ON THE APPLICATION OF THE GALLAVOTTI-COHEN FLUCTUATION THEOREM TO THERMOSTATTED STEADY STATES NEAR EQUILIBRIUM

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ABSTRACT

We analyze time dependent fluctuations in the phase space compression factor for constant temperature equilibrium states and near equilibrium steady states. We show that these fluctuations are not correctly described by the Gallavotti Cohen Fluctuation Theorem (GCFT) either at, or near, equilibrium. At equilibrium the probability distributions of the fluctuations is an even function of the phase space compression, while the GCFT incorrectly predicts an asymmetry in this equilibrium probability distribution. Near equilibrium we show that the GCFT also does not hold, since for such systems the GCFT is incompatible with Green-Kubo relations for fluctuations in the phase space compression factor. We believe that a possible reason for the breakdown of the GCFT for these systems, may be that the Chaotic Hypothesis of Gallavotti and Cohen fails to apply to thermostatted near equilibrium systems.

1. INTRODUCTION

In 1993, Evans, Cohen and Morriss proposed a relation meant to describe the fluctuation properties of N-particle systems in nonequilibrium steady states that were maintained at constant energy by an appropriate deterministic time reversible *ergostat* [1]. This relation was based on heuristic theoretical arguments, and supported by computer simulation data. The authors of reference [1] borrowed the idea from the theory of nonlinear dynamical systems, that the expanding rates of trajectory separation along the unstable directions of the phase space in chaotic systems can be used to compute the steady state averages of smooth phase functions. For the first time they tested this idea in numerical calculations of nonequilibrium many particle systems (at that time, the same had been done using periodic orbit expansions, but only in calculations concerning low dimensional dynamical systems [2]). Evans, Cohen and Morriss [1] used the symmetry properties of these expansion rates for time reversible systems, to propose a relation which we refer to as a steady state Fluctuation Theorem (FT). Reference [1] motivated a number of papers in which various fluctuation theorems were derived or tested, the first of which were the Evans-Searles Transient Fluctuation Theorem (TESFT) [3], and the Gallavotti-Cohen Fluctuation Theorem (GCFT) [4] described in Sections 2 and 3.

A typical nonequilibrium system may consist of a relatively small number of particles that interact with an external field (the driven system). This system may be in thermal contact with a very much larger number of particles on which no external field acts. The reservoir particles could act as a heat bath effectively maintaining the smaller system of interest at a constant average temperature at least over the characteristic relaxation time required for the system of interest to relax to a (quasi) steady state. Although the whole system (driven

system plus reservoirs) is Hamiltonian, the driven system by itself is non-autonomous and non-Hamiltonian.

An alternative way of modeling such systems is to replace the large number of reservoir particles by a much smaller number of reservoir particles, each of which is subject to a time reversible deterministic force that imposes a constraint on their equations of motion. Among the most common constraints are the one which fixes the internal energy of the constrained particle system, called an “ergostat”, and the one that fixes the kinetic energy of that system, called a “thermostat”. These modified equations of motion were proposed simultaneously and independently by Hoover [6] and Evans [7] in the mid 1980's and they have been studied theoretically and successfully employed in molecular dynamics computer simulations for two decades. As it turns out, one finds that heat is on average removed from the non-Hamiltonian modified system, and that the phase space compression factor is nonzero and on average is negative.

Reference [1] considered a very long phase space (steady state) trajectory of a Gaussian ergostatted, (*i.e.* isoenergetic) N-particle system [5]. This long trajectory was divided into (non overlapping) segments of duration t. Along each of the trajectory segments, the instantaneous phase space compression rate, Λ

$$\Lambda \equiv \frac{\partial}{\partial \mathbf{\Gamma}} \bullet \dot{\mathbf{\Gamma}} \tag{1}$$

was calculated. Here we denote the phase space vector describing the microstate (coordinates and momenta) of the N-particle system in d Cartesian dimensions by $\mathbf{\Gamma} \equiv (\mathbf{q}_1, \mathbf{q}_2, .. \mathbf{q}_N, \mathbf{p}_1, .. \mathbf{p}_N)$. In [1], the dynamics is assumed to be chaotic and therefore the

averaged value of the phase space compression factor computed along the trajectory segments $\overline{\Lambda}_t$, can be considered to be a random variable whose probability distribution, $\Pr(\overline{\Lambda}_t)$, can be constructed from the histogram of its observed values for the set of such trajectory segments. Because of time reversibility of the dynamics, if the compression factor takes a value A, then it can also take the value -A, albeit with different probability. The fluctuation relation tested in reference [1] states that:

$$\lim_{t\to\infty}\frac{1}{t}\ln\frac{\Pr(\overline{\Lambda}_t = A)}{\Pr(\overline{\Lambda}_t = -A)} = -A. \qquad (2)$$

Remark 1. *One may find it odd to consider fluctuations in the phase space volume of mechanical systems. As a matter of fact, although the phase space compression factor is identically zero for Hamiltonian particle systems, it is non-zero for the (non-autonomous) dynamical systems obtained by restricting one's attention to an arbitrary subset of particles of that Hamiltonian system [8], (i.e. projecting out the coordinates and momenta of some of the particles). This is the case of the Hamiltonian system (driven system plus reservoirs) described above, if the degrees of freedom of the reservoirs are projected out.*

In reference [1], equation (2) was verified in nonequilibrium molecular dynamics computer simulations. Because the system studied in [1] was maintained at constant energy, equation (2) can be written in an alternative but mathematically equivalent form,

$$\lim_{t\to\infty}\frac{1}{t}\ln\frac{\Pr(\overline{[\beta\mathbf{J}]}_t V\bullet\mathbf{F}_e = A)}{\Pr(\overline{[\beta\mathbf{J}]}_t V\bullet\mathbf{F}_e = -A)} = -A \qquad (3)$$

where for systems in d Cartesian dimensions,

$$[\beta \mathbf{J}](\mathbf{\Gamma}) \equiv \frac{dN\mathbf{J}(\mathbf{\Gamma})}{2K(\mathbf{\Gamma})}. \tag{4}$$

K is the (peculiar) kinetic energy and the dissipative flux J, is defined in the usual way in terms of the adiabatic derivative of the internal energy, H_0, and the system volume V, [5],

$$\dot{H}_0^{ad}(\mathbf{\Gamma}) \equiv -\mathbf{J}(\mathbf{\Gamma})V \bullet \mathbf{F}_e. \tag{5}$$

This shows how in the ergostatted (constant energy) case, the instantaneous phase space contraction rate can be equated with a physical quantity, which is recognizable as the (instantaneous) irreversible entropy production $\Sigma(\mathbf{\Gamma}) = -[\beta \mathbf{J}](\mathbf{\Gamma})V \bullet \mathbf{F}_e$. This rate is a product of a thermodynamic force, $\mathbf{F}_e$, a thermodynamic flux, $\beta\mathbf{J}$ and the system volume V. In reference [1] both ways of writing the steady state FT were exploited almost interchangeably.

2. THE GALLAVOTTI-COHEN FLUCTUATION THEOREM

In 1995 Gallavotti and Cohen [4] obtained equation (2) within a novel framework, meant to extend Boltzmann's ergodic hypothesis to both equilibrium and nonequilibrium statistical mechanics, using the language of modern dynamical systems theory. To this purpose, Gallavotti and Cohen stated the following:

Chaotic Hypothesis (CH): *A reversible N-particle system in a stationary state can be regarded as a transitive Anosov system, for the calculation of its macroscopic properties*.

The main result of reference [4] is the proof of equation (2) for time reversible, dissipative dynamical systems in which the CH holds. This proof is known as the Gallavotti Cohen Fluctuation Theorem or GCFT for short [9]. It should be noted that the GCFT only refers to phase space compression rates and only to steady states. Nowhere in the proof is there a direct requirement that the system should be maintained at constant energy, constant kinetic energy or even that it be maintained at constant volume. The GCFT only seems to require dynamics that is time reversible, smooth and to some degree hyperbolic, which makes the system a reversible Anosov diffeomorphism. Therefore, equation (2) should then apply to a rather wide class of dynamical systems, including, for instance, isothermal-isobaric as well as isoenergetic-isochoric N-particle systems, and also non-particle systems as long as their dynamics is sufficiently similar to that of reversible, transitive Anosov systems.

Reference [4] motivated numerical tests (e.g. [10-12]) in different types of dynamical systems, where equation (2) or similar relations, were verified. The Gallavotti and Cohen work also motivated attempts at experimental verifications of the GCFT (see, for example,

references [13, 14]), even though these experimental systems cannot be considered isoenergetic, and even though the experimental measurement of phase space contraction rates in thermostatted systems is highly problematic.

Quite obviously, realistic models of physical systems can hardly be expected to be transitive Anosov dynamical systems. Nevertheless, just as the mathematical notion of ergodicity is known to be violated by most common physical models and yet turns out to be extremely useful *for practical purposes,* the CH of [4] should be interpreted as saying that deviations from the transitive Anosov property cannot be observed at the macroscopic level, for certain dynamical systems. The CH then allows the use of the techniques of differentiable dynamics in the description of the steady states for a wide class of systems of physical interest, as long as one is interested the behavior of macroscopic observables. In particular, the CH allows one to describe the steady state of a given N-particle system as if it was describable by a Sinai-Ruelle-Bowen (SRB) measure, *i.e.* a probability distribution which is smooth along the unstable directions of the dynamics, and which can be approximated by means of dynamical weights attributed to the cells of finer and finer Markov partitions.

However, at the present time the only test which has been attempted to determine whether a system satisfies the CH, is the numerical or experimental check of whether the system satisfies equation (2). This is somewhat circular because if the CH is satisfied, then the system will also satisfy GCFT. A more precise characterization of the CH is desirable. The experience accumulated so far seems to suggest that **time reversible**, **chaotic** systems should satisfy the CH.

Perhaps surprisingly, chaos (meaning the presence of at least one positive Lyapunov exponent) does not seem to be necessary for expressions such as equation (2) to be verified in numerical simulations of simple N-particle systems [15, 16]. In addition, although there is no known mathematical reason why thermostatted (constant temperature) systems should behave differently from ergostatted systems, there is a considerable body of numerical evidence that the GCFT fails to be satisfied for thermostatted systems in the weak field regime (near equilibrium), hence that the CH does not hold in that case [17]. Reference [18] gives numerical evidence that thermostatted systems seem to satisfy the CH at very high shear rates, while they apparently violate the CH (and the GCFT) at small shear rates [17] . As a matter of fact, the numerical results of [17] suggest that as the system departs further from equilibrium, the data become more consistent with equation (2). This is in apparent contradiction with the expectation that the CH should be satisfied better as the system approaches the equilibrium state and therefore becomes more chaotic (*i.e.* has a larger sum of positive Lyapunov exponents).

Dissipation, which has been invoked in derivations of equation (2) (p.936 of [4], and p.414 of [19]), does not seem to play an essential role in those derivations, and the GCFT would therefore seem to apply to non dissipative stationary states - (*i.e.* equilibrium states). One can see this by repeating Ruelle's proof of the GCFT, given in [19], with minor variations (see appendix A below) .

Thus, the domain of applicability of the CH is an open and quite intriguing question. In this paper we argue that the GCFT, and the CH, do not apply to thermostatted systems that are near, or at, equilibrium. Note the distinction between *thermostatted* systems, where the kinetic energy is constrained or fixed, and *ergostatted* systems where the internal energy is

fixed. Also note that for hard discs or spheres, fixing the kinetic energy and the total energy is equivalent and therefore equation (2) is expected to apply to hard N-particle systems under these forms of thermostat since for hard systems both thermostats are in fact identical. Reference [10] gives evidence for the validity of the GCFT for hard discs. However, if the kinetic energy is constrained using a Nosé-Hoover thermostat, then we show that the GCFT and the CH do not apply, even to hard core particles.

3. EVANS-SEARLES FLUCTUATION THEOREMS

A number of authors, inspired by [1, 4], have obtained a range of fluctuation theorems for steady state systems which are similar in form to equation (2) but have different content or are applicable to a different class of system including both deterministic and stochastic systems. See, for example, references [20-24]. Still other authors, refined the GCFT, cf. references [19, 25, 26].

Independently of this activity, in 1994 Evans and Searles derived the first of a set of fluctuation theorems (ESFT) for nonequilibrium N-particle systems which focused on the corresponding "dissipation rate" Ω, rather than on the phase space contraction rate, Λ [27, 28]. For thermostatted or ergostatted systems the time average "dissipation rate" is identical to the average rate of entropy absorption (positive or negative) by the thermostat. For homogeneously thermostatted systems the entropy absorbed by the thermostat is equal and opposite to the so-called spontaneous entropy production rate defined in linear irreversible thermodynamics, $\Sigma=\sigma V$. Further for homogeneously thermostatted systems Evans and Rondoni [8] have recently shown that the entropy production rate is also equal and opposite to the rate of change of the fine grained Gibbs entropy. These ESFTs apply at all times to particular ensembles [29] of transient trajectories (TESFTs), or particular ensembles of steady state trajectories in the long time limit [28] (SESFTs). The form of the resulting ESFTs is identical to equation (2), but contain different information since they are based on the statistics of ensembles of trajectories. This difference is explained in detail below [30, 31].

Jarzynski and Crooks have taken an approach similar to the transient approach of Evans and Searles, to calculate the free energy difference between equilibrium states [32, 33].

To derive the TESFT one considers an ensemble of trajectories that originate from a known initial distribution (which may be an equilibrium or nonequilibrium distribution, it does not matter) and proceed under the possible application of external fields and/or thermostats. One then obtains general transient fluctuation theorems (TESFTs) stating that

$$\ln \frac{\Pr(\overline{\Omega}_t = A)}{\Pr(\overline{\Omega}_t = -A)} = At \tag{6}$$

which is of similar form to (2) but where the phase space contraction rate is replaced by the so-called dissipation rate or function, $\Omega(\mathbf{\Gamma})$. In all the TESFTs the time averages are computed from t=0 when the system is characterized by its initial distribution, $f(\mathbf{\Gamma},0)$, to some arbitrary later time t. The dissipation function depends on the initial probability distributions (different ensembles) and on the dynamics, and is defined by the equation,

$$\int_0^t ds\, \Omega(\mathbf{\Gamma}(s)) \equiv \ln\left(\frac{f(\mathbf{\Gamma}(0),0)}{f(\mathbf{\Gamma}(t),0)}\right) - \int_0^t \Lambda(\mathbf{\Gamma}(s))ds = \overline{\Omega}_t t \tag{7}$$

For ergostatted dynamics conducted over an ensemble of trajectories which is initially microcanonical, the dissipation function is identical to the phase space compression factor,

$$\Omega(t) = -\Lambda(t) = -[\beta \mathbf{J}](t) V \bullet \mathbf{F}_e, \quad \text{when } dH_0/dt = 0, \tag{8}$$

while for thermostatted dynamics, the dissipation function is subtly different,

$$\Omega(t) = -\beta \mathbf{J}(t) V \bullet \mathbf{F}_e \neq \Lambda(t), \quad \text{when } dK/dt = 0. \tag{9}$$

In both cases $\beta = 2K(\mathbf{\Gamma})/dN$ where d is the Cartesian dimension of the system. Also, in both cases $\lim_{t\to\infty} \overline{[\beta \mathbf{J}]}_t V \bullet \mathbf{F}_e = \lim_{t\to\infty} \overline{\Sigma}_t$ where Σ is the extensive entropy production that one would identify for near equilibrium systems from the theory of irreversible thermodynamics. It is a product of the thermodynamic force $\mathbf{F}_e$ and the time average of its conjugate thermodynamic flux, $\overline{[\beta \mathbf{J}]}_t$.

TESFTs have been derived for an exceedingly wide variety of ensembles, dynamics and processes [28]. For example TESFTs have been derived for dissipative isothermal isobaric systems and for relaxation systems where there is no applied external field but where the system is not at equilibrium by virtue of its initial distribution $f(\mathbf{\Gamma},0)$. In all cases the TESFTs have been verified in numerical experiments. Two TESFTs have recently been confirmed in laboratory experiments on colloidal suspensions: one involving the transient motion of a colloid particle in a moving optical trap; and the other involving the relaxation of a trapped particle in an optical trap whose trapping constant is suddenly changed [34, 35]. One should not be surprised by the diversity of FTs - they refer to *fluctuations* and fluctuations are well known to be ensemble and dynamics dependent - even at equilibrium.

The TESFT can now be stated as follows:

Theorem (Evans-Searles): *For any time reversible N-particle system, and for all times* $t \in \Re$, *there exists a dissipation function* $\overline{\Omega}_t$ *and a smooth probability distribution* $d\mu(\mathbf{\Gamma}) = f(\mathbf{\Gamma})d\mathbf{\Gamma}$ *in phase space, such that:*

$$\frac{1}{t}\ln\frac{\Pr(\overline{\Omega}_t \in B_{p,\varepsilon})}{\Pr(\overline{\Omega}_t \in B_{-p,\varepsilon})} = p \qquad (10)$$

up to corrections of order ε. *Here,* $\Pr(\overline{\Omega}_t \in B_{p,\varepsilon})$ *is the probability assigned by* μ *to the set* E_p *of initial conditions* $\mathbf{\Gamma}$ *for which the dissipation* $\overline{\Omega}_t$ *lies in* $B_{p,\varepsilon} = (p-\varepsilon, p+\varepsilon)$.

It is interesting to observe that the probability measure μ, *i.e.* its density, is not necessarily unique, and that different probability measures lead to the same result as long as $\ln\frac{f(\mathbf{\Gamma})}{f(S^t\mathbf{\Gamma})}$ exists for all initial conditions $\mathbf{\Gamma}$ in the support of μ, and for all $t \in [0,\infty)$.

In contradistinction to the GCFT, these TESFTs are not *only* true asymptotically in time but rather are valid for all times t. To better appreciate the differences between the GCFT and the TESFT we summarize their derivations in an Appendix B.

Evans and Searles have also argued [28] that for transitive **chaotic** systems where the **steady state exists and is unique**, the statistics of properties averaged over trajectory segments selected from a single steady state trajectory are equivalent to a carefully constructed ensemble of steady state trajectory segments [28, Section 2.2]. This can be seen as an extension of the ergodic hypothesis to nonequilibrium steady states. Clearly there will be systems for which this extension fails, even if the system is ergodic at equilibrium.

Assuming the hypothesis of [28] holds, then one can derive asymptotic steady state FTs (SESFTs) that apply to segments along a single trajectory, from the relevant ESFTs. The corresponding fluctuation formula for an ergostatted steady state system is then identical to (2), and contains the same information [31]. However, for nonergostatted systems the predictions of the SESFTs are different in general from the corresponding predictions of the GCFT. This is because in general the dissipation function is different from the phase space compression rate. To check the validity of the SESFTs, numerical simulations have been performed for various ensembles and dynamics, showing that numerical results are indistinguishable when sampling either from a single long steady state trajectory or from an ensemble of steady state trajectory segments [17].

Remark 2. *This equivalence of statistics requires a sufficiently long relaxation time to allow an accurate representation of the steady state, and long trajectory segments. Thus as is the case for the GCFT, the SESFTs, in contradistinction to the TESFTs, are asymptotic in time.*

The dissipation function that appears in the SESFT for a single steady state trajectory is defined by (7), where the initial distribution function is the equilibrium distribution function generated by the same dynamics that is responsible for the steady state except that the dissipative field is set to zero [28]. This requires that the zero field system is ergodic and is at equilibrium.

Table I summarizes the differences between the GCFT and the TESFT for ergostatted dynamics (first two columns). The asymptotic version of the ESFT is introduced in the third column for comparison with the previous two and with the SESFT [30, 31].

4. EQUILIBRIUM FLUCTUATIONS

For thermostatted equilibrium systems the phase space compression factor fluctuates about zero. As a result of the time reversal invariance of all properties of the equilibrium state, we know that,

$$\frac{\Pr(\overline{\Lambda}_t(F_e = 0) = A)}{\Pr(\overline{\Lambda}_t(F_e = 0) = -A)} = 1 \quad \forall t . \tag{11}$$

However, if the GCFT is assumed to apply to thermostatted equilibrium states as in Appendix A, then we find from (2) that it is more likely that the zero field phase space compression factor is negative rather than positive. This is obviously not correct.

By way of contrast, for an ensemble of isothermal systems, the TESFT (6), can be rewritten as,

$$\frac{1}{t}\ln\frac{\Pr(\bar{J}_t = A)}{\Pr(\bar{J}_t = -A)} = -\beta A V F_e \tag{12}$$

where the trajectory segments begin from the isothermal equilibrium ensemble and proceed for a time t, under zero field $F_e = 0$, thermostatted dynamics. However since the external field is zero, equation (12) predicts that at equilibrium time averages of the dissipative flux are as expected, equally like to be positive or negative, regardless of the duration of the averaging time.

We conclude that for *thermostatted* dynamics the GCFT does not properly describe equilibrium fluctuations in the phase space compression factor, whereas for *ergostatted* equilibrium states the TESFT and the GCFT both make correct statements about the equilibrium symmetry of fluctuations. For example the TESFT for ergostatted systems can be written as

$$\frac{1}{t}\ln\frac{\Pr(\overline{[\beta J]}_t = A)}{\Pr(\overline{[\beta J]}_t = -A)} = -AVF_e. \qquad (13)$$

In (13) J refers to the component of **J** that is parallel to $\mathbf{F}_e$, so when the field is zero, the TESFT states that time averages of the thermodynamic flux $[\beta J]$ are equally likely to be positive as negative, regardless of the averaging time. This is obviously a correct statement.

It may be argued that the SRB measure and therefore the GCFT cannot be applied to thermostatted *equilibrium* states - that dissipation is required before they can be applied sensibly. In the next section we discuss the application of the GCFT to thermostatted near equilibrium steady states.

5. THE APPROACH TO EQUILIBRIUM

Consider a thermostatted or ergostatted dissipative system,

$$\begin{aligned} \dot{\mathbf{q}}_i &= \frac{\mathbf{p}_i}{m} + \mathbf{C}_i \bullet \mathbf{F}_e \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i + \mathbf{D}_i \bullet \mathbf{F}_e - \alpha \mathbf{p}_i \end{aligned} \quad . \qquad (14)$$

The system is time reversible and chaotic. Gallavotti (in 1996) [36] was the first to point out that, at least in the case of ergostatted dynamics, the GCFT (and hence equivalently the SESFT), can be used to derive the well known Green-Kubo relations for linear (near equilibrium) transport coefficients [37]. Later Searles and Evans [38] showed that the SESFT for thermostatted systems could also be used to derive correct Green-Kubo relations for linear transport coefficients [39, 40]. We now show that in the Nosé-Hoover thermostatted case where,

$$\dot{\alpha} = \frac{1}{Q}\left(2K - dNk_B T\right) = \frac{2K_0}{Q}\left(K/K_0 - 1\right) \equiv \left(K/K_0 - 1\right)/\tau^2 \qquad (15)$$

(where Q is related to the relaxation time τ, of the thermostat, K is the peculiar kinetic energy and K_0 is some chosen fixed value of the peculiar kinetic energy, $Q = 2K_0\tau^2$), the GCFT does not correctly describe near equilibrium fluctuations in the phase space compression factor and therefore does not lead to the correspondingly correct Green-Kubo relations for linear transport coefficients. This would seem to imply that the Chaotic Hypothesis is not applicable to Nosé-Hoover thermostatted near equilibrium steady states.

The Nosé-Hoover canonical (equilibrium) distribution is:

$$f_c(\mathbf{\Gamma},\alpha) = \frac{\exp(-\beta(H_0 + \frac{1}{2}Q\alpha^2)}{\int d\alpha \int d\mathbf{\Gamma} \exp(-\beta(H_0 + \frac{1}{2}Q\alpha^2)}, \tag{16}$$

from which the distribution of $\{\alpha\}$ can be obtained by integration,

$$f_c(\alpha) = \frac{\exp(-\frac{1}{2}\beta Q\alpha^2)}{\int d\alpha \exp(-\frac{1}{2}\beta Q\alpha^2)} = \sqrt{\frac{\beta Q}{2\pi}} \exp(-\frac{1}{2}\beta Q\alpha^2) \tag{17}$$

which is Gaussian with a variance $\sigma_\alpha^2 = 1/(\beta Q)$. At equilibrium, the distribution of $\overline{\alpha}_t$ is also Gaussian because it is just the time integral of α. For any value of the external field, F_e, and any fixed number, m, of standard deviations from the mean, the distribution of time averaged values of α, namely $f_c(\overline{\alpha}_t)$, will become more and more Gaussian as the averaging time increases. This is a result of the Central Limit Theorem (CLT) which is valid for chaotic systems and is independent of the particular distribution of α,

$$\lim_{t\to\infty} f_c(\overline{\alpha}_t) = \frac{1}{\sqrt{2\pi\sigma^2_{\overline{\alpha}_t}}} e^{(-(\overline{\alpha}_t - \overline{\overline{\alpha(F_e)}})^2/(2\sigma^2_{\overline{\alpha}_t}))}, \quad -m\sigma_{\overline{\alpha}_t} < \overline{\alpha}_t - \overline{\overline{\alpha(F_e)}} < m\sigma_{\overline{\alpha}_t}. \tag{18}$$

The variance of the time average of α, $\overline{\alpha}_t$, is,

$$\lim_{t\to\infty} \sigma^2_{\overline{\alpha}_t} = c/(t\beta Q) = O(1/Nt). \tag{19}$$

where c is a constant. Thus the variance goes to zero as the averaging time goes to infinity. In the weak field limit the mean of the distribution (18) is,

$$\lim_{F_e \to 0} \overline{\overline{\alpha(F_e)}} = -\beta \bar{\bar{\mathbf{J}}} V \bullet \mathbf{F}_e / dN = \beta L(F_e = 0) V F_e^2 / dn = O(F_e^2). \qquad (20)$$

Now we want to consider the limit $t \to \infty$, so that we can simultaneously:

- generate fully converged Green-Kubo integrals;
- ensure that (near the mean) the distribution of $\overline{\alpha}_t$ can be exactly described by a Gaussian and,
- ensure that the GCFT, which is only valid asymptotically in time, yields accurate predictions.

However as we increase the integration time the variance of the distribution of $\overline{\alpha}_t$ gets ever smaller. This implies that for fixed F_e, the mean of the distribution of $\overline{\alpha}_t$, which has a fixed mean value $\overline{\overline{\alpha}}$, moves more and more standard deviations away from zero. To ensure that the GCFT applies to typical fluctuations of $\overline{\alpha}_t$, namely $\pm\overline{\overline{\alpha}}$, and to have the distribution described accurately as a Gaussian at these typical conjugate values $\pm\overline{\overline{\alpha}}$, we propose to take the following limits simultaneously: $t \to \infty$ AND $F_e \to 0$ while keeping $\overline{\overline{\alpha}} / \sigma_{\overline{\alpha}_t} = r$ constant. Thus we take the limit $t \xrightarrow[(F_e = r^{1/2} t^{-1/4})]{} \infty$. To simplify notation we denote this limit simply as $\lim_{\substack{t \to \infty \\ F_e \to 0}}$.

Using this procedure, the CLT ensures,

$$\frac{1}{t}\ln\frac{\Pr(\overline{\alpha}_t = A)}{\Pr(\overline{\alpha}_t = -A)} = \frac{2A\overline{\overline{\alpha(F_e)}}}{\sigma^2_{\overline{\alpha}_t} t} + \varepsilon, \tag{21}$$

where ε becomes arbitrarily small in the limit: $\lim_{\substack{t\to\infty \\ F_e\to 0}}$. This procedure restricts us to the linear regime, close to equilibrium since the field must tend to zero.

If the GCFT applies then,

$$\lim_{t\to\infty}\frac{1}{t}\ln\frac{\Pr(\overline{\Lambda}_t = A)}{\Pr(\overline{\Lambda}_t = -A)} = -A \tag{22}$$

where $\overline{\Lambda}_t$ is the time-average phase space contraction rate. For a Nosé-Hoover thermostatted system,

$$\Lambda = -dN\alpha \tag{23}$$

and equation (22) yields,

$$\lim_{t\to\infty}\frac{1}{t}\ln\frac{\Pr(\overline{\alpha}_t = A)}{\Pr(\overline{\alpha}_t = -A)} = dNA. \tag{24}$$

Combining equation (24) with equation (21) gives,

$$\lim_{\substack{t\to\infty \\ F_{e\to 0}}}\left[\overline{\overline{\alpha(F_e)}} = \frac{dN\sigma^2_{\overline{\alpha}_t} t}{2}\right]. \tag{25}$$

This result is obviously incorrect. The value of the LHS, $\overline{\overline{\alpha(F_e)}}$ approaches zero as $F_e^2 = O(t^{-1/2}) \to 0$. While for Nosé-Hoover dynamics, the RHS approaches a constant as $t \to \infty$. The application of the CLT in this double limit cannot be questioned, therefore we must conclude that the GCFT incorrectly describes these time averaged fluctuations in the phase space compression factor. If we look at (25) more closely we can see what is wrong. The correct limiting expression for the average value of α is [5],

$$\lim_{\substack{t\to\infty \\ F_{e\to 0}}}\left[\overline{\overline{\alpha(F_e)}} = -\beta V \mathbf{F}_e \bullet \int_0^\infty ds\langle \mathbf{J}(0)\alpha(s)\rangle\right]$$

$$= -\beta V \mathbf{F}_e \bullet \int_0^\infty ds\left\langle \mathbf{J}(0)\sum_i (\mathbf{p}_i(s)\bullet \mathbf{D}_i(s))/(2K_0)\right\rangle_{F_e=0} \bullet \mathbf{F}_e, \qquad (26)$$

$$= O(F_e^2)$$

where the second line is only applicable to isokinetic systems; whereas lines 1 and 3 are valid for both Nose-Hoover and isokinetic thermostats. In both cases this shows that the mean value of α goes to zero quadratically with the field strength. In contrast, equation (25), which is derived under the assumption that the GCFT holds, omits important cross correlations between fluctuations in α and the dissipative flux J, without which a correct expression for $\overline{\overline{\alpha(F_e)}}$ cannot be obtained.

We now repeat these arguments assuming that the SESFT holds. The steady state version of the ESFT for thermostatted systems states,

$$\lim_{t\to\infty}\frac{1}{t}\ln\frac{\Pr(\beta\bar{\mathbf{J}}_t V\bullet\mathbf{F}_e=A)}{\Pr(\beta\bar{\mathbf{J}}_t V\bullet\mathbf{F}_e=-A)}=-A. \tag{27}$$

Combining this with the CLT applied to fluctuations in the dissipative flux, and adopting the same procedure for the long time, small field limits, i.e. keeping $\bar{\bar{\alpha}}/\sigma_{\bar{\alpha}_t}=r$ constant, one obtains:

$$\frac{1}{t}\ln\frac{\Pr(\bar{J}_t=A)}{\Pr(\bar{J}_t=-A)}=-A\beta VF_e+\varepsilon_1=\frac{2A\bar{\bar{J}}}{t\sigma^2_{\bar{J}_t}}+\varepsilon_2. \tag{28}$$

where ε_1 and ε_2 become arbitrarily small in these limits. Note, we again take the limits simultaneously keeping, $F_e t^{1/4}$ constant (that is, $\bar{\bar{\alpha}}/\sigma_{\bar{\alpha}_t}=r$ is constant).

From (28) we see that,

$$L(F_e=0)\equiv\lim_{\substack{t\to\infty\\F_e\leftrightarrow 0}}\left[\frac{-\bar{\bar{\mathbf{J}}}\bullet\mathbf{F}_e}{F_e^2}=\frac{\beta Vt\sigma^2_{\bar{J}_t}}{2}\right]. \tag{29}$$

After some tedious manipulations of the integrals (see [38]) we find that

$$L(F_e=0)=\beta V\int_0^\infty ds\left\langle J_\gamma(0)J_\gamma(s)\right\rangle_{F_e=0}\quad,\gamma=x,y,z. \tag{30}$$

The notation $\langle ... \rangle_{F_e=0}$ denotes an ensemble average taken over thermostatted trajectories with the external field set to zero. This is the correct Green-Kubo expression for a linear transport coefficient $L(F_e = 0)$, of a thermostatted system [5].

6. CONCLUSION

Our analysis indicates that the GCFT does not apply to equilibrium or near equilibrium thermostatted steady states, since it does not correctly describe the corresponding fluctuations in time averages of the phase space compression factor. The same holds for the isothermal isobaric systems, and for any other thermostatted system whose phase space volumes are not conserved by the equilibrium dynamics. This conclusion is supported by the inability of current computer simulation calculations to verify the GCFT for thermostatted or barostatted near equilibrium dynamics [17]. These calculations show that the convergence of the left hand side of equation (2) becomes slower and slower as the steady state approaches an equilibrium state, and it is impossible to determine if equation (2) is valid. Even future simulations are likely to lead to the same conclusions, if the trend to slower and slower convergence rates for equation (2) is confirmed at ever smaller external fields. This is easy to understand, considering that the width of the probability distributions appearing in equation (2) typically has order $O(1/\sqrt{t})$. If the convergence rate of equation (2) drops below $O(1/\sqrt{t})$, it becomes impossible (even in principle) to check its validity. Fluctuations in time averages in the phase space compression factor would disappear before convergence of equation (2) is achieved. Therefore, we are lead to the conclusion that thermostatted systems are not sufficiently similar to Anosov systems for the CH to hold.

We find it hard to understand why changing the thermostatting mechanism from an ergostat to a thermostat, can have such drastic effects, since for *ergostatted* systems, the GCFT correctly describes equilibrium and near equilibrium fluctuations. In spite of the fact that there is little difference between the Lyapunov spectra of ergostatted and thermostatted

systems at the same macroscopic state point, evidently ergostatted near equilibrium microstates are Anosov-like whereas their thermostatted analogues are not Anosov-like.

In contrast, all numerical and experimental tests have validated the ESFTs. Moreover, when a corresponding theoretical analysis is made of the near equilibrium fluctuations, that analysis simply yields the well known and correct Green-Kubo expressions for the relevant linear transport coefficients.

We interpret our results as implying that the natural measures of thermostatted systems at, or close to equilibrium, are quite different from the SRB measures, from which the GCFT is derived. This is undoubtedly related to the fact that at equilibrium, phase space volumes are not preserved by the thermostatted dynamics.

We can demonstrate this quite clearly through the following example. Consider a constant kinetic energy system (rather than the Nosé-Hoover thermostatted systems considered previously in this paper). For such a system where the equations of motion take the form given in (14), consider the particular case where $\mathbf{C}_i = \mathbf{0}$. We can separate the contributions to the thermostat multiplier, $\alpha = \sum_i [(\mathbf{F}_i + \mathbf{D}_i \bullet \mathbf{F}_e) \cdot \mathbf{p}_i] / (2K_0)$, that are due to the external field from those that are intrinsic to the field free system. In such a case one can show that if one rewrites equation (2) so that it refers only to the fluctuations in the phase space compression factor that are *explicitly* due to the external field, we then obtain the correct description of both the near and at equilibrium fluctuations in the redefined phase space compression factor.

Furthermore, in the above example, as the field is increased, the full isokinetic thermostat multiplier α, will be increasingly dominated by the second, field dependent term. Thus even

if we do not separate the explicit field dependent contribution from the phase space compression factor it is clear that as the field increases the argument of the GCFT will be increasingly dominated by the explicitly field dependent term. Hence the GCFT given in equation (2) will be approximated more and more accurately as the field strength is increased (as long as fluctuations remain observable). This is not because the CH is more likely to apply at large fields (in fact the opposite is true) but because at larger field strengths fluctuations in the phase space compression factor more closely approximate those of the Evans Searles dissipation function, and ESFT then predicts the fluctuations correctly. This is consistent with the numerical results [17], and may explain the better numerical verification of FT for some systems as the chaoticity of a system decreases and field strength increases [17, 18].

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APPENDIX A: THE RUELLE DERIVATION OF GCFT APPLIED TO EQUILIBRIUM SYSTEMS

In his review, Ruelle [19] presents a derivation of the GCFT in which a geometric approach is taken, based on shadowing. Ruelle considers nonequilibrium steady states in the presence of a Gaussian isoenergetic thermostat (or ergostat), except when he treats the pairing theorem.

In Ruelle's notation [19], the dimensionless phase space contraction rate at x over time τ, $\varepsilon_\tau(x)$ is given by,

$$\varepsilon_\tau(x) = \frac{1}{\tau e_f} \sum_{k=0}^{\tau-1} \log J(f^k x)^{-1} \qquad \text{(A1)}$$

where e_f the average phase space contraction per unit time, f^k gives the time evolution of x, and J is the Jacobian of f with respect to the chosen metric. Comparing with the notation introduced above $\tau \equiv t$, $\varepsilon_\tau(x) \equiv \overline{\Lambda}_t / \overline{\overline{\Lambda}}$ and $e_f \equiv -\overline{\overline{\Lambda}}$. Equation (A1) excludes the cases with $e_f = 0$, and normalizes ε_τ to 1. Nevertheless, the division by e_f does not seem to be an essential ingredient of the proof of the GCFT, and the calculations presented in Sections 3.6-3.9 of reference [19] can apparently be carried out even when ε_τ is not normalized to 1. Assuming that this is the case, dynamics with $e_f = 0$ can be considered under the assumption that the CH holds for them, and Ruelle's derivation may then be repeated for the non-normalized phase space contraction rate,

$$\varepsilon_f^\circ(x) = \frac{1}{\tau} \sum_{k=0}^{\tau-1} \log J(f^k x)^{-1} \qquad \text{(A2)}$$

instead of the *dimensionless* phase space contraction rate. In general, $\varepsilon_f^\circ(x)$ takes a range of values for any system, even for equilibrium systems, but not for isoenergetic equilibrium systems which yield $\frac{1}{\tau}\sum_{k=0}^{\tau-1}\log J(f^k x)^{-1} = 0$ for any τ and any x. The range of possible values of $\varepsilon_f^\circ(x)$ can be written as $[-p^*, p^*]$ which is symmetric about 0 due to time-reversibility. Following Ruelle's derivation we obtain the result

$$p-\delta \le \lim_{\tau\to\infty}\frac{1}{\tau}\log\frac{\rho_f(\{x:\varepsilon_\tau^\circ(x)\in(p-\delta,p+\delta)\})}{\rho_f(\{x:\varepsilon_\tau^\circ(x)\in(-p-\delta,-p+\delta)\})} \le p+\delta \qquad \text{(A3)}$$

Here, as in Ruelle [19], ρ_f is the probability measure for x, undergoing the dynamics specified by f, and such that $\varepsilon_\tau^\circ(x)$ takes on a value in the specified range; $p\in[-p^*,p^*]$ while $\delta>0$ is a constant. To obtain this result the dynamics is assumed to be reversible, and f is assumed to be an Anosov diffeomorphism. However, if the dynamical system is a physical system at equilibrium (or more generally, $e_f = 0$), one has

$$\frac{1}{\tau}\log\frac{\rho_f(\{x:\varepsilon_\tau^\circ(x)\in(p-\delta,p+\delta)\})}{\rho_f(\{x:\varepsilon_\tau^\circ(x)\in(-p-\delta,-p+\delta)\})} = 0 \qquad \text{(A4)}$$

for *all* values of p and τ, which is in conflict with equation (A3). Thus the assumption that f is an Anosov diffeomorphism must not be verified by these equilibrium systems.

APPENDIX B: THE GCFT AND TESFT FOR ISOENERGETIC SYSTEMS

For the GCFT, consider a time reversible, dissipative and chaotic system. Take a long trajectory and break it in consecutive segments, each of duration t, and possibly separated by a decorrelation time t_d. The GCFT concerns the probability distribution (the normalized frequency of observation) of the quantity defined by:

$$\overline{\Lambda}_{t,k} = \frac{1}{t}\int_{kt_d+kt}^{kt_d+(k+1)t} d\tau\, \Lambda(\mathbf{\Gamma}(\tau)), \qquad k = 0,1,\ldots \tag{B1}$$

That is, $\overline{\Lambda}_{t,k}$ is the phase space contraction along the trajectory segment of length t. *If the system is Anosov,* and in the long t limit, the frequency with which $\overline{\Lambda}_{t,k}$ takes a value in the interval $B_{p,\varepsilon} = (p-\varepsilon, p+\varepsilon)$ can be approximated summing over the weights attributed by the SRB measure to certain cells of finer and finer Markov partitions. These are the cells whose "center" can be taken as the middle point of a trajectory segment of length t, whose phase space compression falls in $B_{p,\varepsilon}$. Their weights are approximated by the reciprocal of the Jacobians of the dynamics restricted to the unstable manifold of their center, over longer and longer time intervals. Let us denote by $J^{u}_{i,t}{}^{-1}$ such quantities, where i labels the cells, and t the length of the trajectory segment whose middle point lies in the ith cell.

If we denote by Pr the probability distribution of the values of $\overline{\Lambda}_t$, then, apart from errors which can be made arbitrarily small refining the partition and taking longer t, one can write

$$\Pr(\overline{\Lambda}_t \in B_{p,\varepsilon}) = \frac{1}{M}\sum_{E_p,\,\overline{\Lambda}_t \in B_{p,\varepsilon}} J^{u}_{i,t}{}^{-1} \tag{B2}$$

where M is a normalization constant, and the sum is carried over the cells E_p containing the middle point of a segment with phase space contraction in $B_{p,\varepsilon}$. *If the support of the SRB measure is the whole phase space,* as in the presence of weak dissipation, time reversibility guarantees that the support of Pr is symmetric around 0, and one can consider the ratio

$$\frac{\Pr(\overline{\Lambda}_t \in B_{p,\varepsilon})}{\Pr(\overline{\Lambda}_t \in B_{-p,\varepsilon})} = \frac{\sum_{E_p, \overline{\Lambda}_t \in B_{p,\varepsilon}} J_{i,t}^{u\ -1}}{\sum_{E_p, \overline{\Lambda}_t \in B_{-p,\varepsilon}} J_{i,t}^{u\ -1}} \qquad \text{(B3)}$$

Moreover, for every trajectory segment whose phase space contraction is $\overline{\Lambda}_t$, there is a trajectory segment whose phase space contraction is $\overline{\Lambda}_t$, so that all terms in the numerator of the right hand side of (B3) have a counterpart in the denominator, and the division of each term in the numerator by its counterpart approximately equals $\exp(pt)$. This value, then, approximately equals the ratio in (B3), and one obtains:

Theorem (Gallavotti-Cohen): *For a transitive, Anosov, time reversal invariant dynamical system, the following holds:*

$$\lim_{t\to\infty} \frac{1}{t} \frac{\Pr(\overline{\Lambda}_t \in B_{p,\varepsilon})}{\Pr(\overline{\Lambda}_t \in B_{-p,\varepsilon})} = p \qquad \text{(B4)}$$

apart from errors of order ε.

This is an equivalent way of writing equation (2). The right hand side of equation (B4) is p as long as dissipation is not too high, so that the unstable manifold is dense in the phase space.

We now give a derivation of the TESFT for isoenergetic systems, presented in a way in which the differences between this theorem and the GCFT are made clear. Consider a microcanonical ensemble of time reversal invariant, dissipative systems; but do not require any chaos. Denote by E_p the set of all initial conditions $\mathbf{\Gamma}$ in the phase space, for which the phase space contraction

$$\overline{\Lambda}_t(\mathbf{\Gamma}) = \frac{1}{t}\int_0^t d\tau\, \Lambda(\mathbf{\Gamma}(\tau)) \qquad \text{(B5)}$$

lies in $B_{p,\varepsilon}$, and denote its volume by $V(E_p)$. Denote by S^tE_p the evolution of the set E_p for a time t under the isoenergetic dynamics. Then, the definition of p implies $V(S^tE_p) = e^{-pt}V(E_p)$, apart from small errors which can be made arbitrarily small taking ε correspondingly small. Consider the time reversal involution i, and set $A_p = iS^tE_p$, so that $\mathbf{\Gamma}^* \in A_p$ means that there is $\mathbf{\Gamma} \in E_p$ for which $\mathbf{\Gamma}^* = iS^t\mathbf{\Gamma}$. Then,

$$V(A_p) = \int_{A_p} d\mathbf{\Gamma}^* = \int_{E_p} J(iS^t\mathbf{\Gamma})d\mathbf{\Gamma} = \left[e^{-pt} + O(\varepsilon)\right]V(E_p) \qquad \text{(B6)}$$

because the Jacobian $J(iS^t\mathbf{\Gamma})$ is approximately constant in E_p. In fact, taking a point $iS^t\mathbf{\Gamma}$ with $\mathbf{\Gamma} \in E_p$ and computing its phase space contraction along a trajectory of length t starting at this point, and using time reversibility, one obtains,

$$\frac{1}{t}\int_0^t d\tau\ \Lambda(S^\tau i S^t \Gamma) = \frac{1}{t}\int_0^t d\tau\ \Lambda(S^\tau \Gamma) \in B_{-p,\varepsilon} \qquad \text{(B7)}$$

One also realizes that all points with phase space contraction in $B_{-p,\varepsilon}$ belong to A_p. This leads to:

$$\frac{V(E_p)}{V(E_{-p})} = \frac{V(E_p)}{V(A_p)} = e^{-pt} \qquad \text{(B8)}$$

except for corrections of order ε. Taking the logarithm of both sides of equation (B8), and considering the microcanonical probabilities of observing particular values of the phase space contraction are proportional to the volumes of the phase space sets, one obtains a relation formally similar to equation (B4).

This approach needs to be modified somewhat to obtain TESFTs for other ensembles since in general, the probabilities assigned by such ensembles to a given set of trajectories is not simply proportional to the volume occupied by their initial conditions: there will be different volume elements with the same values of $\overline{\Lambda}_t$, but with different probabilities. As a consequence, the probability of particular values of the phase space contraction over a time t will no longer be just the volume ratio, and the corresponding TESFTs will no longer be just an expression in terms of the phase space contraction. For a derivation of these FTs see [28].

However, the difference between the GCFT and the TESFT for the isoenergetic case is now clear. The first theorem is a statement on the relative frequency with which positive and negative phase space contractions occur along one long steady state trajectory. The second,

theorem is a statement on the relative frequency with which positive and negative phase space contractions are observed if we carry out many experiments starting from equilibrium states described by the microcanonical ensemble. Clearly, the TESFT remain valid under all circumstances, e.g. even under non-fluctuating dynamics, whereas the GCFT requires the dynamics to be chaotic in order to have fluctuations.

The ratio considered by the GCFT and the one considered by the TESFT turn out to be rather similar in form. This fact is not a mere accident, it is a consequence of the particular choice of the dissipation function and of the ensemble made in the TESFT, in the case of isoenergetic dynamics. A similar TESFT construction can be given for any thermostatted dynamics, by choosing the proper dissipation function, and the proper ensembles for each kind of dynamics. In all cases, the result turns out to be formally similar to equation (2), with $\overline{\Lambda}_t$ replaced by the appropriate dissipation function $\overline{\Omega}_t$ (cf. [28]).

This shows that equations formally similar to equation (2), although with a different content, can be obtained without recourse to the phase space steady state probability distribution.

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[41] Comparing with the notation used in our paper, $\rho_f(\{x:\varepsilon_\tau^\circ(x) \in (p-\delta, p+\delta)\}) \equiv \Pr(\overline{\Lambda}_t = -p)$ where $\overline{\Lambda}_t \in (p-\delta, p+\delta)$. Therefore (A3) can be written (in our notation) $p - \delta \le \lim_{t\to\infty} \frac{1}{t} \log \frac{\Pr(\overline{\Lambda}_t = -p)}{\Pr(\overline{\Lambda}_t = p)} \le p + \delta$.

Table I. Main ingredients of the GCFT and of the ESFT.

	GCFT (single trajectory; SS)	**TESFT (ensemble; transient)**	**SESFT (ensemble;SS)**	**SESFT (single trajectory; SS)**
Exploited dynamical symmetry	Time reversal invariance	Time reversal invariance	Time reversal invariance	Time reversal invariance
Domain of validity	$t \to \infty$	Any t	$t \to \infty$	$t \to \infty$
Initial distribution	Independent of initial (absolutely continuous) distribution.	Any known ergodically consistent, smooth distribution	Any known ergodically consistent, smooth distribution	For suitably ergodic systems, independent of initial distribution.
Conditions for validity	(i) Chaos needed (ii) Weak dissipation	(i) Chaos not explicitly needed	(i) Chaos not explicitly needed if the dissipation function is bounded	(i) Chaos needed (ii) ergodic/ unique steady state (iii) Weak dissipation
Argument of the FT	Probability of observing phase space contraction $\overline{\Lambda}_t$ in a time t along one steady state trajectory. For constant energy only, $\overline{\Lambda}_t = -\overline{\Omega}_t$	Probability of observing dissipation function $\overline{\Omega}_t$ in a time t along different trajectories sampled from a known initial distribution. For constant energy only, $\overline{\Lambda}_t = -\overline{\Omega}_t$	Probability of observing dissipation function $\overline{\Omega}_t$ in a time t along different trajectories that are allowed to reach a steady state before measurement of $\overline{\Omega}_t$ commences. For constant energy only, $\overline{\Lambda}_t = -\overline{\Omega}_t$	Probability of observing dissipation function $\overline{\Omega}_t$ in a time t along one steady state trajectory. For constant energy only, $\overline{\Lambda}_t = -\overline{\Omega}_t$