

On the Relation Between Dissipation and the Rate of Spontaneous Entropy Production from Linear Irreversible Thermodynamics

Stephen R. Williams,^a Debra J. Searles^b and Denis J. Evans^a

^a Research School of Chemistry, Australian National University, Canberra, ACT 0200,
Australia

^b Australian Institute of Bioengineering and Nanotechnology and School of Chemistry
and Molecular Biosciences, The University of Queensland, Brisbane, Qld 4072, Australia

Abstract

When systems are far from equilibrium, the temperature, the entropy and the thermodynamic entropy production are not defined and the Gibbs entropy does not provide useful information about the physical properties of a system. Furthermore, far from equilibrium, or if the dissipative field changes in time, the spontaneous entropy production of linear irreversible thermodynamics becomes irrelevant. In 2000 we introduced a definition for the dissipation function and showed that for systems of arbitrary size, arbitrarily near or far from equilibrium, the time integral of the ensemble average of this quantity can never decrease. In the low field limit its ensemble average becomes equal to the spontaneous entropy production of linear irreversible thermodynamics. We discuss how these quantities are related and why one should use dissipation rather than entropy or entropy production for nonequilibrium systems.

Historical background

Over the last 150 years, a number of difficulties to do with entropy have remained unresolved. If one considers an initial state that is constructed as a collection of macroscopic equilibrium states at different temperatures and densities and one allows these states to interact, the equilibrium state towards which this initial collection of equilibrium states evolves, does indeed have a higher entropy than the sum of the entropies of the initial macrostates. This is a comparison of entropies of equilibrium states. It doesn't tell us anything about the entropy of time-evolving *nonequilibrium* states.

In this paper we will explore a number of issues connected with entropy and its rate of production. Firstly, the identity of the change in thermodynamic entropy and the Gibbs entropy has only been given plausibility at equilibrium. The change in thermodynamic entropy, ΔS , is defined as $\Delta S_{\text{sys}} = \int_{\text{rev}} \frac{dQ}{T}$ where Q is the heat transferred reversibly to the system from the reservoir and T is the temperature of the system. The Gibbs entropy is defined as $S_G = -k_B \int f(\mathbf{\Gamma}) \ln f(\mathbf{\Gamma}) d\mathbf{\Gamma}$ where $f(\mathbf{\Gamma})$ is the phase space density at the phase point $\mathbf{\Gamma} \equiv (\mathbf{q}_1, \dots, \mathbf{q}_N, \mathbf{p}_1, \dots, \mathbf{p}_N)$ of an N -particle classical system and k_B is Boltzmann's constant. We will investigate the existence of entropy and its rate of change away from equilibrium, when $f(\mathbf{\Gamma})$ is not the phase space distribution of an equilibrium system.

Secondly, Gibbs realized [1] that in an autonomous Hamiltonian system the Gibbs entropy is simply a constant of the motion! It manifestly does *not* increase until it reaches a maximum and the system is at equilibrium [1-3]. If the initial distribution is not

an equilibrium distribution, if the equations of motion are simply Newton's equations for a group of interacting particles and if the system is T-mixing [4, 5], the system will evolve *towards* equilibrium but the Gibbs entropy is simply constant in time. This is at odds with what is written in many textbooks.

Thirdly Clausius' Inequality, $\oint \frac{dQ}{T} \leq 0$, where Q is the heat transferred to the system from the reservoir, had only been rigorously demonstrated regarding the heat that flows from large thermal reservoirs that are so large compared to the system of interest, that they can be regarded as being in thermodynamic equilibrium. We have shown [6] that in this case the temperature in the Clausius Inequality should be the temperature of the reservoir. This inequality is perfectly consistent with the assumption that constructing a perpetual motion machine of the second kind is impossible.

Clausius's inequality for a cyclic process [7] becomes an equality if the process is carried out reversibly, implying the system and reservoir are both at equilibrium at all times. It becomes an inequality otherwise. If the process is being carried out irreversibly, it means that at least one part of the composite system must be out of equilibrium, and for that component there is no legitimate definition of the thermodynamic temperature or of the entropy. At equilibrium there are infinitely many phase functions, whose ensemble average is equal to the equilibrium thermodynamic temperature. Away from equilibrium these different phase functions each have different average values. The notion of a "nonequilibrium thermodynamic temperature" becomes meaningless. This means that the widespread application of the Clausius inequality to systems that are not in equilibrium, is not rigorously justified.

Ever since Clausius proposed his inequality, this particular difficulty has been discussed [8-11]. In 1904, Orr [9] criticised both Clausius' and Planck's use of thermodynamic temperatures when systems are far from equilibrium. Planck responded [10] in 1905 saying in part: "If a process...takes place so violently that one can no longer define temperature and density, then the usual definition of entropy is inapplicable."

Throughout the century and a half since Clausius' time some thermodynamicists including Truesdell [6], have argued that statements about entropy should be confined to equilibrium systems or to systems so close to equilibrium that they can, with high accuracy, be regarded as being locally at equilibrium. Truesdell was very critical of linear irreversible thermodynamics [12].

To address the issue of S_G remaining constant rather than increasing in an autonomous Hamiltonian system, Gibbs [1] proposed that phase space should be coarse grained. However, unknown to Gibbs, this did not provide a solution because the coarse-grained Gibbs entropy so obtained is *not* an objective material property [3,13] and its time dependence in nonequilibrium systems is determined by the grain size [13].

Since the late 1940's it has been known from ergodic theory that a mixing, autonomous, Hamiltonian system will eventually relax towards microcanonical equilibrium. However this proof [14] is not very revealing. It does not give us any property that is extremal at equilibrium. It simply tells us that eventually averages of sufficiently smooth phase functions, *approach* the corresponding equilibrium microcanonical average of the specified phase function.

Many undergraduate physics, chemistry or engineering textbooks do not mention these issues! Indeed in 1905 Buckingham [11] discussed the problems associated

with writing textbooks for the average students while being aware (at the time) of some of the difficulties mentioned above. He realized that smarter students might recognize the logical inconsistencies in applying Clausius' *inequality* to nonequilibrium systems.

Recently, we discussed [3] differences between entropy and dissipation in relaxing autonomous Hamiltonian systems. In the present paper we concentrate on discussing the differences between dissipation and entropy production in driven thermostatted steady states and transients.

The Solution

With the proof of Fluctuation Theorems in 1993 [15-17], the microscopic proof of the Clausius Inequality [14] and the proof of the Equilibrium Relaxation Theorems (for both autonomous Hamiltonian systems [15] and for systems in contact with thermal reservoirs [16]), these dilemmas have finally been resolved for equilibrium and nonequilibrium molecular systems whose dynamics is deterministic and time reversible.

In 2000 we defined a new microscopic quantity, the dissipation function [17] that provided the key to resolve these problems. The time-integral of the dissipation function can be considered as a measure of the irreversibility. It can be considered as the logarithm of the ratio of the probability observing a trajectories sampled from an infinitesimal phase volume, $P(\delta\Gamma)$, and their time-reversed conjugates, $P(\delta\Gamma^*)$. Dissipation can also be shown to be related to the energy dissipation, or irreversible work, in many cases [17]. If the initial distribution of states, $f(\Gamma;0)$, and the time reversible autonomous dynamics $\dot{\Gamma} = \dot{\Gamma}(\Gamma)$ are known, if the initial distribution is even in the momenta and the system is ergodically consistent

(i.e. $f(\mathbf{\Gamma};0) \neq 0, \mathbf{\Gamma} \in D \Rightarrow f(\mathbf{\Gamma}(t);0) \neq 0, \forall t > 0$), then the time integral of the dissipation function is defined as [17, 18]

$$\Omega_t(\mathbf{\Gamma}) \equiv \ln \left[\frac{P(\delta\mathbf{\Gamma})}{P(\delta\mathbf{\Gamma}^*)} \right] = \ln \left[\frac{f(\mathbf{\Gamma},0) \exp \left(- \int_0^t ds \Lambda(S^s\mathbf{\Gamma}) \right)}{f(M^T S^t \mathbf{\Gamma},0)} \right]. \quad (1)$$

and assuming $f(\mathbf{\Gamma},0) = f(M^T \mathbf{\Gamma},0)$ (as in an equilibrium distribution function), then

$$\Omega(\mathbf{\Gamma}) = - \frac{\partial}{\partial \mathbf{\Gamma}} \cdot \dot{\mathbf{\Gamma}}(\mathbf{\Gamma}) - \dot{\mathbf{\Gamma}}(\mathbf{\Gamma}) \cdot \frac{\partial}{\partial \mathbf{\Gamma}} \ln f(\mathbf{\Gamma},0). \quad \text{In (1), } M^T \text{ is the time reversal map,}$$

$$M^T \mathbf{\Gamma} \equiv (\mathbf{q}_1, \dots, \mathbf{q}_N, -\mathbf{p}_1, \dots, -\mathbf{p}_N), \quad S^t \text{ is the time evolution operator for a time } t \text{ and}$$

$$\Lambda \equiv \frac{\partial}{\partial \mathbf{\Gamma}} \cdot \dot{\mathbf{\Gamma}} \text{ is the phase space expansion factor due to the thermostating mechanism (if}$$

present). We use the notation $\Omega_t(\mathbf{\Gamma}) = \int_0^t \Omega(S^s \mathbf{\Gamma}) ds$ to refer to the time-integral of the

dissipation ($\Omega(S^t \mathbf{\Gamma})$) along a phase space trajectory $S^s \mathbf{\Gamma}; 0 < s < t$ and

$$\bar{\Omega}_t(\mathbf{\Gamma}) \equiv \frac{1}{t} \int_0^t ds \Omega(S^s \mathbf{\Gamma}) \text{ is the associated time average.}$$

A key point in the definition of dissipation is that $\mathbf{\Gamma}$ and $M^T S^t \mathbf{\Gamma}$ are the origin phases for a trajectory $S^s \mathbf{\Gamma}; 0 < s < t$ and its conjugate antitrajectory $S^s M^T S^t \mathbf{\Gamma}; 0 < s < t$ respectively. This places constraints on the propagator, S^t . It *must* have a definite parity under time reversal over the interval $(0,t)$. In (1) ergodic consistency [17] simply ensures that dissipation is well defined everywhere inside the phase space domain D . It is worth noting that the time reversibility of the phase space dynamics is explicitly included in the definition of dissipation.

From its definition and these very few assumptions, it is trivial to prove two remarkable results. Firstly, the Fluctuation Theorem: [17,18]

$$\frac{\Pr(\bar{\Omega}_t = A)}{\Pr(\bar{\Omega}_t = -A)} = \exp[At], \quad \forall t > 0 \quad (2)$$

where the notation $\Pr(\bar{\Omega}_t = A)$ denotes the probability that $\bar{\Omega}_t$ takes on a value $A \pm dA$.

The Fluctuation Theorem has been verified in laboratory experiments as well as computer simulations. The Fluctuation Theorem (FT) is exact for systems of arbitrary size, arbitrarily far or near to equilibrium. It is so powerful because its derivation requires almost no assumptions and no approximations.

Secondly one can prove an extremum property that is remarkably similar to what one might expect from the Second Law. This is referred to as the “Second Law Inequality” [19]

$$\langle \bar{\Omega}_t \rangle \geq 0, \quad \forall t > 0 . \quad (3)$$

Calling equation (3) the “Second Law Inequality” is somewhat questionable since traditionally the Second Law Inequality of Clausius refers to the cyclic integral of heat divided by temperature (*i.e.* entropy). Equation (3) refers to a different quantity namely the dissipation. In physics, statements are called “laws” if they cannot be proven from more elementary laws (say of mechanics). The proof of the Second “Law” Inequality is

just a theorem or lemma proven like the Fluctuation Theorem itself from the laws of mechanics.

Equation (3) does *not* imply $\langle \Omega(t) \rangle \geq 0, \forall t > 0$. In textbooks on irreversible thermodynamics one often reads that the rate of spontaneous entropy production is always non-negative, however one should be aware that this is not always the case (*e.g.* in viscoelastic materials subject to periodic shear rates). The ensemble-averaged instantaneous dissipation can be positive or negative which is just as well because in real experiments, relaxation to equilibrium is usually non-monotonic. So this is a first difference between the so-called rate of spontaneous entropy production and dissipation.

The Second Law Inequality (3) shows the profound difference between dissipation and the time derivative of the Gibbs entropy that for autonomous Hamiltonian systems satisfies the equation $\dot{S}_G = 0$ while for thermostatted nonequilibrium steady states (NESSs) even far from equilibrium,

$$\dot{S}_G = \frac{\langle dQ/dt \rangle}{T} = k_B \langle \Lambda \rangle = \text{const} < 0. \quad (4)$$

where Q is the heat transferred to the system of interest from the reservoir and T is the equilibrium thermodynamic temperature of that large reservoir. In (4) we see that the rate of change of the Gibbs entropy corresponds to its calorimetric form. In NESSs the Gibbs entropy is not *steady*. Instead it diverges at a constant rate towards negative infinity. This is related to the constancy of the Gibbs entropy in autonomous Hamiltonian (*i.e.*

unthermostatted) systems. In NESSs there is no time dependence in the ensemble average of sufficiently smooth phase functions such as pressure or energy.

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, $\lim_{t \rightarrow \infty} f(S^t \Gamma; t) \rightarrow +\infty$. 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, $\lim_{t \rightarrow \infty} S_G(t) \rightarrow -\infty$ [3].

What is really happening here is that the dimension of the accessible phase space domain at equilibrium is different from the corresponding dimension in a NESS [20]. In order to correctly calculate the Gibbs entropy we need to know the dimension of the phase space, within which the phase space distribution is nonsingular. In general for NESSs this is unknown and therefore, for these systems, entropy ceases to be a useful quantity.

In the Appendix we illustrate the relationship between the dissipation, thermodynamic and Gibbs entropy for a simple system, and the difficulties with the Gibbs entropy. 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.

Dissipation in Nonequilibrium Steady States (NESSs)

We begin by considering a system of N particles subject to the following equations of motion [20]:

$$\dot{\mathbf{q}}_i = \mathbf{p}_i / m + C_i \mathbf{F}_e, \quad \dot{\mathbf{p}}_i = \mathbf{F}_i + D_i \mathbf{F}_e - S_i \alpha_{IK} \mathbf{p}_i + S_i \mathbf{F}_{th} \quad (5)$$

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

This condition is known as the adiabatic incompressibility of phase space condition or AIT 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 [14]. If these same systems are thermostatted as in (5) above, they will eventually relax towards canonical equilibrium [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.

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 NESS averages.

In our system the application of infinite checkerboard boundary conditions means that space is translationally homogeneous but orientationally anisotropic. There are no walls to stop particle currents. Space charge can never develop and the flow (at least parallel to the field) can continue forever. This does not contradict the equilibrium relaxation theorems [4, 14, 21], discussed above, because those theorems only apply to finite systems. Our use of these boundary conditions means that our system is effectively infinite. In infinite checkerboard boundary conditions, the system is infinite and the initial condition is spatially periodic at time zero. Time evolution is governed by the equations of motion (5) and the initial periodicity will be preserved forever. This periodicity means that we need only follow the coordinates and momentum of one unit cell of particles. All other particle positions can be calculated by symmetry.

In the present paper we consider only those particles that are initially located in the unit cell at time zero. The equations of motion given in (5), 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 so-called 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, $f_K(\mathbf{\Gamma})$, augmented with the necessary delta functions [4]:

$$f(\mathbf{\Gamma}, 0) = f_K(\mathbf{\Gamma}) = \frac{\exp[-\beta_{th} H_0(\mathbf{\Gamma})] \delta(\mathbf{P}_{th}) \delta(K_{th}(\mathbf{\Gamma}) - K_{\beta, th})}{\int d\mathbf{\Gamma} \exp[-\beta_{th} H_0(\mathbf{\Gamma})] \delta(\mathbf{P}_{th}) \delta(K_{th}(\mathbf{\Gamma}) - K_{\beta, th})}, \quad (6)$$

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

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

and $K_{\beta, th} = (3N_{th} - 4)\beta_{th}^{-1} / 2$ 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 $\beta_{th} = 1 / k_B T_{th}$ 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 (see below), the driving force is set to zero and the whole system is allowed time to relax towards thermodynamic equilibrium [6]. 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 $H_0(\Gamma) = K(p) + \Phi(q)$ where K, Φ are respectively the kinetic and 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). In principle the particle momenta are unbounded. Clearly the delta functions in (6) 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 thermostating region that is unnatural can be made arbitrarily remote from the natural system of interest. The thermostating particles may be buried far inside realistic walls that contain the nonequilibrium flow. 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.

For a system satisfying (5) and satisfying the AIT condition and having an initially equilibrium distribution of states (6), it is easy to show that the dissipation function (3) can be written as [17],

$$\Omega(\Gamma) \equiv -\beta_{th} J(\Gamma) V F_e = \beta_{th} \sum_i [\mathbf{p}_i D_i / m - \mathbf{F}_i C_i] \cdot \mathbf{F}_e \quad (7)$$

where J 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

$-JV = \sum_i c_i \dot{x}_i$, the electric current in the x -direction. Such a dissipation function is called

a primary dissipation function. When the field is zero the system remains in equilibrium and there is no dissipation. An equilibrium distribution is any distribution within which dissipation is identically zero everywhere in the accessible phase space.

Irreversible Entropy Production in near Equilibrium NESSs

Now we consider the macroscopic concept of the so-called irreversible entropy production as detailed in De Groot and Mazur [22]. They make the assumption of local thermodynamic equilibrium (equation (16), page 23 of [22]) which enables them to write the entropy per unit mass $s = s(u, v)$ in terms of the energy per unit mass u , and the volume per unit mass, v , (eq (14) p23 of [22]); assuming a single component system. They note, “This hypothesis of ‘local’ equilibrium can, from a macroscopic point of view, only be justified by virtue of the validity of the conclusions derived from it.” Writing $s = s(u, v)$ assumes that the dependence of s on any applied fields is zero to at least quadratic order in the external fields. It would not apply to the example of a straining solid where the entropy per unit mass certainly varies quadratically with strains, γ , for sufficiently small strains, *i.e.* $s = s(u, v, \gamma^2)$. The rate of increase of entropy is given by the flux into a volume element plus any entropy produced inside the volume, assuming that the system is so close to equilibrium that its temperature can be defined. One then obtains (equation (10) on p22 of de Groot and Mazur [22]),

$$\frac{\partial \rho s}{\partial t} = -\text{div}(J_{s, \text{tot}}) + \sigma \quad (8)$$

where ρ is the mass density, s is the entropy per unit mass, σ is the so-called spontaneous entropy production per unit volume and unit time and $J_{s, \text{tot}}$ is the total entropy flux per unit time and per unit area.

From (8) it can then be written:

$$T \frac{ds}{dt} = \frac{du}{dt} + p \frac{dv}{dt} \quad (9)$$

Following the standard arguments of linear irreversible thermodynamics, one then uses the *exact* conservation equations for mass and energy to discover that

$$\rho \frac{ds}{dt} = \frac{-1}{T} [\nabla \cdot \mathbf{J}_q + \mathbf{P}^T : \nabla \mathbf{u} - p \nabla \cdot \mathbf{u} + \mathbf{J} \cdot \mathbf{F}_e] \quad (10)$$

where \mathbf{F}_e are external conservative forces and \mathbf{J} are the conjugate fluxes.

By combining (10) with (8) and using the assumption that the diffusive entropy flux is

$\mathbf{J}_s = \mathbf{J}_q / T$ and therefore $\nabla \cdot \mathbf{J}_s = \nabla \cdot [\mathbf{J}_q / T]$ we find,

$$\sigma = \mathbf{J}_q \cdot \nabla T^{-1} - \frac{\mathbf{P} : \nabla \mathbf{u} + p \nabla \cdot \mathbf{u}}{T} - \frac{\mathbf{F}_e \cdot \mathbf{J}}{T} \quad (11)$$

This equation does *not* assume the system is in a steady state. It does assume the entropy is not dependent on the strain rate, the temperature gradient or the dissipative field etc.

Because of this limitation one cannot expect (11) to yield correct results if the system is moving between regimes with different shear rates or temperature gradients etc. This expression is $O(F_e^2)$, however since terms of this order were neglected when we assumed local thermodynamic equilibrium and $s = s(u, v)$, if there is any change in the field with time then there would be an additional term in (11) that cannot be neglected.

In computer simulations of shearing atomic fluids at fixed kinetic temperature, the energy and pressure are found to vary quadratically with strain rate. This implies that the single particle and the pair distribution functions (at least) vary quadratically with strain rate. If these distributions are put into the Green expansion for the Gibbs entropy [23] as a sum of single-particle pair,.. etc. contributions, we see that the first two terms (at least) in the Green expansion of the entropy contain components that vary quadratically with strain rate. The entropy, s , for sufficiently small deviations from equilibrium, contains terms which are quadratic in driving fields like the strain rate $F_e = \dot{\gamma}$ and it would be useful to be able to treat such systems. The magnitude of these contributions is likely to be very large in polymeric systems because at equilibrium these systems are dominated by entropic considerations. So it would seem that this is then a second limitation in the linear irreversible thermodynamic formalism. In any event it becomes very difficult to approach this problem using a generalisation of linear irreversible thermodynamics [24]. However, in an analysis using the dissipation function rather than the rate of entropy production, there is no such restriction on the field.

It is assumed in the irreversible thermodynamic view of the world that if a system is time independent then the entropy density should also be time independent. In the steady state the left hand side of (8) vanishes, and,

$$\sigma = \nabla \cdot \mathbf{J}_s = \nabla \cdot (\mathbf{J}_q / T) \quad (12)$$

(Note: from the heat equation, if there is no time dependence then $\nabla \cdot \mathbf{J}_q = 0$). Equation (12) is true even if the entropy is strain rate dependent. This in turn implies that the

temperature will be strain rate dependent but asymptotically, for small strain rates, this effect only leads to a quartic variation in the entropy production. The quartic term may be ignored in the small field limit.

If we consider a system composed of 3 parts: a system of interest where the dissipative field acts $x \approx 0$ within a very narrow region dx , an inert trunk of length L and finally a thermostatted region at $x \approx S$, at a fixed kinetic temperature $T_{th} = k_B \beta_{th}^{-1}$. For simplicity we assume the dissipative field and the dissipative flux are both scalars. In the steady state for a fixed value of the dissipative field F_e , there is a flow of heat

$\langle J_Q(x) \rangle A(x)$ where $A(x)$ is the cross sectional area at position x and $J_Q(x)$ is the heat flux at position x , away from the system of interest. In the steady state

$\langle J_Q(x) \rangle A(x) = -\langle J \rangle V F_e, \quad \forall x, A(x)$. The total entropy production per unit time Σ , would be

$$\Sigma = \frac{-\langle J \rangle V F_e}{T_{soi}} - \int_0^L dx \frac{d\langle J_S(x) \rangle}{dx} = \frac{-\langle J \rangle V F_e}{T_{soi}} - \int_0^S dx \frac{d\langle J_Q(x) \rangle A(x) / T(x)}{dx} \quad (13)$$

where $\langle J_S \rangle$ is the steady state entropy flux per unit time and per unit area. In deriving this equation it is assumed that every part of the extended system is in thermodynamic equilibrium but the equilibrium thermodynamic temperature varies along the extended system. Then infinitesimal amounts of heat are transported along the system. The total change in the equilibrium entropy is obtained by summing $dS(x) = dQ(x) / T(x)$ along the system. This is all assumed to take place without violating local thermodynamic

equilibrium. Clearly if the system was really in equilibrium then the Zeroth Law of thermodynamics would tell us that the heat fluxes would be zero and the extended system would be isothermal.

In the steady state

$$\langle J_Q(x) \rangle A(x) = \langle J \rangle V F_e = -L V F_e^2, \forall x \quad (14)$$

The steady state entropy production per unit time is the integral over the entire system volume of the local products of local thermodynamic forces and thermodynamic forces.

We can rewrite this steady state, entropy production per unit time as

$$\begin{aligned} \lim_{t \rightarrow \infty} \Sigma(t) &= \frac{L V F_e^2}{T(0)} + L V F_e^2 \int_0^S dx \frac{dT(x)^{-1}}{dx} = L V F_e^2 \left[\frac{1}{T(0)} + \frac{1}{T(S)} - \frac{1}{T(0)} \right] \\ &= \frac{L V F_e^2}{T(S)} \equiv \frac{L V F_e^2}{T_{th}} = \langle \Omega \rangle \end{aligned} \quad (15)$$

The derivation does not require a constant thermal conductivity along the trunk. It only uses the fact that in the steady state the *total* heat flow (across any varying cross sectional area) at any value for x must equal the average rate the field does work on the system of interest.

The equality, on average, of the dissipation function and the total “entropy production per unit time” helps to clarify another matter. The dissipation function seems

non-local in space. For driven systems the work term is usually evaluated at a different position to where the temperature is measured. However the total entropy production per unit time in equations (10,11) involve sums and integrals of products of quantities that are each evaluated at the same position. It is a sum of locally evaluated products. Yet in the steady state this inherently local quantity is equal to the average *nonlocal* dissipation function. All that is required, is for the entire system to be in a steady state.

If this is not the case the average dissipation will differ from the entropy production rate and thus the entropy production probably cannot be expected to satisfy an exact Evans-Searles [17] transient fluctuation theorem (ESFT). Whether the entropy production satisfies a steady state FT is not easy to say. The temperature appearing in the ESFT is a constant [17]. It has no fluctuations. It is just the thermodynamic temperature of the underlying equilibrium state. There is ambiguity in how to write the entropy production as a microscopic expression - the temperatures appearing in equation (13) are time and position dependent. Certainly we can understand the fluctuations in $J(t)VF_e$ but it is not easy to understand how to compute or measure $T_{soi}(t)$ especially far from equilibrium. In fact the thermodynamic temperature is defined by the equation

$T^{-1} \equiv \left. \frac{\partial S}{\partial E} \right|_V$ and since the equilibrium entropy is according to Gibbs, a functional of the

full equilibrium phase space distribution function, the thermodynamic temperature too must be a property of the ensemble. Therefore it should be devoid of fluctuations. The equality $J_Q(x,t)A(x) \approx -J(t)VF_e$ is only true on average (see equation (14)). Unless the absolute differences between these two quantities are bounded we do not expect the entropy production to even satisfy an asymptotic steady state FT.

There are regimes where neither the concept of entropy or entropy production are defined. In cases where linear irreversible thermodynamics can be applied, the treatment based on dissipation will lead to linear response theory and Green-Kubo relations that are consistent with linear irreversible thermodynamics [25]. However, the dissipation function treatment can be applied under much more general conditions including strongly driven and/or small, systems.

Conclusion

In a NESS, averages of suitably smooth phase functions like energy, pressure, stress, etc are time independent. The Gibbs entropy that contains a supremely non-smooth $\ln[f(\mathbf{\Gamma};t)]$, decreases towards minus infinity at a constant average rate. This is a manifestation of the fact that the phase space density, or its logarithm, is not a thermodynamic observable. However it is possible that by using the Green expansion, the entropy can be regularized [20]. It is highly likely that the lower order distribution functions like the number density itself the single and the two particle distribution functions, are completely smooth. It is only when the distribution function dimension exceeds the Kaplan-Yorke dimension of the steady state attractor that singularities arise [20, 26]. In most many-particle systems that we are interested, the Kaplan-Yorke dimension [20, 27] is only very slightly less than the ostensible phase space dimension (literally a few parts in Avogadro's Number for Navier-Stokes transport in atomic fluids like argon [27]). No matter how small this dimensional reduction is, the standard Gibbs entropy diverges to negative infinity in any NESS.

However this small reduction in dimensionality means that in NESSs the Green expansion will likely converge to a finite nonequilibrium entropy long before the divergence occurs. There is likely to be a very long plateau region where the N -dimensional Green entropy, $S_{Gr,N}$ is independent of N the dimension of the distribution employed in the Green series summation.

We call this plateau entropy computed from the Green expansion for distributions of lower dimension than the Kaplan-Yorke dimension, the Green expansion entropy. This is very different from the coarse grained Gibbs entropy which is a subjective rather than objective quantity. The Green expansion entropy is the only objective nondivergent nonequilibrium entropy that we know of.

The Green expansion may provide a theoretical mechanism for microscopically defining the entropy for nonequilibrium systems. However it cannot solve the problem that irreversible thermodynamics ignores the quadratic dependence of this regularized entropy, on the driving external field. Close to equilibrium this dependence is precisely the same order as that of the entropy production itself! This is not a problem if the driving field is fixed and we only consider one steady state, but if we move between different steady states it will be problematic even in the weak field limit.

We know from simulations [20] that the various singlet, pair and three particle, distribution functions contain components that are quadratic in the shear rate. This means that the Green expansion entropy must also contain these terms. Due to symmetry, it is impossible for the quadratic strain rate contributions to vanish, because, because entropy is a scalar as is the energy and the trace of the pressure tensor, and these latter quantities do show quadratic components.

A second problem with the regularized Green expansion of the entropy is that to actually perform the summation has proven extremely difficult. At equilibrium the distribution functions factorize into products of configurational and kinetic terms. In steady states this does not happen. At equilibrium, distribution functions for fluids possess a high degree of symmetry. In steady states this is not the case. It has been shown that it is exceedingly difficult to compute even the two-body terms in the Green expansion for a shearing atomic fluid. [24] The dimensionality of the nonequilibrium pair distributions is just too high to yield the required integrals accurately.

It turns out that although computing any Green expansion entropy of a NESS system has proven impossible, it appears to be completely unnecessary. All the necessary theoretical tools involve dissipation rather than entropy production. The Fluctuation Theorem, Second Law inequality, the Dissipation Theorem our microscopic proof of the Clausius Inequality and the various Relaxation Theorems all refer in some way to dissipation. They do not mention entropy production. They are each exact results, valid for systems of arbitrary size and arbitrarily near to, or far from, equilibrium. This is also precisely why the nonequilibrium entropy is so difficult to calculate. Unlike dissipation it is not related to other measureable physical properties. This makes the nonequilibrium entropy impossible to measure or to infer from other measurements.

The only exception to this is that in NESSs close to equilibrium the average entropy production (9), equals the ensemble average of the time-averaged dissipation. However this doesn't make the entropy itself computable because its dependence on dissipative fields is unknown.

In the very first papers on the subject[15, 16], FT's were developed to explain the 2nd law for isoenergetic systems where phase space contraction rate and the dissipation are instantaneously proportional. However, the dissipation is much more widely applicable, and therefore the fact that these two quantities are equal under constant energy conditions might be regarded as being a coincidence. The average rate of change (divergence) of the Gibbs entropy, the average spontaneous entropy production rate and the average dissipation function each have the same average absolute values for any given NESS close to equilibrium. It is by no means obvious why this should be so. Of course once we move further from equilibrium this equality breaks down and the only useful quantity is dissipation.

Finally we should mention that many of our theoretical results have been demonstrated in laboratory experiments. The Fluctuation Theorem both for transients and for steady states has been demonstrated in optical tweezer experiments [28] and other kinds of laboratory experiment [29]. Each of the other theorems has been validated in computer simulation experiments [30].

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APPENDIX

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 at 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 time-symmetric 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.

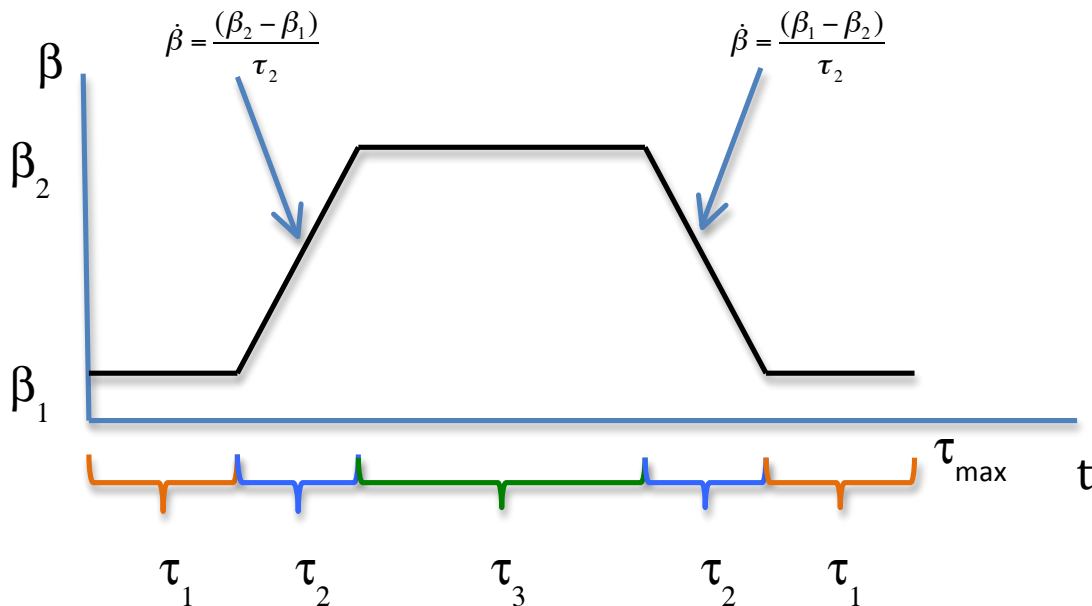


Figure 1. Schematic diagram of the protocol used for the change of temperature in the example considered.

The equations of motion are:

$$\begin{aligned}\dot{\mathbf{q}}_i &= \mathbf{p}_i / m \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i - \alpha \mathbf{p}_i \\ \dot{\alpha} &= \frac{1}{\tau_{th}^2} \left(\frac{2\mathbf{p}_i \cdot \mathbf{p}_i}{3NkT(t)m} - 1 \right)\end{aligned}\tag{A.1}$$

and the initial distribution function is:

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

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]:

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

Noting,

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

so,

$$\frac{3}{2} N \tau_{th}^2 (\alpha(\tau_{\max})^2 - \alpha(0)^2) = \int_0^{\tau_{\max}} \left(\frac{2K(t)\alpha(t)}{k_B T(t)} - 3N\alpha(t) \right) dt \quad (\text{A.5})$$

and substituting into (A.3) gives,

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

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,

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

Now consider some special cases:

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

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

$$\langle \Omega_{\tau_{\max}} \rangle = - \int_0^{\tau_{\max}} \frac{\langle \dot{Q}(t) \rangle}{k_B T(t)} dt = 0. \quad (\text{A.8})$$

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

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

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

and from the Second Law Inequality [19], $\langle \Omega_{\tau_{\max}} \rangle \geq 0$, so

$$\langle \Omega_{\tau_{\max}} \rangle = - \int_0^{\tau_{\max}} \frac{\langle \dot{Q}(t) \rangle}{k_B T(t)} dt = -1/k_B \int_0^{\tau_{\max}} \dot{S}_G(t) dt \geq 0 \quad (\text{A.10})$$

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_{ih} .

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_{ih} . 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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