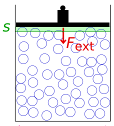
Extended Lagrangian methods in MD: NPT

A dynamic variable (degree of freedom) is added.

Andersen: $\vec r_i = V^{1/3}\vec\xi_i$ $\quad \dot{\vec r}_i = V^{1/3}\dot{\vec\xi}_i$

NO: $\dot{\vec r}_i \overset{?}{=} \mathrm{d}\vec r_i/\mathrm{d}t = \mathrm{d}(V^{1/3}\vec\xi_i)/\mathrm{d}t = \dot V V^{-2/3}\vec\xi_i/3 + V^{1/3}\dot{\vec\xi}_i$

pressure $P\downarrow$



piston area = $\mathcal{A}$

Lagrangian $\mathcal L = \mathcal L(\vec\xi^N, \dot{\vec\xi}^N, V, \dot V)$:

$$\mathcal L = \frac12\sum_{i=1}^N m_i (V^{1/3}\dot{\vec\xi}_i)^2 + \frac12 M_V \dot V^2 - U(V^{1/3}\vec\xi^N) - PV$$

Lagrange equations:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial\mathcal L}{\partial \dot q}\right) = \frac{\partial \mathcal L}{\partial q}$$

Equations of motion:

$$M_V\ddot V = \frac{1}{3V}\left(\sum_{i=1}^N \vec r_i\cdot\vec f_i + 2E_{\mathrm{kin}}\right) - P \equiv P_{\mathrm{cfg}} - P$$

$$V^{1/3}\ddot{\vec\xi}_i = \frac{\vec f_i}{m_i}, \quad \text{back in real variables: } \ddot{\vec r}_i = \frac{\mathrm{d}}{\mathrm{d}t}V^{1/3}\dot{\vec\xi} = \frac{\vec f_i}{m_i} + \frac{\dot V \dot{\vec r}_i}{3V}$$

Extended Lagrangian methods in MD: NPT

The Hamiltonian of the extended system is preserved:

canonically conjugate momentum p

$$\mathcal H = \sum_q \dot q \frac{\partial\mathcal L}{\partial\dot q} - \mathcal L = \frac12\sum_{i=1}^N \frac{p^2}{V^{2/3}m_i} + \frac12\frac{p_V^2}{M_V} + U(V^{1/3}\vec\xi^N) + PV$$
$$\equiv E_{\mathrm{kin}} + E_{\mathrm{kin.\ piston}} + E_{\mathrm{pot}} + PV$$

Other methods:

- generalization (for crystals): Parrinello–Rahman
- Berendsen (friction) method (thermostat required because of dissipation)

$$\dot V = -\mathrm{const}\times(P_{\mathrm{cfg}} - P)$$

- Constraint dynamics

$$P = P_{\mathrm{cfg}}(\vec\xi^N, \dot{\vec\xi}^N, V, \dot V)$$

Nosé–Hoover thermostat

Nosé originally proposed: $\quad \mathcal L = \sum_{i=1}^N \frac{m_i}{2} s^2 \dot{\vec r}_i'^2 - U(\vec r'^N) + \frac{M_s}{2}\dot s^2 - f' k_B T \ln s$

"Rescaling of the kinetic energy by means of velocity, $\dot{\vec r} = s\dot{\vec r}'$; the scaling degree of freedom s has a kinetic as well as potential energy"

Equations of motion (why we write t': see below)

$$\frac{\mathrm{d}}{\mathrm{d}t'}(m_i s^2 \dot{\vec r}_i') = \vec f_i$$
$$M_s \frac{\mathrm{d}^2 s}{\mathrm{d}t'^2} = \sum_{i=1}^N m_i s \dot{\vec r}_i'^2 - \frac{f' k_B T}{s}$$

Hamiltonian

$$\mathcal H = \sum_{i=1}^N \frac{\vec p_i'^2}{2m_i s^2} + U(\vec r'^N) + \frac{p_s'^2}{2M_s} + f'k_BT\ln s$$

Canonically conjugate impulses (momenta):

$$\vec p_i' = \frac{\partial\mathcal L}{\partial \dot{\vec r}_i} = m_i s^2 \dot{\vec r}_i', \qquad p_s' = \frac{\partial \mathcal L}{\partial\dot s} = M_s\dot s$$

Nosé–Hoover thermostat

Nosé: For f' = # of degrees of freedom incl. s we get the canonical distribution od static variables (but see below. . .)

N particles in a general conservative field: $f' = 3N + 1$

Problems: correct velocity is $\dot{\vec r}_i = s\dot{\vec r}_i'$, so if s changes a lot, the integration step should change accordingly

Hoover: $\dot{\vec r}_i = s\dot{\vec r}_i'$ is the same as time rescaling, $\dot{\vec r}_i = s\,\mathrm{d}\vec r_i/\mathrm{d}t'$, i.e.:

$$s\,\mathrm{d}t = \mathrm{d}t' \quad \text{or} \quad \frac{\mathrm{d}}{\mathrm{d}t'} = \frac1s\frac{\mathrm{d}}{\mathrm{d}t}$$

this trick brings us back to the physical (unscaled) velocities and momenta:

$$\vec r_i = \vec r_i', \qquad \dot{\vec r}_i \equiv \frac{\mathrm{d}\vec r_i}{\mathrm{d}t} = s\frac{\mathrm{d}\vec r_i}{\mathrm{d}t'} \equiv s\dot{\vec r}_i', \qquad \vec p_i = \vec p_i'/s, \qquad p_s = p_s'/s$$

Equations of motion:

$$m_i\frac1s\frac{\mathrm{d}}{\mathrm{d}t}s\dot{\vec r}_i = \frac{m_i}{s}[\dot s\dot{\vec r}_i + s\ddot{\vec r}] = \vec f_i$$
$$M_s\frac1s\frac{\mathrm{d}}{\mathrm{d}t}\frac1s\frac{\mathrm{d}}{\mathrm{d}t}s = \frac{M_s}{s}\left[\left(\frac{\ddot s}{s}\right) - \left(\frac{\dot s}{s}\right)^2\right] = \frac1s\left(\sum_{i=1}^N m_i\dot{\vec r}_i^2 - fk_BT\right)$$

Nosé–Hoover thermostat

Another trick: substitution $\xi = \ln s$. Then:

$$\ddot{\vec r}_i = \frac{\vec f_i}{m_i} - \dot{\vec r}_i\dot\xi$$
$$\ddot\xi = \left(\frac{T_{\mathrm{kin}}}{T}-1\right)\tau^{-2}$$

time constant of the thermostat:

$$\tau = \sqrt{\frac{M_s}{fk_BT}}$$

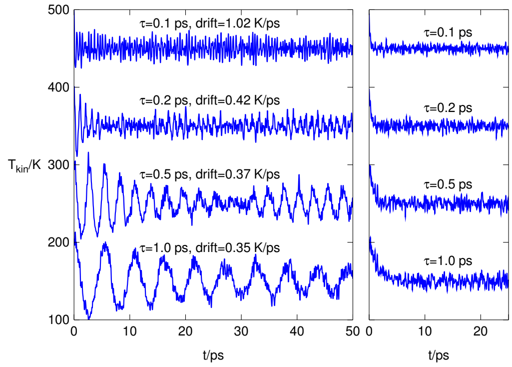
Conserved quantity (not a Hamiltonian because not a function of coordinates and conjugate momenta), can be proven by taking a derivateve:

$$E_{\text{Nosé–Hoover}} = \sum_{i=1}^N \frac12 m_i\dot{\vec r}_i^2 + U + fk_BT\left[\xi + \frac{\tau^2\dot\xi^2}{2}\right] = \mathrm{const}$$

Hoover showed that these equations give the canonical distribution if f is the number of degrees of freedom (without ξ or s)

N particles in a general conservative field: $f = 3N$

Nosé–Hoover $\qquad$ Berendsen



Nosé–Hoover derivation I

Problem of time scaling ($\dot r = s\dot r'$, i.e., $\mathrm{d}t = \mathrm{d}t'/s$)

$$\langle A\rangle = \frac{\int_{t_0}^{t_1}A(t)\mathrm{d}t}{\int_{t_0}^{t_1}\mathrm{d}t} = \frac{\int_{t_0}^{t_1}A(t)\mathrm{d}t'/s}{\int_{t_0}^{t_1}\mathrm{d}t'/s} = \frac{\langle A/s\rangle'}{\langle 1/s\rangle'}$$

The expectation value for $\mathcal H = E$:

$$\langle A\rangle = \frac{\langle A/s\rangle'}{\langle 1/s\rangle'} = \frac{\int \frac As \mathrm{d}p_s' \mathrm{d}\vec p'^N \mathrm{d}s\, \mathrm{d}\vec r'^N \delta(\mathcal H - E)}{\int \frac1s \mathrm{d}p_s'\mathrm{d}\vec p'^N \mathrm{d}s\, \mathrm{d}\vec r'^N\delta(\mathcal H - E)}$$

Nosé–Hoover derivation II

Trick: We will integrate over $\vec p$, not $\vec p'$.

After transformation $\mathrm{d}\vec p_i' = s^3 \mathrm{d}\vec p_i$ we get:

$$\langle A\rangle = \frac{\int A s^{f-1} \mathrm{d}p_s' \mathrm{d}\vec p^N \mathrm{d}s\, \mathrm{d}\vec r^N \delta\left(\mathcal H_0 + \frac{p_s'^2}{2M_s} + fk_BT\ln s - E\right)}{\int s^{f-1} \mathrm{d}p_s' \mathrm{d}\vec p^N \mathrm{d}s\, \mathrm{d}\vec r^N \delta\left(\mathcal H_0 + \frac{p_s'^2}{2M_s} + fk_BT\ln s - E\right)}$$

Where we have donoted

$$\mathcal H_0(\vec p^N,\vec r^N) = \sum_{i=1}^N \frac{\vec p_i^2}{2m_i} + U(\vec r^N)$$

and where the number of degrees of freedom is $f = 3N$.
(If a quantity like the total momentum is conserved, a substitution must be used.)

Nosé–Hoover derivation III

We will integrate over s first. We shall use the formula:

$$\delta(F(s)) = \sum_{s_0, F(s_0)=0}\frac{\delta(s-s_0)}{|F'(s_0)|}$$

So we need all roots of the argument of $\delta()$; there is only one:

$$s_0 = \exp\left[-\frac{1}{fk_BT}\left(\mathcal H_0 + \frac{p_s'^2}{2M_s} - E\right)\right], \qquad F'(s_0) = \frac{fk_BT}{s_0}$$

After integration:

$$\langle A\rangle = \frac{\int A\mathrm{d}p_s' \mathrm{d}\vec p^N \mathrm{d}\vec r^N \exp\left[-\frac{f}{fk_BT}\left(\mathcal H_0 + \frac{p_s'^2}{2M_s}-E\right)\right]}{\int \mathrm{d}p_s' \mathrm{d}\vec p^N \mathrm{d}\vec r^N \exp\left[-\frac{f}{fk_BT}\left(\mathcal H_0 + \frac{p_s'^2}{2M_s}-E\right)\right]}$$

Nosé–Hoover derivation IV

The last integration is over $\mathrm{d}p_s'$. Many terms then cancel out:

$$\langle A\rangle = \frac{\int A \mathrm{d}\vec p^N \mathrm{d}\vec r^N \exp(-\mathcal H_0/k_BT)}{\int \mathrm{d}\vec p^N \mathrm{d}\vec r^N\exp(-\mathcal H_0/k_BT)}, \quad \text{q.e.d}$$

Exercise: thermostats

- Simulate liquid water SPC/E and compare the following thermostats:
  – Berendsen
  – Nosé-Hoover
  – Andersen (for the center of mass)
  – Maxwell (for the center of mass)

The cutoff-electrostatics version `cookce` is recommended (it is faster than Ewald)

The needed files are in /home/guest/termostaty.zip:

```
guest@403-a324-01:~/VY$ unzip ../termostaty.zip
```

`spce.ble` = force field definition of SPC/E
`water.def` = commented simulation parameters

- To start simulation, use the Berensen thermostat and the default method Verlet+Shake:

```
guest@403-a324-01:~/VY$ cookce spce water -s
thermostat="Berendsen"
init="crystal"
```

Stop the simulation by pressing ctrl-C at temperature around 500 K

Exercise: thermostats

- Now try various thermostats (`-w0` prevents writing the final configuration):

```
guest@403-a324-01:~/VY$ cookce spce water -s -w0
tau.T=...
thermostat="..."
```

Nosé–Hoover combined with Verlet+Shake uses a velocity predictor (there are other methods, too)

You may try also the Gear integration combined with the Berendsen and Nosé–Hoover thermostat (Gear 4th order = option `-m4`), e.g.:

```
guest@403-a324-01:~/VY$ cookce spce water -m4 -s -w0
thermostat="Nose-Hoover"
```

The Gear integration is less accurate with `thermostat="Andersen"` and `"Maxwell"` (higher-order terms are not accurate)

- After a few ps run look at the convergence profile of temperatures:

```
guest@403-a324-01:~/VY$ showcp -p water Tkin
```

(white = total $T_{\rm kin}$, yellow = rotational, cyan = translational)