Berendsen and Nose-Hoover thermostats

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Abstract

This is just a brief summary about the Berendsen and Nose-Hoover thermostats which is far away from being complete. For a more detailed description see e.g. [1].

1 Temperature in MD

The instantaneous value of the temperature is related to the kinetic energy via the particles' momenta as follows:

$$\sum_{i=1}^{N} \frac{|\mathbf{p}_i|^2}{2m_i} = \frac{k_b T}{2} \left(3N - N_c \right) \tag{1}$$

where N_c is the number of constraints and so $3N - N_c = N_{df}$ is the total number of degrees of freedom. The average temperature $\langle T \rangle$ is identical to the macroscopic Temperature.

The standard MD is performed in the microcanonical (NVE) ensemble. Additionally, the linear momentum $\mathbf{p}$ as well as the angular momentum $\mathbf{L}$ are conserved. When using periodic boundary conditions , the angular momentum is **not** conserved!

2 MD at constant Temperature - NVT ensemble

2.1 Velocity scaling

Unfortunately, the microcanonical ensemble does not correspond to the conditions under which most experiments are carried out. If one is interested in the behavior of the system at a specific temperature, a NVT simulation using a thermostat is required. Another reason to simulate using a thermostat is to avoid steady energy drifts caused by the accumulation of numerical errors during MD simulations.

An obvious way to alter the temperature of the system is velocity scaling. If the temperature at time t is $T(t)$ and the velocities are multiplied by a factor λ, then the associated temperature change can be calculated as

$$\Delta T = \frac{1}{2} \sum_{i=1} 2 \frac{m_i \left(\lambda v_i \right)^2}{N_{df} k_B} - \frac{1}{2} \sum_{i=1} 2 \frac{m_i v_i^2}{N_{df} k_B} \tag{2}$$

$$\Delta T = \left(\lambda^2 - 1 \right) T(t) \tag{3}$$

$$\lambda = \sqrt{T_0 / T(t)} \tag{4}$$

The simplest way to control the temperature is thus to multiply the velocities at each time step by the factor $\lambda = \sqrt{T_0 / T(t)}$, where $T(t)$ is the current temperature as calculated from the kinetic energy and T_0 is the desired temperature. One problem with this approach is, that it does not allow fluctuations in temperature which are present in the canonical ensemble.

2.2 Berendsen temperature coupling

A weaker formulation of this approach is the **Berendsen thermostat**. To maintain the temperature the system is coupled to an external heat bath with fixed Temperature T_0. The velocities are scaled at each step, such that the rate of change of temperature is proportional to the difference in temperature:

$$\frac{dT(t)}{dt} = \frac{1}{\tau}\left(T_0 - T(t)\right) \tag{5}$$

where τ is the coupling parameter which determines how tightly the bath and the system are coupled together. This method gives an exponential decay of the system towards the desired temperature. The change in temperature between successive time steps is:

$$\Delta T = \frac{\delta t}{\tau}\left(T_0 - T(t)\right). \tag{6}$$

Thus, the scaling factor for the velocities is

$$\lambda^2 = 1 + \frac{\delta t}{\tau}\left\{\frac{T_0}{T(t - \frac{\delta t}{2})} - 1\right\}. \tag{7}$$

The $T(t - \frac{\delta t}{2})$ is due to the fact that the called leap-frog algorithm is used for the time integration. In practice, τ is used as an empirical parameter to adjust the strength of the coupling. Its value has to be chosen with care. In the limit $\tau \to \infty$ the Berendsen thermostat is inactive and the run is sampling a microcanonical ensemble. The temperature fluctuations will grow until they reach the appropriate value of a microcanonical ensemble. However, they will never reach the appropriate value for a canonical ensemble. On the other hand, too small values of τ will cause unrealistically low temperature fluctuations. If τ is chosen the same as the timestep δt, the Berendsen thermostat is nothing else than the simple velocity scaling. Values of $\tau \approx 0.1ps$ are typically used in MD simulations of condensed-phase systems. The ensemble generated when using the Berendsen thermostat is not a canonical ensemble!

2.3 Nose-Hoover temperature coupling

The Berendsen thermostat is extremely efficient for relaxing a system to the target temperature, but once your system has reached equilibrium, it might be more important to probe a correct canonical ensemble.

The extended system method was originally introduced by Nose and subsequently developed by Hoover. The idea is to consider the heat bath as an integral part of the system by addition of an artificial variable $\tilde{s}$, associated with a "mass" $Q > 0$ as well as a velocity $\dot{\tilde{s}}$. The magnitude of Q determines the coupling between the reservoir and the real system an so influences the temperature fluctuations. The artificial variable $\tilde{s}$ plays the role of a time-scaling parameter, more precisely, the timescale in the extended system is stretched by the factor $\tilde{s}$

$$d\tilde{t} = \tilde{s}dt \tag{8}$$

The atomic coordinates are identical in both systems. This leads to

$$\tilde{\mathbf{r}} = \mathbf{r}\,,\ \dot{\tilde{\mathbf{r}}} = \tilde{s}^{-1}\dot{\mathbf{r}}\,,\ \tilde{s} = s\,\text{and}\,\dot{\tilde{s}} = \tilde{s}^{-1}\dot{s} \tag{9}$$

The Lagrangian for the extended system is chosen to be

$$\mathcal{L} = \sum_i \frac{m_i}{2}\tilde{s}^2\dot{\tilde{\mathbf{r}}}_i^2 - U(\tilde{\mathbf{r}}) + \frac{1}{2}Q\dot{\tilde{s}}^2 - gk_bT_0\ln\tilde{s} \tag{10}$$

The first two terms of the Lagrangian represent the kinetic energy minus the potential energy of the real system. The additional terms are the kinetic energy of $\tilde{s}$ and the potential, which is

chosen to ensure that the algorithm produces a canonical ensemble where $g = N_{df}$ in real-time sampling (Nose-Hoover formalism) and $g = N_{df} + 1$ for virtual-time sampling (Nose-formalism). This leads to the Nose equations of motion

$$\ddot{\tilde{\mathbf{r}}}_i = \frac{\tilde{\mathbf{F}}_i}{m_i \tilde{s}^2} - \frac{2\dot{\tilde{s}}\dot{\tilde{\mathbf{r}}}_i}{\tilde{s}}, \tag{11}$$

$$\ddot{\tilde{s}} = \frac{1}{Q\tilde{s}} \left(\sum_i m_i \tilde{s}^2 \dot{\tilde{\mathbf{r}}}_i^2 - gk_b T_0 \right). \tag{12}$$

These equations sample a microcanonical ensemble in the extended system $(\tilde{\mathbf{r}}, \tilde{\mathbf{p}}, \tilde{\mathbf{t}})$. However, the energy of the real system is not constant. Accompanying the fluctuations of $\tilde{s}$, heat transfers occur between the system and a heat bath, which regulate the system temperature. It can be shown, that the equations of motion sample a canonical ensemble in the real system.

The Nose equations of motion are smooth, deterministic and time-reversible. However, because the time-evolution of the variable $\tilde{s}$ is described by a second-order equation, heat may flow in and out of the system in an oscillatory fashion, leading to nearly periodic temperature fluctuations.

The stretched timescale of the Nose equations is not very intuitive and the sampling of a trajectory at uneven time intervals is rather impractical for the investigation of dynamical properties of a system. However, as shown by Nose and Hoover, the Nose equations of motion can be reformulated in terms of real system variables. The transformation is achieved through

$$s = \tilde{s}, \ \dot{s} = \tilde{s}\dot{\tilde{s}}, \ \ddot{s} = \tilde{s}^2\ddot{\tilde{s}} + \tilde{s}\dot{\tilde{s}}^2,$$
$$\mathbf{r} = \tilde{\mathbf{r}}, \ \dot{\mathbf{r}} = \tilde{s}\dot{\tilde{\mathbf{r}}}, \ \ddot{\mathbf{r}} = \tilde{s}^2\ddot{\tilde{\mathbf{r}}} + \tilde{s}\dot{\tilde{\mathbf{r}}}^2 \tag{13}$$

and with substituting

$$\gamma = \frac{\dot{s}}{s} \tag{14}$$

the Lagrangian equations of motion can be written as

$$\ddot{\mathbf{r}}_i = \frac{\mathbf{F}_i}{m_i} - \gamma \mathbf{r}_i, \tag{15}$$

$$\dot{\gamma} = \frac{-k_B N_{df}}{Q} T(t) \left(\frac{g}{N_{df}} \frac{T_0}{T(t)} - 1 \right). \tag{16}$$

In both algorithms, some care must be taken in the choice of the fictious mass Q and extended-system energy E_e. On the one hand, too large values of Q (loose coupling) may cause a poor temperature control (Nose-Hoover thermostat with $Q \to \infty$ is MD which generates a microcanonical ensemble). Although any finite (positive) mass is sufficient to guarantee in principle the generation of a canonical ensemble, if Q is too large, the canonical distribution will only be obtained after very long simulation times. On the other hand, too small values (tight coupling) may cause high-frequency temperature oscillations. The variable $\tilde{s}$ may oscillate at a very high frequency, it will tend to be off-resonance with the charactersistic frequencies of the real system, and effectively decouple from the physical degrees of freedom (slow exchange of kinetic energy).

As a more intuitive choice for the coupling strength, the Nose equations of motion can be expressed as

$$\dot{\gamma} = -\frac{1}{\tau_{NH}} \left(\frac{g}{N_{df}} \frac{T_0}{T(t)} - 1 \right) \tag{17}$$

with the effective relaxation time

$$\tau_{NH}^2 = \frac{Q}{N_{df} k_B T_0}. \tag{18}$$

The relaxation time can can be estimated when calculating the frequency of the oscillations for small deviations $\delta\tilde{s}$ from the average $\langle \tilde{s} \rangle$.

3

3   Remarcs

One problem is encountered when simulating molecular systems involving distinct sets of degrees of freedom with either (i) very different characteristic frequencies of (ii) very different heating rates caused by algorithmic noise. In this case, the joint coupling of all degrees of freedom to a thermostat may lead to different effective temperatures for the distinct subsets of degrees of freedom, due to a too slow exchange of kinetic energy between them. A typical example is the so-called "hot solvent - cold solute problem" in simulations of macromolecules. Because the solvent is significantly affected by algorithmic noise (e.g. due to the use of an electrostatic cutoff), the coupling of the whole system to a single thermostat may cause the average solute temperature to be significantly lower than the average solvent temperature. A solution to this problem is to couple separately the solute and solvent degrees of freedom to two different thermostats.

A second problem is encountered when using a simulation program that (incorrectly) applies the thermostatization directly to the atomic velocities rather than to the internal velocities. In this case, the system linear and angular momenta are not conserved, unless they exactly vanish. However, even if these quantities are set to zero, numerical errors alter these initial values. It may appear, that a termostat pumps kinetic energy from high frequencies to low-frequency degrees of freedom which leads to the "flying ice cube effect".

A good way to do a simulation in the NVT ensemble is first to do the equilibration with the Berendsen thermostat at a small value of τ (e.g. $\tau = 0.01 fs$). After the system is equilibrated, τ should be increased to get a good equilibrium run (see gromacs manual). If a real canonical ensemble with correct fluctuations is needed, the Nose-Hoover thermostat must be used.

References

[1] P.H. Hünenberger, Thermostat algorithms for molecular dynamics simulations, Adv. Polymer. Sci., 173, 105-149 (2005).