Computational Statistical Physics

Part II: Interacting particles and molecular dynamics

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Canonical ensemble

Canonical Ensemble

Experiments are often conducted at constant temperature and not at constant energy. This is a common situation, since systems are usually able to exchange energy with their environment. We therefore first couple our system to a heat bath to realize this situation. There are various options to do this

- Rescaling of velocities,
- Introducing constraints (Hoover),
- Nosé-Hoover thermostat,
- Stochastic method (Anderson).

Canonical Ensemble

However, before focusing on the discussion of the latter methods, we shall define the concept of temperature used in the subsequent sections. We start from the equipartition theorem

$$\left\langle q_\mu \frac{\partial \mathcal{H}}{\partial q_\nu} \right\rangle = \left\langle p_\mu \frac{\partial \mathcal{H}}{\partial p_\nu} \right\rangle = \delta_{\mu\nu} kT \tag{1}$$

for a Hamiltonian $\mathcal{H}$ with the generalized coordinates $\mathbf{q}$ and $\mathbf{p}$.

Canonical Ensemble

We consider a classical system whose Hamiltonian is given by

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + V\left(\mathbf{x}_1, \ldots, \mathbf{x}_N\right) \tag{2}$$

and we define the instantaneous temperature

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

Velocity rescaling

Intuitively, we should be able to adjust the system's instantaneous temperature by rescaling the velocities of the particles according to

$$\mathbf{v}_i \to \alpha \mathbf{v}_i. \tag{4}$$

The measured tempereature is proportional to the squared velocities and thus

$$\mathcal{T} \to \alpha^2 \mathcal{T}. \tag{5}$$

Therefore, we have to set

$$\alpha = \sqrt{\frac{T}{\mathcal{T}}} \tag{6}$$

to stay at a fixed desired temperature T.

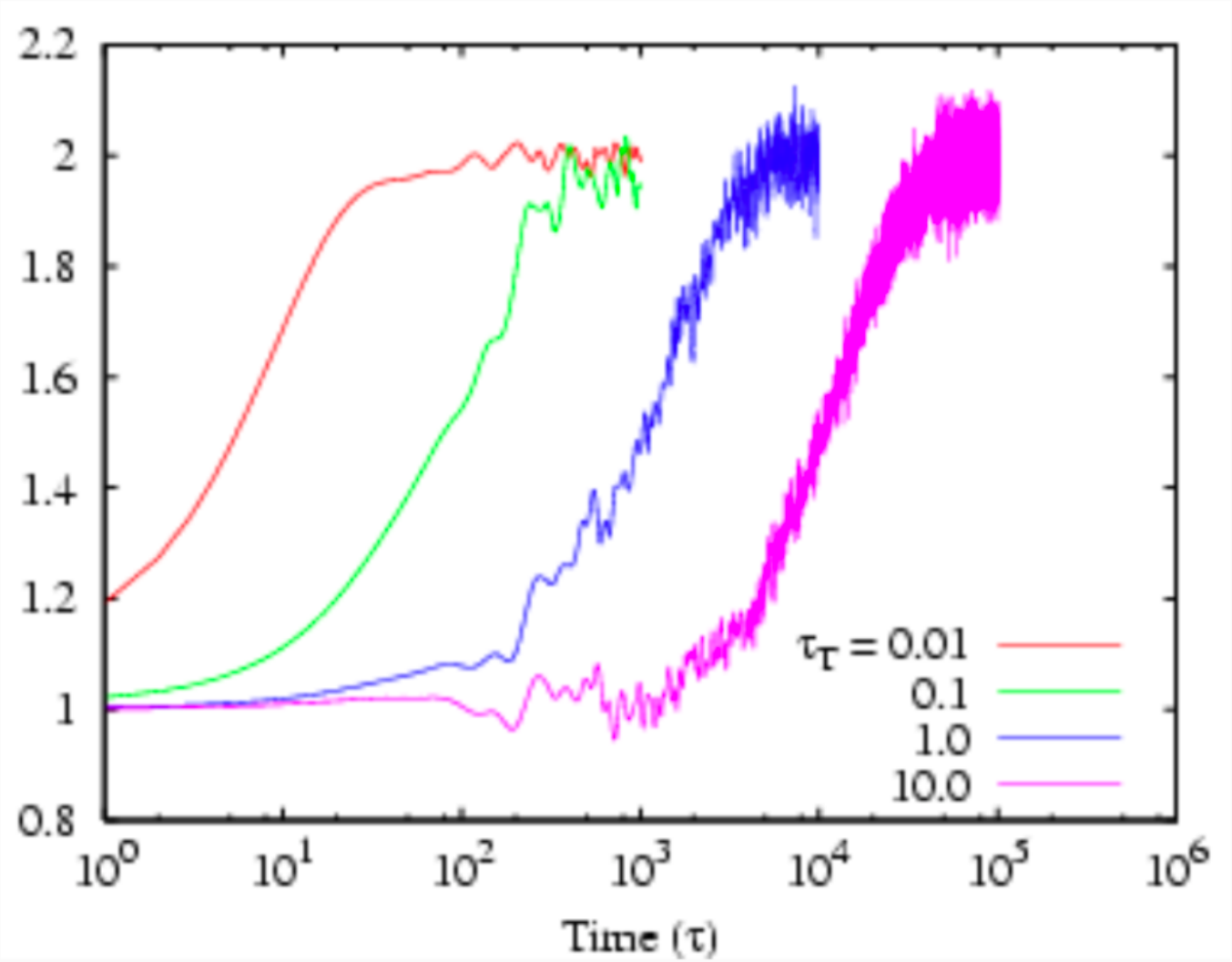
Velocity rescaling

This method is very easy to implement. However, the problem is that we change the physics and in particular the time and the resulting velocity distribution deviates from the canonical one. This method might seems to be very effective. A modification of this method makes use of an additional parameter t_T (relaxation time) which describes the coupling to heat bath. The scaling factor is then (Berendsen thermostat)

$$\alpha = \sqrt{1 + \frac{\Delta t}{t_T}\left(\frac{T}{\mathcal{T}} - 1\right)}. \tag{7}$$

Still we do not recover the canonical velocity distribution (Maxwell–Boltzmann). Velocity rescaling should be only applied to initialize a configuration at given temperature.

Velocity rescaling



Constraint method

Another possiblity to adjust the system's temperature is to add a friction term to the equation of motion, i.e.,

$$\dot{\mathbf{p}}_i = \mathbf{f}_i - \xi \mathbf{p}_i, \tag{8}$$

where $\mathbf{p}_i = m_i \dot{\mathbf{x}}_i$. Various definitions of the friction coefficient ξ are possible. Hoover's original porposal is based on the following constant temperature condition:

$$\dot{\mathcal{T}} \sim \frac{\mathrm{d}}{\mathrm{d}t} \left(\sum_{i=1}^{N} \mathbf{p}_i^2 \right) \sim \sum_{i=1}^{N} \dot{\mathbf{p}}_i \mathbf{p}_i = 0. \tag{9}$$

Constraint method

By combining Eqs. (52) and (53), we find

$$\xi = \frac{\sum_{i=1}^{N} \mathbf{f}_i \mathbf{p}_i}{\sum_{i=1}^{N} |\mathbf{p}_i|^2}. \tag{10}$$

This method makes it necessary to already start at the desired temperature. Another possibility is to determine the friction coefficient according to (Berendsen)

$$\xi = \gamma \left(1 - \frac{T}{\mathcal{T}}\right). \tag{11}$$

or (Hoover)

$$\dot{\xi} = \frac{f k_B}{Q}(\mathcal{T} - T). \tag{12}$$

The parameters γ and Q determine the temperature adaption rate, and f is the number of degrees of freedom.

Nosé-Hoover thermostat [S. Nosé '81, S. Nosé '84]

In order to overcome the problem of the wrong velocity distribution, we are now going to discuss the Nosè-Hoover thermostat as the correct method to simulate heat bath particle dynamics. Shuichi Nosé introduced a new degree of freedom s that describes the heath bath.The corresponding potential and kinetic energy are

$$\begin{aligned} \mathcal{V}(s) &= (3N+1)\, k_B T \ln s, \\ K(s) &= \frac{1}{2} Q \dot{s}^2. \end{aligned} \tag{13}$$

Nosé-Hoover thermostat

The new degree of freedom s rescales the time step $\mathrm{d}t$ and momenta $\mathbf{p}_i$ according to

$$\mathrm{d}t' = s\mathrm{d}t \qquad \text{and} \qquad \mathbf{p}'_i = s\mathbf{p}_i. \tag{14}$$

Similarly, velocities are also rescaled since

$$\mathbf{v}'_i = \frac{\mathrm{d}\mathbf{x}_i}{\mathrm{d}t'} = \frac{\mathrm{d}\mathbf{x}_i}{\mathrm{d}t}\frac{\mathrm{d}t}{\mathrm{d}t'} = \frac{\mathbf{v}_i}{s}. \tag{15}$$

Note that we also used the chain rule in the second step of the equation for the rescaling of momenta:

$$\mathbf{p}'_i = \nabla_{\mathbf{v}'_i}\left(\frac{1}{2}\sum_{i=1}^{N} m_i {\mathbf{v}'_i}^2\right) = s\nabla_{\mathbf{v}_i}\left(\frac{1}{2}\sum_{i=1}^{N} m_i {\mathbf{v}_i}^2\right) = s\mathbf{p}_i, \tag{16}$$

Nosé-Hoover thermostat

The Hamiltonian is thus

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\mathbf{p}_i'^2}{2m_i s^2} + \frac{1}{2} Q \dot{s}^2 + V\left(\mathbf{x}_1, \ldots, \mathbf{x}_N\right) + \mathcal{V}\left(s\right), \tag{17}$$

with $p_s = Q\dot{s}$ being the momentum corresponding to s. The velocities are

$$\begin{aligned} \frac{\mathrm{d}\mathbf{x}_i}{\mathrm{d}t'} &= \nabla_{\mathbf{p}_i'} \mathcal{H} = \frac{\mathbf{p}_i'}{m_i s^2}, \\ \frac{\mathrm{d}s}{\mathrm{d}t'} &= \frac{\partial \mathcal{H}}{\partial p_s} = \frac{p_s}{Q}. \end{aligned} \tag{18}$$

Nosé-Hoover thermostat

With $\mathbf{p}_i' = m_i s^2 \dot{\mathbf{x}}_i$ we find

$$\mathbf{f}_i = \frac{\mathrm{d}\mathbf{p}_i'}{\mathrm{d}t'} = -\frac{\partial \mathcal{H}}{\partial \mathbf{x}_i} = -\nabla_{\mathbf{x}_i} V\left(\mathbf{x}_1, \ldots, \mathbf{x}_N\right) = 2 m_i s \dot{s} \dot{\mathbf{x}}_i + m_i s^2 \ddot{\mathbf{x}}_i \tag{19}$$

and

$$\frac{\mathrm{d}\mathbf{p}_s}{\mathrm{d}t'} = -\frac{\partial \mathcal{H}}{\partial s} = \frac{1}{s}\left[\sum_{i=1}^{N} \frac{{\mathbf{p}_i'}^2}{m_i s^2} - \left(3N+1\right) k_B T\right]. \tag{20}$$

Nosé-Hoover thermostat

Based on the latter Hamilton equations, we find for the equations of motion in virtual time t'

$$m_i s^2 \ddot{\mathbf{x}}_i = \mathbf{f}_i - 2m_i \dot{s} s \dot{\mathbf{x}}_i \quad \text{with} \quad i \in \{1, \ldots, N\} \tag{21}$$

and

$$Q\ddot{\mathbf{s}} = \sum_{i=1}^{N} m_i s \dot{\mathbf{x}}_i^2 - \frac{1}{s} \left(3N + 1\right) k_B T. \tag{22}$$

Nosé-Hoover thermostat

In order to obtain the equations of motion in real time, we have to remind ourselfs that $\mathrm{d}t = \mathrm{d}t'/s$ and $\mathbf{p}_i' = s\mathbf{p}_i$. Thus, we find for the velocities

$$\begin{aligned} \frac{\mathrm{d}\mathbf{x}_i}{\mathrm{d}t} &= s\frac{\mathrm{d}\mathbf{x}_i}{\mathrm{d}t'} = \frac{\mathbf{p}_i'}{m_i s} = \frac{\mathbf{p}_i'}{m_i}, \\ \frac{\mathrm{d}s}{\mathrm{d}t} &= s\frac{\mathrm{d}s}{\mathrm{d}t'} = s\frac{\mathbf{p}_s}{Q}, \end{aligned} \tag{23}$$

and for the forces

$$\begin{aligned} \frac{\mathrm{d}\mathbf{p}_i}{\mathrm{dt}} &= s\frac{\mathrm{d}}{\mathrm{d}t'}\left(\frac{\mathbf{p}_i'}{s}\right) = \frac{\mathrm{d}\mathbf{p}_i'}{\mathrm{d}t'} - \frac{1}{s}\frac{\mathrm{d}s}{\mathrm{d}t'}\mathbf{p}_i' = \mathbf{f}_i - \frac{1}{s}\frac{\mathrm{d}s}{\mathrm{d}t}\mathbf{p}_i, \\ \frac{\mathrm{d}\mathbf{p}_s}{\mathrm{d}t} &= s\frac{\mathrm{d}p_s}{\mathrm{d}t'} = \sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{m_i} - (3N+1)\,kT. \end{aligned} \tag{24}$$

Nosé-Hoover thermostat

With $\xi = \frac{\mathrm{d}\ln(s)}{\mathrm{d}t} = \frac{\dot{s}}{s}$ representing a friction term, the equations of motions (65) and (66) are given in real time by

$$\ddot{\mathbf{x}}_i = \frac{\mathbf{f}_i}{m_i} - \xi \dot{\mathbf{x}}_i \tag{25}$$

and

$$Q\dot{\xi} = \sum_{i=1}^{N} m_i \dot{\mathbf{x}}_i^2 - (3N+1)\, k_B T. \tag{26}$$

Nosé-Hoover thermostat

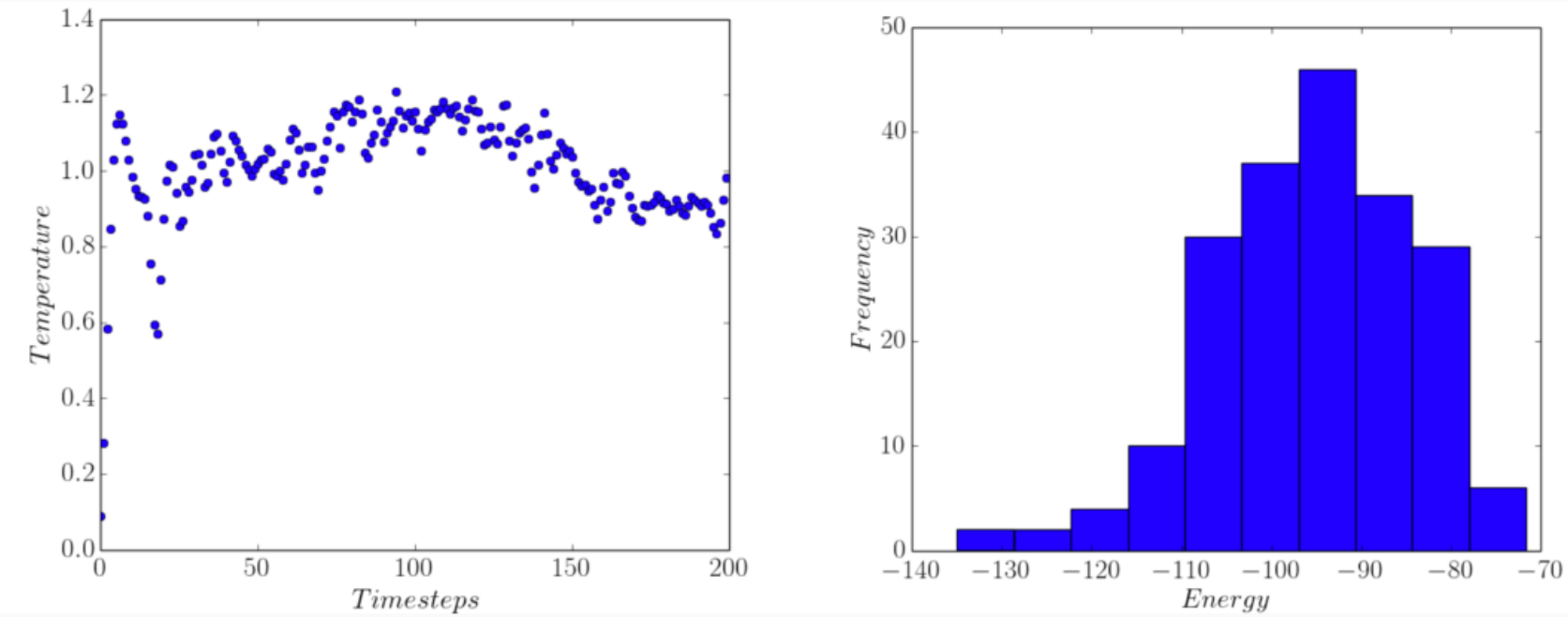
The first term in Eq. (70) denotes the **measured** kinetic energy whereas the second one corresponds to the **desired** kinetic enery. The quantity Q represents the coupling to the heat bath and the higher the value of Q, the stronger the system reacts to temperature fluctuations. For $Q \to \infty$, we recover microcanonical MD.

A reasonable value of Q is characterized by the fact that normal temperature fluctuations are observed, i.e.,

$$\overline{\Delta T} = \sqrt{\frac{2}{Nd}}\overline{T}, \tag{27}$$

where d is the system's dimension and N the number of particles.

Nosé-Hoover thermostat



Nosé-Hoover thermostat

We now show that the Nosé–Hoover thermostat recovers the canonical partition function. Therefore, we start from microcanonical MD and the corresponding partition function

$$Z = \int \delta\left(\mathcal{H} - E\right) \mathrm{d}s \, \mathrm{d}p_s \, \mathrm{d}^3x' \, \mathrm{d}^3p', \tag{28}$$

where the x and p integration has to be taken over a three dimensional space with N particles. With $\mathcal{H} = \mathcal{H}_1 + (3N+1)\, kT \ln(s)$ and in real time, we find

$$\begin{aligned} Z &= \int \delta\left[\left(\mathcal{H}_1 - E\right) + (3N+1)\, kT \ln(s)\right] s^{3N} \mathrm{d}s \, \mathrm{d}p_s \, \mathrm{d}^3x \, \mathrm{d}^3p \\ &= \int \delta\left[s - e^{-\frac{\mathcal{H}_1 - E}{(3N+1)kT}}\right] \frac{s^{3N+1}}{(3N+1)\, kT} \mathrm{d}s \, \mathrm{d}p_s \, \mathrm{d}^3x' \, \mathrm{d}^3p', \end{aligned} \tag{29}$$

where we used the identity $\delta\left[f(s)\right] = \delta\left(s - s_0\right) / f'(s)$ with $f(s_0) = 0$ in the second step.

Nosé-Hoover thermostat

Integrating Eq. (73) over s yields

$$\begin{aligned} Z &= \int \frac{1}{(3N+1)\,kT} e^{-\frac{\mathcal{H}_1 - E}{kT}} \mathrm{d}p_s \, \mathrm{d}^3x \, \mathrm{d}^3p \\ &= \int e^{-\frac{\mathcal{H}_1 - E}{kT}} \mathrm{d}^3x \, \mathrm{d}^3p \int \frac{1}{(3N+1)\,kT} \mathrm{d}p_s, \end{aligned} \tag{30}$$

with $\mathcal{H}_1 = \mathcal{H}_0 + \frac{p_s^2}{2Q}$. The first term of the last equation is the canonical partition function and the last term a constant prefactor.

Stochastic method

This method, proposed by Andersen in 1980, is a combination of the velocity rescaling and Monte Carlo. At temperature T, one expects the velocity distribution to recover the Maxwell-Boltzmann distribution:

$$P(\mathbf{p}) = \frac{1}{(\pi k_B T)^{\frac{3}{2}}} e^{-\frac{\mathrm{p}^2}{k_B T}}. \tag{31}$$

Every n time steps, the simulation will be suspended and particles are selected selected uniformly at random and given a new momentum according to (75). If n is too small, one has pure Monte Carlo and looses the real time scale, e.g., the long time tail of the velocity correlation. If n is too large the coupling to the heat bath is too weak, equilibration is slow and one will essentially work microcanonically.

Constant pressure

Another important situation is the one of constant pressure.

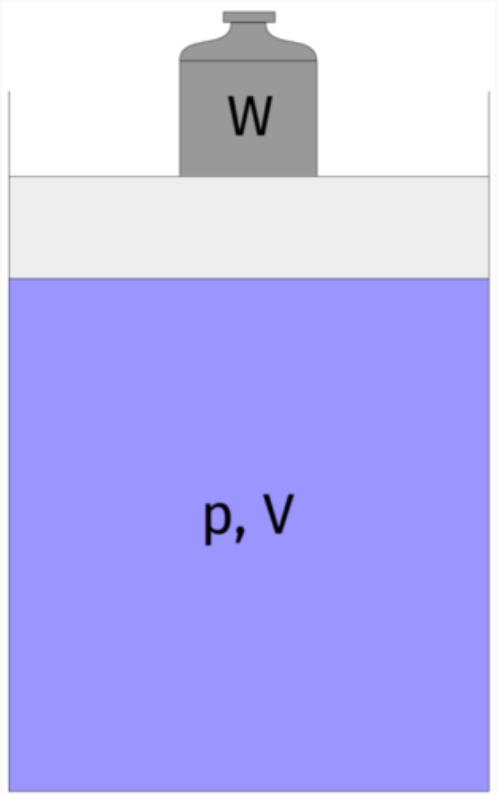


Figure 1: A weight of mass W exerts a pressure p on the system with volume V.

Constant pressure

We will again consider the equipartition theorem (45) with the Hamiltonian

$$\mathcal{H} = K(\mathbf{p}) + V(\mathbf{x})$$

Taking the derivative of the $\mathcal{H}$ with respect to the spatial component yields

$$\frac{1}{3}\left\langle \sum_{i=1}^{N} \mathbf{x}_i \cdot \left[\nabla_{\mathbf{x}_i} V(\mathbf{x})\right] \right\rangle = NkT.$$

Constant pressure

We now distinguish between particle-particle and particle-wall interactions, $\mathbf{f}_i^{\text{part}}$ and $\mathbf{f}_i^{\text{ext}}$, respectively. We then get:

$$\frac{1}{3}\left\langle \sum_{i=1}^{N} \mathbf{x}_i \cdot \left[\nabla_{\mathbf{x}_i} V\left(\mathbf{x}\right)\right] \right\rangle = -\frac{1}{3}\left\langle \sum_{i=1}^{N} \mathbf{x}_i \cdot \left(\mathbf{f}_i^{\text{ext}} + \mathbf{f}_i^{\text{part}}\right) \right\rangle \tag{32}$$

$$= -\frac{1}{3}\left\langle \sum_{i=1}^{N} \mathbf{x}_i \cdot \left(\mathbf{f}_i^{\text{ext}}\right) \right\rangle \underbrace{-\frac{1}{3}\left\langle \sum_{i=1}^{N} \mathbf{x}_i \cdot \left(\mathbf{f}_i^{\text{part}}\right) \right\rangle}_{w \equiv \text{virial}}. \tag{33}$$

Constant pressure

We define

$$w = -\frac{1}{3}\left\langle \sum_{i=1}^{N} \mathbf{x}_i \cdot (\mathbf{f}_i^{\text{part}}) \right\rangle \tag{34}$$

as the viral. Based on

$$\frac{1}{3}\left\langle \sum_{i=1}^{N} \mathbf{x}_i \cdot (\mathbf{f}_i^{\text{part}}) \right\rangle = -\frac{1}{3}\int_{\Gamma} p\mathbf{x}\mathrm{d}\mathbf{A} = -\frac{1}{3}p\int_{V} (\nabla \cdot \mathbf{x})\,\mathrm{d}\mathbf{V} = -pV \tag{35}$$

we define the instantaneous pressure $\mathcal{P}$ by

$$\mathcal{P}V \equiv Nk_BT + \langle w \rangle \tag{36}$$

Constant pressure

Similarly to Nosé-Hoover thermostat, we introduce a sort of "pressure bath',', i.e a parameter W which adjusts the pressure of the system. The volume change can be written as:

$$V = 1 - \alpha_T \frac{\Delta}{t_p} (p - \mathcal{P}) \tag{37}$$

where α_T is the isothermal compressibility and t_p is a relaxation time for the pressure.

Solving Nosé-Hoover – modified velocity Verlet

[Exercise 10]Coupling of the system of particles to a heat bath at fixed temperature T cannot be solved using neither (velocity) Verlet discussed in class, nor Leapfrog algorithm.

One way to solve the system of equations by introducing a small modification of the velocity Verlet algorithm.

Event-driven Molecular Dynamics

Elastic Collisions

One of the first examples for event-driven programming applied to molecular dynamics is a work by Alder in 1957.

In this method only the exchange of the particles' momenta is taken into account and no forces are calculated. Furthermore, only binary collisions are considered and interactions between three or more particles are neglected. Between two collision events, the particles follow ballistic trajectories. To perform an event-driven MD simulation, we need to determine the time t_c between two collisions to then obtain the velocities of the two particles after the collision from the velocities of the particles before the collision using a look-up table.

Elastic Collisions

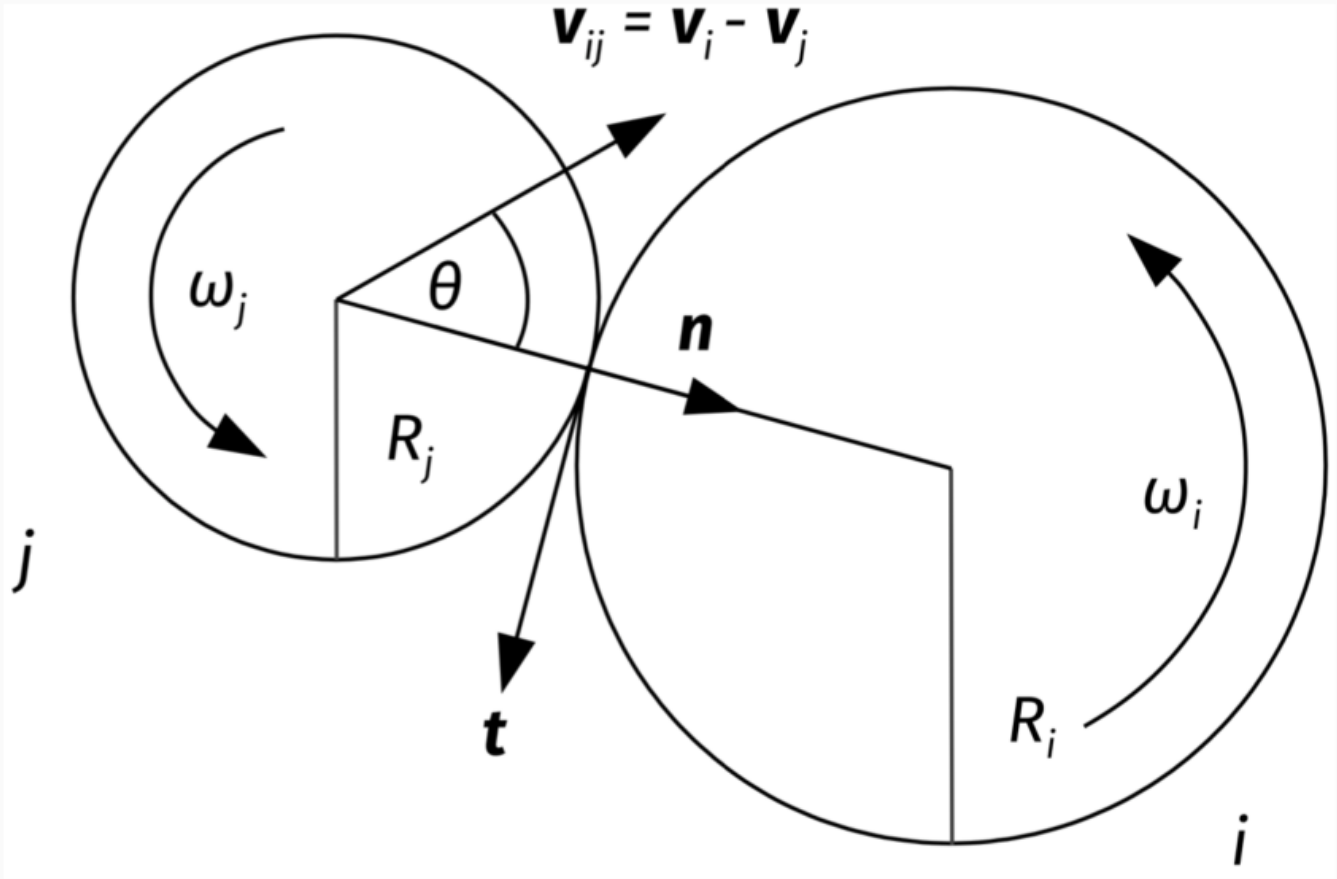


Figure 2: Two particles collide elastically.

Elastic Collisions

For the moment, we are not taking into account the influence of friction and thus neglect the exchange of angular momentum. We compute the times t_{ij}, at which the next collision between the particle i and the particle j would occur. At time t_{ij}, the distance between the two particles is

$$|\mathbf{r}_{ij}(t_{ij})| = |R_i + R_j| \tag{38}$$

Given a relative velocity v_{ij} at time t_0, the contact time t_{ij} of two particles can be obtained from

$$v_{ij}^2 t_{ij}^2 + 2\left[\mathbf{r}_{ij}(t_0)\,\mathbf{v}_{ij}\right] t_{ij} + \left[r_{ij}(t_0)\right]^2 - (R_i + R_j)^2 = 0. \tag{39}$$

Elastic Collisions

We should bear in mind that Eq. (83) are only meaningful if the trajectories of particles i and j cross with each other. The time t_c when the next collision occurs, is the minimum over all pairs, i.e.,

$$t_c = \min_{ij} \left(t_{ij} \right) . \tag{40}$$

Thus, in the time interval $[t_0, t_c]$ the particles' positions and angular orientations evolve according to

$$\mathbf{r}_i \left(t_0 + t_c \right) = \mathbf{r}_i \left(t_0 \right) + \mathbf{v}_i \left(t_0 \right) t_c \quad \text{and} \quad \phi_i \left(t_0 + t_c \right) = \phi_i \left(t_0 \right) + \omega_i \left(t_0 \right) t_c . \tag{41}$$

Lubachevsky method

Instead of going through all the particle pairs ($\mathcal{O}\left(N^2\right)$), we create a list of events for each particle. The reordering of the event list takes a time in the order of $\mathcal{O}\left(N \log N\right)$.

In practice, this can be implemented in six arrays (event times, new partners, positions and velocities) of dimension N (number of particles in the system). Alternatively, one creates a list of pointers pointing to a data structure for each particle consisting of six variables.

Lubachevsky method

Storing the last event is needed as particles are only updated after being involved in an event. For each particle i, the time $t^{(i)}$ is the minimal time of all possible collisions involving this particle, i.e.,

$$t^{(i)} = \min_j \left(t_{ij} \right) . \tag{42}$$

Comparing particle i with $N-1$ others can be improved by dividing the systems in sectors such that only neighboring sectors have to be considered in this step.

Lubachevsky method

These sector boundaries have to be treated similar to obstacles such that when particles cross sector boundaries a collision event happens. For each particle i, this step would then be of order $\mathcal{O}(1)$ instead of $\mathcal{O}(N)$. The next collision occurs at time

$$t_c = \min_i \left(t^{(i)} \right). \tag{43}$$

Lubachevsky method

We store $t^{(i)}$ in increasing order in a stack:

- The vector $\mathrm{part}[m]$ points to particle i which is at position m in the stack. (Sometimes also a vector $\mathrm{pos}[i]$ is used to store position m of particle i in the stack.)
- This constitutes an implicit ordering of the collision times $t^{(i)}$, where $m = 1$ points to the smallest time.
- $\mathrm{part}[1]$ is the particle with minimal collision time: $t_c = t^{(\mathrm{part}[1])}$
- After the event for both particles all 6 entries (event times, new partners, positions and velocities) have to be updated. Additionally, the vector $\mathrm{part}[m]$ has to be reordered.

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- After the event for both particles all 6 entries (event times, new partners, positions and velocities) have to be updated. Additionally, the vector $\mathrm{part}[m]$ has to be reordered.

Lubachevsky method

Reordering the times $t^{(i)}$ after each event is of order $\mathcal{O}(\log N)$ when using, e.g., binary trees for sorting. The advantages of this method are that it is not necessary to minimize all the collision times of all the pairs at every step, and that it is unnecessary to update the positions of particles that do not collide. Only the position and velocity of the particle involved in the collision event are updated.

Collision with perfect slip

We now approximate a collision by neglecting the tangential exchange of momentum – i.e. we assume a perfect slip. Only linear momentum and no angular momentum is exchanged. The conservation of momentum leads to

$$\mathbf{v}_i^{\text{after}} = \mathbf{v}_i^{\text{before}} + \frac{\Delta \mathbf{p}}{m_i}, \tag{44}$$

$$\mathbf{v}_j^{\text{after}} = \mathbf{v}_j^{\text{before}} - \frac{\Delta \mathbf{p}}{m_j}, \tag{45}$$

and energy conservation:

$$\frac{1}{2} m_i \left(\mathbf{v}_i^{\text{before}}\right)^2 + \frac{1}{2} m_j \left(\mathbf{v}_j^{\text{before}}\right)^2 = \frac{1}{2} m_i \left(\mathbf{v}_i^{\text{after}}\right)^2 + \frac{1}{2} m_j \left(\mathbf{v}_j^{\text{after}}\right)^2. \tag{46}$$

Collision with perfect slip

The exchanged momentum is

$$\Delta \mathbf{p} = -2m_{\text{eff}} \left[\left(\mathbf{v}_i^{\text{before}} - \mathbf{v}_j^{\text{before}} \right) \cdot \mathbf{n} \right] \mathbf{n} \tag{47}$$

with $m_{\text{eff}} = \frac{m_i m_j}{m_i + m_j}$ being the *effective mass* and $\mathbf{n} = \mathbf{r}_{ij}/|\mathbf{r}_{ij}|$. If $m_i = m_j$, the velocity updates are

$$\mathbf{v}_i{}^{\text{after}} = \mathbf{v}_i^{\text{before}} - v_{ij}^n \cdot \mathbf{n}, \tag{48}$$

$$\mathbf{v}_j{}^{\text{after}} = \mathbf{v}_j^{\text{before}} + v_{ij}^n \cdot \mathbf{n}, \tag{49}$$

with $v_{ij}^n = \left(\mathbf{v}_i^{\text{before}} - \mathbf{v}_j^{\text{before}} \right) \cdot \mathbf{n}$.

Collision with rotation

We now consider two spheres i and j of the same radius R and mass m. Due to friction, angular momentum is exchanged if particles collide with nonzero tangential velocity. The equations of motion for rotation are

$$I\frac{\mathrm{d}\boldsymbol{\omega}_i}{\mathrm{d}t} = \mathbf{r} \wedge \mathbf{f}_i, \tag{50}$$

where I denotes the moment of inertia and $\mathbf{f}_i$ the forces exerted on particle i.

In the case of two colliding disks of radius R, moment of inertia I and mass m, the exchange of angular momentum is

$$\begin{aligned} I\left(\boldsymbol{\omega}_i' - \boldsymbol{\omega}_i\right) &= -Rm\mathbf{n} \wedge \left(\mathbf{v}_i' - \mathbf{v}_i\right), \\ I\left(\boldsymbol{\omega}_j' - \boldsymbol{\omega}_j\right) &= Rm\mathbf{n} \wedge \left(\mathbf{v}_j' - \mathbf{v}_j\right), \end{aligned} \tag{51}$$

with the primed velocities representing the ones after the collision.

Collision with rotation

Together with the conservation of momentum

$$\mathbf{v}_i' + \mathbf{v}_j' = \mathbf{v}_i + \mathbf{v}_j, \tag{52}$$

we obtain the rule for computing the new angular velocities after the collision, i.e.,

$$\boldsymbol{\omega}_i' - \boldsymbol{\omega}_i = \boldsymbol{\omega}_j' - \boldsymbol{\omega}_j = -\frac{Rm}{I}\left(\mathbf{v}_i' - \mathbf{v}_i\right) \wedge \mathbf{n}. \tag{53}$$

The relative velocity between particles i and j is

$$\mathbf{u}_{ij} = \mathbf{v}_i - \mathbf{v}_j - R(\boldsymbol{\omega}_i + \boldsymbol{\omega}_j) \wedge \mathbf{n}. \tag{54}$$

We decompose the relative velocities $\mathbf{u}$ of the particles into their normal and tangential components $\mathbf{u}^n$ and $\mathbf{u}^t$, respectively.

Collision with rotation

It is important to keep in mind that we are at this point not interested in the relative velocities of the centers of mass of the particles. For the angular momentum exchange, the relevant quantity to consider is the relative velocity of the particle surfaces at the contact point. The normal and tangential velocities are given by

$$\begin{aligned} \mathbf{u}_{ij}^{n} &= (\mathbf{u}_{ij}\mathbf{n})\,\mathbf{n}, \\ \mathbf{u}_{ij}^{t} &= \mathbf{u}_{ij} \wedge \mathbf{n} = [(\mathbf{v}_i - \mathbf{v}_j) - R\,(\boldsymbol{\omega}_i + \boldsymbol{\omega}_j)] \wedge \mathbf{n}. \end{aligned} \tag{55}$$

Collision with rotation

General slips are described by

$$\mathbf{u}_{ij}^{t\,\prime} = e_t \mathbf{u}_{ij}^t, \tag{56}$$

where the the *tangential restitution coefficient* e_t accounts for different slip types. The perfect slip collision is recovered for $e_t = 1$ which implies that no rotation energy is transferred from one particle to the other. No slip at all corresponds to $e_t = 0$. Energy conservation only holds if $e_t = 1$. In the case of $e_t < 1$, energy is dissipated.

If we compute the difference of the relative tangential velocities before and after the slip we get

$$\begin{aligned}(1 - e_t)\,\mathbf{u}_{ij}^t &= \mathbf{u}_{ij}^t - \mathbf{u}_{ij}^{t\,\prime} \\ &= -\left[\left(\mathbf{v}_i' - \mathbf{v}_i - \mathbf{v}_j' + \mathbf{v}_j\right) - R\left(\boldsymbol{\omega}_i' - \boldsymbol{\omega}_i + \boldsymbol{\omega}_j' - \boldsymbol{\omega}_j\right) \wedge \mathbf{n}\right].\end{aligned} \tag{57}$$

Collision with rotation

Combining the previous equation with Eq. (97), we obtain an expression without angular velocities

$$\mathbf{u}_{ij}^{t} - \mathbf{u}_{ij}^{t\,\prime} = (1 - e_t)\,\mathbf{u}_{ij}^{t} \tag{58}$$

$$= -\left[2\left(\mathbf{v}_i^{t\prime} - \mathbf{v}_i^{t}\right) + 2q\left(\mathbf{v}_i^{t\prime} - \mathbf{v}_i^{t}\right)\right] \tag{59}$$

and finally

$$\mathbf{v}_i^{t\prime} = \mathbf{v}_i^{t} - \frac{(1 - e_t)\,\mathbf{u}_{ij}^{t}}{2\,(1+q)} \quad \text{with} \quad q = \frac{mR^2}{I}. \tag{60}$$

Collision with rotation

Analogously, we find for the remaining quantities

$$\begin{aligned}
\mathbf{v}_j^{t\prime} &= \mathbf{v}_j^t + \frac{(1-e_t)\,\mathbf{u}_{ij}^t}{2\,(1+q)}, \\
\boldsymbol{\omega}_i' &= \boldsymbol{\omega}_i - \frac{(1-e_t)\,\mathbf{u}_{ij}^t \wedge \mathbf{n}}{2R\,(1+q^{-1})}, \\
\boldsymbol{\omega}_j' &= \boldsymbol{\omega}_j - \frac{(1-e_t)\,\mathbf{u}_{ij}^t \wedge \mathbf{n}}{2R\,(1+q^{-1})}.
\end{aligned} \tag{61}$$

And the updated velocities are

$$\begin{aligned}
\mathbf{v}_i{}' &= \mathbf{v}_i - \mathbf{u}_{ij}^n - \frac{(1-e_t)\,\mathbf{u}_{ij}^t}{2\,(1+q)}, \\
\mathbf{v}_j{}' &= \mathbf{v}_j + \mathbf{u}_{ij}^n + \frac{(1-e_t)\,\mathbf{u}_{ij}^t}{2\,(1+q)}.
\end{aligned} \tag{62}$$

Inelastic collisions

The kinetic energy of interacting and colliding particles is not constant due to friction, plastic deformation or thermal dissipation. We account for energy dissipation effects in an effective manner by introducing the *restitution coefficient*. The restitution coefficient is defined as the ratio of the energy before and after the interaction event, and it describes multiple physical effects, i.e.,

$$r = \frac{E^{\text{after}}}{E^{\text{before}}} = \left(\frac{v^{\text{after}}}{v^{\text{before}}} \right)^2 , \tag{63}$$

where E^{after} and E^{before} are the energies before and after the interaction event, and v^{after} and v^{before} are the corresponding velocities.

Inelastic collisions

Elastic collisions correspond to $r = 1$ whereas perfect plasticity is described by $r = 0$. Similar to our previous discussion of collisions with rotations, we also distinguish between normal and tangential energy transfer and define the corresponding coefficients

$$e_n = \sqrt{r_n} = \frac{v_n^{\text{after}}}{v_n^{\text{before}}}, \tag{64}$$

$$e_t = \sqrt{r_t} = \frac{v_t^{\text{after}}}{v_t^{\text{before}}}. \tag{65}$$

In the case of a bouncing ball, the restitution coefficient accounts for effects such as air friction, deformations and thermal dissipation.