{\max}} \right\rangle = -\int_0^{\tau_{\max}} \frac{\left\langle \dot{Q}(t) \right\rangle}{k_B T(t)} dt = -1/k_B \int_0^{\tau_{\max}} \dot{S}_G(t) dt \tag{A6.9}$$

and from the Second Law Inequality [19], $\left< \Omega_{\tau_{max}} \right> \ge 0$, so

$$\left\langle \Omega_{\tau_{\max}} \right\rangle = -\int_0^{\tau_{\max}} \frac{\left\langle \dot{Q}(t) \right\rangle}{k_B T(t)} dt = -1/k_B \int_0^{\tau_{\max}} \dot{S}_G(t) dt \ge 0 \tag{A6.10}$$

If the process is irreversible, the inequality applies. The equality will apply for the reversible case. So this says that for the irreversible cycle, the time integral of the average dissipation function (multiplied by k_B), the change in the Gibbs entropy and the integral of $\langle \dot{Q} \rangle / T$, where the temperature is the target temperature of the Nosé-

Hoover thermostat, are all equal and will be positive, independent of the Nosé-Hoover time constant τ_{th} .

The target temperature will in general be different from the instantaneous kinetic temperature and furthermore those differences will vary with respect to the time constant, τ_{th} . The same equation exactly can be derived using an isokinetic rather than Nosé-Hoover thermostat. These facts show that the temperature T(t), in the equation (A.10) is in fact the equilibrium thermodynamic temperature of the underlying equilibrium system at time t. This temperature can be discovered by halting the execution of the protocol at time t, and allowing the entire system to relax to equilibrium. From the equilibrium relaxation theorems, for isokinetic dynamics this temperature is the instantaneous kinetic temperature at time t. For the Nosé-Hoover thermostat it is the Nosé-Hoover target temperature at time t, regardless of the value of the feedback time constant.

Equation (A.10) also shows the lack of utility of the Gibbs entropy in this work. Although its time derivative is: $\langle \dot{Q}(t) \rangle / T(t)$, the difference in the Gibbs entropy of the initial and final states is not zero. This is in spite of the fact that an unlimited amount of time is allowed for relaxation towards the final state! For any relaxation time no matter how large, the final distribution at time τ_{max} , is not precisely an equilibrium distribution and the Gibbs entropy detects these minute differences and $S_G(0) > S_G(\tau_{max}), \forall \tau_{max}$. If it did relax to true equilibrium we could never retrieve the initial distribution of states by applying a time reversal operator. For any τ_{max} no matter how large, the initial distribution of states can always be retrieved using a time reversal operator. True equilibrium distributions are invariant in time with or without the application of time reversal operators.

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