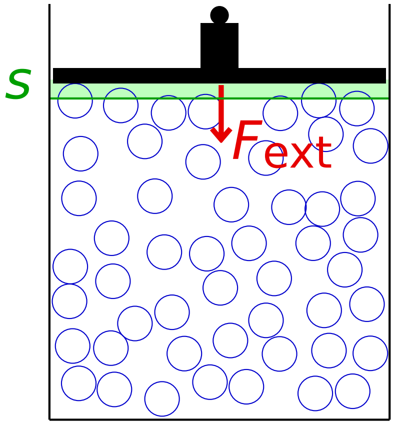
Extended Lagrangian methods in MD: NPT

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: $\dot{\vec r}_i \overset{?}{=} \mathrm{d}\vec r_i/\mathrm{d}t = \mathrm{d}(V^{1/3}\vec\xi_i)/\mathrm{d}t = \dot V V^{-2/3}\vec\xi_i/3 + V^{1/3}\dot{\vec\xi}_i$



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

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

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:

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

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

Extended Lagrangian methods in MD: NPT

The Hamiltonian of the extended system is preserved:

canonically conjugate momentum p

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

$$\equiv E_{\text{kin}} + E_{\text{kin. piston}} + E_{\text{pot}} + PV$$

Other methods:

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

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

- Constraint dynamics

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

Nosé–Hoover thermostat

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

"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)

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

Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\vec{p}_i'^2}{2 m_i s^2} + U(\vec{r}'^N) + \frac{p_s'^2}{2M_s} + f' k_\mathrm{B} T \ln s$$

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.:

$$s\mathrm{d}t = \mathrm{d}t' \quad \text{or} \quad \frac{\mathrm{d}}{\mathrm{d}t'} = \frac{1}{s}\frac{\mathrm{d}}{\mathrm{d}t}$$

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:

$$m_i\frac{1}{s}\frac{\mathrm{d}}{\mathrm{d}t}s\dot{\vec{r}}_i = \frac{m_i}{s}[\dot{s}\dot{\vec{r}}_i + s\ddot{\vec{r}}] = \vec{f}_i$$

$$M_s\frac{1}{s}\frac{\mathrm{d}}{\mathrm{d}t}\frac{1}{s}\frac{\mathrm{d}}{\mathrm{d}t}s = \frac{M_s}{s}\left[\left(\frac{\ddot{s}}{s}\right) - \left(\frac{\dot{s}}{s}\right)^2\right] = \frac{1}{s}\left(\sum_{i=1}^{N} m_i\dot{\vec{r}}_i^{\,2} - fk_\mathrm{B}T\right)$$

Nosé–Hoover thermostat

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

$$\ddot{\vec{r}}_i = \frac{\vec{f}_i}{m_i} - \dot{\vec{r}}_i \dot{\xi}$$

$$\ddot{\xi} = \left(\frac{T_{\text{kin}}}{T} - 1 \right) \tau^{-2}$$

time constant of the thermostat:

$$\tau = \sqrt{\frac{M_s}{f k_{\text{B}} T}}$$

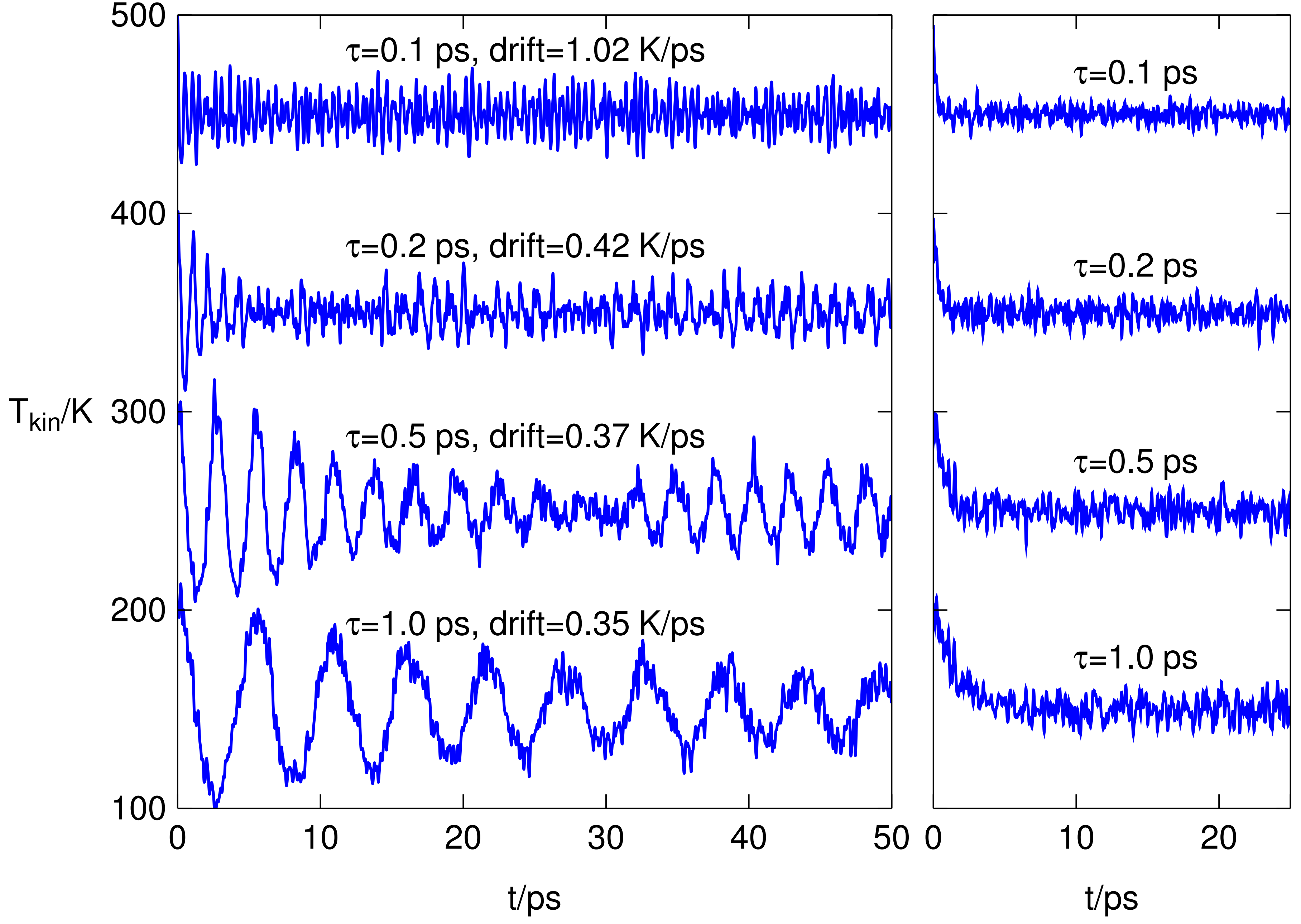
Conserved quantity (not a Hamiltonian because not a function of coordinates and conjugate momenta), can be proven by taking a derivateve:

$$E_{\text{Nosé–Hoover}} = \sum_{i=1}^{N} \frac{1}{2} m_i \dot{r}_i^2 + U + f k_{\text{B}} T \left[\xi + \frac{\tau^2 \dot{\xi}^2}{2} \right] = \text{const}$$

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   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 $\mathcal{H} = E$:

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

Nosé–Hoover derivation II

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

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

$$\langle A \rangle = \frac{\int A s^{f-1} dp_s' d\vec{p}^N ds d\vec{r}^N \delta\left(\mathcal{H}_0 + \frac{p_s'^2}{2M_s} + f k_B T \ln s - E\right)}{\int s^{f-1} dp_s' d\vec{p}^N ds d\vec{r}^N \delta\left(\mathcal{H}_0 + \frac{p_s'^2}{2M_s} + f k_B T \ln s - E\right)}$$

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:

$$s_0 = \exp\left[-\frac{1}{fk_\mathrm{B}T}\left(\mathcal{H}_0 + \frac{p_s'^2}{2M_s} - E\right)\right], \qquad F'(s_0) = \frac{fk_\mathrm{B}T}{s_0}$$

After integration:

$$\langle A \rangle = \frac{\int A\,\mathrm{d}p_s'\,\mathrm{d}\vec{p}^N\,\mathrm{d}\vec{r}^N \exp\left[-\frac{f}{fk_\mathrm{B}T}\left(\mathcal{H}_0 + \frac{p_s'^2}{2M_s} - E\right)\right]}{\int \mathrm{d}p_s'\,\mathrm{d}\vec{p}^N\,\mathrm{d}\vec{r}^N \exp\left[-\frac{f}{fk_\mathrm{B}T}\left(\mathcal{H}_0 + \frac{p_s'^2}{2M_s} - E\right)\right]}$$

Nosé–Hoover derivation IV

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

$$\langle A \rangle = \frac{\int A \mathrm{d}\vec{p}^N \mathrm{d}\vec{r}^N \exp(-\mathcal{H}_0/k_\mathrm{B}T)}{\int \mathrm{d}\vec{p}^N \mathrm{d}\vec{r}^N \exp(-\mathcal{H}_0/k_\mathrm{B}T)}, \quad \text{q.e.d}$$

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_{kin}, yellow = rotational, cyan = translational)