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

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ABSTRACT

We analyze time dependent fluctuations in the phase space compression factor of a class of N-particle systems that are at equilibrium or in steady states close to equilibrium. This class does not seem to include Anosov systems, and excludes isoenergetic systems, but includes most steady state systems considered in molecular dynamics. The fluctuation relation of the Gallavotti-Cohen Fluctuation Theorem (GCFT) has been proven for Anosov systems, but it is expected to apply more generally. This raises the question of which non-Anosov systems satisfy the fluctuation relation. The fluctuations of the equilibrium and near-equilibrium systems considered here do not seem to satisfy the fluctuation relation, although they seem to satisfy it when they are moderately far from equilibrium. We provide arguments to explain these facts.

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 that we refer to as a steady state Fluctuation Relation (FR). 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 (ESTFT) [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 each other and 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 peculiar kinetic energy of that system, called a "thermostat". These modified equations of motion were proposed simultaneously and independently by Hoover et al. [5] and Evans [6] in the mid 1980's and they have been studied theoretically and successfully employed in molecular dynamics computer simulations for two decades.

Reference [1] considered a very long phase space (steady state) trajectory of a Gaussian ergostatted, (*i.e.* isoenergetic) N-particle system [7]. 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 FR tested in reference [1] states that:

$$\frac{1}{t}\ln\frac{\Pr(\overline{\Lambda}_t = A)}{\Pr(\overline{\Lambda}_t = -A)} = -A \qquad \text{for large t.} \qquad (2)$$

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 for the Hamiltonian system described above (driven system plus reservoirs), if the degrees of freedom of the reservoirs are projected out.*

As it turns out, one finds that heat is on average removed from the non-Hamiltonian modified system, and that the corresponding phase space compression factor is nonzero and on average is negative.

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,

$$\frac{1}{t}\ln\frac{\Pr(\overline{[\beta\mathbf{J}]}_t V \bullet \mathbf{F}_e = A)}{\Pr(\overline{[\beta\mathbf{J}]}_t V \bullet \mathbf{F}_e = -A)} = -A \qquad \text{for large t,} \qquad (3)$$

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, [7],

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

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 FR were exploited almost interchangeably.

In this paper, we analyze time dependent fluctuations in the phase space compression factor for a class of systems that are at equilibrium or in steady states close to equilibrium. The particles are assumed to interact via the usual potentials used to represent atomic and molecular interactions in statistical mechanics and molecular modeling. The equilibrium dynamics for this class of system does not preserve the phase space volume instantaneously, therefore isoenergetic systems are excluded, but most molecular dynamics systems are included in our analysis.

Our work is motivated by the fact that numerical data do not seem to satisfy the FR of the GCFT (equation (2)) if the state of the systems under consideration is too close to an equilibrium state, while they seems to satisfy it if the systems are moderately far from equilibrium [9-11].

The GCFT has been proven for time reversible, dissipative, transitive Anosov systems, but it has been argued that the FR should apply more generally to systems of physical interest. Most of these systems can hardly be thought to be of the Anosov type, just as they cannot be considered ergodic. Therefore, the Chaotic Hypothesis (CH) was proposed in [4] in the hope that the class of systems satisfying the FR would be significantly larger than the class of Anosov systems. In a similar way the Ergodic Hypothesis justifies the equality of the time averages and ensemble averages of macroscopic variables to classes of system that are not strictly speaking ergodic.

This raises the question of which non-Anosov systems satisfy the FR of the GCFT, and the CH. To address this question, it is important to understand why certain molecular dynamics systems do not seem to satisfy the FR. This will lead to a better understanding of the meaning of the CH. To this purpose, we provide two theoretical arguments to explain the numerical results of [9-12]. Perhaps surprisingly, we find that the particle systems of the class mentioned above should not satisfy the FR of the GCFT when their steady states are close to equilibrium states.

In Section 2 we give a brief description of the CH and the GCFT, including a discussion of the conditions necessary for the GCFT. In Section 3 we describe the Evans-Searles FTs and highlight the differences between these theorems and the GCFT. In Section 4 we investigate

the possibility of extending the proof of the GCFT and its associated FR to equilibrium dynamics. We argue that except for constant energy dynamics, such an extension may lead to contradictions. This implies that the CH does not hold for these non-constant energy equilibrium systems. In Section 5 we reach an analogous conclusion for systems that are in the linear response regime close to equilibrium. We show that the GC FR is in contradiction with the known Green-Kubo relations for transport coefficients in thermostatted systems. Section 6 summarizes our results.

2. THE GALLAVOTTI-COHEN FLUCTUATION THEOREM

In 1995 Gallavotti and Cohen [4] justified 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. More precisely, for a dynamical system ($\mathcal{C}$,S) they assumed the following (p. 936 of [4]):

(A) *Dissipation:* The phase space volume undergoes a contraction at a rate, on the average, equal to $D\langle\sigma(x)\rangle_+$, where 2D is the phase space $\mathcal{C}$ dimension and $\sigma(x)$ is a model-dependent "rate" per degree of freedom.

(B) *Reversibility:* There is an isometry, i.e., a metric preserving map i in phase space, which is a map $i: x \to ix$ such that if $t \to x(t)$ is a solution, then $i(x(-t))$ is also a solution and furthermore i^2 is the identity.

(C) *Chaoticity:* The above chaotic hypothesis holds and we can treat the system ($\mathcal{C}$,S) as a transitive Anosov system.

The chaotic hypothesis that they referred to states (p. 935 of [4]):

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

Gallavotti and Cohen then showed the following (p. 963 of [4]):

Fluctuation Theorem: *Let (C,S) satisfy the properties (A)-(C) (dissipativity, reversibility, and chaoticity). Then the probability* $\pi_\tau(p)$ *that the total entropy production* $D\tau t_0\sigma_\tau(x)$ *over a time interval* $t = \tau t_0$ *(with* t_0 *equal to the average time between timing events) has a value* $Dt\langle\sigma(x)\rangle_+ p$ *satisfies the large-deviation relation*

$$\frac{\pi_\tau(p)}{\pi_\tau(-p)} = e^{Dt\langle\sigma\rangle_+ p} \qquad (6)$$

with an error in the argument of the exponential which can be estimated to be p, τ *independent.*

This means that if one plots the logarithm of the left-hand side of (6) as a function of p, one observes a straight line with more and more precision as τ becomes large…"

The above theorem is known as the Gallavotti Cohen Fluctuation Theorem or GCFT for short [13]. It should be noted that the GCFT only refers to phase space compression rate (called entropy production rate in [4], cf. p.936) and only to steady states. Apparently there is no 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 behave as though it was a time reversible Anosov diffeomorphism. Therefore, equation (2) should in principle 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. As a matter of fact, Gallavotti and Cohen, on p. 939 of [4] state: "*The details of the models described here* will not *be used in the following, since our main*

point is the generality of the derivation of a fluctuation formula from the chaotic hypothesis and its (ensuing) model independence." They then give various examples of models for which the CH is expected to hold.

The FR (6) of the GCFT is equivalent to equation (2), but written in different notation.

Reference [4] motivated numerical tests (e.g. [11, 14-16]) 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 [17, 18]), even though these experimental systems cannot be considered isoenergetic, and the experimental measurement of phase space contraction rates in non-isoenergetic 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 that has been attempted to determine whether a dissipative 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 dissipative 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, dissipative** systems in a steady state 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 [19, 20]. In addition, reference [10] gives numerical evidence that thermostatted systems satisfy equation (2) at very high shear rates, while at small shear rates [9, 11] it becomes very problematic, or even impossible to verify equation (2). As a matter of fact, the numerical results of [9, 11] suggest that as the system departs further from equilibrium, the data become more consistent with equation (2). If equation (2) affords the only possible characterization of the CH, these results appear in 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).

This is rather puzzling because there is no obvious reason why thermostatted (constant temperature) systems should behave so differently from ergostatted systems. Furthermore, it is our impression that the distance from equilibrium, or the amount of dissipation, which is invoked in the proof of the GCFT does not play an essential role in the derivation of equation

(2), as long as this dissipation is not exceedingly high [14]. Therefore, close to equilibrium and far from equilibrium thermostatted systems should not behave as differently as they do.

Thus, the domain of applicability of equation (2) and the CH is an open and quite intriguing question. In this paper we argue that equation (2) and the CH do not apply to thermostatted systems that are near, or at, equilibrium. Note the distinction between *thermostatted* systems, where the peculiar 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 [14] gives evidence for the validity of the GCFT for one such system, i.e. for a system of thermostatted-ergostatted hard discs. However, if the kinetic energy is constrained using a Nosé-Hoover thermostat, then we show that the CH does 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 relations for steady state systems which are similar in form to equation (2) but have different content or are applicable to systems including both deterministic and stochastic systems. See, for example, references [21-25]. Still other authors, refined the GCFT, cf. references [26-28].

Independently of this activity, in 1994 Evans and Searles derived the first of a set of fluctuation theorems (ESFTs) for nonequilibrium N-particle systems which focused on a quantity Ω, called the "dissipation rate", rather than on the phase space contraction rate, Λ [29, 30]. For thermostatted or ergostatted nonequilibrium steady state 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 given ensembles [31] of transient trajectories (ESTFTs), or given ensembles of steady state trajectories in the long time limit [30] (ESSFTs). The form of the resulting FRs is identical to equation (2), but contain different information since they are based on the statistics of the given ensembles of trajectories.

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 ESTFT 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 proceeds under the possible application of external fields and/or thermostats. One then obtains general transient fluctuation theorems (ESTFTs) stating that

$$\ln \frac{\Pr(\overline{\Omega}_t = A)}{\Pr(\overline{\Omega}_t = -A)} = At \tag{7}$$

which is of similar form to (2) but where the time averaged phase space contraction rate is replaced by the so-called time averaged dissipation rate or function, $\overline{\Omega}_t(\mathbf{\Gamma})$, and Pr represents the probability which is influenced by the chosen ensemble. In all the ESTFTs 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,

$$\int_0^t ds\, \Omega(\mathbf{\Gamma}(s)) \equiv \ln\left(\frac{f(\mathbf{\Gamma}(0),0)}{f(\mathbf{\Gamma}(t),0)}\right) - \int_0^t \Lambda(\mathbf{\Gamma}(s))ds = \overline{\Omega}_t t \tag{8}$$

for all positive times t.

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

$$\Omega(t) = -\Lambda(t) = -[\beta \mathbf{J}](t) V \bullet \mathbf{F}_e, \quad \text{when } dH_0 / dt = 0, \tag{9}$$

while for thermostatted dynamics (both isokinetic and Nose-Hoover), the dissipation function is subtly different,

$$\Omega(t) = -\beta \mathbf{J}(t) V \bullet \mathbf{F}_e, \qquad \text{constant temperature}$$

$$\neq \Lambda(t) = -\beta \mathbf{J}(t) V \bullet \mathbf{F}_e - \beta \dot{H}_0(t) \quad . \tag{10}$$

For isokinetic and isoenergetic dynamics, $\beta = 2K(\mathbf{\Gamma}) / dN$ where d is the Cartesian dimension of the space in which the system exists. For Nose-Hoover dynamics $\beta = 1/k_B T$ where k_B is Boltzmann's constant and T is the absolute temperature appearing in the Nose-Hoover equations of motion – see equation (20). It is clear that for constant temperature dynamics the dissipation function is different from the phase space compression factor. However, in all cases the time averaged dissipation function is equal (with probability one) to the average entropy production since $\lim_{t \to \infty} \overline{[\dot{H}_0]}_t = 0$ and $\lim_{t \to \infty} \overline{[\beta \mathbf{J}]}_t V \bullet \mathbf{F}_e = \lim_{t \to \infty} \overline{\Sigma}_t$ where Σ is the extensive entropy production that one would identify for near equilibrium systems from the theory of irreversible thermodynamics. The entropy production is a product of the thermodynamic force $\mathbf{F}_e$ and the time average of its conjugate thermodynamic flux, $\overline{[\beta \mathbf{J}]}_t$.

ESTFTs have been derived for an exceedingly wide variety of ensembles, dynamics and processes [30]. For example ESTFTs 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 ESTFTs have been verified in numerical experiments. Two ESTFTs 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 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 ESTFT can be stated as follows:

Theorem (Evans-Searles): *For any time reversible N-particle system, and for all positive 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:*

$$\frac{1}{t}\ln\frac{\Pr(\overline{\Omega}_t \in B_{p,\varepsilon})}{\Pr(\overline{\Omega}_t \in B_{-p,\varepsilon})} = p \qquad (11)$$

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 ESTFTs are not *only* true asymptotically in time but rather are valid for all times t.

Evans and Searles have also argued [30] 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 [30, Section 2.2].

Assuming the arguments of [30] holds, then one can derive asymptotic steady state FTs (ESSFTs) 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 [36]. It should also be noted that for nonergostatted systems the predictions of the ESSFTs 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 ESSFTs, 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 [9].

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 ESSFTs, in contradistinction to the ESTFTs, apply to steady states and are only valid at large t.*

The dissipation function that appears in the ESSFT for a single steady state trajectory is defined by (8), 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 [30]. This requires that the zero field system is ergodic and is at equilibrium.

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,

$$\frac{\Pr(\overline{\Lambda}_t(F_e = 0) = A)}{\Pr(\overline{\Lambda}_t(F_e = 0) = -A)} = 1 \quad \forall t\,. \tag{12}$$

This equation states that for all averaging times, the distribution of time averaged values of the phase space compression is precisely symmetric about zero. This is the special property of any equilibrium state. Comparing equation (2) with equation (12), one can see that for any finite averaging time t (no matter how large) with $A \neq 0$, equation (2) incorrectly predicts an asymmetry in the equilibrium distribution of time averaged values of the phase space compression factor. Therefore, for such systems, some assumptions that are invoked in the derivation of (2) must not hold. We argue below that the systems modeled by equilibrium thermostatted dynamics are of this type.

For simplicity, let us focus on systems whose equations of motion are:

$$\begin{aligned} \dot{\mathbf{q}}_i &= \frac{\mathbf{p}_i}{m} \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i - \alpha \mathbf{p}_i \end{aligned} \quad . \tag{13}$$

where α is a reversible thermostat multiplier that constrains the kinetic energy. We argue that the usual derivation of the FR might be adapted to consider non-dissipative systems of the kind (13), if the CH is assumed to hold for them. We show below that in this case we still get equation (2) – although this equation cannot be correct for these systems. This might imply that such systems violate the requirements of the CH in a rather substantial way. It would suggest that they might also do so even if driven to nonequilibrium steady states that are close to equilibrium. This suggestion, if correct, would provide one explanation of the numerical results of [9, 11].

This argument might also contribute to the clarification of the meaning of the CH, delimiting the range within which it yields correct results in a rather unexpected way. Equation (2), in fact, has been observed to describe systems quite similar to those considered here (see, for example, [1, 10]).

To understand this point, we analyze the proof of the GCFT given by Ruelle in Section 3 of reference [26]. In Ruelle's notation [26], the dimensionless phase space contraction rate at x over time τ, $\varepsilon_\tau(x)$ is given by,

$$\varepsilon_\tau(x) = \frac{1}{\tau e_f} \sum_{k=0}^{\tau-1} \log J(f^k x)^{-1} \qquad (14)$$

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 (14) 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 in [26], and the calculations presented in Sections 3.6-3.9 of reference [26] 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,

$$\varepsilon_f^\circ(x) = \frac{1}{\tau}\sum_{k=0}^{\tau-1} \log J(f^k x)^{-1} \tag{15}$$

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. If our assumption is correct then, following the same steps of Ruelle's proof, one would obtain a relation formally identical to that reported in Section 3.9 of [26]. Differently from Ruelle's case, this procedure would not yield a dimensionless expression, and whether e_f is equal to zero or not would seem to make no difference. One could then write,

$$p - \delta \le \lim_{\tau\to\infty} \frac{1}{\tau} \log \frac{\rho_f(\{x:\varepsilon_\tau^\circ(x) \in (p-\delta, p+\delta)\})}{\rho_f(\{x:\varepsilon_\tau^\circ(x) \in (-p-\delta, -p+\delta)\})} \le p + \delta \tag{16}$$

Here, as in Ruelle [26], ρ_f would be the probability, under the dynamics specified by f, that $\varepsilon_\tau^\circ(x)$ took on a value $p \in [-p^*, p^*]$, while $\delta > 0$ would be an arbitrarily small constant.

To obtain this result the dynamics is assumed to be of the Anosov type, which should imply that the phase space contraction rate is a bounded function (assumed to be Holder continuous in [26]). For equilibrium isokinetic dynamics, the width of the interval $[-p^*,p^*]$ can be easily estimated. One finds that the average phase space contraction rate, over a time t, is proportional to $(\Phi(t)-\Phi(0))/t$ where $\Phi(t)$ is the value of the interaction potential at time t. If Φ is bounded, the largest fluctuation goes as 1/t, and one then obtains $p^* = 0$. Differently, if Φ is not bounded, one may have $p^* > 0$, and indeed, even $p^* = \infty$. According to the derivation above, in the case of bounded Φ, (16) is not bracketed between $p-\delta$ and $p+\delta$, but between $-\delta$ and $+\delta$, and is then not in contradiction with equation (12). The content of (16) would be trivially correct. In the case of unbounded Φ, (16) could be valid for $p \in (-\infty,\infty)$, i.e. for all p. However, in this case, equation (16) does not describe the fluctuations of $\varepsilon_f^\circ(x)$. This suggests that one of the assumptions made in the derivation is not met by these systems, and might mean that these systems are not encompassed by the CH. The Nosé-Hoover thermostat is another thermostat that is widely used, and generates the canonical equilibrium distribution. In this case $p \in (-\infty,\infty)$, irrespective of the boundedness of the interaction and again, if the CH holds, the derivation above leads to (16) which contradicts equation (12) and does not describe the fluctuations of $\varepsilon_f^\circ(x)$ correctly.

The equilibrium systems considered above are clearly not Anosov, however equation (2) has been tested numerically for a wide range of systems, none of which, to the best of our knowledge, meets all the conditions that the proof [26] requires. For instance, the models of [1, 10, 15, 16] are not expected to be uniformly hyperbolic; those of [14, 19, 20] have singularities; and the flat billiards of [19, 20] are not even chaotic (that is, have no positive

Lyapunov exponents). But for them the FR has been shown to hold, and the CH considered appropriate to describe them. In other words, although the Anosov property is violated for these systems, this violation did not appear substantial. In some cases [10] the systems would collapse to the equilibrium systems considered above if the field was set to zero. It therefore seems interesting to consider the derivation above for equilibrium thermostatted systems in order to see what result is obtained.

The above analysis directs our attention towards the role of p^* in the proof of the GCFT, and could provide one explanation of the results of [9, 11, 12]. Indeed, assume that the FR fails at equilibrium for certain systems because they have $p^* = \infty$. Then, the FR would have to fail for the same systems when they are driven to nonequilibrium steady states that are sufficiently close to equilibrium. Indeed, if the range of fluctuations is $(-\infty,\infty)$ at equilibrium, it remains so under a small driving field because application of the external field does not remove the singularities in the phase space contraction rate.

However, this explanation is not satisfactory as the systems of reference [10] have singular phase space contraction rates (hence $p^* = \infty$) and yet satisfy (2). One could argue that the large fields of [10] make the largest fluctuations so rare (cf. Section 1 of [10]) that p* practically reduces to a finite constant.

However, many other scenarios are consistent with the available numerical evidence. For instance, one subtle violation of the CH could be inferred from the fact that the number of positive finite time Lyapunov exponents fluctuates along phase space trajectories of our thermostatted systems. This indicates that the continuous splitting of the tangent space of our

dynamics, required by the Anosov condition, does not even approximately hold for our systems.

Another possible scenario which will be investigated in section 5, concerns the times of convergence of equation (2). If these times are too long the CH is invalid in a practical sense.

In contrast to the discrepancy between (2) and (12) for isothermal systems, for an ensemble of isothermal systems the ESTFT (7), can be rewritten as,

$$\frac{1}{t}\ln\frac{\Pr(\bar{J}_t = A)}{\Pr(\bar{J}_t = -A)} = -\beta A V F_e \qquad (17)$$

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 (17) 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.

In the above, we concluded that the FR given in equation (2) does not apply to *thermostatted* equilibrium systems. However for *ergostatted* equilibrium states the ESTFT (equation (7)) and equation (2) both make correct statements about the equilibrium symmetry of fluctuations. For equation (2) this is due to the fact that $p^* = 0$, while for the ESTFT for ergostatted systems can be written as

$$\frac{1}{t}\ln\frac{\Pr(\overline{[\beta J]}_t = A)}{\Pr(\overline{[\beta J]}_t = -A)} = -A V F_e. \qquad (18)$$

In (18) J refers to the component of **J** that is parallel to $\mathbf{F}_e$, so when the field is zero, the ESTFT 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.

In the next section we discuss the application of the FR to thermostatted near equilibrium steady states.

5. THE APPROACH TO EQUILIBRIUM

Consider a thermostatted or ergostatted dissipative system,

$$\begin{aligned} \dot{\mathbf{q}}_i &= \frac{\mathbf{p}_i}{m} + \mathbf{C}_i \bullet \mathbf{F}_e \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i + \mathbf{D}_i \bullet \mathbf{F}_e - \alpha \mathbf{p}_i \end{aligned} \quad . \tag{19}$$

The system is time reversible and chaotic. Gallavotti (in 1996) [37] was the first to point out that, at least in the case of ergostatted dynamics, the GCFT (and hence equivalently the ESSFT), can be used to derive the well known Green-Kubo relations for linear (near equilibrium) transport coefficients [38]. Later Searles and Evans [39] showed that the ESSFT for thermostatted systems could also be used to derive correct Green-Kubo relations for linear transport coefficients [40, 41]. We now show that in the Nosé-Hoover thermostatted case where,

$$\dot{\alpha} = \frac{1}{Q}\left(2K - dNk_B T\right) = \frac{2K_0}{Q}\left(K/K_0 - 1\right) \equiv \left(K/K_0 - 1\right)/\tau^2 \tag{20}$$

(where $Q = 2K_0\tau^2$ is related to the arbitrary 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), the FR for phase space compression (equation (2)) makes incorrect predictions, and is inconsistent with the 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:

$$f_c(\mathbf{\Gamma},\alpha) = \frac{\exp(-\beta(H_0 + \frac{1}{2}Q\alpha^2)}{\int d\alpha \int d\mathbf{\Gamma} \exp(-\beta(H_0 + \frac{1}{2}Q\alpha^2)}, \tag{21}$$

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

$$f_c(\alpha) = \frac{\exp(-\frac{1}{2}\beta Q\alpha^2)}{\int d\alpha \exp(-\frac{1}{2}\beta Q\alpha^2)} = \sqrt{\frac{\beta Q}{2\pi}} \exp(-\frac{1}{2}\beta Q\alpha^2) \tag{22}$$

which is Gaussian with a variance $\sigma_\alpha^2 = 1/(\beta Q)$. [42] Assuming equations (21) and (22) hold for our equilibrium systems, the distribution of $\overline{\alpha}_t$ is also Gaussian because it is just the time integral of α. From the equations of motion (19, 20) we see that the rate of change of the extended Nose-Hoover Hamiltonian $H_0' \equiv H_0 + \frac{1}{2}Q\alpha^2$, is

$$dH_0'/dt = -JVF_e - dNk_B T\alpha. \tag{23}$$

The external field contributes to the fluctuations in the phase space compression factor. This contribution cannot be expected to be Gaussian except when long time averages are made near the mean of the distribution.

From (23) we see that,

$$(H_0'(t) - H_0'(0))/t \equiv \Delta H_0'(t)/t = -\bar{J}_t V F_e - dNk_B T\bar{\alpha}_t \qquad (24)$$

So the variance of time averages of α contains, to leading order, two contributions,

$$\sigma^2_{\bar{\alpha}_t} = (\sigma^2_{\Delta H_0'(t)}/t^2 + V^2F_e^2\sigma^2_{\bar{J}_t})/(dNk_BT)^2 . \qquad (25)$$

Because we assume a steady state, in the long time limit, $\sigma^2_{\Delta H_0'(t)}$ is independent of t. From [39] we know that for sufficiently long times,

$$t\sigma^2_{\bar{J}_t} = 2L(F_e)k_BT/V + O(F_e^2t^{-1}N^{-1}) \qquad (26)$$

and we also know from the Green-Kubo relations that, $\lim_{F_e\to 0} L(F_e) = L(0)$ is the linear transport coefficient defined by the linear constitutive relation,

$$\lim_{F_e\to 0}\lim_{t\to\infty}\frac{\bar{J}_t}{F_e} = L(0). \qquad (27)$$

We also note that at nonzero fields $L(F_e)$ has no simple relation to the nonlinear transport coefficient for the process [39].

Substituting (26) into (25) gives, at long times and small fields,

$$\begin{aligned}\sigma^2_{\bar{\alpha}_t} &= \sigma^2_{\Delta H_0'(t)}/(dNk_BTt)^2 + 2VF_e^2L(F_e)/(tk_BT(dN)^2) + O(F_e^4t^{-2}N^{-1}) \\ &= O(t^{-2}N^{-1}) + O(F_e^2t^{-1}N^{-1})\end{aligned} \qquad (28)$$

.

For any fixed non zero field, no matter how small, at sufficiently long times the second term dominates.

In the weak field limit the mean of α is,

$$\overline{\overline{\alpha(F_e)}} = -\beta \bar{\bar{\mathbf{J}}} V \bullet \mathbf{F}_e / (dN) \sim \beta L(F_e = 0) V F_e^2 / (dN) = O(F_e^2) \quad \text{for small } F_e. \qquad (29)$$

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

- generate fully converged Green-Kubo integrals;
- ensure that t is a large as required by the FR of equation (2); and
- ensure that (near the mean) the distribution of $\bar{\alpha}_t$ can be described by a Gaussian,

However as we increase the integration time t, the variance of the distribution of $\bar{\alpha}_t$ gets ever smaller. This implies that for fixed F_e, the mean of the distribution of $\bar{\alpha}_t$, which has a fixed mean value $\bar{\bar{\alpha}}$, moves more and more standard deviations away from zero. This makes it dubious that symmetric fluctuations, like $\pm\bar{\bar{\alpha}}$, which are the object of equation (2), be described by a Gaussian distribution at long times with fixed F_e. To ensure that the typical fluctuations of $\bar{\alpha}_t$, namely $\pm\bar{\bar{\alpha}}$, have their distribution described accurately as a Gaussian, we propose to take the following limits simultaneously: $t \to \infty$ AND $F_e \to 0$ while keeping $\bar{\bar{\alpha}} / \sigma_{\bar{\alpha}_t} = r$ constant.

Substituting from equations (28) and (29) gives,

$$r^2 = \frac{\bar{\bar{\alpha}}^2}{\sigma^2_{\bar{\alpha}_t}} = \frac{F_e^4}{a/t^2 + bF_e^2/t} \tag{30}$$

where a,b are constants independent of t, F_e. Solving this quadratic equation for F_e^2 shows that we must take the limit $t \xrightarrow[(F_e = ct^{-1/2})]{} \infty$, where c is a constant. To simplify notation we denote this limit simply as $\lim_{\substack{t\to\infty \\ F_e\to 0}}$.

Using this double limit, if we compute the left hand side of equation (2) then the distribution of alpha will be Gaussian near the typical values of A required by equation (2) for longer and longer t. This gives:

$$\lim_{\substack{t\to\infty \\ F_e\to 0}} \frac{1}{t} \ln \frac{\Pr(\bar{\alpha}_t = A)}{\Pr(\bar{\alpha}_t = -A)} \sim \frac{2A\bar{\bar{\alpha}}(F_e)}{\sigma^2_{\bar{\alpha}_t} t}$$

$$= \frac{2A\beta LVF_e^2/(dN)}{\sigma^2_{\Delta H'_0(t)}/(t(dNk_BT)^2) + 2VF_e^2L/(k_BT(dN)^2)} \tag{31}$$

$$= \frac{dNA}{(\sigma^2_{\Delta H'_0(t)}/(2VF_e^2Ltk_BT) + 1)}$$

$$= dNA(1 + O(1)) \neq dNA$$

This result is contrary to the result inferred from equation (2), namely dNA.

Of course, equation (2) requires the time to become very large at fixed F_e, hence one might question the relevance of our procedure that requires double limits to be taken. However, we see just two possible scenarios that can be considered. For any field, there will be a

maximum t for which the distribution of the phase space contraction can be considered to be Gaussian at $\pm\overline{\overline{\alpha}}$. The first scenario assumes that this time, ($t = c^2F_e^{-2}$) is sufficient for equation (2) to be verified with good accuracy. In this case, equation (31) shows that the prediction of equation (2) is incorrect, indicating that the CH is violated. The second scenario assumes that the value of t required for an accurate verification of equation (2) is longer than $c^2F_e^{-2}$. Clearly, for sufficiently small F_e, the verification of equation (2) becomes out of reach, and therefore in this case the CH must be violated for any practical purpose. We conclude that, in accord with Section 4, fluctuations in the Nose`-Hoover near equilibrium thermostatted dynamics are not consistent with (2) at finite times, and therefore these systems must violate the requirements of the CH in a rather substantial way.

The results of [9], and the argument here suggest that if equation (2) is to apply to the systems considered, the error term in equation (2), which is of order O(1/t) for Anosov systems must be strongly field dependent, and that the error term cannot be neglected at sufficiently small fields.

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

$$\frac{1}{t}\ln\frac{\Pr(\beta\overline{\mathbf{J}}_t V \bullet \mathbf{F}_e = A)}{\Pr(\beta\overline{\mathbf{J}}_t V \bullet \mathbf{F}_e = -A)} = -A \qquad \text{for large t.} \qquad (32)$$

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 $\overline{\overline{\Omega}}/\sigma_{\overline{\Omega}_t} = \left|\overline{\overline{J}}\right|/\sigma_{\overline{J}_t} = r$ constant, one obtains:

$$\frac{1}{t}\ln\frac{\Pr(\bar{J}_t = A)}{\Pr(\bar{J}_t = -A)} = -A\beta V F_e + \varepsilon_1 = \frac{2A\bar{\bar{J}}}{t\sigma^2_{\bar{J}_t}} + \varepsilon_2. \tag{33}$$

where ε_1 and ε_2 become arbitrarily small in these limits. Note, we again take the limits simultaneously keeping, $F_e^2 t$ constant (Note, keeping $\bar{\bar{\Omega}}/\sigma_{\bar{\Omega}_t} = \left|\bar{\bar{J}}\right|/\sigma_{\bar{J}_t} = r$ constant implies $F_e^2 t$ is constant. This is the same limit as that taken for equation (2).).

From (33) we see that,

$$L(F_e = 0) \equiv \lim_{\substack{t\to\infty \\ F_{e\to 0}}} \left[\frac{-\bar{\bar{\mathbf{J}}} \bullet \mathbf{F}_e}{F_e^2} = \frac{\beta V t \sigma^2_{\bar{J}_t}}{2} \right]. \tag{34}$$

After some tedious manipulations of the integrals (see [39]) we find that

$$L(F_e = 0) = \beta V \int_0^\infty ds \left\langle J_\gamma(0) J_\gamma(s) \right\rangle_{F_e = 0} \quad , \gamma = x, y, z. \tag{35}$$

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 [7].

6. CONCLUSION

Our analysis indicates that equation (2) does not apply to equilibrium or near equilibrium thermostatted steady states. 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. For equilibrium systems, adaptation of the derivation of equation (2) for Anosov systems [26] suggests that if the phase space contraction rate is bounded, equation (2) is only expected to be valid for A=0, and hence is trivially correct. However, if the phase space contraction is unbounded, this is not the case (cf Section 4). Furthermore equation (2) may not be applicable *in practice*, even if it does apply in the $t \to \infty$ limit (cf Section 5), and hence for the practical inapplicability of equation (2), the unboundedness of the phase space contraction rate does not seem to be necessary. Our conclusion is supported by the inability of current computer simulation calculations to accurately verify equation (2) for thermostatted or barostatted near equilibrium dynamics [9, 11, 12]. 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 for fixed values of the external field, 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.

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

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 seems to correctly describe 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 may be considered Anosov-like whereas their thermostatted analogues may not.

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, although the implications of this fact are not fully understood yet.

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 (19), 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.

Furthermore, in the above example, as the field is increased, the full isokinetic thermostat multiplier α, could be increasingly dominated by the second, field dependent term. In that case 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 FR will be increasingly dominated by the explicitly field dependent term. Hence the relation 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 could be related to the fact that, at larger field strengths, fluctuations in the phase space compression factor more closely approximate those of the dissipation function, Ω, which is the object of the ESFTs. These fluctuations are well behaved and satisfy the ESFTs for the presently accessible observation timescales. This is consistent with the numerical results [9, 11, 12], and may explain the better numerical verification of equation (2) for some systems as the field strength increases, and chaoticity decreases [9-12].

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its rigorous derivation from the dynamics is not yet possible. However, we adopt this f_c assuming that it describes the statistics of the Nosé-Hoover equilibrium dynamics, as is usually done.