Thermostats in Molecular Dynamics Simulations

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December 6th, 2012
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.
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 $\langle f \rangle$.

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

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

where $\mu$ is the ensemble measure and $\Gamma$ is the phase space of the observable.
Phase space is collection of positions $q$ and momenta $p$ of particles in system

The Hamiltonian Form

\[
\begin{align*}
\frac{dq_t}{dt} &= \nabla_p H(q_t, p_t) dt \\
\frac{dp_t}{dt} &= -\nabla_q H(q_t, p_t) dt
\end{align*}
\]

\[
H(q, p) = E_{kin}(p) + V(q), \quad E_{kin}(p) = \frac{1}{2}p^T M^{-1}p
\]
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 → 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 \( q'_i = q_i \)
  - Momenta \( p'_i = p_i / s \)
  - Time \( t' = \int_0^t \frac{dt}{s} \)
  - \( s \): additional degree of freedom, acts as external system
Nosé-Hoover

- Hamiltonian given by

\[ H = \sum_{i=1}^{N} \frac{p_i^2}{2m_is^2} + V(q) + \frac{Q\dot{s}^2}{2} + (3N + 1)k_B T\ln s \]

- 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 thermostatting 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

\[ \frac{dq_i}{dt} = \frac{p_i}{m_i} \]

\[ \frac{dp_i}{dt} = -\frac{\delta V(q)}{\delta q_i} - \gamma p_i + \sigma G_i \]

- Viscous drag force proportional to velocity \(-\gamma p_i\)
- 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: $\gamma$ related to particle radius
  - Momentum transfer lost: cannot compute diffusion coefficients

- **Advantages**
  - Damping + random force $\rightarrow$ 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 $\nu$, 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

<table>
<thead>
<tr>
<th>Thermostat</th>
<th>Description</th>
<th>Canonical?</th>
<th>Stochastic?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Velocity Rescaling</td>
<td>KE fixed to match $T$</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Nosé-Hoover</td>
<td>extra degree of freedom acts as thermal reservoir</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>Langevin</td>
<td>noise and drag balance to give correct $T$</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>Andersen</td>
<td>momenta occasionally re-randomized</td>
<td>yes</td>
<td>yes</td>
</tr>
</tbody>
</table>
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

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

where \( r \) is the distance between the two particles, and \( \epsilon \) and \( \sigma \) are constants that define the energy and length scale, respectively. The potential is repulsive for small distances and attractive for large distances.
**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**
  \[ p_i \rightarrow \sqrt{\frac{T}{T_c}} p_i \]

- **Anderson**
  \[ \nu = 1\%, 0.1\%, 0.05\% \]
  Velocities are sampled from \( \mathcal{N}(0, \sqrt{T}) \)

- **Langevin**
  BBK algorithm
  \[
  p^{n+1/2} = p^n - \frac{\Delta t}{2} \nabla V(q^n) - \frac{\Delta t}{2} \gamma(q^n) M^{-1} p^n + \sqrt{\frac{\Delta t}{2}} \sigma(q^n) G^n
  \]
  \[
  q^{n+1} = q^n + \Delta t M^{-1} p^{n+1/2}
  \]
  \[
  p^{n+1} = p^{n+1/2} - \frac{\Delta t}{2} \nabla V(q^{n+1}) - \frac{\Delta t}{2} \gamma(q^{n+1}) M^{-1} p^{n+1} + \sqrt{\frac{\Delta t}{2}} \sigma(q^{n+1}) G^{n+1}
  \]

  - \( \gamma \) chosen to be constant
  - \( \sigma = \sqrt{2/\gamma M k_B T} \)
  - \( G \) sampled from a standard normal distribution
Velocity Rescaling - Instantaneous Temperature

![Graph showing velocity rescaling over time with temperature on the y-axis and time step on the x-axis.](chart.png)
Anderson - Instantaneous Temperature

![Graph showing instantaneous temperature over time steps with lines for different ν values: ν = 1%, ν = 0.1%, ν = 0.05%.](image)

- **ν = 1%**
- **ν = 0.1%**
- **ν = 0.05%**

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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

Thermostat Algorithms for Molecular Dynamics Simulations

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