“What Is Liquid?”, as seen in Thermostated Manybody Simulations : Hamiltonian Statistical Mechanics, Molecular Dynamics, & Irreversibility

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Ruby Valley Nevada USA

Condensed Matter Symposium
Celebrating Doug Henderson’s 80th Birthday
Saturday, 16 August 2014

1. Historical Geography with Doug Henderson

DH : IBM San Jose → BYU

WGH : U Michigan/Duke → Berni Alder at LLNL

CGH : So CA → LLNL /UCD

[Retired, Ruby Valley NV]

J Barker & D Henderson :
West Coast Statistical Mechanics Meetings
1973-1989
IBM UCLA UCB UCD LLNL

Vitaly Kuzkin met with Doug and Dean Wheeler in 2013 ;
He & Diana have Emilia now

The Second Law and Irreversibility From Thermostated Simulations

1. Historical Geography

2. Isothermal Equilibrium Liquids according to Gibbs
3. Barker + Henderson's Liquid Perturbation Theory
4. Nosé-Hoover Isothermal Equilibrium Dynamics

5. Nonequilibrium from Hamiltonian Mechanics ?
6. Puzzle solved *via* Liouville's Theorem !
7. Nonequilibrium from Nosé-Hoover Mechanics ?
8. Fractal Explanation of the Second-Law Puzzle !
9. Time-Reversibility and Lyapunov Instability

10. Summary

2. Equilibrium ← Gibbs' Statistical Mechanics

$e^{(-A/kT)} = \Sigma\, e^{(-E/kT)} = e^{(+S/k)} e^{(-E/kT)}$

(Canonical $dA \equiv -PdV - SdT$) where

$kT = \langle p^2 / m \rangle$ or $k(\partial E / \partial S)_V$ or $-\langle F^2 \rangle / \langle F' \rangle$

van der Waals' : $P = P_{repulsive} - P_{attractive}$

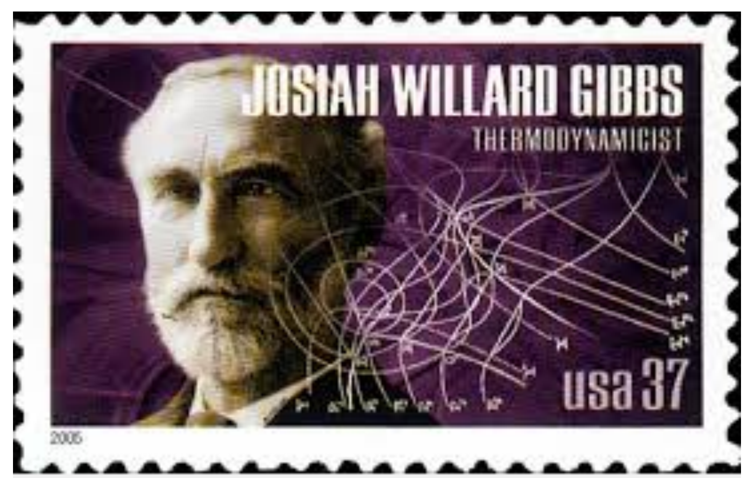
Virial Series (12 terms known for spheres)

Liquid Perturbation Theory :

(Φ = Reference + Perturbed)

This idea can replace

Monte Carlo Sampling $e^{(-\Delta\Phi/kT)}$



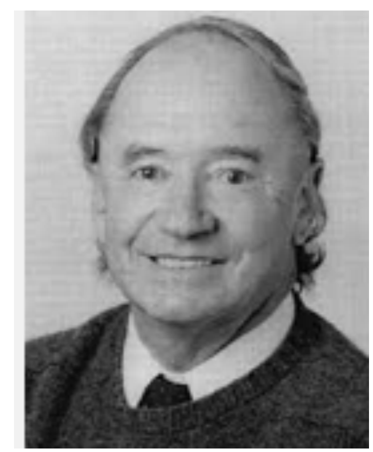
3. Equilibrium ← Barker-Henderson

$A = A_o + \langle \Delta\mathcal{H} \rangle_o$ [Bob Zwanzig]

$dA = -PdV - SdT$

A successful theory of liquids. Percus-Yevick g(r) made Monte Carlo sampling unnecessary.

The results of the theory are easy to check with molecular dynamics, especially isothermal molecular dynamics



4. Equilibrium ← Nosé-Hoover MD : Hamiltonian Motion Equations for the Canonical Ensemble !

Shuichi Nosé's Good Idea :

$$\mathcal{H}_N = \Sigma\,(\,p^2/2ms^2\,) + \Phi(q) + NDkT\,\ln(\,s\,) + (\,p_s^2/2M\,)\,;$$

"Scale the time", multiplying time derivatives by s and replace { (p/s) → p } . Then { (dp/dt) = F – ζp } where (dζ/dt) = Σ [(p²/mkT) – 1]/τ² .

Carl Dettmann's Better Idea : $\mathcal{H}_D \equiv s\mathcal{H}_N \equiv 0$

Exactly the same **NH equations of motion result, but without any time-scaling .**

4. Equilibrium ← Nosé-Hoover MD

Best Idea : The continuity equation shows that Gibbs' canonical distribution, f $\propto e^{(-\mathcal{H}/kT)}$, is a stationary solution of the equations of motion :

$$\{ (dp/dt) = F(q) - \zeta p \} .$$

provided that the friction coefficient ζ is generated by the integral feedback equation :

$$d\zeta/dt = [< (p^2/mkT) > - 1] / \tau^2$$

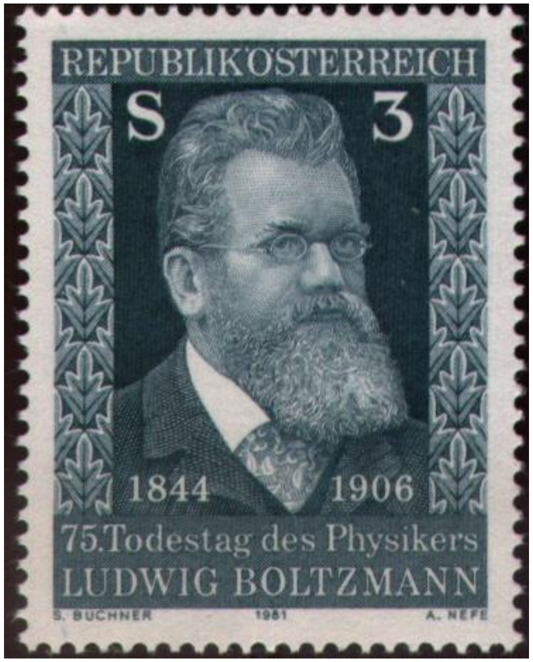
These motion equations are deterministic and time-reversible, *not* Hamiltonian. Nosé's "time-scaling variable" s has *disappeared* .

4. Equilibrium ← Nosé-Hoover MD

Bauer, Bulgac, and Kusnezov considered a much more general situation, including one, two, or more "friction coefficients" { ζ } , enough to generate Brownian Motion with time-reversible motion equations .

5. Nonequilibrium Simulations using Hamiltonian Mechanics ?

The Kinetic Temperature , T ≡ < mv²/k > , can be constrained by using a Lagrange Multiplier → an *Isokinetic* Hamiltonian :

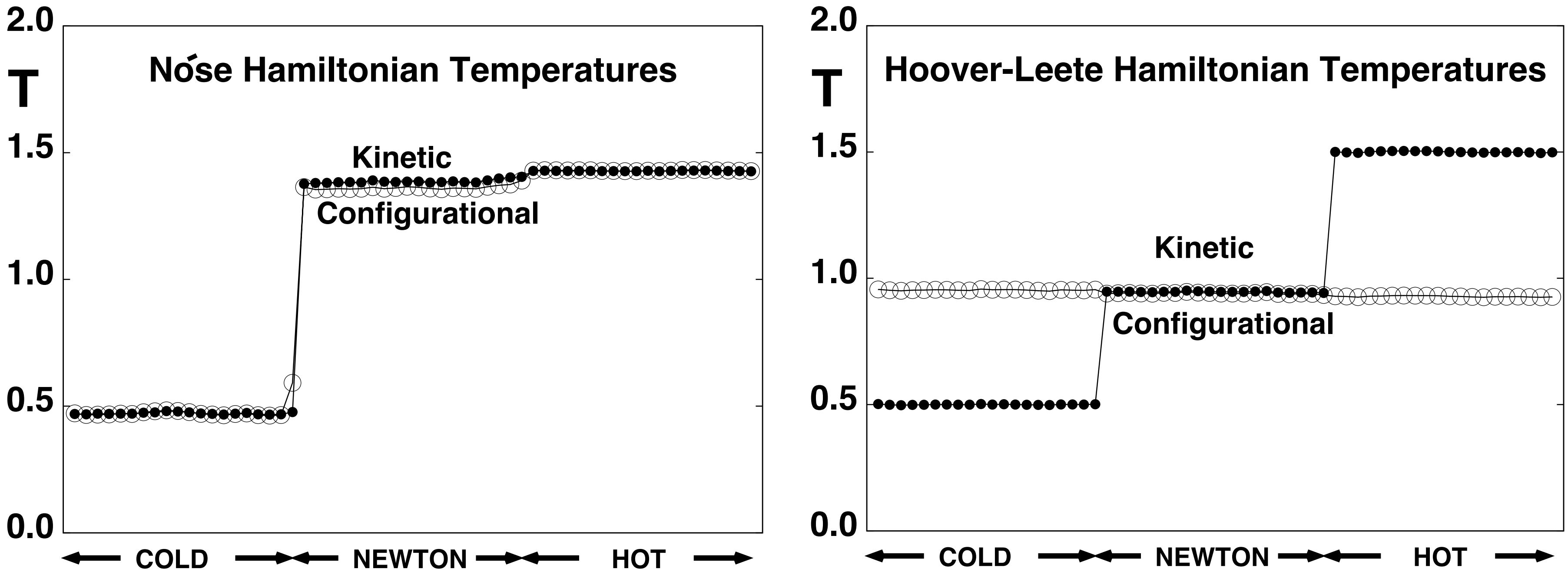


$$\mathcal{H} = 2[\ (K(v)K(p)\ ]^{1/2} - K(v) + \Phi(q)$$

Here K(v) is a *fixed* kinetic energy .

An Alternative to $\mathcal{H}_{Nosé}$.

5. Puzzling Hamiltonian Thermostating



Despite tremendous temperature gradients there is no heat flow in these 60-particle ϕ^4 chains. The results are similar for the canonical and the kinetic thermostats. The interparticle forces are harmonic, with quartic tethers.

6. Puzzle Solved *via* Liouville Theorem

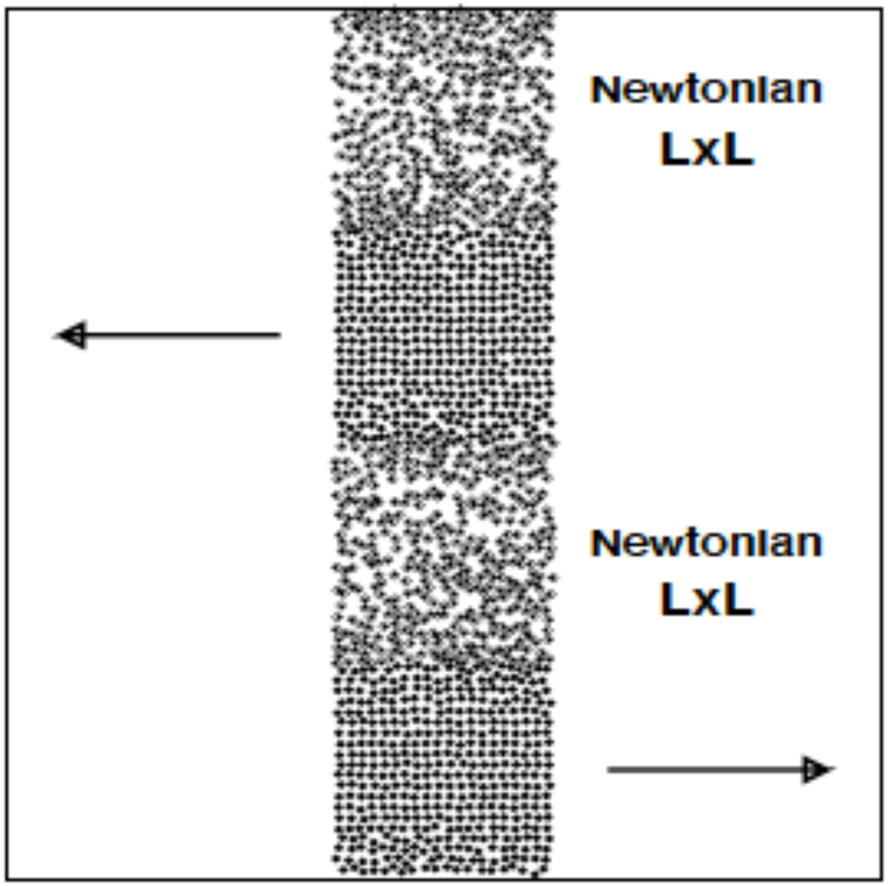
Liouville's phase-space continuity equation implies (for Hamiltonian systems) that the comoving phase volume is conserved .

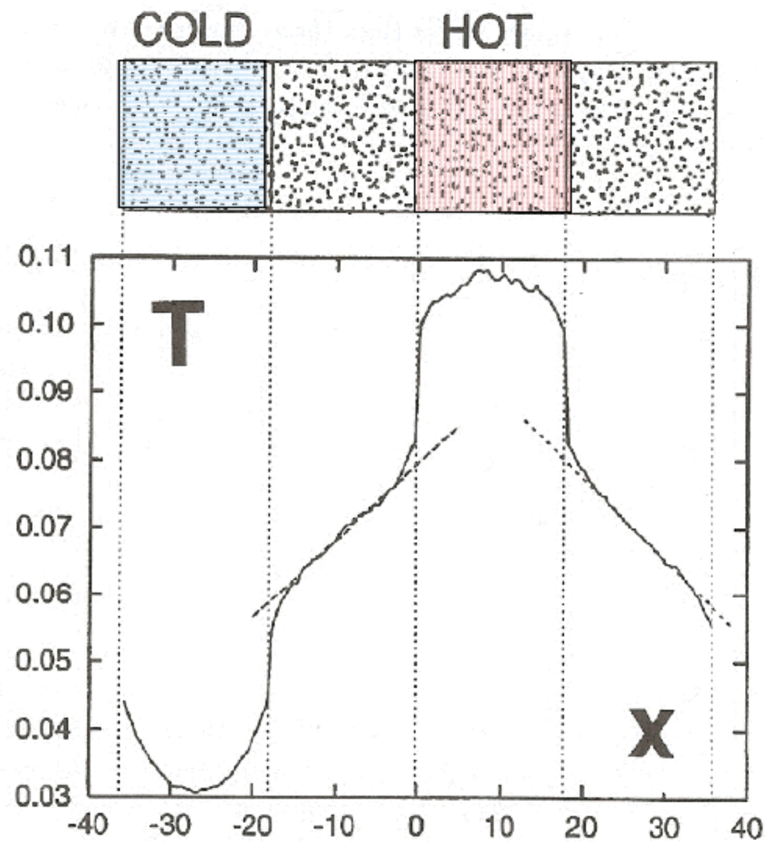
But Heating *increases* phase volume.
Cooling *decreases* phase volume.

Conclusion :

Hamilton cannot work for Nonequilibrium Steady States
[There can be no Heat Flow !]

7. Pictures of Shear and Heat Flow using Nosé-Hoover thermostats





7. Nonequilibrium MD ← Nosé-Hoover

Equations of motion do *add* or *subtract* heat :

$\{ dp/dt = F - \zeta p \} \rightarrow$ Heat out $= \int \zeta (p^2/m)\, dt$

Heat out/T $\equiv \Delta S = \int \zeta dt (p^2/T) = \int \zeta\, dt$

ζ is the entropy production rate in the thermostat

Steady heat flow or shear flow →

$(d \ln f/dt) \equiv \Sigma \zeta > 0 \rightarrow$ Phase volume $\rightarrow 0$

Puzzle : How *can* phase volume vanish ?

8. Fractal Explanation of the Puzzle

Phase Volume does Vanish !

The "Lyapunov Spectrum" describes rate-of-change of 1, 2, . . . 6N-dimensional phase-space volumes :

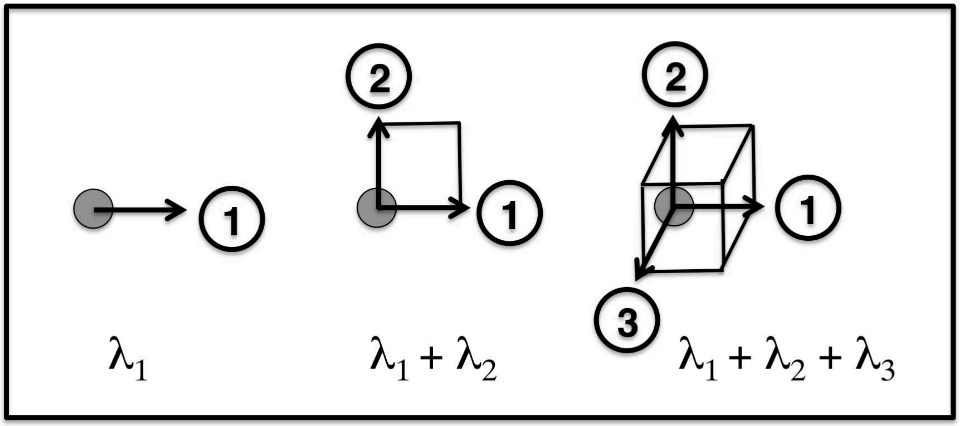
λ_1 for a line segment

$\lambda_1 + \lambda_2$ for a triangle

$\lambda_1 + \lambda_2 + \lambda_3$ for a tetrahedron

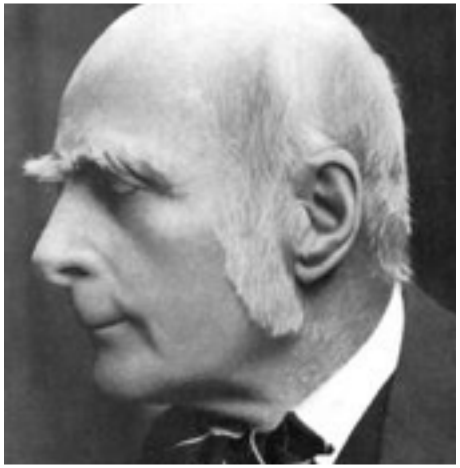
Using Gram-Schmidt-Benettin

8. Definition of the Lyapunov Spectrum

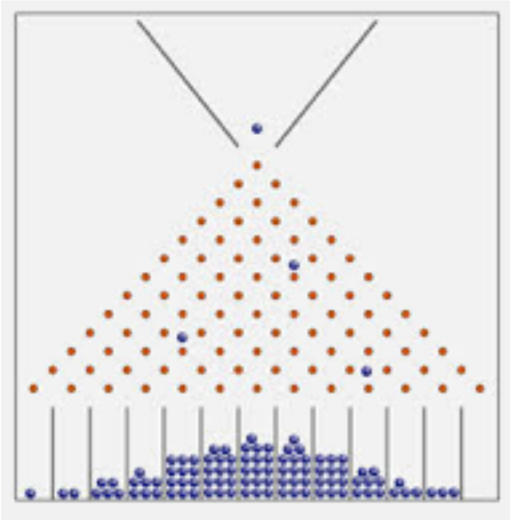


By following the motion of N satellite systems orthonormally constrained about an N-dimensional reference system, the N Lyapunov exponents are given by forces needed to maintain orthonormality. The algorithm was developed by Benettin's group.

9. Interesting Example of Lyapunov Fractal Instability → vanishing phase volume

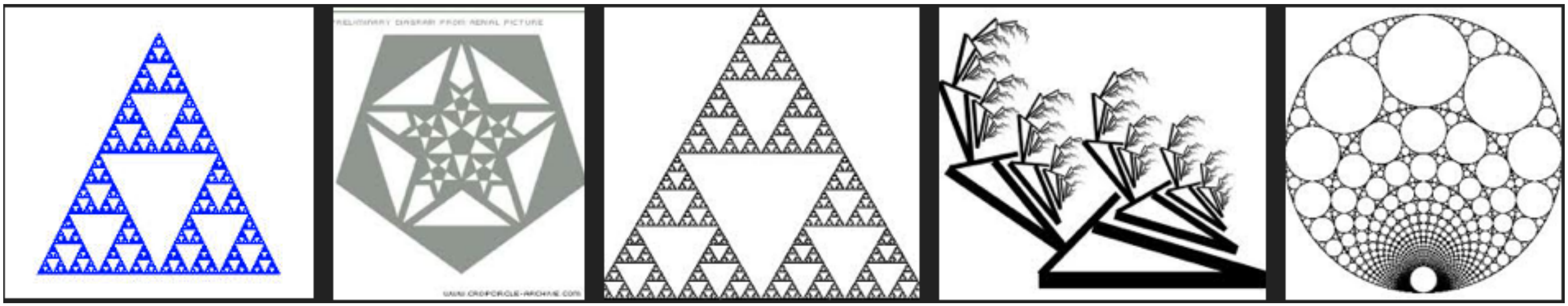


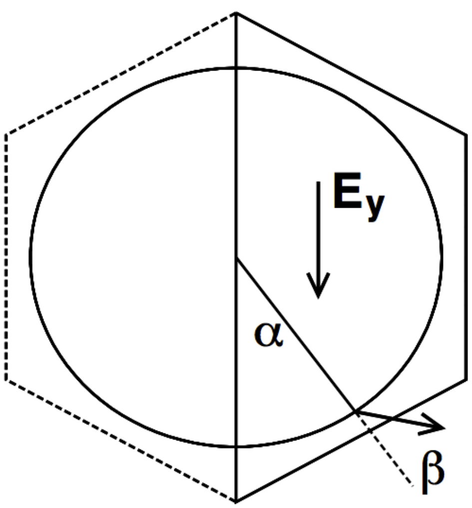
Isokinetic Galton Board : gravitational Work is Converted to extracted Heat *via* frictional ζ .

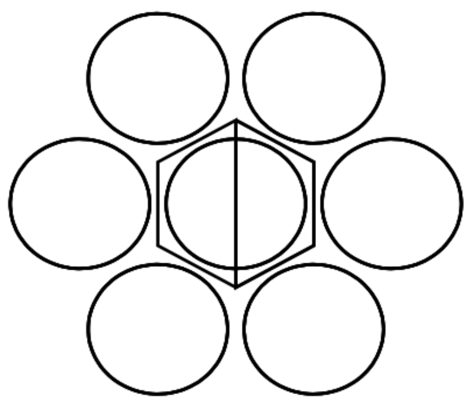


Cross sections of phase space at Fields of strength E = 1, 2, 3, and 4 . There can be a mix of conservative + dissipative parts of phase space .

9. Classical Textbook Fractals (with holes)

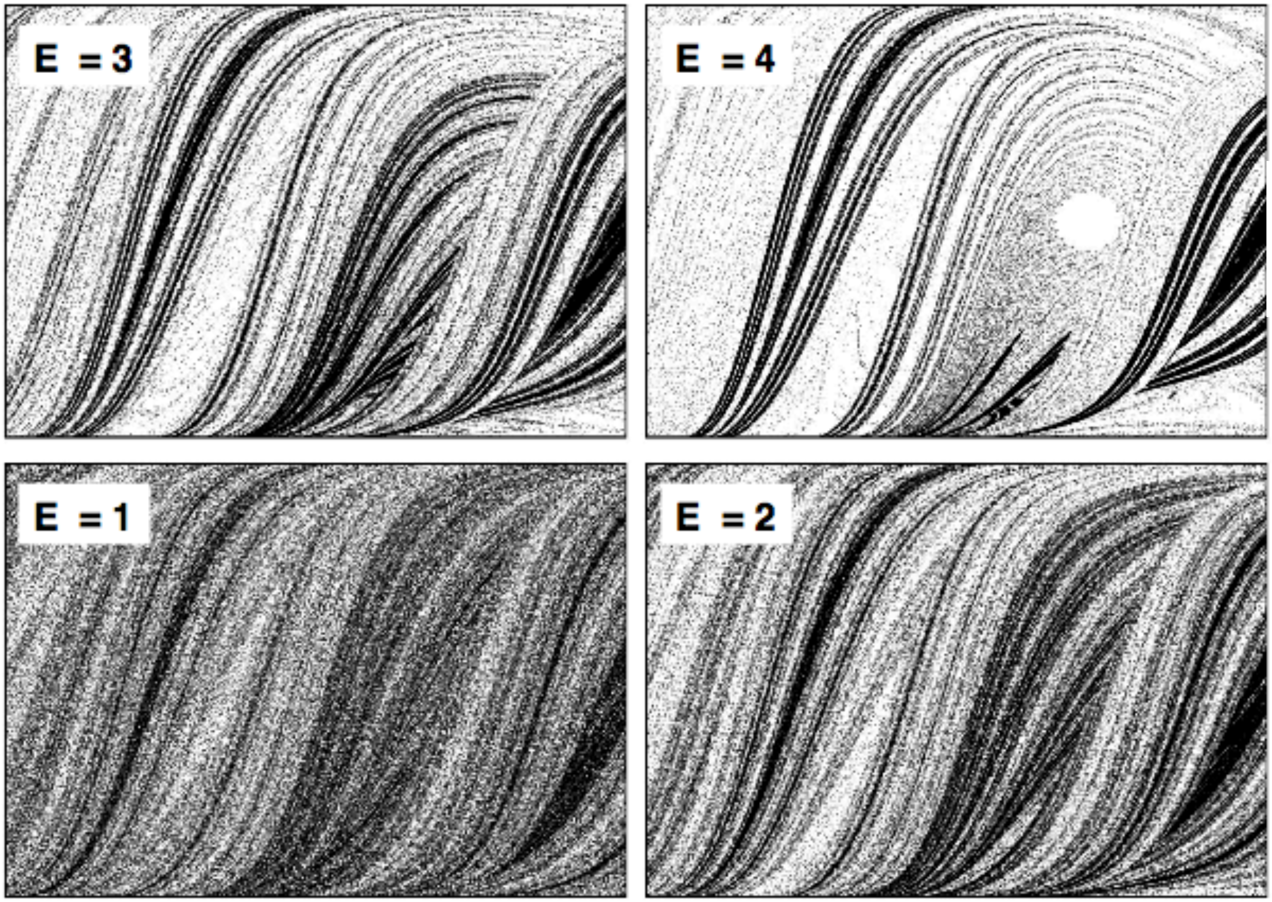


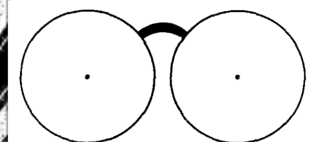




Isokinetic Galton Board
Generates Fractal
Phase-space
Cross Sections

9. MultiFractal Galton Board Sections
[$-1 < \sin(\beta) < +1$ as function of $\alpha < \pi$]

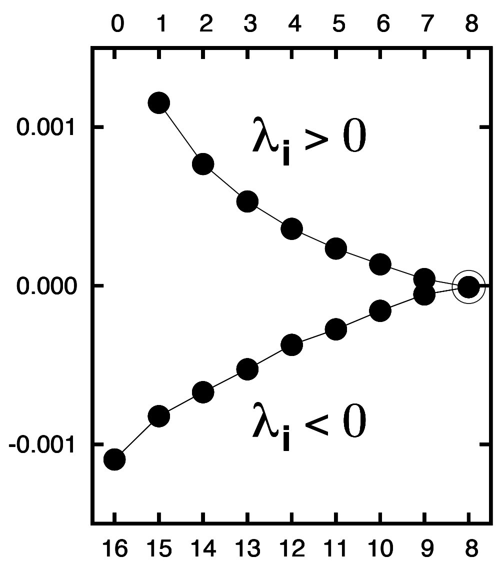


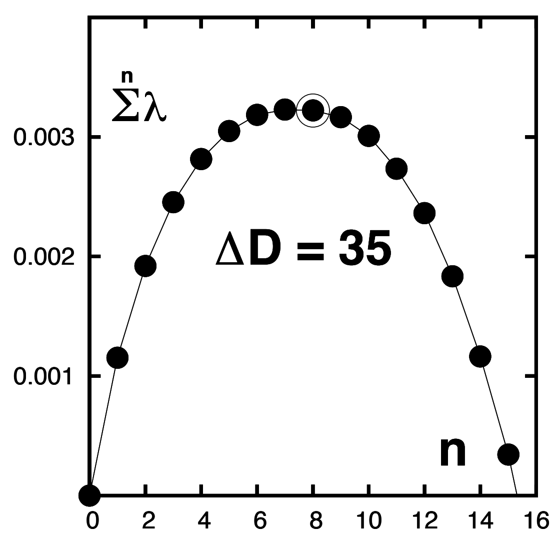


9. Another Interesting Example of Fractal Lyapunov Instability

ϕ^4 Heat Flow (Hooke's Law + quartic tethers)

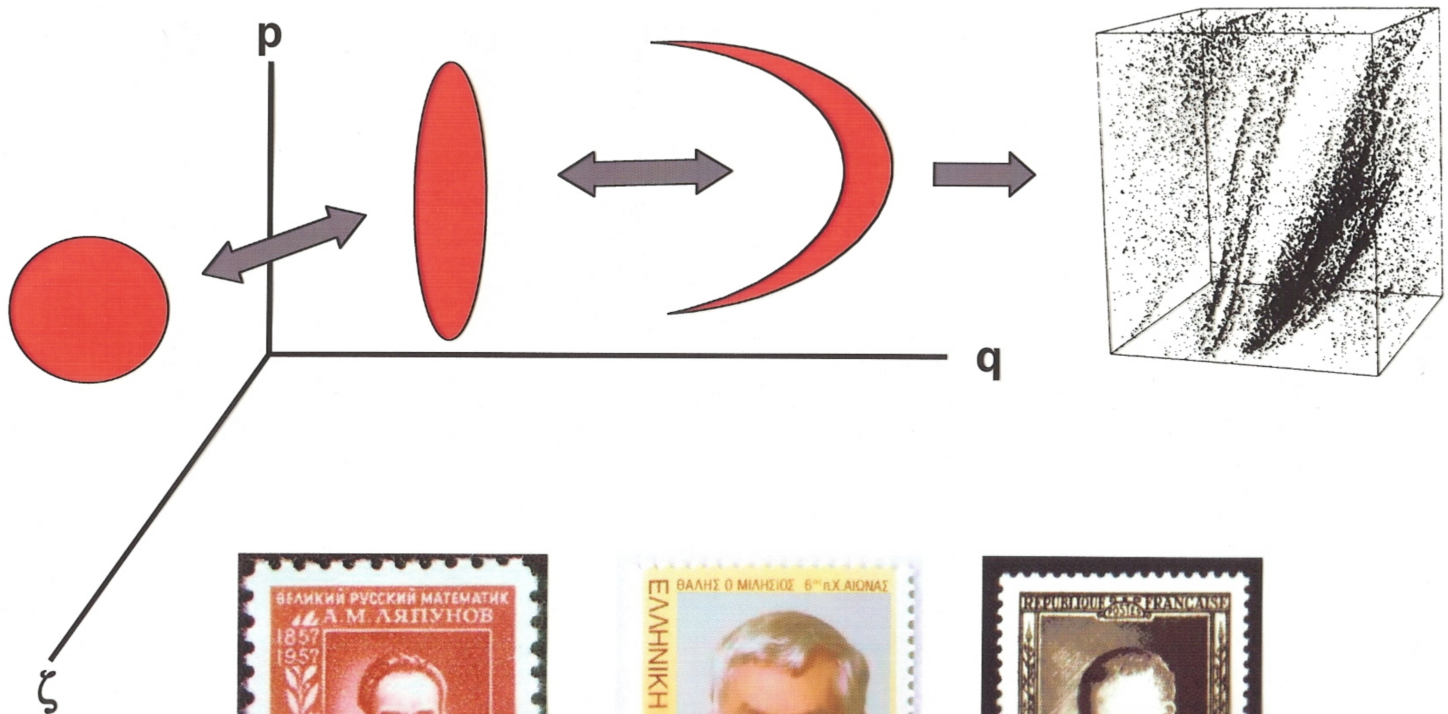
The dimensionality loss, 35/50, implies zero phase volume with entropy of minus infinity.

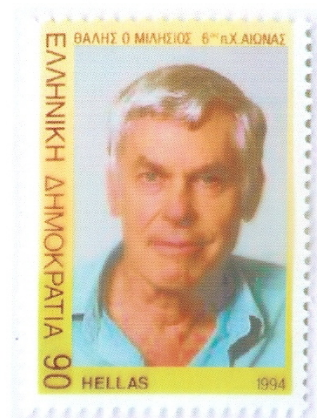


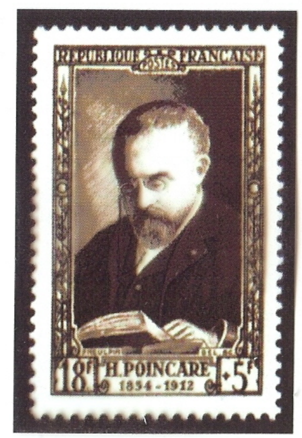


Aoki + Kusnezov in Venice

Generic Nonequilibrium Phase Space Flow





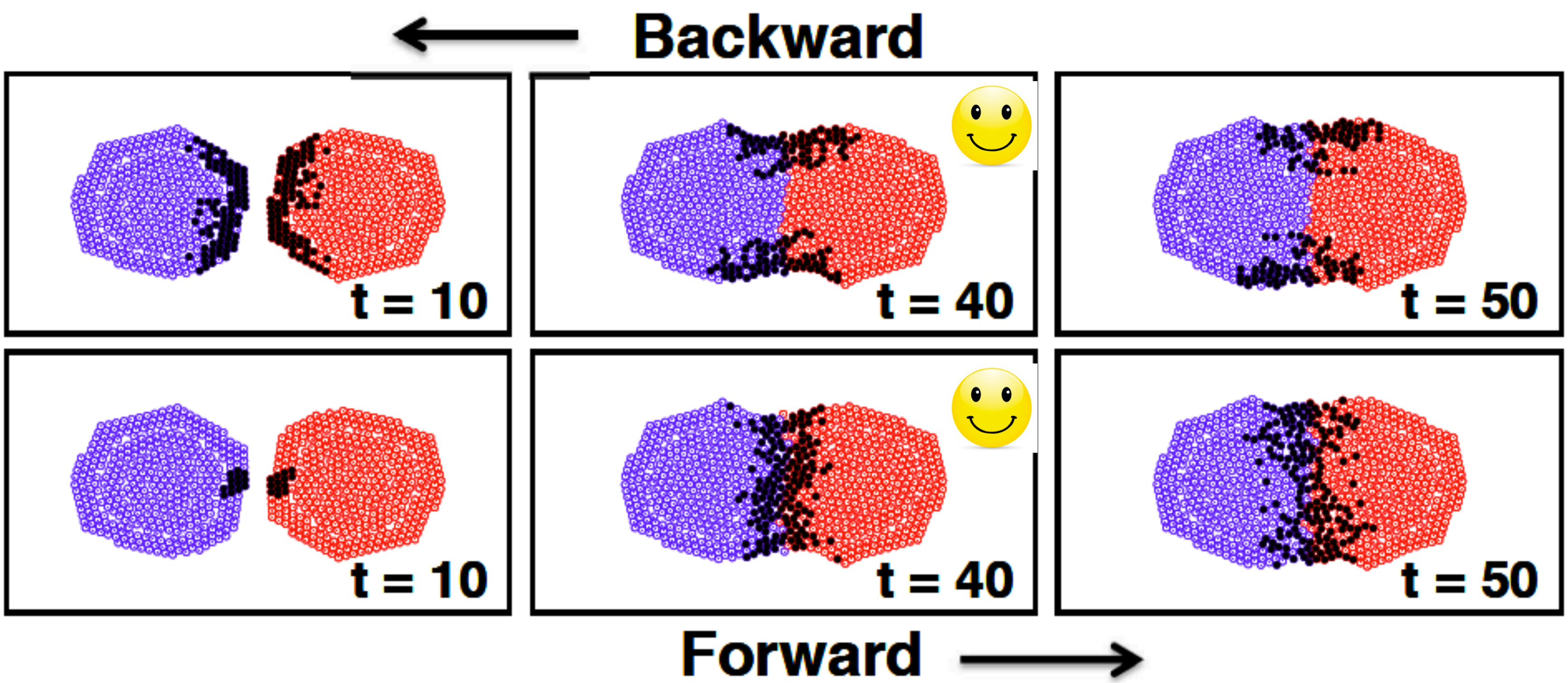


9. Hamiltonian Irreversibility and Symmetry Breaking

Levesque-Verlet bit-reversible trajectories can be followed either way by using integer arithmetic.

$$q(t+dt) - 2q(t) + q(t-dt) = \text{Integer}\,[\,F(t)dt^2/m\,]\,.$$

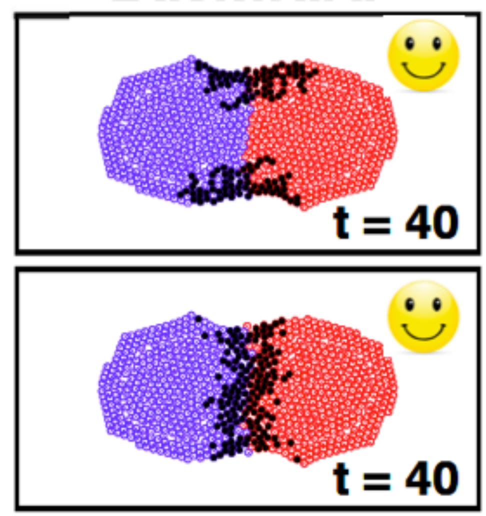
Two neighboring trajectories → important particles .



9. Hamiltonian Irreversibility & Symmetry Breaking!

Two symmetrized trajectories → important particles .
By considering Lyapunov instability we can distinguish two trajectories going forward/backward in time .

Lyapunov exponents serve to distinguish future from past .



10. Summary from our Simulations

Equilibrium is well understood (Monte Carlo, Perturbation Theory, Molecular Dynamics) .

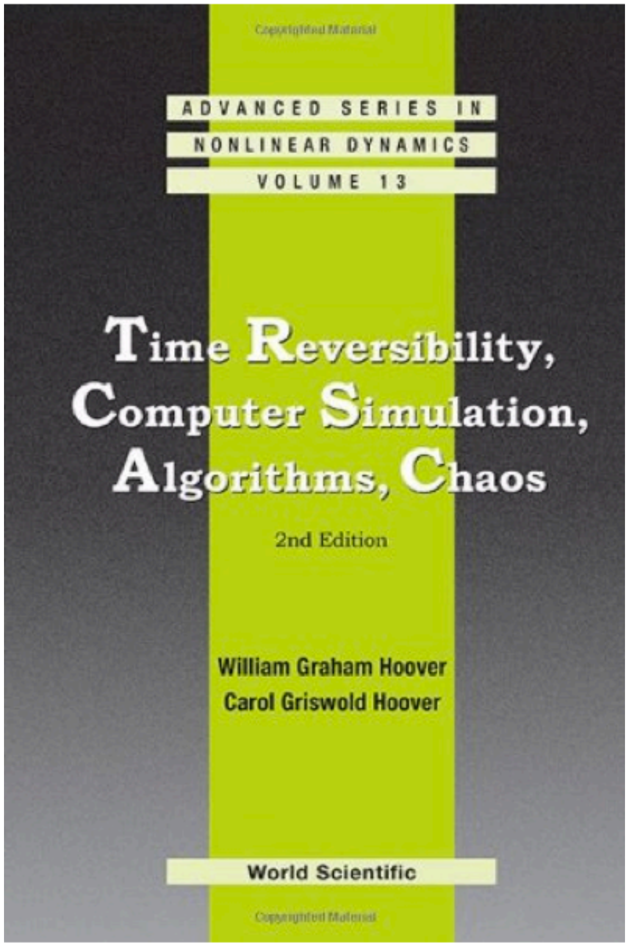
Nonequilibrium is quite complex. Hamiltonian Mechanics fails for heat flow. ***Despite time reversibility*** **$(dS/dt) < 0$ is not observed. The phase-volume of stationary states is zero.**

The Second Law is the result, with a fractal, rather than smooth, phase-space distribution . Still, for Hamiltonian nonequilibrium systems Lyapunov distinguishes the past from the future .

For additional details see
www.williamhoover.info

Simulation and Control of
Chaotic Nonequilibrium Systems

is our current project, which
should be completed by this
year's end, in plenty of time
For Doug's 90th Birthday !



Happy Birthday Doug