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Comment on "Toward a Statistical Thermodynamics of Steady States"

Tuckerman, Mundy, and Klein (TMK) [1] criticized our belief [2–4] that fractal distribution functions result from simulations of nonequilibrium steady states. TMK's argument includes an erroneous version of Liouville's phase-space continuity equation [5,6], as well as an unconventional *ad hoc* prescription for evaluating Gibbs' entropy from the phase-space distribution function f. Although it is universally agreed that Gibbs' system entropy is $-S_G/k \equiv \langle \ln f(q,p) \rangle$, and that steady nonequilibrium processes generate external entropy, TMK include an additional "Jacobian" J in the average:

$$J_t(q,p) \equiv (dqdp)_0/(dqdp)_t \equiv f_t/f_0.$$

TMK then define the nonequilibrium entropy as follows:

$$-S_{TMK}/k \equiv \int (dqdpJf)_t \ln f_t \equiv \int (dqdp)_0 f_t \ln f_t,$$

and claim that this leads to (i) a smooth steady-state distribution function f_∞ and (ii) finite steady-state entropy S_{TMK} and free energy A_{TMK}.

These results contradict those from a host of nonequilibrium simulations [2–4], using from one [3] to one hundred [4] particles. All these simulations have indicated multifractal distributions, with the many-body simulations establishing extensive order-N decreases in information dimension. All the phase-space distributions correspond to divergent steady-state entropies, $S_G = -\infty$. The qualitative nature of the one-body results has been established, rigorously, for the simplest one-particle model, by Chernov *et al.* The multifractal nature of the corresponding one-particle "Galton-Board" distribution function is quite apparent in the sample $\{qp\}$ Poincaré section shown in Fig. 1.

We see no reason to abandon either Liouville's continuity equation or Gibbs' definition for entropy. And because $S_G \neq S_{TMK}$, it is not surprising that the theoretical properties of entropy found by TMK are qualitatively different from those inferred from the simulations described in Refs. [2–4]. A further difficulty with S_{TMK} lies in the fact that J_t is well defined only for times t which are shorter than the phase-space mixing time.

TMK claim [1] that their entropy S_{TMK} and free energy A_{TMK} never deviate from those of the (completely arbitrary) initial state. TMK likewise "show" that the product Jf obeys the continuity equation—as also must the probability density—but TMK provide no means to evaluate either J or f, separately. Evidently the new results [1] found by TMK are artifacts based on an arbitrary phase-space flow equation and an equally unconventional definition of entropy. For a proper general treatment see [6].
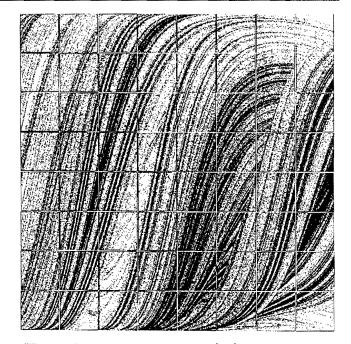
FIG. 1. Multifractal Galton-Board $\{qp\}$ Poincaré section.

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Comment on "Toward a Statistical Thermodynamics of Steady States"

In a recent Letter [1], Tuckerman, Mundy, and Klein propose a new framework for the statistical thermodynamics of nonequilibrium systems. Their starting point is an N-particle dynamical system in d dimensions, described by the phase space vector $\mathbf{\Gamma}(t) = (\mathbf{q}_1(t), \ldots, \mathbf{q}_N(t), \mathbf{p}_1(t), \ldots, \mathbf{p}_N(t))$. Next, they introduce a statistical mechanical ensemble of such systems, giving rise to the phase space distribution function $f(\mathbf{\Gamma}, t)$. The system is, furthermore, assumed to be closed in the sense that members of the ensemble may not appear or disappear in the course of time [2]. As a simple example, let us consider an ensemble consisting of a finite number of realizations $\mathbf{\Gamma}_m(t)$, $m = 1, \ldots, M$. An explicit definition of the phase space distribution function $f(\mathbf{\Gamma}, t)$ is not given in [1], implying that the usual (and natural) definition is adopted implicitly, namely that in our simple example $M f(\mathbf{\Gamma}, t) d\mathbf{\Gamma}$ equals the number of realizations contained in the infinitesimal phase space volume $d\mathbf{\Gamma}$ at time t. Thus, the phase space distribution function takes the explicit form:

$$f(\mathbf{\Gamma}, t) = \frac{1}{M} \sum_{m=1}^{M} \delta(\mathbf{\Gamma} - \mathbf{\Gamma}_m(t)). \qquad (1)$$

The systems addressed in [1] are not required to be isolated, i.e., they may exchange energy with a thermostat, and so, in general, the incompressibility of the phase space flow does not hold:

$$\nabla_{\mathbf{\Gamma}} \cdot \dot{\mathbf{\Gamma}} \neq 0. \qquad (2)$$

Notwithstanding, it follows from (1) that

$$\frac{d}{dt} \int d\mathbf{\Gamma} \, f(\mathbf{\Gamma}, t) = 0. \qquad (3)$$

By an appropriate limiting procedure $M \to \infty$ in (1) the same property (3) carries over to arbitrary smooth phase space distribution functions $f(\mathbf{\Gamma}, t)$ as considered in [1]. In any case, Eq. (3) is not affected by the compressibility of the dynamical flow, in close analogy to the mass conservation law in fluid dynamics.

The basic equation underlying all the conclusions in [1] is given by [see Eq. (4) in [1]]

$$\frac{\partial}{\partial t} [J(\mathbf{\Gamma}) f(\mathbf{\Gamma}, t)] = -\nabla_{\mathbf{\Gamma}} \cdot [\dot{\mathbf{\Gamma}} f(\mathbf{\Gamma}, t) J(\mathbf{\Gamma})], \qquad (4)$$

where the Jacobian $J(\mathbf{\Gamma})$ associated with the phase space flow satisfies [see Eq. (1) in [1]]

$$\frac{dJ(\mathbf{\Gamma})}{dt} = -J(\mathbf{\Gamma}) \nabla_{\mathbf{\Gamma}} \cdot \dot{\mathbf{\Gamma}}. \qquad (5)$$

The purpose of this Comment is to point out that Eqs. (2)–(5) are not compatible. To this end the conser-

vation law (3) is taken for granted and rewritten as

$$0 = \int d\mathbf{\Gamma} \frac{\partial}{\partial t} f(\mathbf{\Gamma}, t) = \int d\mathbf{\Gamma} \frac{1}{J(\mathbf{\Gamma})} \frac{\partial}{\partial t} [J(\mathbf{\Gamma}) f(\mathbf{\Gamma}, t)]. \qquad (6)$$

With (4) it follows that

$$0 = \int d\mathbf{\Gamma} \\ \times \frac{[\dot{\mathbf{\Gamma}} f(\mathbf{\Gamma}, t)] \cdot \nabla_{\mathbf{\Gamma}} J(\mathbf{\Gamma}) + J(\mathbf{\Gamma}) \nabla_{\mathbf{\Gamma}} \cdot [\dot{\mathbf{\Gamma}} f(\mathbf{\Gamma}, t)]}{J(\mathbf{\Gamma})}. \qquad (7)$$

The last term amounts to a surface term and, according to the general reasoning adopted in [1] [see below Eq. (5) therein], is zero. Moreover, Eq. (7) must hold for arbitrary (smooth, non-negative) phase space distribution functions $f(\mathbf{\Gamma}, t)$, implying

$$0 = \frac{\dot{\mathbf{\Gamma}} \cdot \nabla_{\mathbf{\Gamma}} J(\mathbf{\Gamma})}{J(\mathbf{\Gamma})} = \frac{\frac{d}{dt} J(\mathbf{\Gamma})}{J(\mathbf{\Gamma})} = -\nabla_{\mathbf{\Gamma}} \cdot \dot{\mathbf{\Gamma}}, \qquad \forall \mathbf{\Gamma}; \qquad (8)$$

where we exploited (5) in the last step. We, thus, end with a contradiction to (2).

In conclusion, there appears to be a basic inconsistency in the entire work [1]. As a simple way of curing the problem one might think of replacing (3) by

$$\frac{d}{dt} \int d\mathbf{\Gamma} J(\mathbf{\Gamma}) f(\mathbf{\Gamma}, t) = 0. \qquad (9)$$

However, while (3) is an immediate consequence of the conservation of members of the ensemble, Eq. (9) is in contradiction to that property and, therefore, not acceptable. Another way out would be to include an artificial extra factor $1/J(\mathbf{\Gamma})$ into the definition of $f(\mathbf{\Gamma}, t)$ (without ever saying so). However, in such a case the major results (4) and (11) [with (8)] in [1] would boil down to trivialities.

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[2] This assumption is not stated explicitly but is used implicitly throughout [1], especially in the derivation of Eq. (4) therein.

Tuckerman *et al.* Reply: The statistical mechanics of nonequilibrium steady states is a topic that has generated a fair amount of controversy. It has been recently argued by Hoover *et al.* [1], Reimann [1], and by Chernov *et al.* [2] that the thermodynamics of steady states, based on, for example, the Gibbsian notion of entropy, is not defined. These authors suggest that a smooth distribution function does not exist for a nonequilibrium steady state, but rather takes on a "fractal" character [1]. In a recent Letter [3], we showed that the analysis carried out by Hoover *et al.* that leads, to this conclusion was based on an improper treatment of the geometry of phase space, and that a correct treatment leads to a generalization of the Gibbs entropy that *is* well defined. Our analysis was based on a generalized form of the Liouville equation that accounts for the compressibility of phase space.

It is well known that a nonvanishing phase space compressibility gives rise to a metric $g(x)$ on a phase space [4–6] that can be related to a Jacobian $J(x)$. $x = (p, q)$ represents the set of phase space variables. This metric must be incorporated into the measure for the integral of any function over the phase space [3,5,7]. In particular, the Gibbs entropy, being an integral over the phase space, must be generalized according to [3,5]: $S(t) = -k \int dx \sqrt{g(x)} f(x, t) \ln f(x, t)$.

Up to now, no generalization of the Liouville equation [4–6] has properly incorporated the geometry of the phase space arising from compressibility. Liouville's theorem is a general statement of the invariance of the phase space volume element [4,6]. This concept was recognized in the work of Refs. [4] but was incorrectly generalized: therein, one finds the statement $f(x_{t_1}, t_1)dx_{t_1} = f(x_0, t_0)dx_{t_0}$. However, preservation of the volume element for *all* time t can be found in Ref. [6] and leads to the definition of the invariant ensemble of microstates, $f(x_t, t)J(x_t, t)dx_t$ rather than $f(x_t, t)dx_t$. The latter definition was also employed by Reimann [1], thus leading to his contradictory result. Indeed, Eq. (9) in Reimann's Comment is the starting point in our derivation of the generalized Liouville equation. Equating the time derivative of the ensemble of microstates to the negative of the flux of this quantity leaving a surface leads unambiguously to Eq. (4) in Ref. [3] as the correct generalized form of Liouville's equation [7].

Further mathematical justification of the generalized Liouville equation given in our Letter [3] begins with a general statement of continuity. Consider an n-dimensional Riemannian manifold with metric G. In an arbitrary coordinate system $x^1, \ldots, x^n$, the volume n form is generally given by $\tilde{\omega} = \sqrt{g} \, dx^1 \wedge \cdots \wedge dx^n$, where g is the determinant of the metric in this basis. For a flow field on the manifold prescribed by $\dot{x}^i = F^i(x)$ with density $f(x, t)$, it is well known that the general form of the continuity equation is [8]: $(\partial/\partial t + \mathcal{L}_\xi)(f\tilde{\omega}) = 0$, where $\xi^i \equiv \xi^i(t) = dx^i/dt$ is tangent to $x^i \equiv x^i(t)$ and $\mathcal{L}_\xi$ is the Lie derivative [see, for example, Eq. (5.68) of

Ref. [8]]. By applying standard rules of differential geometry and tensor calculus for acting with the Lie derivative on $f\tilde{\omega}$ [9], it is straightforward to deduce a form of the Liouville equation valid on any Riemannian manifold with a metric G: $(\partial/\partial t)(f\sqrt{g}) + \nabla \cdot (f\sqrt{g}\,\xi) = 0$. The relationship between $\sqrt{g}$ and the Jacobian J can be established by considering an arbitrary change of coordinates, with the well known result $\sqrt{g'} = \sqrt{g} J$ [10], where g' and g are the metric determinants in the two representations, and J is the Jacobian of the transformation. The coordinate transformation produced by the dynamical evolution on the space yields, for the metric, $\sqrt{g(x_{t'})} = \sqrt{g(x_t)} J(t \to t')$. Note that this relationship does not imply that the underlying manifold is changing with time, only the representation of the metric in the different coordinate bases generated by the dynamics. If the manifold is locally flat, then a coordinate system $q^1, \ldots, q^n$ can always be chosen such that the metric tensor components g'_{ij} in this basis are $g'_{ij} = \delta_{ij}$ (see, for example, exercise 2.14 from Ref. [8]). It then follows that in any other representation,
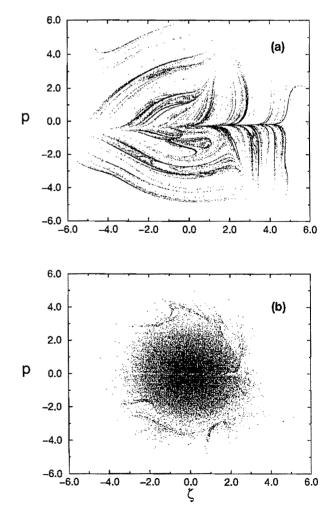

FIG. 1. Poincaré sections p vs ζ for the Galton staircase. (a) corresponds to a choice of $\nu = 0.316$ as in Ref. [11]; (b) corresponds to a choice of $\nu = 1.0$.

$\sqrt{g} = J$, where J is the Jacobian of the transformation to the new representation. Substituting this relation into the general definition of S given above gives the general definition of entropy employed in our Letter [3], $S(t) = - \int dx J(x) f(x, t) \ln f(x, t)$ and justifies such a generalization.

The procedure for obtaining f and J separately can be deduced from Eqs. (1) and (4) of Ref. [3]. One simply solves (1) for J and substitutes it into (4) and solves for f, i.e., there are two equations and two unknowns.

To address the question of the fractal nature of the example presented by Hoover et $al.$ [1], we present a counter example below, that of the Galton staircase treated in Ref. [11]. Note that a simple Nosé-Hoover thermostat was used in [11], which does not guarantee complete sampling of the entire available phase space [12]. Figure 1(a) shows the Poincaré section p vs ζ for a value of $\nu = 0.316$, and Fig. 1(b) shows the same section for a value of $\nu = 1.0$. While Fig. 1(a) shows a strong fractal character, Fig. 1(b) exhibits a densely filled phase space. When the system is coupled to the more ergodic Hoover-Holian thermostat [13], the Poincaré section is similar to that shown in Fig. 1(b). The suggestion is that the fractal nature of Fig. 1(a) could be the result of incomplete phase space sampling. Although this example is not, in itself, definitive, it should provide an impetus for further investigation of the effect of different thermostating mechanics and time scales on the nature of the phase space.

Finally, we would like to note that the generalized Gibbs entropy employed in Ref. [3] is a fine-grained entropy that carries all the microscopic details of phase space. It is well known that the fine-grained entropy must satisfy $dS/dt = 0$ [14]. It is expected that a suitable coarse-graining procedure [14] applied to the generalized definition of S given above will yield an entropy suitable for the description of nonequilibrium steady states.

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