

Independence of the transient fluctuation theorem to thermostating detailsStephen R. Williams,¹ Debra J. Searles,² and Denis J. Evans^{1,*}¹*Research School of Chemistry, Australian National University, Canberra, Australian Capital Territory 0200, Australia*²*School of Science, Griffith University, Brisbane, Queensland 4111, Australia*

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The fluctuation theorems show how macroscopic irreversibility arises from time reversible microscopic dynamics. They have been confirmed in computer simulations and in laboratory experiments. The standard proofs of the transient fluctuation theorems involve the use of time reversible deterministic thermostats to control the temperature of the system of interest. These mathematical thermostats do not occur in Nature. However, since in a gedanken experiment the thermostating regions can be removed arbitrarily far from the system of interest, it has been argued that the precise details of the thermostat cannot be important and that the resulting fluctuation theorems apply to natural systems. In this paper we give a detailed analysis showing how the fluctuation theorem is independent of the precise mathematical details of the thermostating mechanism for an infinite class of fictitious time reversible deterministic thermostats. Our analysis reinforces the implications of the gedanken experiment and implies that thermostats used in the derivations of fluctuation theorems are a convenient but ultimately irrelevant device.

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INTRODUCTION

If one wants to treat nonequilibrium dissipative systems that are maintained at a constant temperature, some form of thermostating mechanism must be employed. A natural procedure would be to surround the nonequilibrium system of interest with an extremely large inert block of heat conducting material—the thermal reservoir. If the heat capacity of the reservoir is much greater than that of the system of interest, then we can expect that the composite system may relax to a nonequilibrium quasi-steady-state in which the rate of temperature rise for the composite system is so small that it can be regarded as being zero. This approach is mathematically and computationally complex.

Twenty years ago Hoover *et al.* [1] and Evans [2] independently but simultaneously developed time reversible deterministic thermostats to enable convenient and efficient computer simulations of thermostatted dissipative systems. These thermostats do not exist in Nature but nonequilibrium statistical mechanics has been used to prove that under specific circumstances thermodynamic properties and transport coefficients computed from simulations using these thermostats are free of artifacts [3].

The development of fictitious mathematical thermostats and algorithms for simulating transport coefficients of nonequilibrium thermodynamic systems has led to an enormous advancement of nonequilibrium statistical mechanics [3]. These two developments have allowed the mathematical apparatus of dynamical systems theory to be brought to bear on statistical mechanics. Recently, thermostating mechanisms have been made more realistic by thermostating only part of a system (such as the walls). The synthetic thermostat does not directly modify the dynamics of the particles in the rest

of the system—the system of interest. An excellent review on thermostating has appeared recently [4].

One of the major achievements in this field was the discovery [5] and subsequent proof [6–9] (and references therein) of fluctuation theorems. The fluctuation theorem is also closely related to the Jarzynski equality, otherwise known as the nonequilibrium work relation [10]. For further information on fluctuation theorems see reviews [7,8]. These theorems showed for the first time how macroscopic irreversibility arises from time reversible microscopic equations of motion. A number of experimental tests have confirmed the predictions of some of these fluctuation theorems in the laboratory [11–13].

The standard proofs of the transient fluctuation theorems (TFTs) [7] involve the use of time reversible deterministic thermostats to control the temperature of the system of interest. These mathematical thermostats do not occur in Nature. In the present paper we give a detailed analysis showing how the fluctuation theorem is independent of the precise mathematical details of the thermostating mechanism for an infinite class of fictitious time reversible deterministic thermostats. Our analysis reinforces the view that the thermostats used in the derivations of fluctuation theorems are a convenient but ultimately irrelevant device [7].

THEORY

We denote the phase space vector $\Gamma \equiv (\mathbf{q}, \mathbf{p})$ of our system to consist of $2DN$ variables, \mathbf{q} being the position vector, \mathbf{p} the momentum vector, D the Cartesian dimension of the system, and N the number of particles. We divide the system into N_w wall or reservoir particles that are thermostatted, and are in contact with N_s particles that are not thermostatted. These latter particles comprise the nonequilibrium system of interest. They experience a dissipative field \mathbf{F}_e which does work on the system of interest, driving it away from equilibrium. This work is converted (irreversibly) into heat. This

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heat is removed by the thermostatted wall particles, allowing a nonequilibrium steady state to develop at sufficiently long times after the application of the dissipative field.

Consider the family of thermostats which, following Gauss's principle of least constraint [3,14,15], maintain the μ th moment of the momentum distribution for the wall particles,

$$g(\mu) = \sum_{i=1}^{N_w} (\mathbf{p}_i \cdot \mathbf{p}_i)^{\mu/2} = \sum_{i=1}^N s_i (\mathbf{p}_i \cdot \mathbf{p}_i)^{\mu/2} = g_0(\mu), \quad (1)$$

as a constant of the motion. In Eq. (1) \mathbf{p}_i denotes the momentum vector for the i th particle and $s_i=1$ for $i \leq N_w$ while $s_i=0$ for $i > N_w$, where we choose μ to be any real number with the provision $\mu > 1$ for $D=1$ and $\mu > 1-D/2$ for all higher dimensions, thus ensuring that the averages of all variables used in this paper converge. Using Gauss's principle of least constraint [3,14,15] we obtain the equations of motion for the system subject to the thermostating constraint $g(\mu)$:

$$\begin{aligned} \dot{\mathbf{q}}_i &= \mathbf{p}_i/m + (1-s_i)\mathbf{C}_i(\mathbf{\Gamma}) \cdot \mathbf{F}_e, \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i(\mathbf{q}) + (1-s_i)\mathbf{D}_i(\mathbf{\Gamma}) \cdot \mathbf{F}_e - (\mathbf{p}_i \cdot \mathbf{p}_i)^{\mu/2-1} s_i \alpha \mathbf{p}_i, \\ \alpha &= \frac{\sum_{i=1}^{N_w} (\mathbf{p}_i \cdot \mathbf{p}_i)^{\mu/2-1} \mathbf{p}_i \cdot \mathbf{F}_i}{\sum_{i=1}^{N_w} (\mathbf{p}_i \cdot \mathbf{p}_i)^{\mu-1}}. \end{aligned} \quad (2)$$

In these equations the dissipative field \mathbf{F}_e couples to the system via the dyadic phase functions $\mathbf{C}_i(\mathbf{\Gamma})$ and $\mathbf{D}_i(\mathbf{\Gamma})$. The phase space compression factor for the full system is defined as [3]

$$\Lambda(\mathbf{\Gamma}) = \frac{\partial}{\partial \mathbf{\Gamma}} \cdot \dot{\mathbf{\Gamma}}, \quad (3)$$

and determines the evolution of an infinitesimal volume element of phase space δV_{Γ} surrounding a trajectory $\mathbf{\Gamma}(t)$,

$$\delta V_{\Gamma}[\mathbf{\Gamma}(t)] = \exp \left[\int_0^t \Lambda(\mathbf{\Gamma}(s)) ds \right] \delta V_{\Gamma}(\mathbf{\Gamma}(0)). \quad (4)$$

Assuming in the absence of the thermostating terms that the phase space compression factor is zero (known as the adiabatic incompressibility of phase space) [3] and ignoring terms involving the momentum dependence of α [which is of $O(1/N_w)$ relative to the terms involving \mathbf{p}_i explicitly] we obtain the phase space compression factor for the μ th thermostat:

$$\Lambda(\mathbf{\Gamma}, \mu) = -\alpha(D + \mu - 2) \sum_{i=1}^{N_w} (\mathbf{p}_i \cdot \mathbf{p}_i)^{\mu/2-1}. \quad (5)$$

If the ratio N_w/N_s is large enough, the perturbation caused to the wall particles by the nonequilibrium system of interest can be regarded as infinitesimal. In this limit, the thermostating particles can be described by the appropriate equilibrium distribution.

Under these conditions we will now show that the phase space compression factor is solely determined by the rate of loss of energy (heat) from the total system due to the thermostat divided by the absolute temperature of that thermostat. Furthermore, the phase space compression factor is independent of the precise momentum moment μ that is constrained by the thermostat. The rate of change of the total internal energy [$H = \sum_i p_i^2/2m + \Phi(\mathbf{q})$] may be split into an adiabatic (or work) component $\dot{W}(t)$ and a heat transfer $\dot{Q}_{\mu}(t)$ component,

$$\dot{H}(t) = \dot{W}(t) + \dot{Q}_{\mu}(t),$$

$$\dot{Q}_{\mu}(t) = \frac{-\alpha(t)}{m} \sum_{i=1}^{N_w} (\mathbf{p}_i \cdot \mathbf{p}_i)^{\mu/2},$$

$$\dot{W}(t) = - \sum_{i=N_w+1}^N \left[\frac{\mathbf{p}_i}{m} \cdot \mathbf{D}_i - \mathbf{F}_i \cdot \mathbf{C}_i \right] \cdot \mathbf{F}_e \equiv -\mathbf{J}(\mathbf{\Gamma})V \cdot \mathbf{F}_e. \quad (6)$$

The term $\dot{Q}_{\mu}(t)$ is the change in energy due to the thermostat. It involves only the reservoir particles, as the particles in the system of interest are not thermostatted. In Eq. (6) \mathbf{J} is the so-called dissipative flux and V is the volume of the system of interest [3]. By construction the rate of change of the work $\dot{W}(t)$ only involves the coordinates and momenta of the particles in the system of interest—see Eq. (6). We will show that for sufficiently large N_w ,

$$\dot{Q}_{\mu} - k_B T \Lambda(\mathbf{\Gamma}, \mu) = 0 \quad \forall \quad \mu > 2 - D. \quad (7)$$

For the special case of $\mu=2$ this will be so regardless of the chosen value of N_w . Note that for a system with a large reservoir undergoing reversible heat transfer Eq. (7) shows that the phase space compression factor is related to the entropy lost from the thermostating reservoir region

$$\dot{Q}_{\mu}/T = \dot{S}_{res} = k_B \Lambda(\mathbf{\Gamma}, \mu) \quad \forall \quad \mu > 2 - D. \quad (8)$$

The kinetic temperature of the reservoir is defined by

$$k_B T \equiv \frac{1}{DmN_w} \sum_{i=1}^{N_w} \mathbf{p}_i \cdot \mathbf{p}_i. \quad (9)$$

Since the reservoir is very large compared to the dissipative system of interest, temperature gradients in the reservoir will be negligible, and we can assume that the momentum is distributed according to an equilibrium Maxwell-Boltzmann distribution in this region. The synthetic thermostat regulates the temperature of the reservoir and plays the role that circulating water often does in an experiment. The sum $\sum_{i=1}^{N_w} \mathbf{p}_i \cdot \mathbf{p}_i$ may be treated as an average $N_w \langle \mathbf{p}_i \cdot \mathbf{p}_i \rangle$. It is convenient to define

$$I(a,b) \equiv \int_0^\infty dx x^a \exp(-bx^2) \\ = \frac{1}{2} b^{-(1+a)/2} \Gamma((1+a)/2) \quad \forall a > -1, \quad (10)$$

where Γ denotes the gamma function, and then one can show that

$$\dot{Q}_\mu = \frac{-\alpha N_w I(D + \mu - 1, \beta/2m)}{mI(D - 1, \beta/2m)} \quad (11)$$

and

$$\Lambda = \frac{-\alpha(D + \mu - 2)N_w I(D + \mu - 3, \beta/2m)}{I(D - 1, \beta/2m)}. \quad (12)$$

Using Eqs. (11) and (12) and the relation $I(a,b) = (a-1) \times I(a-2,b)/2b$ it is easy to prove Eq. (7).

We can now derive the equilibrium distribution function for a large system of particles where the μ th moment of the momentum distribution is constrained using the dynamics defined by Eq. (2). The Liouville equation may be written as [3]

$$\frac{d}{dt} \ln f(\mathbf{\Gamma}(t), t) = -\Lambda(\mathbf{\Gamma}(t)), \quad (13)$$

where $f(\mathbf{\Gamma}, t)$ is the phase space distribution function at time t . When combined with Eq. (7) and the fact that the system is at equilibrium [$\dot{W}=0$ and thus $\dot{Q}(t)=\dot{H}(t)$] gives

$$\frac{d}{dt} \ln f(\mathbf{\Gamma}(t), t) = -\frac{\dot{H}(\mathbf{\Gamma}(t))}{k_B T}. \quad (14)$$

Upon integrating both sides with respect to time we obtain the distribution function

$$f_\mu(\mathbf{\Gamma}) = \frac{\exp[-\beta H(\mathbf{\Gamma})] \delta(g(\mu, \mathbf{\Gamma}) - g_0(\mu))}{\int d\mathbf{\Gamma} \exp[-\beta H(\mathbf{\Gamma})] \delta(g(\mu, \mathbf{\Gamma}) - g_0(\mu))}, \quad (15)$$

where $g_0(\mu)$ is the value to which the μ th moment is constrained, and $\beta=1/k_B T$ is the inverse thermal energy. In the case of the Gaussian isokinetic thermostat ($\mu=2$) the kinetic degrees of freedom are distributed microcanonically and the configurational degrees of freedom are distributed canonically; thus we have a clear link with equilibrium thermodynamics. For our system involving thermostatted wall particles this distribution function will be correct for the whole system given that there are enough thermostatted particles to make Eq. (7) valid: here $g(\mu, \mathbf{\Gamma})$ is only a function of the wall particle momenta.

After some rather tedious algebra one can prove that for systems in D Cartesian dimensions the μ th moments of the momenta are related to the equilibrium thermodynamic temperature by the equation

$$g_0(\mu) = N_w \frac{\Gamma((\mu+D)/2)}{\Gamma(D/2)} (2mk_B T)^{\mu/2}. \quad (16)$$

Since the distribution function for the thermostatted system is known, we can apply the TFT to these systems. The dissipation function appearing in the TFT is defined as [7]

$$\bar{\Omega}_t = \int_0^t ds \Omega(\mathbf{\Gamma}(s)) \equiv \ln \left[\frac{f(\mathbf{\Gamma}(0), 0)}{f(\mathbf{\Gamma}(t), 0)} \right] - \int_0^t \Lambda(\mathbf{\Gamma}(s)) ds. \quad (17)$$

The TFT then gives the probability ratio

$$\frac{p(\bar{\Omega}_t = A)}{p(\bar{\Omega}_t = -A)} = \exp[At]. \quad (18)$$

We may now combine Eqs. (7), (15), and (17) to show that, when the number of degrees of freedom in the walls is large and much larger than the number of degrees of freedom in the system of interest,

$$\bar{\Omega}_t = \beta(\Delta H(t) - \Delta Q_\mu(t)) \\ = \beta \Delta W(t) = -\beta \int_0^t ds \mathbf{J}(\mathbf{\Gamma}(s)) \cdot \mathbf{F}_e \quad \forall \mu > 2 - D. \quad (19)$$

Substituting into Eq. (18) gives

$$\frac{p(-\beta \bar{\mathbf{J}}_t \cdot \mathbf{F}_e = A)}{p(-\beta \bar{\mathbf{J}}_t \cdot \mathbf{F}_e = -A)} = \exp[AVt] \quad \forall \mu > 2 - D. \quad (20)$$

Equation (20), which is independent of the value of μ , is the central result of this paper.

SIMULATION

We test this theory by carrying out simulations using two thermostats, the usual Gaussian isokinetic thermostat $\mu=2$ and the higher constrained moment of $\mu=4$. We choose an application of the TFT that has been investigated in the past by both simulation and experiment [11]. A particle, immersed in a fluid, is held by a stationary harmonic well (optical trap in the experiment [11]) at equilibrium. At an arbitrary time $t=0$ the trap suddenly moves at a constant velocity. In the large thermostat limit we have just proved that the dissipation function is independent of the thermostating moment μ . The dissipation function has been given before [11] and is

$$\bar{\Omega}_t = \beta \int_0^t ds \mathbf{v}_{opt} \cdot \mathbf{F}_{opt} \quad \forall \mu > 2 - D. \quad (21)$$

Computer simulations were carried out in two dimensions using periodic boundary conditions and a Weeks-Chandler-Anderson (WCA) potential, the fluid number density was $\rho = N\sigma^3/V = 0.4$ where σ is the particle diameter from the WCA potential. The number of fluid particles in the system of interest was $N_s = 32$ and for the $\mu=2$ thermostat the num-

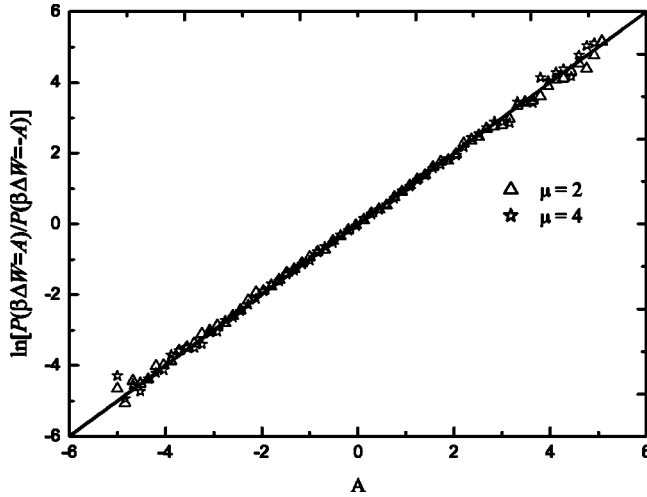


FIG. 1. TFT data. The $\mu=2$ thermostat simulation has 28 wall particles while the $\mu=4$ thermostat simulation has 112 wall particles.

ber of thermostatted wall particles was $N_w=28$ while for the $\mu=4$ thermostat systems with $N_w=28$ and $N_w=112$ were simulated. The thermostatted wall particles were harmonically bound to an ideal hexagonal lattice, with close packed layers aligned in the x direction of the Cartesian axis having seven particles per layer. The distance between these layers in the y direction was 1.1066 σ and the periodic distance in the y direction was such that the fluid was bound by close packed layers whose axes were separated by 8.9443 σ : the periodic distance in the x direction was 8.9443 σ . For both thermostats 2×10^5 trajectories were computed to form the averages with the trajectories being of duration $t=5.0$, in dimensionless time units. All other details were as reported by Wang *et al.* [11].

For all systems the kinetic temperature of the fluid particles increased, on average, by $\sim 2\%$ over the full duration of the trajectory, while the kinetic temperature of the wall particles did not change. For the $\mu=4$ thermostats the nominal dimensionless wall temperature was set at $T=1$ by fixing the constraint Eq. (1) to the value specified by Eq. (16). This resulted in an average kinetic temperature for the wall particles of $T=1.01$ for the $N_w=112$ system and $T=1.03$ for the $N_w=28$ system.

A direct test of Eq. (20) is plotted in Fig. 1 for the time $t=5.0$ where the trajectory finishes. This shows the logarithm of the probability ratio of observing a trajectory which has had a positive value for the time integral of the dissipation function relative to its negative, as a function of the integral value. For a dissipative field coupled with a large volume of particles or for long times this probability ratio diverges to infinity recovering the second law of thermodynamics. Equation (20) is expected to be valid for all N_w when $\mu=2$, and for large N_w in other cases. The figure shows excellent agreement between the data for both thermostats and the plotted prediction of Eq. (20). Note that in the case of the $\mu=4$ thermostat only the large $N_w=112$ system results are shown here.

The TFT Eq. (18) may be partially summed to obtain the integrated fluctuation theorem:

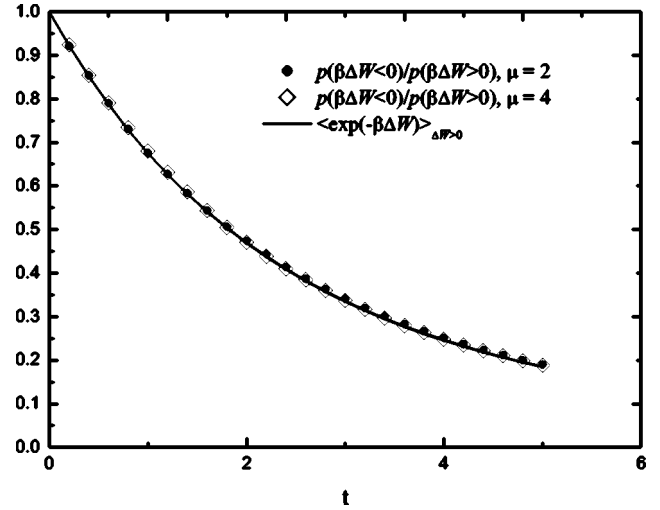


FIG. 2. IFT data. The $\mu=2$ thermostat simulation has 28 wall particles while the $\mu=4$ thermostat simulation has 112. The difference between $\langle \exp(-\beta\Delta W) \rangle_{\Delta W>0}$ for the two thermostats cannot be resolved on the scale of this figure.

$$\frac{p(\bar{\Omega}_t < 0)}{p(\bar{\Omega}_t > 0)} = \langle \exp(-\bar{\Omega}_t t) \rangle_{\bar{\Omega}_t > 0}. \quad (22)$$

The left-hand side (LHS) is the probability of observing a negative value for the dissipation function $\bar{\Omega}_t$, divided by the probability of observing a positive value. The RHS is an ensemble average formed from the set of trajectories which have a positive value for the dissipation function at time t . In Fig. 2 we plot both sides of Eq. (22) which have been calculated directly from our simulation data for both thermostats (again in the case of the $\mu=4$ thermostat only the large $N_w=112$ system results are shown). In both cases we observe excellent agreement.

In the case of the smaller $N_w=28$, $\mu=4$ thermostat system, systematic differences between the fluctuation relation that is derived for large thermostating regions and the simulation results are observed and this is shown in Fig. 3 for the case of the integrated fluctuation theorem. The systematic difference is a result of the distribution function for the wall particles' momentum being somewhat non-Gaussian due to both the heat flow from the system of interest and the constraint Eq. (1). As the number of wall particles is increased, while keeping both the system of interest and the field \mathbf{F}_e fixed, the heat flow per particle into the wall will decrease as will the effect of the constraint on its momentum distribution. As the number of wall particles increases, the wall can be approximated more and more accurately by equilibrium distributions. Again this difference would become insignificant for a system with a very large number of wall particles.

CONCLUSION

In this paper we have shown that if we study a nonequilibrium system which is in contact with a thermostat then when the number of degrees of freedom in the thermostat is large and also large compared to the number of degrees of

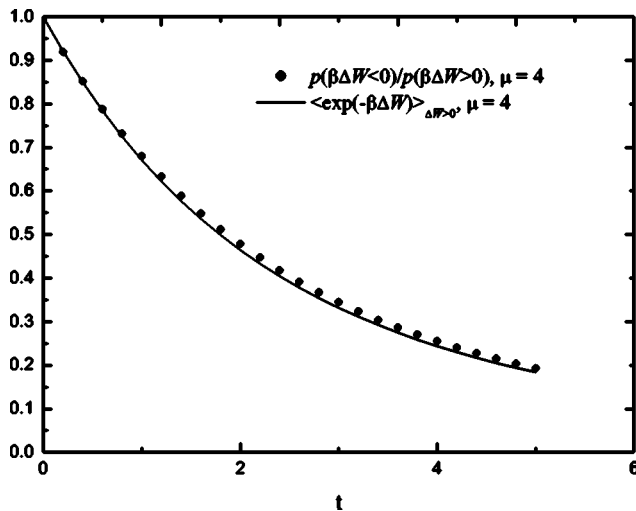


FIG. 3. IFT data. The simulation has 28 wall particles with a $\mu=4$ thermostat. A small systematic disagreement between the theory and the simulation may be seen.

freedom in the nonequilibrium system, the transient fluctuation relation is insensitive to the details of the thermostating mechanism. We have shown this both theoretically and numerically for a class of time reversible deterministic thermostats that fix various moments of the momentum distribution. In this large thermostat limit the TFT is independent of the precise moment that the thermostat fixes.

These results are thus consistent with the previous gedanken arguments that for large thermostats the fluctuation theorem is insensitive to the precise details of the thermostating mechanism, and although the fluctuation theorems may be derived using fictitious (i.e., unnatural) thermostats, the theorems nevertheless apply to natural systems.

One of the key results of this paper is Eq. (7). In a literal sense this equation says that there is an instantaneous relationship between the instantaneous phase space compression factor for the composite system and the instantaneous energy lost from the composite system due to the thermostat and the absolute temperature of the thermostat. This happens for any thermostat among the infinite family of thermostats considered here as long as the thermostat is sufficiently large that the thermostating region can be regarded as being at equilibrium. Because the thermostat can be regarded as at equilibrium, the energy lost to the thermostat can be regarded as *heat*. Furthermore, the heat loss divided by the absolute temperature is precisely the thermodynamic entropy lost from

the composite system through the boundary region to the thermostat. Again this relation is independent of the precise details of the thermostat.

Since Eq. (7) is true regardless of the mathematical form of the thermostat we propose the following conjecture. Consider a nonequilibrium dissipative system (the system of interest) embedded in an (initially) equilibrium nondissipative Hamiltonian system. This system of interest has a fixed number of particles and a fixed dissipative field F_e is applied for $t > 0$. Assume the initial equilibrium thermodynamic temperature of the embedding system is T . Very far from the system of interest, beyond the embedding system, there may be some form of μ thermostating region or the Hamiltonian embedding system may simply continue on forever, at temperature T .

If we consider a composite system (system of interest plus a surrounding sphere of the embedding system) of radius r , then for a fixed time $t > 0$, as r increases the embedding system located in the spherical shell region at $r \pm dr$ will be closer and closer to thermodynamic equilibrium. We can now apply Eq. (7) to relate the phase space compression of the composite (system of interest plus embedding) of radius r , $\Lambda_r(\Gamma)$, to the entropy lost from the composite system at radius r to the surrounding equilibrium (embedding) system \dot{S}_r :

$$\lim_{r \rightarrow \infty} \Lambda_r(\Gamma) = \dot{S}_r. \quad (23)$$

This equation is expected to be true regardless of whether ultimately at very large distances the composite system contains a time reversible deterministic thermostat or whether the Hamiltonian embedding system continues indefinitely. This equation relates entropy loss through an equilibrium boundary to the phase space compression of the phase space of the system enclosed within that boundary. In this sense phase space compression can occur in purely Hamiltonian (sub)systems, which is consistent with results obtained from theoretical work on simple models [16,17]. This occurs in spite of the obvious fact that in the full phase space of any Hamiltonian system the phase space compression is identically zero [18].

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