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Ergodicity, mixing, and time reversibility for atomistic nonequilibrium steady states

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Ergodic mixing is prerequisite to any statistical-mechanical calculation of properties derived from atomistic dynamical simulations. Thus the time-reversible thermostats and ergostats used in simulating Gibbsian equilibrium dynamics or nonequilibrium steady-state dynamics should impose ergodicity and mixing. Though it is hard to visualize many-dimensional phase-space distributions, recent developments provide several practical numerical approaches to the problem of ergodic mixing. Here we apply three of these approaches to a useful nonequilibrium test problem, an oscillator in a temperature gradient. [S1063-651X(97)09711-0]

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I. INTRODUCTION

The simplest equilibrium and nonequilibrium many-body problems are steady states. These include Gibbs' equilibrium ensembles, for which the stationary smooth phase-space distributions are exactly known, as well as the prototypical nonequilibrium flows which define the basic diffusive, viscous, and heat-conducting transport coefficients. The steady nonequilibrium flows generate relatively complicated multifractal phase-space structures. Because the work done by the special boundary conditions, or driving forces, used to stimulate nonequilibrium flows, is inevitably converted to heat, heat reservoirs, capable of extracting the generated heat, must be included in the simulations [1,2]. For the application of statistical mechanics to such dynamical simulations, it is desirable that the overall dynamics be simultaneously ''ergodic,'' ''mixing,'' and ''time reversible.'' Let us begin by defining these terms.

An ''ergodic'' dynamics must eventually approach each and every one of the microstates which could serve as an initial condition. Thus an isolated ergodic system would be required to approach all the energy states consistent with the initial energy, for example. An ergodic equilibrium system, with a volume V, and in contact with a thermal bath, or ''thermostat,'' at temperature T, would be required to approach all the energy states possible within the fixed volume. Any computationally useful ergodic dynamics would necessarily generate these energy states with a probability density given by Gibbs' canonical distribution, $f_{\text{Gibbs}} \propto e^{-H/kT}$. Ergodicity becomes computationally irrelevant for large systems, because the time required to access all states diverges strongly with system size. Ergodicity is likewise computationally irrelevant for very high energy states, due to their negligible probability.

A ''mixing'' dynamics eventually loses all correlations linking the developing trajectory to its initial conditions. The mixing property, in the full phase space, is fundamental to the simulation of stationary nonequilibrium states [3], for it ensures that the time-averaged properties are independent of the initial conditions. For the dynamics to be mixing, the trajectories initiated at two neighboring initial conditions must eventually separate from each other and become uncorrelated. Mixing is important for statistical mechanics in that it implies the independence of measured averages to the initial conditions. Without mixing, the results of numerical experiments would not be reproducible. Mixing typically relies on the ''Lyapunov instability'' of the dynamics—the exponential separation of neighboring trajectories. But Lyapunov instability does not guarantee mixing. Consider, for example, the equations of motion for a particular Nosé-Hoover oscillator [4–6] with mass, force constant, and temperature all chosen as unity:

$$\dot{q} = p; \quad \dot{p} = -q - \zeta p; \quad \dot{\zeta} = p^2 - 1.$$

Here q, p, and ζ are, respectively, the oscillator coordinate, momentum, and friction coefficient. These equations provide both chaotic and regular solutions, depending on the initial values. The boundaries separating such solutions are, without doubt, complicated. Choosing the initial values $\{q_0, p_0, \zeta_0\} = \{0,5,0\}$, and integrating numerically, the motion is found to be chaotic in the three-dimensional $\{q,p,\zeta\}$ space, with a Lyapunov exponent of order 0.01 [5]. Although the chaotic region covered by this solution has the same dimensionality as that of the full space, three, the solution does not completely fill the space. Other initial conditions, separated only infinitesimally from chaotic ones, occupy instead two-dimensional quasiperiodic tubular regions which surround a countable infinity of stable periodic orbits. The measures of the chaotic and regular regions are roughly equal. A slightly more complicated set of equations, with two thermostatting variables rather than one,

$$\dot{q} = p; \quad \dot{p} = -q - \zeta p - \xi p^3; \quad \dot{\zeta} = p^2 - 1; \quad \dot{\xi} = p^4 - 3p^2,$$

provides a dynamics which is simultaneously chaotic, ergodic, and mixing [11].

A ''time-reversible'' dynamics can be made to return to its time-reversed initial state by changing the initial conditions, with no change to the equations which generate the

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dynamics. In the examples given above, integrating from $\{q_0,p_0,\zeta_0\}$ or $\{q_0,p_0,\zeta_0,\eta_0\}$ for a time t, changing the signs of p_t and ζ_t, and once again integrating for a time t, results in the time-reversed initial state $\{q_0,-p_0,-\zeta_0\}$ or $\{q_0,-p_0,-\zeta_0,\eta_0\}$. All the fundamental equations of physics are time reversible, suggesting that the thermostats and ergostats for physical simulations should have this property too [7–9]. In fact, the most successful model thermostats have this property, which greatly simplifies theoretical analyses [1,2].

Many types of heat reservoirs, designed to control temperature, or energy, or stress, have been developed as generalizations of the simpler Nosé-Hoover approach. We select three of them [6,8,10] for detailed discussion in Sec. II. All three time-reversible methods appear to be both ergodic and mixing for that prototypical hard-to-mix problem, the one-dimensional harmonic oscillator. For that reason, these more general thermostats would appear to be useful for nonequilibrium simulations. In Sec. III we study the ergodicity and mixing properties for all three types of time-reversible thermostats, by applying them to a nonequilibrium oscillator problem [11]. Two of the three thermostats perform quite well away from equilibrium. In Sec. IV we summarize the conclusions drawn from this work.

II. MODEL HEAT RESERVOIRS AND THERMOSTAT FORCES

Nonequilibrium steady states necessarily involve the interaction of a driven system with at least one heat reservoir. Typically, a heat reservoir is characterized by its ideal-gas-thermometer temperature T [12]. A physical picture of such a heat reservoir is a gas of very small weakly interacting particles. In practice, such a heat reservoir is modeled by adding ‘‘thermostat forces’’ to the dynamics of all those degrees of freedom subject to the thermostat. The thermostat forces, like the heat reservoir which they represent, are chosen for their ability to reproduce a Gibbsian canonical distribution for the system velocities $f_{\mathrm{Gibbs}} \propto e^{-mv^2/2kT}$ *independent of the initial conditions*. Energy reservoirs, represented by ‘‘ergostat forces’’ can be similarly defined. It has recently been shown that the fractal structures generated by the time-reversible thermostatted equations of motion have exact counterparts in systems free of the thermostats, provided that hard-disk or hard-sphere interactions are used [13].

Probabilistic thermostats have their roots in kinetic theory and the Langevin equation, and can be represented in simulations by stochastically reflecting walls. The intrinsic irreversibility of the stochastic dynamics which results precludes theoretical analyses based on trajectory properties. See the discussion of this point in the proceedings of a recent NATO conference [14]. We do not consider such stochastic irreversible boundary conditions here. There are many alternative descriptions of boundaries which are both deterministic and time reversible. For example, walls can be composed of ‘‘tethered particles’’ [15]. The oscillations of these tethered boundary particles are governed by feedback forces which control their kinetic or total energy. Ashurst's more sophisticated ‘‘fluid walls’’ [16] are closer to reality. Ashurst's walls confine a group of collectively thermostatted, or ergostatted, particles between two elastic reflecting surfaces.

Computational thermostats were first constructed in an *ad hoc* way [16,17]. The algorithm representing the thermostatting action was called ‘‘velocity scaling,’’ because all the thermostatted velocities were periodically multiplied by a numerical scale factor, so as to match the instantaneous second moment of the velocity distribution to the desired ideal-gas-thermometer temperature T:

$$kT \equiv \langle mv^2 \rangle.$$

Though this periodic rescaling process is not time reversible, it becomes so in the limiting case of continuous rescaling. In that limit, the thermostatting process can be described by a feedback equation which contains a Lagrange multiplier ζ. The multiplier constrains the second moment to match the temperature:

$$\dot{p} = F - \zeta p; \quad \zeta \equiv \sum F(p/m)/2K \Leftrightarrow \dot{K} = \sum p\dot{p}/m \equiv 0,$$

where K is the kinetic energy. Exactly this same time-reversible motion equation results if Gauss' principle of least constraint [18], or Hamilton's principle of least action [19], is used in conjunction with the requirement of constant kinetic energy. Similar motion equations, but with a different recipe for ζ, result if energy, rather than temperature, is controlled.

Nosé developed a thermostat designed to reproduce Gibbs' canonical ensemble [20,21], and including a ‘‘time-scaling’’ variable s. Hoover emphasized the superiority of the simpler ‘‘Nosé-Hoover’’ form of this thermostat [4]. Very recently, Dettmann, and Morriss [22] showed that these Nosé-Hoover equations of motion follow from a special Hamiltonian which avoids Nosé's time scaling. For a one-dimensional oscillator, with unit mass and force constant, and with temperature and thermostat relaxation time of unity, the time-reversible Nosé-Hoover oscillator equations of motion describe the motion in a three-dimensional $\{q,p,\zeta\}$ space:

$$\dot{q} = p; \quad \dot{p} = -q - \zeta p; \quad \dot{\zeta} = p^2 - 1.$$

In the time-reversed motion both p and ζ change sign. The main advantage of this Nosé-Hoover thermostat is simplicity. For a system which is sufficiently mixing to promote ergodicity, it is hard to imagine a simpler thermostat. A harmonic system, on the other hand, behaves in a very complicated way under the influence of a Nosé-Hoover thermostat. The extended oscillator phase space $\{q,p,\zeta\}$ is typically partitioned into both chaotic and regular regions, with the regular regions enclosing a countable set of stable periodic orbits. See the illustrations in Ref. [5]. Because of this undesirable complexity, special thermostats have been developed. Ideally, such a thermostat will generate ergodic dynamics for relatively small equilibrium systems, and will generate a mixing dynamics both at, and away from, equilibrium.

Kusnezov, Bulgac, and Bauer [9], and Hoover and Holian [8] provide recent general overviews of this approach. See especially Ju and Bulgac's interesting application of a somewhat more complex ‘‘Brownian’’ thermostat to the dynamics of small metal clusters [10]. The most straightforward extension of Nosé's thermostat idea is to include control of additional velocity moments. The harmonic oscillator, with both second- and fourth-moment control, was investigated from this point of view by Hoover and Holian [8]:

$$\dot{q}=p; \quad \dot{p}=-q-\zeta p-\xi p^3; \quad \dot{\zeta}=p^2-T;$$

$$\dot{\xi}=p^4-3p^2; \quad T=1 \quad (\mathrm{HH}).$$

The extra control variable ξ was designed to correct the phase-space partitioning of the Nosé-Hoover thermostat. The partitioning, into chaotic and regular regions, gives long-time averages which depend on the initial conditions. For example, though $\langle K\rangle$ is correctly controlled, lack of ergodicity gives an incorrect fluctuation of the kinetic energy $\langle \Delta K^2\rangle$. Hoover and Holian found that controlling both the second moment $\langle K\rangle$ and the fourth moment $\langle K^2\rangle$ was sufficient to get the complete Gibbs' canonical distribution for a harmonic oscillator. Posch and Hoover [11] showed later that these same $\{q,p,\zeta,\xi\}$ motion equations can be easily extended to a nonequilibrium oscillator, with a temperature varying in space, $T=T(q)$, without losing the ergodicity property. Bulgac, Ju, and Kusnezov [10] controlled the first four moments of the velocity in isothermal simulations of a small cluster of metal atoms. As the result of many trials, not reproduced here, we found that their control variables which interact with the odd moments of the velocity distribution $\langle p\rangle$ and $\langle p^3\rangle$ were not useful for promoting ergodicity in an oscillator. Accordingly, we consider here only the Bulgac-Ju-Kusnezov control of the oscillator's second and fourth moments $\langle p^2\rangle$ and $\langle p^4\rangle$:

$$\dot{q}=p; \quad \dot{p}=-q-\zeta^3 p-\xi p^3; \quad \dot{\zeta}=p^2-T;$$

$$\dot{\xi}=p^4-3p^2; \quad T=1 \quad (\mathrm{BJK}).$$

The control variable ζ has a stationary equilibrium distribution $\propto e^{-\zeta^4/4}$, providing a somewhat stiffer control than Nosé's, together with a relatively erratic dynamics. The fourth-moment control variable ξ is identical to that used by Hoover and Holian [8].

Rather than considering more moments, Martyna, Klein, and Tuckerman [6] took a qualitatively different approach, generalizing the Nosé-Hoover thermostat by introducing a ''chain'' of nearest-neighbor thermostat variables, controlling all the second moments in the chain. At equilibrium, each of the variables in such a chain has a Gaussian distribution and is linked to no more than two adjacent control variables. In the present work we explore the simplest of these thermostat chains, in which just two thermostat variables ζ and ξ control the kinetic energy. The equations of motion are quadratic:

$$\dot{q}=p; \quad \dot{p}=-q-\zeta p; \quad \dot{\zeta}=p^2-T-\xi\zeta;$$

$$\dot{\xi}=\zeta^2-1; \quad T=1 \quad (\mathrm{MKT}).$$

Martyna, Klein, and Tuckerman showed that this system is time-reversible and ergodic at equilibrium. Because the two time averages $\langle\dot{\zeta}\rangle$ and $\langle\xi\zeta\rangle$ both vanish at equilibrium, the long-time-averaged temperature $\langle p^2\rangle$ necessarily converges to its target value, here unity. Martyna, Klein, and Tuckerman had intended their chains to be useful away from equilibrium too. But Holian pointed out that the chain thermostats fail whenever, as is usual away from equilibrium, $\langle\xi\zeta\rangle$ is nonzero [8,23,24]. In what follows, we apply the Hoover-Holian, Bulgac-Ju-Kusnezov, and Martyna-Klein-Tuckerman temperature controls to a classical one-dimensional harmonic oscillator driven from equilibrium by a space-dependent thermostat. The Hoover-Holian and Martyna-Klein-Tuckerman approaches, applied to the harmonic oscillator, give a Gaussian distribution in the phase space, for the four variables $\{q,p,\zeta,\xi\}$. In these cases it is easy to verify that Liouville's theorem for the stationary flow takes the form

$$\partial\dot{p}/\partial p \equiv q\dot{q}+p\dot{p}+\zeta\dot{\zeta}+\xi\dot{\xi} \Rightarrow f(q,p,\zeta,\xi)\propto e^{-(q^2+p^2+\zeta^2+\xi^2)/2}.$$

The Bulgac-Ju-Kusnezov approach leads instead to the very similar relations:

$$\partial\dot{p}/\partial p \equiv q\dot{q}+p\dot{p}+\zeta^3\dot{\zeta}+\xi\dot{\xi} \Rightarrow f(q,p,\zeta,\xi)$$

$$\propto e^{-(q^2+p^2+\xi^2)/2}e^{-\zeta^4/4}.$$

We discuss the extension of all these ideas to the nonequilibrium case in the following section.

III. ERGODICITY TESTS FOR A THERMOSTATTED NONEQUILIBRIUM OSCILLATOR

For simplicity, we continue to consider the illustrative problem of a single harmonic oscillator, with unit mass and force constant. Such an oscillator, if isolated from external forces or controls, simply traces out a constant-energy circle in its $\{q,p\}$ phase space. At thermal equilibrium, with a heat reservoir at temperature T, a thermostatted oscillator should arrive at any combination of coordinate q and momentum p with a relative frequency given by Gibbs' stationary canonical distribution. For a temperature of unity

$$f(q,p)\propto e^{-(q^2+p^2)/2}.$$

The two-moment thermostat explored by Hoover and Holian (HH) and the similar, but somewhat stiffer thermostat based on Bulgac, Ju, and Kusnezov's work (BJK), together with the ''chain thermostat'' invented by Martyna, Klein, and Tuckerman (MKT), can all three provide ergodic phase-space distributions for the harmonic oscillator in $\{q,p,\zeta,\xi\}$ space [1,6,8]. In the stationary equilibrium state, despite their different dynamics, the three thermostats correspond to similar extended canonical distributions,

$$f_{\mathrm{HH}}\equiv f_{\mathrm{MKT}}\propto e^{-(q^2+p^2+\zeta^2+\xi^2)/2};$$

$$f_{\mathrm{BJK}}\propto e^{-(q^2+p^2+\xi^2)/2}e^{-\zeta^4/4}.$$

For simplicity, we continue to set all the adjustable parameters equal to unity in the nonequilibrium case too. Careful equilibrium investigations had previously been carried out in the HH and MKT cases, establishing that the entire four-dimensional Gaussian distribution results from an arbitrary initial condition. The equilibrium results, which we include in Table I, indicate that the BJK case is likewise ergodic. Here, and in what follows, we exclude from consideration exceptional zero-measure sets of initial conditions with

TABLE I. Dependence of the time-averaged ‘‘energies’’ $E_{\rm HH}=E_{\rm MKT}=(q^2+p^2+\zeta^2+\xi^2)/2$ or $E_{\rm BJK}=(q^2+p^2+\xi^2)/2+\zeta^4/4$ and external entropy production $\dot S/k$: $\langle \dot S/k\rangle \equiv \langle -\epsilon\zeta^p \tanh(q)\rangle$ on the deviation from equilibrium ϵ for the Hoover-Holian, Bulgac-Ju-Kusnezov, and Martyna-Klein-Tuckerman thermostatted oscillators. Time averages are given for 10^7, 10^8, and 10^9 time steps of 0.001, where the maximum- and mimimum-energy trajectories after 10^7 steps were then followed, and compared, for an additional 10^9 time steps.

t	ϵ	$E_{\rm HH}$	$\dot S_{\rm HH}/k$	$E_{\rm BJK}$	$\dot S_{\rm BJK}/k$	$E_{\rm MKT}$	$\dot S_{\rm MKT}/k$
10^4	0.0	1.89< 2.11	0.000,0.000	1.69< 1.81	0.000,0.000	1.97< 2.03	0.000,0.000
10^5	0.0	1.99, 2.00	0.000,0.000	1.76, 1.75	0.000,0.000	2.00, 2.00	0.000,0.000
10^6	0.0	2.00, 2.00	0.000,0.000	1.75, 1.75	0.000,0.000	2.00, 2.00	0.000,0.000
10^4	0.1	1.89< 2.17	0.001,0.002	1.50< 1.83	0.038,0.007	1.95< 2.04	0.001,0.002
10^5	0.1	2.03, 2.02	0.001,0.001	1.49, 1.52	0.038,0.035	2.00, 2.00	0.001,0.001
10^6	0.1	2.01, 2.01	0.001,0.001	1.49, 1.50	0.038,0.038	2.01, 2.00	0.001,0.001
10^4	0.2	1.91< 2.15	0.002,0.007	1.73< 1.88	0.026,0.030	1.96< 2.03	0.003,0.006
10^5	0.2	2.04, 2.04	0.004,0.004	1.81, 1.80	0.025,0.025	2.00, 1.99	0.005,0.005
10^6	0.2	2.04, 2.04	0.004,0.004	1.81, 1.81	0.025,0.025	2.00, 2.00	0.005,0.005
10^4	0.3	2.00< 2.20	0.006,0.010	1.78< 1.90	0.049,0.070	1.94< 1.99	0.008,0.011
10^5	0.3	2.06, 2.06	0.008,0.008	1.84, 1.83	0.063,0.063	1.97, 1.96	0.010,0.009
10^6	0.3	2.08, 2.07	0.008,0.008	1.84, 1.84	0.062,0.062	1.97, 1.96	0.010,0.010
10^4	0.4	2.04< 2.25	0.013,0.021	1.95< 2.07	0.112,0.123	1.88< 1.96	0.017,0.019
10^5	0.4	2.14, 2.14	0.016,0.016	2.01, 2.01	0.122,0.121	1.92, 1.91	0.019,0.018
10^6	0.4	2.15, 2.13	0.016,0.016	2.02, 2.02	0.121,0.120	1.92, 1.92	0.018,0.018
10^4	0.5	2.15< 2.38	0.024,0.036	2.18< 2.41	0.172,0.197	1.82< 1.88	0.033,0.039
10^5	0.5	2.26, 2.29	0.031,0.029	2.29, 2.28	0.185,0.182	1.85, 1.85	0.037,0.036
10^6	0.5	2.28, 2.27	0.029,0.028	2.30, 2.29	0.184,0.185	1.85, 1.85	0.036,0.035
10^4	0.6	2.29< 2.61	0.040,0.063	2.70< 2.88	0.325,0.325	1.75< 1.91	0.049,0.080
10^5	0.6	2.44, 2.44	0.050,0.048	2.85, 2.82	0.219,0.243	1.82, 1.82	0.065,0.064
10^6	0.6	2.45, 2.45	0.051,0.051	2.85, 2.84	0.213,0.215	1.83, 1.82	0.066,0.065
10^4	0.7	2.44< 4.17	0.059,0.064	3.03< 7.98	0.398,0.428	1.74< 3.32	0.065,0.236
10^5	0.7	4.14, 4.10	0.059,0.058	7.51, 7.99	0.425,0.427	3.02, 3.33	0.205,0.233
10^6	0.7	4.17, 4.16	0.058,0.058	7.95, 7.99	0.426,0.426	3.30, 3.33	0.230,0.233
10^4	0.8	1.22< 2.83	0.002,0.115	2.51< 2.68	0.250,0.271	1.74< 3.41	0.106,0.257
10^5	0.8	1.42, 1.36	0.037,0.039	2.53, 2.53	0.251,0.252	3.41, 3.41	0.256,0.257
10^6	0.8	1.30, 1.30	0.039,0.039	2.53, 2.53	0.252,0.252	3.41, 3.41	0.257,0.257
10^4	0.9	2.99< 3.33	0.135,0.230	1.11< 1.37	0.090,0.175	1.86< 2.07	0.228,0.249
10^5	0.9	3.19, 3.18	0.257,0.255	1.11, 1.11	0.090,0.091	1.87, 1.87	0.239,0.239
10^6	0.9	3.19, 3.19	0.263,0.263	1.11, 1.11	0.090,0.090	1.87, 1.87	0.239,0.239
10^4	1.0	2.95< 3.35	0.212,0.250	3.00<10.41	1.446,0.730	1.88< 2.02	0.279,0.286
10^5	1.0	3.13, 3.12	0.227,0.233	3.09,10.42	1.511,0.729	1.88, 1.88	0.283,0.283
10^6	1.0	3.15, 3.14	0.236,0.234	3.09,10.42	1.512,0.729	1.88, 1.88	0.283,0.283

$q=p=0$. Martyna, Klein, and Tuckerman [6] carefully verified that these negligible sets repel, rather than attract, the phase-space flow.

Here we apply all three thermostat approaches HH, BJK, and MKT to a one-parameter nonequilibrium problem [11], an oscillator with a coordinate-dependent temperature:

$$T(q)=1.0+\epsilon\tanh(q).$$

Though it is plausible that linear-response theory could be applied to this problem, for small ϵ, the known multifractal nature of the phase-space distributions which result, suggests that the theory would be difficult to work out. In the present work we carry out numerical explorations of these nonequilibrium systems, considering a range $0\leqslant\epsilon\leqslant 1$. We would expect the corresponding heat-flux perturbation to become asymptotically linear, for small ϵ, which in turn would imply that the external thermodynamic dissipation is quadratic in ϵ:

$$d\ln f/dt\equiv\dot S/k\equiv -[\partial\dot q/\partial q+\partial\dot p/\partial p+\partial\dot\zeta/\partial\zeta+\partial\dot\xi/\partial\xi]$$

$$\Rightarrow \dot S_{\rm HH}/k=\zeta+3\xi p^2\propto\epsilon^2;$$

$$\dot S_{\rm BJK}/k=\zeta^3+3\xi p^2\propto\epsilon^2;\quad \dot S_{\rm MKT}/k=\zeta+\xi\propto\epsilon^2.$$

The numerical results we obtain for the HH and MKT thermostats appear to be consistent with this expectation for ϵ up to about 0.5. The BJK thermostat, on the other hand, exhibits considerable nonlinearity, including limit cycles, in this same range of ϵ.

Holian pointed out to us that the time averages of these various expressions for the dissipation $\langle\dot S/k\rangle$ can all be ex-

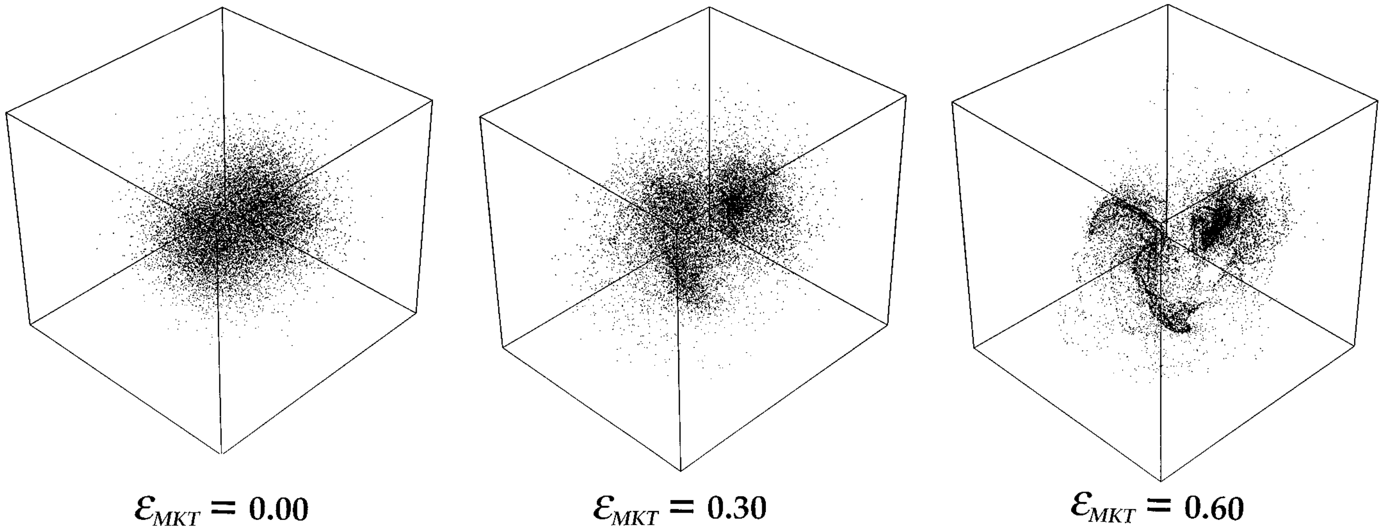

FIG. 1. Poincaré sections $p=0$ for a harmonic oscillator in a temperature gradient. The three $\{q,\zeta,\xi\}$ cases shown here, for the MKT thermostat, suggest the gradual shift from a smooth equilibrium distribution function to a limit cycle through intermediate multifractal distributions. The systems studied in the present work all appear to provide distributions independent of initial conditions with the exception of the BJK thermostat at $\epsilon=1.0$.

pressed in a simple form which emphasizes the importance of the temperature perturbation proportional to tanh(q):

$$\langle \dot{S}/k\rangle \equiv \langle -\epsilon\zeta^{p}\tanh(q)\rangle; \quad p_{\mathrm{HH}}=p_{\mathrm{MKT}}=1; p_{\mathrm{BJK}}=3.$$

These three alternative expressions for $\dot{S}$ follow from taking time averages of the time derivative of an energylike quadratic form:

$$\langle \dot{E}_{\mathrm{HH,MKT}}\rangle \equiv \langle \dot{q}q+\dot{p}p+\dot{\zeta}\zeta+\dot{\xi}\xi\rangle \equiv 0;$$

$$\langle \dot{E}_{\mathrm{BJK}}\rangle \equiv \langle \dot{q}q+\dot{p}p+\dot{\zeta}\zeta^{3}+\dot{\xi}\xi\rangle \equiv 0.$$

What about ergodicity and mixing for the nonequilibrium cases? Here, since the distributions are multifractal, rather than Gaussian, ergodicity is arguably less significant than the slightly different requirement, implied by mixing, that time-averaged values be independent of the initial conditions. In far-from-equilibrium problems the multifractal distributions can even collapse to one-dimensional limit cycles, stable to machine accuracy and independent of the initial conditions. Space-filling ergodicity is evidently impossible under such conditions. Figure 1 illustrates the kinds of flows which result, through a series of typical Poincaré sections for the MKT thermostat. These are three-dimensional sections cut through the four-dimensional solution space. The sections for the HH thermostat are similar. The sections show quite clearly the structural changes induced by increasing the temperature gradient. The Poincaré section of the space-filling equilibrium distribution becomes transformed, by increasing the temperature gradient, through a series of more-and-more singular attractors, until a limit cycle is reached. The HH and MKT trajectories converge to limit cycles at $\epsilon=0.7$. For the MKT trajectory the corresponding Poincaré section reduces to four isolated points. The existence of such robust limit-cycle solutions, for time-reversible motion equations, appears somewhat paradoxical. The BJK thermostat behaves differently. It already shows a limit cycle at a relatively small temperature gradient, with $\epsilon=0.1$. See the representative BJK trajectory projection shown in Fig. 2.

Just as no experiment can exclude uncertainty in its result, no numerical experiment, or test of ergodicity, can be completely definitive. Let us consider the implications of ergodicity for computation. At equilibrium, where the distribution is usually known, any allowed state should eventually occur, and recur. Likewise, any two trajectories, independent of their initial conditions, will eventually, and repeatedly, approach one another. Though these recurrence and concurrence properties could certainly be tested, for sufficiently low-dimensional systems such as ours, they are of no significance whatever for statistical mechanics. This is because the recurrence and concurrence times, even for very small systems, exceed the age of the universe. Accordingly, we do not investigate recurrence and concurrence numerically. Away from equilibrium there is no guarantee that a measure can be determined throughout space. The limit cycles indicate that, sufficiently far from equilibrium, the measure can vanish almost everywhere.

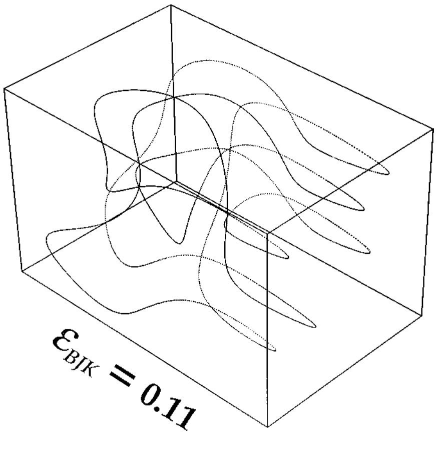

FIG. 2. Projected $\{q,p,\zeta\}$ trajectory for a harmonic oscillator, using the BJK thermostat with $\epsilon=0.11$. This trajectory is a limit cycle.

What are some practical tests of the dynamics which *do* have significance for statistical mechanics, both at and away from equilibrium? At equilibrium, ergodicity requires that mean values, fluctuations, and dynamical measures of instability and dissipation must all be independent of the initial conditions. Away from equilibrium the equivalent mixing property simply corresponds to the reproducibility of experimental averages. Thus the time averages of various moments, such as $\langle q^i p^j \zeta^k \xi^l \rangle$, together with the Lyapunov exponents $\langle \{\lambda_i\} \rangle$, and their fluctuations, and the external entropy production $\langle \dot{S} \rangle$ and its fluctuation, must all converge to values independent of the initial choice $\{q,p,\zeta,\xi\}_0$.

Based on preliminary investigations of all the quantities just mentioned, we have chosen to tabulate here time averages for two useful diagnostic quantities, the ''energies'' $(q^2+p^2+\zeta^2+\xi^2)/2$ and $[(q^2+p^2+\xi^2)/2]+[\zeta^4/4]$ and the external entropy production rate $\dot{S}/k=-\Sigma\lambda_i$. We generated these data by first selecting 100 sets of initial conditions $\{q,p,\zeta,\xi\}$ drawn at random from the equilibrium probability density

$$f_{\mathrm{HH,MKT}} \propto e^{-(q^2+p^2+\zeta^2+\xi^2)/2}; \quad f_{\mathrm{BJK}} \propto e^{-(q^2+p^2+\xi^2)/2} e^{-\zeta^4/4}.$$

These initial data would allow us to detect the presence of topologically isolated phase-space regions with measures of order of 0.01 or more. The 100 sets of differential equations corresponding to the initial data were first integrated forward for ten million time steps, with $dt=0.001$, to a time of 10 000, using the classic fourth-order Runge-Kutta method. Next, the two trajectories corresponding to the extreme time-averaged energy values in the set, the maximum and the minimum, were integrated forward in time for an additional billion time steps. The resulting data are displayed in Table I.

For small deviations from equilibrium the maximum and minimum values of energy and entropy production evidently approach a common limit fairly quickly, with the separation between the two diminishing, roughly as the inverse square root of the run length. Near $\epsilon=0.7$, where all three thermostats lead to limit cycles, it is evident that the situation is becoming more complicated. ''Short'' calculations, corresponding to millions of time steps and thousands of oscillations, can have very different time averages. Quite remarkably, longer calculations, with billions of time steps, indicate that all of the three approaches to thermostatting considered here lead to averages free of dependence on the initial conditions. The only apparent exception which we found in the nonequilibrium states shown in the table is the Bulgac-Ju-Kusnezov thermostat, at the highest value of ϵ, 1.0. Here the minimum- and maximum-energy sets of $\{q,p,\zeta,\xi\}$ lead to periodic orbits, appearing as four- and two-point limit cycles in the $p=0$ Poincaré plane.

For all three thermostat types, the rate of convergence is dramatically slowed by the multifractal nature of the distribution functions in the vicinity of $\epsilon=0.7$. Here the dissipation rate and the largest Lyapunov exponent λ_1 have roughly equal magnitudes. For the chaotic states which preceded the cycle at $\epsilon=0.7$ we show the HH and MKT Lyapunov spectra in Fig. 3. These two thermostats evidently provide relatively simple space-filling ergodic nonequilibrium trajectories for a relatively wide range of oscillator temperature gradients. The change occurring in the rate of convergence of the time averages is reflected in the Lyapunov spectra $\{\lambda\}$. The magnitude of the dissipative shrinking in phase space, $\Sigma\lambda=-\dot{S}/k$, exceeds the spreading tendency expressed by the largest exponent λ_1 when the temperature gradient magnitude ϵ reaches about 0.7 in these two cases. Evidently the strong nonlinearity associated with the cubic control variable ζ_{BJK} destroys the relatively simple response of the oscillator to a temperature gradient.

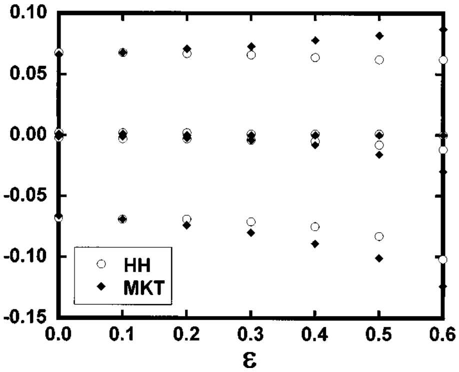

FIG. 3. Lyapunov spectra for thermostatted nonequilibrium oscillators using the HH and MKT thermostats. Both sets of four flow equations are characterized here by their four Lyapunov exponents. For higher values of the dimensionless temperature gradient ϵ the spectra reveal limit cycles.

IV. CONCLUSION

In principle, equilibrium tests for ergodicity can be based on recurrence and concurrence, as well as on time-averaged values of moments, entropy production, and the Lyapunov spectrum. In practice, only the time averages can have significance for statistical mechanics. We have studied a variety of phase functions to check the ergodicity and dependence of dynamical averages on the initial conditions, all for the same simple nonequilibrium system, but with three different thermostat types. We found that any of them, Hoover-Holian, Bulgac-Ju-Kusnezov, or Martyna-Klein-Tuckerman, can easily provide stationary nonequilibrium states which are mixing, so giving dynamical averages independent of the initial conditions. The Lyapunov spectra reveal the erratic unpredictable nature of the BJK thermostat more clearly than do the simple averages of phase variables.

The Hoover-Holian and Bulgac-Ju-Kusnezov temperature controls have the advantage of precise temperature control, even far from equilibrium. The Martyna-Klein-Tuckerman thermostat, which lacks this characteristic, does have the virtue of additional simplicity—the underlying equations are quadratic forms. Both the MKT and HH thermostats appear to exhibit a roughly linear response over a wide range of nonequilibrium conditions. The minimum-to-maximum energy ranges shown in the table indicate considerably smaller fluctuations for the MKT chain approach than for the others. The more elaborate forms of the Bulgac-Ju-Kusnezov thermostats, given in the references, could be particularly desirable if the details of the moment fluctuations were specially important. The extra flexibility of the BJK thermostat is not specially helpful in sampling the phase-space efficiently for the heat-flow problem studied here and leads to a particularly erratic dynamics.

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