On the entropy of relaxing deterministic systems

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In this paper, we re-visit Gibbs' second (unresolved) paradox, namely the constancy of the fine-grained Gibbs entropy for autonomous Hamiltonian systems. We compare and contrast the different roles played by dissipation and entropy both at equilibrium where dissipation is identically zero and away from equilibrium where entropy cannot be defined and seems unnecessary in any case. Away from equilibrium dissipation is a powerful quantity that can always be defined and that appears as the central argument of numerous exact theorems: the fluctuation, relaxation, and dissipation theorems and the newly derived Clausius inequality. © *2011 American Institute of Physics*. [doi:10.1063/1.3660203]

I. INTRODUCTION

For autonomous Hamiltonian systems, the expression Gibbs proposed for the equilibrium entropy[1] is, when applied to the time dependent nonequilibrium phase space distribution, a constant of the motion.[1,2] That is for a system whose equations of motion can be derived from a time independent Hamiltonian, $S_G(t) \equiv -k_B \int d\mathbf{\Gamma}\ f(\mathbf{\Gamma}, t) \ln[f(\mathbf{\Gamma}, t)]$ does not vary with time (S_G is Gibbs' entropy, k_B is Boltzmann's constant, and $f(\mathbf{\Gamma}, t)$ is the N-particle phase space distribution function at the phase space vector $\mathbf{\Gamma} \equiv (\mathbf{q}_1, \ldots \mathbf{q}_N, \mathbf{p}_1, \ldots \mathbf{p}_N)$, at time t).

If you decompose a large equilibrium system with no externally applied fields, with a total energy E, total number of particles N in a volume V, into a set of macroscopic but smaller *equilibrium* systems each at different temperatures or densities such that the total energy, total number of particles, and total volume remains unchanged at (E, N, V), then it is easy to show that the single (uniform) equilibrium (E, N, V) system has the maximum total equilibrium entropy.[1,2] Further, if we assemble this set of equilibrium systems in such a way as to allow the equalization of temperatures and pressures, we know from the relaxation theorem,[3] that this composite system will eventually relax to an *apparently* uniform equilibrium (E, N, V) system. This observation has lead many text book authors to state that for a given set (E, N, V), an initial nonequilibrium system will relax to equilibrium at long times and that this equilibrium state is the state of maximum entropy. This appears to contradict the fact that in a closed Hamiltonian system, the Gibbs entropy is in fact a constant of the motion.

This paradox was known to Gibbs[1] and is sometimes referred to as his second paradox. The first more widely known paradox refers to the nonextensivity of the entropy when identical classical particles are treated as distinguishable.

We note that the Hamiltonian formulation of classical mechanics is only equivalent to a subset of Newtonian classical mechanics. The Hamiltonian formulation cannot represent systems with various non-holonomic constraints.[4] It is also incompatible with homogenous planar shear. This can be seen from the so-called SLLOD equations of motion, which reduce to Newton's equations of motion for planar Couette flow[5,6] for $t > 0$, yet cannot be represented using the Hamiltonian formulation of classical mechanics. Gibbs' second paradox applies to all classical deterministic systems that are not thermostated and obey the adiabatic incompressibility of phase space, $AI\mathbf{\Gamma}$.[5]

There have been many attempts over the years to resolve this second paradox; however, Paul and Tatiana Ehrenfest's encyclopedia article[2] published in 1911 still represents the state of the science on this subject (at least until the discovery of the fluctuation theorems in 1993). This article points out that there is no resolution of this issue. A more recent article by Callender[7] in 1999 presents a more recent summary of this unsatisfactory situation with many references updated to that time. However, the state of the science has not really progressed since the Ehrenfests.

In 1993, the discovery of the first fluctuation theorem[8] started to change things. The proof of the fluctuation[9] and related theorems[10] shows how irreversible macroscopic behaviour arises from time reversible microscopic equations of motion. The two new theoretical results that illustrate this most clearly are the second law inequality[11] and the very recent mechanical proof[12] of Clausius' inequality without the prior assumption of the second "law" of thermodynamics. None of these results refer to the nonequilibrium entropy. They refer instead to a quantity first defined in 2000 namely the dissipation function, $\Omega(\mathbf{\Gamma})$.[13] The time integral of the dissipation function or the dissipation over a period t, Ω_t is defined *for an autonomous Hamiltonian system* as[13]

$$\int_0^t ds\ \Omega(\mathbf{\Gamma}(s)) = \ln\left(\frac{f(\mathbf{\Gamma}(0), 0)}{f(\mathbf{\Gamma}(t), 0)}\right) = \Omega_t. \tag{1}$$

(Note: if the system obeys $AI\mathbf{\Gamma}$, but is not adiabatic and thus gains or looses heat from its surroundings, Eq. (1) contains an additional term.[10]) The second law inequality states that

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the ensemble averaged time integral of the dissipation is nonnegative. It does not refer to entropy production directly although it is true that for weakly driven systems the average dissipation is, to leading order in the driving field, equal to the entropy production one meets in linear irreversible thermodynamics. Unlike linear irreversible thermodynamics, the fluctuation and related theorems are exact for systems of arbitrary size and for systems arbitrarily near to, or far from, equilibrium. Far from equilibrium, the entropy production, like the thermodynamic temperature and the entropy, cannot be defined.

By combining the so-called dissipation theorem[14] and the second law inequality one can even prove the relaxation to equilibrium.[3] Again, the discussion revolves around dissipation. Indeed, we now define an equilibrium system as any system in which the dissipation function is identically zero everywhere in the accessible phase space. At equilibrium, entropy is a very useful quantity while dissipation is not, because it is identically zero.

These results seem to show that away from equilibrium we do not *need* the concept of entropy or entropy production. It is ironic that it was the Clausius equality that introduced the equilibrium entropy but our recent proof of Clausius' *inequality* refers only to heat and dissipation and only when the system is at equilibrium, is the concept of entropy introduced. In the present paper, we give a new derivation of the constancy of the fine-grained Gibbs entropy for Hamiltonian systems. Although this result is not new, the arguments are. We believe these new arguments show more precisely why the nonequilibrium entropy is not a useful concept.

II. CONVENTIONAL DERIVATION OF GIBBS' SECOND PARADOX

Because the constancy of the Gibbs entropy for Hamiltonian systems is so little known but so important, we now give three derivations of this result. First, we give the standard differential derivation based on the time reversible phase continuity equation.[15] We consider an autonomous Hamiltonian system, and note that the phase space expansion rate, Λ, is zero in all Hamiltonian systems, that is, $\Lambda = \partial/\partial\mathbf{\Gamma}\cdot\dot{\mathbf{\Gamma}} = 0$. We compute the rate of change of the Gibbs entropy using successive integrations by parts. Consider an N-particle system in three dimensions. Here we take the time derivative of the fine-grained Gibbs entropy $S_G(t)$:

$$\begin{aligned}\dot{S}_G(t) &= -k_B\int d\mathbf{\Gamma}\ \frac{\partial}{\partial t}[f(\mathbf{\Gamma},t)\ln(f(\mathbf{\Gamma},t))]\\ &= -k_B\int d\mathbf{\Gamma}\ (1+\ln(f(\mathbf{\Gamma},t)))\frac{\partial f(\mathbf{\Gamma},t)}{\partial t}\\ &= k_B\int d\mathbf{\Gamma}\ (1+\ln(f(\mathbf{\Gamma},t)))\frac{\partial}{\partial\mathbf{\Gamma}}\cdot[\dot{\mathbf{\Gamma}}f(\mathbf{\Gamma},t)]\\ &= -k_B\int d\mathbf{\Gamma}\ \dot{\mathbf{\Gamma}}f(\mathbf{\Gamma},t)\cdot\frac{\partial}{\partial\mathbf{\Gamma}}(1+\ln(f(\mathbf{\Gamma},t)))\\ &= -k_B\int d\mathbf{\Gamma}\ \dot{\mathbf{\Gamma}}\cdot\frac{\partial}{\partial\mathbf{\Gamma}}f(\mathbf{\Gamma},t))\\ &= k_B\int d\mathbf{\Gamma}\ f(\mathbf{\Gamma},t))\frac{\partial}{\partial\mathbf{\Gamma}}\cdot\dot{\mathbf{\Gamma}} = 0.\end{aligned} \tag{2}$$

It is easily seen that the boundary terms in the integrations by parts vanish. This result was known to Gibbs[1] (1902) and as we said in the introduction, this result has been discussed a number of times in the century since.[2,3]

We should point out that Eq. (2) applies to an isolated relaxing system of interacting particles that obey Newton's equations. Thus as the system relaxes to equilibrium, the entropy does not increase. It just stays constant. Equation (2) also applies to an adiabatic system of charged particles subject to a dissipative electric field. In this case too, the phase space expansion factor is zero. Although the system is driven away from equilibrium and in general becomes hotter as time increases, the Gibbs entropy just remains constant.

III. DIRECT CALCULTATION OF THE TIME DEPENDENT ENTROPY

We can also compute the Gibbs entropy directly. We do this in two different ways.

The solution of the Lagrangian form of the phase continuity equation[15] for an autonomous system gives $f(\mathbf{\Gamma}(t),t) = \exp[-\int_0^t ds\ \Lambda(\mathbf{\Gamma}(s))]f(\mathbf{\Gamma}(0),0)$, and for a Hamiltonian system this means that

$$f(\mathbf{\Gamma}(t),t) = f(\mathbf{\Gamma}(0),0). \tag{3}$$

The physical argument for Eq. (3) is the following. In an autonomous Hamiltonian system, the number of ensemble members within a differential volume element near $\mathbf{\Gamma}(t)$ at time t, namely $f(\mathbf{\Gamma}(t),t)d\mathbf{\Gamma}(t)$ is equal to the number of ensemble members that started near $\mathbf{\Gamma}(0)$ at time *zero* namely $f(\mathbf{\Gamma}(0),0)d\mathbf{\Gamma}(0)$. Since phase space volumes are preserved under Hamiltonian dynamics, $|\partial\mathbf{\Gamma}(t)/\partial\mathbf{\Gamma}(0)| = 1$: $f(\mathbf{\Gamma}(t),t) = f(\mathbf{\Gamma}(0),0)$, which is identical to Eq. (3).

Substituting this equation into the expression for the Gibbs entropy and using $\mathbf{\Gamma}(t)$ as a dummy variable gives,

$$\begin{aligned}S_G(t) &= -k_B\int d\mathbf{\Gamma}(t)\ f(\mathbf{\Gamma}(t),t)\ln[f(\mathbf{\Gamma}(t),t)]\\ &= -k_B\int d\mathbf{\Gamma}(t)\ \left|\frac{\partial\mathbf{\Gamma}(0)}{\partial\mathbf{\Gamma}(t)}\right| f(\mathbf{\Gamma}(0),0)\ln[f(\mathbf{\Gamma}(0),0)]\\ &= -k_B\int d\mathbf{\Gamma}(0)\ f(\mathbf{\Gamma}(0),0)\ln[f(\mathbf{\Gamma}(0),0)] \equiv S_G(0),\end{aligned} \tag{4}$$

where in the second last line the Jacobian is unity (for Hamiltonian dynamics only).

We can also calculate the change in the entropy from the dissipation function. The time integral of the dissipation function, $\Omega(\mathbf{\Gamma})$, is defined above in Eq. (1). The dissipation theorem[14] gives the following exact expression for the time dependent N-particle phase space distribution function,

$$f(\mathbf{\Gamma}(0),t) = \exp\left[-\int_0^{-t} ds\ \Omega(\mathbf{\Gamma}(s))\right]f(\mathbf{\Gamma}(0),0). \tag{5}$$

This equation is valid for driven or relaxing systems with or without a thermostat. However, here we only apply it to a field free autonomous Hamiltonian system.

From the definition of the dissipation function (1), we see that for autonomous Hamiltonian

systems,

$$\exp\left[-\int_0^{-t} ds\ \Omega(\mathbf{\Gamma}(s))\right] = \left(\frac{f(\mathbf{\Gamma}(-t),0)}{f(\mathbf{\Gamma}(0),0)}\right). \tag{6}$$

Combining Eqs. (5) and (6) gives

$$f(\mathbf{\Gamma}(0),t) = f(\mathbf{\Gamma}(-t),0). \tag{7}$$

This equation is obviously true from a physical point of view. It simply shows how to switch from the Heisenberg to the Schrodinger representations when computing time dependent averages.

The physical argument for Eq. (7) is the following. In an autonomous Hamiltonian system, the number of ensemble members within a differential volume element near $\mathbf{\Gamma}(0)$ at time t, namely $f(\mathbf{\Gamma}(0),t)d\mathbf{\Gamma}(0)$ is equal to the number of ensemble members that started trajectories at $\mathbf{\Gamma}(-t)$ at time *zero* namely $f(\mathbf{\Gamma}(-t),0)d\mathbf{\Gamma}(-t)$. Since phase space volumes are preserved under Hamiltonian dynamics, $|\partial\mathbf{\Gamma}(0)/\partial\mathbf{\Gamma}(-t)| = 1$: $f(\mathbf{\Gamma}(0),t) = f(\mathbf{\Gamma}(-t),0)$, which is identical to Eq. (7).

Substituting this equation into the expression for the Gibbs entropy gives,

$$\begin{aligned} S_G(t) &\equiv -k_B \int d\mathbf{\Gamma}(0)\ f(\mathbf{\Gamma}(0),t)\ln[f(\mathbf{\Gamma}(0),t)] \\ &= -k_B \int d\mathbf{\Gamma}(0)\ f(\mathbf{\Gamma}(-t),0)\ln[f(\mathbf{\Gamma}(-t),0)] \\ &= -k_B \int d\mathbf{\Gamma}(-t)\ \left|\frac{\partial\mathbf{\Gamma}(0)}{\partial\mathbf{\Gamma}(-t)}\right| f(\mathbf{\Gamma}(-t),0) \\ &\quad \times \ln[f(\mathbf{\Gamma}(-t),0)] \\ &= -k_B \int d\mathbf{\Gamma}\ f(\mathbf{\Gamma},0)\ln[f(\mathbf{\Gamma},0)] \equiv S_G(0), \end{aligned} \tag{8}$$

where in the second last line, the Jacobian is unity (for Hamiltonian dynamics only) and in last line, we have made a change in the dummy integration variable ($\mathbf{\Gamma}(-t) \to \mathbf{\Gamma}$).

IV. DISCUSSION OF A RELAXING, DETERMINISTIC, HAMILTONIAN SYSTEM

These "physicist's derivations" hide some subtleties. As we have seen the proof relies on conservation of probabilities of observing sets of ensembles members: $f(\mathbf{\Gamma}(t),t)d\mathbf{\Gamma}(t) = f(\mathbf{\Gamma}(0),0)d\mathbf{\Gamma}(0)$. The problem is that in all thermodynamic systems, the phase space dynamics is chaotic. This means that although for autonomous Hamiltonian dynamics $|\partial\mathbf{\Gamma}(t)/\partial\mathbf{\Gamma}(0)| = 1$ and therefore $|d\mathbf{\Gamma}(0)| = |d\mathbf{\Gamma}(t)|$, if we let $dl_{\mathbf{\Gamma}}$ be the radius spanning the differential volume $d\mathbf{\Gamma}$, then $\lim_{t\to\infty} dl_{\mathbf{\Gamma}(t)} = dl_{\mathbf{\Gamma}(0)}\exp[\lambda_{\max}t]$, where $\lambda_{\max}$ is the largest Lyapunov exponent for our N-particle system. Since the system is chaotic this largest exponent is necessarily positive. This means that if we let time go to *infinity* before we let the differential volume go to zero, $S_G(t)$ is not Lebesgue integrable. In at least one direction, the differential volume element ceases to be infinitesimal. This applies to both equilibrium systems and to adiabatic or thermostated nonequilibrium systems.

The fundamental component of Gibbs' second paradox is that in autonomous Hamiltonian systems, be they driven or relaxing, the entropy is time independent. The reason why entropy is a constant of the motion for autonomous Hamiltonian systems is that first, phase space volumes are preserved and second, we can at any point in the relaxation process, reverse the momenta leaving the coordinates unchanged and return to the initial state from which the system evolved. Entropy measures information and for exact deterministic dynamics, we never loose the information about the initial state from which the system evolved. This was commented on by Gibbs in 1902.[1]

Numerous schemes have been advanced to resolve Gibbs' second paradox. Most explanations try to introduce some form of coarse graining.[2,3] The problem with this approach is that the resultant values for the coarse-grained entropy are dependent on the grain size. Also the time dependence of the coarse-grained Gibbs entropy is grain size dependent.

Others claim that there is always some form of external noise (no matter how small) that upsets the accuracy of the deterministic equations of motion. When you add noise to the otherwise deterministic dynamics you smooth out the N-particle distribution function effectively coarse graining that function. Once again the computed entropy becomes a function of the noise amplitude and therefore is not a property of the system of interest alone. Once again the nonequilibrium entropy looses its utility.

In contrast to the dissipation function, the entropy is not useful in describing the relaxation to equilibrium. In contradistinction to the dissipation function, the entropy also plays no direct role in response theory and because of its constancy for autonomous Hamiltonian systems, it plays no role in the fluctuation theorem. It appears that entropy's usefulness is limited to describing equilibrium and local equilibrium states. This point has been made in the past by several authors.

These results can only be described as somewhat shocking to most students of physics. Most textbooks reiterate the important role played by entropy in the process of relaxation to equilibrium. We quote Clausius himself:[16]

> "The energy of the Universe is constant.
>
> The entropy of the Universe approaches a maximum."

Close to equilibrium where local thermodynamic equilibrium holds, we have seen that the extensive entropy production is in fact equal to the instantaneous dissipation divided by Boltzmann's constant. This appears to be the only nonequilibrium circumstance where entropy (or at least its production!) plays a significant role away from equilibrium.

We can also compare the change in entropy of a Hamiltonian system with the change of the ensemble average of the dissipation. Using Eq. (4), we can express the change in Gibbs' entropy, $\Delta S_G(t) = S_G(t) - S_G(0)$, as

$$\begin{aligned} \Delta S_G(t) &= -k_B \int d\mathbf{\Gamma}\ f(\mathbf{\Gamma},t)\ln[f(\mathbf{\Gamma},t)] \\ &\quad + k_B \int d\mathbf{\Gamma}\ f(\mathbf{\Gamma},0)\ln[f(\mathbf{\Gamma},0)] \\ &= -k_B\langle\ln[f(\mathbf{\Gamma},t)]\rangle_{f(\mathbf{\Gamma},t)} + k_B\langle\ln[f(\mathbf{\Gamma},0)]\rangle_{f(\mathbf{\Gamma},0)} \\ &= -k_B\langle\ln[f(\mathbf{\Gamma}(-t),0)]\rangle_{f(\mathbf{\Gamma}(-t),0)} \\ &\quad + k_B\langle\ln[f(\mathbf{\Gamma},0)]\rangle_{f(\mathbf{\Gamma},0)} = 0. \end{aligned} \tag{9}$$

In obtaining the third line of Eq. (9), we use the Schrödinger-Heisenberg equivalence for phase space averages (see Sec. 3.3 of Ref. 5). The last equality is clearly zero since $\mathbf{\Gamma}(-t)$ can obviously be treated as a dummy integration variable.

By contrast, the change in the dissipation function is clearly different. From the second law inequality proved in Ref. 11, the change in the ensemble averaged dissipation, $\langle \Omega_t \rangle$ is

$$k_B \langle \Omega_t \rangle_{f(\mathbf{\Gamma},0)} = -k_B \langle \ln[f(\mathbf{\Gamma}(t),0)] \rangle_{f(\mathbf{\Gamma},0)} + k_B \langle \ln[f(\mathbf{\Gamma},0)] \rangle_{f(\mathbf{\Gamma},0)} \geq 0. \quad (10)$$

The second term on the right hand side of Eq. (10) is identical to the corresponding term in the entropy change of Eq. (9). However, in the first term on the right hand side of Eq. (10) is ($\ln[f(\mathbf{\Gamma}(t),0)] = \ln[f(\mathbf{\Gamma}(2t),t)]$ rather than $\ln[f(\mathbf{\Gamma}(-t),0)] = \ln[f(\mathbf{\Gamma},t)]$). Also the first term in Eq. (10) is averaged with respect to the *initial* distribution while in Eq. (9), we see from Eq. (7) that the corresponding term is averaged with respect to the distribution at time t.

Dissipation measures at any time, the relative probabilities of seeing a set of trajectories compared to its conjugate set of anti-trajectories. In driven systems that satisfy the adiabatic incompressibility of phase space condition, the average dissipation is, to leading order close to equilibrium, equal to the average value of the spontaneous entropy production—as we meet in linear irreversible thermodynamics. In this limit, it becomes the average of the dissipative flux (e.g., the shear stress multiplied by the volume), the thermodynamic driving force (e.g., the strain rate), and the reciprocal of the absolute temperature of a reservoir the system is in contact with (see Appendix 1 of Ref. 17). Further from equilibrium, the thermodynamic temperature defined as the derivative of the internal energy with respect to the entropy $T = \partial U/\partial S|_V$ cannot be computed because the fine-grained Gibbs entropy of a nonequilibrium steady states diverges to negative infinity.

In isolated relaxing Hamiltonian systems, the internal energy is constant like the fine-grained Gibbs entropy, so nothing is learned about the relaxation of the system to equilibrium by studying the entropy. Unlike entropy, dissipation is a profoundly useful quantity for studying exactly solved deterministic dynamics. Furthermore, it is usually easy to calculate. The initial distribution is usually known: $f(\mathbf{\Gamma},0) = \exp(-G(\mathbf{\Gamma}))$ for some real function, $G(\mathbf{\Gamma})$. The equations of motion are usually known and allow the computation of $G(\mathbf{\Gamma}(t))$ as a function of t. Substituting this information into the definition of dissipation for Hamiltonian systems (1) shows that $\Omega_t(\mathbf{\Gamma}(0)) = G(\mathbf{\Gamma}(t)) - G(\mathbf{\Gamma}(0))$.

V. FOR THERMOSTATED SYSTEMS, THE HELMHOLTZ FREE ENERGY IS A CONSTANT OF THE MOTION

Consider a thermostated system in contact with a very large isokinetic heat bath.[13] Because the bath is much larger than the system of interest, the heat bath may be approximated as being in thermodynamic equilibrium while the system of interest which is in thermal contact with the bath, relaxes to equilibrium.

There are no external dissipative fields applied to the system but the initial distribution for the system of interest is not the equilibrium distribution. The nonequilibrium system of interest is relaxing towards equilibrium. From Eq. (2), since the phase space expansion term is non-zero, the change in the fine-grained entropy for the combined system of interest and reservoir is

$$\dot{S}_G(t) = k_B \int d\mathbf{\Gamma}\ f(\mathbf{\Gamma},t)) \frac{\partial}{\partial \mathbf{\Gamma}} \cdot \dot{\mathbf{\Gamma}} = -k_B \langle 3N_{\text{th}} \alpha_{\text{th}}(t) \rangle, \quad (11)$$

where N_{th} is the number of thermostated particles and α_{th} is the usual isokinetic thermostat multiplier.[5] We also know that the rate of change of the total energy of the system of interest and heat bath is

$$\langle \dot{H}_0(t) \rangle = -2K_{\text{th}} \langle \alpha_{\text{th}}(t) \rangle \equiv -3N_{\text{th}} k_B T_{\text{th}} \langle \alpha_{\text{th}}(t) \rangle, \quad (12)$$

where T_{th} is the kinetic temperature of the equilibrium reservoir. However, since the reservoir is in equilibrium, T_{th} is of course also equal to the equilibrium thermodynamic temperature of the reservoir.

If we generalize the Helmholtz free energy so that it takes the form for the composite system

$$A \equiv U - T_{\text{th}} S. \quad (13)$$

From Eqs. (11) and (12), we deduce that the Helmholtz free energy for the composite system is a constant of the motion,

$$\dot{A} = \langle \dot{H}_0 \rangle - T_{\text{th}} \dot{S} = 0. \quad (14)$$

This is precisely the type of system treated by the relaxation theorem. In that case, however, the time integral of the ensemble average of the dissipation is positive for all times and the instantaneous dissipation eventually decays to zero everywhere in phase space (i.e., The system has relaxed to equilibrium).

If the heat bath is not very large compared to the system of interest then both the system of interest and the heat bath will be out of equilibrium during the relaxation process. The heat bath could be subject to a Gaussian isokinetic thermostat in which case T_{th} is not the equilibrium thermodynamic temperature of the reservoir but is in fact the kinetic temperature of the nonequilibrium reservoir. If the thermostat employed is the Nosé-Hoover thermostat, T_{th} is the target temperature of the integral feedback mechanism. The relaxation pathway will be entirely different for the two thermostats and indeed in the Nosé-Hoover case, the relaxation pathway will also be dependent on the adjustable Nosé-Hoover time constant. Nevertheless, Eq. (14) referring to T_{th} is valid for all these systems. The only temperature any of these systems has in common is the equilibrium thermodynamic temperature that they all relax to, in the long time limit. This *equilibrium* thermodynamic temperature is of course T_{th}.

It may seem odd that the Helmholtz free energy for a nonequilibrium system refers to the thermodynamic temperature of the large thermal reservoir or the final equilibrium temperature to which the small systems relax. However, as we pointed out in our recent proof[12] of the Clausius inequality, the temperature appearing at any stage in a Clausius cycle or in the present thermal relaxation process, is in fact the

equilibrium temperature that the system will relax to if it is allowed to do so. In the Clausius case, this temperature changes in time as a cyclic protocol is executed. In the present (relaxation) case, there is no time dependent parametric protocol and there is only one temperature to which the system will ultimately relax.

VI. CONCLUSION

We have given detailed arguments for the point of view that the entropy and indeed any of the thermodynamic free energies are not useful concepts far from equilibrium (by which we mean that local thermodynamic equilibrium is not an accurate approximation). The very fact that our recent derivation[12] of Clausius' *inequality* and our earlier derivations of the relaxation,[3] the dissipation,[14] and the fluctuation theorems[8–10] each do not refer to entropy, shows that away from equilibrium a knowledge of entropy is not even necessary. We can accomplish all that we require using the definitions of energy, dissipation, and the equilibrium thermodynamic temperatures to which our nonequilibrium systems will relax. It is no accident that the proof of the relaxation to equilibrium could not be given until after the mathematical definition of dissipation. Without this concept, progress in this direction was simply not possible.

A more detailed description of the deterministic relaxation process reveals that if we start with a smooth nonequilibrium distribution and allow the system to relax to equilibrium following field free autonomous Hamiltonian dynamics, we expect that at long times the distribution will at low resolution resemble the smooth equilibrium microcanonical distribution. However, if you examine this distribution at ever finer resolution you will see that the distribution will in fact be a fractal approximation to the smooth microcanonical distribution. The last structures remaining from the initial nonequilibrium distribution will in fact be the unstable periodic orbits consistent with the initial distribution. The reason is obvious: these unstable periodic orbits are precisely those phase space structures that have the longest decay times. These are the analogues of the fractal structures that form in thermostated nonequilibrium steady states. These structures present profound mathematical difficulties in the calculation of the singular function known as the fine-grained entropy.[18] The logarithm appearing in the Gibbs entropy reacts strongly to the singular structures inherent in these unstable periodic orbits.

The relaxation theorem proves that subject to certain mathematical conditions, the magnitude of the ensemble averaged dissipation function goes to zero in the infinite time limit. In that limit, we know that for our field free Hamiltonian system, the only state with zero dissipation everywhere in phase space is in fact the microcanonical distribution with a uniform probability density in phase space. For any *finite* time no matter how large, in general there will be *some* ensemble-averaged dissipation and the distribution will not be *exactly* microcanonical. The distribution always contains information about its initial distribution of states. Indeed for any ensemble member, the equations of motion can always be reversed to recover the initial state (and distribution of states). During relaxation to equilibrium, the entropy is just constant while the dissipation tends to zero.

Our observations concerning the fine-grained Gibbs entropy are completely consistent with the recent results of Falcioni *et al.*[19] In this paper, Falcioni *et al.* make a number of observations:

- The single-particle Boltzmann entropy (in μ-space), of course obeys the Boltzmann H-theorem. This entropy can be calculated from the (possibly fractal) N-particle phase space distribution by projecting out all the degrees of freedom except those of a single particle. This is the same type of projection as that discussed by Evans and Rondoni.[18] This projection generates a smooth 1-particle, μ-space distribution. In the projection process, the loss of information means that unlike the fine-grained Gibbs entropy, the Boltzmann entropy is not constant and instead obeys an H-theorem.
- Starting from a smooth initial distribution, the course grained Gibbs entropy is initially a constant of the motion, but as time increases and the characteristic size of phase space structures become smaller than the grain size, the loss of information in resolving these structures again means that this coarse-grained Gibbs entropy is no longer constant and instead (as Gibbs already proved), obeys its own generalized H-theorem.
- The time scale for the transition of the coarse-grained Gibbs entropy, from constancy to an H-theorem regime is controlled by the Kolmogorov-Sinai entropy (an objective system property) and the grain size. The dependence on grain size introduces subjectivity into the coarse-grained Gibbs entropy which means that this quantity is *not* an objective material and system property but instead depends upon the spatial and momentum resolution with which you *choose* to observe system behaviour. To quote Ref. 19: "the onset of entropy variation in the (coarse-grained) Gibbs case has no intrinsic meaning."

If the system of interest is made of N non-interacting particles, the phase space distribution factorizes into N single-particle distributions, each of which is at once the phase space distribution of a single-particle system and the single-particle projection on μ-space of the N-body phase space distribution. The Boltzmann equation has no collision term, and is formally a phase continuity equation for a system made of just one particle. No H-theorem can thus be satisfied and the Boltzmann and Gibbs entropies are one and the same and are both constants of the motion.

For systems made up of *interacting* particles, there are characteristic scales that make the Boltzmann entropy and its relaxation time, objective material properties of the system that do not depend on the accuracy of measurements.

Lastly, we should comment on the relationship of our work with linear irreversible thermodynamics. Linear irreversible thermodynamics assumes that there is a nonequilibrium entropy that is an *analytic* function of the driving fields and of spatial position, close to equilibrium. This entropy must be equal to the equilibrium entropy at zero field. However, the theory does not

give any microscopic expression for this nonequilibrium entropy.

We know that this entropy cannot be the fine-grained Gibbs entropy that always diverges to $-\infty$ in any nonequilibrium steady state, no matter how close that state is to equilibrium. It also cannot be the Boltzmann entropy since that only reduces to the equilibrium entropy when the system at zero density. For the reasons given above this entropy likewise cannot be the coarse-grained Gibbs entropy.

The only entropy that we know of that has the desired properties is obtained by expanding the fine-grained Gibbs entropy into terms involving the single particle distribution, the pair distribution, the triplet, ... etc. This is the Green-expansion of the entropy first discussed (for equilibrium systems only) by H. S. Green[20] in 1952. In 1989, one of us (D.J.E.) pointed out[21] that below the Kaplan-Yorke dimension of the nonequilibrium steady state attractor, the distribution functions will be smooth and the resulting contributions to the entropy will be finite. The divergences inherent in the steady state attractor are only resolved in the high order distribution functions. Because the dimensional contraction of the steady state attractor is known to be quadratic in the field and also very small for real physical systems, the Green expansion is expected to converge to a finite value very early in the series. Further the dimensional reduction goes to zero in the zero field limit. This entropy is therefore expected to have all the properties required for the establishment of linear irreversible thermodynamics. Unfortunately in practice, this entropy is impossible to compute except in the dilute gas limit where it is equal to the Boltzmann entropy.

However, it seems that once again even the irreversible entropy production defined in linear irreversible thermodynamics is unnecessary since its average value is, in the weak field limit, equal to the average dissipation. That average dissipation of course satisfies the second law inequality and therefore all the results of linear irreversible thermodynamics can be derived using dissipation (in the weak field limit) rather than entropy production. The dissipation, relaxation, and fluctuation theorems do not require either the weak field limit or the thermodynamic limit and so they are vastly more general than irreversible thermodynamics.

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