MD Ensembles and Thermostats

Konstanze R. Hahn

Department of Physics, University of Cagliari, Italy

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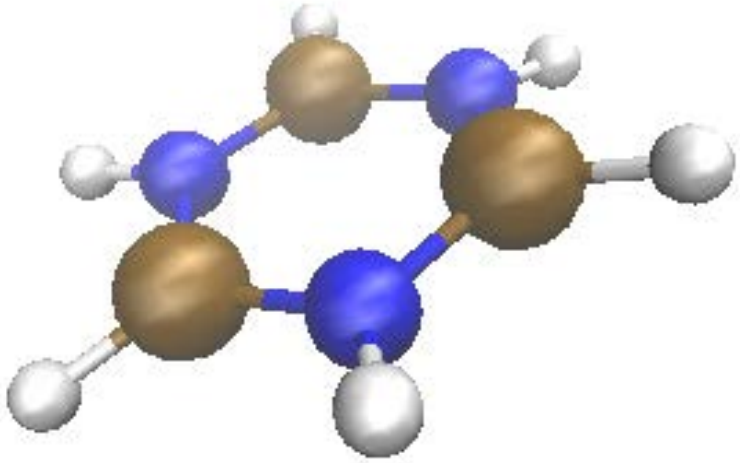


Goal of MD simulations

- obtain ensemble average from trajectory

$$\langle A \rangle = \int P(p,t)A(p,r)dpdr = \int A(p(t),r(t))dt$$

P: probability p: momenta

A: property r: position

- solve equations of motion

$$F_i = m_i \ddot{\mathbf{r}}_i$$

Newton

$$\mathcal{H}(\mathbf{r},\mathbf{p}) = \frac{|\mathbf{p}|^2}{2m} + \mathcal{U}(r)$$

Hamiltonian

Ensembles in MD

- ensemble: all microstates ($\mathbf{r}$, $\mathbf{p}$) that are accessible to the simulation and provide probability of each microstate

particle number *N*	chemical potential *μ*
volume *V*	pressure *P*
energy *E*	temperature *T*

- *NVE* microcanonical
- *NVT* canonical
- *NPT* isothermal-isobaric

Ensembles in MD

- ideal MD conserves energy and entropy: microcanonical ensemble (*NVE*)

- realistic systems change energy, volume and particles with external reservoirs → more difficult

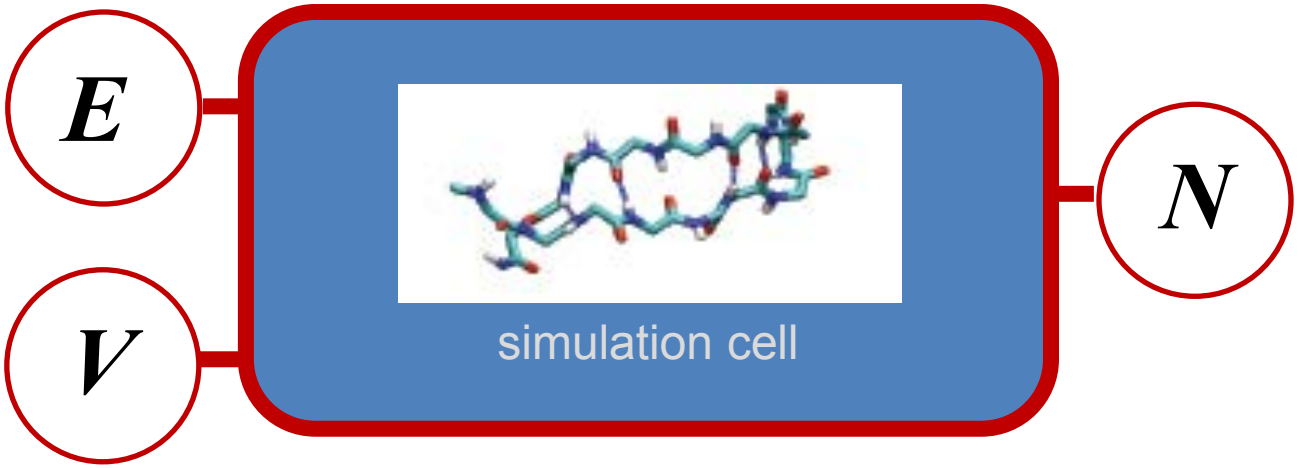
- canonical (*NVT*) most frequently used

$$P \propto e^{-\frac{E(\mathbf{r})}{k_b T}}$$

NVE – microcanonical ensemble

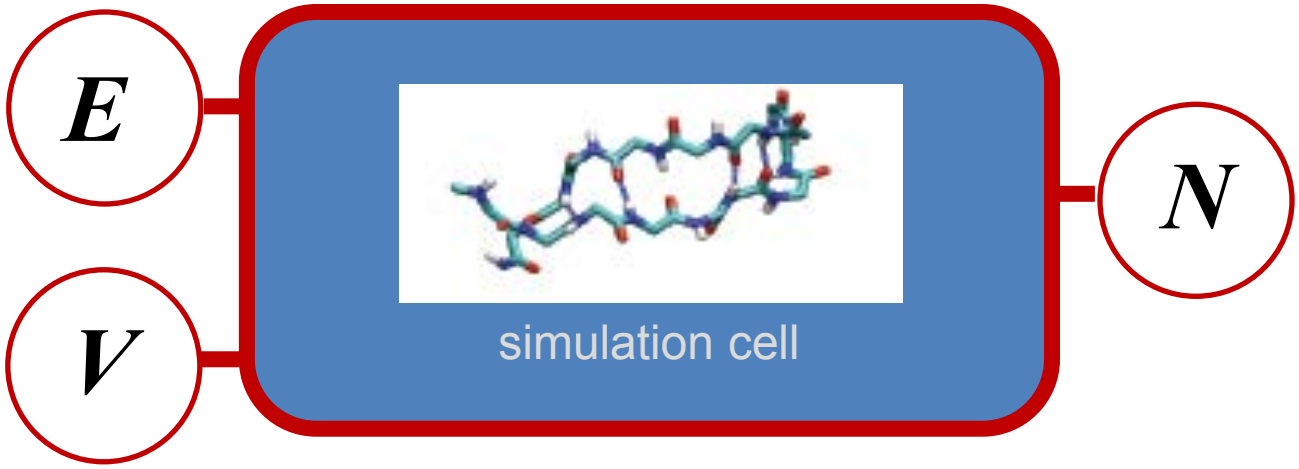
- system isolated with constant number of particles *N*, volume *V* and energy *E*
- solving equations of motion without temperature or pressure control

$$F_i = m_i \ddot{\mathbf{r}}_i$$



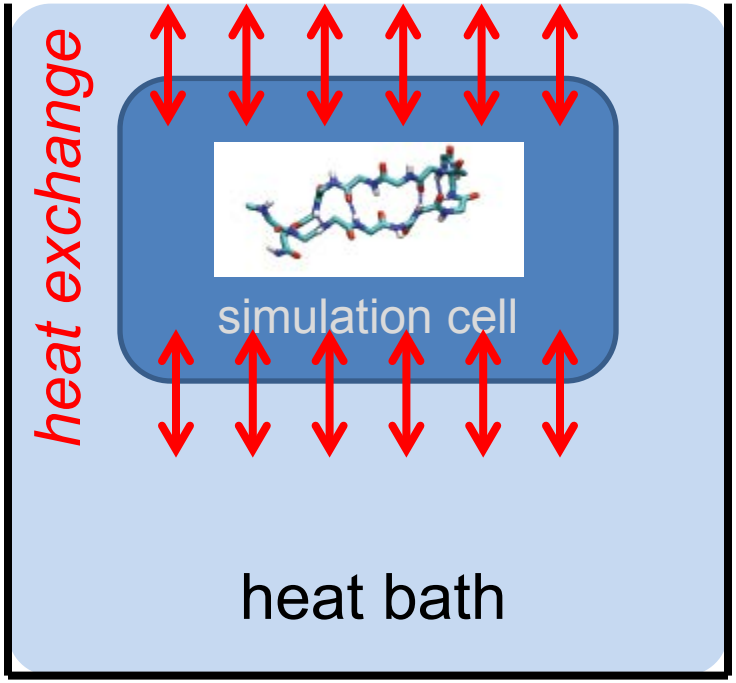
NVE – microcanonical ensemble

- drift in *E* resulting from rounding and truncation errors
- time reversible
- dynamical variables well defined
- required initial conditions: position and velocity



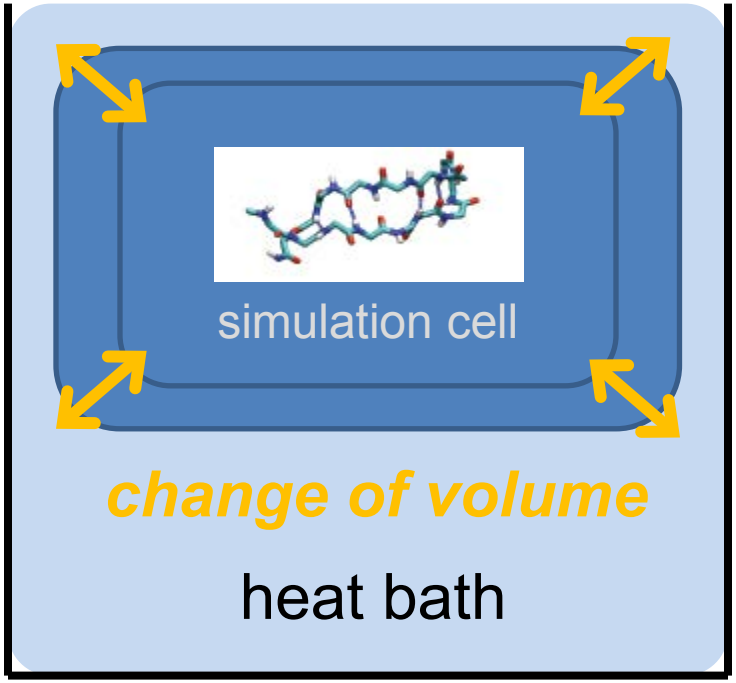
NVT – canonical ensemble

- constant number of particles *N* and volume *V*
- system in thermal contact with heat bath



NPT – isothermal-isobaric ensemble

- constant number of particles *N*, pressure *p* and temperature *T*
- use of thermostat and barostat



Lagrangian equations of motion

- extended ensemble
- difference between kinetic and potential energy

$$\mathcal{L}\left(\mathbf{r}^N, \mathbf{v}^N\right) = K\left(\mathbf{v}^N\right) - U\left(\mathbf{r}^N\right)$$

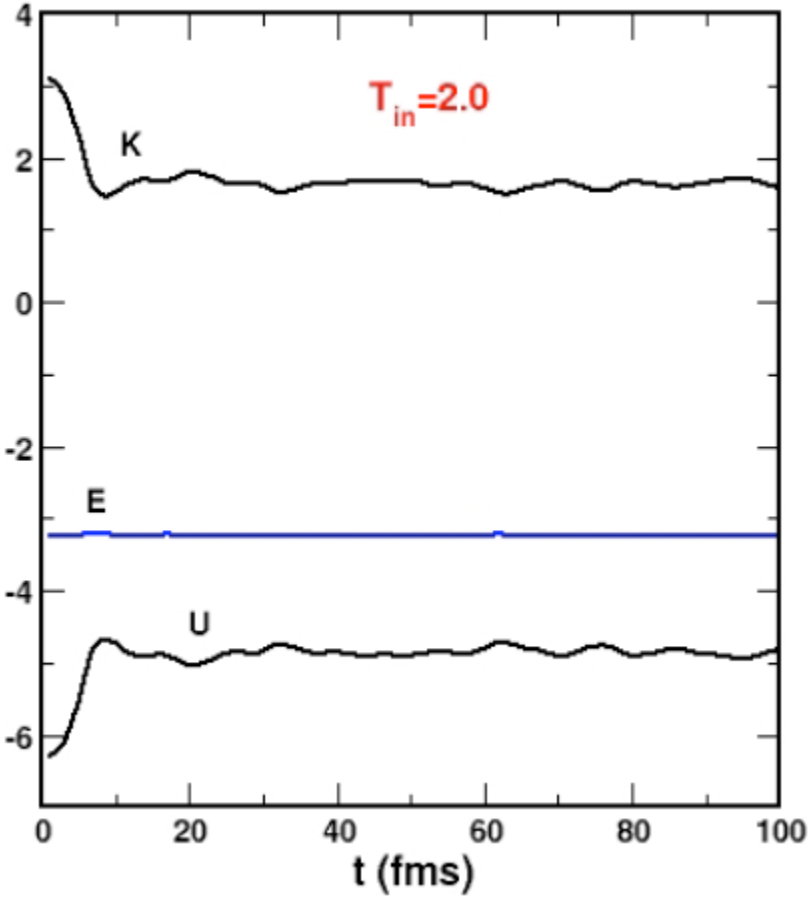
- assumption: K only dependent on v, U only on r

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \mathbf{v}_i} - \frac{\partial \mathcal{L}}{\partial \mathbf{r}_i} = 0$$

- Hamiltonian $\mathcal{H} = \sum_i \mathbf{p}_i \cdot \mathbf{v}_i - \mathcal{L} = \sum_i \mathbf{p}_i \cdot \mathbf{v}_i + \mathcal{U}$

kinetic energy *potential energy*

Lagrangian equations of motion



$$\mathcal{H} = \sum_i \mathbf{p}_i \cdot \mathbf{v}_i - \mathcal{L} = \sum_i \mathbf{p}_i \cdot \mathbf{v}_i + \mathcal{U}$$

Calculation of temperature

$$\langle K \rangle = \frac{N_f}{2} k_B T$$

K: kinetic energy

$$K = \sum_i \frac{p_i^{\,2}}{2m_i}$$

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

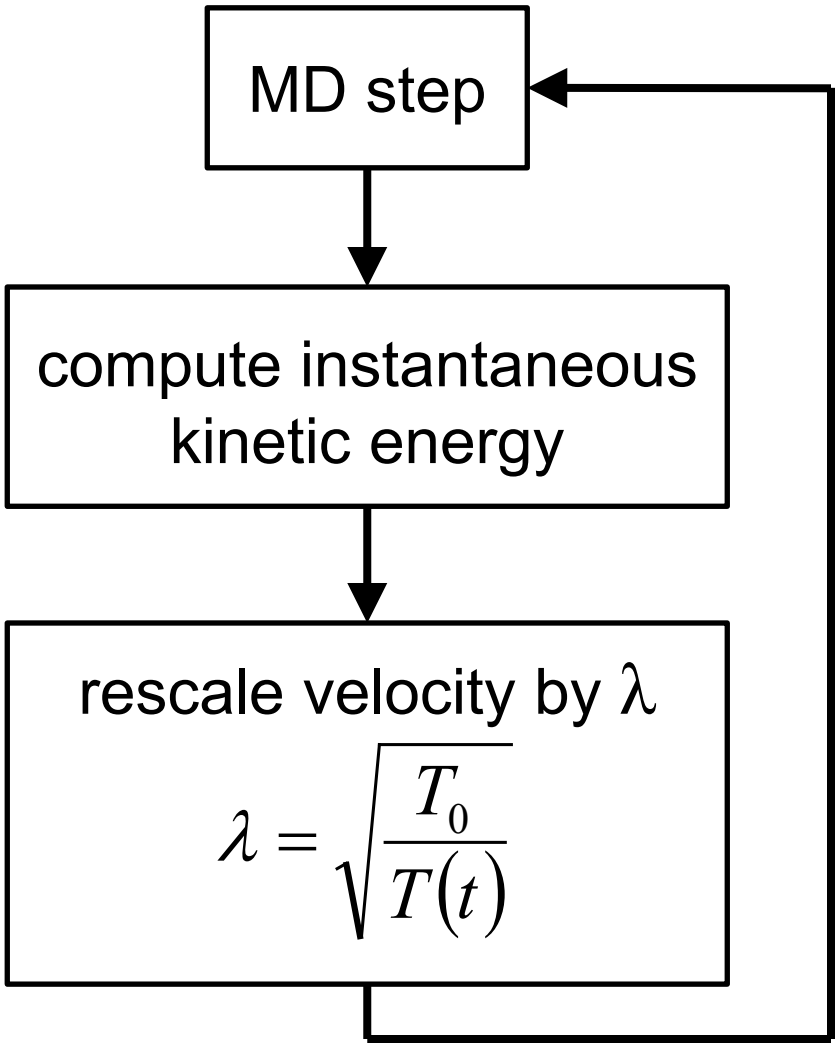
Velocity rescaling

- multiply velocities by a factor λ to obtain desired temperature T_0

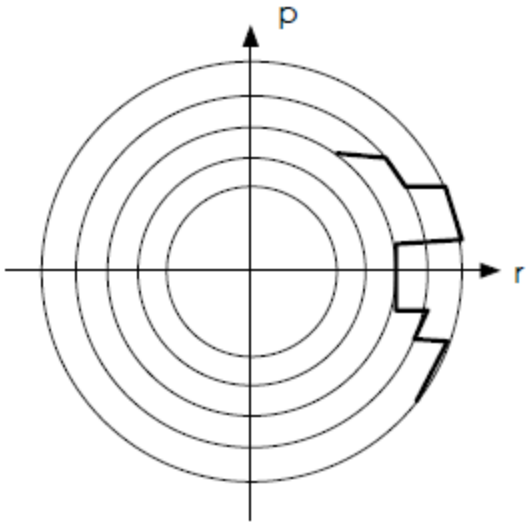
$$\Delta T = \frac{1}{2}\sum_{i=1}^{N}\frac{2}{3}\frac{m_i\left(\lambda v_i\right)^2}{Nk_B} - \frac{1}{2}\sum_{i=1}^{N}\frac{2}{3}\frac{m_i v_i^2}{Nk_b} = \left(\lambda^2 - 1\right)T(t)$$

$$\lambda = \sqrt{\frac{T_0}{T(t)}}$$

Velocity rescaling



- straight forward
- does not correspond to any ensemble



Berendsen thermostat

- system weakly coupled to heat bath with temperature T_{bath}

$$\frac{dT(t)}{dt} = \frac{1}{\tau}\left(T_{\text{bath}} - T(t)\right)$$

τ : coupling parameter

- rescaling at each step, with temperature change

$$\Delta T = \frac{\partial t}{\tau}\left(T_{\text{bath}} - T(t)\right)$$

- scaling factor

$$\left(\lambda^2 - 1\right)T(t) = \frac{\partial t}{\tau}\left(T_{\text{bath}} - T(t)\right)$$

Berendsen, JCP (1984)

Berendsen thermostat

- smoother than velocity rescaling
- suppresses fluctuations in kinetic energy

  → no ensemble
- global thermostat
- for large systems good approximation

Andersen thermostat

- random collisions of molecules with an imaginary heat bath (randomize velocities)

$$P(p_1, p_2, \ldots) \propto \exp\left(-\frac{p_1^2}{2k_B T m_1}\right) \times \exp\left(-\frac{p_2^2}{2k_B T m_2}\right) \times \ldots$$

$$p_{new} = \sqrt{mk_B T}\,R$$

random Gaussian number

Andersen, JCP (1980)

Andersen thermostat

- canonical ensemble (*NVT*)
- stochastic
- local thermostat
- destroys momentum transport (true molecular kinetics are not preserved)

  → cannot be used to calculate transport properties (diffusion coefficient)

Langevin thermostat

- velocity corrected by random force and constant friction

$$m\ddot{\mathbf{r}}_i = -\frac{\partial U}{\partial \mathbf{r}_i} - m\Gamma\dot{\mathbf{r}}_i + \mathrm{W}_i(t)$$

Γ : friction coefficient

W: random force

- relation between magnitude of force and friction

$$\left\langle \mathbf{W}_i(t), \mathbf{W}_j(t') \right\rangle = \partial_{ij}\partial(t-t')\,6m\,\Gamma k_B T$$

Schneider and Stoll, PRB (1978)

Langevin thermostat

- canonical ensemble (*NVT*)
- local thermostat
- ergodic
- allows the use of large time steps
- destroys momentum transport → cannot be used to calculate transport properties (diffusion coefficient)

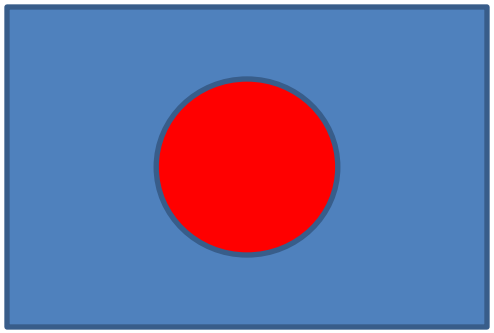
Local and global thermostats

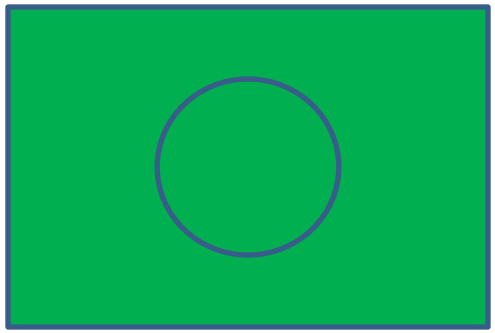
Berendsen (global)

$$\dot{p}_i = -\gamma\, p_i = -\left[\frac{1}{2\tau}\left(\frac{\overline{K}}{K} - 1\right)\right] p_i$$

Langevin (local)

$$\dot{p}_i = -\gamma\, p_i + \sqrt{2 m_i k_B T \gamma}\,\eta_i$$





if needed: different thermostats for different atoms

Nosé thermostat

- add two additional degrees of freedom the system:

  s – position of imaginary heat reservoir

  p_s – conjugate momentum of imaginary heat reservoir

- additional parameter

  Q – effective mass $\quad p_s = \frac{\partial \mathcal{L}}{\partial \dot{s}} = Q\dot{s}$

- momenta conjugate to $\mathbf{r}_i$ $\quad \mathbf{p}_i = \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}_i} = m_i s^2 \dot{\mathbf{r}}_i$

- Hamiltonian $\quad H_N = \sum_i \frac{\mathbf{p}_i^2}{2m_i s^2} + \mathcal{U}(\mathbf{r}^N) + \frac{p_s^2}{2Q} + gk_B T \ln s$

Nose, JCP (1984)

Nosé thermostat

- canonical ensemble (*NVT*)
- smooth
- deterministic
- time-reversible

- fluctuation of real time step resulting from scaling factor *s*

$$dt' = sdt$$

Nosé-Hoover thermostat

- eliminate problem of “real”-time averages

$$H_{NH} = \sum_i \frac{\mathbf{p}_i}{2m_i} + \mathcal{U}\left(\mathbf{r}^N\right) + \frac{1}{2} Q \xi^2 - g k_B T \ln s$$

$$g = 3N$$

- friction coefficient

$$\dot{\xi} = \frac{1}{Q}\left(\sum_i \frac{\mathbf{p}_i}{m_i} - g k_B T \right)$$

$$\xi = \frac{\dot{s}}{s} = \frac{d \ln s}{dt}$$

Hoover, PRA (1985)

Nosé-Hoover thermostat

- second order equation on *K*
- proper sampling
- deterministic (can be non-ergodic)
- second order → can be oscillating

Nosé-Hoover chains

- canonical ensemble (*NVT*)

$$\dot{\xi}_1 = \frac{1}{Q_1}\left(\sum_i \frac{\mathbf{p}_i^2}{m_i} - gk_BT\right) - \xi_1\xi_2$$

$$\dot{\xi}_j = \frac{1}{Q_j}\left(Q_{j-1}\xi_{j-1}^2 - k_BT\right) - \xi_j\xi_{j+1}$$

$$\dot{\xi}_M = \frac{1}{Q_M}\left(Q_{M-1}\xi_{M-1}^2 - k_BT\right)$$

Martyna et al., JCP (1992)

Nosé-Hoover chains

- higher order equation on K
- canonical
- ergodic
- additional equations for chaotic behavior

Basic input in CP2K

```
&GLOBAL
  PROJECT  MD_NVE
  RUN_TYPE MD
  PRINT_LEVEL LOW
  WALLTIME 600
&END GLOBAL

&MOTION
  &MD
    ENSEMBLE NVE
    STEPS 1000
    TIMESTEP 0.5
    TEMPERATURE  300.0
  &END MD
&END MOTION
```

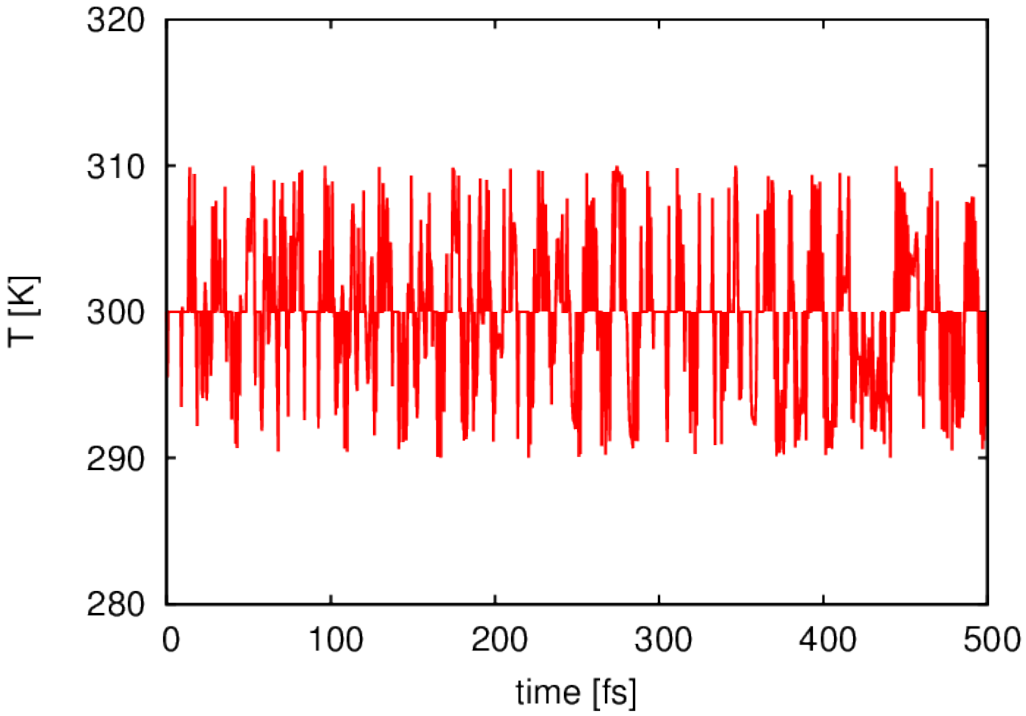
Ensembles in CP2K

```
&MOTION
  &MD
    ENSEMBLE NVE
    STEPS 1000
    TIMESTEP 0.5
    TEMPERATURE  300.0
  &END MD
&END MOTION
```

- microcanonical: **NVE**
- canonical: **NVT**
- canonical using Langevin: **LANGEVIN**
- isobaric-isothermic: **NPT_F**
- isobaric-isothermic in isotropic cell: **NPT_I**
- constant pressure: **NPE_F**
- constant pressure in isotropic cell: **NPE_I**
- constant kinetic energy: **ISOKIN**
- HYDROSTATICSHOCK, MSST, MSST_DAMPED, NVT_ADIABATIC,…

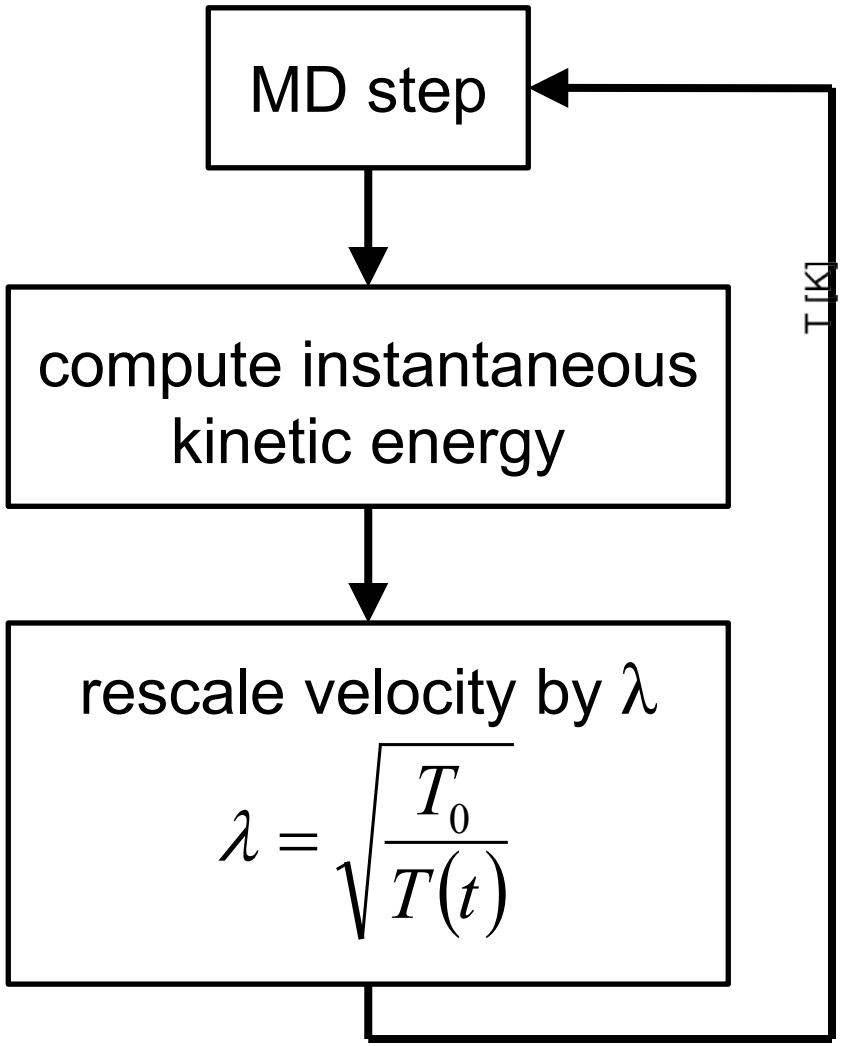
Ensembles in CP2K

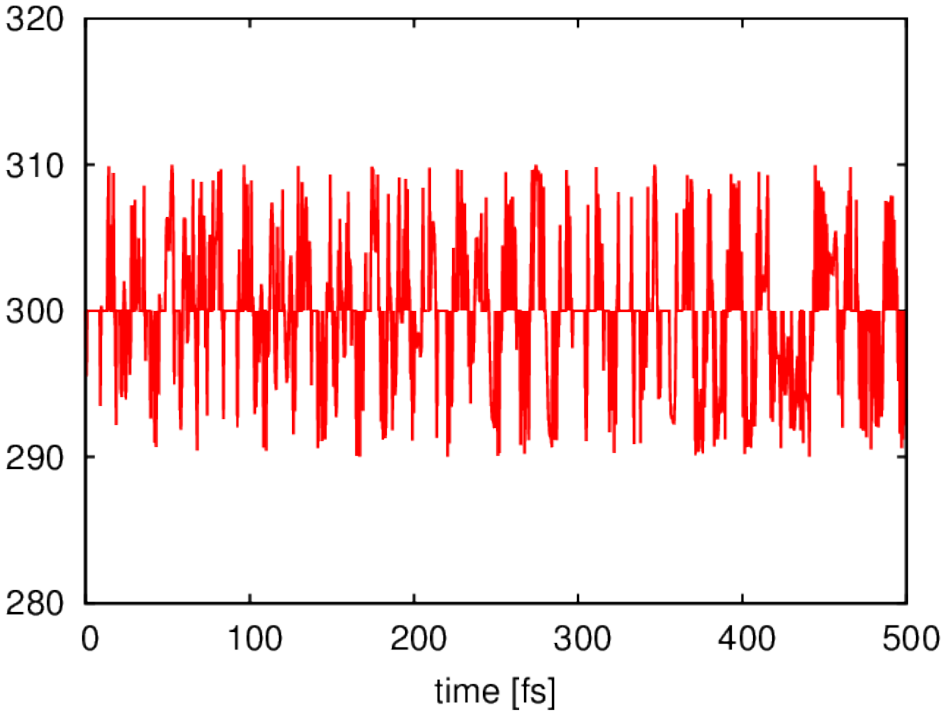
```
&MOTION
  &MD
    ENSEMBLE NVE
    STEPS 1000
    TIMESTEP 0.5
    TEMPERATURE  300.0
    TEMP_TOL 10
  &END MD
&END MOTION
```



enable **velocity rescaling**
when $T < 290$ K or $T > 310$ K

Velocity rescaling





$T < 290$ K or $T > 310$ K

Ensembles in CP2K - CSVR

Kinetic energy

$$dK = \sum_i \frac{f_i \cdot p_i}{m_i} dt + \left(\overline{K} - K\right)\frac{dt}{\tau} + 2\sqrt{\frac{K\overline{K}}{N_f}}\frac{dW}{\sqrt{\tau}} \quad \left(\tau = \frac{1}{2\gamma}\right)$$

thermostat part

$$dK = \left(\overline{K} - K\right)\frac{dt}{\tau} + 2\sqrt{\frac{K\overline{K}}{N_f}}\frac{dW}{\sqrt{\tau}}$$

Berendsen thermostat

noise gives correct fluctuations

Bussi, Donadio and Parrinello, JCP (2007)

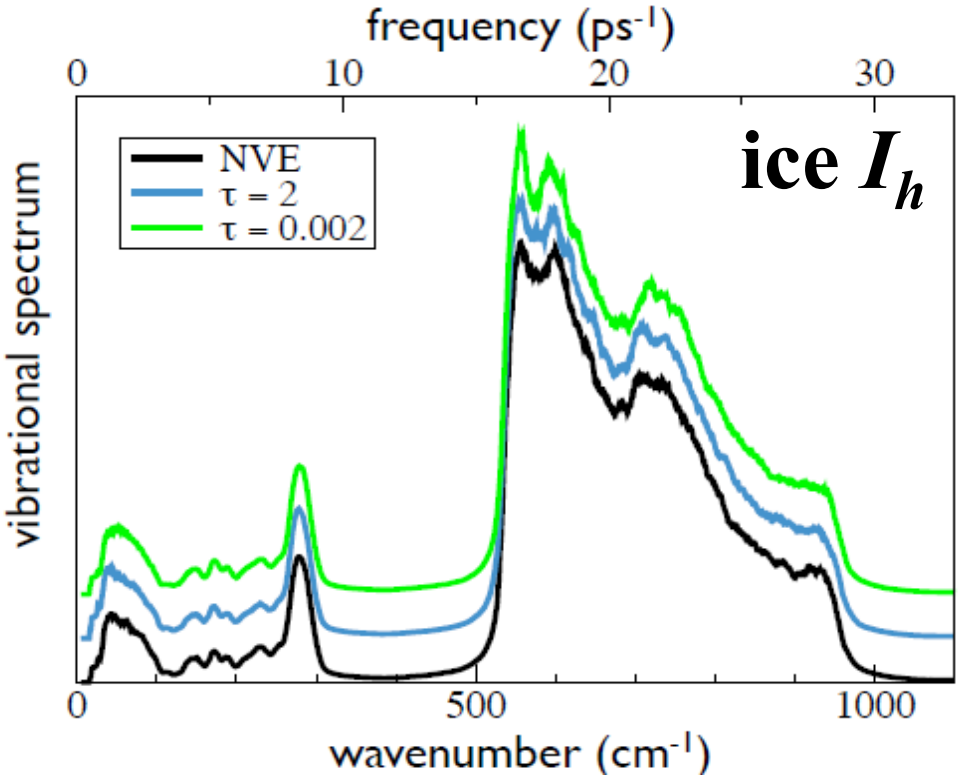
Ensembles in CP2K - CSVR

$$dK = \left(\overline{K} - K\right)\frac{dt}{\tau} + 2\sqrt{\frac{K\overline{K}}{N_f}}\frac{dW}{\sqrt{\tau}}$$

- stochastic velocity rescaling for $\tau = 0$
- global
- correct fluctuations
- preserves dynamic properties
- recovers Langevin for single degree of freedom

Ensembles in CP2K - CSVR

```
&MOTION
  &MD
    ENSEMBLE NVT
    STEPS 1000
    TIMESTEP 0.5
    TEMPERATURE  300.0
    &THERMOSTAT
       TYPE CSVR
       REGION GLOBAL
       &CSVR
          TIMECON 50.
       &END CSVR
    &END THERMOSTAT
  &END MD
&END MOTION
```

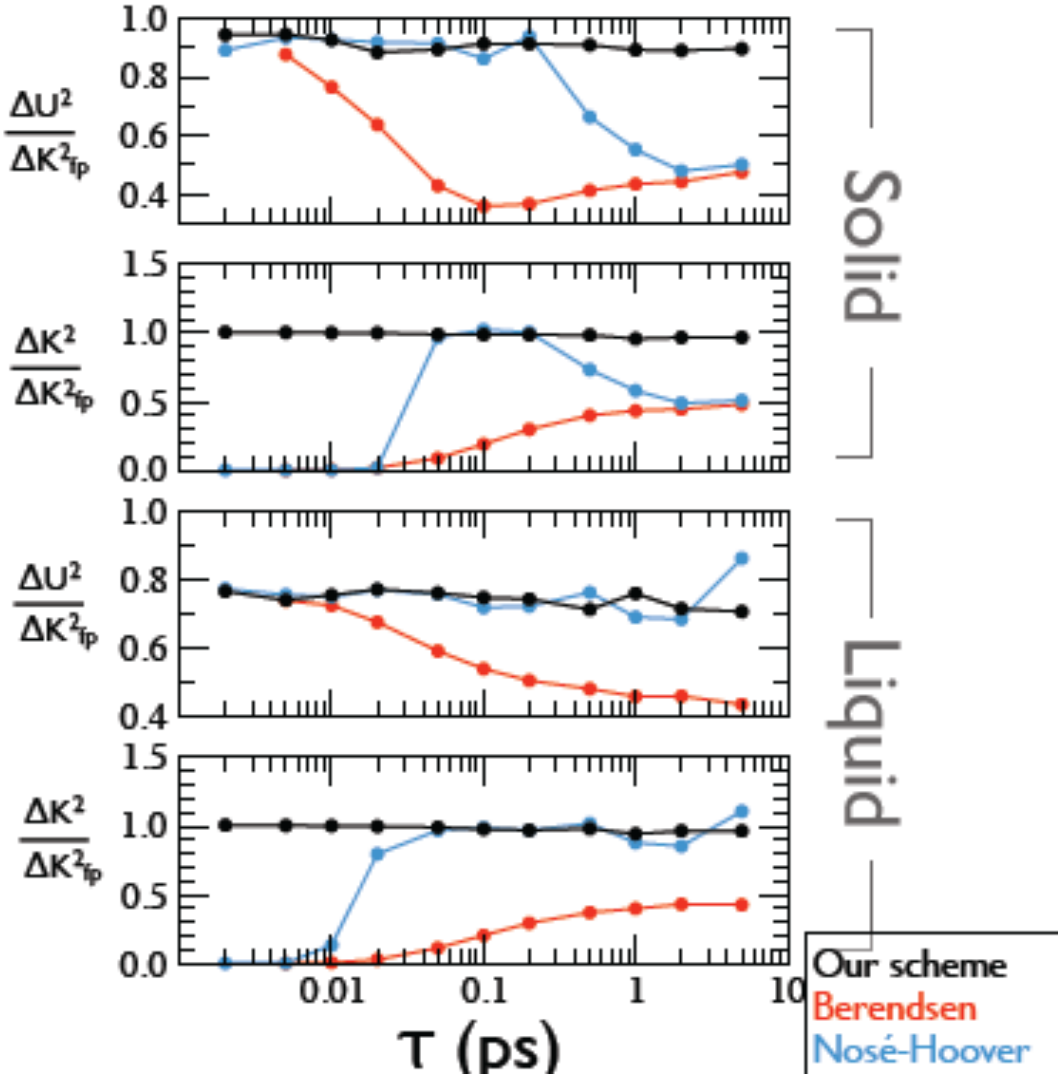


Ensembles in CP2K - CSVR

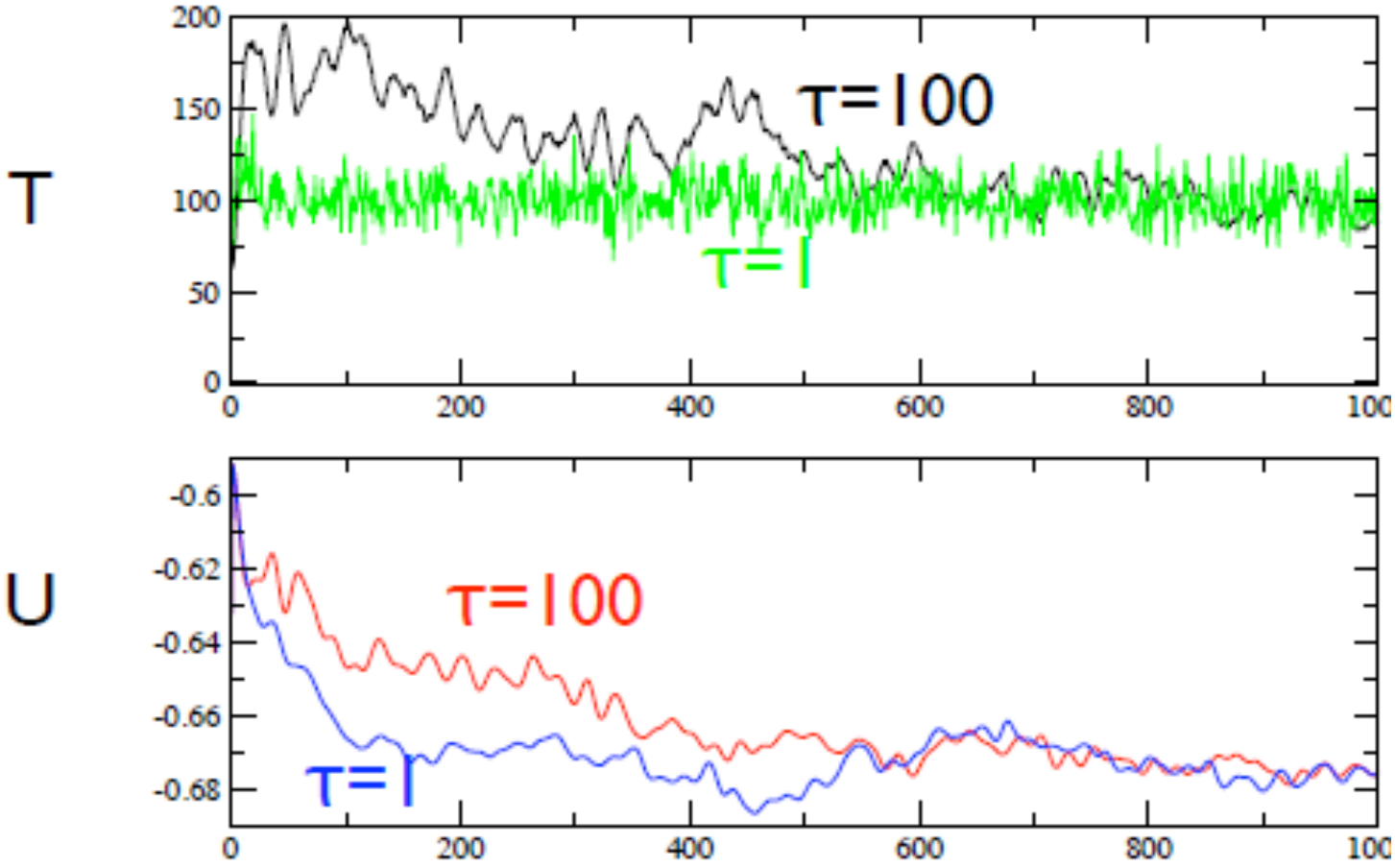
Energy fluctuations (in units of $N_f k_b^2 T^2/2$) from a 1.0 ns run.

Berendsen: wrong ensemble

Nosé-Hoover: not-ergodic, especially in solid (NHC solve this)



Ensembles in CP2K - CSVR



Overview of thermostats

	tune	cont.	L/G	correct	ergodic	cons. q.	determ.	cp2k
Velocity rescaling			G		?		X	
Andersen	X		L	X	X			
Berendsen	X	X	G		?		X	
Nosé-Hoover	X	X	L/G	X		X	X	NOSE*
Nosé-Hoover chains	X	X	L/G	X	X	X	X	NOSE
Langevin	X	X	L	X	X	X		CSVR**
Stochastic velocity rescaling	X	X	L/G	X	X	X		CSVR

*use "LENGTH=1"
**use "MASSIVE"

Recipes for MD calculations

- equilibration:
  - strong thermostat (small τ)
  - local for ab initio; local or global for classical
- normal production:
  - global, τ=1-100 fs
- difficult temperature control:
  - local, τ=1-100 fs
- two or more “separate” subsystems (solid-liquid, QMMM,…)
  - global, one per subsystem

- always check energy conservation
- always check kinetic energy fluctuations

Analysis of trajectories

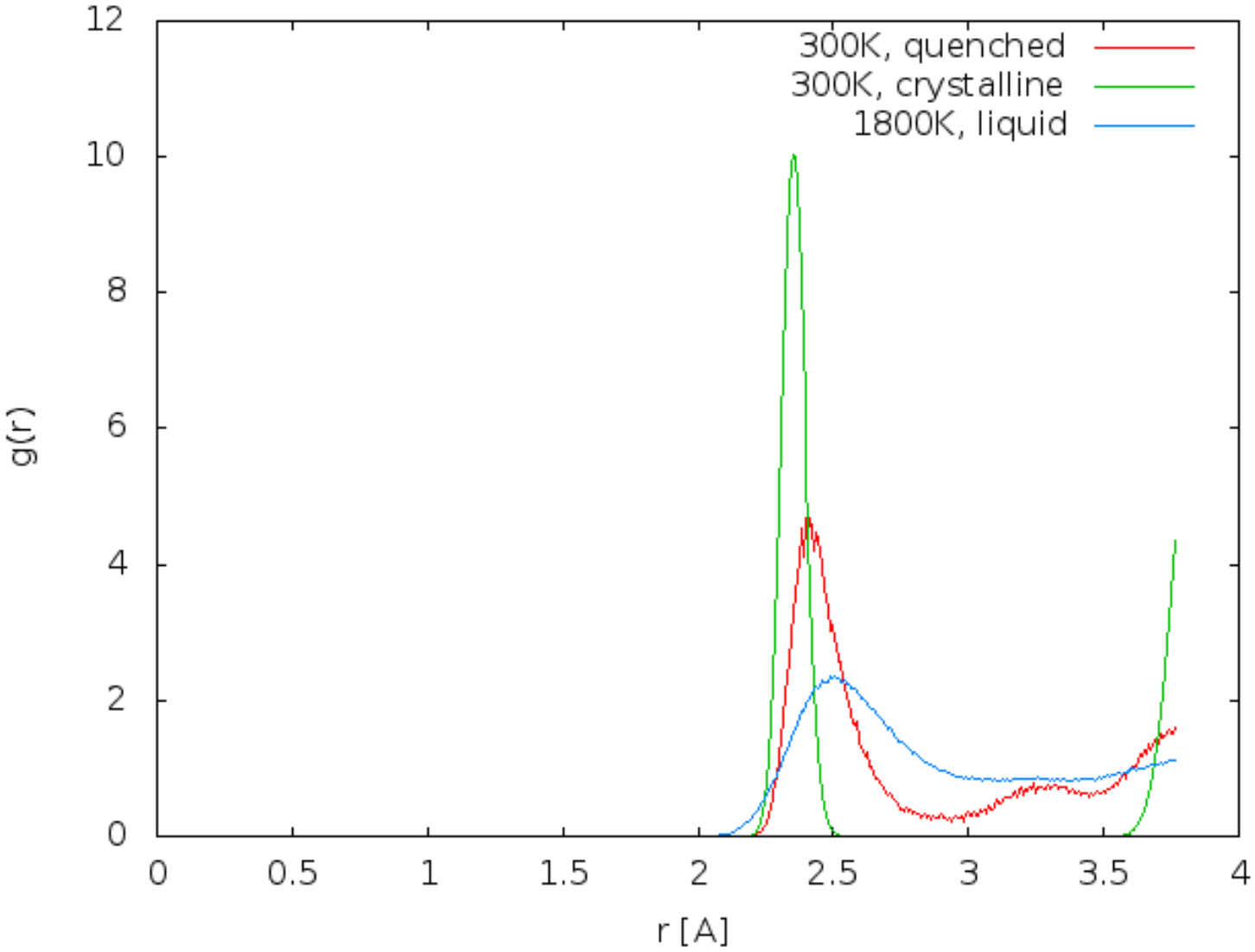
$$\langle A \rangle = \int P(p,t)A(p,r)dpdr = \int A(p(t),r(t))dt$$

from trajectory file *[project]-pos-1.xyz*

property A

- *g* or *r*

g(r) of Si


300K, quenched
300K, crystalline
1800K, liquid
g(r)
r [A]
0
2
4
6
8
10
12
0
0.5
1
1.5
2
2.5
3
3.5
4

Analysis of trajectories

$$\langle A \rangle = \int P(p,t)A(p,r)dpdr = \int A(p(t),r(t))dt$$

from trajectory file *[project]-pos-1.xyz*

property A

- *g* or *r*
- mean square displacement (MSD)
- bond length
- coordination number
- …..

REFTRAJ in CP2K

```
&MOTION
  &MD
    ENSEMBLE REFTRAJ
    STEPS 5
    &REFTRAJ
      TRAJ_FILE_NAME traj.xyz
      FIRST_SNAPSHOT 1
      LAST_SNAPSHOT 5
    &END REFTRAJ
  &END MD
&END MOTION
```

```
&SUBSYS
...
  &COLVAR
     &COORDINATION
       KINDS_FROM  O
       KINDS_TO   Si
       R_0 [angstrom]  1.8
     &END COORDINATION
  &END COLVAR
&END SUBSYS
```

Mean square displacement

$$\mathrm{MSD}(t) = \left\langle \Delta \mathbf{r}_i(t)^2 \right\rangle = \left\langle \left(\mathbf{r}_i(t) - \mathbf{r}_i(0)\right)^2 \right\rangle$$

```
&MOTION
  &MD
    ENSEMBLE REFTRAJ
    STEPS 5
    &REFTRAJ
      TRAJ_FILE_NAME traj.xyz
      FIRST_SNAPSHOT 1
      LAST_SNAPSHOT 5
      &MSD
        MSD_PER_KIND
        REF0_FILENAME ref0.xyz
      &END MSD
    &END REFTRAJ
  &END MD
&END MOTION
```

reference cell