Theory of Hamiltonian Thermostats for Molecular Dynamics Simulations

Wm G Hoover & C G Hoover
Great Basin College, Nevada
http://williamhoover.info

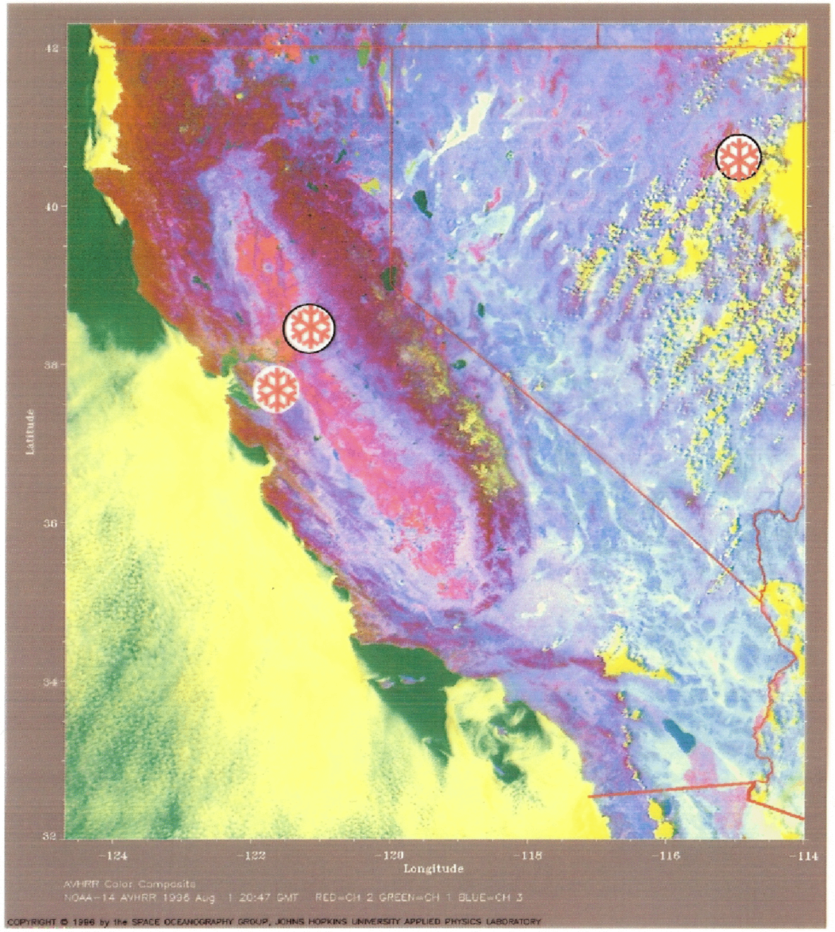
1. Molecular Dynamics Simulations .
2. Why Thermostats are Needed .
3. Four Example $\mathcal{L}$ and $\mathcal{H}$ Thermostats :

   Gauss-Rescaling and Nosé-Hoover ;
   Configurational and Kinetic .
4. Problems for $\mathcal{L}$ and $\mathcal{H}$ Mechanics .

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

Theory of Hamiltonian Thermostats for Molecular Dynamics Simulations

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University of California &
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1. Molecular Dynamics Simulations

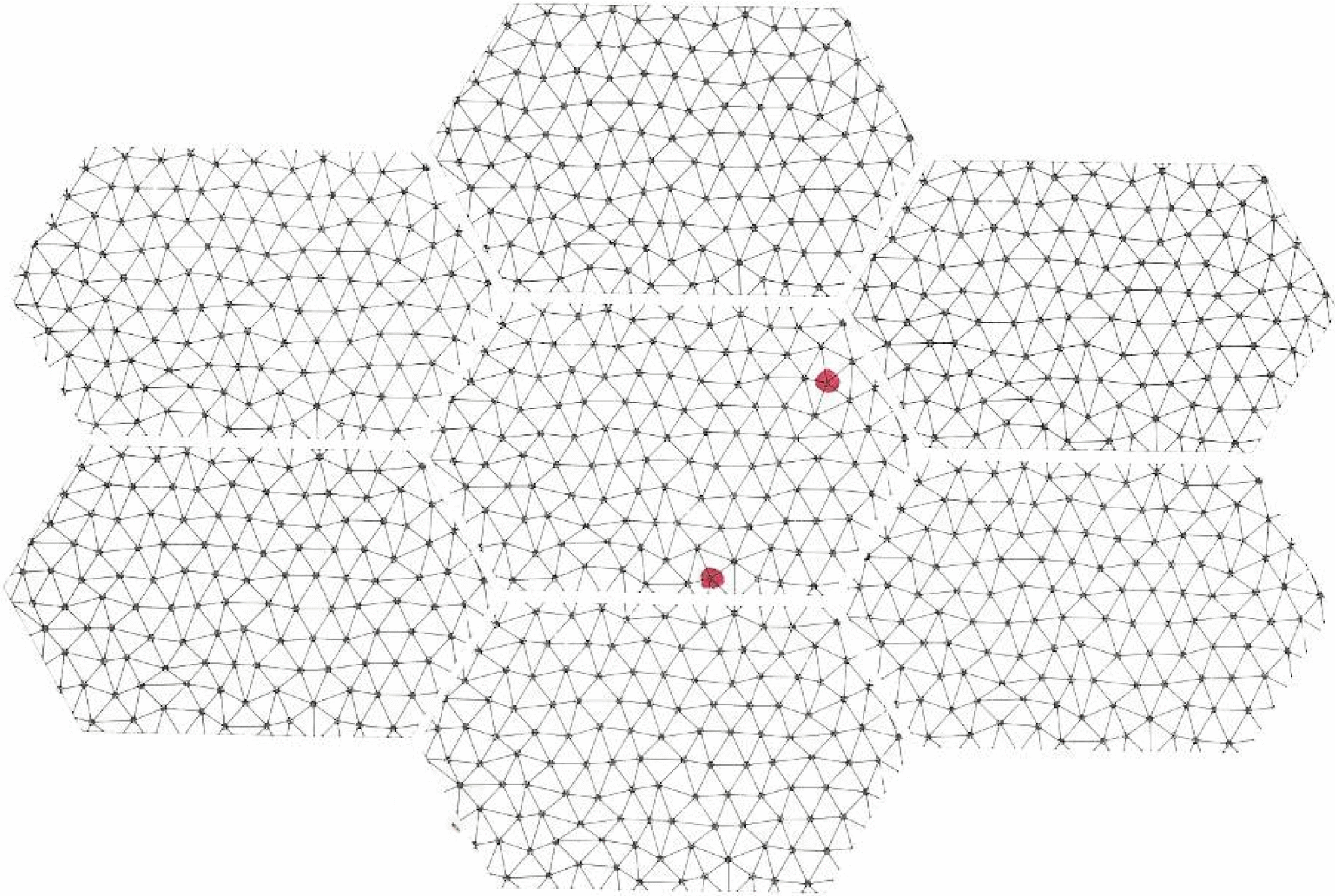
Molecular Dynamics Simulations

- Equations of Motion are either first-order or second-order ordinary differential equations :

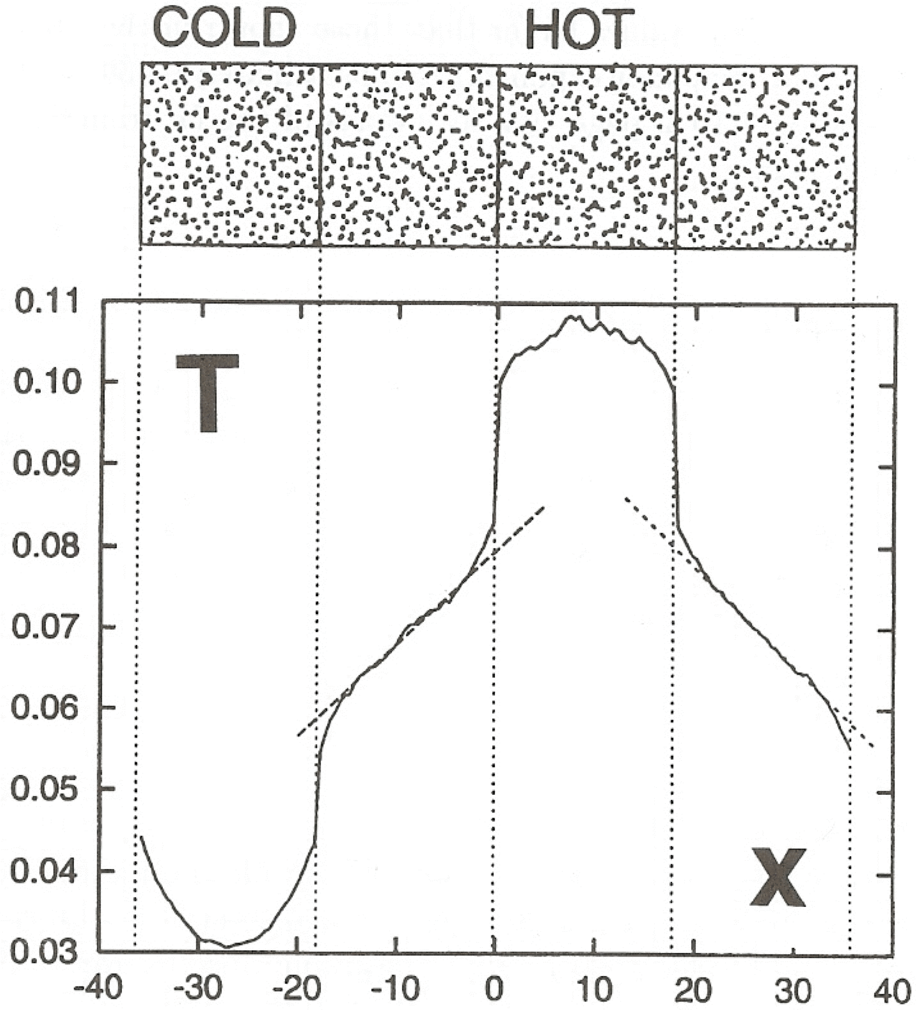
$$\{\dot{q}, \dot{p}\} \text{ or } \{\ddot{q}\}$$

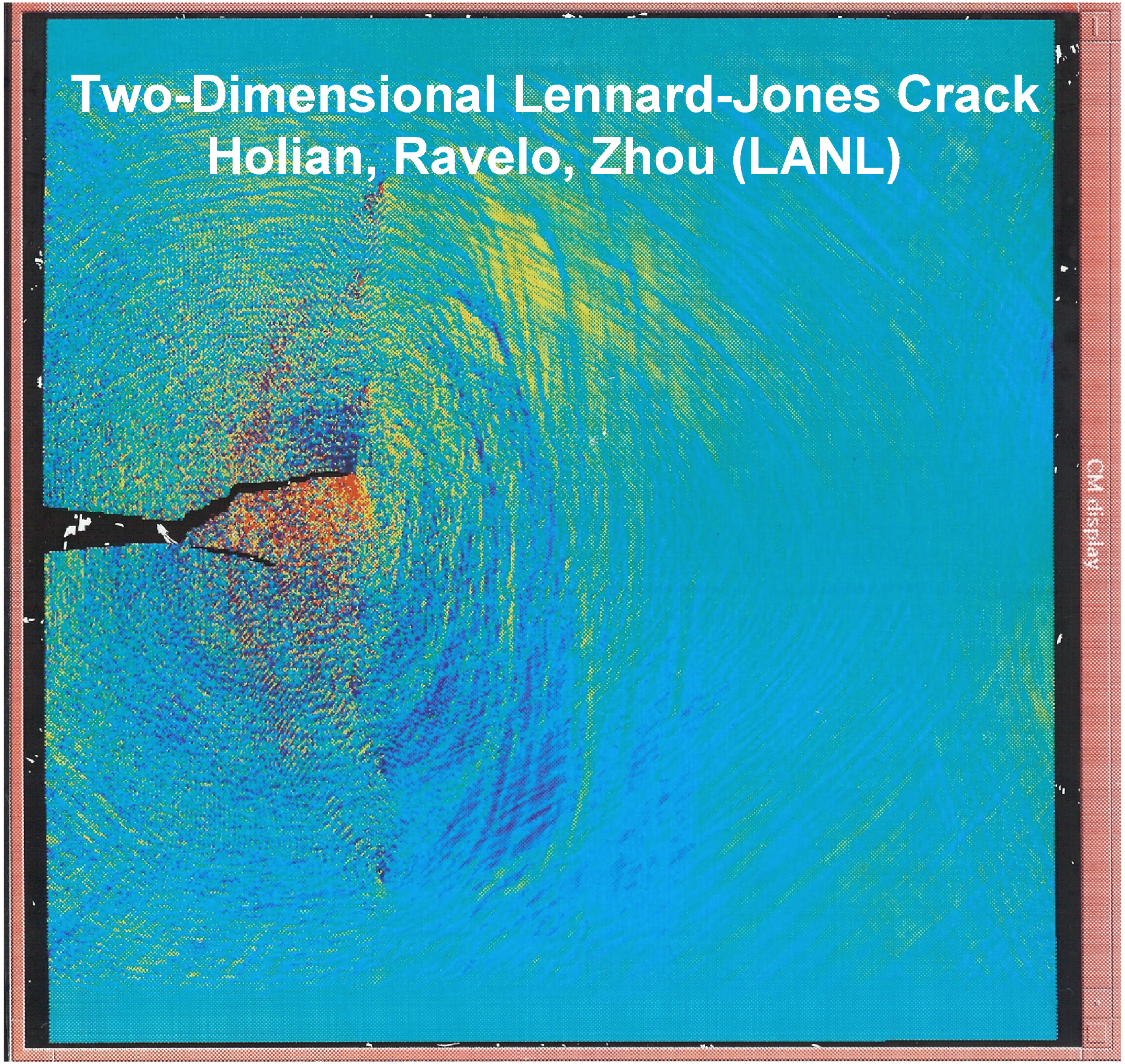
- Periodic Boundary Conditions are the simplest, and have been applied to both shear flows and heat flows .
- Fourth-order Runge-Kutta is the simplest solution algorithm .

Periodic Solid-Phase Shear



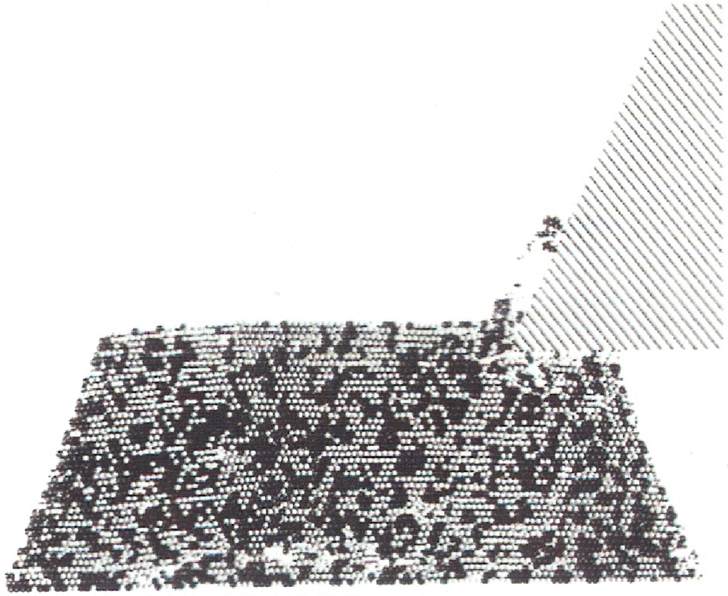
Four-Chamber Periodic Heat Flow



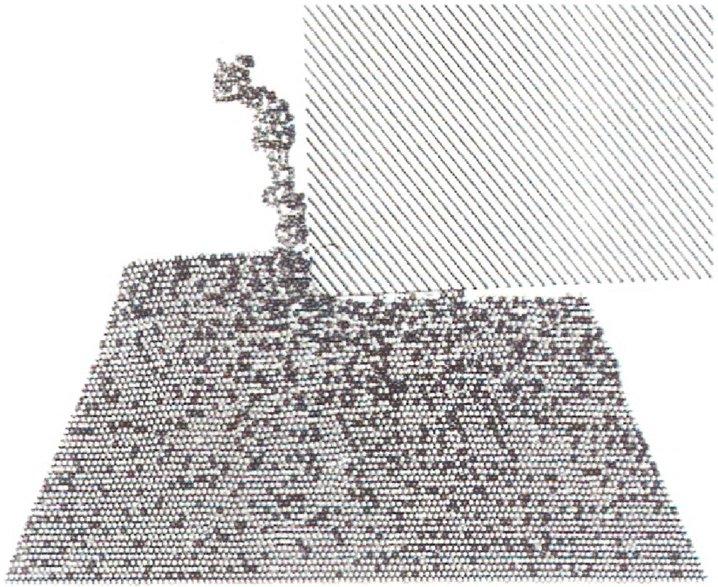

Two-Dimensional Lennard-Jones Crack
Holian, Ravelo, Zhou (LANL)
CM display

ENGINEERING @ LLNL

Thermostatted Metal Cutting



Lennard-Jones Crystal



Embedded-Atom (Metal)

Molecular Dynamics Simulations

- **Temperature and Pressure are typically expressed in terms of momenta and forces, at, and away from, equilibrium :**

$$E = K(p) + \Phi(q);$$

$$PV = \sum_{i<j} Fr + \sum_{i} pp/m;$$

$$kT(p) = \langle p^2/2m \rangle \text{ or } kT_c(q) = \langle F^2/\nabla^2 H \rangle .$$

- **Configurational Temperature T_c is both old (Landau-Lifshitz) and “new” (Rugh) .**

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2. The Need for NEMD Thermostats

Molecular Dynamics Simulations

- Nonequilibrium simulations typically generate **irreversible heat**, proportional to the squares of the velocity or temperature gradients .

- To remove this heat **Thermostats** are required. How can we find appropriate thermostats ?

- We will consider here four thermostat types :
  1. "Velocity scaling" [Woodcock, Ashurst]
  2. "Nose-Hoover" [Dettmann → Morriss]
  3. "Configurational $\mathcal{L}$ and $\mathcal{H}$" [Landau-Lifshitz]
  4. "Constrained $\mathcal{L}$ and $\mathcal{H}$" [Hoover ← Leete]

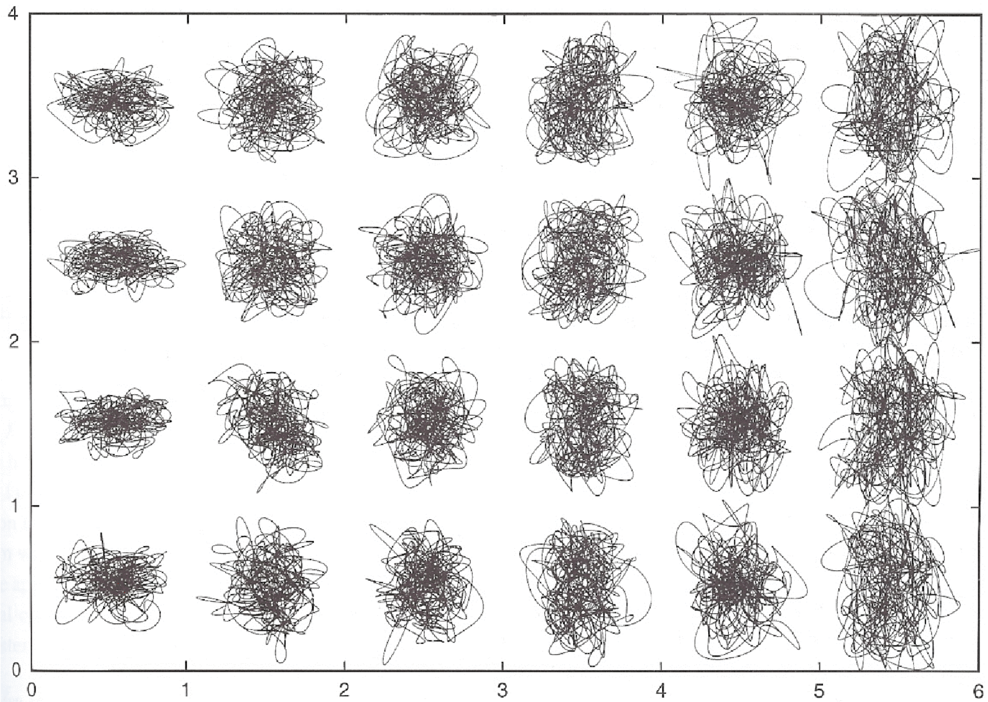
Heat Transfer *via* Two Thermostatted Boundaries

Shūichi Nosé
Keio University
Yokohama
1987

Shūichi Nosé
Keio University
Yokohama
1987

Heat Conduction in 2D ϕ^4 Slab

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



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

Four COLD Particles & Four HOT Particles

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University of California &
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3. Four Example Thermostats

3A. The Isokinetic Thermostat

- Velocity rescaling: $p_0 = p[K_0/K]^{1/2}$.
- Continuous rescaling: $dp/dt = F - \zeta p$, with $\zeta = \Sigma F\cdot p / \Sigma (p^2/m) \rightarrow dK/dt = 0$.
- Dettmann-Morris Hamiltonian : $\mathcal{H}(q,p) = K(p)e^{+\Phi/2K_0} - K_0 e^{-\Phi/2K_0} = 0$!

All three approaches [1971, 1980, 1996] are equivalent!

Isokinetic $\mathcal{H}$(q,p) Details

$$\mathcal{H}(q,p) = K(p)e^{+\Phi/2K_0} - K_0 e^{-\Phi/2K_0} = 0 \;!$$

This implies that $K/K_0 = e^{-\Phi/K_0}$.

Compute Hamiltonian motion equations :

- $m\,dq/dt = pe^{+\Phi/2K_0}$; $dp/dt = Fe^{-\Phi/2K_0}$;

giving the familiar isokinetic equations

- $md^2q/dt^2 = F - \zeta p$; $\zeta = [\,\Sigma F\cdot dq/dt/2K_0\,]$.

3A. Isokinetic Thermostat

- The Isokinetic thermostat preserves Gibbs' configurational distribution :
- $f(q,t) \sim e^{-\Phi/kT} \rightarrow d\ln f/dt = -(d\Phi/dt)/kT = \Sigma Fp/kT$.
- Alternatively, from the isokinetic dynamics and Liouville's Theorem :

$$d\ln f/dt = \Sigma[\partial\dot{q} / \partial q + \partial\dot{p} / \partial p] = \Sigma\varsigma$$

- The two approaches agree with the result of Gauss' $<F_c^2>$ Principle $\rightarrow \zeta = \Sigma Fp/\Sigma p^2/m$.

3B. Nosé-Hoover Thermostat

- Carl Dettmann (Lyon, in 1996) discovered the vanishing Nosé-Hoover Hamiltonian :

$$\mathcal{H}(q,p) = [K(p)/s] + s[\Phi + \zeta^2\tau^2/2 + \#kT\ln s] = 0 \ !$$

Familiar equations of motion result :

$\{ dq/dt = p/m \ ; \ dp/dt = F - \zeta p \}$; where

$$d\zeta/dt = [(K/K_0) - 1]/\tau^2 \ .$$

- Now Liouville's Theorem gives the *full*

$$f(q,p,t) \sim e^{-\mathcal{H}/kT} \rightarrow d\ln f/dt = \Sigma \ \zeta_{\text{Nosé-Hoover}} \ .$$

With Fujiwara-sensei in 1990 @ Keio

STUDIES IN MODERN THERMODYNAMICS 11

Computational Statistical Mechanics

Wm. G. Hoover

ELSEVIER

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

3C. Configurational Thermostat

- The Configurational Temperature* follows from a canonical-ensemble integration by parts :

$$kT\int \nabla^2 \Phi e^{-\Phi/kT} dq = \int (\nabla\Phi)^2 e^{-\Phi/kT} dq \rightarrow$$

$$kT_c = \langle F^2 \rangle / \langle \nabla^2 \Phi \rangle$$

* [Landau & Lifshitz' (1938 or 1958) Equation 33.14]

3C. Configurational Thermostat

The Configurational Temperature (or even several *different* temperatures $\{T_c\}$) can be imposed with a constrained Lagrangian :

$$\mathcal{L}(q,dq/dt) = K(dq/dt) - \Phi + \lambda(T_c - T_0) .$$

Two time differentiations → d^2T_c/dt^2, taking care to choose T_c and dT_c/dt wisely, give λ . Then both T_c and the total energy, $E = K + \Phi$, are constants of the motion.

3D. Hoover-Leete* Thermostat

The Hoover-Leete Kinetic Temperature comes from Goldstein's mechanics using either a Lagrangian or a Hamiltonian approach :

$$\mathcal{L}(q,v = dq/dt) = K(v) - \Phi(q) + \lambda [K(v) - K_0] .$$

$$\mathcal{H}(q,p) = \Sigma p \cdot v - \mathcal{L}(q,v) \text{ , which gives}$$

$$\mathcal{H}(q,p) = [4K(p)K_0]^{1/2} + \Phi(q) - K_0 .$$

In *both* these cases it is evident that two or more temperatures can be included .

* [Tom Leete's Master's Thesis, 1979, U WV]

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4. Problems with the Lagrangian or Hamiltonian Thermostat Approach

4. Problems for the Theory

The Gaussian Isokinetic and Nosé-Hoover *Hamiltonians* both use the trick $\mathcal{H} = 0$. There is no way to include *two* temperatures with such an approach . Instead, the *dynamical equations* have to be adopted. Both these dynamic approaches give Second-Law MultiFractal phase-space distributions .

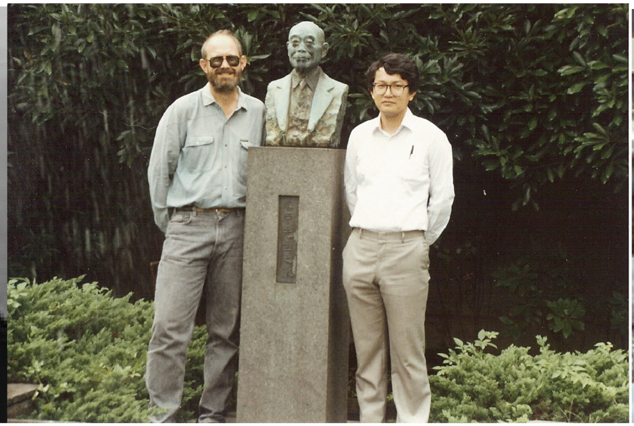
The Configurational and Hoover-Leete Kinetic Lagrangians and Hamiltonians both can include more than one temperature, but both have *two* constants of the motion . Accordingly, *neither* gives fractals .

Next time we will consider *Computational* Results .

Rogues’ Gallery of Thermostaters






Results with Hamiltonian Thermostats in Molecular Dynamics Simulations

Wm G Hoover & C G Hoover
Great Basin College, Nevada
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1. Four Thermostat Types .
2. Periodic Heat Flow Problem .
3. Aoki-Kusnezov ϕ^4 Model System .
4. Continuum Solution of the Problem .
5. Gauss & Nosé-Hoover Results .
6. Hoover-Leete & Landau-Lifshitz Results .
7. Summary and Suggestions .

Results using Hamiltonian Thermostats in Molecular Dynamics Simulations

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University of California &
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1. Four Thermostat Types

We considered Four Thermostats

Two came from an *ad hoc* friction idea :

$$dq/dt = p/m \; ; \; dp/dt = F - \zeta p \, ,$$

Where ζ is either Isokinetic or Nosé-Hoover .

Two came from Lagrangians :

$$\mathcal{L}_{HL}(q,v) = K(v) - \Phi + \lambda \, [\, K(v) - K_0 \,]$$

$$\mathcal{L}_{LL}(q,v) = K(v) - \Phi + \lambda \, [\, T(q) - T_0 \,] \, .$$

Results using Hamiltonian Thermostats in Molecular Dynamics Simulations

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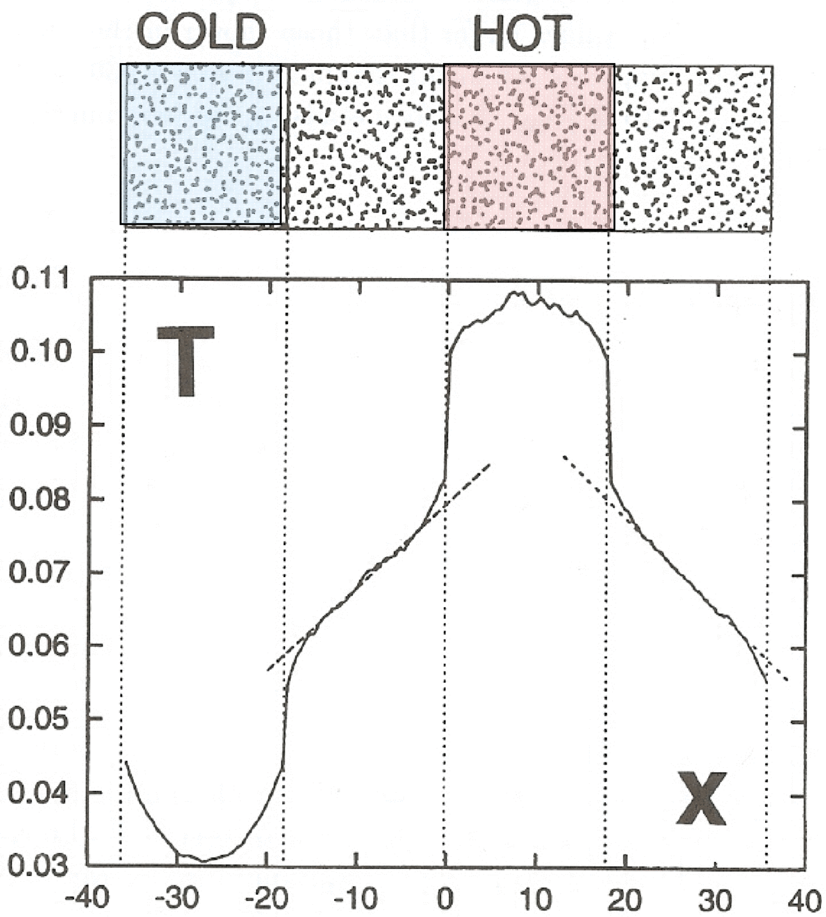
2. Periodic Heat Flow Problem

Four Chamber Periodic Problem



2. Periodic Heat Flow Problem
[HOT + Newton + COLD + Newton]

$$\Phi = \Sigma_{i<j}\, \kappa_{ij}\delta_{ij}^{2}/2 + \Sigma_{i}\, \kappa_{i}\delta_{i}^{4}/4 \,,$$

Plus *control* using HOT and COLD Thermostats .

Aoki and Kusnezov have determined a 1-D heat conductivity for $\kappa_{ij} = \kappa_i = 1$:

$$\kappa_{Heat} \sim 3T^{-4/3}$$

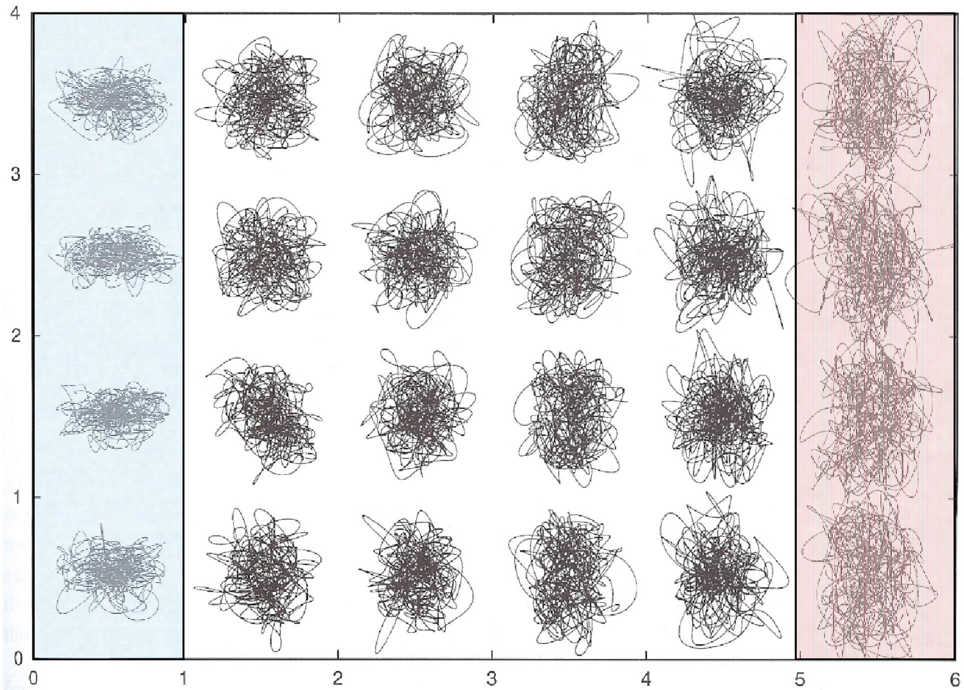
Dimitri Kusnezov & Kenichiro Aoki

Colorado

Tokyo

Heat Conduction in 2D ϕ^4 Slab

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



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

Four COLD Particles + Four HOT Particles

Results using Hamiltonian Thermostats in 1-D Molecular Dynamics Simulations

W G Hoover & C G Hoover
University of California &
Great Basin College, Nevada

3. Aoki-Kusnezov ϕ^4 Model System

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

Results using Hamiltonian Thermostats in Molecular Dynamics Simulations

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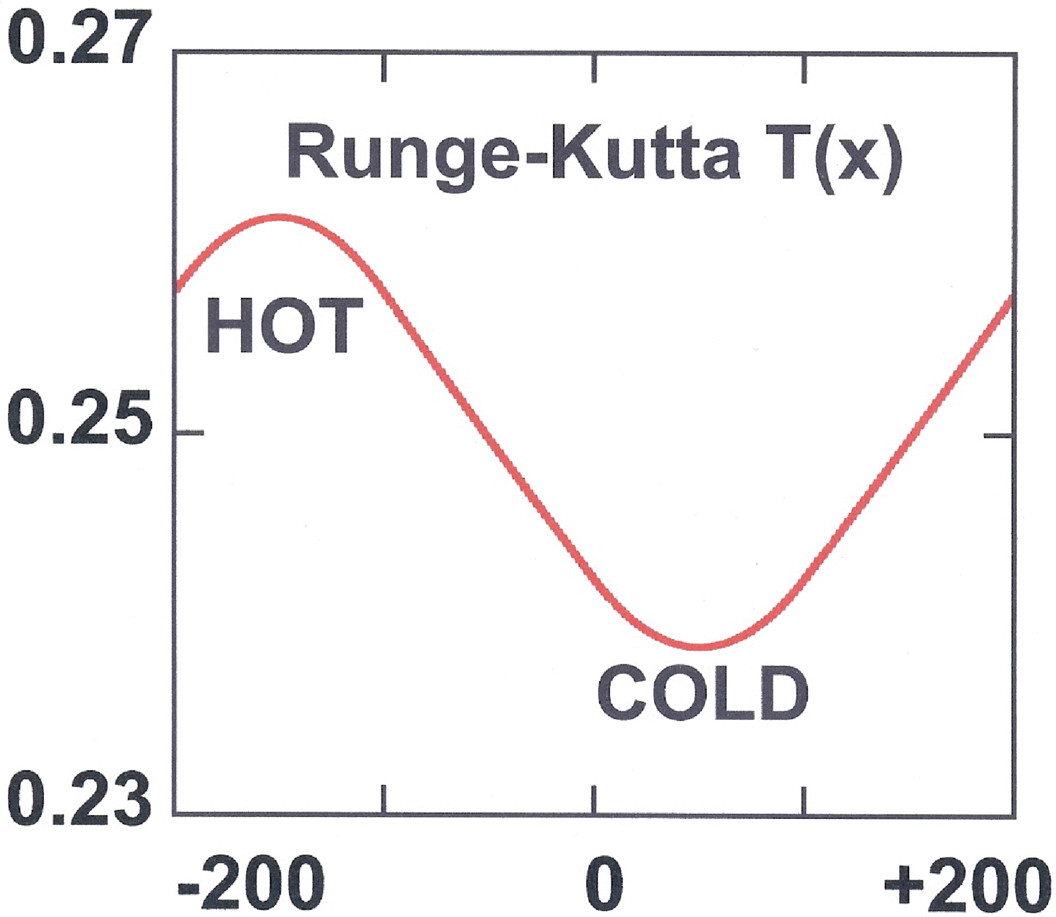
4. The Continuum Solution

Solving the Periodic Heat Flow Problem
[HOT + Newton + COLD + Newton]

$$\dot{T} = \nabla[(3/T^{4/3})\nabla T] \pm \alpha T$$

We can solve this Heat Flow Problem with Fourth-order Runge-Kutta integration on a one-dimensional mesh.

Finite-Difference Temperature



Results using Hamiltonian Thermostats in Molecular Dynamics Simulations

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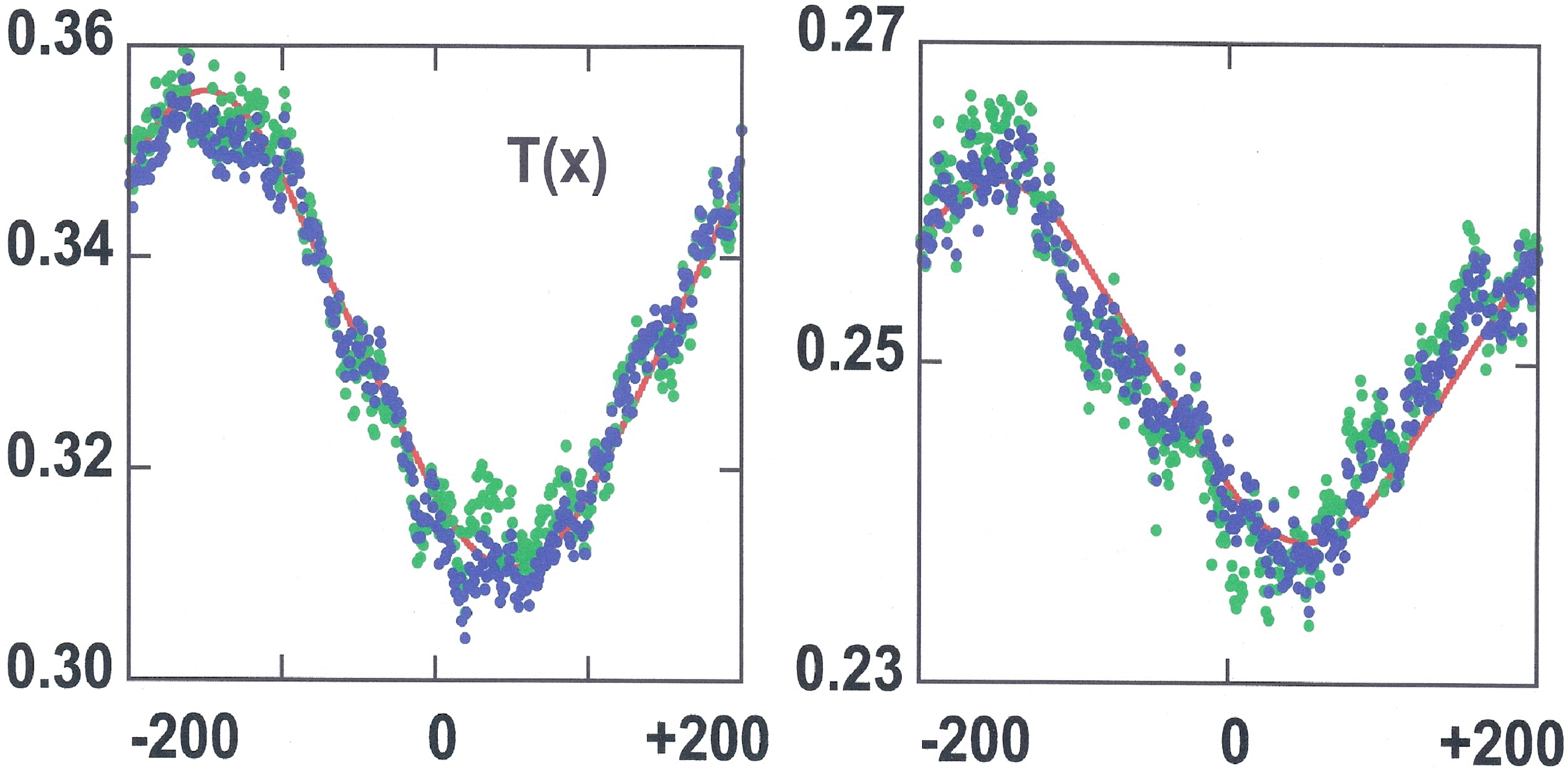
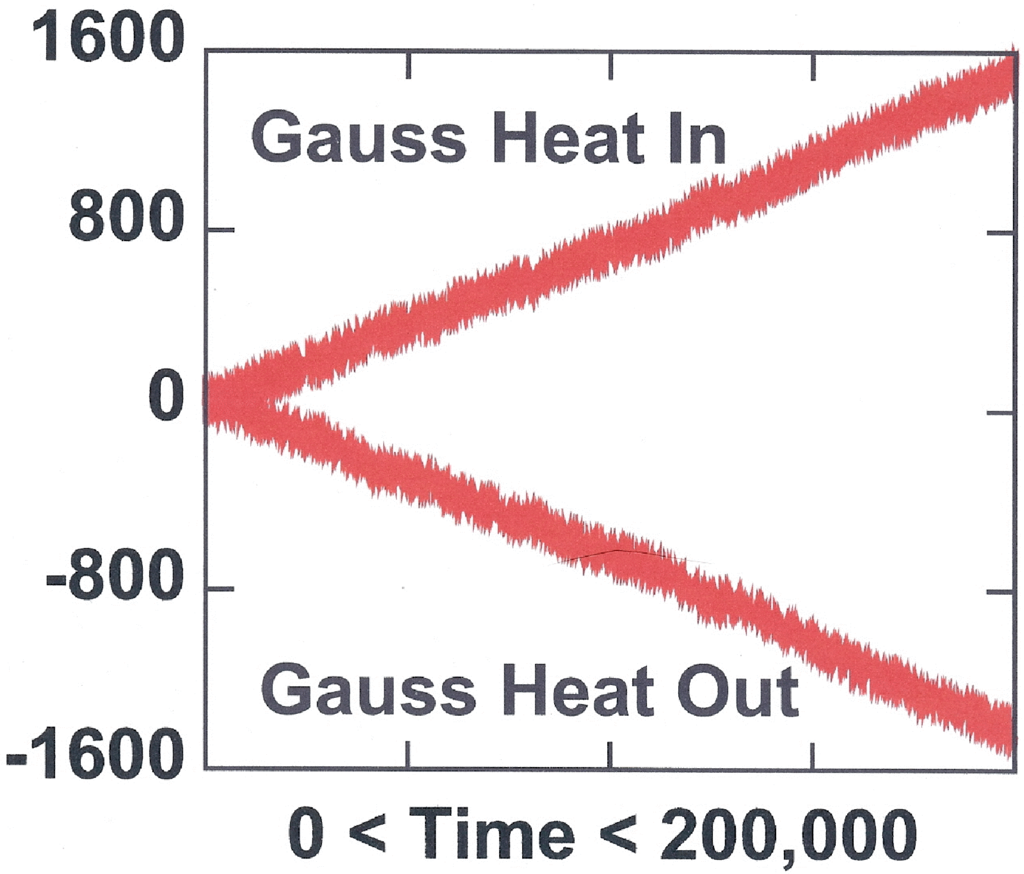
5. Gauss & Nosé-Hoover Thermostats

Gauss & Nosé-Hoover Profiles : Kinetic & Configurational T(x)



HOT and COLD Heat Fluxes



Results using Hamiltonian Thermostats in Molecular Dynamics Simulations

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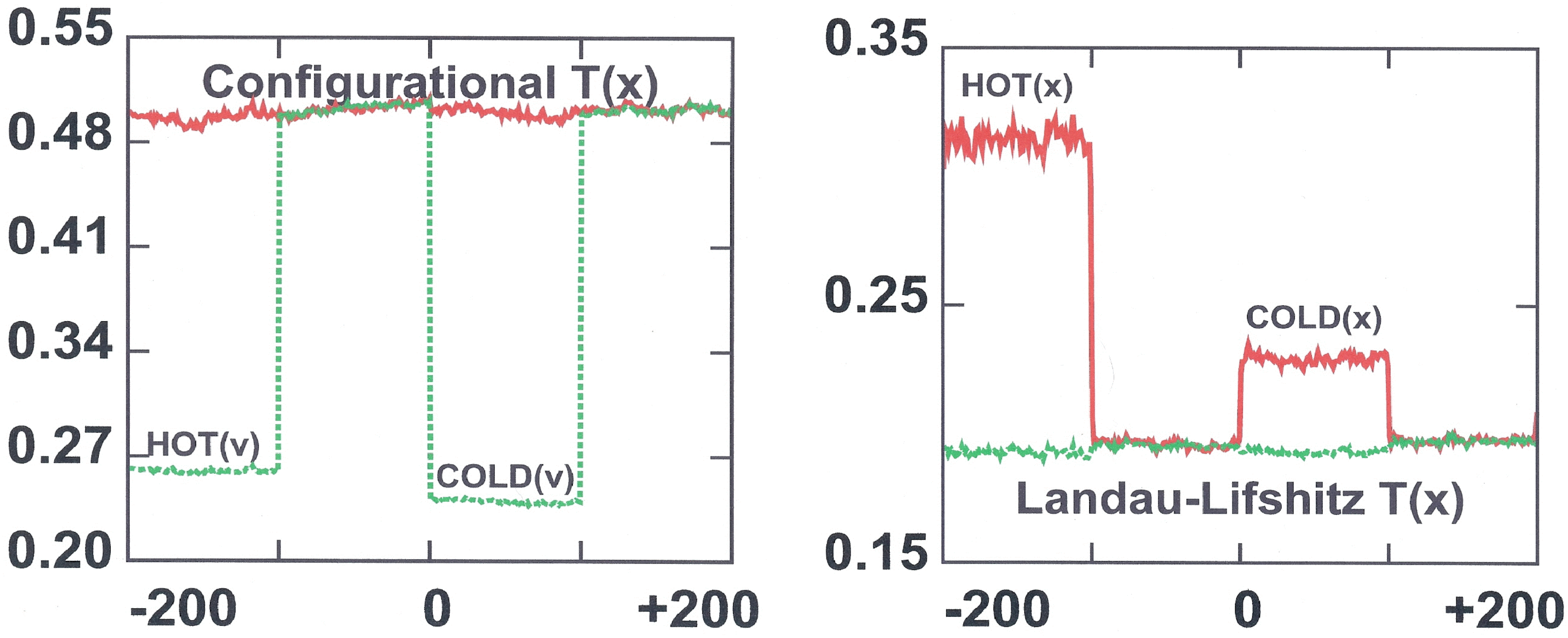
Great Basin College, Nevada

6. Hoover-Leete Thermostat Landau-Lifshitz Thermostat

Hoover-Leete & Landau-Lifshitz
Kinetic & Configurational T(x) .



Characteristics of the Hoover-Leete & Landau-Lifshitz "Nonequilibria"

Though the local T(q) or T(p) can be constrained, no fluxes result .

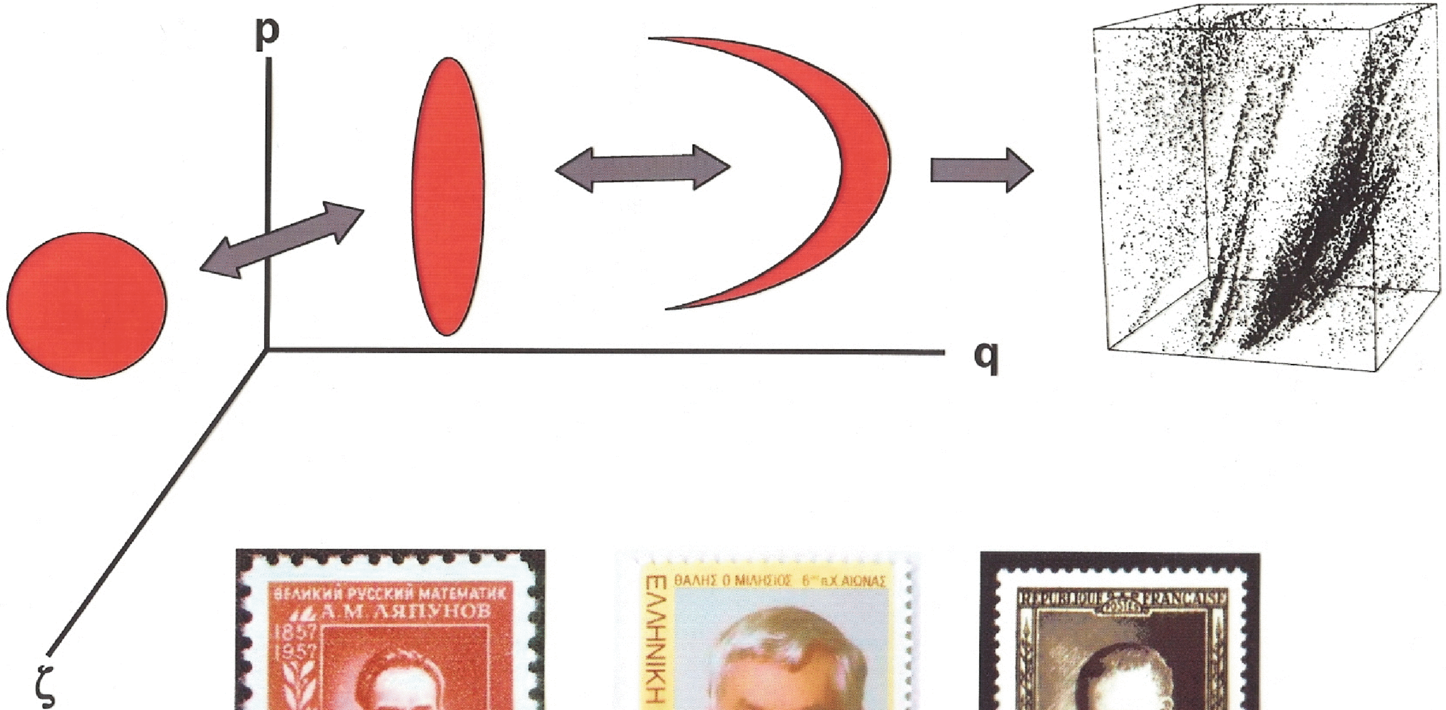
T(p) constrained → T(q) constant ;
T(q) constrained → T(p) constant .

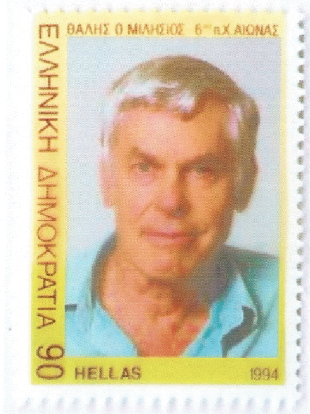
Characteristics of the Hoover-Leete & Landau-Lifshitz “Nonequilibria”

Phase Volume is Conserved, in Violation of the Second Law .

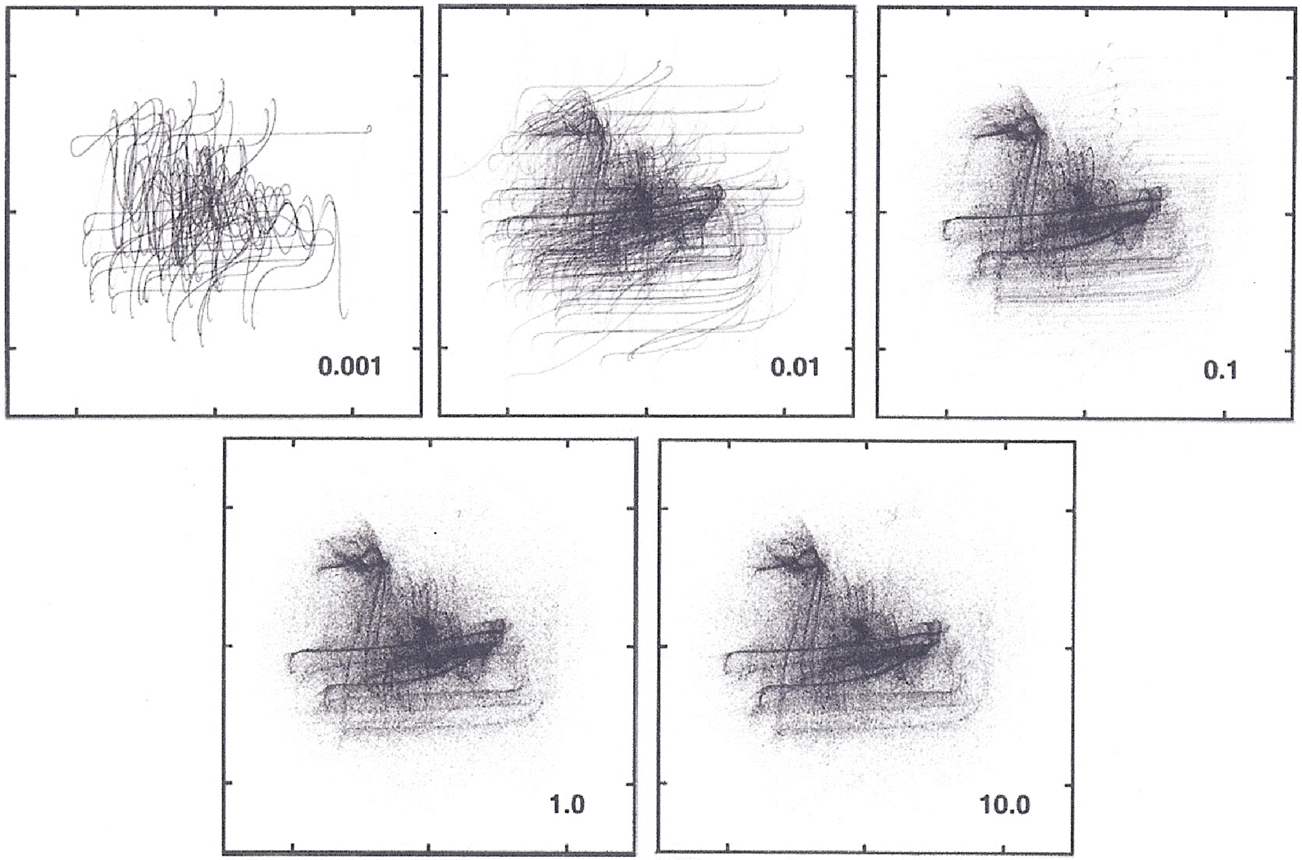
Total Energy is Fixed while some Temperatures are also, in Violation of Thermodynamics .

Generic Nonequilibrium Phase Space Flow





Continuous Orbit → Multifractals



Dimensionality of Skiing Goose: 2.0 or 1.77 .

Results using Hamiltonian Thermostats in Molecular Dynamics Simulations

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University of California &
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7. Summary & Suggestions

7. Summary and Suggestions

1. *All* useful single-T Thermostats *can* be related to Hamiltonian Mechanics .
2. Hamiltonian Thermostats fix *both* the Energy and the Temperature !
3. Hamiltonian Thermostats work, but *cannot* provide Heat Flow . Why Not ?
4. Fractal distributions provide a clue ; Hamiltonians → phase conservation .