Theory of Hamiltonian Thermostats for Molecular Dynamics Simulations

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1. Molecular Dynamics Simulations.
2. Why Thermostats are Needed.
3. Four Example $L$ and $H$ Thermostats: Gauss-Rescaling and Nosé-Hoover; Configurational and Kinetic.
Overview of California and Nevada

Ruby Valley

Davis
Livermore
Nonequilibrium Molecular Dynamics

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

RUBY MOUNTAIN BREWING COMPANY
VIENNA STYLE LAGER
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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)
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:

\[
E = K(p) + \Phi(q);
\]
\[
PV = \sum_i Fr_i + \sum_{i<j} pp_{ij}/m;
\]
\[
kT(p) = \langle p^2/2m \rangle \text{ or } kT_c(q) = \langle F^2/\nabla^2 H \rangle.
\]

- **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 $L$ and $H$” [Landau-Lifshitz]
  4. “Constrained $L$ and $H$” [Hoover ← Leete]
Heat Transfer via
Two Thermostatted Boundaries

Shūichi Nose
Keio University
Yokohama 1987

Shūichi Nosé
Keio University
Yokohama 1987
Heat Conduction in 2D $\phi^4$ Slab

$$\Phi_{\text{Newton}} = \sum_{\text{sites}} \delta^4/4 + \sum_{\text{pairs}} (|r| - 1)^2 / 2.$$
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3. Four Example Thermostats
3A. The Isokinetic Thermostat

- Velocity rescaling: $p_0 = p[\frac{K_0}{K}]^{1/2}$.

- Continuous rescaling: $dp/dt = F - \zeta p$, with $\zeta = \sum F \cdot p / \sum (p^2/m) \rightarrow dK/dt = 0$.

- Dettmann-Morris Hamiltonian:
  $$\mathcal{H}(q,p) = K(p)e^{+\Phi/2K_0} - K_0e^{-\Phi/2K_0} = 0.$$  

All three approaches [1971, 1980, 1996] are equivalent!
Isokinetic $\mathcal{H}(q,p)$ Details

$\mathcal{H}(q,p) = K(p)e^{\Phi/2K_0} - K_0e^{-\Phi/2K_0} = 0$ !
This implies that $K/K_0 = e^{-\Phi/K_0}$.

Compute Hamiltonian motion equations:

- $mdq/dt = pe^{\Phi/2K_0}$; $dp/dt = Fe^{-\Phi/2K_0}$;

  giving the familiar isokinetic equations

- $md^2q/dt^2 = F - \zeta p$; $\zeta = [\sum F \cdot dq/dt/2K_0]$.
3A. Isokinetic Thermostat

- The Isokinetic thermostat preserves Gibbs’ configurational distribution:

\[ f(q,t) \sim e^{-\Phi/kT} \rightarrow \frac{d\ln f}{dt} = -(d\Phi/dt)/kT = \Sigma Fp/kT. \]

- Alternatively, from the isokinetic dynamics and Liouville’s Theorem:

\[ \frac{d\ln f}{dt} = \Sigma \left[ \frac{\partial q}{\partial q} + \frac{\partial p}{\partial p} \right] = \Sigma \zeta \]

- The two approaches agree with the result of Gauss’ \( <F^2> \) 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:

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

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

- Now Liouville’s Theorem gives the full

$$f(q,p,t) \sim e^{-\mathcal{H}/kT} \rightarrow df/dt = \sum \zeta_{\text{Nosé-Hoover}} \! .$$
With Fujiwara-sensei in 1990 @ Keio
3C. **Configurational Thermostat**

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

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

\[ kT_c = < F^2 > / < \nabla^2 \Phi > \]

* [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 \(\lambda\). 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:

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

\[ \mathcal{H}(q,p) = \sum p \cdot v - \mathcal{L}(q,v) , \text{ which gives} \]

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

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

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1. Four Thermostat Types.
3. Aoki-Kusnezov $\phi^4$ Model System.
4. Continuum Solution of the Problem.
5. Gauss & Nosé-Hoover Results.
7. Summary and Suggestions.
Results using Hamiltonian Thermostats in Molecular Dynamics Simulations

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1. Four Thermostat Types
We considered **Four Thermostats**

Two came from an *ad hoc* friction idea:

\[
dq/dt = p/m ; \quad dp/dt = F - \zeta p ,
\]

Where *\zeta* is either isokinetic or Nosé-Hoover.

Two came from **Lagrangians**:

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

\[
\mathcal{L}_{LL}(q,v) = K(v) - \Phi + \lambda \left[ T(q) - T_0 \right].
\]
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2. Periodic Heat Flow Problem
Four Chamber Periodic Problem
2. Periodic Heat Flow Problem
[ HOT + Newton + COLD + Newton ]

\[ \Phi = \sum_{i<j} \kappa_{ij} \delta_{ij}^2/2 + \sum_i \kappa_i \delta_i^4/4, \]

Plus control using HOT and COLD Thermostats.

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

\[ \kappa_{\text{Heat}} \sim 3T^{-4/3} \]
Dimitri Kusnezov & Kenichiro Aoki

Colorado

Tokyo
Heat Conduction in 2D $\phi^4$ Slab

$$\Phi_{\text{Newton}} = \sum_{\text{sites}} \frac{\delta^4}{4} + \sum_{\text{pairs}} \frac{(|r| - 1)^2}{2}.$$
Results using Hamiltonian Thermostats in 1-D Molecular Dynamics Simulations

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3. Aoki-Kusnezov $\phi^4$ Model System

$$\Phi_{\text{Newton}} = \sum \frac{\delta^4}{4} + \sum \left( |r| - 1 \right)^2 / 2 .$$

sites pairs
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 ]

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

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

Runge-Kutta $T(x)$

HOT

COLD
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

Gauss Heat In

Gauss Heat Out

0 < Time < 200,000
Results using Hamiltonian Thermostats in Molecular Dynamics Simulations

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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 $\rightarrow$ $T(q)$ constant; $T(q)$ constrained $\rightarrow$ $T(p)$ constant.
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 $\rightarrow$ Multifractals

Dimensionality of Skiing Goose: 2.0 or 1.77.
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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.