Canonical ensemble, Thermostats

Lukáš Sukeník

March 13, 2017

Canonical ensemble

Ensemble in statistical mechanics

- Represents the possible states of a mechanical system
- In thermal equilibrium with a heat bath(fixed temperature)
- The system can exchange energy with the heat bath
  - The states of the system will differ in total energy
- Describe Boltzmann distribution

Principal variables

- Thermodynamic - absolute temperature (symbol: T)
  - Determine the probability distribution of states
- Mechanical - number of particles (N), system's volume (V)
  - Influence the nature of the system's internal states

Thermostats in Molecular dynamics

- Newton equations $\rightarrow$ NVE
- Reality $\rightarrow$ NpT
- In vast majority of system $\rightarrow$ little difference between NVT and NpT

Thermostats

- Modulate the temperature of a system
- Ensure that the average temperature of a system is the desired one
- For NVT - Couple the system to a heat bath that imposes desired T
- Deterministic:
    - Velocity rescale
    - Nose-Hoover
    - Berendsen
- Stochastic:
    - Langevin
    - Anderson

Anderson thermostat

- Coupling by stochastic collisions
  - Act periodically on a random particle
  - Instantaneous event
- Between stochastic collisions, system evolves in NVE

Simulation

- Select two parameters T and f
  - T - desired temperature of the system
  - f - frequency of stochastic collisions, strength of coupling to heat bath
- The simulations proceeds in NVE until a stochastic collision
- Particle suffering a "collision"
  - Given a random Momentum from a Boltzmann distribution at T
- repeat with frequency f

Anderson thermostat

Newtonian dynamics + stochastic collisions

- Turns MD simulation into a Markov process
- Canonical distribution in phase space is invariant under repeated collisions
- Anderson's algorithm generates canonical distribution
  - If Markov chain irreducible and aperiodic

Disadvantages

- Algorithm randomly decorrelates velocities
- Dynamics is not physical
  - Can't measure dynamical properties

Langevin thermostat

- Motion of large particles through a continuum of smaller particles
- Langevin equation $\ddot{r} = \nabla\phi - \gamma\dot{r} + \sigma\xi$
  - $\nabla\phi$ - force from positions of particles
    - similar term to $\frac{\partial V}{\partial q_i}$
  - damping force $\gamma\dot{r}$
  - $\sigma\xi$ - Random force
    - The smaller particles move with kinetic energy
    - Give random nudges to large particles
    - Fluctuation-dissipation relation $\sigma^2 = 2\gamma m_i k_B T$
    - To recover the canonical ensemble distribution

Langevin thermostat

- Use Langevin equation
- Assume that atoms being simulated are embedded in a sea of much smaller fictional particles
- Instances of solute-solvent systems
  - Solute is desired
  - Solvent is non-interesting
  - Solvent influences Solute via random collisions and a frictional force

Langevin thermostat

Langevin thermostat

- At each time step Δt the Langevin thermostat changes the equation of motion so that the change in momenta is
  - $\Delta p_i = (\frac{\partial \phi(q)}{\partial q_i} - \gamma p_i + \delta p)\Delta t$
    - γp_i - damp the momenta
    - δp - Gaussian distributed random number represents the thermal kicks from the small particles

Langevin thermostat

Advantages

- Fewer computations per time step since we eliminate many atoms
  - Include them implicitly by stochastic terms
- Relatively large time step
  - Δt - different fastest frequency motions, slower degree of freedom

Disadvantages

- Excluded volume effects of solvent not included
- Not trivial to implement drag force for non-spherical particles
- Solute-solvent system, solvent molecules must be small compared to the smallest molecules explicitly considered

Berendsen thermostat

Main problem of velocity-rescaling method

- Does NOT allow T fluctuations as in NVT

Berendsen thermostat

- Weak coupling method to external heat bath
- Corrects deviations of actual T to T_0 by multiplying the velocities by a factor λ
- Allows the temperature fluctuations
- Tries to minimize local disturbances (like stochastic thermostat does) while keeping the global effects unchanged

Proportional time-rescaling

- Velocities scaled at each time step
- Rate of change of T is proportional to the difference in temperature

Berendsen thermostat

Proportional time-rescaling

- $\frac{dT}{dt} = \frac{1}{\tau}(T_0 - T)$
    - τ coupling parameter
    - Exponential decay of the system towards the desired temperature
- This lead to a modification of the momenta $p_i \rightarrow \lambda p_i$
    - Rescaling parameter λ
    - $\lambda^2 = 1 + \frac{\Delta t}{\tau_T}(\frac{T_0}{T} - 1)$
    - Note: Velocity rescale $\lambda^2 = \frac{T_0}{T}$

Drawbacks

- Cannot be mapped onto a specific thermodynamic ensemble
- Interpolation between the canonical and microcanonical ensemble
    - $\Delta t = \tau_T$, fluctuations of E_{kin} vanish and phase space distribution reduces to NVT
    - $\tau_T \rightarrow \infty$, corresponds to an isolated system (NVE)

Nose-hoover thermostat

Idea

- Simulate a system which in the NVT ensemble
- Introduce a fictitious dynamical variable = friction
- Friction slows down or accelerates particles
- Measure kinetic energy and energy given by bipartition theorem
  - $\frac{1}{2}K_B T$ per degree of freedom
- Scale velocities of particles so that we have desired T
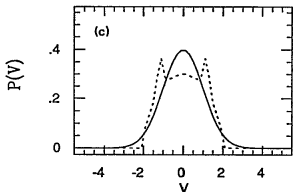
Nose-hoover thermostat

Varibles

- r_i, - positions
- $v_i = \dot{r}_i = \frac{dr_i}{dt}$, - velocities
- $p_i = m_i \cdot r_i$, - momentum
- $\dot{p}_i = m_i \dot{v}_i = m_i a_i$, - force

Dynamical equations

- $\dot{r}_i = \frac{p_i}{m_i}$
- $\dot{p}_i = f_i - p_i \cdot \zeta(t)$
  - $f_i = -\frac{\partial V(q)}{\partial q_i}$
  - ζ physical meaning friction, changes with time
- $\dot{\zeta} = \frac{1}{Q} \left[\sum_{i=1}^{N} m_i \cdot \frac{v_i^2}{2} - \frac{3N+1}{2} k_B T \right]$
  - Q determines the relaxation of the dynamics of the friction, heat-bath mass, large Q denotes weak coupling
 - T denotes the target temperature
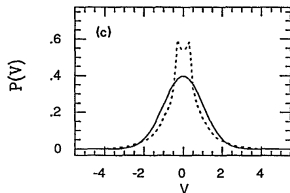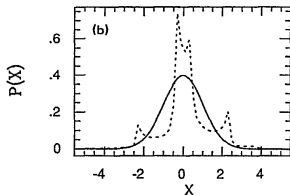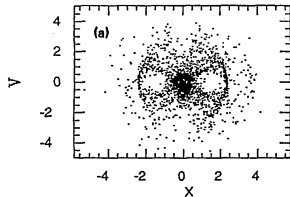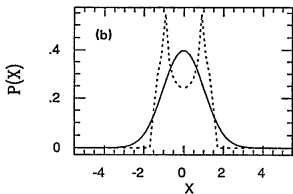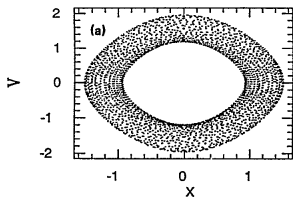
Nose-hoover thermostat Wrong behavior - Solution

- Need invariant probability distribution

Nose-Hoover chain method

- $\dot{p}_i = f_i - p_i \cdot \zeta_1(t)$
- $\dot{\zeta}_1 = \frac{1}{Q_1} \left[\sum_{i=1}^{N} m_i \cdot \frac{v_i^2}{2} - \frac{3N+1}{2} k_B T \right] + p_2 \zeta_2$
- $\dot{\zeta}_j = \frac{1}{Q_j} \left[Q_{j-1} \zeta_{j-1}^2 - \frac{1}{2} k_B T \right] + p_{j+1} \zeta_{j+1}$
- Thermostat masses affect dynamics in achieving canonical distribution
  - Large masses - microcanonical distribution (NVE)
  - Small masses - fluctuations of the momenta greatly inhibited
  - $Q_1 = \frac{3N+1}{2} k_B T / \omega^2$
  - $Q_j = \frac{1}{2} k_B T / \omega^2$
  - Allows the thermostats to be in approximate resonance with both the system variables, which are assumed to have fundamental frequency ω, and each other
  - Mass choice in chain method less critical than in single metllod

Harmonic oscilator, $r(0) = 0, p(0) = 1, \frac{\zeta}{Q}(0) = 1$
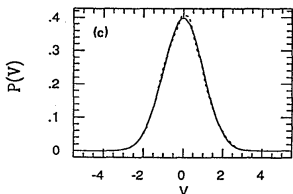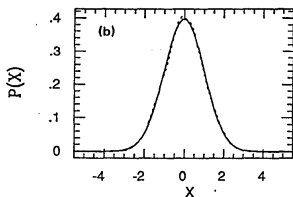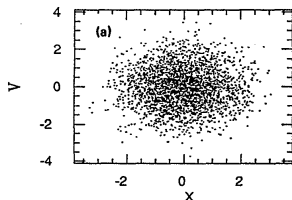
- Chain dynamics (M=2)
- Distribution good approximation to NVT
- Dynamics fills phase space
- Changes in the initial conditions dont have an appreciable effect on the results
- Choice of thermostat mass is not critical

The Lyapunov exponent

The Lyapunov exponent

- Measure of the degree of chaos present in a dynamical system
- More chaotic the dynamics of a system $\rightarrow$ the more quickly it fills phase space

Calculation

- Systems containing M = 1-15 thermostats
- Wide variety of initial conditions (Q= 1)

Lyapunov exponent of harmonic oscillator as a function of the number of thermostats, Q=1

Nose-hoover thermostat - Conclusion
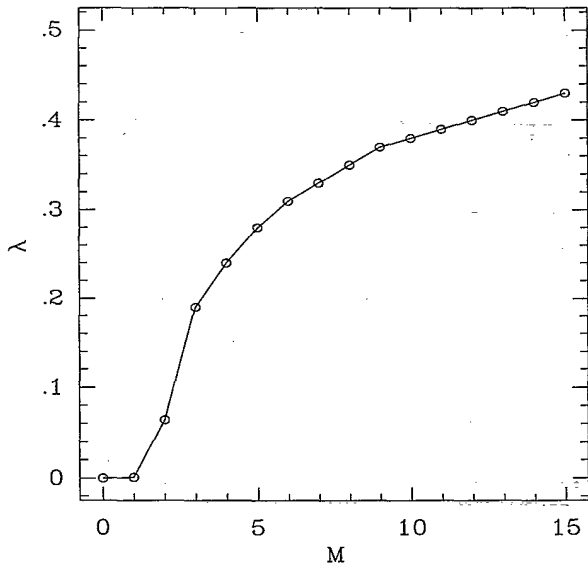
Thermostating the extended variable

- Stiff complex systems (proteins)
  - Difficult to start near equilibrium
  - Large unphysical oscillations in T may develop
  - Additional thermostats will effectively damp such oscillations
  - More stable simulations

Summary

- Very good approximation to the canonical ensemble even in pathological cases
- Wide application

Thermostat Artifacts in Replica Exchange Molecular Dynamics Simulations

Replica exchange molecular dynamics (REMD) simulations

- Enhance the conformational sampling of molecular dynamics
- Several "replicas" simulated in parallel at different T
- At regular intervals - attempts to exchange replicas to increase conformational sampling efficiency at lower T
- After accepted exchange - Particle velocities:
  - Reassigned from a Maxwell-Boltzmann distribution at T
  - Old velocities are scaled $(T_1/T_2)^{(\frac{1}{2})}$ and vice versa
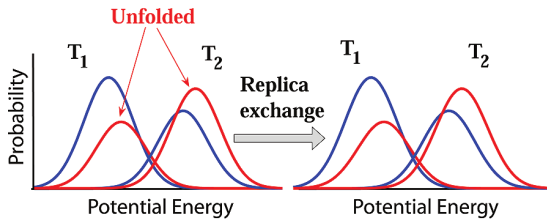
REMD

Berendsen Thermostat

- Dont produce correct NVT
- Detailed balance condition of replica exchange is not satisfied

Protein folding in water

- Helix-forming peptide with a weak-coupling Berendsen thermostat
- Conformational equilibrium is altered
    - Folded state is overpopulated by about 10 % at low T
    - Underpopulated at high T
    - Enthalpy of folding deviates by almost 3 kcal/mol
- Non-canonical ensembles with narrowed potential energy fluctuations
    - Artificially bias toward replica exchanges between low-energy folded structures at high T and high-energy unfolded structures at low T

Folding probabilities
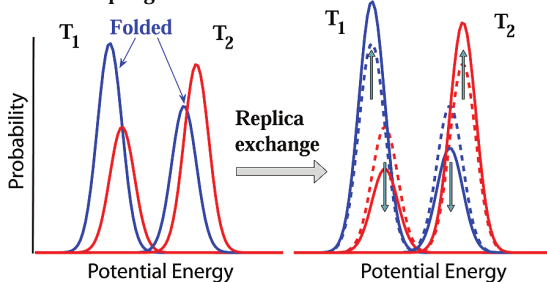
REMD

Folding probabilities

- For NVT REMD does not affect folding populations
- Berendsen - REMD alters the relative populations
    - Folded states become overpopulated at low T
    - Underpopulated at high T

Replica exchange molecular dynamics (REMD) simulations

- Thermostats producing incorrect canonical ensemble
- REMD distort the configuration-space distributions
- For REMD use only thermostats correctly representing NVT

Simple Quantitative Tests to Validate Sampling from Thermodynamic Ensembles

- Some aspects of molecular distributions can be checked directly

NVE

- Total energy is conserved with statistically zero drift

NVT

- Potential energy independent on particle momenta (except in systems with magnetic forces)
- Kinetic energy will follow the Maxwell–Boltzmann distribution
  - Consistency of distribution, estimated using standard statistical methods
- Average kinetic energy corresponding to the desired T

NPT

- Proper average instantaneous pressure computed from the virial and kinetic energy

- Proper distribution for the potential energy
- Proper distribution for total energy of an arbitrary simulation system
- Many possible distributions which have the correct average temperature or pressure but do not satisfy the proper Boltzmann probability distributions for our specific ensemble of interest

Basis of the ensemble validation techniques

- Thermodynamic ensembles all have similar probability distributions with respect to macroscopic intensive parameters and microstates
  - $P(\vec{x}|\beta) \propto exp(\beta H(\vec{p}, \vec{r}))$ canonical
    - where $P(x|y)$ indicates the probability of a microstate determined by variable(s) x given a macroscopic parameter(s) y
- The probability density of observing a specific energy in the canonical ensemble
  - $P(E|\beta) = Q(\beta)^{-1}\Omega(E)exp(-\beta E)$
    - $\Omega(E)$ density of states, Q canonical partition function
- No knowledge of $\Omega(E)$ distribution, cant identify proper distribution
  - Ratio of distributions from two simulations performed at different T
    - Two different β, other parameters the same
    - Unknown $\Omega(E)$ cancels
  - $ln\frac{P(E|\beta_1)}{P(E|\beta_2)} = [\beta_2 A_2 - \beta_1 A_1] - [\beta_2 - \beta_1] E$
    - which is of the linear form $\alpha_0 + \alpha_1 E$. Note that linear coefficient $\alpha_1 = -[\beta_2 - \beta_1]$ is independent of the (unknown in general) Helmholtz free energies A_2 and A_1.
    - Helmholtz free energy $A = -\beta^{-1}lnQ$

General and easy

- Can be derived for any of the standard thermodynamic ensembles
- Require only energy(NVT), volume(NpT) and particle numbers(μVT)

NVT

- Bin Total energies
- Distributions must be sufficiently close together
    - Statistically well-defined probabilities at overlapping values of E
- Fit the ratio of the histogram probabilities to a line in overlap region
    - Slope deviates from $-(\beta_2 - \beta_1) \rightarrow$ not canonical distribution

Shortcomings

- Necessary test for canonical distribution
- Not sufficient - not a direct test of ergodicity
- No info whether states of same energy sampled with equal probability
- No info whether there are states that are not sampled
- Can be trapped in a portion of allowed phase space
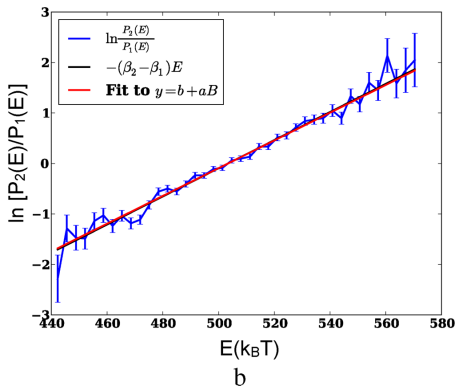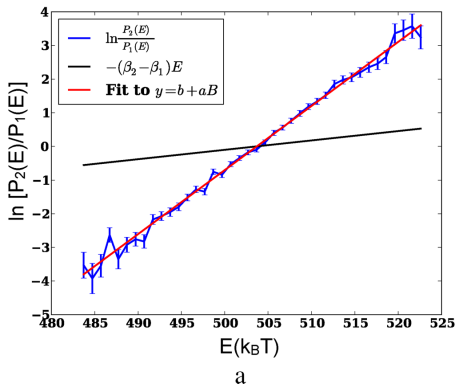- Additional tests of convergence or ergodicity required

a

b
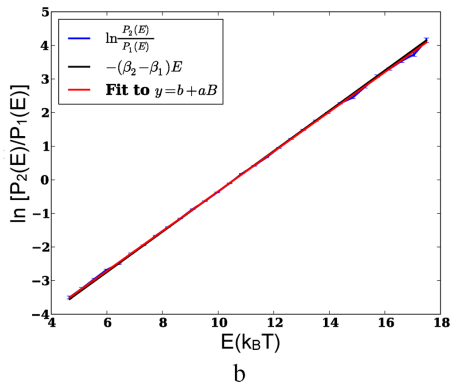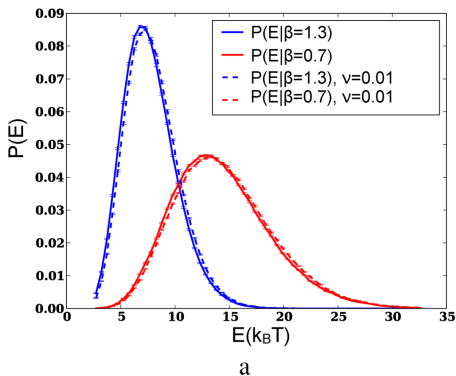
Ensemble validation of water simulations
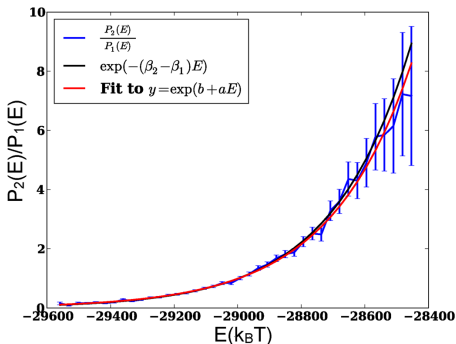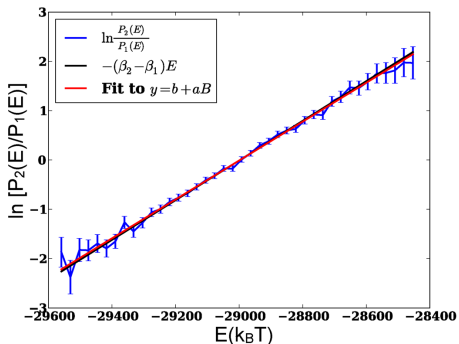
- 900 TIP3P water molecules in NVT
- Nosé – Hoover algorithm

Lennard-Jones system

a

b

- a - Berendsen thermostat
  - Slope of energy ratios 7 times higher than expected
  - Low β (high T) simulation over-samples that particular kinetic energy
  - Incorrect, overly narrow kinetic energy distribution
- b - Nosé – Hoover thermostat

Conclusion

Validity checks

- Molecular distributions characterized by Boltzmann distributions
- Easily check for consistency with the intended ensemble
- Robust and general method
    - Regardless of the details of a simulation
    - Require only 2 simulations with differing external parameters such as T, p or μ
        - Cancel out system-dependent properties(densities of states)
        - Result in linear relationship between the distributions of extensive quantities (energy, volume, enthalpy and number of particles)
        - Slope of the relationship completely determined by the intensive variables set by user
- Necessary, but not sufficient condition
    - Ergodicity
    - Full sampling of phase space

The End