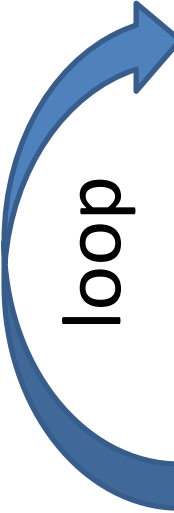# CHE-E4115 Computational Chemistry 1

Molecular dynamics in other ensembles beyond NVE

Chapters 7.5-
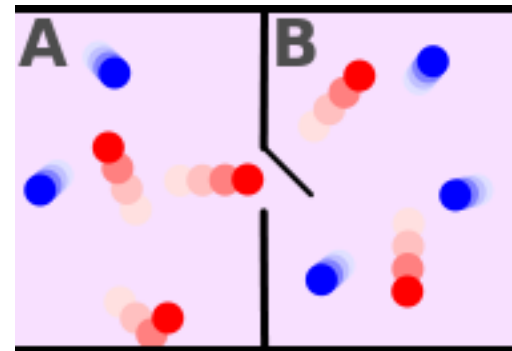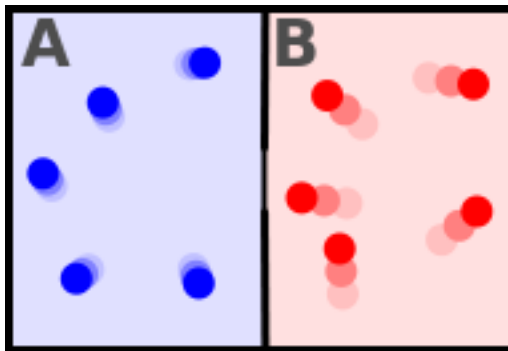
Revision: Molecular dynamics algorithm

- 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

loop

- 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)

- Set the initial conditions (r, v)

- Update neighborlist
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- Make ensemble scaling (V, T, p)
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loop
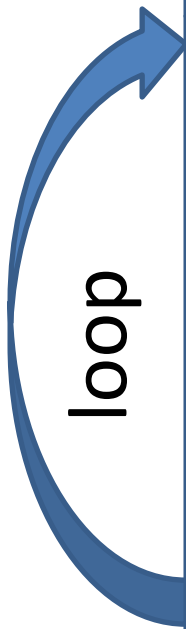
Summary of this lecture

- 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

Thermostat algorithms

- **Trivial example: Isokinetic thermostat**
- **Berendsen thermostat**
- Andersen thermostat
- Nose-Hoover thermostat
  - Nose-Hoover chains thermostat
- Langevin thermostat
- **Stochastic velocity rescaling thermostat**

Molecular dynamics with simple scaling: Isokinetic thermostat

- Trivial T scaling: force during every time step the system 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!!!!
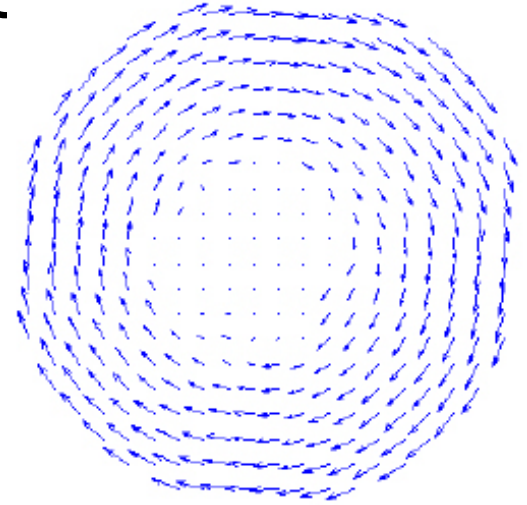
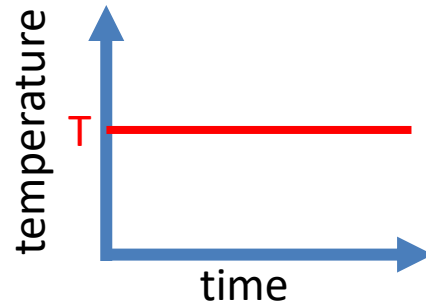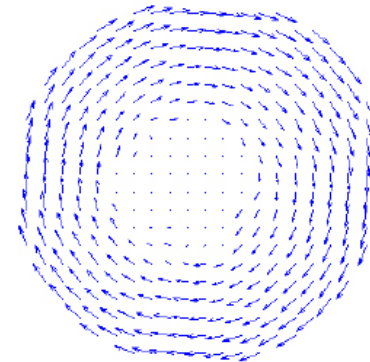# Isokinetic thermostat loop

loop
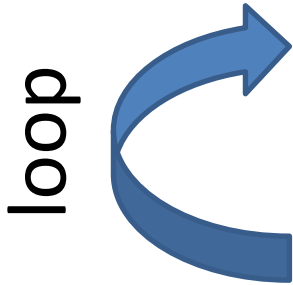
- Perform one (or more) MD steps

- Compute the instantaneous kinetic energy

- Rescale the velocities by a factor $\lambda = \sqrt{T/T_i}$

Not for production runs!
Ensemble scalings usually
much better idea!!!!

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

$$\Delta T = \frac{\delta t}{\tau}\left(T_0 - T(t)\right).$$
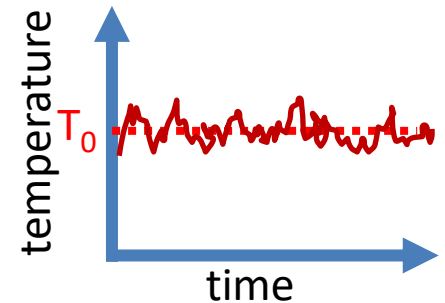
- Fluctuations are wrong! (Incorrect statistical ensemble, never canonical)

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, $K = \sum \frac{1}{2} m_i v_i^2$

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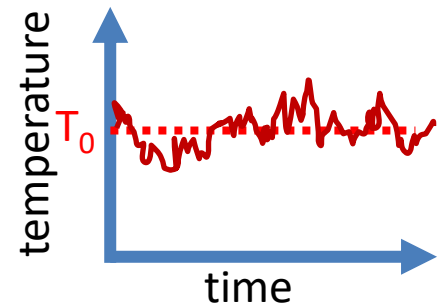
same as Berendsen

noise gives correct fluctuations

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

Barostat algorithms (pressure control in molecular dynamics simulations)

- **Berendsen barostat**
- Andersen barostat
- **Parrinello-Rahman barostat**
- Martyna-Tuckermann-Tobias-Klein (MTTK)

Pressure in molecular dynamics simulations calculated

$$\boldsymbol{P} = \frac{2}{V}(\boldsymbol{E_{kin}} - \Xi),$$ where virial tensor $\Xi = -\frac{1}{2}\sum \boldsymbol{r_{ij}} \otimes \boldsymbol{F_{ij}}$

and $\boldsymbol{E_{kin}} = \frac{1}{2}\sum m_i \boldsymbol{v_i} \otimes \boldsymbol{v_i}$

$\boldsymbol{r_{ij}}$ distance (vector) btw j and i particle, $\boldsymbol{v_i}$ velocity (vector) of particle i, m_i mass, $\boldsymbol{F_{ij}}$ force (vector) btw j and I particle; vectors / tensors so that pressure control can be different for different simulation box facets
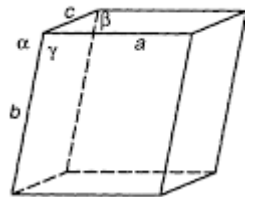
$\otimes$: tensor product. For more information see, for example
https://www.math3ma.com/blog/the-tensor-product-demystified

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 $\dfrac{d\boldsymbol{P}}{dt} = \dfrac{P_0 - P}{\tau_p}$

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

- β_{ij} isothermal compressibility (matrix), τ_p coupling constant
- Compare with Berendsen thermostat: analogous idea

NPT ensemble methods
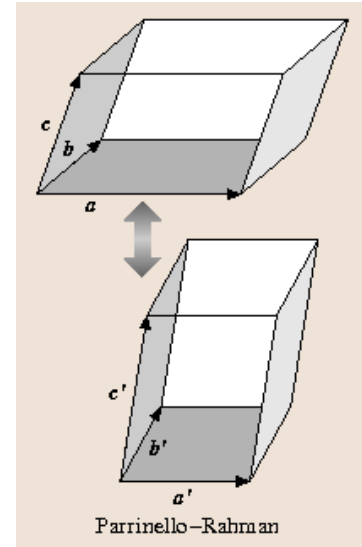## **Parrinello-Rahman-pressure control**
[Parrinello and Rahman, *J. Appl. Phys.* 52 (1981) 7182]

- allows a variable simulation cell shape, that is, the angles between the axes do not have to be 90º.

- box vectors follow an equation of motion & the equations of motion of the particles are also changed

Parrinello–Rahman

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

$$\frac{\mathrm{d}^2\boldsymbol{r}_i}{\mathrm{d}t^2} = \frac{\boldsymbol{F}_i}{m_i} - \boldsymbol{M}\frac{\mathrm{d}\boldsymbol{r}_i}{\mathrm{d}t},$$

$$\boldsymbol{M} = \boldsymbol{b}^{-1}\left[\boldsymbol{b}\frac{\mathrm{d}\boldsymbol{b}'}{\mathrm{d}t} + \frac{\mathrm{d}\boldsymbol{b}}{\mathrm{d}t}\boldsymbol{b}'\right]\boldsymbol{b}'^{-1}.$$

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

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
- 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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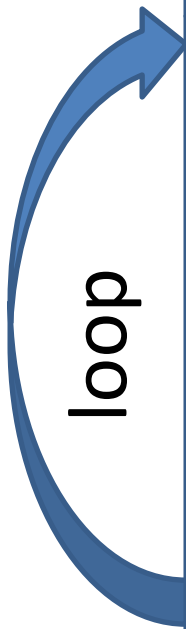
Revision

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Other thermostat and barostat algorithms

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 $Q \sim gk_BT$ 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 Andersen thermostat, Langevin acts on single 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=1/2mv²

- 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)

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=1/2mv²

Hamiltonian equations of motion for generalized coordinates q and momenta p

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

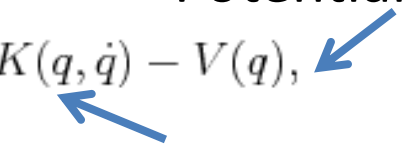$$\dot{p} = -\frac{\partial H}{\partial q} = -\frac{\partial U}{\partial q} = f(q)$$

Hamiltonian mechanics equations of motion 1

- q_i generalized coordinates

- p_i generalized momenta $\qquad p_i = \dfrac{\partial L}{\partial \dot{q}_i}.$

  Potential energy

- Lagrangian (function) $\qquad L(q, \dot{q}) = K(q, \dot{q}) - V(q),$
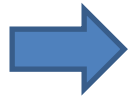
  Kinetic energy

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

  - Interpretation: Total energy of a conservative system

Hamiltonian mechanics equations of motion 2

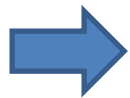$$H(p,q) = p \cdot \dot{q} - L(q, \dot{q}) = \sum_{i=1}^{n} p_i \dot{q}_i - L(q, \dot{q})$$

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

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

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

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

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

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