

Chapter 2

The Dissipation Function: Its Relationship to Entropy Production, Theorems for Nonequilibrium Systems and Observations on Its Extrema

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Abstract In this chapter we introduce the dissipation function, and discuss the behaviour of its extrema. The dissipation function allows the reversibility of a nonequilibrium process to be quantified for systems arbitrarily close to or far from equilibrium. For a system out of equilibrium, the average dissipation over a period, t , will be positive. For field driven flow in the thermodynamic and small field limits, the dissipation function becomes proportional to the rate of entropy production from linear irreversible thermodynamics. It can therefore be considered as an entropy-like quantity that remains useful far from equilibrium and for relaxation processes. The dissipation function also appears in three important theorems in nonequilibrium statistical mechanics: the fluctuation theorem, the dissipation theorem and the relaxation theorem. In this chapter we introduce the dissipation function and the theorems, and show how they quantify the emergence of irreversible behaviour in perturbed, steady state, and relaxing nonequilibrium systems. We also examine the behaviour of the dissipation function in terms of the extrema of the function using numerical and analytical approaches.

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2.1 Introduction

The treatment of thermodynamic systems can be considered to be split between systems that are in or near equilibrium, and nonequilibrium systems. Equilibrium systems are well quantified by a variety of state functions, such as entropy, temperature and free energy, that are independent of the moment to moment behaviour of the system. Nonequilibrium systems can exhibit a variety of behaviours including relaxation, ageing, various meta-stable states, and steady states. Even in a steady state, they are generally more difficult to classify as many of the basic state functions, including the temperature and entropy, are undefined for far from equilibrium states and the nonequilibrium distribution function of a steady state system is fractal and non-analytic.

As discussed recently [1], the Gibbs' entropy,

$$S_G(t) \equiv -k_B \int d\mathbf{\Gamma} f(\mathbf{\Gamma}, t) \ln(f(\mathbf{\Gamma}, t)) \equiv -k_B \langle \ln(f(\mathbf{\Gamma}, t)) \rangle_{f(\mathbf{\Gamma}, t)}, \quad (2.1)$$

is not useful for the description of the relaxation of nonequilibrium Hamiltonian systems or for steady states because it is constant in the first case and divergent in the latter. Here the notation $\langle \dots \rangle_{f(\mathbf{\Gamma}, t)}$ is an ensemble average with respect to the distribution function $f(\mathbf{\Gamma}, t)$. Close to equilibrium and in the thermodynamic limit, the spontaneous entropy production rate from nonlinear irreversible thermodynamics [2] can be well defined and is a useful quantity. However, far from equilibrium where temperature is not well defined a new quantity needs to be considered. Recently we have shown that the dissipation function, Ω , is a powerful quantity which reduces to the spontaneous entropy production rate at small fields for field driven flow [3]. As discussed below, it also satisfies the inequality, $\langle \Omega_t \rangle > 0$ for nonequilibrium systems and therefore it is considered an entropy-like quantity or a generalisation of the entropy for far from equilibrium systems.

In this chapter we will first define the dissipation function and give an overview of some recently derived theorems where dissipation plays a key role. We will also consider the extremal behaviour of the dissipation function by referring to some results from previously published work.

2.2 The Dissipation Function and the Fluctuation Theorem

The dissipation function quantifies the thermodynamic reversibility of a trajectory. It compares the probability of observing an arbitrary system trajectory with the probability of observing the time reverse of that trajectory (its conjugate anti-trajectory) in the same ensemble of trajectories [3]:

$$\Omega_t(\mathbf{\Gamma}(0)) = \ln \frac{P(\mathbf{\Gamma}(0), 0)}{P(\mathbf{\Gamma}^*(t), 0)}. \quad (2.2)$$

Here $\Gamma \equiv \{q_1, p_1, \dots, q_N, p_N\}$ is the phase space vector of the system which corresponds to a system trajectory, $\Omega_t(\Gamma(0))$ is the total dissipation (or time integral of the dissipation) for a trajectory originating at $\Gamma(0)$ and evolving for a time t , $P(\Gamma(0), 0) = f(\Gamma(0), 0)d\Gamma(0)$ is the probability of observing a system in an infinitesimal region around $\Gamma(0)$ in the initial system distribution with distribution function $f(\Gamma(0), 0)$, and $\Gamma^*(t)$ is the result of applying a time reversal map to $\Gamma(t)$. It can therefore be written in expanded form as,

$$\Omega_t(\Gamma(0)) = \ln \frac{f(\Gamma(0), 0)d\Gamma(0)}{f(\Gamma^*(t), 0)d\Gamma^*(t)}. \quad (2.3)$$

While the expression above is for a deterministic system, the dissipation function can be defined for a general dynamic system [4], and has been applied to quantum and stochastic systems in addition to deterministic ones [5–7].

The time integral of the dissipation is positive when the observed system trajectory, starting at $\Gamma(0)$, is more probable than the conjugate trajectory, starting at $\Gamma(t)$, and negative when the observed trajectory is less likely than its conjugate. In order for the dissipation function to be well defined for a system we need the conjugate trajectory to exist for every possible trajectory in the accessible phase space of the system,¹ which for a deterministic system requires ergodic consistency (that the volume of phase space occupied at time t is congruent with or a subset of the volume at time 0) and time reversal symmetric (any time dependent external parameters are even around $t/2$). We can also define an instantaneous dissipation function:

$$\Omega(\Gamma(t)) = \frac{d\Omega_t(\Gamma(0))}{dt}. \quad (2.4)$$

For clarity of notation, we note that $\Omega_t(\Gamma(0)) = \int_0^t \Omega(\Gamma(s))ds$.

The dissipation function evaluates the relative reversibility of a single observation of a system. To understand the overall system behaviour, we need to look at the distribution of the dissipation function. The fluctuation theorem does this by considering the relative probability of observing processes that have positive and negative total dissipation in nonequilibrium systems. This theorem was first derived by Evans and Searles [3, 8], and results in the relationship:

$$\frac{P(\Omega_t = A \pm dA)}{P(\Omega_t = -A \pm dA)} = e^A, \quad (2.5)$$

where $P(\Omega_t = A \pm dA)$ is the probability of observing a trajectory with a dissipation total infinitesimally close to A .

The fluctuation theorem was derived to solve one of the fundamental paradoxes of statistical mechanics, Lochsmidt's paradox. In 1876, Lochsmidt pointed out a fundamental problem associated with nonequilibrium thermodynamics: the

¹ Note that this is often trivially satisfied in a stochastic system.

macroscopic behaviour of a system is irreversible, as embodied in the second law, but the microscopic motion of all of the individual components is fully time reversible. Therefore for any system change, the opposite system change must also be possible. Even at that time, a resolution to the paradox was recognised by some. As noted by Maxwell [9]:

The truth of the second law is... a statistical, not a mathematical, truth, for it depends on the fact that the bodies we deal with consist of millions of molecules...

Hence the second law of thermodynamics is continually being violated, and that to a considerable extent, in any sufficiently small group of molecules belonging to a real body.

and Boltzmann [10]:

...as soon as one looks at bodies of such small dimension that they contain only a very few molecules, the validity of this theorem [the Second Law] must cease.

This means that the second law of thermodynamics is the limiting result of a statistical effect where the probability of observing the behaviour predicted from thermodynamics becomes more and more likely as the system size grows. However for sufficiently small systems monitored for short periods, we would expect to observe both types of behaviour. The fluctuation theorem quantifies this result.

The fluctuation theorem is an exact expression that applies to any system for which the dissipation function is well defined. It tells us that positive dissipation is exponentially more likely to be observed than negative dissipation. Furthermore, consideration of the ensemble *average* of the dissipation function, that is the average over all the available initial points, must be positive, $\langle \Omega_t \rangle \geq 0$, a result known as the second law inequality [11]. These two results expand the generally irreversible behaviour of macroscopic thermodynamic systems into a finite size regime where the second law only holds probabilistically, as demonstrated by a variety of experiments on systems as diverse and optically trapped colloids, torsional pendulums, and electric circuits [12–14].

It is instructive to consider a simple, nonequilibrium, thermostatted system of volume, V consisting of charged particles driven by a field, F_e . In this case, $\Omega_t = \beta V F_e \int_0^t J_c(s) ds$ where $\beta = 1/(k_B T)$, T is the temperature that the system would relax to in the absence of the field (i.e. the temperature of the surroundings), and J_c is the current density in the direction of the field. Writing the time-average of the current density along a trajectory as $\bar{J}_{c,t} = \frac{1}{t} \int_0^t J_c(s) ds$, the fluctuation relation can then be stated:

$$\frac{P(\bar{J}_{c,t} = A \pm dA)}{P(\bar{J}_{c,t} = -A \pm dA)} = e^{A\beta F_e V t}, \quad (2.6)$$

From this equation, we can see that as the system size or time of observation is increased, the relative probability of observing positive to negative current density increases exponentially so the current density has a definite sign and the second law of thermodynamics is retrieved. Furthermore, $\langle \bar{J}_{c,t} \rangle \geq 0$. In obtaining these results, nothing is assumed about the form of the distribution of current density (it

does not have to be Gaussian), and their application is not restricted to this special case of a field driven system, but is very widely applicable. The conditions of ergodic consistency and microscopic time reversibility (that is reversibility of the equations of motion of the particles in the system) are all that are required. Furthermore, in the weak field limit, the rate of entropy production, \dot{S} , is given from linear irreversible thermodynamics as $\dot{S} \equiv \sum \langle J_i \rangle V X_i / T$ where the sum is over the product of all conjugate thermodynamic fluxes, J_i and thermodynamics forces, X_i divided by the temperature of the system, T . Clearly the dissipation here is related to this: $\lim_{F_e \rightarrow 0} \dot{S}(t) = k_B \langle \Omega(t) \rangle$. The difference at high fields is because the temperature that appears in the dissipation function is that which the system would relax to if the fields were removed rather than any non-equilibrium system temperature observed with the field on.² The change in entropy for a process will be similarly related to the time-integral of the dissipation $\lim_{F_e \rightarrow 0} \Delta S = k_B \langle \Omega_t \rangle$.

The second law of thermodynamics is often stated in terms of the thermodynamic entropy and this is equivalent to the dissipation in some cases. However we note that the argument of the fluctuation theorem and second law inequality is the dissipation function and these results apply widely: to field driven, boundary driven and relaxation processes arbitrarily close to, or far from, equilibrium. Therefore we argue that away from equilibrium the dissipation function is the appropriate property to consider. It is a well defined, unambiguous quantity for deterministic nonequilibrium systems, given by Eq. (2.3).

2.3 The Dissipation Theorem and the Relaxation Theorem

The dissipation function appears as the central argument of the fluctuation theorem and the second law inequality. Dissipation is also important in quantifying a range of nonequilibrium behaviours, including appearing as the argument of exact expressions for nonlinear response (the dissipation theorem [16]) and relaxation towards equilibrium (the relaxation theorem [17, 18]).

From the definition of the dissipation function, it can be shown that the time-evolution of the phase space distribution function is given by [16]:³

$$f(\Gamma, t) = \exp\left(-\int_0^t \Omega(\Gamma(s)) ds\right) f(\Gamma, 0) \quad (2.7)$$

² Outside of equilibrium, microscopic temperature expressions are ill defined. Often expressions such as the kinetic temperature (the equipartition expression in momenta) or configurational temperature (a similar expression in position) are used, however these expressions only correspond to the temperature of the system, and each other, at equilibrium [15].

³ Equation (2.7) applies to systems with no field or a constant field. For the case of a time-dependent field see [19].

The time argument in $f(\Gamma, t)$ represents the time over which the distribution function has evolved from the initial distribution function. Using this result, the dissipation theorem enables the time evolution of ensemble averages of arbitrary phase variables to be calculated for systems that are arbitrarily close or far from equilibrium. In its transient time-correlation form it is written [16]:

$$\langle B(\Gamma(t)) \rangle = \langle B(\Gamma(0)) \rangle + \int_0^t \langle \Omega(\Gamma(0)) B(\Gamma(s)) \rangle ds, \quad (2.8)$$

where $B(\Gamma)$ is a phase function (i.e. a function whose value can be obtained from the instantaneous value of Γ) and $\Omega(\Gamma(0))$ is the instantaneous dissipation at time 0. It was first derived in [16], however a simpler derivation is presented in [20].⁴ While it may initially appear redundant, as the ensemble average of the quantity of interest can always be measured directly using the same experiment as the dissipation theorem, in some systems, such as weakly driven ones, the dissipation average converges more quickly than the direct average [22–25]. It also proves useful in understanding the response of a system. This relationship is exact at arbitrary field, and therefore it gives the nonlinear response of a system to an external field. However, it also applies to nonequilibrium systems where there is no external field, but there is a change to the system, such as a change in temperature, removal of an applied pressure gradient etc.

The question of how a system relaxes towards equilibrium, and how to determine the functional form of the equilibrium distribution function can also be answered by considering the dissipation. Applying the dissipation theorem to a relaxing system, using the second law inequality and assuming the property of T-mixing [26] (that is the decay of time-correlations in transients), it has been proven that a system will relax to a unique equilibrium state. This result is referred to as the relaxation theorem [17, 18]. If a system that is initially out of equilibrium has a well defined dissipation function and time decay of correlations then the relaxation theorem predicts that [17, 18]:

- The instantaneous dissipation will be zero for a system in equilibrium ($\Omega(\Gamma(t)) = 0$).
- The state where the instantaneous dissipation remains 0 with time is unique and is the canonical distribution for a thermostatted system [17, 18] and the microcanonical distribution for a constant energy system [17, 18].
- The ensemble average of the instantaneous dissipation will go to zero as the relaxing system approaches equilibrium ($\lim_{t \rightarrow \infty} \langle \Omega(\Gamma(t)) \rangle = 0$).
- The ensemble average of the time-integrated dissipation will always be positive, following the second law inequality ($\langle \Omega_t \rangle > 0$), and will reach a limiting value $\langle \Omega_\infty \rangle$ at long times. Therefore if the conditions on an equilibrium system are changed, the system will relax to a new equilibrium state and the total dissipation during the process will be finite and positive.

⁴ Note that a special case of this relation was derived much earlier, see [21] for details.

The relaxation theorem does not however say that the average *instantaneous* dissipation function must be greater than zero at all times, accommodating non-monotonic relaxation [27].

We can consider applying Eq. (2.7) to the case where a system initially in equilibrium state 1 with distribution function $f_1(\mathbf{\Gamma}) = f(\mathbf{\Gamma}, 0)$ is subject to a change in conditions and allowed to relax to a new equilibrium state 2 with distribution function $f_2(\mathbf{\Gamma}) = \lim_{t \rightarrow \infty} f(\mathbf{\Gamma}, t)$. As mentioned previously, the change in Gibbs' entropy, $-k_B \langle \ln f_2 \rangle_{f_2} + k_B \langle \ln f_1 \rangle_{f_1}$ is zero if the dynamics are Hamiltonian and will be equal to the heat removed from the system divided by the thermodynamic temperature of the underlying equilibrium state, with a non-Hamiltonian thermostat [1]. Taking the ensemble average with respect to the *initial* distribution function, for the left and right hand side of Eq. (2.7), it can be shown that:⁵

$$k_B \langle \Omega_\infty \rangle_{f_1} = k_B \langle \ln f_2 \rangle_{f_1} - k_B \langle \ln f_1 \rangle_{f_1} \quad (2.9)$$

In obtaining this result, we have made use of the fact that the equilibrium distributions do not change when the sign of the momentum is changed [16]. This looks similar to the change in Gibbs' entropy, however the ensemble averages are *both* with respect to the distribution function of the *initial* state. This clearly shows the difference between the change in the Gibbs' entropy and the total dissipation.

The importance of dissipation in all these results shows that apart from being an entropy-like quantity for field driven flow, it is an important general property for all nonequilibrium systems.

2.4 Extrema of the Dissipation Function

The dissipation function is similar to the entropy production, and while not directly connected to a state function, the various fluctuation theorems provide exact, nonequilibrium relations that are fundamentally important to describing nonequilibrium systems. Given the similarity between the two functions, it is interesting to consider whether a phenomenological theory such as MaxEnt (maximum entropy) for equilibrium systems, and MaxEP (maximum entropy production rate) for nonequilibrium systems can be applied to the dissipation. Several papers have considered the links between entropy production, maximum entropy production

⁵ We note that $-\int_0^{-t} \Omega(\mathbf{\Gamma}(s))ds = \int_0^t \Omega(\mathbf{\Gamma}^*(s))ds$ if the dynamics are time reversible and that $\int \Omega(\mathbf{\Gamma}^*, s)f(\mathbf{\Gamma})d\mathbf{\Gamma} = \int \Omega(\mathbf{\Gamma}^*, s)f(\mathbf{\Gamma}^*)d\mathbf{\Gamma}^* = \langle \Omega(s) \rangle$ since the probability of observing ensemble members is constant ($f(\mathbf{\Gamma})d\mathbf{\Gamma} = f(\mathbf{\Gamma}^*)d\mathbf{\Gamma}^*$, see [1]). We assume that the system eventually relaxes to an equilibrium state, $f_2(\mathbf{\Gamma}) = \lim_{t \rightarrow \infty} \ln f(\mathbf{\Gamma}, t)$. From Eq. (2.7), $\lim_{t \rightarrow \infty} \ln f(\mathbf{\Gamma}, t) = \lim_{t \rightarrow \infty} (-\int_0^{-t} \Omega(\mathbf{\Gamma}(s))ds + \ln f(\mathbf{\Gamma}, 0))$, which can be expressed $\ln f_2(\mathbf{\Gamma}) = \int_0^\infty \Omega(\mathbf{\Gamma}^*(s))ds + \ln f_1(\mathbf{\Gamma})$. Then taking the ensemble average with respect to the initial distribution function we obtain $\langle \ln f_2 \rangle_{f_1} = \langle \Omega_\infty \rangle_{f_1} + \langle \ln f_1 \rangle_{f_1}$.

rates, fluctuation theorems and nonlinear response [19, 28–33]. As noted by Williams and Evans [19], MaxEP cannot be applied rigorously to nonequilibrium systems in general, as the distribution function at any time (including in the steady state) is not just a function of the dissipation at that time. However it might provide a good approximation in some cases.

A system that relaxes towards equilibrium can do so in one of two ways: conformally and non-conformally.⁶ From the relaxation theorem, it can be shown that a system that behaves conformally relaxes monotonically to equilibrium at t_{eq} .⁷ Given the bounds on the instantaneous dissipation function, $\langle \Omega(t_{eq}) \rangle = \langle \Omega(0) \rangle = 0$, we expect it to peak at some time before returning to zero. The total dissipation will therefore reach a maximum at equilibrium, $\langle \Omega_{t_{eq}} \rangle > \langle \Omega_{t_{eq}-\Delta t} \rangle$, $\forall \Delta t < t_{eq}$. That is, the ensemble of systems will move through a number of different states (with different distribution functions and average values of the average instantaneous dissipation) as it evolves towards the equilibrium state. However, because the total dissipation is maximised when the system reaches equilibrium, we can use Eq. (2.9) to note that the final stable state will have a greater value of $\langle \ln f(\mathbf{\Gamma}, t) \rangle_{f_i}$ than any other state it passes through. This is a special case where it is clear that this function is a maximum compared with other states that it passes through. If a system relaxes non-conformally then there is no such extremal result. This is the most common form of relaxation in nature, and is the one we will study using numerical simulations.

For systems that reach a nonequilibrium steady state, qualitatively different behaviour is expected. From the relaxation theorem and the second law inequality, we know that if a field is applied to a system that is initially at equilibrium the total dissipation will be positive at all times after application of a field. If a steady state is ultimately reached, this implies that the ensemble average of the instantaneous dissipation function in the steady state must be positive, and that the average of the total dissipation function will approach infinity at long times. Furthermore, considering Eq. (2.8) with $B = \Omega$, if the time autocorrelation function $\langle \Omega(\mathbf{\Gamma}(0)) \Omega(\mathbf{\Gamma}(t)) \rangle$ decays monotonically with time, then the value of the ensemble average of the instantaneous dissipation function, $\langle \Omega(t) \rangle$ will be higher when it reaches its steady state than for any another state it passes through. Therefore the system is in the state that maximises the dissipation function (rate of entropy production). Again this is a special case, so we use numerical simulations to study the behaviour of the instantaneous dissipation function more generally; examining whether it is a maximum in the steady state or if a transient state has a higher average instantaneous dissipation value.

⁶ A conformal system relaxes such that the nonequilibrium distribution is of the form $f(\mathbf{\Gamma}, t) = \exp(-\beta H(\mathbf{\Gamma}) + \lambda(t)g(\mathbf{\Gamma}))/Z, \forall t$ and the deviation function, g , is a constant over the relaxation.

⁷ Strictly a system relaxes as time tends towards infinity, but in practice at t_{eq} the system has relaxed.

2.4.1 Relaxing System: Trapped Particle

We choose a system with non-monotonic relaxation based on an optical trapping experiment called the capture experiment [12]. In this model a particle is bound by a harmonic potential to a point in space within a two dimensional fluid surrounded by thermostatted walls [27]. At the beginning of the experiment we begin with the test particle in equilibrium with a trapping constant of k_0 , then at time $t = 0^+$ we discontinuously change the trap constant to k_t , and allow the system to relax to equilibrium with k_t . The system contains a number of energy storage modes including the optical trap of the particle, the harmonic binding of the walls, and an integral feedback thermostat; all of which can phase shift the response in dissipation and cause non-monotonic relaxation.

To study this system nonequilibrium molecular dynamics simulations (NEMD) were performed using a 4th order Runge–Kutta algorithm with $k_0 = 2$, $k_t = 8$, and therefore it is expected that the particle will move closer to the trap on average.⁸ From the equations of motion for the system:

$$\dot{\mathbf{q}}_i(t) = \mathbf{p}_i(t)/m, \quad (2.10)$$

$$\dot{\mathbf{p}}_i(t) = \mathbf{F}_{I,i}(t) - \delta_{1,i}k_t\mathbf{q}_i(t) - S_w\alpha(t)\mathbf{p}_i(t) + S_w\mathbf{F}_{w,i}(t), \quad (2.11)$$

$$\dot{\alpha}(t) = \frac{3k_B}{Q}(T_k(t) - T), \quad (2.12)$$

and from our definition of the dissipation function, Eq. (2.2), we can derive a dissipation function of the form:

$$\Omega_i(\Gamma(0)) = \frac{\beta(k_0 - k_t)}{2}(\mathbf{q}_1^2(t) - \mathbf{q}_1^2(0)). \quad (2.13)$$

Here i is the particle index, m is the mass of the particles, δ is the Kronecker delta, S_w is the thermostat switch that is 1 for the wall particles and 0 for the fluid and trapped particles, $\mathbf{F}_{I,i}$ is the intermolecular force acting on the particle, $\mathbf{F}_{w,i}$ is the harmonic force constraining the wall particles to their positions, α is the thermostat multiplier that constrains the momenta of the system, Q is the thermal mass of the thermostat, T is the thermostat target temperature, and T_k is the kinetic temperature of the walls, $\beta = 1/k_B T$, \mathbf{q}_1 is the position of the trapped particle relative to the harmonic trap centre. The particles interact via the Weeks, Chandler and Andersen (WCA) potential (i.e. a Lennard-Jones potential that is truncated at the potential energy minimum) [34].

From this we can fully describe the behaviour of the dissipation: if the initial trapping constant is greater than the final trapping constant, $k_0 > k_t$, then the function will be positive when the trapped particle finishes further from the trap

⁸ Simulation parameters: 50 Fluid particles, 22 Wall particles, $T = 1$, $\rho = 0.3$, 100,000 trajectories.

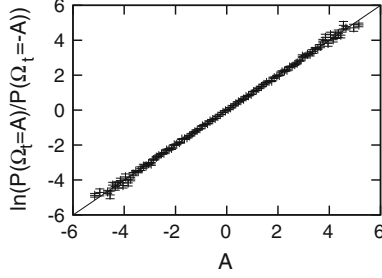


Fig. 2.1 Plot of the logarithm of both sides of Eq. (2.5) at the end of the simulation, with standard error bars, and a line that shows the expected relation. Reprinted with permission from Reid et al. [27]. Copyright 2012 American Institute of Physics

centre than it started and negative when it is closer, and if the initial trapping constant is less than the final trapping constant, $k_t > k_0$, then the function will be positive when the trapped particle finishes closer to the trap centre than it started and negative when it is further away. However, there is always a possibility of observing a negative value for the total dissipation in this system. Finally the instantaneous form of the dissipation function for this system is easily derived to be:

$$\Omega(\Gamma(t)) = \beta(k_0 - k_t)\mathbf{q}_1(t)\dot{\mathbf{q}}_1(t). \quad (2.14)$$

Again it can be seen that its sign is connected to the difference in trapping constants. For example, when the initial trapping constant is greater than the final trapping constant, $k_0 > k_t$, then the function will be positive when the particle is travelling away from the trap centre.

We will first examine the fluctuation theorems for this system to show that it is consistent with their predictions. In Fig. 2.1 we plot the logarithm of both sides of Eq. (2.5) at the end of the simulation, and see extremely good agreement with the straight line of slope one predicted by the fluctuation theorem. To test the dissipation theorem, we can take advantage of the fact that the instantaneous dissipation function is a phase function and can be the argument of the theorem, $B(\Gamma) = \Omega(\Gamma)$ in Eq. (2.8). In Fig. 2.2 we see extremely close agreement between the average as directly measured, and the average as calculated from the dissipation theorem. We also observe that the average of the instantaneous dissipation function goes to zero as predicted by the relaxation theorem at long times (Fig. 2.2).

Looking at the extrema, the average of the instantaneous dissipation function against time in Fig. 2.2 is reminiscent of an underdamped harmonic oscillator; this means that the maximum and minimum are reached in the first ‘cycle’, before going to zero at long times. In Fig. 2.3 we plot the average dissipation function against time. It appears that the average of the total dissipation reaches a maxima at equilibrium. This suggests that the non-conformal modes relax more quickly

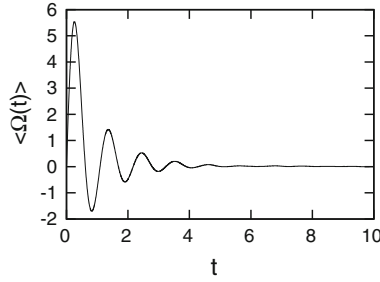


Fig. 2.2 Plot of the average instantaneous dissipation ($\langle \Omega(\Gamma(t)) \rangle$, —), and the dissipation theorem estimate of the average instantaneous dissipation ($\theta(\Omega, t) = \text{RHS of Eq. (2.8)}$, - - -), with time. Note that these results are indistinguishable at this scale. Also note how the function approaches zero at long time as predicted by the relaxation theorem. Reprinted with permission from Reid et al. [27]. Copyright 2012 American Institute of Physics

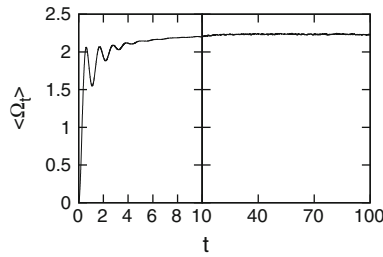


Fig. 2.3 Plot of the average dissipation ($\langle \Omega(\Gamma(t)) \rangle$, —) with time over two time scales. Note how the trend of the function is to increase in spite of the oscillations. Reprinted with permission from Reid et al. [27]. Copyright 2012 American Institute of Physics. Note that it has been modified to show two time scales

than the conformal modes, leading to an overall relaxation to the state with maximum Ω_i . This is an interesting result, and bears further study to determine if it is a universal feature of relaxing systems, or merely a feature of this system.

2.4.2 Transient and Steady State System: Poiseuille Flow

Here we examine a simple system, thermostatted Poiseuille flow, that produces a nonequilibrium steady state. A fluid of identical particles in equilibrium is subjected to a field at time $t = 0^+$ that exerts a constant force on the fluid particles in the positive x-direction. At short times, the system will exhibit a transient state as particles begin to accelerate in the appropriate direction, while at long times the particles will have velocities that are mediated by their interactions with the walls of the system, and a steady state will be reached with a maximum streaming

velocity in the center of the system, and a minimum streaming velocity proximate to the walls.

We study this system using nonequilibrium molecular dynamics simulations.⁹ The equations of motion for the N particles are given by:

$$\dot{\mathbf{q}}_i(t) = \mathbf{p}_i(t)/m, \quad (2.15)$$

$$\dot{\mathbf{p}}_i(t) = \mathbf{F}_{l,i}(t) + S_f F_e \mathbf{i} - S_w \alpha(t) \mathbf{p}_i(t) + S_w \mathbf{F}_{w,i}(t), \quad (2.16)$$

$$\alpha(t) = \frac{\sum S_w (\mathbf{F}_{l,i} + \mathbf{F}_{w,i}) \cdot \mathbf{p}_i}{\sum S_w \mathbf{p}_i \cdot \mathbf{p}_i}. \quad (2.17)$$

F_e is the field which acts in the x-direction on each of the N_f fluid particles and S_f is the field switch that is 1 for the fluid particles and 0 for the wall particles. As in the previous example, a WCA interparticle potential is used. In order to better observe non-linear behaviour in this system, a polymer melt consisting of chains of 4 particles bound by a Finite Extensible Nonlinear Elastic Potential (FENE) [35] was studied in addition to studying an atomistic fluid. This adds an additional term into the interparticle force, $\mathbf{F}_{l,i}$, due to interactions of the particle with its neighbours in the chain. We can again derive the dissipation using Eq. (2.2),

$$\Omega(\Gamma(t)) = \beta F_e \sum_{i=1}^{N_f} \frac{p_{xi}(t)}{m}. \quad (2.18)$$

This dissipation function is extensive with the number of fluid particles in the field. Particles give a positive contribution to the dissipation function when they move in the same direction as the field, and a negative dissipation they move in the opposite direction to the field, and the dissipation function can be expressed in terms of a particle current, $J_x = \sum_{i=1}^{N_f} \dot{q}_{xi}/N_f$, as $\Omega(t) = \beta J_x(t) N_f F_e$.

In Fig. 2.4 we plot the logarithm of both sides of Eq. (2.5) at the end of the simulation, and see extremely good agreement with the straight line of slope one predicted by the fluctuation theorem. To test the dissipation theorem for this system, we use the particle current J_x instead of the instantaneous dissipation as they are proportional, but the particle current is a more familiar property. The second law inequality predicts that $\langle \Omega_t \rangle > 0$ and hence $\langle J_{x,t} \rangle > 0$ at all times for a nonequilibrium system, however it says nothing about $\langle \Omega_x(t) \rangle$ or $\langle J_x(t) \rangle$. Indeed it is well known that $\langle \Omega(t) \rangle$ can be negative (see [36]). The results presented in Fig. 2.5 show that $\langle J_x(t) \rangle$, and hence the average instantaneous dissipation function, is positive at all times. It would be interesting to determine if this will always be the case for systems with a constant field. In Fig. 2.5 we also observe the numerical utility of the dissipation theorem: at high field the agreement between the directly calculated current and that obtained from the dissipation theorem is

⁹ Simulation parameters: 64 Fluid particles, 64 Wall particles, $T = 1$, $\rho = 0.8$, 100,000 Trajectories.

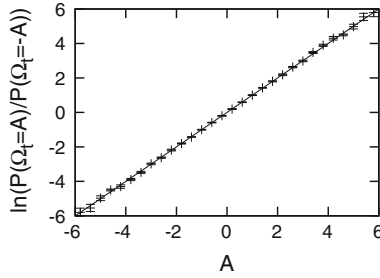


Fig. 2.4 Plot of the logarithm of both sides of Eq. (2.5) at the end of the simulation, with standard error bars, and a line that shows the expected relation. Reprinted from [24], with modifications to formatting. Published under licence in Journal of Physics: Conference Series by IOP Publishing Ltd

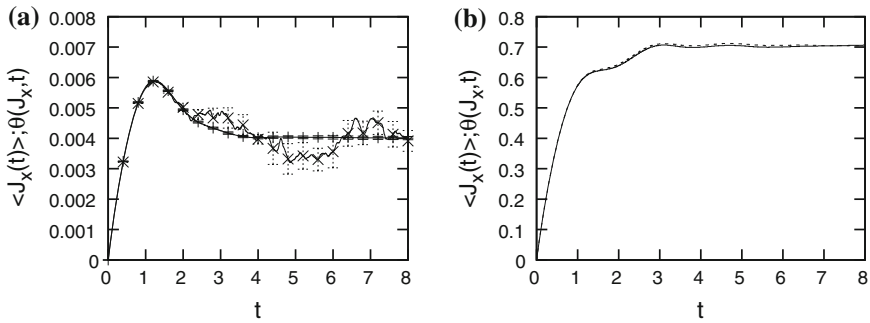


Fig. 2.5 Plot of the average particle current ($J_x(t)$), - - -, and the dissipation theorem estimate of the average particle current ($\theta(J_x, t) = \text{RHS of Eq. (2.8)}$), —, with time for a 4-atom polymer system at two field strengths. Note how the dissipation theorem gives better convergence at low field for this system. Reprinted from [24], with modifications to formatting. Published under licence in Journal of Physics: Conference Series by IOP Publishing Ltd. **a** $F_e = 0.01$. **b** $F_e = 1.00$

similar as in the case of the capture experiment; but at low field the dissipation theorem does a much better job of determining the behaviour of the particle current. In Fig. 2.6 we plot the average of the particle current normalised by the field against time for various field strengths. It is notable that the dissipation average peaks before dropping to a steady state for most field values. Therefore it is clear that the instantaneous dissipation is not a maximum in the steady state—the system evolves through an unstable maximum. However for strong fields in the polymer melt we reach a value that is higher than the transient response. This is consistent with the arguments of Williams and Evans [19] where they suggest that under some conditions, (large fields in this case), the state with the maximum dissipation (or rate of “entropy” production) might be the steady state that is observed. From these results we infer that the linear response of the system has a transient peak, but the non-linear response increases with time. In Fig. 2.7, we

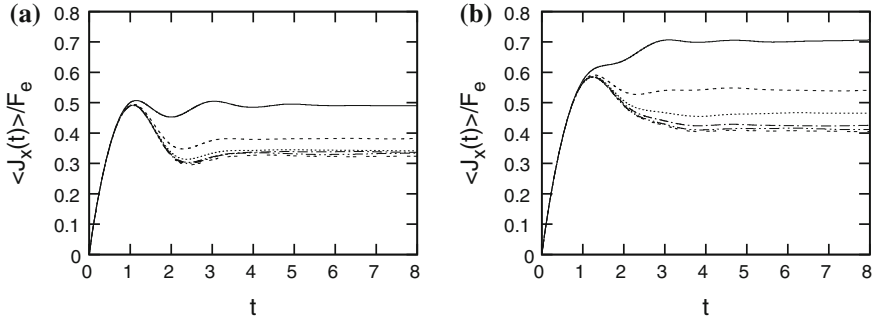


Fig. 2.6 Plot of the average particle current divided by the field ($\langle J_x \rangle / F_e$) for an atomic fluid and a melt of 4-atom long polymers. The field strengths of the lines are, from lowest to highest at $t = 8$, ($F_e = 0.01$, - - - -), ($F_e = 0.1$, - . - .), ($F_e = 0.2$, - . - .), ($F_e = 0.3$, ...), ($F_e = 0.5$, - - -), ($F_e = 1$, —). Note that as the field increases, the value of the asymptotic particle current rises relative to the peak of the transient response, and for the polymer melt, the high field asymptotic value exceeds the transient peak. Reprinted from [24]; **a** is a rescale of Fig. 2a from [24], and **b** is a modified version of Fig. 6b. Published under licence in Journal of Physics: Conference Series by IOP Publishing Ltd. **a** Atomic fluid. **b** 4-Atom polymer melt

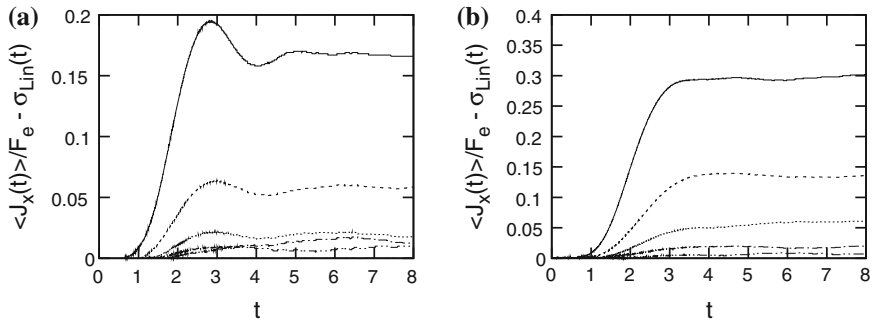


Fig. 2.7 Plot of the non-linear response in the particle current ($\langle J_x \rangle / F_e - \sigma_{Lin}(t)$, $\sigma_{Lin}(t) = \langle J_x(F_e = 0.01) \rangle / 0.01$) for an atomic fluid and a melt of 4-atom long polymers. The field strengths of the lines are, from lowest to highest at $t = 8$, ($F_e = 0.01$, - - - -), ($F_e = 0.1$, - . - .), ($F_e = 0.2$, - . - .), ($F_e = 0.3$, ...), ($F_e = 0.5$, - - -), ($F_e = 1$, —). Note that the difference in peak to asymptotic particle current is 0.17 for the atomic system and 0.18 for the polymer melt. **a** Atomic fluid. **b** 4-Atom polymer melt

subtract the smallest field response (as a good approximation for the linear response), and see that this is indeed the case for the polymer melt. Since the instantaneous dissipation function settles to a steady value as the steady state is reached, the time integral of the dissipation will be positive at all times (as determined from the second law inequality), but will diverge to infinity with time.

2.5 Discussion and Conclusion

The dissipation function is like entropy production in that it can be used to indicate whether a system's behaviour is in accord with the Second "Law" of Thermodynamics. Positive entropy production or dissipation is taken to be in accord with the Second "Law". Negative dissipation is against the Second "Law" and is seen by the fluctuation theorems as being unlikely. In most text books negative entropy production is seen as not only against the Second "Law" but is expressly impossible.

Close to equilibrium in large systems, where entropy production can be defined, the average dissipation is equal to the entropy production. However unlike entropy production, the dissipation function is well defined arbitrarily near or far from equilibrium and for systems of arbitrary size. Furthermore it obeys a number of exact theorems: the Fluctuation Theorem, the Second "Law" Inequality and the various Relaxation Theorems. Dissipation is also the fundamental quantity required for all linear and nonlinear response theory both for driven and relaxing systems. Dissipation is the central quantity of nonequilibrium statistical mechanics. It also gives for the first time a definition of equilibrium. An equilibrium phase space distribution has the property that the dissipation is identically zero everywhere in the ostensible phase space.

The most profound aspect of these theorems concerning the role played away from equilibrium by dissipation is that the logical status of thermodynamics has changed. The "laws" of thermodynamics were termed "laws" because, apart from the first law, they were deemed unprovable from the laws of mechanics. Indeed the Second "Law" was thought for over 100 years to be in conflict with the time reversible laws of classical and quantum mechanics. All this changed with the first proof of a fluctuation theorem in 1994.

In the present chapter we have presented numerical results that demonstrate many of the various properties of the dissipation, and also provide insight into its temporal extrema and evolution for relaxing systems and driven T-mixing systems that must have a unique steady state.

We found that while the time integrated dissipation appears to approach a maximum for relaxation to equilibrium, in thermostatted, relaxing systems the instantaneous dissipation function has a peak in the transient response, subsequently decaying to zero at equilibrium. For driven thermostatted T-mixing systems the average instantaneous dissipation often passes through one or more unstable maxima before reaching a stable final time independent state—a non-equilibrium steady state. This suggests that a theorem of maximum instantaneous dissipation for steady states does not generally apply.

MaxEP is a theory focused on identifying which steady state a system will select if multiple steady states are possible. In order to provide further information on the behaviour of the dissipation, we can consider a simple system where multiple steady state solutions are known to exist: the heat flow in a one-dimensional lattice [37]. Here two possible steady states exist which depend on the initial

conditions: a soliton and a diffusive heat flow. The state with maximum dissipation should stay the same at all field strengths, however at low fields, the soliton does not form whereas at high fields it does. This is not consistent with the state of maximum dissipation being the one that it observed. It would be of interest to study this system in more detail.

Our results might be interpreted as being in contradiction with MaxEP. However this may not be the case. We note that the irreversibility defined in Chap. 3, “A theoretical basis of maximum entropy production“, is equivalent to the time integral of the dissipation function given by Eq. (2.2) (see discussion in Sect. 3.5.2). However, the results that we have presented are not necessarily in conflict with current understanding of MaxEP (see Chap. 3) because MaxEP requires the external forcing to be sufficiently large that low entropy states are unstable and because the system is also subject to various constraints. It is clear that the results will depend on the constraints imposed, and therefore the problem can be reformulated as a problem in identification of the appropriate constraints. Ideally, a fundamental maximal principle would justify *a priori* all constraints that are required, but a theoretical basis for this has not yet been established. Indeed this might not be possible. However, as discussed above, it may be possible to determine under what conditions an extremum principle will apply through systematic analysis of systems at a microscopic level.

As MaxEP is useful at very extreme forcing, it will be difficult to study this numerically at a microscopic level for the types of system we have considered here. This is because most systems that generate multiple steady states, such as convection or turbulent flow, are computationally expensive as they require huge numbers of particles and strong fields or both. These instabilities are hydrodynamic rather than molecular in origin and they require large system sizes to increase the Reynolds numbers above various turbulent thresholds. Traditionally, turbulence has rarely been studied using molecular dynamics (for early work see [38, 39]). However modern computing facilities are making this more accessible (see [40, 41]) and it would be interesting to carry out simulations of these systems.

If some objective way can be found to select these constraints, the MaxEP formalism, if applied exactly, could still be impractical. This can be seen for the derivation of the dissipation theorem for driven systems from an extremum principle. The problem in this case was that the number of constraints required in order to obtain the exact answer, was in fact infinite [32, 42].

Whether MaxEP can be established as a useful approximation is an open question. We still need a more objective way of selecting the necessary constraints.

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Beyond the Second Law

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