



MD at constant T

MD at constant temperature

- In an experiment, constant temperature T means thermal equilibrium with a reservoir at T .
- In the canonical ensemble the system is also in thermal equilibrium with a bath at T .
- However thermal equilibrium doesn't mean constant temperature!
- The instantaneous temperature of a system is related to the kinetic energy, and KE fluctuates

$$kT = m\langle v_u^2 \rangle$$

In equilibrium, the momenta are distributed according to Boltzman statistics:

$$P(p) \sim (\beta / 2\pi m)^{3/2} \exp\{-\beta p^2 / 2m\}$$

With this distribution

$$\langle p^2 \rangle = 3mkT$$

$$\langle p^4 \rangle = 15 (mkT)^2$$

$$\sigma_T^2 / \langle T \rangle^2 = 2 / (3N)$$

- In a canonical ensemble of a finite system, the instantaneous kinetic temperature T_k fluctuates.

- In fact, if we were to keep the average kinetic energy per particle rigorously constant, as is done in the so-called isokinetic MD scheme or velocity-scaling schemes, then we would NOT simulate the true constant-temperature ensemble.

- **In practice**, the difference between isokinetic and canonical schemes is often negligible.

- Problems can be expected if isokinetic simulations are used to measure equilibrium averages that are sensitive to fluctuations .

- Any kind of temperature regulation can be used while preparing the system at a desired temperature (i.e., during **equilibration**).

MD in a Canonical Ensemble: The Andersen Thermostat

- The system is coupled to a heat bath that imposes the desired temperature.
- The coupling to a heat bath is represented by stochastic impulsive forces that act occasionally on randomly selected particles.
- These stochastic collisions with the heat bath can be considered as Monte Carlo moves that transport the system from one constant-energy shell to another.

- Between stochastic collisions, the system evolves at constant energy according to the normal Newtonian laws of motion (MD).
- The stochastic collisions ensure that all accessible constant-energy shells are visited according to their Boltzmann weight.
- Before starting such a constant-temperature simulation, we should first select the strength of the coupling to the heat bath.
- This coupling strength is determined by the frequency of stochastic collisions: ν

A constant-temperature simulation now consists of the following steps:

1. Start with an initial set of positions and momenta $\{r^N(0), p^N(0)\}$ and integrate the equations of motion for a time Δt .
2. A number of particles are selected to undergo a collision with the heat bath. The probability that a particle is selected in a time step of length Δt is $\nu \Delta t$.
3. If particle i has been selected to undergo a collision, its new velocity will be drawn from a Maxwell-Boltzmann distribution corresponding to the desired temperature T . All other particles are unaffected by this collision.

The mixing of Newtonian dynamics with stochastic collisions turns the Molecular Dynamics simulation into a Markov process

The Andersen algorithm does, indeed, generate a canonical distribution.

Implementation:

In subroutine SOLVE:

```
sigma=sqrt(temp)
do i=1,npart
  if(ranf.lt.nu*dt) then
    v(i)=gauss(sigma)
  endif
enddo
```

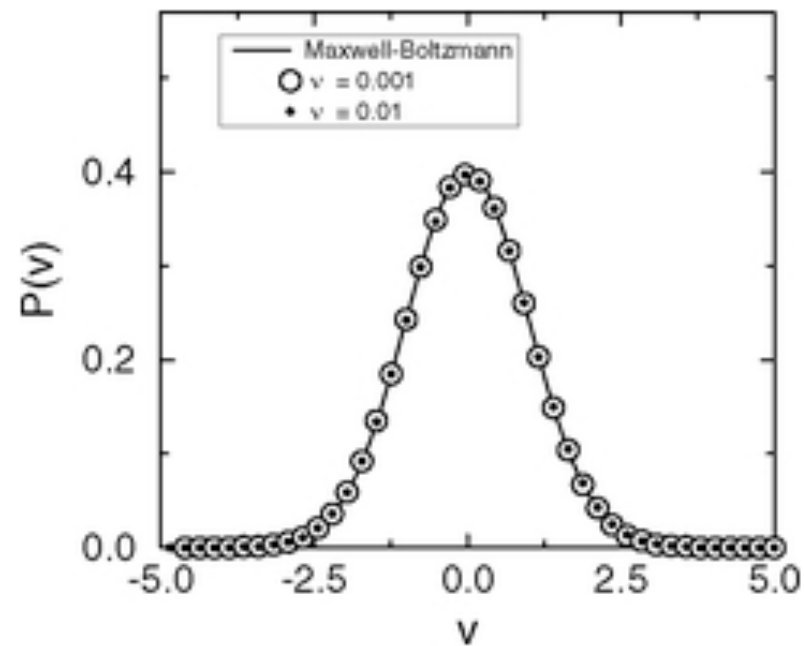
nu is a parameter (the frequency of collisions)

The results should be independent of the value of nu.

$$P(v) \sim (1/2\pi T)^{3/2} \exp\{-v^2/2T\}$$

$$\sigma^2 = T$$

Distribution of velocities obtained with Andersen Thermostat



Andersen method is NOT deterministic, but STOCHASTIC.

- The Andersen thermostat yields good results for time-independent properties, such as the equation of state.
- However, as the method is based on a stochastic scheme, is not good for dynamic properties, such as the diffusion coefficient.
- The stochastic collisions disturb the dynamics in a way that is not realistic—it leads to sudden random decorrelation of particle velocities.
- This effect will result in an enhanced decay of the velocity autocorrelation function, and hence the diffusion constant
- Clearly this effect will be more pronounced as the collision frequency ν is increased.

MD NVT: Nose-Hoover thermostat

Extended Lagrangian for the original system S + one additional coordinate s

$$Lagrangian(r_i, \dot{r}_i, s, \dot{s}) = \sum (m/2) \dot{r}_i^2 - U(r^{3N}) + (Q/2) \dot{s}^2 - (L/\beta) \ln s$$

- s is the coordinate of an extra particle representing the “heat bath”
- Q is a coupling constant, (~the mass of the extra particle)
- The system S can now exchange energy with the extra particle
- The total energy of the extended system is constant
- L is a constant

Extra degree of freedom: s, p_s

$$\mathcal{L}_{\text{Nose}} = \sum_{i=1}^N \frac{m_i}{2} s^2 \dot{\mathbf{r}}_i^2 - \mathcal{U}(\mathbf{r}^N) + \frac{Q}{2} \dot{s}^2 - \frac{L}{\beta} \ln s,$$

L : parameter

Q : effective “mass” of the extra particle

momenta:

$$p_i = \frac{\partial L}{\partial \dot{r}_i} = m_i s^2 \dot{r}_i$$
$$p_s = \frac{\partial L}{\partial \dot{s}} = Q \dot{s}$$

$$\mathcal{H}_{\text{Nose}} = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i s^2} + \mathcal{U}(\mathbf{r}^N) + \frac{p_s^2}{2Q} + L \frac{\ln s}{\beta}.$$

$$\begin{aligned} Q_{\text{Nose}} &= \frac{1}{N!} \int d\mathbf{p}_s d\mathbf{p}'^N d\mathbf{r}^N ds \frac{\beta s^{3N+1}}{L} \\ &\quad \times \delta \left\{ s - \exp \left[-\beta \frac{\mathcal{H}(\mathbf{p}', \mathbf{r}) + p_s^2/(2Q) - E}{L} \right] \right\} \\ &= \frac{1}{N!} \frac{\beta \exp[E(3N+1)/L]}{L} \int d\mathbf{p}_s \exp \left[-\beta \frac{3N+1}{L} p_s^2/(2Q) \right] \\ &\quad \times \int d\mathbf{p}'^N d\mathbf{r}^N \exp \left[-\beta \frac{3N+1}{L} \mathcal{H}(\mathbf{p}', \mathbf{r}) \right] \end{aligned}$$

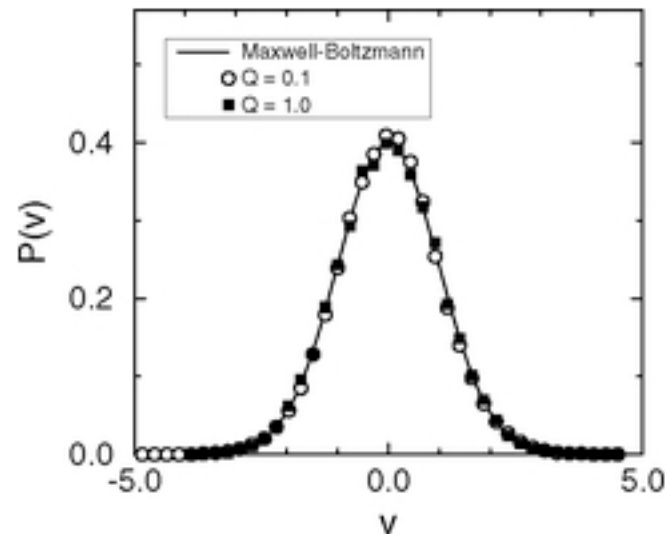
partition function \rightarrow
$$= C \frac{1}{N!} \int d\mathbf{p}'^N d\mathbf{r}^N \exp \left[-\beta \frac{3N+1}{L} \mathcal{H}(\mathbf{p}', \mathbf{r}) \right].$$

With the choice $L = 3N + 1$, this ensemble reduces to the **canonical ensemble**

The Hamiltonian derived from this Lagrangian generates a canonical ensemble for the system S:

$$Z_{\text{Nose}} = \text{constants} \times Z_S(\text{NVT})$$

Distribution of velocities obtained by MD_{Nose-Hoover}



After 12,000 time steps the imposed temperature is suddenly increased from $T = 1$ to $T = 1.5$.

A small value of Q corresponds to a low inertia of the heat bath and leads to rapid temperature fluctuations.

A large value of Q leads to a slow response to the temperature jump.

