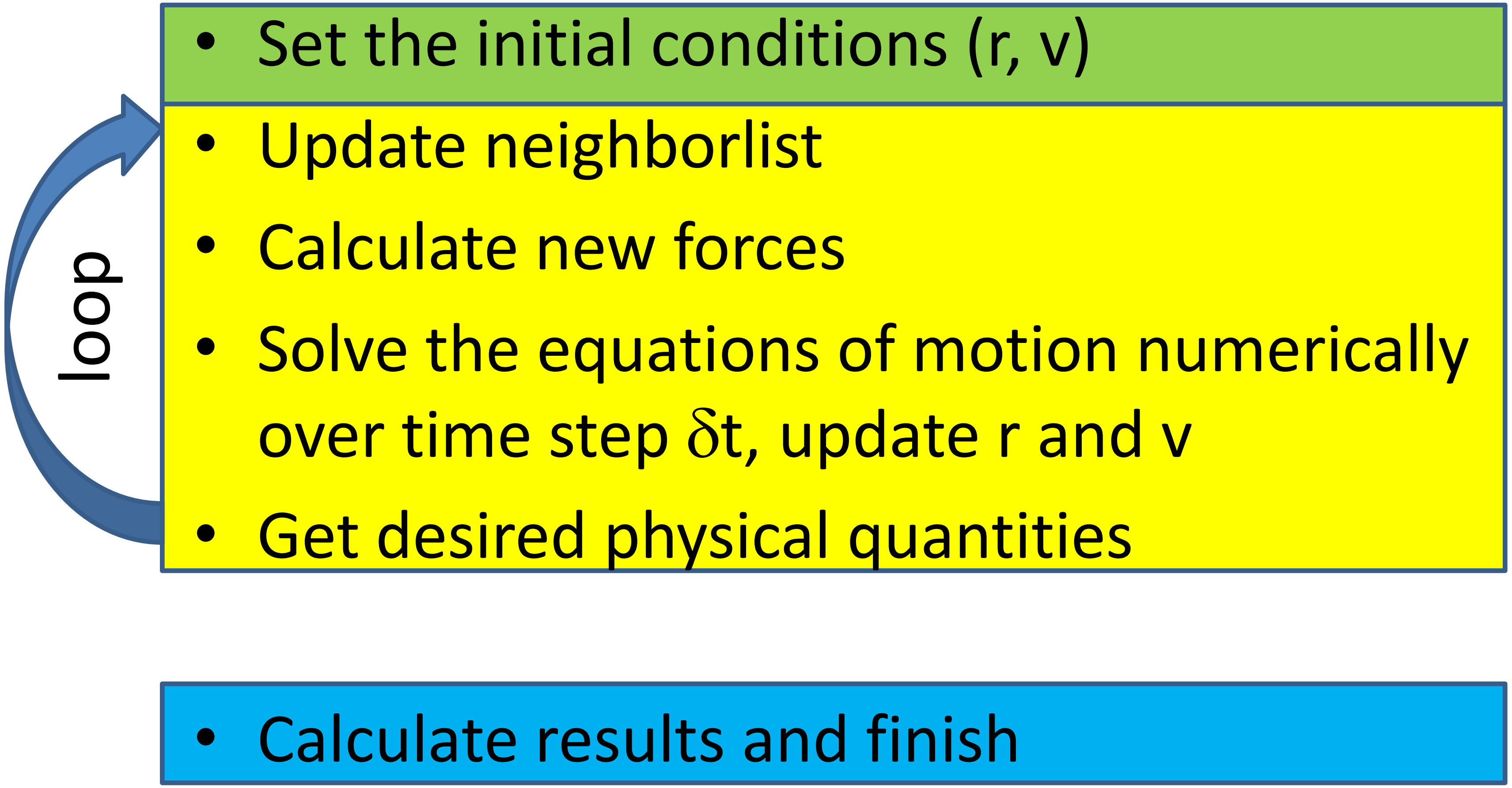
CHE-E4115 Computational Chemistry 1

Molecular dynamics in other ensembles beyond NVE

Chapters 7.5-

Revision: Molecular dynamics algorithm

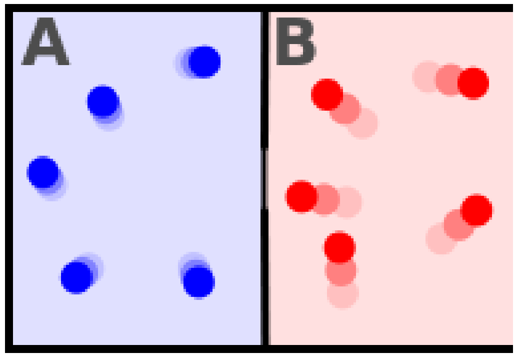


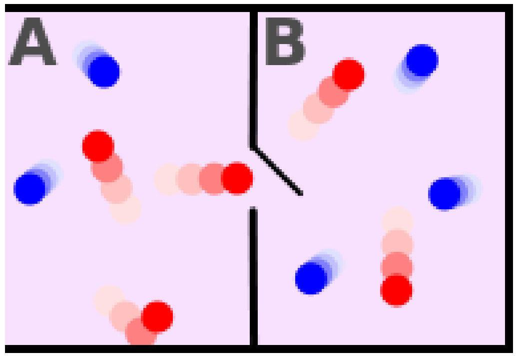
- Set the initial conditions (r, v)
- Update neighborlist
- Calculate new forces
- Solve the equations of motion numerically over time step δt, update r and v
- Get desired physical quantities

- Calculate results and finish

Vocabulary reminder: Statistical mechanics ensembles

- Microcanonical ensemble: NVE constants
- Canonical ensemble: NVT constants
- Isothermal-isobaric ensemble: NTP constants
- Grand canonical ensemble: μ VT constants

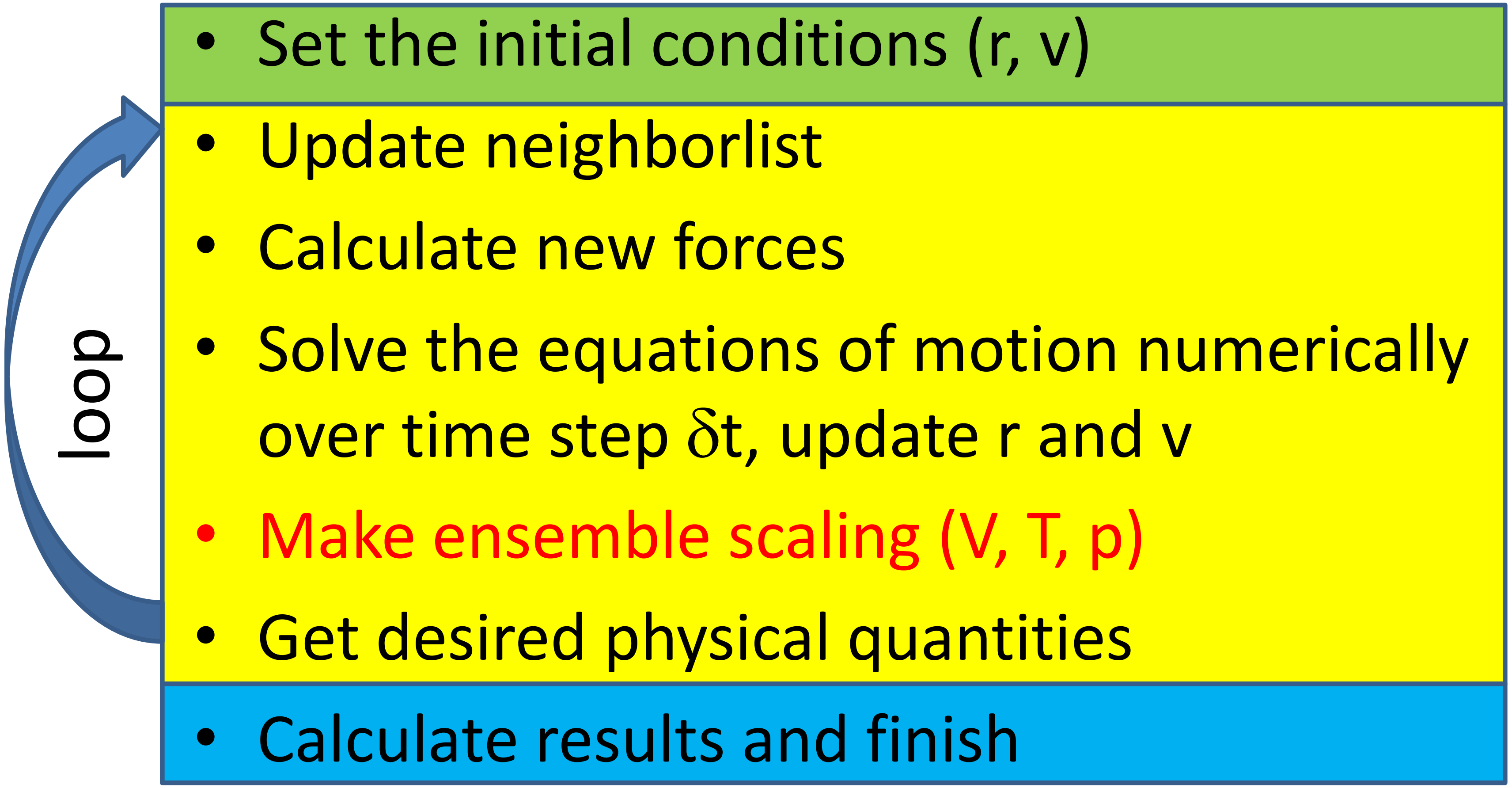




Molecular dynamics in different ensembles

- NVE: innate ensemble of molecular dynamics
  - Note: However, numerical errors and force fluctuations cause fluctuations in energy and possible drifts as well
- NVT or NPT require algorithmic changes
- μ VT possible but rare in molecular dynamics (more later)
- Note: Temperature and pressure are quantities that are typically constant in experiments. Thus, it is natural to take these as the control variables for simulations.

Molecular dynamics in different ensembles (NVE, NVT, NPT)



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Temperature in molecular simulations

Temperature T defined by average kinetic energy of the particles

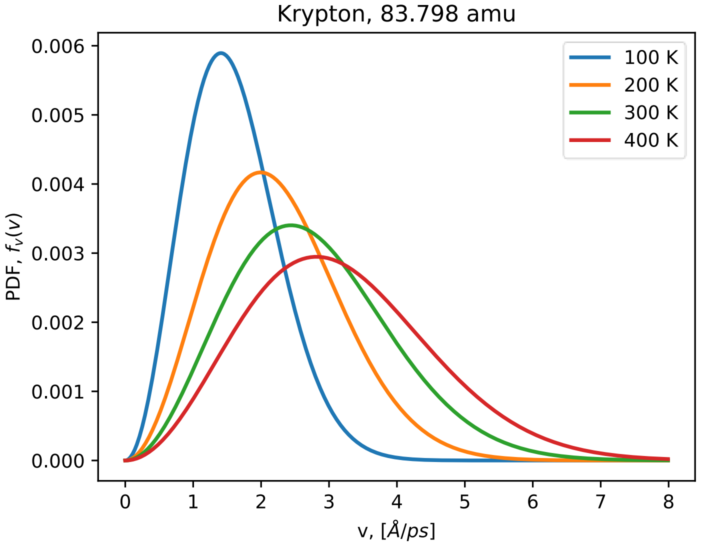
At equilibrium, states (=energy values) distributed to atoms in the most probable way -> Boltzmann distribution! This results in atom velocities *v* following the **Maxwell-Boltzmann distribution**:

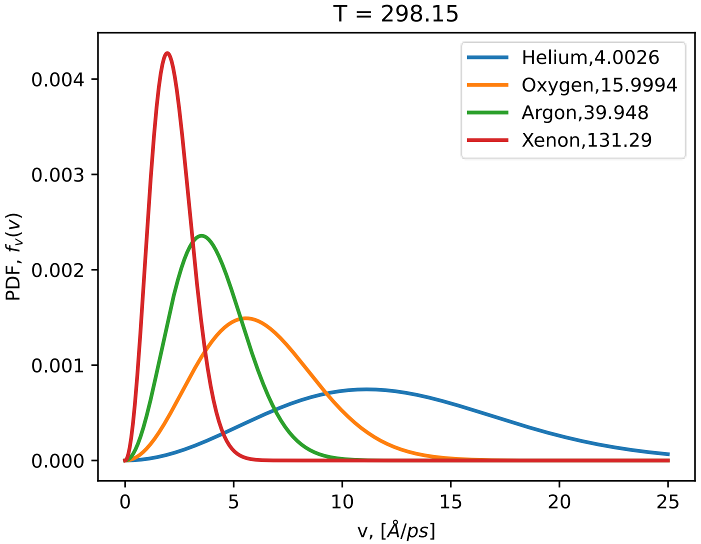
$$f_v(v) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \cdot 4\pi v^2 \cdot \exp(-mv^2/2k_B T)$$

Krypton atoms at different temperatures

Noble gases with different mass at 298K

Probability distribution function for the velocities





https://computecanada.github.io/molmodsim-md-theory-lesson-novice/aio/index.html

Summary of this lecture

- Microcanonical ensemble (NVE) - plain MD
- Canonical ensemble (NVT) - MD + thermostat
- Isothermal-isobaric (NPT) - MD + thermostat + barostat

- Possible to do simple scaling which enforces quantity or more complex ensemble scalings
- Typically the more complex ensemble scalings only resemble the real ensemble

Molecular simulations with T and p control (different thermodynamic ensembles)

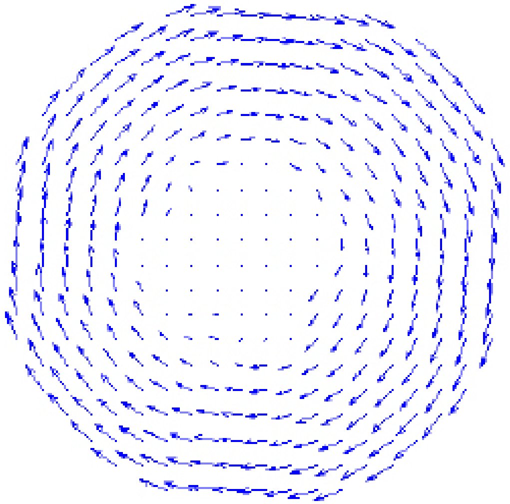
- Microcanonical ensemble (NVE) - plain MD
- Canonical ensemble (NVT) - MD + thermostat
- Isothermal-isobaric (NPT) - MD + thermostat + barostat

- Simulation of NVE ensemble as long as the MD code conserves the energy of the system.
- NVT ensemble is more practically relevant, as managing the temperature of a system is easier than controlling energy -> temperature control algorithm, a thermostat.
- Often, constant ambient pressure and temperature are desired -> both a thermostat and a pressure control algorithm, a barostat.

Thermostat algorithms

- Strong coupling methods
  - **Trivial example: Isokinetic thermostat**
  - Alternative: Periodical assignment of new randomized velocities to set the system to desired temperature
- Weak coupling methods:
  - **Berendsen thermostat**
- Stochastic methods
  - Andersen thermostat
  - Langevin thermostat
  - **Bussi et al. Stochastic velocity rescaling thermostat**
- Extended system thermostats
  - Nose-Hoover thermostat
  - Nose-Hoover chains thermostat

Molecular dynamics with simple scaling: Isokinetic thermostat

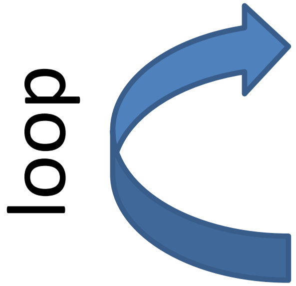


- Trivial T scaling: force during every time step th temperature to be exactly T

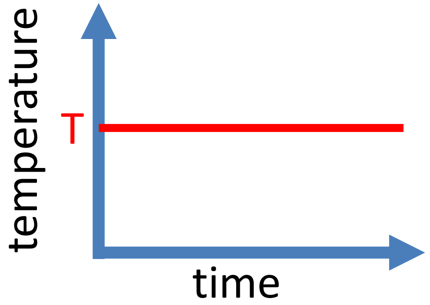
$$T = \frac{\sum m_i v_i^2}{3Nk_b} \qquad \lambda = \sqrt{T / T_i}$$

- Scale velocities by λ –> temperature becomes desired T (T_i instantaneous T)
- Severe perturbation of the atom motion especially if there are only a few atoms
- Suppresses normal T fluctuations, and does still not correspond to a true NVT ensemble.
- May works for large number of (simple) particles in uniform system but extremely likely to cause velocity vortices etc. problem in dynamics
- Not for production runs! Ensemble scalings usually much better idea!!!!

Isokinetic thermostat loop



- Perform one (or more) MD steps
- Compute the instantaneous kinetic energy
- Rescale the velocities by a factor $\lambda = \sqrt{T / T_i}$



Not for production runs!
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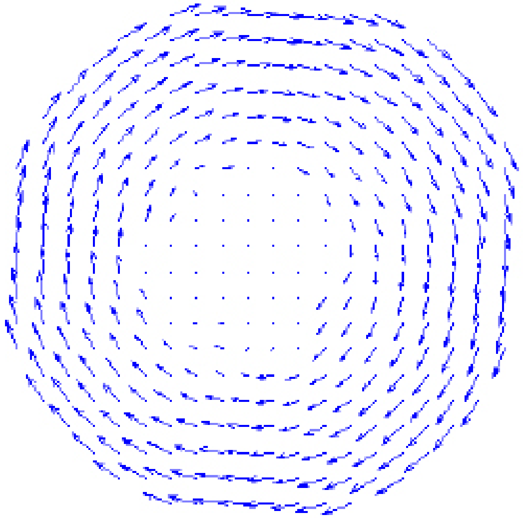
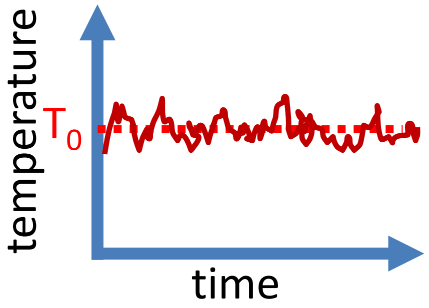


Berendsen thermostat
Berendsen, JCP(1984)

- Smoother approach to scaling (weak coupling)
- velocities scaled at rate of change of temperature proportional to the difference in temperature

$$\frac{dT(t)}{dt} = \frac{1}{\tau}\left(T_0 - T(t)\right)$$



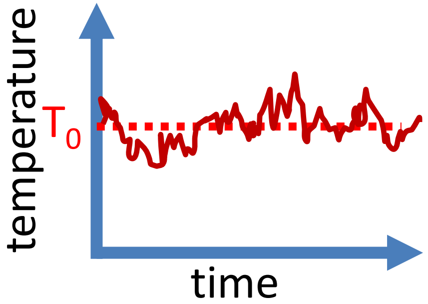
- T_0 heat bath temperature
- τ heat bath coupling constant
- change in temperature between successive time steps

$$\Delta T = \frac{\delta t}{\tau}\left(T_0 - T(t)\right).$$

- Fluctuations are wrong! (Incorrect statistical ensemble, never canonical)

Stochastic velocity rescaling thermostat: [Bussi, Donadio and Parrinello, JCP (2007)]

- Combines ~Berendsen ”friction” and Langevin random noise to produce correct fluctuations
- Currently the ”state of art”
- Note on correct τ
- K kinetic energy, $K = \sum \frac{1}{2} m_i v_i^2$



same as Berendsen — noise gives correct fluctuations

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

Selecting thermostats in molecular dynamics packages

Thermostat/MD package	GROMACS
velocity rescaling	
velocity reassignment	
Andersen	tcoupl = andersen
massive-Andersen	tcoupl = andersen-massive
Lowe-Andersen	
Berendsen	tcoupl = berendsen
Langevin	
Bussi	tcoupl = V-rescale
Nose-Hoover	tcoupl = nose-hoover
Nose-Hoover-chains	nh-chain-length (default 10)

You have this in exercises. No need to change anything

Notes on molecular dynamics velocity distributions

- Initial velocities most commonly set as Boltzmann distributed so that $T=T_0$ (desired temperature)
- Center of mass should not drift (neither initially nor during simulation)
- Rotational moments should vanish for whole system (both initially and during the simulation)
- Numerical error will cause center of mass and rotational drift: software typically set to correct for this as simulation run parameters
  - If correction specified for subgroups of the system, may cause difficult artefacts

Pressure in molecular simulations

- Pressure control algorithms (barostats) keep pressure in the simulation system constant or apply an external stress onto the simulated system.

Pressure is kept at target value by adjusting the volume of a periodic simulation system.

- Pressure is a force that rises from collision of particles with the walls of a closed container. The virial equation is used to obtain the pressure:

$$P = \frac{NK_BT}{V} + \frac{1}{3V}\langle \sum r_{ij}F_{ij} \rangle$$

- First term: pressure of an ideal gas (no interaction between molecules).
- Second term: contributions from internal forces acting on each atom.
- Virial approach is well suited for MD because forces are evaluated at each simulation step.

Barostat algorithms (pressure control in molecular dynamics simulations)

- **Weak coupling methods:**
  - **Berendsen barostat**
- Extended system methods
  - Parrinello-Rahman barostat
  - Nosé-Hoover barostat
  - Martyna-Tuckermann-Tobias-Klein (MTTK)
- **Stochastic methods**
  - Langevin piston pressure control
  - Stochastic Cell Rescaling

Bernetti M, Bussi G
Pressure control using stochastic cell rescaling.
J Chem Phys. 2020;153:114107 doi:10.1063/5.0020514

NPT ensemble methods: Berendsen barostat [J. Chem. Phys. 81 (1984) 3684]

- box vectors scaled every n_{PC} steps with a matrix μ so that pressure P approaches reference pressure P_0 as $\frac{d\boldsymbol{P}}{dt} = \frac{P_0 - P}{\tau_p}$

$$\mu_{ij} = \delta_{ij} - \frac{n_{\mathrm{PC}}\Delta t}{3\tau_p}\beta_{ij}\{P_{0ij} - P_{ij}(t)\}$$

- β_{ij} isothermal compressibility (matrix), τ_p coupling constant
- Compare with Berendsen thermostat: analogous idea
- Does not sample the NPT statistical ensemble
- Induces artifacts into simulations of inhomogeneous systems such as aqueous biopolymers or liquid/liquid interfaces because of uniform scaling
- Should be avoided for production MD simulations

Stochastic Cell Rescaling

Bernetti M, Bussi G
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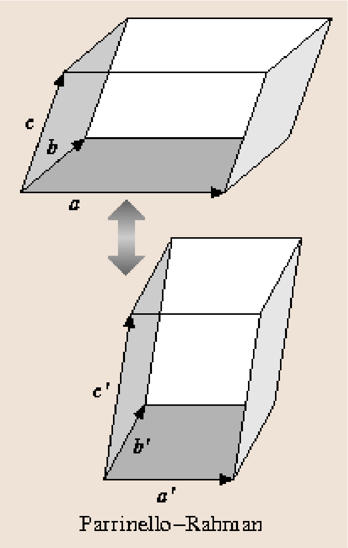
- Improved version of the Berendsen barostat.
- Adds stochastic term to rescaling matrix.
- Produces correct fluctuations of local pressure for NPT ensemble.
- Pressure converges fast without oscillations.
- Can be used for all stages of MD, including production.

NPT ensemble methods

Parrinello-Rahman-pressure control

[Parrinello and Rahman, *J. Appl. Phys.* 52 (1981) 7182]

- allows a variable simulation cell shape, that is, the angles between the axes do not have to be 90°.
- box vectors follow an equation of motion & the equations of motion of the particles are also changed



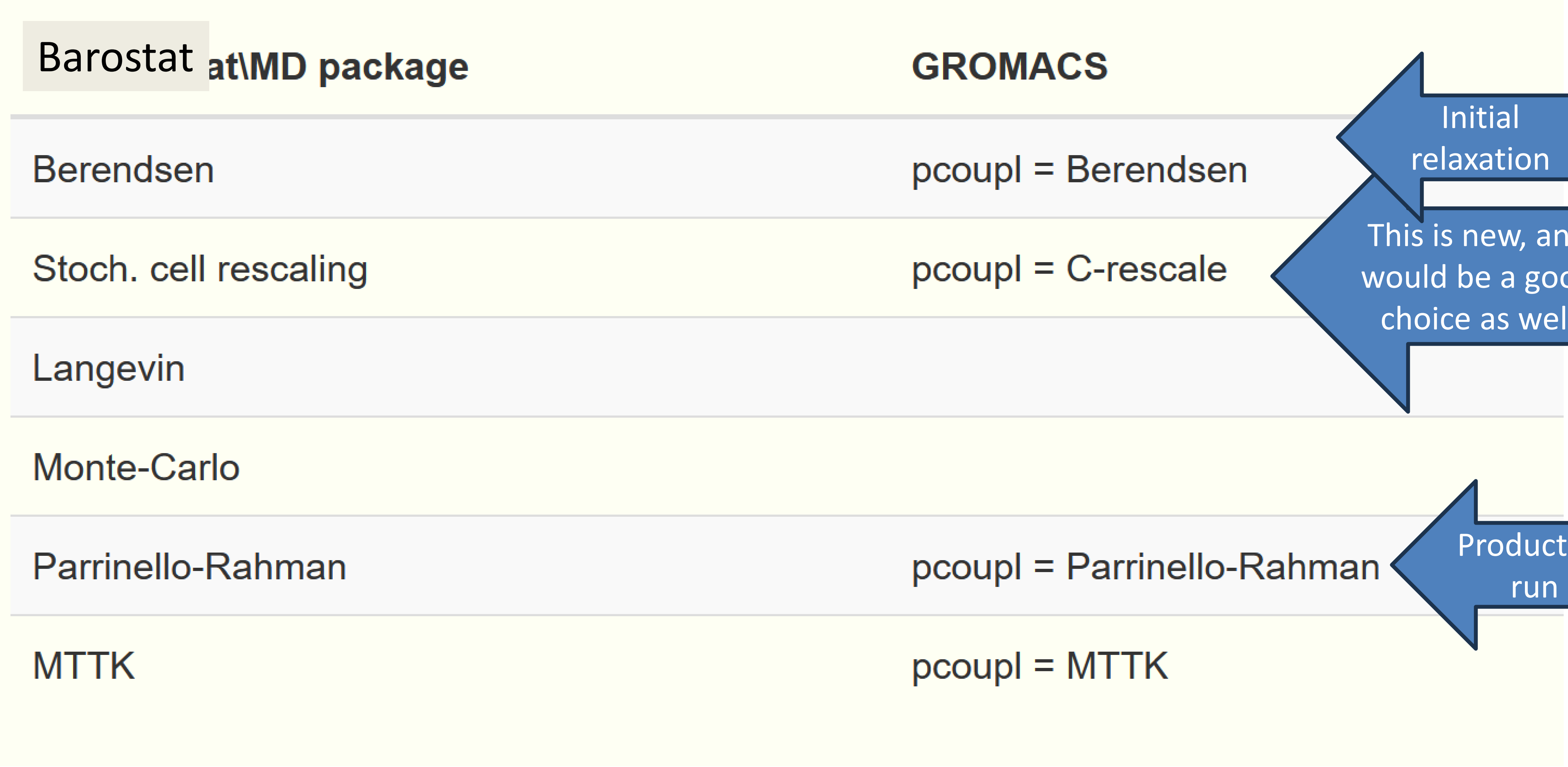
$$\frac{\mathrm{d}\boldsymbol{b}^2}{\mathrm{d}t^2} = V\boldsymbol{W}^{-1}\boldsymbol{b}'^{-1}\left(\boldsymbol{P} - \boldsymbol{P}_{ref}\right)$$

$$\begin{aligned} \frac{\mathrm{d}^2\boldsymbol{r}_i}{\mathrm{d}t^2} &= \frac{\boldsymbol{F}_i}{m_i} - \boldsymbol{M}\frac{\mathrm{d}\boldsymbol{r}_i}{\mathrm{d}t}, \\ \boldsymbol{M} &= \boldsymbol{b}^{-1}\left[\boldsymbol{b}\frac{\mathrm{d}\boldsymbol{b}'}{\mathrm{d}t} + \frac{\mathrm{d}\boldsymbol{b}}{\mathrm{d}t}\boldsymbol{b}'\right]\boldsymbol{b}'^{-1}. \end{aligned}$$

b matrix of the box vectors, V box volume, **W** strength of the coupling (matrix), P pressure, P_{ref} target reference pressure
F_i force on particle i (vector), r_i position of particle i (vector)
M matrix determining the prefactor for the Parrinello-Rahman change to particle equations of motion

M. Parrinello and A. Rahman:
(i) Phys. Rev. Lett. 45 (1980) 1196
(ii) J. Appl. Phys. 52 (1981) 7182
(iii) J. Chem. Phys. 76 (1982) 2662

How to choose barostat in Gromacs



Barostat at\MD package	GROMACS
Berendsen	pcoupl = Berendsen
Stoch. cell rescaling	pcoupl = C-rescale
Langevin	
Monte-Carlo	
Parrinello-Rahman	pcoupl = Parrinello-Rahman
MTTK	pcoupl = MTTK

Initial relaxation

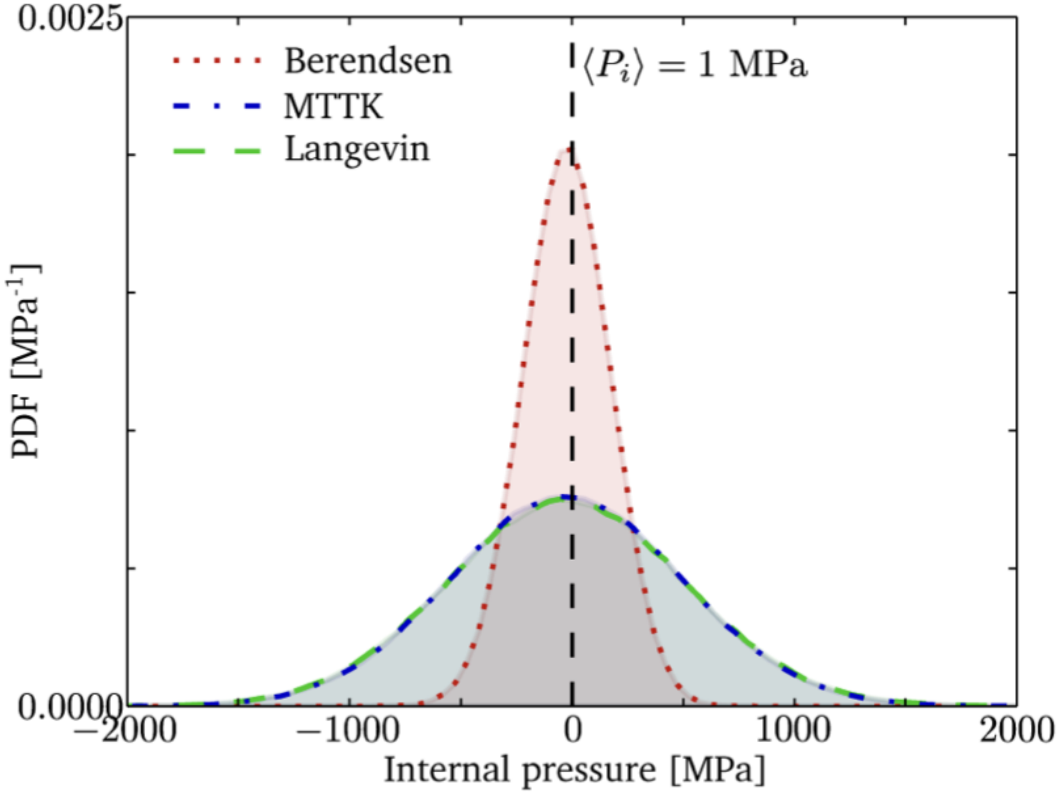
This is new, and would be a good choice as well

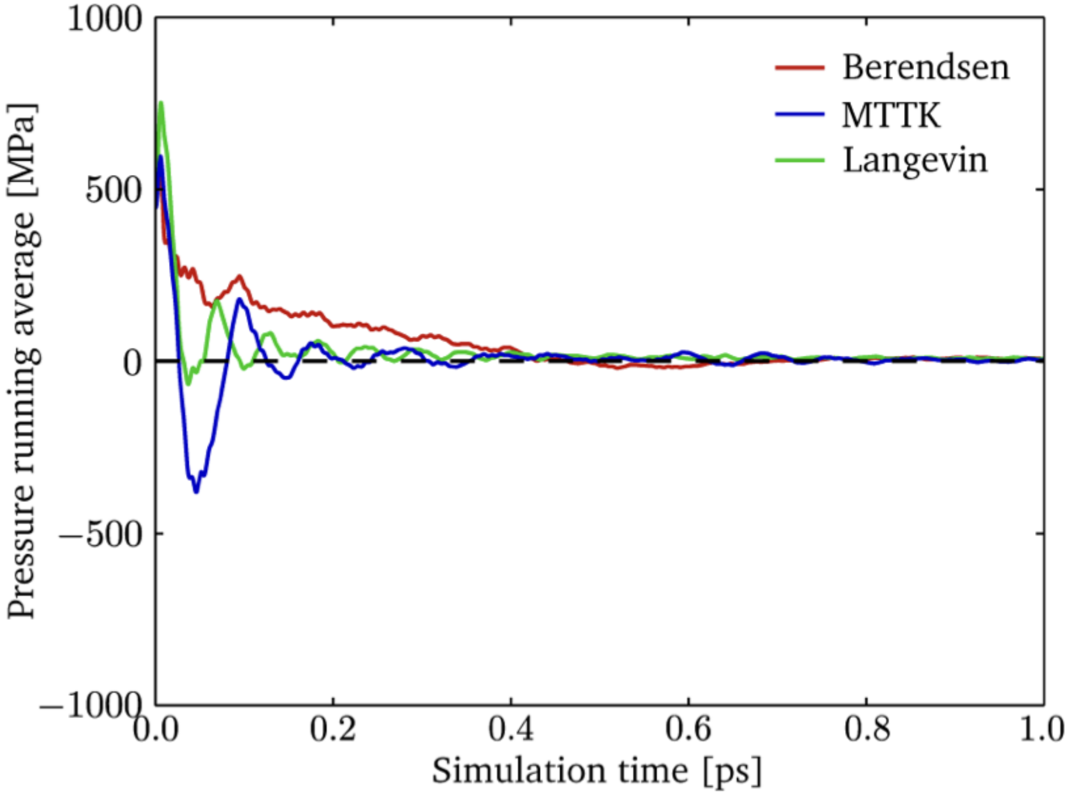
Production run

Barostat produced pressure distribution

MTTK and Langevin barostats produce identical ensembles

Langevin barostat oscillates less then MTTK and converges faster due to stochastic collisions and damping.





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Which ones to use

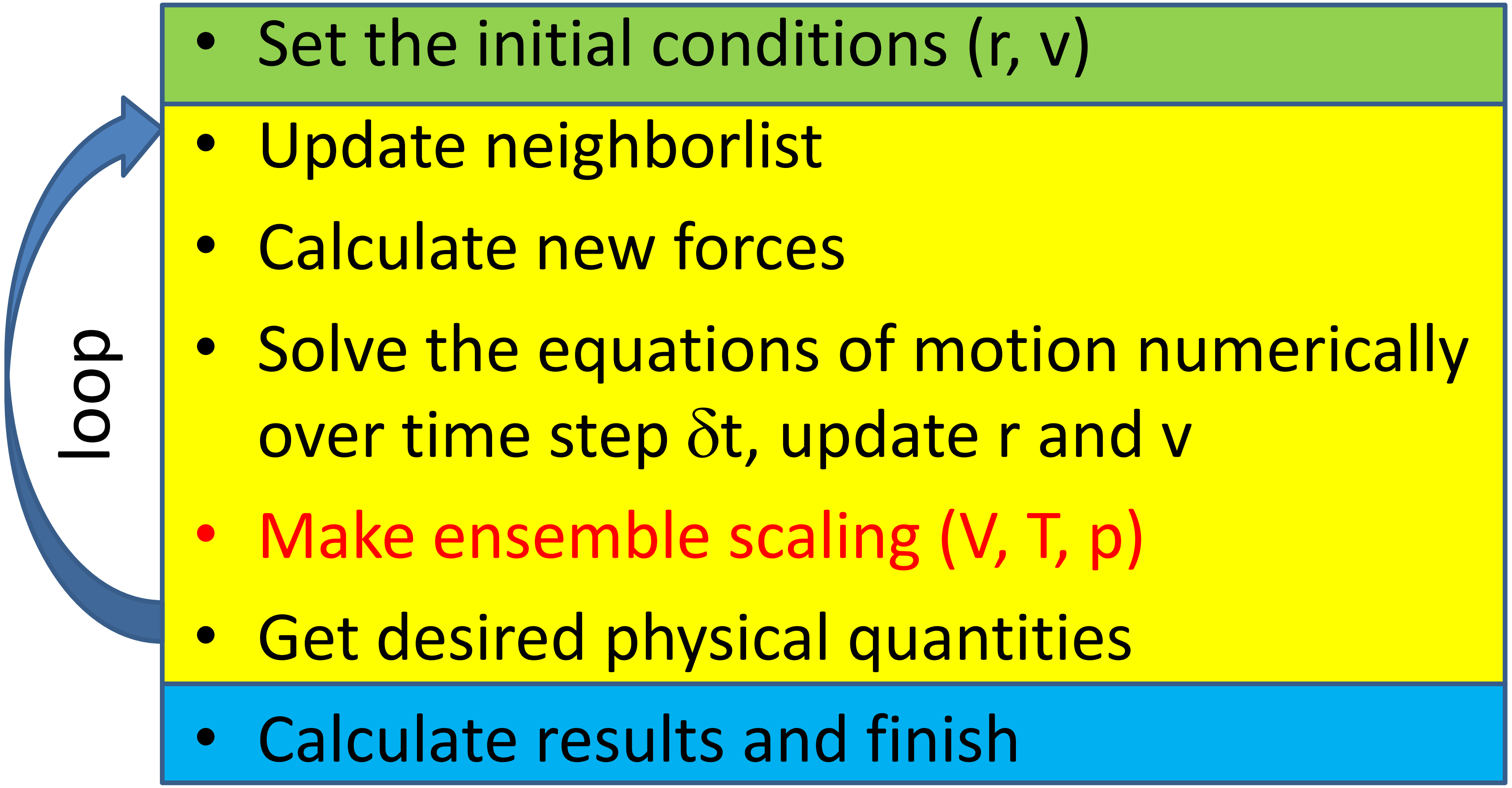
- Do not use trivial scalings!
- Berendsen *T* and *p* control are simple to implement and use. In addition, they can steadily drive the system far from equilibrium toward equilibrated state. This is very handy at the start of the simulation, where significant fluctuations may take place.
- If you need to produce the correct statistical ensemble, you will need to use other methods.
- Stochastic velocity rescaling is currently the state-of-the-art thermostat. It is usually combined with Parrinello-Rahman barostat. A more recent, new choice is the stochastic cell rescaling barostat
- Another good option is the Nosé-Hoover thermostat with Parrinello-Rahman barostat

μVT methods

- Chemical potential μ stays constant, number of atoms fluctuates
- Rarely used in molecular dynamics
- More often in Monte Carlo simulations (more natural to add and remove atoms from the system)
- Can be alternatively implemented by adding or removing “control volume”.
- just adding an atom on a random place can easily lead to completely unphysical configurations.
- adding or removing control volume without distorting the system state too much may be tricky

- Algorithms: [Lynch, Pettitt: *J. Chem. Phys.* **107** (1997) 8594] or [Heffelfinger, *J. Chem. Phys.* **100** (1994) 7548].

Revision: Molecular dynamics in different ensembles (NVE, NVT, NPT)



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Other thermostat and barostat algorithms (not covered on lectures)

NVT ensemble methods

The Andersén thermostat

[H. C. Andersén, *J. Chem. Phys.* **72**, 2384 (1980)]

- Give an atom with some probability $P(t) = \nu e^{-\nu t}$ a new velocity
- ν stochastic collision frequency
- Upon a 'collision event' the new momentum of the lucky atom (or molecule) is chosen at random from a Boltzmann distribution at desired temperature T
- Physical interpretation: connection to external heat bath
- should only be used for time-independent properties (thermodynamic averages), but not for looking at atomic processes in detail such as diffusion, since the random velocity is an unphysical perturbation on the motion of a single atom
- Optimal choice of ν: $$\nu = \frac{2a\kappa V^{1/3}}{3k_B N} = \frac{2a\kappa}{3k_B\rho^{1/3}N^{2/3}}$$

a is dimensionless constant, κ is thermal conductivity, V is volume, k_B is Boltzmann constant, and ρ is number density of particles

NVT ensemble methods
Nosé-Hoover-method
[W. Hoover, *Phys. Rev. A* **31**, 1695-1697 (1985).]

- A fictional degree of freedom *s* which has its own kinetic and potential energy is added to the system, and this degree of freedom controls the temperature. The system total energy, i.e. Hamiltonian:

$$H = \sum_i \frac{p_i}{2m_i} + V(q_i) + \frac{Q}{2} p_s^2 + qkT \ln s$$

Reminder: Hamiltonian formalism for equations of motion

$$\dot{q}_k = \frac{\partial}{\partial p_k} H(\mathbf{q}, \mathbf{p}) \quad \dot{p}_k = -\frac{\partial}{\partial q_k} H$$

Resulting equations of motion

$$\frac{dq_i}{dt} = \frac{p_i}{m_i}; \qquad \frac{dp_i}{dt} = -\frac{dV}{dq_i} - p_s p_i, \qquad \frac{dp_s}{dt} = \left(\sum_i \frac{p_i}{m_i} - gkT \right) / Q$$

- p_s is the momentum associated with the degree of freedom.
- Q is a fictional mass related to the extra degree of freedom, which describes the rate at which the temperature changed

NVT ensemble methods

Nosé-Hoover-method

[W. Hoover, *Phys. Rev. A* **31**, 1695-1697 (1985).]

$$H = \sum_i \frac{p_i}{2m_i} + V(q_i) + \frac{Q}{2} p_s^2 + qkT \ln s$$

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- Nosé suggested Q ~gk_BT where g is the number of degrees of freedom in the system, typically 6N. Issues: for large Q the connection to the heat bath weakens, and for small Q the energy E may oscillate too much.
- Proper sampling, but deterministic
  - Can be non-ergodic in pathological cases (e.g. harmonic oscillator)
  - Second order: can end up in oscillating behavior (especially far from equilibrium)

Nosé-Hoover chains method

[Martyna et al, JCP, 1992]

- performance of Nose-Hoover algorithm can be improved by controlling the extra degree of freedom s with another Nosé-Hoover thermostat
- After that, control *that* degree of freedom with yet another thermostat
- And so on...

Langevin thermostat
[Schneider and Stoll, Phys. Rev. B (1978)]

- Langevin: partial stochastic refreshment of momenta (random)

$$p_{new} = p_{old} - \gamma p_{old}\Delta t + \sqrt{2mk_BT\gamma}\sqrt{\Delta t}R$$

- Like with
  particles: should only be used for time-independent properties (thermodynamic averages), but not for looking at atomic processes in detail such as diffusion.

Hamiltonian mechanics briefly

$$\mathcal{H} = T + V, \quad T = \frac{p^2}{2m}, \quad V = V(q) = V(x).$$

Hamiltonian

Kinetic energy

Potential energy

$p=mv$ (momentum)

$T=1/2mv^2$

- reformulation of classical mechanics (Newtonian mechanics)
- first-order constraints on a 2n-dimensional phase space
- For a closed system, Hamiltonian is sum of the kinetic and potential energy in the system
- q are generalized coordinates (for each degree of freedom)

http://en.wikipedia.org/wiki/Hamiltonian_mechanics

Hamiltonian mechanics briefly

$$\mathcal{H} = T + V, \quad T = \frac{p^2}{2m}, \quad V = V(q) = V(x).$$

Hamiltonian

Kinetic energy

Potential energy

$T=1/2mv^2$

$p=mv$ (momentum)

Hamiltonian equations of motion for generalized coordinates q and momenta p

$$\dot{q} = \frac{\partial H}{\partial p} = \frac{p}{m}$$

$$\dot{p} = -\frac{\partial H}{\partial q} = -\frac{\partial U}{\partial q} = f(q)$$

Hamiltonian mechanics equations of motion 1

- q_i generalized coordinates
- p_i generalized momenta

$$p_i = \frac{\partial L}{\partial \dot{q}_i}.$$

- Lagrangian (function)

Potential energy

$$L(q, \dot{q}) = K(q, \dot{q}) - V(q),$$

Kinetic energy

- Hamiltonian

$$H(p, q) = p \cdot \dot{q} - L(q, \dot{q}) = \sum_{i=1}^{n} p_i \dot{q}_i - L(q, \dot{q})$$

  - Interpretation: Total energy of a conservative system

Hamiltonian mechanics equations of motion 2

$$H(p,q) = p \cdot \dot{q} - L(q,\dot{q}) = \sum_{i=1}^{n} p_i \dot{q}_i - L(q,\dot{q})$$

$$dH = \sum_{i=1}^{n} \frac{\partial H}{\partial p_i} dp_i + \sum_{i=1}^{n} \frac{\partial H}{\partial q_i} dq_i.$$

⇒ $$dH = \sum_{i=1}^{n} \dot{q}_i \, dp_i + \sum_{i=1}^{n} p_i \, d\dot{q}_i - \sum_{i=1}^{n} \frac{\partial L}{\partial \dot{q}_i} d\dot{q}_i - \sum_{i=1}^{n} \frac{\partial L}{\partial q_i} dq_i.$$

Cancel since $p_i = \frac{\partial L}{\partial \dot{q}_i}.$

⇒ $$dH = \sum_{i=1}^{n} \dot{q}_i \, dp_i - \sum_{i=1}^{n} \frac{\partial L}{\partial q_i} dq_i.$$

Hamiltonian mechanics equations of motion 3

So (from last slide): $dH = \sum_{i=1}^{n} \dot{q}_i \, dp_i - \sum_{i=1}^{n} \frac{\partial L}{\partial q_i} dq_i.$

Remembering $\dot{p} = \frac{\partial L}{\partial q_i}.$

We get $dH = \sum_{i=1}^{n} \dot{q}_i \, dp_i - \sum_{i=1}^{n} \dot{p}_i \, dq_i.$

Hamiltonian mechanics equations of motion: Last slide

- So, we ended up with 2 expressions for dH:

$$dH = \sum_{i=1}^{n} \frac{\partial H}{\partial p_i} dp_i + \sum_{i=1}^{n} \frac{\partial H}{\partial q_i} dq_i.$$

$$dH = \sum_{i=1}^{n} \dot{q}_i \; dp_i - \sum_{i=1}^{n} \dot{p}_i \; dq_i.$$

2n equations called Hamilton’s equations

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \qquad\qquad \dot{p}_i = \frac{\partial H}{\partial q_i},$$