

10 Controlling temperature

Many real systems are not even close to isolated. They exchange heat with their surroundings. And even with NVE simulations, usually some certain temperature is wished. At infinite size limit thermodynamic properties can be transformed from ensemble to another

- Thermodynamic limit
- For thermodynamics NVE is therefore, in principle, good enough
- Other properties are a ?

Obviously we want

- to keep the model system as small as possible
- simulate as long times as possible
- possibly do something else than thermodynamics
- trajectories at **given** T

Therefore we would like to explicitly sample the canonical ensemble (constant-NVT). For this purpose we need to be able to control the temperature of our system.

10.1 Velocity rescaling

We already know how the temperature is related to velocities calculate the definition of temperature in the system

$$\left\langle \frac{1}{2} m_i v_{i,\alpha}^2 \right\rangle = \frac{1}{2} k_B T, \quad \langle \mathcal{K} \rangle_{NVT} = \frac{N_f}{2} k_B T$$

- and how to calculate instantenous temperature at moment t

$$T(t) = \frac{1}{k_B N_f} \sum_{i,\alpha} m_i v_{i,\alpha}^2(t) \quad (10.1)$$

- of course want to argue ergodicity holding

$$T = \bar{T} = \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t T(t') dt$$

Velocity rescaling is a **constraint method** where velocities of particles are scaled with parameter λ for $T(t)$ of (10.1) to match T .

- scaling velocities by λ results in

$$T^{(new)} = \frac{1}{k_B N_f} \sum_{i,\alpha} m_i (\lambda v_{i,\alpha}(t))^2 = \lambda^2 T(t)$$

and

$$T^{(new)} - T(t) = (\lambda^2 - 1)T(t).$$

- This allows identifying required λ for T

$$\lambda = \sqrt{\frac{T}{T(t)}}$$

Velocity rescaling method is simple but it does not sample the canonical ensemble. It also can lead to hot solvent – cold solute problem, where the solute molecules have smaller $\langle \mathcal{K} \rangle$ than the solvent. Different thermostats for different parts of the system can be used, but still sampling will not be that of canonical ensemble. Velocity rescale method is good for starting runs in obscure cases as lot of heat can be transferred at each time step.

10.2 Berendsen weak coupling

Instead of crudely scaling velocities to yield proper $\langle \mathcal{K} \rangle_{NVT}$ a more gentle way can be established by scaling with

$$\chi = \left(1 + \frac{\Delta t}{\tau_T} (T/T(t) - 1) \right)^{1/2}$$

This method

- allows temperature to fluctuate in the system (we are still simulating a microscopic system)
- Can be cast in EoMs

$$\begin{aligned} \dot{\mathbf{r}} &= \mathbf{p}/m \\ \dot{\mathbf{p}} &= \mathbf{f} - \xi \mathbf{p} \\ \xi &= \frac{1}{2\tau_T k_B T(t)} (k_B T(t) - k_B T) \end{aligned} \tag{10.2}$$

The Berendsen method results exponentially dampened approach to the desired temperature. It

- Scales velocities towards desired temperature
- Has explicit relaxation time τ_T that adjusts the coupling (for liquid water $\tau_T = 0.4$ ps is good)
- Can be used to effectively drive the system close to microcanonical ensemble
- Does not sample canonical ensemble (NVT)

The velocity rescale and Berendsen thermostats do not sample NVT ensemble. The following ones do.

10.3 Stochastic collisions

In stochastic methods velocities of randomly chosen particle (minor collision), several or all particles (massive collision) are adjusted to values generated from the Maxwell-Boltzmann distribution. These methods

- run NVE between the stochastic collisions
- jump to new E-surface in each collision
- do not provide smooth trajectories
- can produce proper sampling – a canonical collection of microcanonical trajectories

For example the method of Andersen uses single particle adjustments (collisions). The rate that each particle should suffer a stochastic collision is given by

$$\nu = \frac{2a\kappa}{3k_B\rho N^{2/3}},$$

where a is a constant, κ is thermal conductivity and $\rho = N/V$. For thermal collision rate ν_c , the choice $\nu = \nu_c/N^{2/3}$ will do.

- Too high collision rates do not allow kinetic energy fluctuations
- Too low collision rates result in bad sampling
- Massive collisions require smaller rates.

10.4 Extended system methods

Extended system methods provide an alternative way to treat the heat bath. We actually have an imaginary reservoir that is coupled to the system. Dynamics is performed for both – the system and the imaginary bath.

10.4.1 Nose thermostat

The simplest of the extended system thermostats is the original Nose thermostat. Here we assign additional generalized coordinate s and its conjugate momentum p_s to the heat bath. We define s to be the scaling factor of velocities

$$\mathbf{v} = s\dot{\mathbf{r}} = s\mathbf{p}/m.$$

in addition, we will define the potential and kinetic energies associated with s to be

$$\mathcal{U}_s = (N_f + 1)k_B T \ln s, \quad \mathcal{K}_s = \frac{1}{2}Q\dot{s}^2 = \frac{p_s^2}{2Q},$$

where Q is "thermal inertia". Q looks like a mass, but due to units of s $[Q]=[E]/[t^2]$. Having simply defined this way, now there's the fun part

- Lagrangian for the extended system reads

$$\mathcal{L} = \mathcal{K} + \mathcal{K}_s - \mathcal{U} - \mathcal{U}_s = \sum_i \frac{\mathbf{p}_i^2}{2m_i s^2} + \frac{p_s^2}{2Q} - \mathcal{U}(\mathbf{r}) - (N_f + 1)k_B T \ln s$$

- Since there is no explicit time dependence,

$$\mathcal{H}_N = \mathcal{K} + \mathcal{K}_s + \mathcal{U} + \mathcal{U}_s \quad (10.3)$$

$$= \sum_i \frac{\mathbf{p}_i^2}{2m_i s^2} + \mathcal{U}(\mathbf{r}) + \frac{p_s^2}{2Q} + (N_f + 1)k_B T \ln s \quad (10.4)$$

is also conserved. This is a good check for numerical stability. The Hamiltonian equations of motion for \mathcal{H}_N (Cartesian choice).

$$\begin{aligned} \dot{\mathbf{r}}_i &= \frac{\partial \mathcal{H}_N}{\partial \mathbf{p}_i} = \mathbf{p}_i / (m_i s^2) \\ \dot{\mathbf{p}} &= -\frac{\partial \mathcal{H}_N}{\partial \mathbf{r}_i} = \mathbf{f}_i \\ \dot{s} &= \frac{\partial \mathcal{H}_N}{\partial p_s} = p_s / Q \\ \dot{p}_s &= -\frac{\partial \mathcal{H}_N}{\partial s} = \sum_i \frac{\mathbf{p}_i^2}{m_i s^3} - (N_f + 1)k_B T / s \end{aligned} \quad (10.5)$$

The Nose thermostat therefore treats the system+bath=extended system as an NVE ensemble. It can be shown¹⁴ to yield NVT ensemble for the system in coordinates $(\mathbf{r}, \mathbf{p}/s)$, which was of course the whole purpose of the definitions of s , p_s , \mathcal{K}_s and \mathcal{U}_s . However we have introduced a parameter Q that controls the coupling

- Too small Q (inertia) causes oscillations. The bath should be large!
- Too large Q results in poor coupling and long thermalization time.
- Q needs to be found by trial and error.

Nose thermostat is a great tool but it has one small problem. As velocities are scaled with s , actually time is scaled. There is no direct correspondence between the velocities and time in real and extended systems.

- s can change and therefore
- Δt can fluctuate
- Regular time step dynamics of extended system corresponds to dynamics univently spaced times for real system¹⁵

10.4.2 Nose-Hoover thermostat

Hoover version¹⁶ of Nose thermostat uses different parametrization avoiding use of velocity (and time) scaling parameter s in EoMs. This is the real thing! With slightly different definitions for the bath (now ηp_η)¹⁷, the Nose-Hoover equations read

$$\begin{aligned}
 \dot{\mathbf{r}}_i &= \mathbf{p}_i / (m_i) \\
 \dot{\mathbf{p}} &= \mathbf{f}_i - \frac{p_\eta}{Q} \mathbf{p}_i \\
 \dot{\eta} &= p_\eta / Q \\
 \dot{p}_\eta &= \sum_i \frac{\mathbf{p}_i^2}{m_i} - N_f k_B T
 \end{aligned}
 \tag{10.6}$$

¹⁴Nose paper or Tuckerman p. 180

¹⁵Interested reader can resort to Tuckerman book.

¹⁶Phys. Rev. A **31** 1695 (1984)

¹⁷Again, Tuckerman book

Comparison with Berendsen (10.2) is now easy. Whereas Berendsen gives damped temperature oscillations, Nose-Hoover has \dot{p}_η in the last equation and coupling between the bath (bath is affected too).

- Nose-Hoover thermostat drives the system much softer than Berendsen thermostat
- Due to true coupling, Nose-Hoover can result in slowly dampening oscillations and very long thermalization.
- Nose-Hoover needs to be started close to equilibrium.

10.4.3 Nose-Hoover chain thermostat and massive thermostating

Nose-Hoover thermostat fails in cases where there more than one conservation law in the real system. As each conservation law fixes on degree of freedom, they may affect the dynamics of the bath. This can be counteracted by applying Nose thermostating on the thermostat itself. For a chain of M thermostats one has

$$\begin{aligned}\dot{\mathbf{r}}_i &= \mathbf{p}_i/m_i \\ \dot{\mathbf{p}} &= \mathbf{f}_i - \frac{p_{\eta 1}}{Q_1} \mathbf{p}_i \\ \dot{\eta}_j &= p_{\eta j}/Q_i \quad \forall j = 1, \dots, M \\ \dot{p}_{\eta 1} &= \sum_i \frac{\mathbf{p}_i^2}{m_i} - N_f k_B T - \frac{p_{\eta 2}}{Q_2} p_{\eta 1}\end{aligned}\tag{10.7}$$

$$\begin{aligned}\dot{p}_{\eta 2} &= \frac{p_{\eta 1}^2}{Q_1} - k_B T - \frac{p_{\eta 3}}{Q_3} p_{\eta 2} \\ &\dots \\ \dot{p}_{\eta M} &= \frac{p_{\eta M-1}^2}{Q_{M-1}} - k_B T\end{aligned}\tag{10.8}$$

Naturally there is a conserved energy in this case too. We are left only with discussion about choice of Q s.

- One suggestion $Q_1 = N_f k_B T \tau^2$ and $Q_j = k_B T \tau^2$, where $j = 2 \dots M$ and τ is characteristic time scale for the system.
- Tuckerman states that $\tau > 20\Delta t$ is fine.
- Note that in NH formalism $[Q]=[E][t^2]$

Nose-Hoover chains are probably the best way to thermostat a canonical system. However, as with the Nose case one may have long-lived oscillations during thermalization. One can circumvent this and guarantee proper thermalization by applying each particle of the system a separate thermostat. This is called "massive thermostating". To avoid oscillations in Nose-related thermostating it is a good idea to run system close to equilibrium using other thermostats, like Berendsen.

10.5 Use of different thermostats

For a simulation to sample the NVT (canonical) ensemble a proper thermostat needs to be used in the last part of equilibration and production runs.

- Other thermostats like v-rescale can still be useful.
 - Starting simulation and driving it to a proper temperature
 - v-rescale is a good way to input or remove thermal energy in a quick fashion
 - If system heats up due to large potential energy in the Γ_0 , velocities do not grow too large for time step used (simulation will not crash)

For a realistic equilibrium MD in NVT one can for example take subsequent steps

- Pick up a \mathbf{r}_0 close to the system you want to study
- Minimize energy by minimization to remove bad contacts
- Generate velocities (possibly first at a low temperature)
- Run v-rescale to establish proper temperature (possibly first at a low temperature)
- Drive system close to the ensemble by Berendsen weak coupling method
- Continue with the equilibration with the thermostat you want to use (Nose, Nose-Hoover, Nose-Hoover chain,...)
- Once thermalized, run production

11 Controlling pressure

As well as specifying temperature in MD simulation, it may be desired to maintain the system at constant pressure. This may be crucial in some cases, like phase transitions.

- Many of the experiments are performed in NPT (a bottle in a lab)
- Simulations at constant NPT are closest to experiments

A macroscopic system maintains constant pressure by changing its volume. In simulations of isobaric ensembles,

- the system is allowed to change its volume.

Many of the methods are very similar to those of temperature control.

11.1 Calculating pressure

Defining the pressure is somewhat more difficult than temperature. With the use of scaled coordinates (4.2), one can evaluate the internal pressure in NVT ensemble by

$$P^{(int)} = k_B T \frac{\partial}{\partial V} \ln Q(N, V, T) = \frac{Nk_B T}{V} + \frac{1}{3V} \left\langle \sum_i \mathbf{r}_i \cdot \mathbf{f}_i \right\rangle_{NVT}$$

where we can insert temperature definition $3Nk_B T = \langle \sum_i \mathbf{p}_i^2 / m_i \rangle_{NVT}$ to obtain

$$P^{(int)} = \frac{1}{3V} \left\langle \sum_i \mathbf{p}_i^2 / m_i \right\rangle_{NVT} + \frac{1}{3V} \left\langle \sum_i \mathbf{r}_i \cdot \mathbf{f}_i \right\rangle_{NVT}$$

This suggests that we can define an instantaneous pressure function

$$P(\mathbf{\Gamma}(t)) = \frac{1}{3V} \sum_i \left[\frac{\mathbf{p}_i^2}{m_i} + \mathbf{r}_i \cdot \mathbf{f}_i \right] \quad (11.1)$$

using which we could estimate internal pressure over a trajectory by

$$P^{(int)} = \langle P(\mathbf{\Gamma}) \rangle_{NVT} = \overline{P(\mathbf{\Gamma})}$$

Now we will only need to find out the relation between $P^{(int)}$ and P of our ensemble (NPT). The result of the calculation¹⁸ indeed is

$$\langle P^{(int)} \rangle_{NPT} = P.$$

However, a calculation for $\langle P^{(int)}V \rangle_{NPT}$ yields

$$\langle P^{(int)}V \rangle_{NPT} - P \langle V \rangle_{NPT} = k_B T$$

which can be interpreted as additional energy related to degree of freedom V . Energy is equipartitioned on this quantity too. In addition, pressure function $P^{(int)}(t)$ oscillates wildly due to virial $\sum_i \mathbf{r}_i \cdot \mathbf{f}_i$ varying a lot during the simulation.

11.2 Berendsen barostat

The Berendsen barostat is analogous to the Berendsen thermostat. The box-center-of mass coordinates are scaled at each MD step

$$\mathbf{r}' = \chi^{1/3} \mathbf{r}$$

$$\chi = 1 - \kappa \frac{\Delta t}{\tau_P} (P - P^{(int)}(t)),$$

where $\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$ is isothermal compressibility, and τ_P is relaxation time for the coupling. The Berendsen method drives the system pressure according to equation

$$\frac{dP^{(int)}(t)}{dt} = \frac{1}{\tau_P} (P - P^{(int)}(t))$$

As the Berendsen thermostat, the barostat is exponentially damped and drives the system nicely to the desired temperature.

- Good in directing the system close to equilibrium
- Does not yield the proper ensemble
- for water $\tau_P = 0.01$ ps and $\tau_P = 0.1$ ps were found to be OK.
- For liquid water $\kappa \approx 4.5 \times 10^{-5} \text{bar}^{-1}$.

¹⁸Tuckerman p. 225

11.3 Andersen barostat

The Andersen barostat is similar to Nose temperature coupling. It uses the extended system scheme

- This time volume V is used as the additional degree of freedom. The associated generalized momentum is p_V .

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$$\mathcal{K}_V = \frac{1}{2} \frac{p_V^2}{2W}, \quad \mathcal{U}_V = PV$$

- In addition, positions and momenta are scaled

$$\mathbf{s}_i = V^{-1/3} \mathbf{r}_i, \quad \pi_i = V^{-1/3} \mathbf{p}_i$$

The Andersen Hamiltonian reads

$$\mathcal{H}_A = \sum_i \frac{V^{-2/3} \pi_i^2}{2m_i} + U(V^{1/3} \mathbf{s}) + \frac{p_V^2}{2W} + PV$$

and we know how to proceed. The equations of motion are

$$\begin{aligned} \dot{\mathbf{s}}_i &= \frac{\partial \mathcal{H}_A}{\partial \pi_i} = \frac{V^{-2/3} \pi_i}{m_i} \\ \dot{\pi}_i &= -\frac{\partial \mathcal{H}_A}{\partial \mathbf{s}_i} = -\frac{\partial U}{\partial (V^{1/3} \mathbf{s}_i)} V^{1/3} \\ \dot{V} &= \frac{\partial \mathcal{H}_A}{\partial p_V} = p_V / W \\ \dot{p}_V &= -\frac{\partial \mathcal{H}_A}{\partial V} = \frac{1}{3} V^{-5/3} \sum_i \frac{\pi_i^2}{m_i} - \frac{1}{3} V^{-1/3} \sum_i \frac{\partial U}{\partial (V^{-2/3} \mathbf{s}_i)} \cdot \mathbf{s}_i - P \end{aligned} \quad (11.2)$$

which can be written ¹⁹

$$\begin{aligned} \dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i^2}{m_i} + \frac{1}{3} \frac{\dot{V}}{V} \mathbf{r}_i \\ \dot{\mathbf{p}}_i &= \mathbf{f}_i - \frac{1}{3} \frac{\dot{V}}{V} \mathbf{p}_i \\ \dot{V} &= p_V / W \\ \dot{p}_V &= \frac{1}{3V} \sum_i \left[\frac{\mathbf{p}_i^2}{m_i} - \frac{\partial U}{\partial \mathbf{r}_i} \cdot \mathbf{r}_i \right] - P \end{aligned} \quad (11.3)$$

¹⁹You can do it: $\mathbf{s}_i = V^{-1/3} \mathbf{r}_i$; $\dot{\mathbf{s}}_i = V^{-1/3} \dot{\mathbf{r}}_i - \frac{1}{3} V^{-4/3} \dot{V} \mathbf{r}_i$;
 $\pi_i = V^{1/3} \mathbf{p}_i$; $\dot{\pi}_i = V^{1/3} \dot{\mathbf{p}}_i + \frac{1}{3} V^{-2/3} \dot{V} \mathbf{p}_i$

It is instructive to compare these to Nose-Hoover equations of motion (10.6) for temperature coupling.

- Especially the last equation. Here we simply have $\dot{p}_V = P^{(int)}(t) - P$ on the right.
- Integration of these could be performed and MD run as well.
- Choice of parameter

$$W = (3N + 1)k_B T \tau_P^2$$

- $3N + 1$ since we have $3N$ coordinates and 1 for barostat.
- τ_P characteristic time for volume oscillations.

- There is a conserved energy corresponding \mathcal{H}_A

11.4 Parrinello-Rahman barostat

Andersen barostat treats volume as a single variable. For a cubic box of volume V with isotropic compressibility and simulation of liquids this is fine. For a more general approach

- box sides could be made independent
- box side vectors could be nonorthogonal

$$\mathbf{r} = \mathbf{H}\mathbf{s}, \quad \mathbf{H} = (\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3), \quad V = \mathbf{h}_1 \cdot \mathbf{h}_2 \times \mathbf{h}_3$$

- Phase transitions in solids.

This is the content of Parrinello-Rahman barostat. Ideas behind the formulae will be the same, except for complication due to nonorthogonality.

As with the Nose-Hoover thermostat, large and slowly dampening oscillations can take place with the corresponding barostats. Therefore similar route close to equilibrium needs to be taken. That implies using Berendsen weak coupling barostat first and only afterwards Andersen/Parrinello Rahman.

11.5 Parameters

Apart from the characteristic times τ , the Berendsen barostat has a our barostats have For water $\kappa = 4.5 \times 10^{-5} \text{bar}^{-1}$. It is quite good approximation for other liquids too. For ideal gas $\kappa \approx 1 \text{bar}^{-1}$ instead. The isothermal compressibility fulfills

$$\kappa = \frac{1}{k_B T} \frac{\langle V^2 \rangle - \langle V \rangle^2}{\langle V \rangle}.$$

- For a cubic box of $(20 \text{ \AA})^3$ with volume 8000 \AA^3
 - of water, fluctuations of 121 \AA^3 or 0.1 \AA take place
 - of ideal gas, fluctuations of 18100 \AA^3 take places

To simulate ideal gas with p-coupling LARGE boxes are needed.

Naturally, all sources use different conventions. The Gromacs code defines parameters Q and W by introducing relaxation times τ_T and τ_P in addition to κ . In the excercises we will use values from 1 to a couple ps.

Especially note, that the values for NH and PR are not the same as for Berendsen. Typically $\tau_T^{\text{Nose}} > 5\tau_T^{\text{Berendsen}}$ and $\tau_P^{\text{Parrinello-Rahman}} > 5\tau_P^{\text{Berendsen}}$

However, proper functioning of the NH thermostats and the BR barostats can be checked from the velocity, temperature and volume distributions and oscillations in time. That being said we will happily use a couple of ps times for our short simulations.

12 NPT ensemble (isothermal-isobaric)

For sampling the real thing, the NPT ensemble we will need to combine pressure and temperature coupling. What can be done is to implement pressure and temperature coupling simultaneously to the ensemble. For example

- Berendsen-T and Berendsen-P coupling
- Nose-Hoover-T and Parrinello-Rahman/Andersen-P coupling

The latter is already considered to be a good option for NPT. However, there is an algorithm that rigorously samples NPT that we will shortly discuss.

12.1 MTTK algorithm

Martyna-Tuckerman-Tobias-Klein algorithm is a true NPT implementation of pressure coupling to be used with Nose-Hoover chain thermostat. Again there is a Nose-Hoover chain type equations together with pressure equations that are integrated in time. And a conserved Hamiltonian. The interested reader can refer to Tuckerman p. 239 and onwards.

12.2 Thermalization of NPT simulations

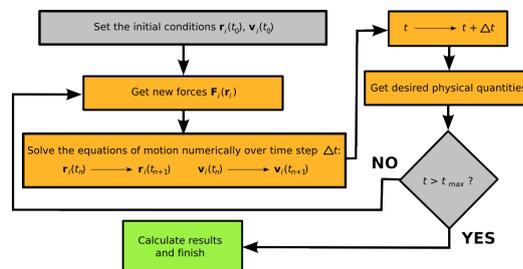
As with thermostating similar pathway of equilibration can be followed when doing pressure coupling too.

- As we naturally start with reasonably good Γ_0 with close-to-proper density, pressure coupling in the first v-rescale run might be
- Prohibits the system to expand due to potential energy stored in Γ_0 .
- So running v-rescale with NVT first
- then turning to NPT for proper thermalization
 - Berendsen thermostat & barostat driving close to equilibrium
 - End of thermalization and production with Nose-Hoover & Andersen or Parrinello-Rahman or MTTK

Summary

We have now gone through the basics of molecular dynamics simulations for equilibrium ensembles.

- We have motivated the method by numerous applications
- We know the basics about sampling ensembles
- We know how the simulation is set up
- We know how to use boundary conditions
- We know how to integrate EoMs in time
- We know how to evaluate forces from pair potentials and simplify calculations with neighbor lists
- We know how to model effects of temperature bath
- We know how pressure on the system is taken into account
- We know



Now we can

- study some small additional things
- dig in some specific interaction models
- study nonequilibrium simulations
- study methods that utilize this stuff for more complicated properties