Nosé-Hoover Nonequilibrium Dynamics and Statistical Mechanics

William Graham Hoover
Great Basin College, Nevada
http://williamhoover.info

1. Thermostatted Oscillators
2. Many-Body Heat Flow → Fractals
3. Lyapunov Spectrum, Kaplan-Yorke
4. Jarzynski's Helmholtz Free Energy
5. Fractal Distributions and Second Law
6. Summary

Wm G Hoover *et ux* @ Grizzly Flat, California

ENGINEERING @ LLNL

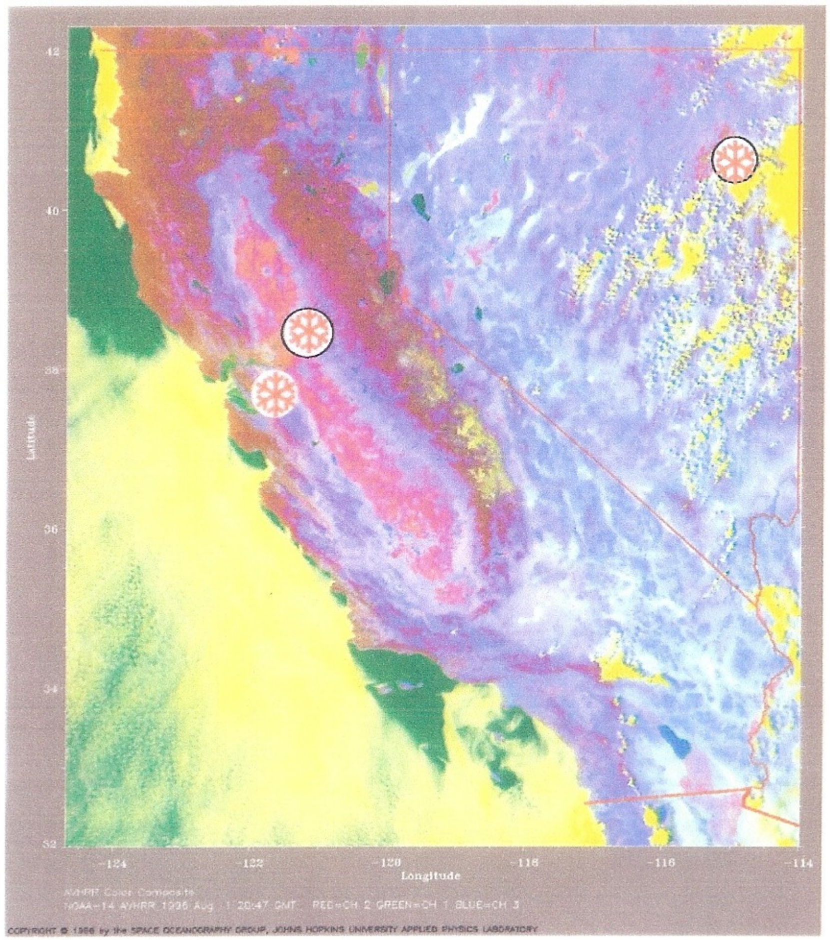
Nonequilibrium Molecular Dynamics

Wm G Hoover and C G Hoover
Lawrence Livermore Laboratory

Overview of California and Nevada

Davis

Livermore



Ruby Valley

ENGINEERING @ LLNL

Nonequilibrium Molecular Dynamics

Wm G Hoover & Carol G Hoover
UCDavis, LLNL, and Ruby Valley NV

Ruby Valley Neighbors

Local Ruby Valley Industry

MICRO-BREWED IN NEVADA'S HIGH COUNTRY

RUBY

MOUNTAIN

BREWING COMPANY

VIENNA STYLE

LAGER

With Fujiwara-sensei in 1990 @ Keio

STUDIES IN MODERN THERMODYNAMICS 11

Computational Statistical Mechanics

Wm. G. Hoover

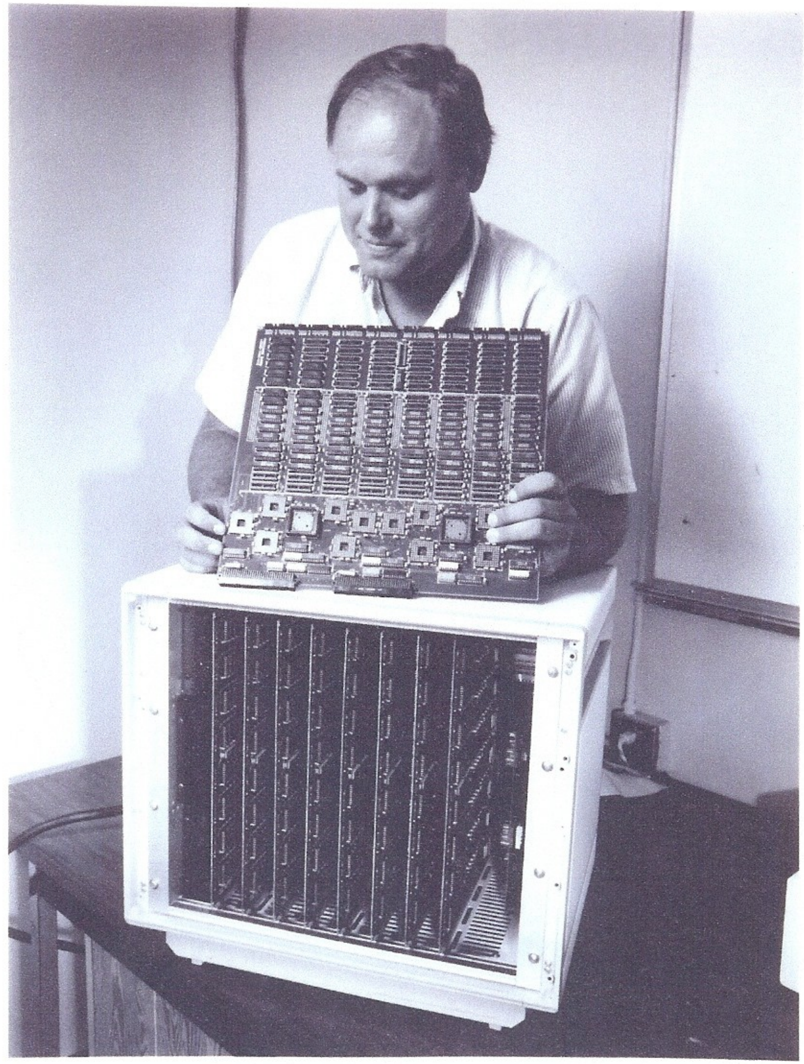
熵

ELSEVIER

Free pdf file available at http://williamhoover.info

Keio University, Yokohama, 1986

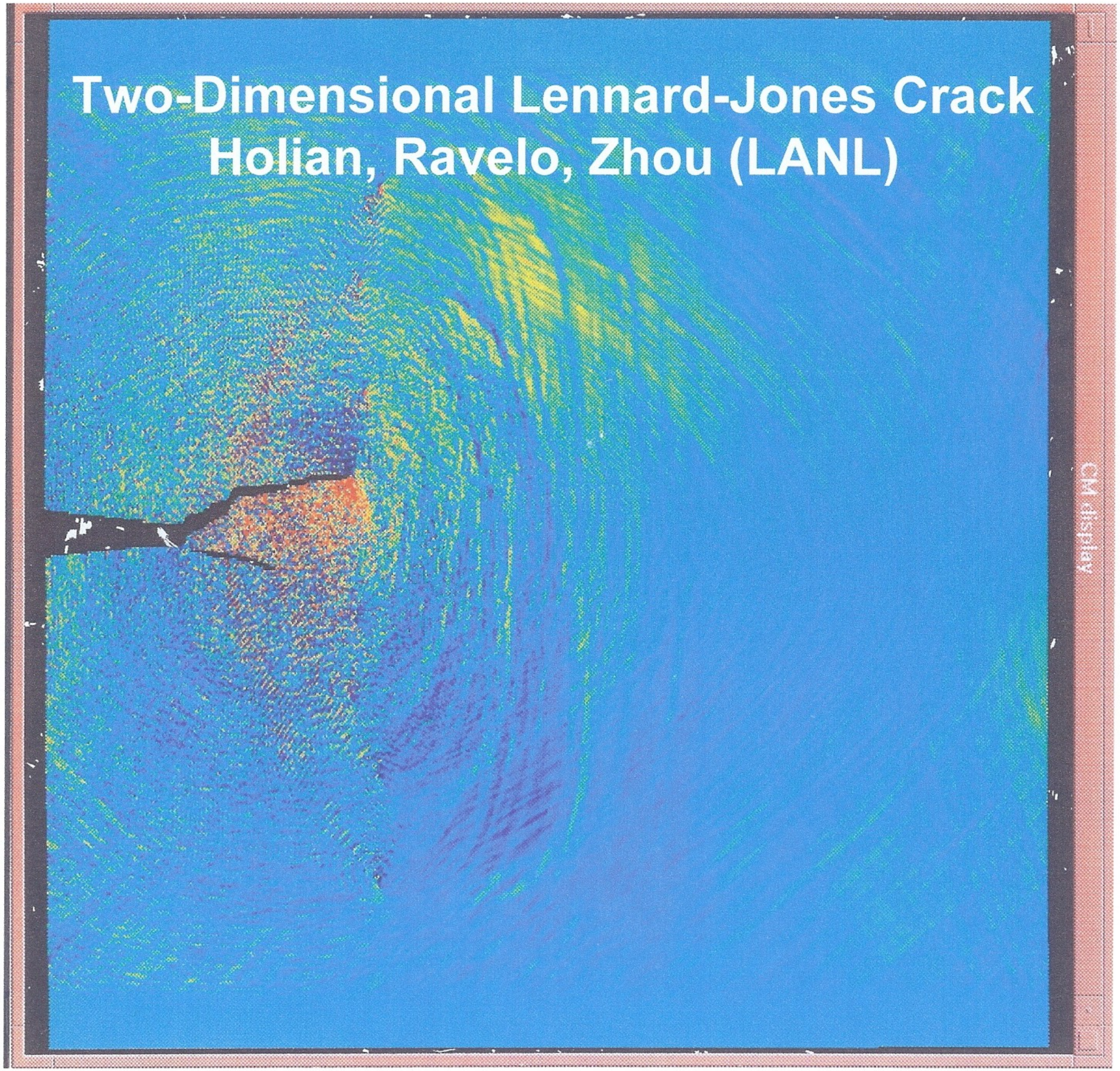
Tony De Groot, Livermore, 1989



Thermostatted Metal Cutting

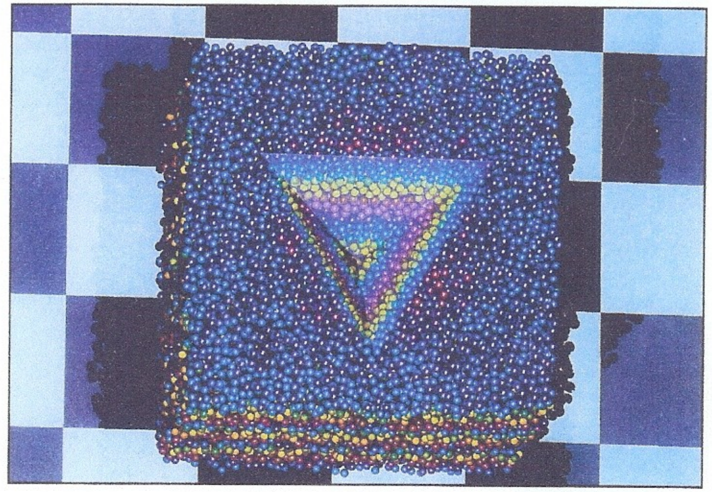
Lennard-Jones Crystal

Embedded-Atom (Metal)

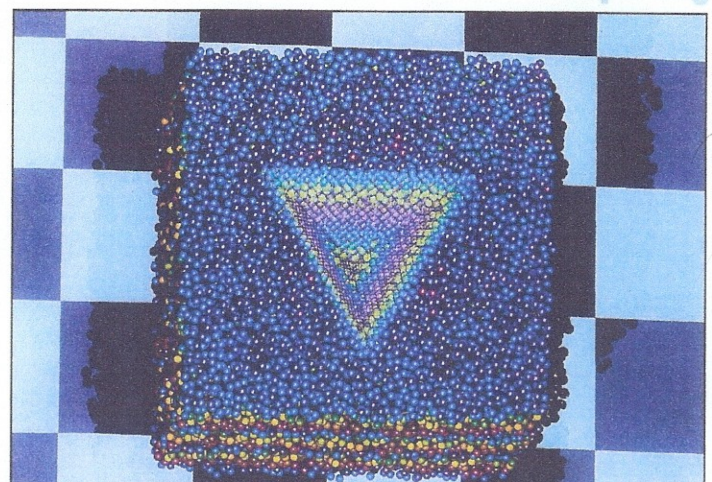

Two-Dimensional Lennard-Jones Crack
Holian, Ravelo, Zhou (LANL)
CM display

COMPUTERS IN PHYSICS

MAR/APR 1992



Parallel Computing



AMERICAN INSTITUTE OF PHYSICS

Nosé-Hoover Nonequilibrium Dynamics and Statistical Mechanics

William Graham Hoover
University of California &
Great Basin College, Nevada

1. Thermostatted Oscillators

Nosé-Hoover Oscillator (Paris, 1984)

$$\mathcal{H}_{\text{Nosé}} = [\,(p/s)^2 + q^2 + \zeta^2\,]/2 + T\ln s\,.$$

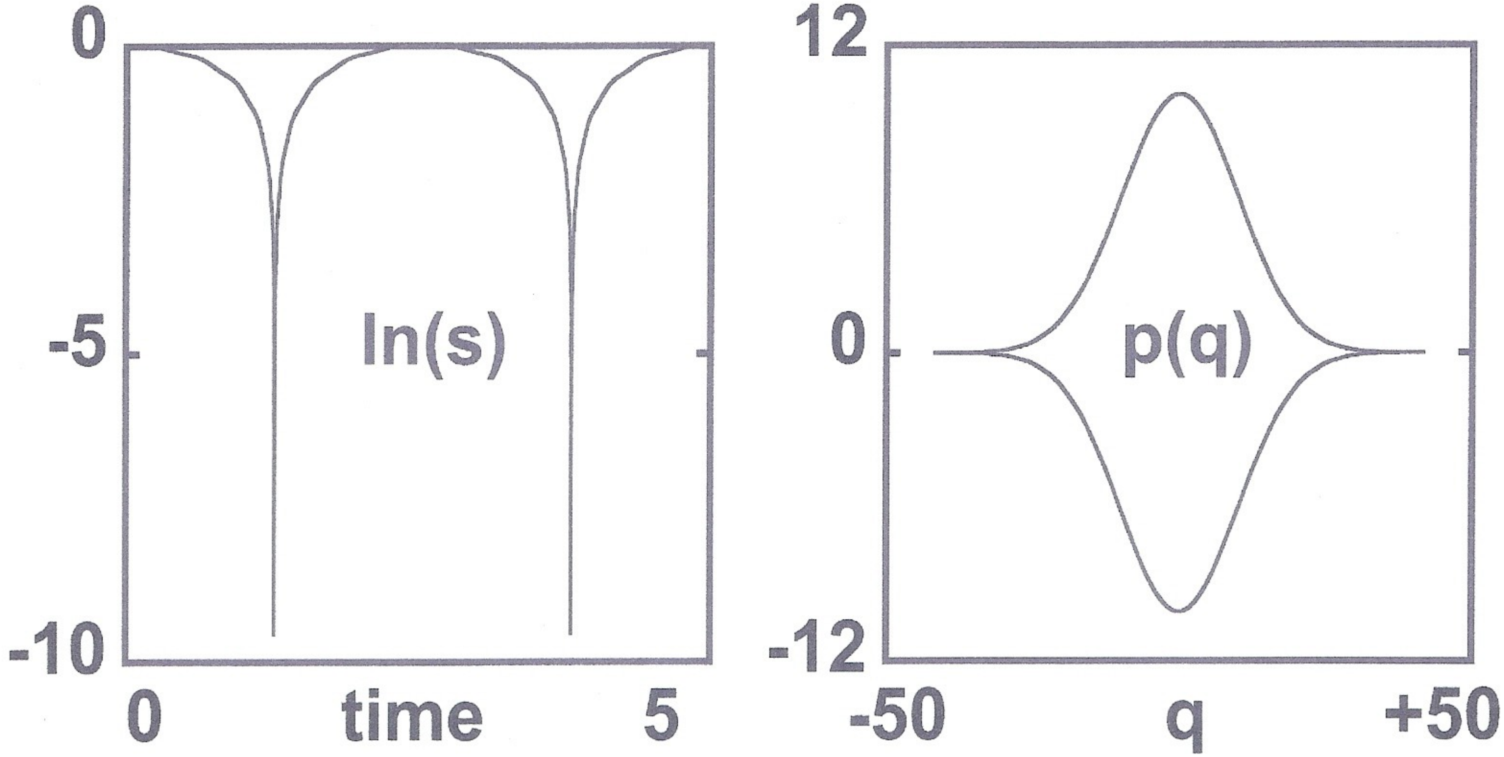
$$\dot{q} = p/s^2\,;\ \dot{p} = -q\,;\ \dot{s} = \zeta\,;$$

$$\dot{\zeta} = \left[p^2/s^3\right] - \left[T/s\right].$$

For T=100 timestep dt = 0.0000001 .

Periodic and Chaotic Orbits

The 1984 Oscillator with dt = 0.0000001 :



Initially { $q = 0$, $p = 10.085$, $s = 1$, $\zeta = 0$ } .

Nosé Oscillator Observations

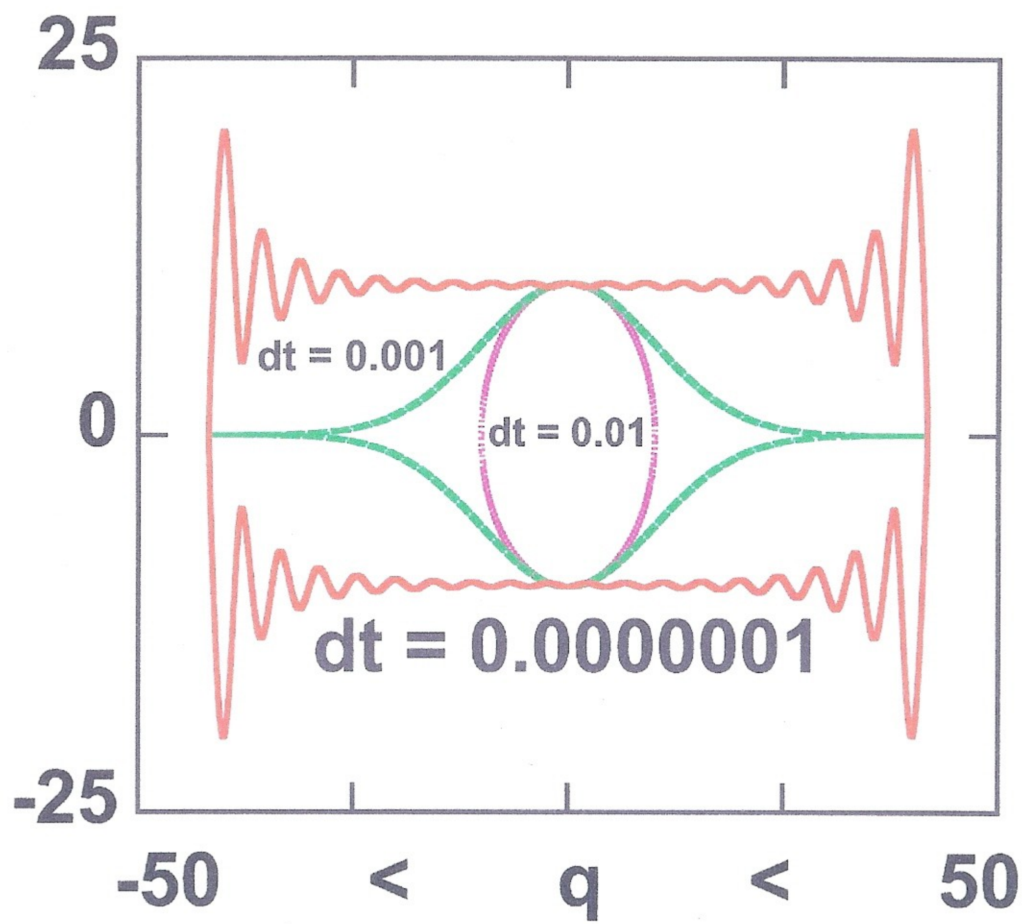
1. *Stiff* Equations: dt = 0.0000001 .
2. Solutions are not Ergodic .
3. Only a Single Temperature .

Remedy for Stiffness: "Time Scaling" :

$$\{ \dot{q} \Rightarrow s\dot{q} \,;\, \dot{p} \Rightarrow s\dot{p} \,;\, \dot{s} \Rightarrow s\dot{s} \,;\, \dot{\zeta} \Rightarrow s\dot{\zeta} \}$$

Now dt = 0.001 rather than 0.0000001.

Periodic Oscillator Trajectories



From { q = 0, p = 10.085, s = 1, ζ = 0 } .

Nosé-Hoover *via* Dettmann (Lyon, 1996)

$$\mathcal{H}_{\text{Nosé}} = [\,(p/s)^2 + q^2 + \zeta^2\,]/2 + T\ln s\,.$$

$$\mathcal{H}_{\text{DETTMANN}} = s\mathcal{H}_{\text{Nosé}} \equiv 0\,!$$

Now the timestep dt is larger, 0.001 ,
without requiring "Time Scaling" .

Nosé-Hoover *from* f(qp) + Dynamics

$$\left\{ \ddot{q} = \dot{p} = -q - \zeta p \;\Rightarrow\; \dot{\zeta} = p^2 - T \right\}$$

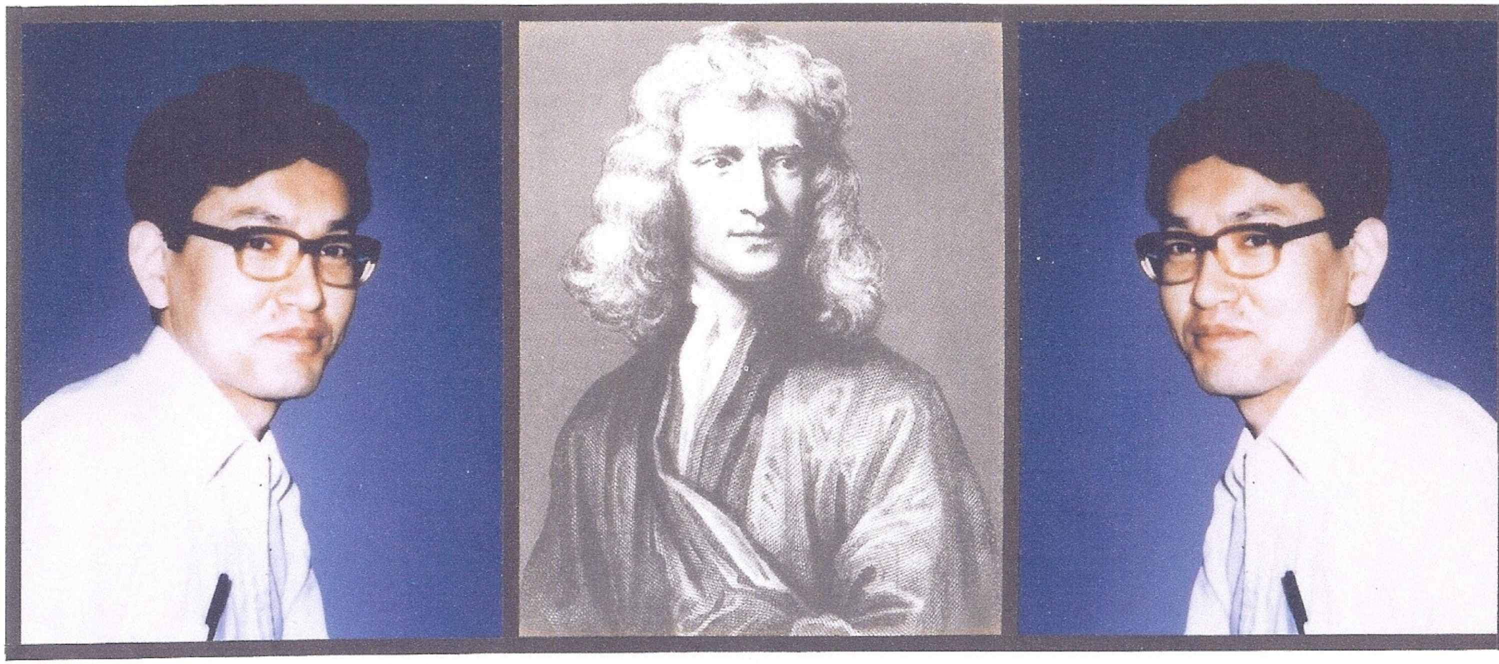
1. The timestep dt is even larger, 0.01 .
2. No "Time Scaling" or "s" is required .
3. No Hamiltonian is required .
4. There is still a constant of the motion .
5. *Many* Temperatures can be used .
6. But the Motion is still *not Ergodic* , though it is consistent with Gibbs .

Nosé-Hoover Nonequilibrium Dynamics and Statistical Mechanics

William Graham Hoover
Great Basin College, Nevada

2. Many-Body Heat Flow → Fractals

Heat Transfer *via* Two Thermostatted Boundaries

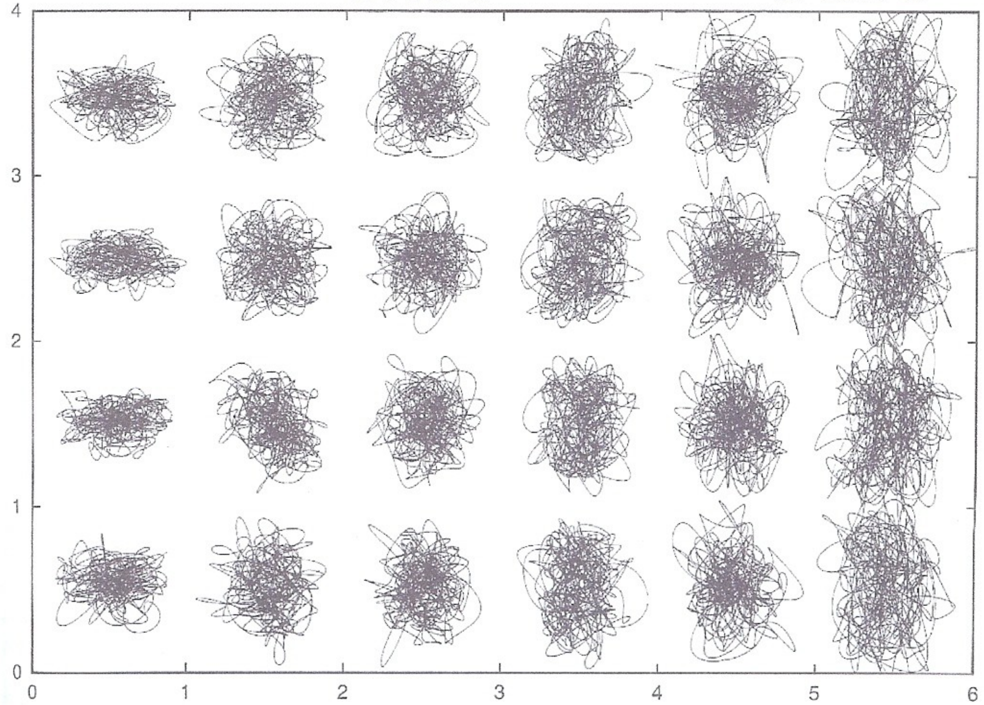


Shūichi Nosé
Keio University
Yokohama
1987

Shūichi Nosé
Keio University
Yokohama
1987

Heat Conduction in 2D ϕ^4 Slab

$$\Phi_{Newton} = \sum_{sites} \delta^4/4 + \sum_{pairs} (|r|-1)^2/2 .$$



Hoover, Aoki, Hoover, and De Groot Physica D (2004)

Four Cold Particles and Four Hot Particles

Heat Conduction Results

The Heat Flux obeys Fourier's Law .

Flux measured for **seven** thermostat types

p^2 , p^4, $< p^2 >$, $< p^4 >$ and combinations

Thermostat contributions are of order 1/L .

Conclusion :

use the Nosé-Hoover thermostat .

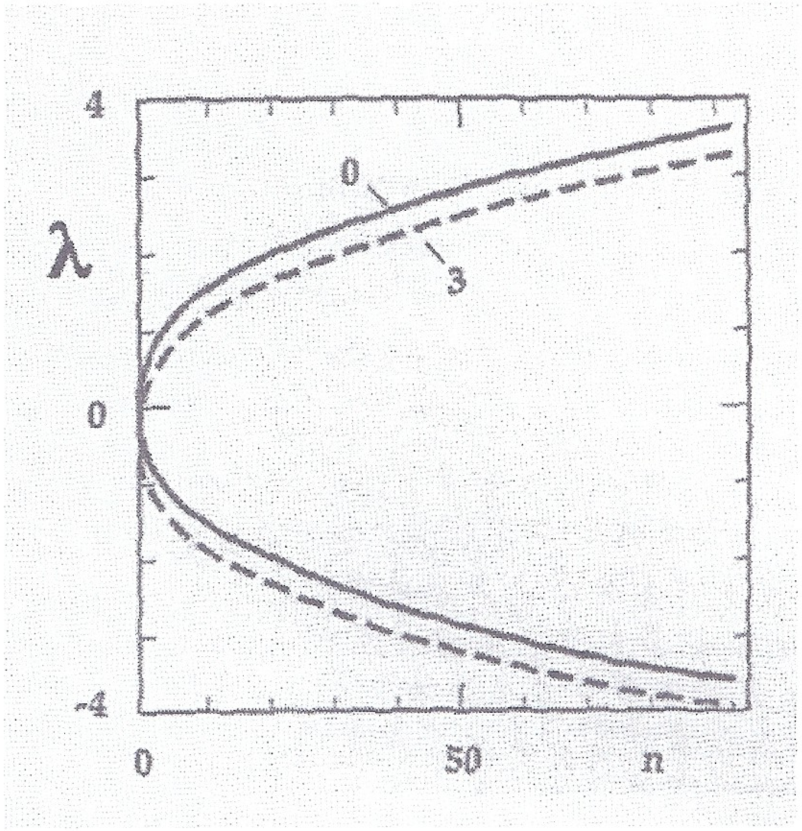
Nosé-Hoover Nonequilibrium Dynamics and Statistical Mechanics

William Graham Hoover
Great Basin College, Nevada

3. Lyapunov Spectrum, Kaplan-Yorke

Lyapunov Spectrum for N = 32

Symmetry Breaking, Lennard-Jones Particles



Time Reversible Dynamics
Dissipative, dS/dt > 0
Zero Phase Volume
Multifractal Attractor

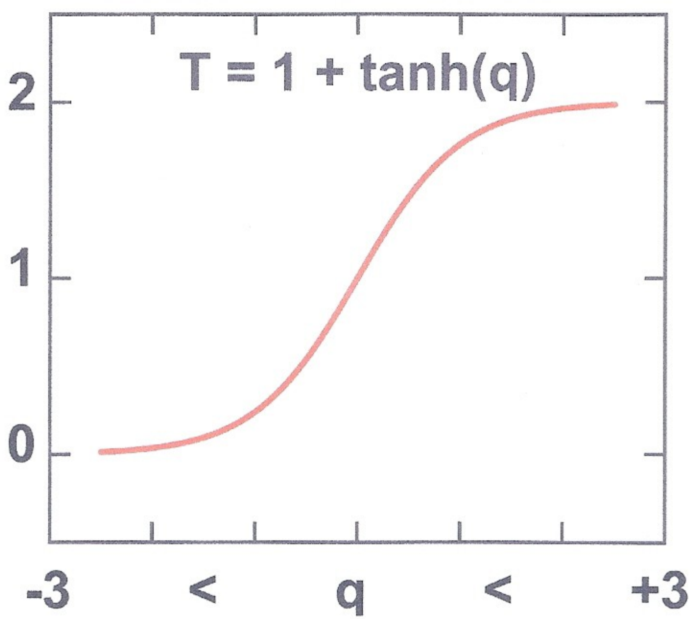
Thermostatted Color Conductivity
External Field in x Direction:
    16 Particles Pushed to the Right
    16 Particles Pushed to the Left

Posch and Hoover, 1987

Ergodicity *and* Multiple Temperatures for Thermostatted Harmonic Oscillator

Two Friction Coefficients **give Ergodicity ($\varepsilon = 0$)**

and **Multifractal Distributions for $\varepsilon > 0$.**



$$\dot{q} = p \ ;$$

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

$$\dot{\zeta} = p^2 - T(q) \ ;$$

$$\dot{\xi} = p^4 - 3p^2 T(q) .$$

$$T(q) \equiv 1 + \varepsilon \tanh(q) .$$

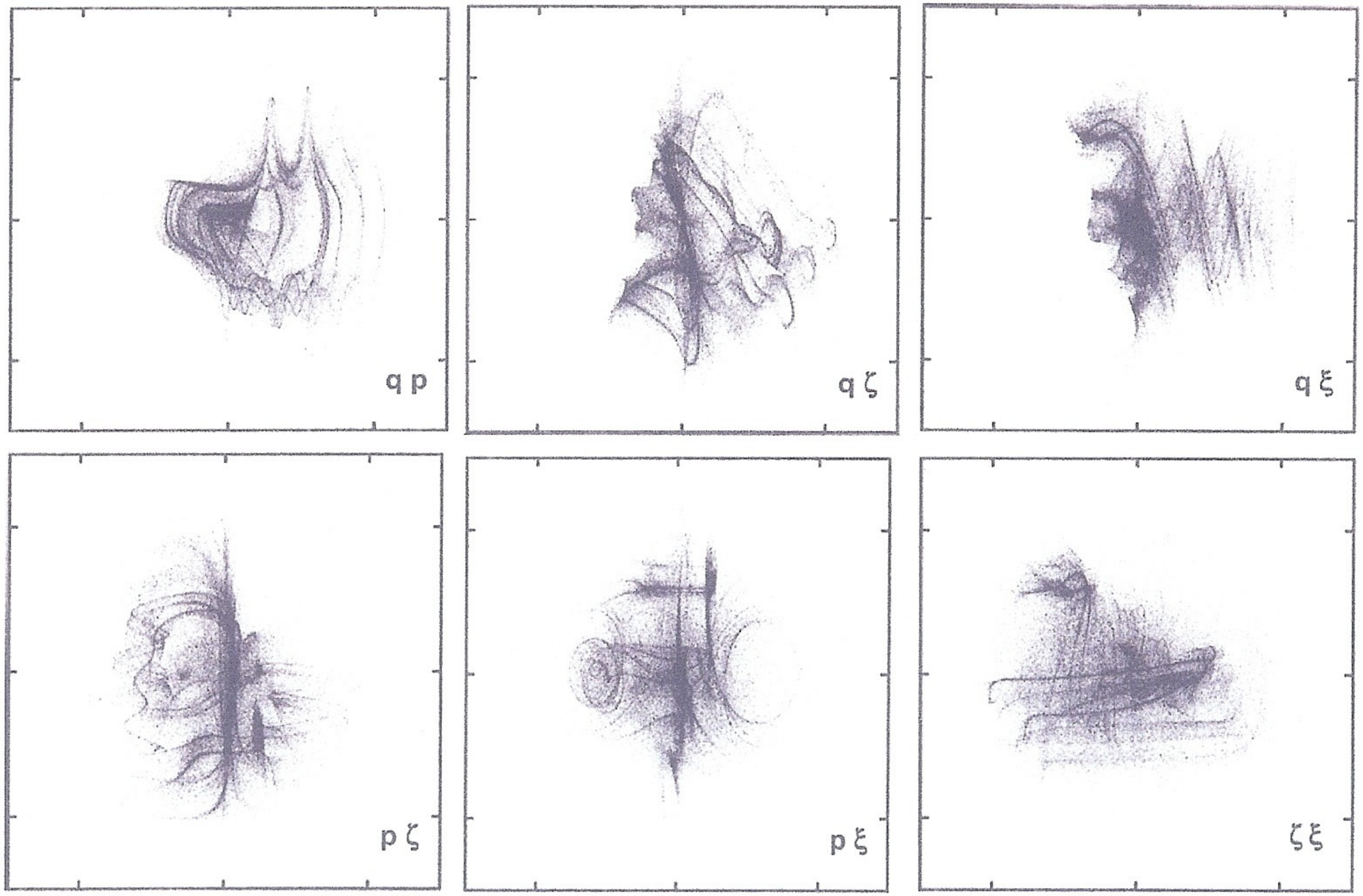
Ergodicity *and* Multiple Temperatures for Thermostatted Harmonic Oscillator

There is still a constant of the motion:

$$C = \left(q^2 + p^2 + \zeta^2 + \xi^2 \right)/2 + \int_0^t T[d(\ln f)/dt]dt'$$

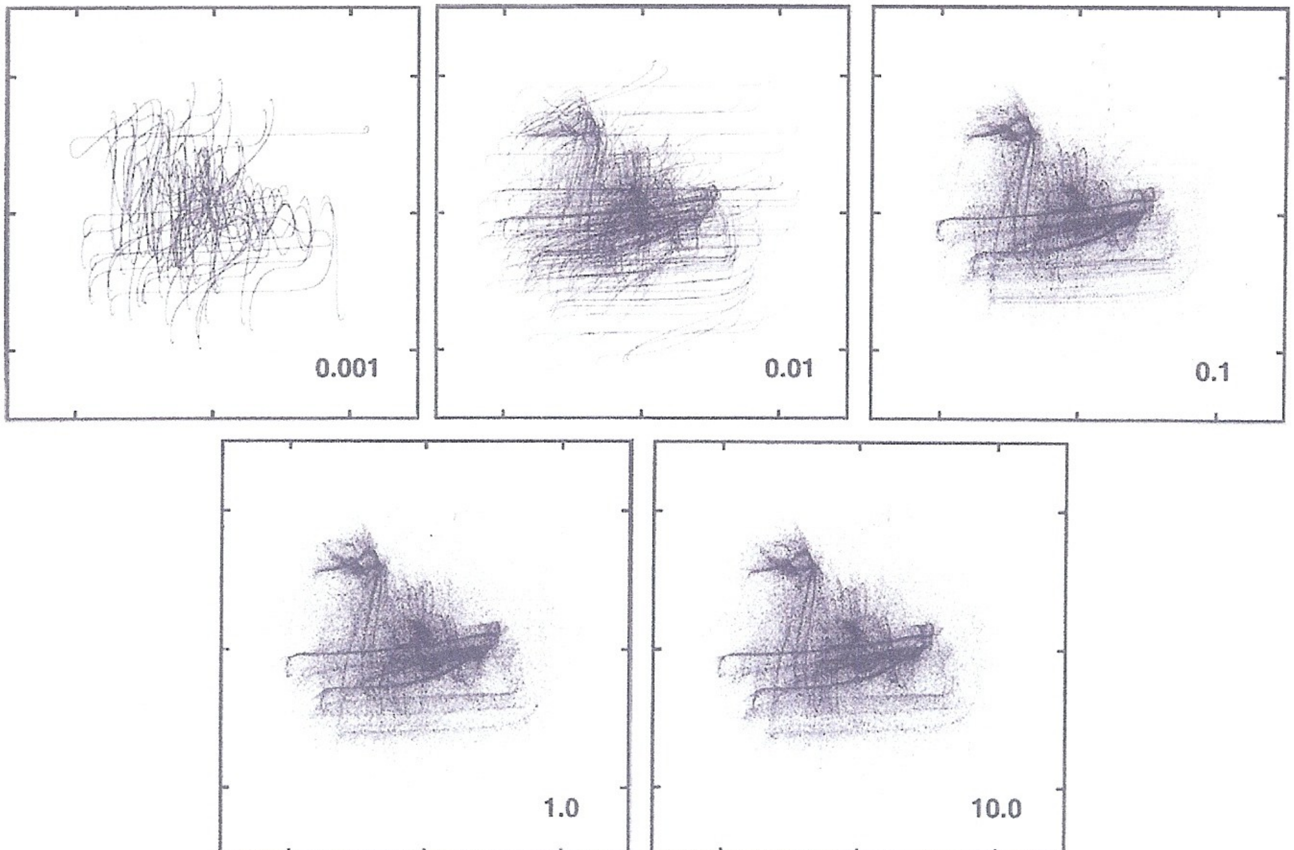
where $[d(\ln f)/dt] = \zeta + 3\xi p^2$.

Six Two-Dimensional Projections: The Distributions are Multifractal .



Dimensionality of 4D Distribution: 2.56 or 2.00 .

Continuous Orbit → Multifractals



Dimensionality of Skiing Goose: 2.0 or 1.77 .

Lyapunov Spectrum / Kaplan-Yorke

$$\{\lambda_{EQ}\} = \{ +0.066, 0.000, 0.000, -0.066 \}$$

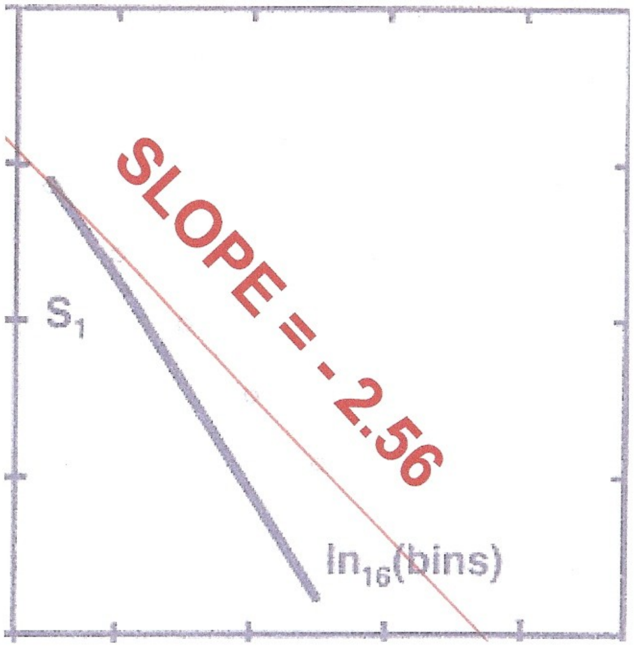
$$\{\lambda_{NEQ}\} = \{ +0.072, 0.000, -0.091, -0.430 \}$$

$$\to D_{KY} = 2.80 \cong D_{INFO} \leftarrow \langle f \ln f \rangle .$$

Note the *symmetry breaking* despite the Time Reversibility of the { qp$\zeta\xi$ } equations .

D_{INFO} is actually 2.56 from a Simulation with 10^{11} timesteps and 268,435,456 sampling bins!

Failure of Kaplan-Yorke Conjecture*



Bin Counting vs. $\{ \lambda \}$

$D_{LYAPUNOV} = D_{KY} = 2.80$

$D_{INFORMATION} = 2.56$

$D_{EQUILIBRIUM} = 4.00$

Based on 2^{28} Bins with 10^{11} phase points .

*Hoover, Hoover, Posch, and Codelli (2006)

Nosé-Hoover Nonequilibrium Dynamics and Statistical Mechanics

William Graham Hoover
Great Basin College, Nevada

4. Jarzynski's Helmholtz Free Energy

Jarzynski's Helmholtz Free Energy

In 1997 Jarzynski used the Nosé-Hoover thermostat equations to show that the Equilibrium Free Energy change can be calculated as a Nonequilibrium average.

$$d(\ln f)/dt = \zeta \equiv \dot{S}/k$$

$$\rightarrow \left\langle e^{W/kT} \right\rangle \equiv e^{-A/kT}$$

Jarzynski* Free Energy Calculations

Example Problem Types :

- Change of Oscillator Force Constant ;
- Expansion/Compression Cycles ;
- Pulling/Unfolding of Proteins .

The Identity seems to hold for a wide variety of Isothermal transformations .

* 1997 Physical Review E and Physical Review Letters

Nosé-Hoover Nonequilibrium Dynamics and Statistical Mechanics

William Graham Hoover
Great Basin College, Nevada

5. Fractal Distributions and Second Law

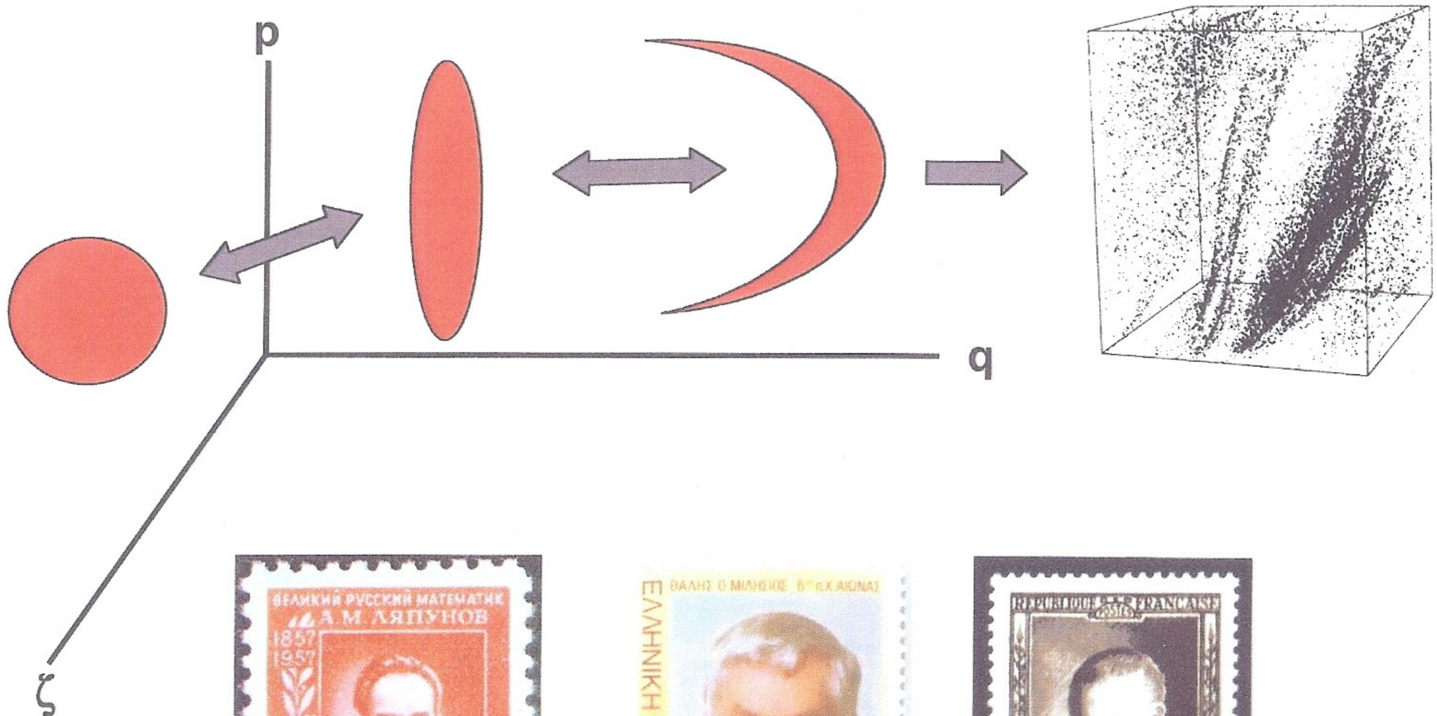
Second Law of Thermodynamics

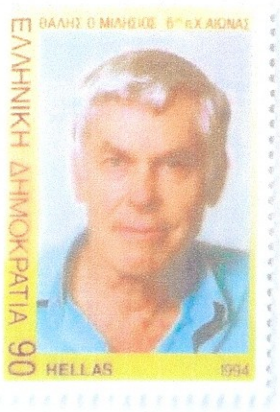
- **Fractal Distributions give Time's Arrow :**
- **Nonequilibrium states are rare .**
- **Nonequilibrium entropy diverges .**
- **Reversed nonequilibrium trajectories are more unstable, and hence unobservable**

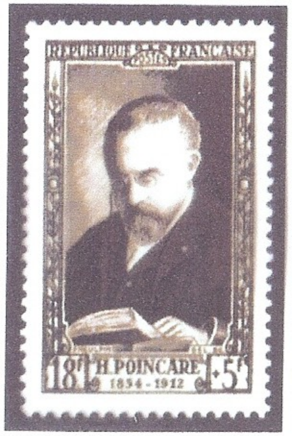
$$d(\ln f)/dt = \dot{S}/k = -\sum \lambda = \sum \zeta > 0 .$$

$$\Rightarrow d(\ln f)/dt = - d(\ln \otimes)/dt < 0 !$$

Generic Nonequilibrium Phase Space Flow







Summary of Nosé's Legacy

- Gibbs' Statistical Mechanics is directly linked to Hamilton's Dynamics .
- Thermostats use only a single degree of freedom, the coefficient ζ .
- Nonequilibrium states are multifractal .
- Free energy from nonequilibrium processes using $d(\ln f)/dt = d(S/k)/dt = \zeta$.
- Symmetry breaking gives Second Law .
- Quantum and Fluid Dynamics also OK .

May 1990 Snapshot, Nestle House