Thermostats in Molecular Dynamics Simulations

Alden Johnson, Teresa Johnson, Aimee Khan

University of Massachusetts Amherst

December 6th, 2012

An Interest in Thermostats

Thermostat: A modification of the Newtonian MD scheme with the purpose of generating a *statistical ensemble* at a constant temperature.

- Match experimental conditions
- Manipulate temperatures in algorithms such as simulated annealing
- Avoid energy drifts caused by accumulation of numerical errors.

Statistical Ensembles

- Ensemble: a large collection of microscopically defined states of a system, with certain constant macroscopic properties
- Microcanonical (NVE)
  - Arises in Newtonian MD simulation
  - Conserves total energy
- Canonical (NVT)
  - Implement thermostats to sample from here
  - Relevant to real behavior in experiment

Microcanonical Ensemble

- Consider an isolated system
- Microstate: complete description of a state of the system, microscopically
- The probabilities of being in a certain microstate for the microcanonical ensemble are uniform over all possible states

Canonical Ensemble

- Follows a Gibbs distribution for probability p_j of being in a given microstate j with energy E_j

$$p_j = \frac{e^{-\beta E_j}}{Z_\beta}, \qquad Z_\beta = \sum_j e^{-\beta E_j}$$

$$\beta = \frac{1}{k_B T}$$

- Derivation follows from maximizing entropy

Ergodic Hypothesis

- The ergodic hypothesis says the long time average of an observable $\overline{f}$ coincides with an ensemble average of the observable $\langle f \rangle$.

$$\overline{f} = \lim_{t\to\infty} \frac{1}{t}\int_0^t f(x(s))\,\mathrm{d}s$$

$$\langle f \rangle = \int_\Gamma f(x)\,\mathrm{d}\mu(x)$$

where μ is the ensemble measure and Γ is the *phase space* of the observable.

- Phase space is collection of positions q and momenta p of particles in system
- The Hamiltonian Form

$$\begin{cases} \mathrm{d}q_t = \nabla_p H(q_t, p_t)\,\mathrm{d}t \\ \mathrm{d}p_t = -\nabla_q H(q_t, p_t)\,\mathrm{d}t \end{cases}$$

$$H(q,p) = E_{kin}(p) + V(q), \qquad E_{kin}(p) = \frac{1}{2} p^T M^{-1} p$$

Sampling from Ensembles

- A canonical ensemble (constant average energy) is a distribution of microcanonical ensembles (constant energy)
- To sample from the canonical ensemble, the following thermostats modulate the energy entering and leaving the boundaries of the system

Velocity Rescaling

- Velocities are described by Maxwell-Boltzmann distribution

$$P(v_{i,\alpha}) = \left(\frac{m}{2\pi k_B T}\right)^{\frac{1}{2}} e^{-\frac{mv_{i,\alpha}^2}{2k_B T}}$$

- Adjust instantaneous temperature by scaling all velocities
- Average E_{kin} per degree of freedom related to T via the equipartition theorem

$$\left\langle \frac{mv_{i,\alpha}^2}{2} \right\rangle = \frac{1}{2} k_B T$$

Velocity Rescaling

- Ensemble average $\rightarrow$ average over velocities of all particles: define instantaneous temperature T_c for a finite system

$$k_B T_c = \frac{1}{N_f} \sum_{i,\alpha} m v_{i,\alpha}^2$$

- $T_c \neq T$ until rescaling

$$v'_{i,\alpha} = \sqrt{\frac{T}{T_c}} v_{i,\alpha}$$

Velocity Rescaling

- Disadvantages
  - Results do not correspond to any ensemble
    - Does not allow the proper temperature fluctuations
  - Localized correlation not removed
  - Not time reversible
- Advantages
  - Straightforward to implement
  - Good for use in warmup / initialization phase

Nosé-Hoover

- Based on extended Lagrangian formalism
  - Deterministic trajectory
  - Simulated system contains virtual variables related to real variables
    - ★ Coordinates $\mathbf{q}_i' = \mathbf{q}_i$
    - ★ Momenta $\mathbf{p}_i' = \mathbf{p}_i / s$
    - ★ Time $t' = \int_0^t \frac{dt}{s}$
    - ★ s: additional degree of freedom, acts as external system

Nosé-Hoover

- Hamiltonian given by

$$H = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i s^2} + V(\mathbf{q}) + \frac{Q\dot{s}^2}{2} + (3N+1)k_B T \ln s$$

- Logarithmic term required for proper time scaling: canonical ensemble
- Effective mass Q associated with s
  - Determines thermostat strength
  - Q too small: system not canonical
  - Q too large: temperature control inefficient
- Microcanonical dynamics on extended system give canonical properties

Nosé-Hoover

- Disadvantages
  - Extended system not guaranteed to be ergodic
- Advantages
  - Easy to implement and use
    - Implement as a chain
    - Each link: apply thermostatting to the previous thermostat variable
  - Increasing Q lengthens decay time of response to instantaneous temperature jump
  - Deterministic and time reversible

Langevin

- Consider the motion of large particles through a continuum of smaller particles

$$\frac{d\mathbf{q}_i}{dt} = \frac{\mathbf{p}_i}{m_i}$$

$$\frac{d\mathbf{p}_i}{dt} = -\frac{\delta V(\mathbf{q})}{\delta \mathbf{q}_i} - \gamma \mathbf{p}_i + \sigma G_i$$

  - Viscous drag force proportional to velocity $-\gamma \mathbf{p}_i$
  - Smaller particles give random pushes to large particle

- Fluctuation-dissipation relation

$$\sigma^2 = 2\gamma m_i k_B T$$

Langevin

- Disadvantages
  - Difficult to implement drag for non-spherical particles: γ related to particle radius
  - Momentum transfer lost: cannot compute diffusion coefficients
- Advantages
  - Damping + random force $\mapsto$ correct canonical ensemble
  - Ergodic
  - Can use larger time step

Andersen

- Couple a system to a heat bath to impose desired temperature
- Equations of motion are Hamiltonian with stochastic collision term
- Strength of coupling specified by ν, the stochastic collision frequency
- When particle has collision, new velocity is sampled from $\mathcal{N}(0, \sqrt{T})$

Andersen

- Disadvantages
  - Newtonian dynamics + stochastic collisions $\rightarrow$ Markov chain
  - Algorithm randomly decorrelates velocity: dynamics are not physical
- Advantages
  - Allows sampling from canonical ensemble

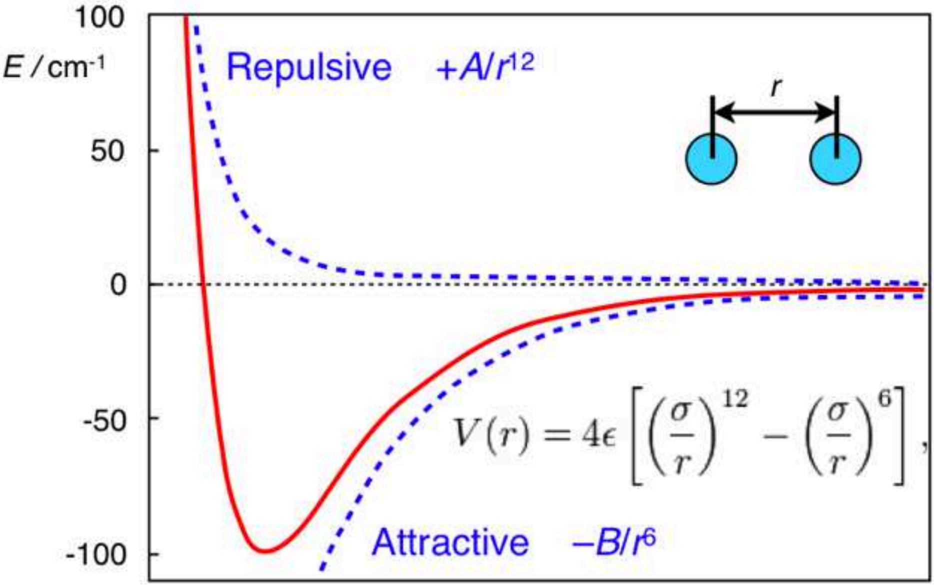
Thermostats Summary

Thermostat	Description	Canonical?	Stochastic?
Velocity Rescaling	KE fixed to match T	no	no
Nosé-Hoover	extra degree of freedom acts as thermal reservoir	yes	no
Langevin	noise and drag balance to give correct T	yes	yes
Andersen	momenta occasionally re-randomized	yes	yes

Applied Math Masters Project

- Molecular Dynamics Simulation
  - Implemented in MATLAB and C++
  - Simulations in 2 and 3 dimensions
  - Periodic and walled boundary conditions
  - External fields such as gravity
  - Optimization
    - OpenMP
    - CUDA

Lennard-Jones Potential



$$V(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right],$$

Numeric Integration

- Verlet Algorithm

$$p^{n+1/2} = p^n - \frac{\Delta t}{2} \nabla V(q^n)$$

$$q^{n+1} = q^n + \Delta t M^{-1} p^{n+1/2}$$

$$p^{n+1} = p^{n+1/2} - \frac{\Delta t}{2} \nabla V(q^{n+1})$$

  - Preserves modified Hamiltonian

Thermostat Implementation

- Velocity Rescaling
  - $p_i \to \sqrt{\frac{T}{T_c}} p_i$
- Anderson
  - $\nu = 1\%, 0.1\%, 0.05\%$
  - Velocities are sampled from $\mathcal{N}(0, \sqrt{T})$
- Langevin
  - BBK algorithm

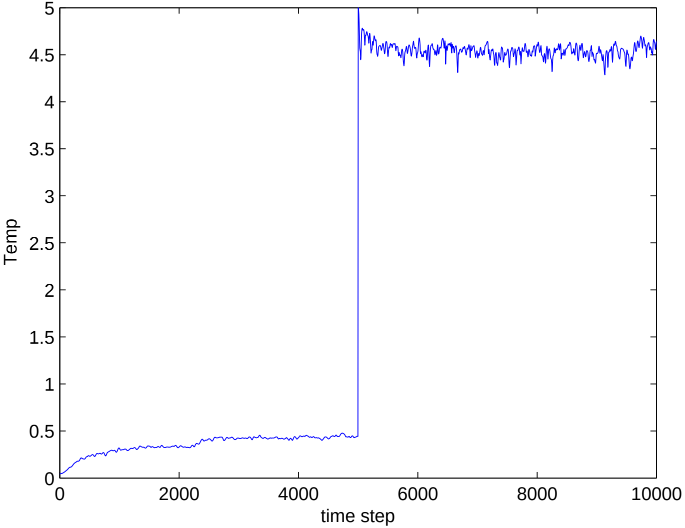
$$p^{n+1/2} = p^n - \tfrac{\Delta t}{2} \nabla V(q^n) - \tfrac{\Delta t}{2} \gamma(q^n) M^{-1} p^n + \sqrt{\tfrac{\Delta t}{2}} \sigma(q^n) G^n$$

$$q^{n+1} = q^n + \Delta t M^{-1} p^{n+1/2}$$

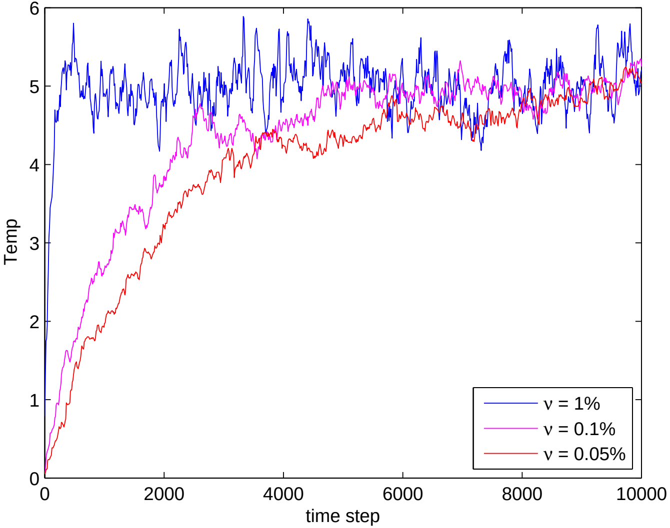
$$p^{n+1} = p^{n+1/2} - \frac{\Delta t}{2} \nabla V(q^{n+1}) - \frac{\Delta t}{2} \gamma(q^{n+1}) M^{-1} p^{n+1} + \sqrt{\frac{\Delta t}{2}} \sigma(q^{n+1}) G^{n+1}$$

  - γ chosen to be constant
  - $\sigma = \sqrt{2\gamma M k_B T}$
  - G sampled from a standard normal distribution

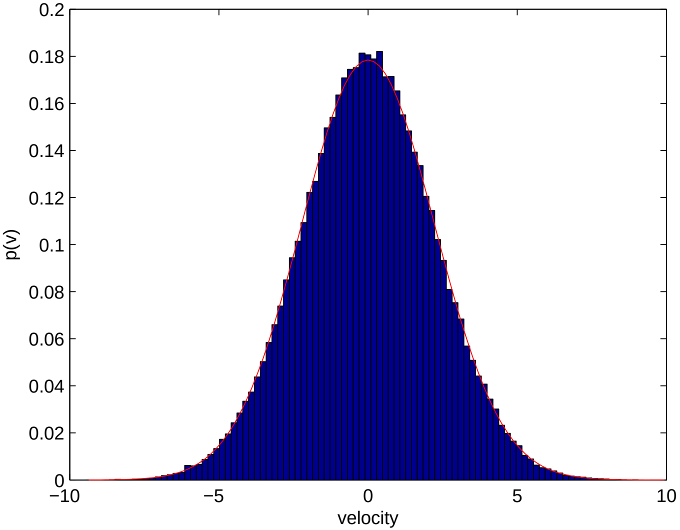
Velocity Rescaling - Instantaneous Temperature



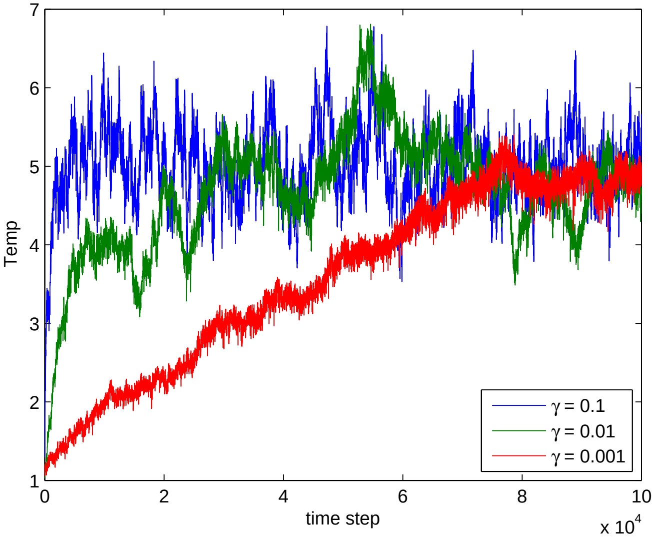
Anderson - Instantaneous Temperature



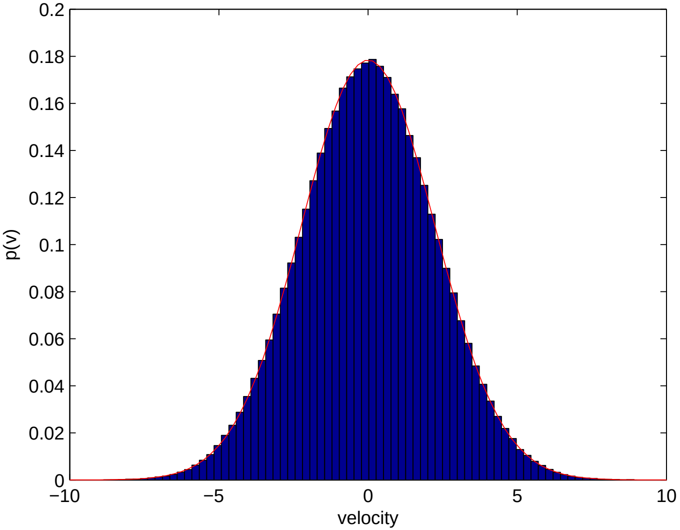
Anderson - Histogram of Velocity Distribution



Langevin Instantaneous Temperature



Langevin - Histogram of Velocity Distribution



References

Barsegov, Valeri (2007)
Different ensembles in molecular dynamics simulations
http://faculty.uml.edu/vbarsegov/teaching/bioinformatics/lectures/MDEnsemblesModified.pdf

Carloni, Paolo (2009)
Simulation of Biomolecules
http://www.grs-sim.de/cms/upload/Carloni/Presentations/Strodel3.pdf

Hunenberger, Philippe H. (2005)
Thermostat Algorithms for Molecular Dynamics Simulations
Adv. Polym. Sci. 173:105-149

Tuckerman, Mark E.(2010)
Statistical Mechanics: Theory and Molecular Simulation
Oxford Graduate Texts

Zhao, Yanxiang (2011)
Brief introduction to the thermostats
http://www.math.ucsd.edu/ y1zhao/ResearchNotes/ResearchNote007Thermostat.pdf