

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

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

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

- Derivation follows from maximizing entropy

Ergodic Hypothesis

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

$$\bar{f} = \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t f(x(s)) ds$$

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

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

Molecular Dynamics Simulation

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

$$\begin{cases} dq_t = \nabla_p H(q_t, p_t) dt \\ dp_t = -\nabla_q H(q_t, p_t) dt \end{cases}$$

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

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

- 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

- 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

- Disadvantages

- ▶ Extended system not guaranteed to be ergodic

- Advantages

- ▶ Easy to implement and use
 - ★ Implement as a chain
 - ★ Each link: apply thermostating to the previous thermostat variable
- ▶ Increasing Q lengthens decay time of response to instantaneous temperature jump
- ▶ Deterministic and time reversible

- 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

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

- 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

- 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 $\mathcal{N}(0, \sqrt{T})$

- Disadvantages

- ▶ Newtonian dynamics + stochastic collisions \rightarrow Markov chain
- ▶ Algorithm randomly decorrelates velocity: dynamics are not physical

- Advantages

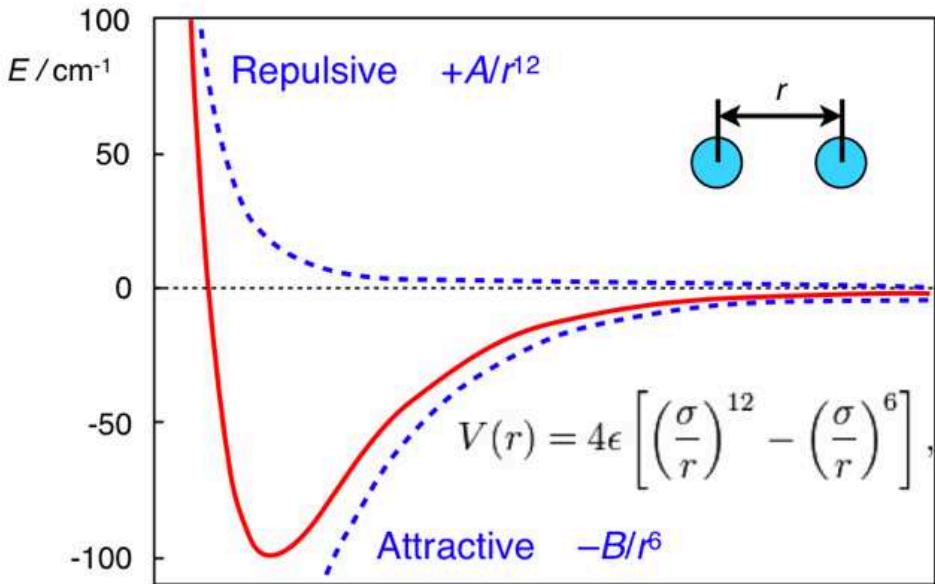
- ▶ Allows sampling from canonical ensemble

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

- 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



- 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

- ▶ $p_i \rightarrow \sqrt{\frac{T}{T_c}} p_i$

- Anderson

- ▶ $\nu = 1\%, 0.1\%, 0.05\%$

- ▶ Velocities are sampled from $\mathcal{N}(0, \sqrt{T})$

- Langevin

- ▶ BBK algorithm

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

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

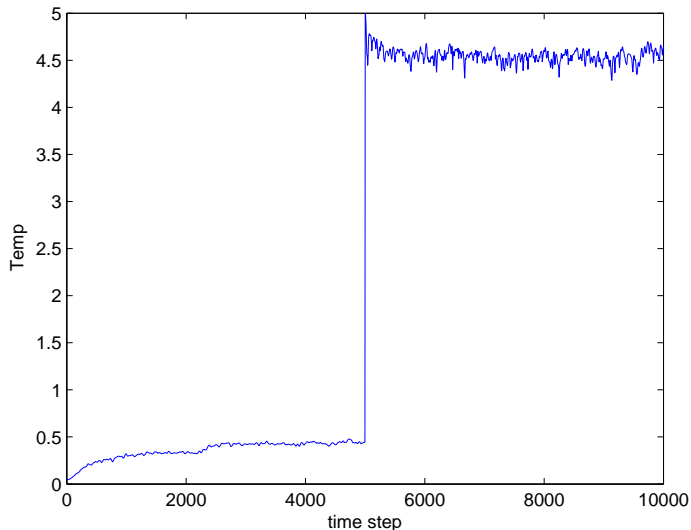
$$p^{n+1} = p^{n+1/2} - \frac{\Delta t}{2} \nabla V(q^{n+1}) - \frac{\Delta t}{2} \gamma(q^{n+1}) M^{-1} p^{n+1} + \sqrt{\frac{\Delta t}{2}} \sigma(q^{n+1}) G^{n+1}$$

- ▶ γ chosen to be constant

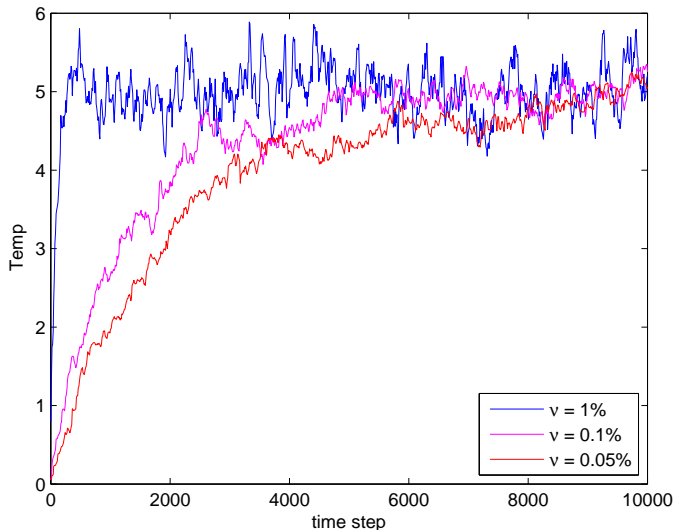
- ▶ $\sigma = \sqrt{2\gamma M k_B T}$

- ▶ G sampled from a standard normal distribution

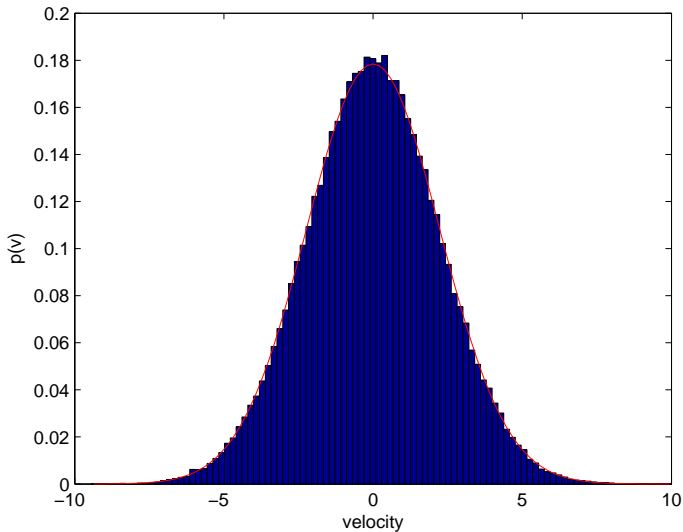
Velocity Rescaling - Instantaneous Temperature



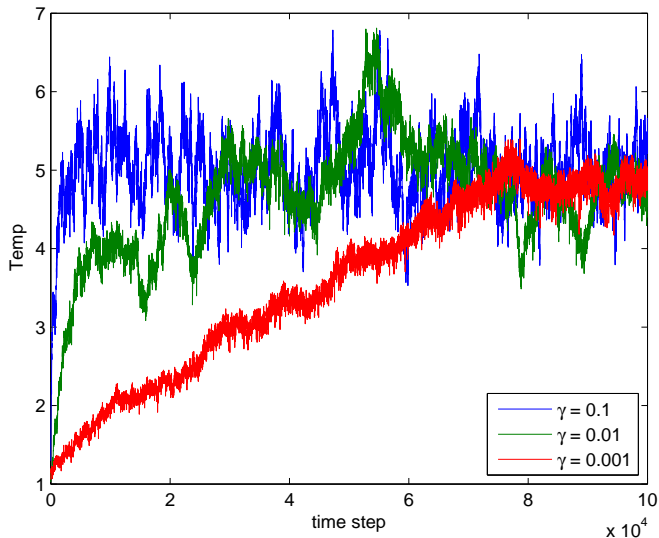
Anderson - Instantaneous Temperature



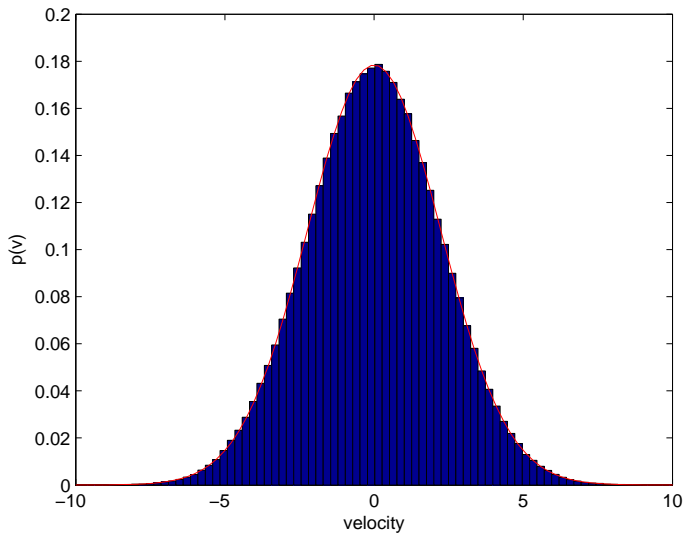
Anderson - Histogram of Velocity Distribution



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>