Chapter 4

The Dissipation Theorem

"…the divergences [in the virial expansion of transport coefficients] somehow implied that the whole classical picture of nonequilibrium statistical mechanics was wrong, that there was an essential nonanalytic, non-controlled feature in the theory, that defied "Boltzmann's dream"."

E.G.D. Cohen, Am. J. Phys., **58**,618(1990)

4.1 Derivation of the Dissipation Theorem

We now derive the *Dissipation Theorem*, which shows that, as well as being the subject of the ESFT, the dissipation function is the central argument of both linear response theory (*i.e.* Green-Kubo theory) and nonlinear response theory. This theorem was first derived in 2008 [25,26].

Taking the solution of the Lagrangian form of the phase continuity equation eq. (2.4.1,4), we can substitute for $f(\boldsymbol{\Gamma},0)$ using the definition of the time-integrated dissipation function (3.1.2), obtaining:

$$\begin{aligned} f(S^t\boldsymbol{\Gamma};t) &= \exp\left[-\int_0^t ds\ \Lambda(S^s\boldsymbol{\Gamma})\right] f(\boldsymbol{\Gamma};0) \\ &= \exp\left[-\int_0^t ds\ \Lambda(S^s\boldsymbol{\Gamma})\right] f(S^t\boldsymbol{\Gamma};0)\exp\left[\int_0^t ds\ \Omega(S^s\boldsymbol{\Gamma}) + \int_0^t \Lambda(S^s\boldsymbol{\Gamma})ds\right] \\ &= f(S^t\boldsymbol{\Gamma};0)\exp\left[\int_0^t ds\ \Omega(S^s\boldsymbol{\Gamma})\right]. \end{aligned} \tag{4.1.1}$$

The first line is obtained from (2.4.1,4). The second line substitutes for $f(\boldsymbol{\Gamma};0)$ using the definition of the dissipation function (3.1.2).

Equation (4.1.1) is valid for any $\boldsymbol{\Gamma}$, so we map $\boldsymbol{\Gamma} \to S^{-t}\boldsymbol{\Gamma}$. Then after this remapping,

$$\begin{aligned} f(\boldsymbol{\Gamma},t) &= f(\boldsymbol{\Gamma},0)\exp\left[\int_0^{-t} ds\ \Omega(S^s S^{-t}\boldsymbol{\Gamma})\right] \\ &= f(\boldsymbol{\Gamma};0)\exp\left[-\int_0^{-t} ds'\ \Omega(S^{s'}\boldsymbol{\Gamma})\right], \end{aligned} \tag{4.1.2}$$

where the second equality is obtained by introducing $\mathrm{s'} = \mathrm{s} - \mathrm{t}$. Replacing the dummy variables gives,

$$\begin{aligned} f(\boldsymbol{\Gamma};t) &= f(\boldsymbol{\Gamma};0)\exp\left[-\int_0^{-t} ds\ \Omega(S^s\boldsymbol{\Gamma})\right] \\ &= f(\boldsymbol{\Gamma};0)\exp\left[\int_0^{t} ds\ \Omega(S^{-s}\boldsymbol{\Gamma})\right] \end{aligned} \tag{4.1.3}$$

This result shows that the forward time propagator for the *N*-particle distribution function, $\exp[-\mathrm{i}L(\boldsymbol{\Gamma})\mathrm{t}]$ - see (2.4.7): $f(\boldsymbol{\Gamma};t) = \exp[-iLt]f(\boldsymbol{\Gamma};0)$ - has a very simple relation (backwards in time) to exponential time integral of the dissipation function. In fact (4.1.3) is a simpler equation. It only involves functions and their path integrals whereas (2.4.7) involves functions and exponential integrals of *operators.*

If we take (4.1.3) and differentiate it in time at a fixed point in phase space we see that

$$\frac{\partial f(\mathbf{\Gamma};t)}{\partial t} = \Omega(S^{-t}\mathbf{\Gamma})f(\mathbf{\Gamma};t) = -iL(\mathbf{\Gamma})f(\mathbf{\Gamma};t) \qquad (4.1.4)$$

where we have used (2.4.6) to relate the time derivative of $f(\mathbf{\Gamma};t)$ to the *f*-Liouvillean. Equation (4.1.4) shows there is a very simple relation between the dissipation function and the *f*-Liouville operator.

In the case of adiabatic (*i.e.* unthermostatted) dynamics for an ensemble that is initially a canonical ensemble, this result is equivalent to (7.2.8) of reference [25], which is the distribution function derived by Yamada and Kawasaki in 1967 [28]. However (20) is much more general and, like the ESFT, can be applied to any initial ensemble and any time reversible, and possibly thermostatted dynamics that satisfies $\mathrm{A}\mathbf{I\Gamma}$. For thermostatted dynamics driven by a dissipative field (4.1.4 was first derived by Evans and Morriss in 1984.

From eq. (4.1.4) we can calculate nonequilibrium ensemble averages in the Schrödinger representation

$$\begin{aligned} \langle B(t)\rangle_{F_e,f(\mathbf{\Gamma};0)} &= \int_D d\mathbf{\Gamma}\, B(\mathbf{\Gamma})\exp[-\int_0^{-t} ds\,\Omega(S^s\mathbf{\Gamma})]f(\mathbf{\Gamma};0) \\ &= \left\langle B(0)\exp[-\int_0^{-t} ds\;\Omega(S^s\mathbf{\Gamma})]\right\rangle_{F_e,f(\mathbf{\Gamma};0)} \end{aligned} , \qquad (4.1.5)$$

and by differentiating and integrating (4.1.5) with respect to time, we find that

$$\begin{aligned}\frac{d\left\langle B(t)\right\rangle_{F_e,f(\boldsymbol{\Gamma};0)}}{dt} &= \int_D d\boldsymbol{\Gamma}\, B(\boldsymbol{\Gamma})\Omega(S^{-t}\boldsymbol{\Gamma})f(\boldsymbol{\Gamma};t) \\ &= \int_D d\boldsymbol{\Gamma}\, B(S^{t}\boldsymbol{\Gamma})\Omega(\boldsymbol{\Gamma})f(\boldsymbol{\Gamma};0) \qquad (4.1.6) \\ &= \left\langle B(t)\Omega(0)\right\rangle_{F_e,f(\boldsymbol{\Gamma};0)}\end{aligned}$$

If we integrate (4.1.6) in time we can write the averages in the Heisenberg representation as

$$\left\langle B(t)\right\rangle_{F_e,f(\boldsymbol{\Gamma};0)} = \left\langle B(0)\right\rangle_{f(\boldsymbol{\Gamma};0)} + \int_0^t ds\left\langle \Omega(0)B(s)\right\rangle_{F_e,f(\boldsymbol{\Gamma};0)}. \qquad (4.1.7)$$

On both sides of eqs. (4.1.7,8,9) the time evolution is governed by the full field-dependent, thermostatted equations of motion (2.2.5). The derivation of eqs. (4.1.7,9) from the definition of the dissipation function (3.1.2), is called the *Dissipation Theorem.* This Theorem is extremely general, and allows the determination of the ensemble average of an arbitrary phase function under very general conditions. We require time reversible, autonomous dynamics; an initial distribution that is invariant under the time reversal map M^T and we require ergodic consistency so that the dissipation function is non-singular.

Like the ESFT (4.1.5,7) are valid arbitrarily far from equilibrium. Equation (4.1.5) can be obtained for time-dependent fields by including the explict time-dependence of $\mathbf{F}_e(t)$, but (4.1.7) cannot [29]. As in the derivation of the ESFT the only unphysical terms in the derivation are the thermostatting terms within the wall region. However, because these thermostatting particles can be moved arbitrarily far from the system of interest, the precise mathematical details of the thermostat are unimportant. Since the number of degrees of freedom in the reservoir is assumed to be much larger than that of the system of interest, the reservoir can always be assumed to be in thermodynamic equilibrium. There is therefore no difficulty in defining the thermodynamic temperature of the walls. This is in marked contrast with the system of interest, which may be very far from equilibrium where the thermodynamic temperature cannot be defined.

4.2 Equilibrium Distributions are preserved by their associated Dynamics

Equation (4.1.4) shows that if at time *t,* the dissipation is nonzero anywhere in the phase space domain, the distribution function is time dependent time.

$$\exists \boldsymbol{\Gamma} \in D \ st \ \Omega(S^t \boldsymbol{\Gamma}) \neq 0 \Rightarrow \frac{\partial f(\boldsymbol{\Gamma};t)}{\partial t} = \Omega(S^{-t}\boldsymbol{\Gamma}) f(\boldsymbol{\Gamma};t) \neq 0 \qquad (4.2.1)$$

and cannot be an equilibrium distribution function. Conversely if the distribution function is an equilibrium distribution at t=0, then from (4.1.4), $\Omega(\boldsymbol{\Gamma}) = 0, \forall \boldsymbol{\Gamma} \in D$ and by (4.1.4)

$$\frac{\partial f_{eq}(\boldsymbol{\Gamma};0)}{\partial t} = \Omega_{eq}(\boldsymbol{\Gamma}) f_{eq}(\boldsymbol{\Gamma};0) = 0, \quad \forall \boldsymbol{\Gamma} \in D \qquad (4.2.2)$$

and the distribution function will stay an equilibrium distribution function forever. This means that if the distribution starts in equilibrium*,* the distribution will be unchanging

$$f_{eq}(\boldsymbol{\Gamma};t) = f_{eq}(\boldsymbol{\Gamma};0), \forall \boldsymbol{\Gamma} \in D, t \qquad (4.2.3)$$

and the time integrated dissipation will be zero for all time. By equation (3.7.1) this system is a time independent equilibrium system. So having zero instantaneous dissipation everywhere in *D* at *t*=0 guarantees the time integrated dissipation is zero forever. Once you start in equilibrium you remain in equilibrium!

Furthermore using (4.2.1), the only unchanging distribution functions are equilibrium distributions where the dissipation is identically zero everywhere in the ostensible phase space domain. Thus distributions that are, over some specified domain *D,* at equilibrium with respect to their specified dynamics, are time independent at every point in phase space!

Definition

This gives us a new definition of equilibrium systems. *Equilibrium systems* are those combinations of dynamics and phase space distribution for which

$$\Omega_{eq}(\mathbf{\Gamma}) = 0, \forall \mathbf{\Gamma} \in D \,. \tag{4.2.4}$$

This is a simple restatement of our original definition (3.7.1) that involved time integrals of dissipation. Our new definition involves the instantaneous dissipation.

Notes:

- Although the partial derivative of the equilibrium distribution function with respect to time is zero, the streaming derivative of an equilibrium distribution function is ***not*** necessarily zero. As we will see in Chapter 6 for isochoric constant energy systems the streaming derivative is zero but for any equilibrium system that exchanges heat with its surroundings $df_{eq} / dt \neq 0$. For thermostatted equilibrium systems the time averaged streaming derivative is zero however.
- Although the Dissipation Theorem shows that an equilibrium distribution is preserved by its dynamics $f_{eq}(\mathbf{\Gamma})$, we do not yet know whether the equilibrium distribution is unique or whether it is stable with respect to small perturbations. Neither do we know whether arbitrary initial distributions will relax to equilibrium at long times. We will return to discuss these issues in the following chapter.
- Equation (4.1.3) shows that for all *nonequilibrium* deterministic systems, the N-particle distribution function has explicit time dependence: $f_{ne}(\mathbf{\Gamma};t)$. This automatically means that nonequilibrium steady state distributions cannot be written in a closed, time-stationary form,

$$f_{ne}(\mathbf{\Gamma}) \neq \frac{\exp[-F(\mathbf{\Gamma})]}{\int_D d\mathbf{\Gamma} \exp[-F(\mathbf{\Gamma})]} \qquad (4.2.4)$$

for some real $F(\mathbf{\Gamma})$. If (4.2.3) were possible,

$$\frac{\partial f_{ne}(\mathbf{\Gamma})}{\partial t} = 0 = \Omega(S^{-t}\mathbf{\Gamma}) f_{ne}(\mathbf{\Gamma},t), \forall t, \mathbf{\Gamma} \in D \qquad (4.2.5)$$

The only way this could happen would be if $\Omega(\mathbf{\Gamma}) = 0, \forall \mathbf{\Gamma} \in D$. But this implies that the distribution is in fact an equilibrium distribution, which is a contradiction. Consequently equations (4.2.4) and (4.2.5) are impossible.

The Jaynes information theory approach to nonequilibrium steady hypothesizes closed forms like (4.2.4) for nonequilibrium steady state distributions. From equation (4.2.4) these can at *most* only be approximations! They cannot possibly be exact.

In writing (4.2.4) we exclude the case where we discontinuously change the dynamics therefore instantaneously changing the form of the equilibrium distribution. In such a case the initial distribution is an equilibrium distribution for the prior dynamics ($t \leq 0$) but is a nonequilibrium distribution for the subsequent ($t > 0$) dynamics.

- As noted in §2.5, in nonequilibrium steady states the distribution function collapses forever towards a steady state attractor of lower dimension than that of the embedding phase space. Therefore although averages of smooth phase functions are time independent, in nonequilibrium steady states the distribution function and its associated Gibbs entropy are not constant. The Gibbs entropy is of course not the average of a simple phase function but rather can be expressed as the ensemble average of the logarithm of the phase space density. The average of the phase function becomes time independent at sufficiently long times but the Gibbs entropy itself diverges linearly in time towards negative infinity.

4.3 Broad characterization of nonequilibrium systems: Driven, Equilibrating and T-mixing systems

Definition

A *driven* system is a system of interacting particles, possibly thermostatted in some way, subject to an external field F_e (or possibly asymmetric boundary condition). For times up to zero the system is in an equilibrium distribution with respect to the *zero field* dynamics. The field dependent dynamics satisfies AI$\mathbf{\Gamma}$. Because the zero field system is at equilibrium with respect to the zero field dynamics, the dissipative field is *solely* responsible for the dissipation.

Definition

For driven systems the *dissipative field* F_e, is defined by the equation,

$$\Omega(\mathbf{\Gamma}) \equiv -[\beta J](\mathbf{\Gamma})VF_e \qquad (4.3.1)$$

where V is the system volume, and $[\beta J](\mathbf{\Gamma})$ is simply the dissipation divided by the volume and the dissipative field.

Definition

We often refer to (4.3.1) as the *primary dissipation function* for the external field F_e. When the field is zero there is no dissipation.

Definition

The dissipative field could be a *mechanical field* appearing in the equations of motion (*e.g.* an electric field applied to an electrical conductor, or it could be the strain rate appearing in the SLLOD equations of motion).

Definition

The dissipative field could be *thermodynamic field* (*e.g.* a velocity or temperature difference between moving walls that sandwich the system of interest). Thermodynamic fields are associated with boundary conditions. These boundary conditions do not usually appear in the actual equations of motion for the atoms or molecules comprising the system. As we have seen the SLLOD equations of motion have the characteristics both of a mechanical dissipative process and a thermal transport process. The equations of motion refer explicitly to the field but the boundary conditions also refer to the field. This points out that although thermal and mechanical dissipative processes look profoundly different, at a deeper level there are similarities between the two types of field.

Sllod is not autonomous but the nonautonomous terms rapidly decrease with system size in systems with short ranged interatomic potentials.

Without loss of generality we define the dissipative field so that the dissipation function is a *linear* functional of that field. If the disspation is explicitly quadratic in some external physical field we just define the dissipative field to be that quadratic physical field. The dissipative field in (4.3.1) is undefined up to some scalar factor. This has no serious mathematical consequences however, because this factor can be simply absorbed into the factor $[\beta J]$.

In order to specify $[\beta J](\mathbf{\Gamma})$ further we need to look at the explicit form for the initial distribution and the dynamics. In Chapter 2 we showed that for for systems whose equations of motion are given by (2.2.5) $\beta = 1 / k_B T_{th}$ where T_{th} was the target temperature of the Nose-Hoover thermostatted reservoir which as will be shown in Chapter 6, is equal to the equilibrium thermodynamic temperature of that the entire system will relax to, if the dissipative field is set to zero and the entire system is allowed sufficient time to relax towards equilibrium.

For ergostatted systems β is not constant and is instead the reciprocal of the instantaneous kinetic temperaure of the ergostatted particles times Boltzmann's constant. This kinetic temperature is *not* a constant of the motion for constant energy dynamics.

Analogous statements are made if the thermostat is in fact an isokinetic thermostat. In this case β is the reciprocal of the constant kinetic temperature multiplied by Boltzmann's constant. Again if the dissipative field is set to zero this kinetic temperature is the equilibrium thermodynamic temperature the system will relax to if the dissipative field is set to zero and the system is allowed to relax.

For all driven systems equation that are at equilibrium when the dissipative field is zero, (4.1.8) can be written as the Transient Time Correlation function expression, [25] for the thermostatted nonlinear response of the phase variable B to the dissipative field F_e:

$$\left\langle B(t)\right\rangle_{F_e,f(\Gamma;0)} = \left\langle B(0)\right\rangle_{f(\Gamma;0)} - V\int_0^t ds\left\langle [\beta J](0)B(s)\right\rangle_{F_e,f(\Gamma;0)} F_e \,. \qquad (4.3.4)$$

Definition

The *Transient Time Correlation Function* (TTCF) eq. (4.3.4) has been used frequently to compute the nonlinear transport behaviour of systems over extremely wide ranges of the applied field [30-36]. It is exact arbitrarily far from equilibrium and for systems of arbitrary size. It applies to systems that are driven by mechanical fields that appear directly in the equations of motion and also to boundary driven systems where it is the boundary conditions that prevent the system from being in quilibrium.

Definition

A system is said to be *Transient, or T-Mixing* over a phase space domain *D*, if ensemble averages over domain *D* of the transient time correlation functions $\left\langle B(\mathbf{\Gamma}(s))\Omega(\mathbf{\Gamma}(0))\right\rangle$, go to zero at long times sufficiently rapidly, that their time integrals, converge to a constant finite value, as the integration time goes to infinity. Since the average of phase functions is not necessarily zero $\langle B(s)\rangle \neq 0$, the T-mixing condition requires that

$$\langle \Omega(0)\rangle = 0 \qquad (4.3.5)$$

and for driven systems,

$$\langle [\beta J](0)\rangle = 0 \, . \qquad (4.3.6)$$

At this stage we do not know whether T-mixing equilibrating systems exist and if the do, we do not yet know what any necessary conditions are. We have already seen that for driven systems (4.3.6) always holds.

The dissipation function is odd under the time reversal mapping and since our initial distributions are always invariant under the time reversal mapping, (4.3.5) always holds. We can make some further remarks about (4.3.6). For isotropic fluids at equilibrium in the absence of external fields (4.3.6) will hold if the dissipative flux is a tensor or pseudo tensor of rank 1 or higher. It will also hold if the dissipative flux is odd under the time reversal map M^T or if it is a pseudo scalar. Only if the dissipative flux is a polar scalar tensor could (4.3.6) fail to hold. If (4.3.6) does not hold the system cannot be T-mixing and we do not treat such systems in this book.

T-mixing is more general than the more common mixing condition. Mixing is for correlation functions over stationary distributions such as equilibrium distributions.

Definition

An *equilibrating* system is a system that evolves under zero-field dynamics, possibly in contact with some form of thermostat. Initially the system is not in equilibrium with respect to the zero field dynamics. The initial form of the distribution is entirely responsible for dissipation.

If the dissipative field is nonzero, the ensemble averaged and time averaged dissipation is, as the Second Law Inequality shows, always strictly positive and the dissipation must be, to leading order, quadratic in the dissipative field. The means if the ensembled averaged steady state dissipation is analytic in the field, as expected for finite times in finite systems with continuous dynamics, and the system is driven

$$\lim_{F_e \to 0} \left\langle [\beta J](t) \right\rangle_{F_e, f(\Gamma,0)} = O(F_e), \forall t \,. \tag{4.3.7}$$

It is possible that this leading order term vanishes because of some symmetry of the system in which case the leading term would be cubic in the field. Since at t=0, the distribution has had no time to adjust to the sudden presence of the field (it was turned on at time zero), we see that for driven systems,

$$\left\langle [\beta J](0) \right\rangle_{F_e, f(\Gamma,0)} = 0 \tag{4.3.8}$$

Equation (4.3.3) is for driven systems, a simple but very powerful result. Note: we assume here that $F_e(t) = 0, \forall t < 0$. We do not treat the case where $F_e(t) = a, t < 0; F_e = b, t > 0$ for two constants *a*,*b.*

For small fields and small systems, the averages of field-induced properties of the system are often swamped by noise from naturally occuring fluctuations. This makes direct calculation of the left hand side of (4.3.4) problematic. This is particularly relevent in calculation of the transport coefficient which can be obtained from ratio of the flux to the field. The TTCF can be applied at any field strength, even zero where it reduces to the Green-Kubo expression for the linear response:

$$\lim_{F_e\to 0}\left\langle B(t)\right\rangle_{F_e,f(\boldsymbol{\Gamma};0)} = \left\langle B(0)\right\rangle_{f(\boldsymbol{\Gamma};0)} - V\int_0^t ds\left\langle [\beta J](0)B(s)\right\rangle_{F_e=0,f(\boldsymbol{\Gamma};0)} F_e \quad (4.3.9)$$

where ensemble average on the right hand side is an equilibrium ensemble average and the dynamics used to compute $B(s)\equiv B(S^s\boldsymbol{\Gamma})$ is the zero field possibly thermostatted dynamics. This is in marked contrast to equation (4.3.4) where everything is computed with the dissipative field applied.

Note: we could consider systems that are being driven by a dissipative field but that are not initially at equilibrium with respect to the zero field dynamics. For simplicity we rarely consider such mixed systems in this book.

Two Trivial Corollaries of the Dissipation Theorem

Two trivial consequences follow for systems that are T-mixing over the specified phase space domain. These systems have two properties:

a. they are physically ergodic over the specified phase space domain at long times and

b. they have *time independent* ensemble averaged values for all smooth phase functions at long times.

These results are true for systems that are driven or equilibrating.

If the system is T-mixing, obviously we have convergent integrals for (4.1.7,8) and a convergent value for the difference in the ensemble average of all smooth, phase variables. If we assume the system was not physically ergodic then we could form time correlation functions involving phase functions that change their values depending on whether you are, or are not, in some ergodic subdomain of the full nonergodic domain: *D*. If the system is not ergodic, by definition these correlation functions never decay. This is a contradiction. Therefore the system is physically ergodic.

Why do we expect correlation functions (4.1.7), (4.3.4) go to zero at long times? Two things happen. Firstly, as we have seen if the system is T-mixing either (4.3.5) or (4.3.6) holds.

Secondly in many (but not all!) systems, correlation functions of zero mean quanities go to zero at long times. [This is guranteed if the system is T-mixing.] At late times these systems loose "memory" of their initial average value for the phase functions appearing in the correlation function. Note: this loss of "memory" has *no* connection with Lyapunov instability or the Kolmogorov-Sinai entropy – as the argument below shows.

From (4.3.5,6) we have $\langle A(0)\rangle = 0$ and many time correlation functions decorrelate over time and we have

$$\lim_{t\to\infty}\langle A(0)B(t)\rangle = \langle A(0)\rangle \lim_{t\to\infty}\langle B(t)\rangle = 0 \; . \qquad (4.3.8)$$

The time correlation function appearing in (4.3.8) is not necessarily an equilibrium or steady state correlation function. It may be a transient time correlation function as in (4.1.8). Systems that do not loose correlations are generally integrable (*e.g.* undamped systems of harmonic oscillators).

Our definition of T-mixing is in fact stronger than (4.3.8). It requires that the correlations vanish sufficiently rapidly that the time integrals converge (4.1.5) to finite values. They must decay faster than t^{-1}. For equilibrium systems in two dimensions, autocorrelation functions of particle velocity, shear stress and heat flux evaluated in the limit of large system size, are all thought to have divergent time integrals because of the so-called long time tails. In three dimensions the corresponding equilibrium autocorrelation functions are thought to decay asymptotically as $t^{-3/2}$, fulfilling the T-mixing convergence criterion.

Historically there has been a lot of interest in systems at the border line of being mixing or T-mixing. The famous Fermi-Pasta-Ulam system which is a chain of anharmonic oscillators where the degree of anharmonicity can be controlled, are right at the border line of T-mixing. They are thought not to be mixing.