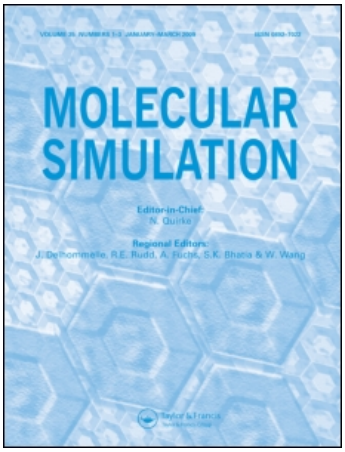

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Dissipative Irreversibility from Nosé's Reversible Mechanics

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DISSIPATIVE IRREVERSIBILITY FROM NOSÉ'S REVERSIBLE MECHANICS

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Nosé's Hamiltonian mechanics makes possible the efficient simulation of irreversible flows of mass, momentum and energy. Such flows illustrate the paradox that *reversible* microscopic equations of motion underlie the *irreversible* behavior described by the second law of thermodynamics. This generic behavior of molecular many-body systems is illustrated here for the simplest possible system, with only one degree of freedom: a one-body Frenkel–Kontorova model for isothermal electronic conduction. This model system, described by Nosé–Hoover Hamiltonian dynamics, exhibits several interesting features: (1) deterministic and reversible equations of motion; (2) Lyapunov instability, with phase-space offsets increasing exponentially with time; (3) limit cycles; (4) dissipative conversion of work (potential energy) into heat (kinetic energy); and (5) phase-space contraction, a characteristic feature of steady irreversible flows. The model is particularly instructive in illustrating and explaining a paradox associated with steady-state statistical mechanics: the Gibbs entropy of a nonequilibrium steady state decreases continuously to minus infinity.

KEY WORDS: Irreversibility, reversibility, Hamiltonian mechanics, steady states, dissipation, entropy.

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INTRODUCTION

In 1984 Nosé [1, 2] introduced a many-body dynamics reproducing the equilibrium canonical ensemble from deterministic Hamiltonian equations of motion. He also showed how to generalize this idea to the isothermal–isobaric ensemble. These same ideas have been simplified [3] and applied not only to equilibrium atomistic simulations [3, 4] but also to nonequilibrium simulations of viscous flow [5] and heat-conducting flows [6], and to molecular vibrational relaxation [7]. The corresponding "Nosé–Hoover" thermostat has proved to be useful in exploring molecular systems far from equilibrium under steady-state conditions.

The theory of nonequilibrium steady states [5, 8–10] can be applied to Nosé's mechanics. The theory has established two surprising results. First, the thermodynamic Gibbs entropy, defined according to Gibbs as $-k\langle \ln f \rangle$, never reaches a steady value but instead decreases continuously to minus infinity. Secondly, the nonequilibrium distribution function, written in the so-called "Kawasaki form" [11], diverges to plus infinity in nonequilibrium steady states. This unsettling and paradoxical state of affairs has cast doubt [12] on the usefulness of phase-space probability densities $f(q, p, t)$, and on the validity of formal results obtained using nonequilibrium generalizations of the Liouville phase-space propagator. To clarify the uncertainties associated with these new many-body techniques, we are applying them to simple systems with only a few degrees of freedom.

A recent investigation [13] of a simple dissipative nonequilibrium system suggests that f really does diverge in the nonequilibrium steady state. This divergence corresponds to the loss, in the phase space, of full dimensionality, with the dynamics restricted to a fractal subspace with zero volume. This picture was confirmed by generating nonequilibrium distribution functions for a simple model system, a two-dimensional "Galton Board", in which a particle "falls", reversibly and at constant kinetic energy, through a regular array of fixed scatterers. The constant-kinetic-energy constraint is applied by using Gauss' "Principle of Least Constraint". Nosé's isothermal mechanics reduces to this special case as the relaxation time associated with the Nosé–Hoover thermostat approaches zero.

Detailed computer calculations show a gradual decrease of the phase-space dimensionality, from 3 to 1, as the field strength is increased. The phase-space contraction occurs relatively rapidly, on the time scale of the scattering particle's collision rate. Thus, a distribution of such particles, followed for only a few collisions, would be confined to a small phase-space volume, approaching zero as the exponential of the elapsed time. This paradoxical vanishing of the phase-space volume applies at all fields, even in the regime where linear-response theory is valid.

Because the Galton Board problem involves singular hard-disk collisions, the phase-space trajectory is composed of a series of disconnected streaming motions that begin and end with collisions. To avoid these discontinuous momentum jumps, we sought a simpler model that incorporates the same qualitative features of dynamic reversibility, thermodynamic irreversibility, and phase-space contraction. The search was successful. The resulting model can be viewed as the weak-coupling limit of a field-driven Frenkel–Kontorova model linked to a Nosé–Hoover thermostat. (The Frenkel–Kontorova model consists of a harmonic chain confined in a periodic sinusoidal potential.) In the present article we describe this new model and present results illustrating deterministic reversible instability as well as dissipative phase-space contraction. We emphasize that the effects found here, for a very simple system, occur

also in many-body molecular systems driven away from equilibrium. In the many-body case it is not necessary that driving forces be applied to *all* particles in the system of interest. Nosé's ideas can be used as true *boundary* conditions, applied only to particular degrees of freedom in a many-body molecular system.

CALCULATIONS

Consider a particle with mass m moving along the x axis under the influence of a periodic (pendulum) potential, $\varepsilon(1 - \cos x)$, and a fixed external field F. The total potential energy of the particle, including the field contribution, is $\phi = \varepsilon(1 - \cos x) - Fx$. In this expression x is a reduced coordinate, where the unit of length is the periodicity of the sinusoidal potential divided by 2π. In addition, reduced variables are introduced by using m and kT as units of mass and energy, respectively, where k is Boltzmann's constant and T is the temperature maintained by the Nosé–Hoover thermostat. Then the equations of motion are as follows:

$$\begin{aligned} \dot{x} &= p; \\ \dot{p} &= F - \varepsilon \sin x - \zeta p; \\ \dot{\zeta} &= \alpha(p^2 - 1). \end{aligned} \tag{1}$$

In reduced variables the definition of temperature, $kT = \langle p^2/m \rangle$, becomes $\langle p^2 \rangle = 1$. Apart from the frictional force $-\zeta p$ the model described by Equations (1) is equivalent to the solid-state Frenkel–Kontorova model [14] with vanishingly small interparticle interactions. The response time of the Nosé–Hoover thermostat is $\alpha^{-1/2}$. If the strength of the cosine potential were made sufficiently large and the field strength F were sufficiently small, $F - \varepsilon \sin x$ could be replaced by $-\varepsilon x$. This special case reduces the dynamics to that of the chaotic Nosé oscillator studied in Reference 4.

New features arise from the presence of the field F. For sufficiently low field strengths, both regular Kolmogorov–Arnold–Moser-like oscillations and irregular chaotic trajectories can be observed, depending on the initial conditions. At higher fields conduction is typically observed, with the conductivity σ = current/field approaching, at high fields, the asymptote $1/F$, which corresponds to maximum-velocity motion parallel to the field.

This conductivity corresponds to periodically repeating "limit cycles", with spatial periods that are multiples of 2π. For an example, see Figure 1. In this case the occupied phase-space dimension is reduced to 1, so that a stable limit cycle, with an entropy minus infinity, results.

One could argue that such a limit cycle, periodically repeating in space and time, is simply mechanics rather than thermodynamics, because no statistical averaging is involved. Figures 2 and 3 illustrate a more paradoxical situation, in which the long-time distribution is determined by following an aperiodic chaotic trajectory and in which the phase-space dimension exceeds 1, but with dissipation. The presence of dissipation (a net conversion of field energy into heat, with the heat extracted by the Nosé thermostat) guarantees that the Gibbs entropy decreases steadily with time.

$$\dot{S} = \dot{\Phi}/T = -F\langle current \rangle. \tag{2}$$

The figures display both the full phase-space trajectory and a typical Poincaré section

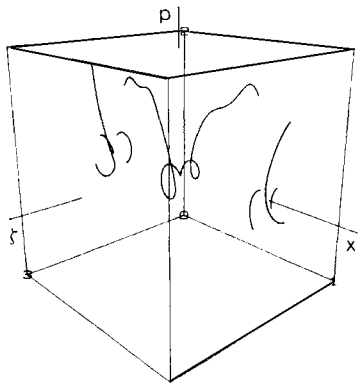

Figure 1. Stable limit cycle, with spatial period 4π and temporal period 47.67. The field strength F is 0.2 and the thermostat strength α is 0.1. The potential parameter ε is 1.0 in this example. The ranges of x, p, and ζ lying within the cube are respectively $\pm 2\pi$, ± 4 and ± 3. The periodic boundary condition in the x direction is clearly displayed.

(at $x = 2n\pi$). Because Nosé's mechanics has a Hamiltonian basis, the system of Equations (1) is time-reversible. Nevertheless, the phase-space trajectories generated by these equations can resemble those generated by dissipative irreversible equations. The typical chaotic, but reversible, Poincaré section shown in Figure 3 bears a qualitative visual resemblance to the *fractal* [15] Poincaré sections previously associated with dissipative irreversible nonlinear systems of equations.

This visual resemblance strongly suggests that the steady-state phase-space distribution is a fractal with a dimensionality lying between 1 (limit cycle) and 3 (mixing over the energetically allowed phase space). Fractal objects reveal a scale-independent structure: enlarging a portion of a fractal Poincaré section in order to examine the nature of the small holes and irregularities only reveals still smaller holes and

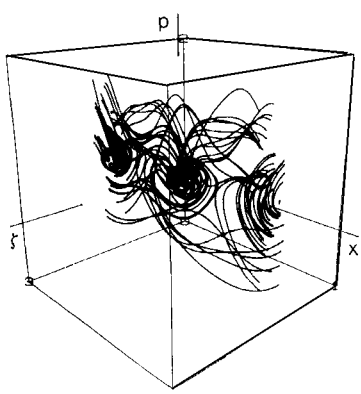

Figure 2. Chaotic phase-space trajectory with field strength 0.3 and thermostat strength 0.1. The potential parameter ε is again 1.0 in this example, as in Figure 1. The initial conditions, with x, p, and ζ all set equal to zero, were followed for 10^5 time steps of 0.01 to a final time of 1000. The total displacement in a 10 times longer run under these conditions was 1414, corresponding to a conductivity $\sigma = 1414/(10\,000F) = 0.47$, with an estimated uncertainty of 0.04. The ranges of x, p, and ζ lying within the cube are again $\pm 2\pi$, ± 4, and ± 3.

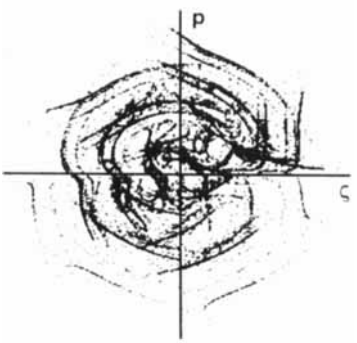

Figure 3 Poincaré surface of section, or "puncture plot", for the trajectory shown in Figure 2. Each point shown corresponds to a value of x equal to $2n\pi$.

irregularities. The existence of fractal phase-space distributions in systems based on Hamiltonian mechanics is surprising, but fully consistent with equation (2).

Kaplan and Yorke describe the fractal dimensionality of phase-space distributions in terms of the spectrum of Lyapunov exponents $\{\lambda_i\}$. The Lyapunov exponents describe the chaotic co-moving deformation of phase-space hypervolumes with time. The largest Lyapunov exponent λ_1 describes the exponential growth rate of a one-dimensional line joining two neighboring trajectories. The sum of the two largest Lyapunov exponents, $\lambda_1 + \lambda_2$, describes the exponential growth rate of an area defined by joining three neighboring trajectories. The sum of the first n exponents likewise describes the growth rate of the corresponding n-dimensional hypervolume. For our model, described by the three differential equations (1), there are three Lyapunov exponents.

Although Kaplan and Yorke's relation between fractal dimensionality and the Lyapunov spectrum is not rigorous, this "Kaplan and Yorke conjecture" has proved to be accurate in a variety of numerical applications. For the chaotic system of Figures 2 and 3, we have evaluated the three Lyapunov exponents $\{\lambda_i\}$, with an uncertainty of 0.001. These are $+0.040$, 0.000, and -0.079, and were obtained by an extension of the constrained-force method outlined in the Appendix and further described in Reference 16. Applications of the Kaplan and Yorke conjecture [17, 18] yields a fractal dimension of 2.50, with an uncertainty of 0.02, in full accord with the visual resemblance mentioned above.

The implications of the thermodynamic irreversibility illustrated by this simple dynamically-reversible conductivity model carry over directly to more macroscopic molecular simulations. In the many-body case, the entropy loss calculated from Liouville's Theorem according to Equation (2) has exactly the same form, so that the many-body phase-space dimensionality must likewise fall as the rate of conversion of work to heat increases. There is some physical evidence for this cooperative loss of dimensionality in the string [19] and sheet [20] phases of high-strain-rate molecular viscous flows simulated by Evans, Heyes, Morriss and Erpenbeck. In these rapidly deforming thermostatted systems, individual particles are collectively forced into ordered arrays reminiscent of liquid crystals. In these systems the steady-state phase-space volume is zero, relative to the equilibrium volume, and the occupied phase-space dimensionality is a fractal dimensionality that can be estimated by applying the Kaplan–Yorke conjecture.

The string and sheet phases are unrealistic caricatures of real fluids because the shear forces driving them were applied homogeneously rather than at physical boundaries, and because the systems were driven *very* far from equilibrium. But the *qualitative* nature of the phase-space distribution is *exactly the same* for systems driven only at boundaries, provided that the boundary forces obey the Nosé–Hoover reversible equations. Empirically, work is converted into heat in nonequilibrium steady-state systems involving two or more particles in two or more dimensions, even when the equations of motion are fully time-reversible. The occupied phase space thus shrinks with time. The corresponding loss of dimensionality in the phase-space trajectories can be estimated directly from the Kaplan and Yorke conjecture, using the collision frequency ν as an estimate for the maximum Lyapunov exponent – the dimensionality loss is of order $\dot{S}/k\nu$, where $\dot{S}$ is the rate of irreversible entropy production. It is noteworthy that this loss of dimensionality is not just a small-system artifact. It persists in the large-system limit.

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APPENDIX

Here we outline the calculation of the Lyapunov exponents for the system of three equations described in the text. The solution of the ordinary differential equations of motion (1) can be obtained using a predictor–corrector method such as Hamming's, or the somewhat simpler fourth-order Runge–Kutta method. This same procedure can be generalized to the study of realistic nonequilibrium many-body systems. The determination of the many-body spectrum is intricate enough to merit a separate report.

At time 0 construct an orthonormal basis of three vectors, δ_1, δ_2, δ_3. As time proceeds, the vectors will span the neighborhood of a phase-space trajectory obtained by solving the three coupled equations of motion. The time-dependence of the vectors requires the construction of the "dynamical matrix" D, which describes the unconstrained time evolution of the basis vectors:

$$\dot{\delta}_i = D \cdot \delta_i.$$

For the equations of motion (1) the nonvanishing elements of the 3×3 matrix D are

$$D_{xp} = 1;\ D_{px} = -\varepsilon \cos x;\ D_{pp} = -\zeta;\ D_{p\zeta} = -p;\ D_{\zeta p} = 2\alpha p.$$

The basis vectors are additionally constrained to remain orthonormal by introducing Lagrange multipliers λ_{11} (which maintains the length of δ_1), λ_{22} (which maintains the length of δ_2), λ_{21} (which maintains the orthogonality of δ_1 and δ_2), λ_{33} (which maintains the length of δ_3), together with λ_{32} and λ_{31} (which maintain the orthogonality of δ_3 to the plane defined by δ_1 and δ_2). The full equations of motion for the basis vectors become

$$\dot{\delta}_i = D \cdot \delta_i - \Sigma \lambda_{i \geq j} \delta_j,$$

where the λ_{ii} (the time-averaged values of which are the Lyapunov exponents) and the $\lambda_{i \geqslant j}$ are constructed from matrix products:

$$\lambda_{ii} = \delta_i^t \cdot D \cdot \delta_i;$$

$$\lambda_{i \geqslant j} = \delta_i^t \cdot D \cdot \delta_j + \delta_j^t \cdot D \cdot \delta_i.$$

The three equations of motion for the basis vectors are added to the set being integrated. It is convenient to add another three differential equations, integrating λ_{11}, λ_{22}, and λ_{33} with respect to time, to determine the Lyapunov exponents.