

Nonequilibrium Molecular Dynamics: Reversible Irreversibility from Symmetry Breaking, Thermostats, Entropy Production, and Fractals.

Wm. G. Hoover

*Highway Contract 60, Box 565,
Ruby Valley, Nevada 89833;
Department of Applied Science,
University of California at Davis/Livermore;
and
Lawrence Livermore National Laboratory,
Livermore, California 94551-7808.*

Abstract.

Nonequilibrium Molecular Dynamics requires an extension of Newtonian and Hamiltonian mechanics. This new extended mechanics includes Gauss' and Nosé's *thermostatted* equations of motion. Here I review the past 20 years' history of the various formulations, solutions, interpretations, and further extensions of these "new" motion equations. I emphasize the fractal nature of the resulting phase-space distributions. I describe the connections of these fractal distributions to irreversibility, to time-symmetry breaking (from reversible motion equations), and to entropy production and the Second Law, far from equilibrium.

1. INTRODUCTION

Molecular dynamics, the numerical solution of atomistic-scale equations of motion, was developed by Enrico Fermi (at the Los Alamos Laboratory), George Vineyard (at the Brookhaven Laboratory), and Berni Alder (at the Livermore Laboratory), about fifty years ago. This usual molecular dynamics, a numerical solution of Newton's equations, $\{m\ddot{q} = F\}$, provides a solid foundation for Gibbs' and Boltzmann's statistical mechanics. Molecular dynamics has provided direct numerical verifications of the detailed statistical theories of bulk behavior which Gibbs and Boltzmann based on smooth equilibrium phase-space distributions. Newton's equations of motion and Gibbs' microcanonical (constant-energy) phase-space distributions were found to be completely compatible in the earliest days of constant-energy molecular dynamics. Molecular dynamics became a reliable method for the determination of equations of state. Gas, fluid, and solid phases were all explored, as were also the phase transitions linking them.

That exploratory work on the microscopic basis for equilibrium thermodynamic properties was finished off by the development of equilibrium perturbation theory. This was very much a joint effort, with about a dozen different investigators collaborating on sev-

eral numerical formulations of a perturbation theory for Helmholtz' free energy. The perturbation theories were based on combining Gibbs' and Boltzmann's ideas with results taken from computer simulation. This body of perturbation theories made it possible to compute equilibrium equations of state for a wide variety of relatively-general systems in terms of the entropic and structural properties of a "reference system" of hard spheres. The hard-sphere properties were available from the results of computer simulation, both Monte Carlo and molecular dynamics.

By 1972 it was high time to concentrate on nonequilibrium properties. Fortunately for me I found a graduate student, both willing and able to take on this challenge. Bill Ashurst had just joined Sandia's Livermore Laboratory, across the street from the "Rad Lab" where I worked, and was eager to take on the challenging doctoral program at "Teller Tech", the graduate Department of Applied Science. This Department, though a part of the University of California's *Davis* Campus, was an oasis of unclassified research excitement, located within the Livermore Laboratory's boundaries. Though by now the founders of the Department are all either dead or retired, a vestige of it remains in Livermore today.

Bill Ashurst and I set out to develop *nonequilibrium* molecular dynamics. Our underlying goal at the start was to understand the large discrepancies between the Green-Kubo transport coefficients found by Levesque, Verlet, and K urkijarvi and the corresponding transport coefficients for that simplest of the real fluids, argon. We measured the transport coefficients by setting up computer simulations of both viscous and heat flows. In order to do this, we developed both *local thermostats* at system boundaries and global *homogeneous thermostats*, which operated throughout systems described by periodic boundaries. In either of these cases the computational "thermostats" extracted the irreversibly-generated heat associated with nonequilibrium flows of momentum and energy.

These thermostatted systems generated steady nonequilibrium flows. The thermostats could constrain either the kinetic energy or the internal energy of a set of thermostatted particles to a fixed value. The kinetic-energy thermostats rely on Boltzmann and Gibbs' identification of the kinetic energy per particle with the mean thermal energy,

$$\langle mv^2/2 \rangle \equiv 3kT/2 .$$

In either the isokinetic or the isoenergetic case we used "velocity rescaling" to impose the constraint. In England, Les Woodcock had used exactly this same kind of temperature control. In the isokinetic case Ashurst multiplied every thermostatted particle's velocity by a factor chosen to return the current kinetic energy of the thermostatted set to its initial value. The resulting modification of Newtonian mechanics was "isokinetic" molecular dynamics. Here the thermostatted set's kinetic temperature was a constant of the motion.

A couple of years later we found that this velocity rescaling was formally equivalent to applying a frictional force $-\zeta p$ proportional to each particle's momentum. I spent considerable time in the libraries at Livermore, looking for a link between our "ad hoc" thermostating recipe and classical mechanics. I found a description of Gauss' Principle (of Least Constraint), in one of Sommerfeld's books. The Principle states that *any* cons-

straint, including “nonholonomic constraints” involving momenta, should be imposed with the least possible constraint forces. Gauss’ Principle turned out to be exactly equivalent to our isokinetic thermostating idea.

Gauss’ thermostat turned out to be specially useful far from equilibrium, where it could provide stress-strainrate relations under extreme shockwave conditions. In the isokinetic case, the equations of motion which result from Gauss’ Principle include constraint forces $\{F_C\}$ linear in the momenta:

$$\{dp/dt = F(q) + F_C(q, p) ; F_C = -\zeta p\} ;$$

$$\zeta_{\text{Gauss}} = \sum F \cdot p / \sum p^2 .$$

At about this same time (1982) Shuichi Nosé discovered a more general means of thermostating, based on *integral* feedback control (as opposed to Gauss’ *differential* feedback control). Nosé was born 17 June 1951 in the small town of Mineyama and attended high school there. His thesis work (D. Sc. in Chemistry, 1981) at Kyoto University involved Monte Carlo simulation. After three years of postdoctoral work in Ottawa, during which he developed his revolutionary thermostating ideas, he moved back to Japan to teach at Keio University in Yokohama. He married Ibuki Kushida in April 1985, and his son Atsushi (“temperature”) was born in January 1986.

It was in summer 1984 that I met Shuichi by accident, on a Paris train platform, several days in advance of a meeting we both planned to attend. My hotel, the Hôtel California at 32, rue des Ecoles, was some distance from Nosé’s thoroughly-Japanese hotel. We arranged to meet outside the Notre Dame cathedral for several hours of intense technical conversations. I learned enough from these to write a paper during the next few weeks, while visiting Philippe Choquard in Lausanne[1]. My study of Nosé’s methods[2] (applied to a single harmonic oscillator) made it clear that the coordinate-space (q, \dot{q}, ζ) version of Nosé’s dynamics (now called “Nosé-Hoover dynamics) was useful, while his alternative (q, p, s, p_s) “time-scaled” phase-space version was not. At Nosé’s invitation, I was in Japan for sabbatical leave 1989-1990, when IBM recognized his work with an elaborate dinner and a ceremony awarding him its Japan Science Prize in 1989.

Nosé’s thermostat forces depend on the system’s past history rather than on its instantaneous state. With # degrees of freedom the Nosé-Hoover motion equations are these:

$$\{\dot{p} = m\dot{q} = F(q) + F_C ; F_C = -\zeta p = -m\zeta\dot{q}\} ;$$

$$\dot{\zeta} = (1/\#) \sum [(p^2/mkT) - 1]/\tau^2 = (1/\#) \sum [(m\dot{q}^2/kT) - 1]/\tau^2 .$$

The coordinate-space form of this dynamics follows directly from Nosé’s *ad hoc* Hamiltonian:

$$\mathcal{H}_{\text{Nosé}} = (K/s) + s[\Phi + (p_s^2/2M) + \#kT \ln s] \equiv 0 .$$

where $M = \#kT \tau^2$. K is the usual kinetic energy, expressed in terms of the $\{p\}$ and p_s is the action variable (which turns out to be proportional to the friction coefficient ζ) conjugate to s . Evidently the friction coefficient ζ depends on the *past*:

$$\zeta_{\text{NH}}(t) = \zeta_{\text{NH}}(0) + (1/\#) \int_0^t \sum [(p^2/mkT) - 1]/\tau^2 dt' .$$

Despite the apparent dependence on the past, the motion equations are themselves precisely time-reversible. Any time-ordered set of coordinates satisfying them provides an alternative solution when the time ordering of the coordinates is reversed. In the reversed solution of the equations the momenta $\{p\}$, velocities $\{\dot{q}\}$, and the friction coefficient(s) ζ all change signs.

In the equilibrium case Nosé's thermostat variable ζ has a Gaussian distribution with zero mean value,

$$f(\zeta) \propto \exp(-\#\zeta^2\tau^2/2) .$$

His thermostats were capable of reproducing Gibbs' *entire* canonical distribution, $f(q, p) \propto \exp(-\mathcal{H}/kT)$, not just the isokinetic one. Analogous equations of motion provided either instantaneous or time-averaged control of the momentum flux (or "stress tensor") and heat flux. By 1985 the various generalizations of mechanics needed for a detailed understanding of Gibbs' statistical mechanics were just about complete. The only piece still missing is a variational principle like Gauss' on which to base Nosé's approach to canonical dynamics.

The pedagogical benefits of Nosé's thermostats should be a part of any physicist's education. This review summarizes the main consequences of his work from my perspective as an actively-involved observer. The consequences for simulation, for statistical mechanics, for thermodynamics, and for nonlinear dynamics make up Secs. 2, 3, 4 and 5. Sec. 6 is devoted to an example problem, a nonequilibrium oscillator exposed to a temperature gradient induced by an extension of Nosé's thermostat ideas.

I have resisted including all of the dozens of literature references germane to this review, expecting that the interested reader can find them on his own through an internet search. Many of the older references can be found in my books[3, 4]. It gives me pleasure to dedicate this manuscript to Shuichi Nosé.

2. CONSEQUENCES FOR SIMULATION

Nosé's main research goal was to make equilibrium simulations more relevant to experimental studies. He wanted to use temperature and pressure as independent variables, rather than energy and volume, facilitating comparisons with experimental equilibrium data. I was much more interested in *nonequilibrium* phenomena, because perturbation theory had made the "problem" of determining simple-fluid properties into a relatively pedestrian nonproblem. Provided that the composition of the system is fixed, Nosé's mechanics can be applied to any reasonable isothermal or isobaric ensemble. It was natural to apply these same ideas to nonequilibrium systems, systems driven from equilibrium, and even "far" from equilibrium, by velocity gradients, temperature gradients, or by the performance of mechanical work.

Because Green and Kubo had formulated transport processes in terms of Gibbsian fluctuations, any credible nonequilibrium algorithm had to reduce to the proper equilib-

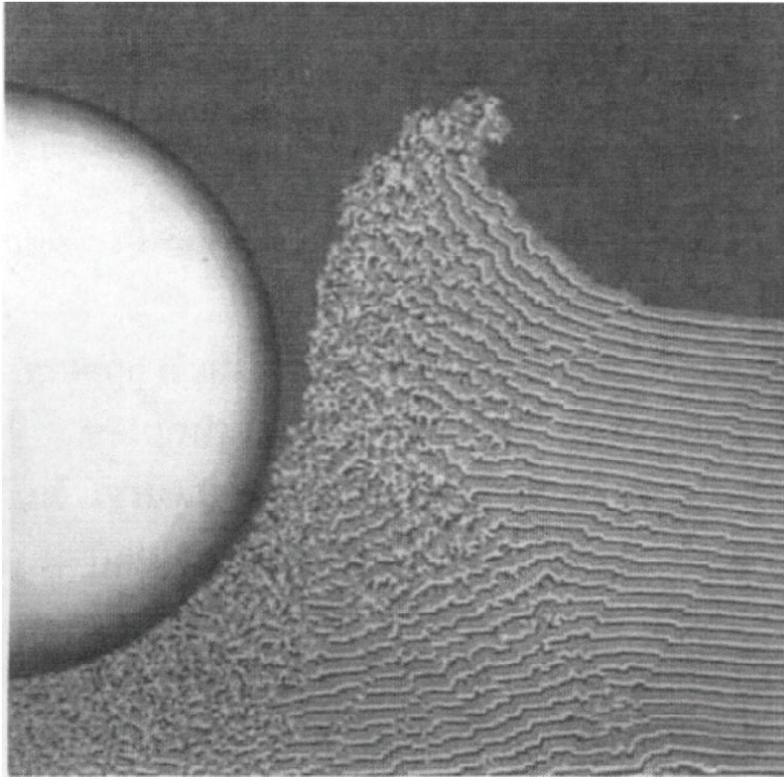


FIGURE 1. Plastic flow using thermostatted nonequilibrium molecular dynamics. The indenter is pressed into the thermostatted workpiece at a speed somewhat less than the sound speed.

rium one so as to reproduce the Green-Kubo results. Ashurst and I and Lees and Edwards independently used homogeneous periodic shear to measure viscosity. Evans and Gillan independently invented an energy field to generate thermal flows consistent with Green-Kubo thermal conductivity.

The thermostats were also applied to a host of interesting problems in materials science. Shockwaves are the simplest of these because the boundary conditions are purely equilibrium ones. But fracture, viscous flows, heat flows, and plastic deformation were also being studied. Nosé's feedback controls were ideally suited to these nonequilibrium problems too, and have since then undergone extensive development, resulting in a detailed foundation for understanding nonequilibrium systems. By 1990 a host of simulations, some with as many as a million particles, had verified many of the simple engineering rules of thumb. Fig. 1 shows a two-dimensional indentation simulation from those days. The new mechanics, besides opening up these new fields of simulation, had profound conceptual consequences for statistical mechanics.

3. CONSEQUENCES FOR STATISTICAL MECHANICS

Gibbs' statistical mechanics is based on following the many-body flow in "phase space", the many-dimensional (q, p) space in which a single point corresponds to all the coordinates q and momenta p of the degrees of freedom composing the system. For a Hamil-

tonian system the flow equations are:

$$\mathcal{H}(q, p) \longrightarrow \{ \dot{q} = +\partial \mathcal{H} / \partial p = p/m ; \dot{p} = -\partial \mathcal{H} / \partial q = F \} .$$

They have the consequence (Liouville's Theorem) that the flow of probability density f through the space occurs at constant density. The only possible stationary solution of this flow law is that the density has a common value throughout the accessible part of the phase space:

$$\dot{f} = 0 \longrightarrow f_{\text{eq}} = \text{constant} .$$

Liouville's Theorem also implies that the (hyper)volume of a comoving phase volume element \otimes , does not change with time:

$$d \ln \otimes / dt \equiv 0 .$$

This constant "microcanonical" distribution implies that any system coupled mechanically to an ideal-gas thermometer obeys the "canonical" distribution, $\propto \exp(-\mathcal{H}/kT)$, where T is the kinetic-theory temperature of the ideal gas.

Now consider flows in phase space governed by Nosé-Hoover thermostats. To characterize them it is specially convenient to rewrite the second-order motion equation in their equivalent "Nosé-Hoover" form:

$$\{ m\dot{q} = p ; \dot{p} = F - \zeta p \} ; \dot{\zeta} = (1/\#) \sum [\frac{p^2}{mkT} - 1] / \tau^2 .$$

These motion equations are fully consistent with Gibbs' distribution. To see this, it is only necessary to apply Liouville's Theorem, appropriately generalized to a $(2\# + 1)$ -dimensional space which includes the friction coefficient ζ :

$$\partial f / \partial t = - \sum \partial (f\dot{q}) / \partial q - \sum \partial (f\dot{p}) / \partial p - \partial (f\dot{\zeta}) / \partial \zeta .$$

Substituting the equations of motion, along with the trial solution,

$$f \propto \exp[- \sum \frac{p^2}{2mkT}] \exp[- \frac{\Phi}{kT}] \exp[- \frac{\# \zeta^2 \tau^2}{2}] ,$$

we can evaluate all the partial derivatives needed to apply Liouville's Theorem:

$$\begin{aligned} \partial f / \partial t &\equiv 0 ; \\ - \sum \partial (f\dot{q}) / \partial q &= \sum (-F \cdot p / mkT) f ; \\ - \sum \partial (f\dot{p}) / \partial p &= \sum [(F - \zeta p) \cdot (p / mkT) f + \zeta f] ; \\ - \partial (f\dot{\zeta}) / \partial \zeta &= + \zeta \sum f [\frac{p^2}{mkT} - 1] / \tau^2 . \end{aligned}$$

Evidently the trial solution satisfies the theorem identically. This is a direct proof that

the Nosé-Hoover equations of motion are consistent with the canonical distribution, extended to include a Gaussian distribution in the friction coefficient. It establishes also that the probability density f and the infinitesimal phase volume \otimes both vary *following* the flow:

$$\begin{aligned} d \ln f / dt &= -d \ln \otimes / dt = \\ \partial \ln f / \partial t + \sum [\dot{q} \cdot \partial \ln f / \partial q + \dot{p} \cdot \partial \ln f / \partial p] + \dot{\zeta} \partial \ln f / \partial \zeta &= \\ - \sum [\partial \dot{q} / \partial q + \partial \dot{p} / \partial p] - \partial \dot{\zeta} / \partial \zeta &= \\ - \sum [0 - \zeta] - 0 = \sum \zeta \neq 0 . \end{aligned}$$

For statistical mechanics the introduction of motion equations leading to changes of phase volume \otimes , with those changes directly linked to heat transfer $-\zeta \sum p^2/m$, and to entropy production, was fundamental, opening up connections to thermodynamics and nonlinear dynamics which were totally new.

4. CONSEQUENCES FOR THERMODYNAMICS

From the pedagogical standpoint it is extremely interesting to see *irreversible* behavior arising from time-reversible equations of motion[5]. The one-way behavior that results from the either-way Nosé-Hoover motion equations is the microscopic analog of the macroscopic Second Law of Thermodynamics. It is significant that the microscopic version, based on limiting the growth of phase volume, involves time averages. One can only argue against an increase in phase volume if that increase were to apply in perpetuity, that is, in either a “steady state” or a cyclic process. In either case Nosé-Hoover mechanics provides a definite sign for the (time-averaged) friction coefficient sum:

$$\langle \sum \zeta \rangle = \langle d \ln f / dt \rangle = - \langle d \ln \otimes / dt \rangle > 0 .$$

The opposite sign, corresponding to an inexorably increasing ultimately diverging phase volume is ruled out, for stable flows.

The friction coefficient sum is precisely equal to the rate at which entropy is generated in the external reservoirs with which the thermostatted system interacts:

$$\langle d(S_{\text{ext}}/k) / dt \rangle = - \langle (dQ_{\text{int}}/dt) / kT_{\text{ext}} \rangle = \langle \sum \zeta p^2 / mkT_{\text{ext}} \rangle = \langle \sum \zeta \rangle ,$$

where the last equality follows from the motion equations:

$$\begin{aligned} \dot{\zeta} &= \sum [(p^2/mkT) - 1] / \tau^2 \longrightarrow \langle \sum \zeta \dot{\zeta} \rangle = 0 \longrightarrow \\ \langle \sum \zeta [(p^2/mkT) - 1] \rangle &= 0 \longrightarrow \langle \sum \zeta (p^2/mkT) \rangle = \langle \sum \zeta \rangle . \end{aligned}$$

Nosé-Hoover mechanics leads directly to the conclusion that the external entropy change associated with a stationary or cyclic process is positive. The corresponding thermodynamic relation,

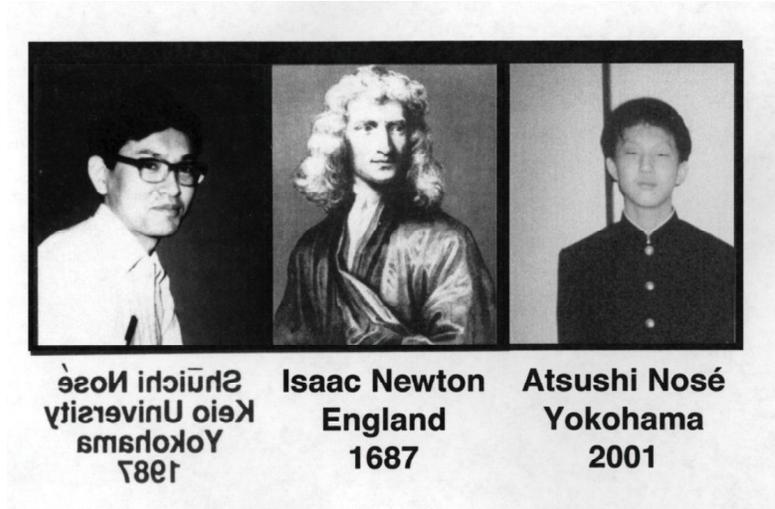


FIGURE 2. A Newtonian region in thermal contact with two Nosé-Hoover reservoirs. For a stable stationary state to exist it is necessary that the positive friction coefficient sum (at the cold reservoir) exceed the negative friction coefficient sum (at the hot reservoir). This guarantees a net flow of heat from hot to cold, in accord with (one of) Clausius' forms of the Second Law of Thermodynamics discussed in Sec. 4.

$$-\langle (dQ_{\text{int}}/dt)/kT_{\text{ext}} \rangle = \langle (dS_{\text{ext}}/dt)/k \rangle > 0 ,$$

is one of Clausius' forms of the Second Law.

Thermodynamics does not discuss the length of time required to make measurements. Once entropy has been defined [as the reversible integral of heat transfer divided by temperature $dS \equiv dQ_{\text{rev}}/T$] the Second Law of Thermodynamics can be stated in many alternative ways[6]. The simplest of these, also attributed to Clausius, is the statement that heat cannot flow from a cold body to a hot one. This particular statement requires a bit of care far from equilibrium: in certain shockwaves the flow of heat is indeed opposite in direction to that predicted by Fourier's law[7]. But in the simple case of Fig. 2, where a Newtonian system interacts with two Nosé-Hoover reservoirs at T_C and $T_H > T_C$, it is easy to prove that the time-averaged friction coefficient sums are consistent with this form of the Second Law also:

$$\langle \sum \zeta_C \rangle > 0 ; \langle \sum \zeta_H \rangle < 0 .$$

The proof is as follows: (i) evidently energy balance requires that the absolute value of the cold sum exceeds that of the hot sum:

$$\langle \sum \zeta_C T_C \rangle + \langle \sum \zeta_H T_H \rangle = 0 \rightarrow |\langle \sum \zeta_C \rangle| > |\langle \sum \zeta_H \rangle| .$$

(ii) If, as is required for stability of the phase volume, the overall sum, $\sum \zeta_C + \sum \zeta_H$, is to be positive, the cold sum *must* be the positive one, corresponding to heat extracted at the cold reservoir and heat inserted at the hot end. Again, Nosé-Hoover mechanics implies the validity of a time-averaged Second Law of Thermodynamics.

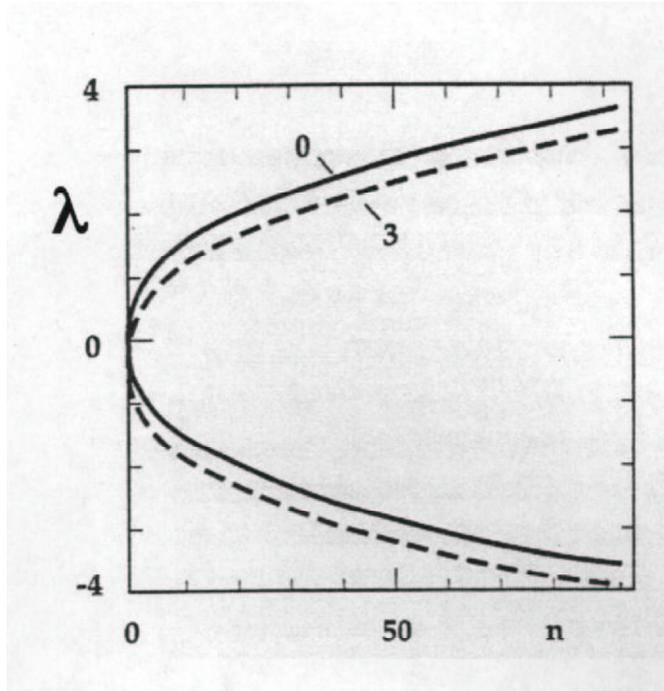


FIGURE 3. Lyapunov spectra, both at (full curve) and away from (dots) equilibrium, for a dense-fluid system of 32 Lennard-Jones particles exposed to an external field. This constant field accelerates half the particles to the left and the other half to the right. The symmetry breaking associated with the shift of the spectrum to more negative values signals the collapse of the ergodic phase-space distribution to a zero-volume strange attractor. The dimensionality loss is about 16. There are 96 pairs of Lyapunov exponents in the 192-dimensional phase space.

5. CONSEQUENCES FOR NONLINEAR DYNAMICS

Nonlinear dynamics studies general “flows”, the solutions of sets of ordinary differential equations in general spaces. Time-reversible flows, such as those following the Nosé-Hoover equations, are much less studied than irreversible “dissipative” flows which generate “strange attractors”. In nonlinear dynamics the Lyapunov instability of flow equations is characterized by the spectrum of Lyapunov exponents, the time-averaged rates of growth (or decay) associated with an infinitesimal hypersphere that moves with the flow. Evidently the number of Lyapunov exponents is equal to the number of dimensions in which the flow occurs.

Hamiltonian systems have a special either-way symmetry, with any phase-space direction corresponding to expansion converted into a compression in the time-reversed version of the same flow. The symmetry of the Lyapunov spectrum can be seen in Fig. 3. The effect of dissipation, even time-reversible dissipation, gives a qualitative change. Because the flow volume can only decrease (to a strange attractor) the Lyapunov spectrum must have a negative sum:

$$\sum \lambda_i \equiv \langle d \ln \otimes / dt \rangle = \langle -d \ln f / dt \rangle < 0 .$$

The specimen calculation in the figure[8] illustrates this shift for a simple system exposed to an accelerating field. We have seen that the consequence of this decreasing phase volume is the microscopic version of the Second Law of Thermodynamics.

There is a vast literature on chaos, nonlinear dynamics, and fractals, much of which can be applied directly to nonequilibrium molecular dynamics. This work has been carried out for the past twenty years by hundreds of interested researchers. An example problem, quite well suited to student exploration, is described in the following section.

6. DOUBLY-THERMOSTATED ERGODIC NONEQUILIBRIUM OSCILLATOR

Here we consider a simple model system to illustrate the ideas discussed in the text[9]. Because the simple Nosé-Hoover oscillator is not ergodic, we generalize Nosé's approach to control the *fourth* moment of the oscillator's momentum, as well as the second. The additional control variable is ξ . Choosing all of the various problem parameters equal to unity and using a thermostat relaxation time τ equal to the corresponding unperturbed oscillator period, $\tau = 2\pi$, the set of four ordinary differential equations we solve is as follows:

$$\begin{aligned}\dot{q} &= p ; \dot{p} = -q - \zeta p - \xi(p^3/T) ; \\ \dot{\zeta} &= [(p^2/T) - 1]/\tau^2 ; \dot{\xi} = [(p^4/T^2) - 3(p^2/T)]/\tau^2 ; \\ T &= 1 + \tanh(q) .\end{aligned}$$

As shown in Fig. 4, the temperature varies from 0, as q approaches $-\infty$ to 2, as q approaches $+\infty$. Had we instead used a constant temperature of unity throughout the equilibrium Gaussian distribution would result:

$$f \propto \exp(-q^2/2) \exp(-p^2/2) \exp(-\tau^2 \zeta^2/2) \exp(-\tau^2 \xi^2/2) .$$

In the nonequilibrium case the projections of the motion into the (q, p) and (ζ, ξ) planes are shown as Fig. 5. Their appearances suggest *fractal* character, with a singular dependence of probability density on location. These fractals are typical of nonequilibrium states, reflecting the rarity of these states in the equilibrium phase space.

The Lyapunov exponents for the four-dimensional flow are:

$$\{\lambda\} = (+0.059, 0.000, -0.018, -0.256) .$$

These provide the time-averaged rate of phase-volume change along with the corresponding rate of probability density divergence:

$$\langle d \ln \otimes / dt \rangle \equiv -\langle d \ln f / dt \rangle = +\langle \sum \lambda \rangle = -0.215 .$$

As an independent check,

$$\langle d \ln f / dt \rangle = \langle \zeta + (3p^2 \xi / T) \rangle = 0.215 .$$

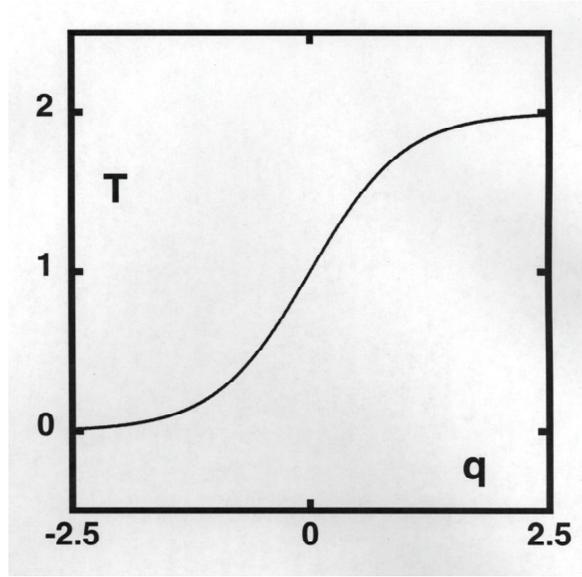


FIGURE 4. The hyperbolic tangent temperature profile for the thermostatted oscillator of Sec. 6 is shown here.

The total heat transfer in this stationary process, must vanish, on average:

$$\langle dQ/dt \rangle = \langle -\zeta p^2 - (\xi p^4/T) \rangle = 0.0 ,$$

while the associated entropy change, obtained by dividing by the thermostat temperature, matches the dissipation, as expected:

$$\begin{aligned} \langle (1/T)dQ/dt \rangle &= \langle -\zeta p^2/T - \xi p^4/T^2 \rangle = \\ &= \langle -\zeta - (3p^2\xi/T) \rangle = \\ &= \langle -d \ln f / dt \rangle = -0.215 . \end{aligned}$$

Fig. 4 shows the temperature profile. The densities of the heat transfer and entropy change, as well as their integrals with respect to the coordinate q are shown in Fig. 6. All these thermodynamic data were obtained as averages over a run of 10^9 timesteps of 0.001 each while the Lyapunov spectrum was obtained using 10^8 such timesteps.

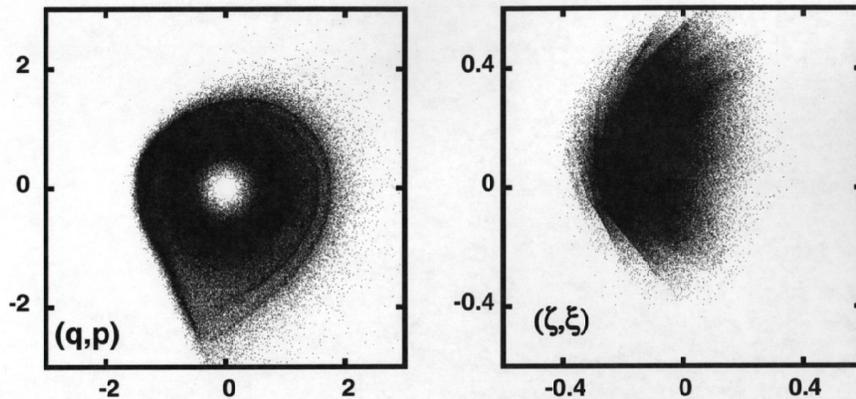


FIGURE 5. Projections of the motion of the thermostatted oscillator into the (q, p) and (ζ, ξ) subspaces. The thermostat variables are smaller than the oscillator variables by roughly a factor of the oscillator relaxation time, $\tau = 2\pi$. The Kaplan-Yorke dimension of the strange attractor is 3.16, significantly less than that of the four-dimensional phase space in which the motion takes place.

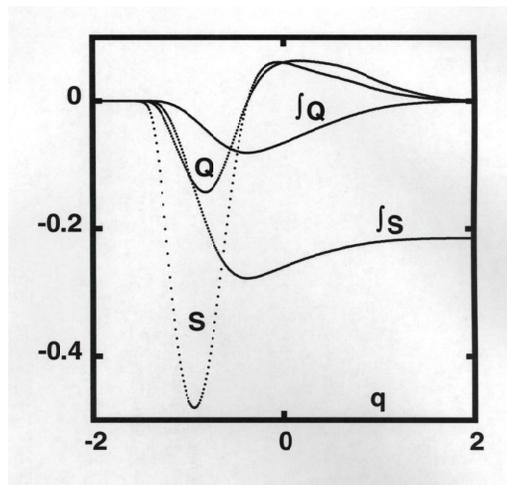


FIGURE 6. The four curves show the densities and their integrals (\int) for both the heat transfer (Q) and the entropy production (S). The total time-averaged heat transfer, $\langle dQ/dt \rangle \equiv 0$ and the total entropy production $\langle dS_{\text{int}}/dt \rangle = \langle (dQ/dt)/T \rangle = -0.215$ are the large- q limits of the two integrated curves.

7. OUTLOOK

Friction coefficients able to control temperature have provided simulators with a useful tool in studying systems far from equilibrium. The discovery that the result of this time-

reversible dissipation is the formation of dissipative fractal strange attractors in phase space, with dimensionality reduced below the equilibrium dimensionality, was surprising. As a consequence, it became clear that a consistent nonequilibrium entropy based on Gibbs' (or Shannon's) $S/k \propto \ln f$ would not be possible. This seems not to be such a serious loss, as the utility of a nonequilibrium entropy is not at all clear. On the other hand, a focus on the structure of nonequilibrium attractors, their homogeneity and fractal dimensions, suggests that further understanding of highly nonequilibrium systems is desirable. The isotropy and homogeneity of these attractors remains to be explored, as does also their connection to Green-Kubo linear response theory. Simple models, such as the four-dimensional oscillator problem mentioned here, can prove very helpful in evaluating and interpreting theoretical advances such as the Fluctuation Hypotheses and Finite-Rate Thermodynamic procedures currently under intense investigation.

8. AFTERWORD

I thank Francisco Uribe, Leopoldo García-Colín, and Enrique Diaz for all their work in organizing and executing the Segunda Reunión Mexicana sobre Física Matemática y Física Experimental in Mexico City. Leopoldo's gentle persistence was responsible for my emphasis here on the Second Law of Thermodynamics. The science and ambiance of the Segunda Reunión Mexicana would be hard to match anywhere. Here is to the goal of achieving more such successes!

ACKNOWLEDGMENTS

Work performed under the auspices of the United States Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-Eng-48. The support of the University of California and my many collaborators over the last four decades is much appreciated. I thank them all.

REFERENCES

1. W. G. Hoover, Phys. Rev. A **31**, 1695 (1985).
2. S. Nosé, Mol. Phys. **52**, 255 (1984); S. Nosé, J. Chem. Phys. **81**, 511 (1984).
3. Wm. G. Hoover, *Computational Statistical Mechanics* (Elsevier, Amsterdam, 1991). A pdf file for this out-of-print book is available at <http://williamhoover.info>.
4. Wm. G. Hoover, *Time Reversibility, Computer Simulation, and Chaos* (World Scientific, Singapore, 1999 and 2001). While my supply lasts I am happy to mail a copy of this book to any interested reader.
5. B. L. Holian, W. G. Hoover, and H. A. Posch, Phys. Rev. Lett. **59**, 10 (1987).
6. Wm. G. Hoover, "Molecular Dynamics, Smooth Particle Applied Mechanics, and Clausius' Inequality", Computational Methods in Science and Technology **3**, 19-23 (1997, Poznań).
7. O. Kum, Wm. G. Hoover, and C. G. Hoover, Phys. Rev. E **56**, 462 (1997).
8. H. A. Posch and W. G. Hoover, Phys. Rev. A **38**, 473 (1988).
9. For some closely-related models, see H. A. Posch and Wm. G. Hoover, Phys. Rev. E **55**, 6803 (1997).