Computational Physics 2023

Sommersemester, 3th April, 2022 – 14th Juli, 2022

1) Introduction

2) Numbers and errors

3) Differentiation and integration

4) Ordinary differential equations

5) Molecular dynamics simulations

6) Partial differential equations

7) Iteration processes

8) Matrixdiagonalisation & Eigenvalue problems

9) Minimization

10) Random numbers

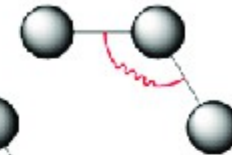11) Monte Carlo (MC) Simulations

12) Perkolation

13) Stochastic Dynamics

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$$U(R) = \sum_{bonds} k_r \left(r - r_{eq}\right)^2 \qquad \text{bond}$$

$$+ \sum_{angles} k_\theta \left(\theta - \theta_{eq}\right)^2 \qquad \text{angle}$$

$$+ \sum_{dihedrals} k_\phi \left(1 + \cos\left[n\phi - \gamma\right]\right) \qquad \text{dihedral}$$

$$+ \sum_{impropers} k_\omega \left(\omega - \omega_{eq}\right)^2 \qquad \text{improper}$$

$$+ \sum_{i<j}^{atoms} \varepsilon_{ij} \left[\left(\frac{r_m}{r_{ij}}\right)^{12} - 2\left(\frac{r_m}{r_{ij}}\right)^6 \right] \qquad \text{van der Waals}$$

$$+ \sum_{i<j}^{atoms} \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \qquad \text{electrostatic}$$

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Lennard-Jones

Lennard-Jones Potential

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

$$\mathbf{F} = \left(-\frac{\partial V}{\partial x}, -\frac{\partial V}{\partial y}\right)$$

Intermolecular Potential (Potential Energy) (V)

NOTE: The deeper the well depth (ε), the stronger the interaction between the two particles. When the bonding potential energy is equal to zero, the distance of separation, r, will be equal to σ

Figure B

$$r = \sqrt{\left(x(i) - x(j)\right)^2 + \left(y(i) - y(j)\right)^2}$$

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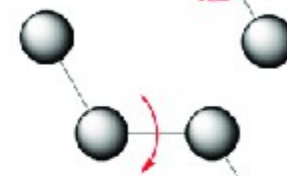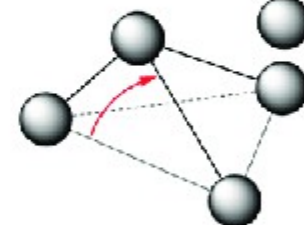
The simulation box: Periodic boundaries
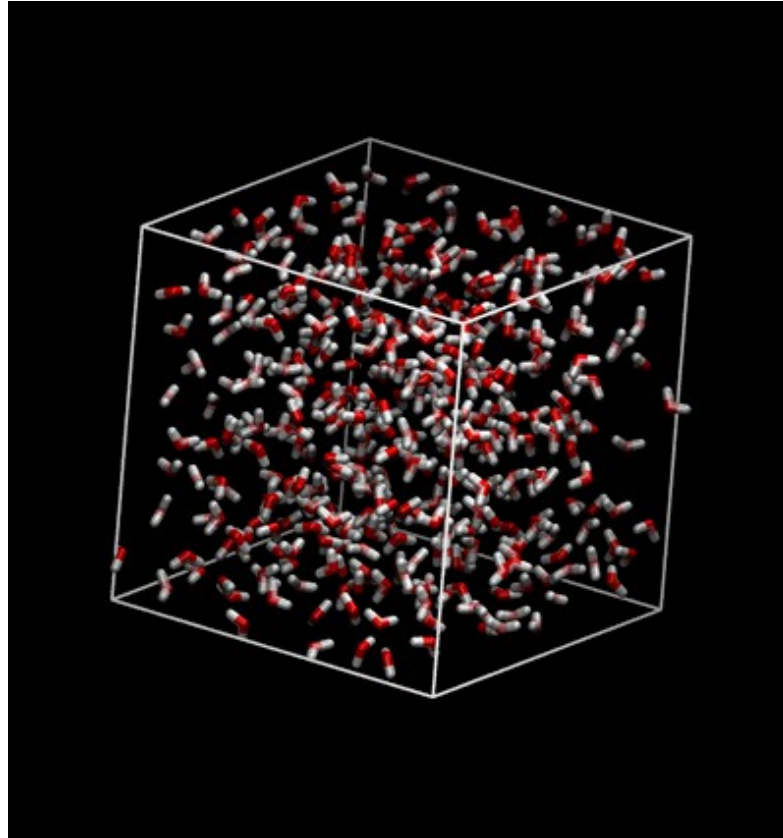
- **Fluid-air (Fluid-vacuum) interfaces are characterized by a substantial surface tension. The water-air surface tension is about 70 mN/m or about 18 k_BT/nm^2.**
- **Periodic boundaries form an excellent and widely used method to obtain bulk properties of fluids (no surface tension) within small, finite systems.**

Periodic boundary Conditions (PBC)

In the "Argon code":
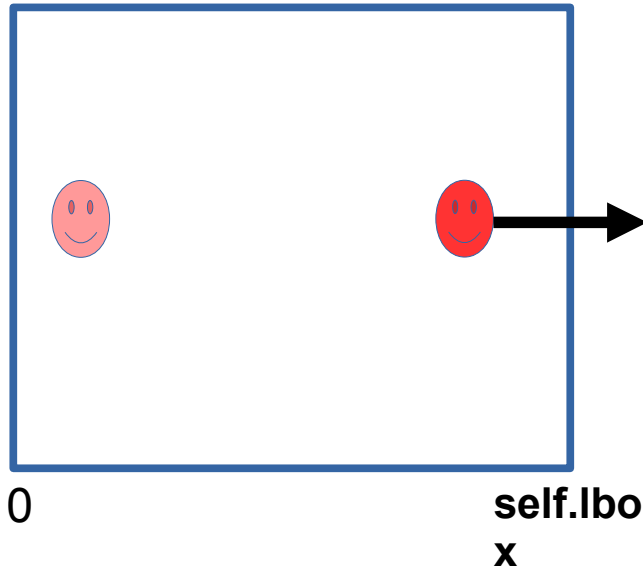
```
# Update current positions (applying PBC)
        if newX < 0:
            self.atoms[atom].x = newX + self.lbox
        elif newX > self.lbox:
            self.atoms[atom].x = newX - self.lbox
        else:
            self.atoms[atom].x = newX

        if newY < 0:
            self.atoms[atom].y = newY + self.lbox
        elif newY > self.lbox:
            self.atoms[atom].y = newY - self.lbox
        else:
            self.atoms[atom].y = newY

        if newZ < 0:
            self.atoms[atom].z = newZ + self.lbox
        elif newZ > self.lbox:
            self.atoms[atom].z = newZ - self.lbox
        else:
            self.atoms[atom].z = newZ
```
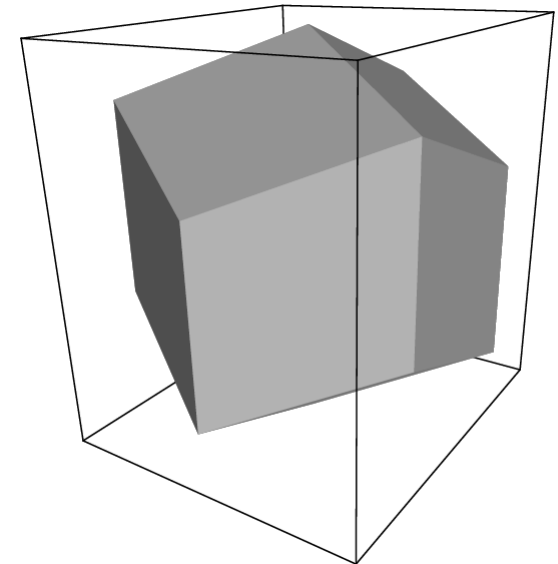
0   self.lbo
                           x

Different simulation boxes

All space-filling periodic boxes can be described by a 3x3 matrix:

Table 6 Overview over different box types

box type	image distance	box volume	box vectors a	b	c	box vector angles ∠ bc	∠ ac	∠ ab
cubic	d	d^3	d	0	0	$90°$	$90°$	$90°$
			0	d	0			
			0	0	d			
rhombic dodcahdron (xy-square)	d	$\frac{1}{2}\sqrt{2}\,d^3$ $0.707\,d^3$	d 0 0	0 d 0	$\frac{1}{2}d$ $\frac{1}{2}d$ $\frac{1}{2}\sqrt{2}\,d$	$60°$	$60°$	$60°$
rhombic dodcahdron (xy- hexagon)	d	$\frac{1}{2}\sqrt{2}\,d^3$ $0.707\,d^3$	d 0 0	$\frac{1}{2}d$ $\frac{1}{2}\sqrt{3}\,d$ 0	$\frac{1}{2}d$ $\frac{1}{6}\sqrt{3}\,d$ $\frac{1}{3}\sqrt{6}\,d$	$60°$	$60°$	$60°$
truncated octahedron	d	$\frac{4}{9}\sqrt{3}\,d^3$ $0.770\,d^3$	d 0 0	$\frac{1}{3}d$ $\frac{2}{3}\sqrt{2}\,d$ 0	$-\frac{1}{3}d$ $\frac{1}{3}\sqrt{2}\,d$ $\frac{1}{3}\sqrt{6}\,d$	$71.53°$	$109.47°$	$71.53°$

rhombic dodecahedron

- The matrix is asymmetric with 0,0,0 below the diagonal. This assures that the 3 box vectors are linear independent!
- The volume of the rhombic dodcahdron is 71% of the volume of a cube having the same image distance. This typically shaves of 29% of solvent and thus speeds up the simulation by a factor of 1.3.
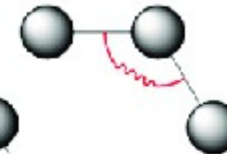
Atomistic force-fields: The main computational cost

$$U(R) = \sum_{bonds} k_r (r - r_{eq})^2 \qquad bond$$

$$+ \sum_{angles} k_\theta (\theta - \theta_{eq})^2 \qquad angle$$

$$+ \sum_{dihedrals} k_\phi (1 + \cos[n\phi - \gamma]) \qquad dihedral$$

$$+ \sum_{impropers} k_\omega (\omega - \omega_{eq})^2 \qquad improper$$

$$+ \sum_{i<j}^{atoms} \varepsilon_{ij} \left[\left(\frac{r_m}{r_{ij}}\right)^{12} - 2\left(\frac{r_m}{r_{ij}}\right)^6 \right] \qquad van\ der\ Waals$$

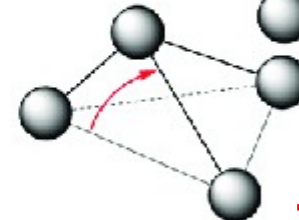$$+ \sum_{i<j}^{atoms} \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \qquad electrostatic$$
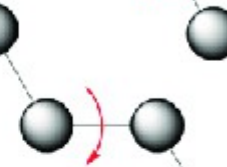
```
for(i=0;i<N;i++)
for(j=i+1;j<N;j++)
{
    f=do_force(x[i],x[j]);
    ft[i] += f;
    ft[j] -= f;
}
```

- **Nonbonded pair-wise interactions are not cheap since there exists $1/2 N^2 - N$ unique pairs in total. This quadratic scaling is killing the performance!**
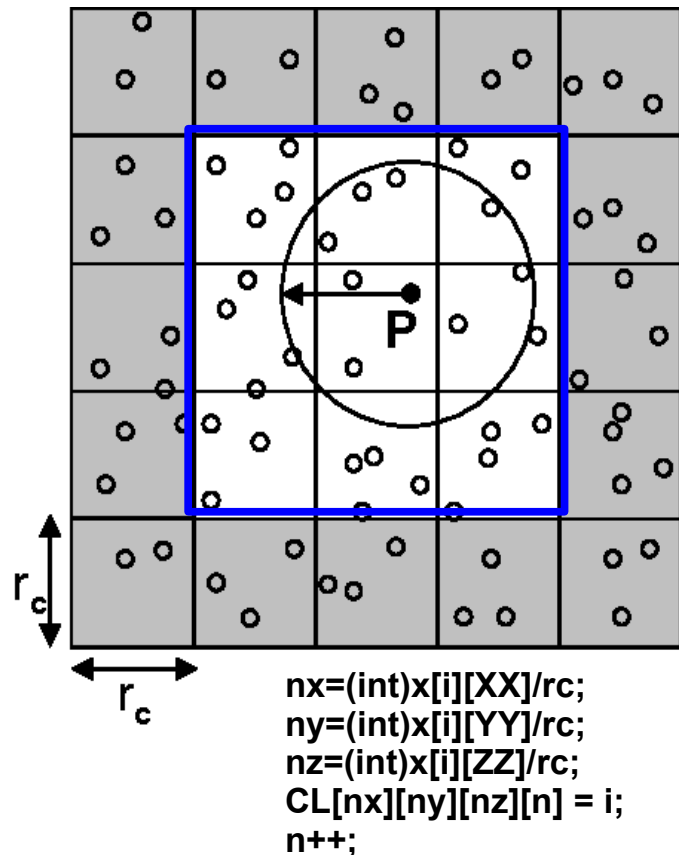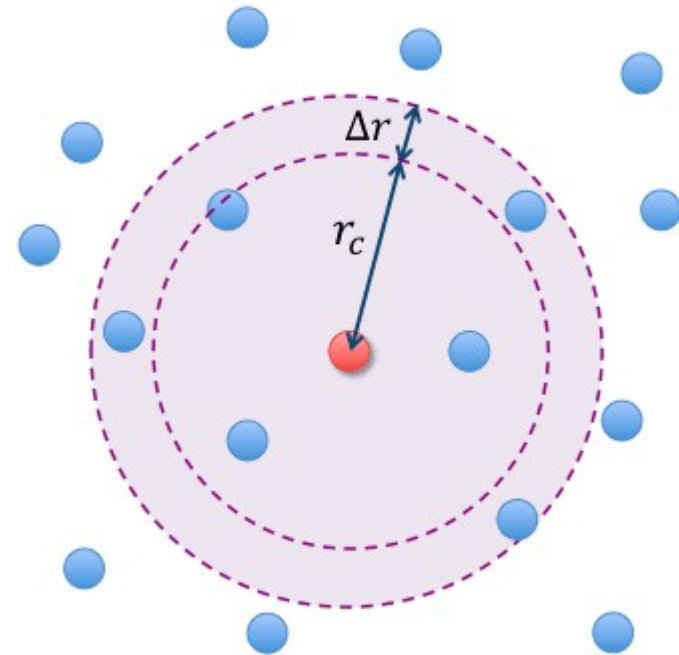
The solution is to introduce "cutoffs"!

Simulation cutoff

Cell list: Finding neighbors efficiently

nx=(int)x[i][XX]/rc;
ny=(int)x[i][YY]/rc;
nz=(int)x[i][ZZ]/rc;
**CL[nx][ny][nz][n] = i;**
n++;

Verlet list:

- The cell list can be used to efficiently generate a Verlet list. A substantial volume mismatch between the cutoff sphere and the corresponding subcells exists. Updating of the cell list itself, however, scales with N_{global}.
- The Verlet list (scales with N_{local}^2) conserves all neighbors until a particle moves beyond "its skin", $r_c + \Delta r$. This check is inexpensive since these distances are anyway calculated to assign the forces.
- Infrequent updating makes the simulation faster but is also a source of noise.

Periodic boundary Conditions (PBC)

$$R_c < \frac{1}{2}\min(\|\mathbf{a}\|, \|\mathbf{b}\|, \|\mathbf{c}\|),$$
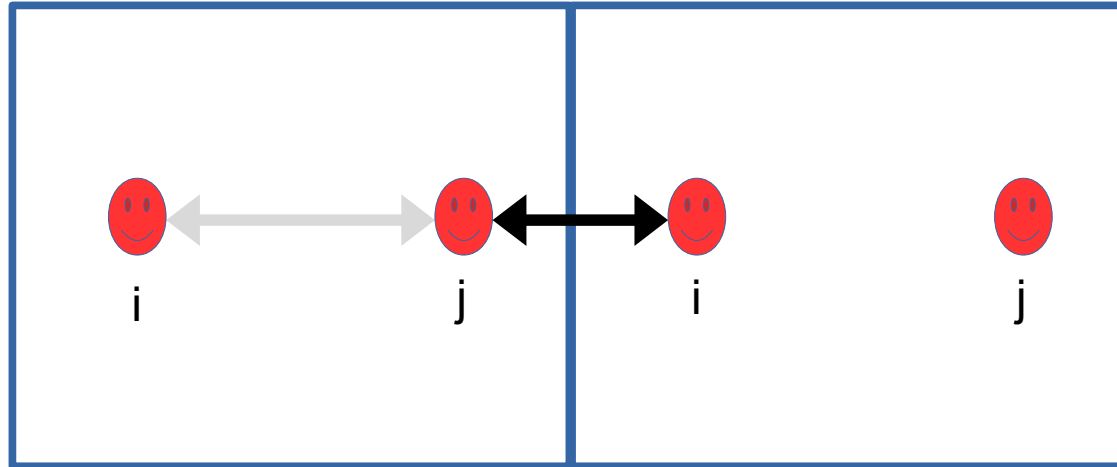

In the "Argon code":

```
def calculateForce(self, atom1, atom2):
    """Calculates the force between two atoms using LJ 12-6 potential"""
    # Calculate distance between two atoms
    dx = self.atoms[atom1].x - self.atoms[atom2].x
    dy = self.atoms[atom1].y - self.atoms[atom2].y
    dz = self.atoms[atom1].z - self.atoms[atom2].z

    # Minimum Image Convention
    dx -= self.lbox*round(dx/self.lbox)
    dy -= self.lbox*round(dy/self.lbox)
    dz -= self.lbox*round(dz/self.lbox)
```

- The minimum image convention implies that the cut-off radius used to truncate non-bonded interactions may not exceed half the shortest box vector.

Simulation cutoff: Lennard-Jones

- The smaller the cutoff the more efficient the speed up. In atomistic simulations the typical ' cutoff for Lennard-Jones interactions is about 1.0-1.2 nm.
- Truncation of energy! Energy derivatives must go to zero at the cutoff!
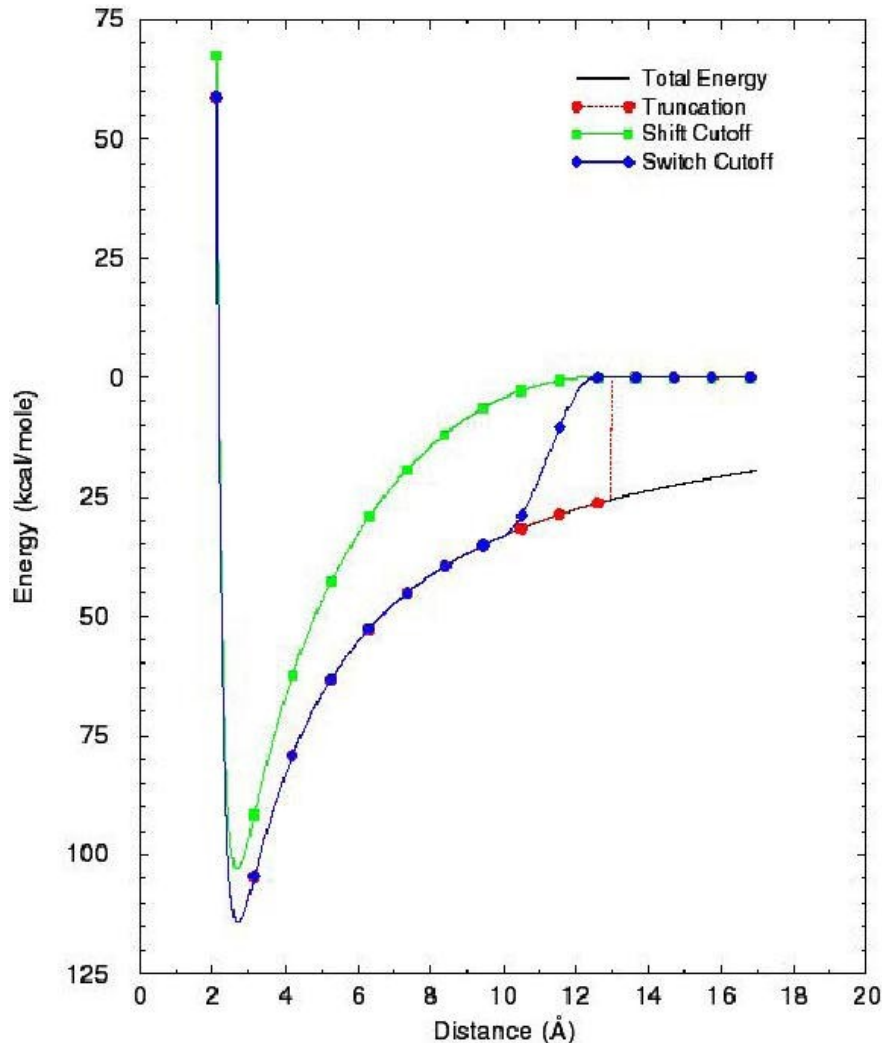
$$\mathbf{F}(\mathbf{x_i}) = -\nabla V(\mathbf{x_i})$$

"Shift" and "Switch" Cutoffs are achieved via addition of the function S(r), if r1 = 0 -> "Shift" Cutoff else "Switch" Cutoff:

$$
\begin{aligned}
F_s(r) &= F_\alpha(r) & r < r_1 \\
F_s(r) &= F_\alpha(r) + S(r) & r_1 \le r < r_c \\
F_s(r) &= 0 & r_c \le r
\end{aligned}
$$

$$S_V(r; r_1, r_c) = \frac{1 - 10(r-r_1)^3(r_c-r_1)^2 + 15(r-r_1)^4(r_c-r_1) - 6(r-r_1)}{(r_c-r_1)^5}$$

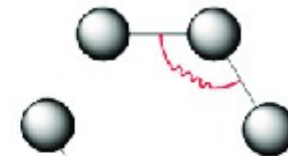# *Atomistic force-fields*

How expensive are chemical bonds?
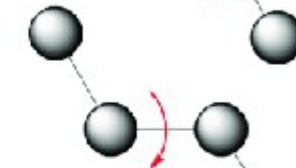
$$U(R) = \sum_{bonds} k_r (r - r_{eq})^2 \quad \text{bond}$$
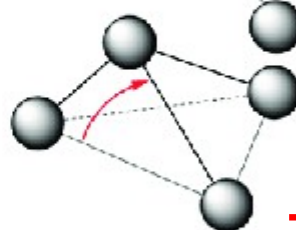
$$+ \sum_{angles} k_\theta (\theta - \theta_{eq})^2 \quad \text{angle}$$

$$+ \sum_{dihedrals} k_\phi (1 + \cos[n\phi - \gamma]) \quad \text{dihedral}$$

$$+ \sum_{impropers} k_\omega (\omega - \omega_{eq})^2 \quad \text{improper}$$

$$+ \sum_{i<j}^{atoms} \varepsilon_{ij} \left[\left(\frac{r_m}{r_{ij}} \right)^{12} - 2 \left(\frac{r_m}{r_{ij}} \right)^6 \right] \quad \text{van der Waals}$$
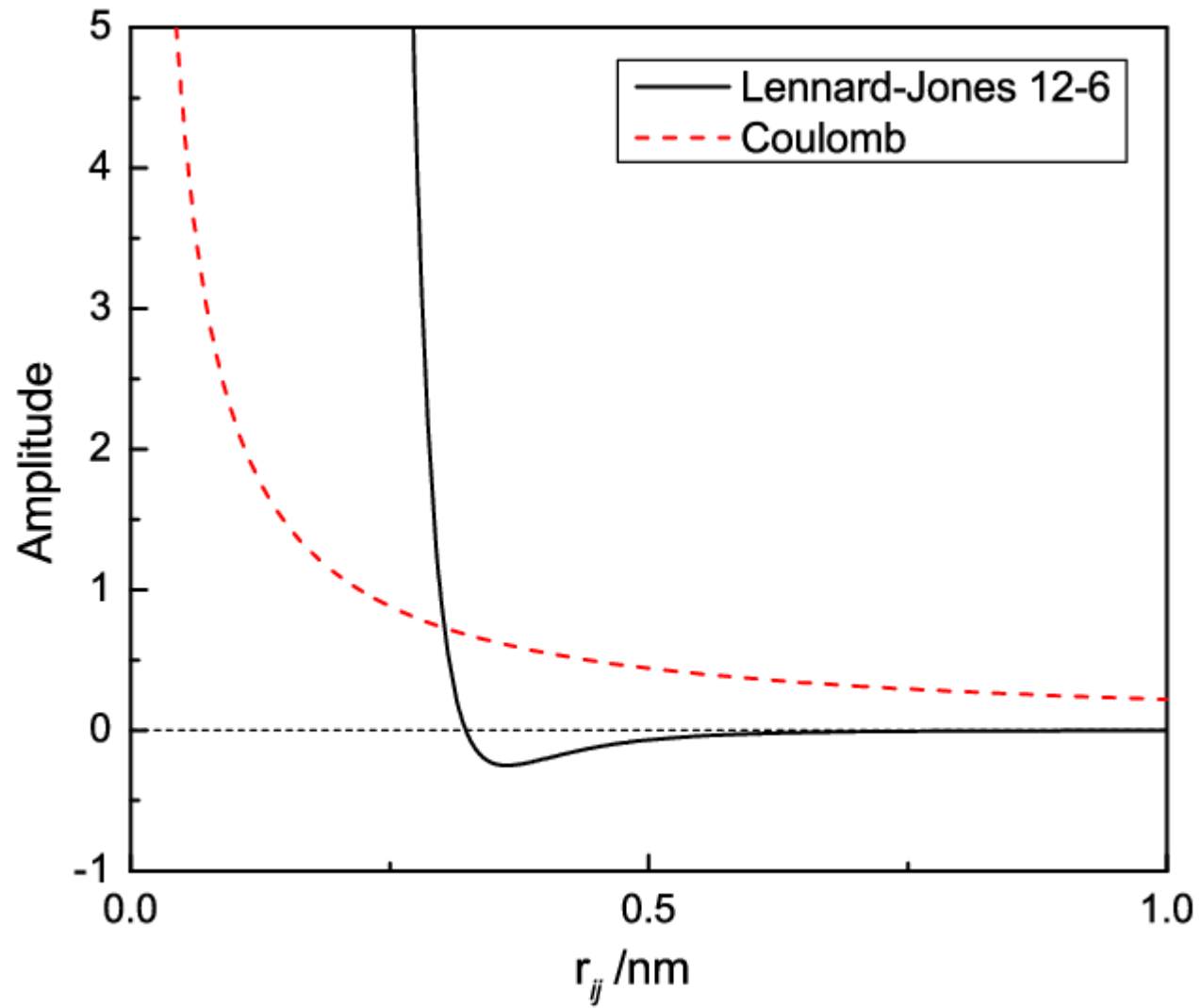
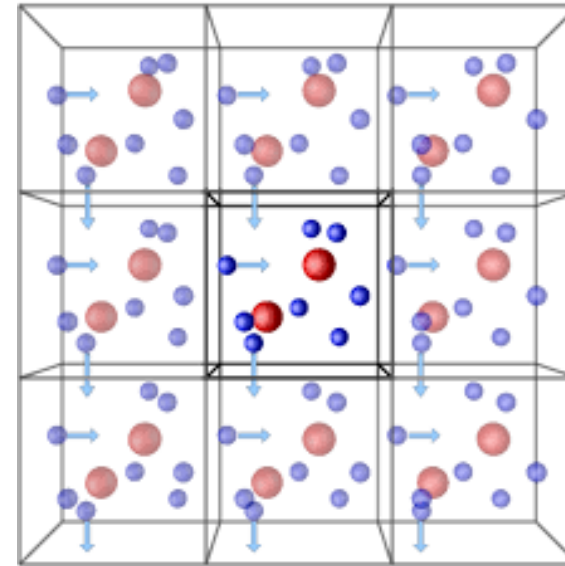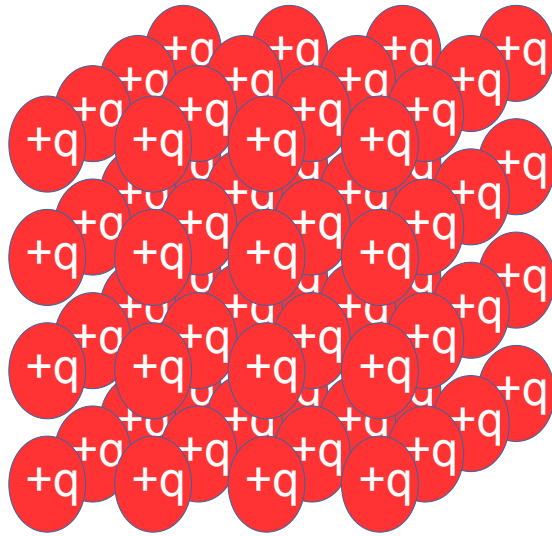$$+ \sum_{i<j}^{atoms} \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \quad \text{electrostatic}$$

```
for(i=0;i<N;i++)
for(j=i+1;j<N;j++)
{
    f=do_force(x[i],x[j]);
    ft[i] += f;
    ft[j] -=  f;
}
```

- Electrostatic interactions only scale with 1/r: The long-range interactions are significant! Shifting or switching neglects these contributions.

Electrostatic interactions: Monopoles

periodic boundary conditions (PBC)

- Coulomb explosion: Potential energy builds up quicker (r^3) than the decay ($1/r$) !
- Accurate description of systems with a net charge is generally challenging in periodic boundary conditions.

Electrostatic interactions: Multipoles

$$V_{total} = V_{mono} + V_{dipole} + V_{quad} + V_{octo} + \dots$$

monopole

+q

$$\frac{1}{r}$$

dipole

+q —— -q

$$\frac{1}{r^2}$$
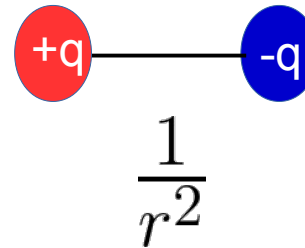
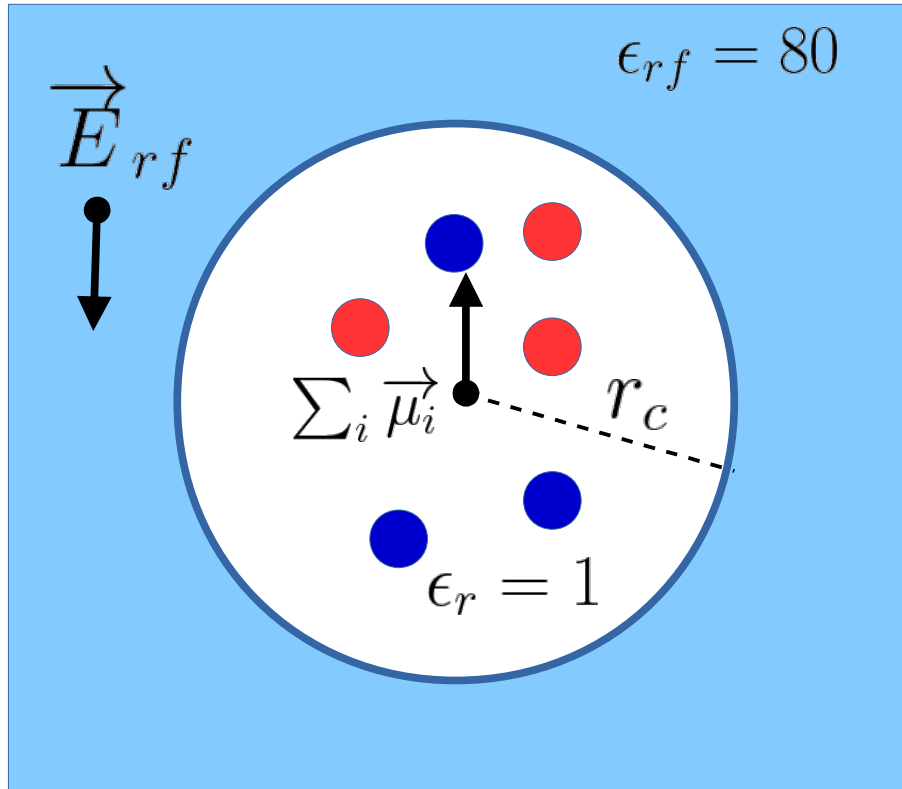$$\sum q \neq 0 \longrightarrow V_{total} \approx V_{monopole}$$

$$\sum q = 0 \longrightarrow V_{total} \approx V_{dipole}$$

- In neutral systems the contribution of monopoles to the potential vanishes and the dipole terms become dominant!

Electrostatics: Onsager reaction field

1) Direct interactions with other particles in R.
2) Treat material outside sphere as continuum dielectric.

$$\epsilon_{rf} = 80$$

$$\vec{E}_{rf}$$

$$\sum_i \vec{\mu_i} \qquad r_c$$

$$\epsilon_r = 1$$

Lars Onsager

$$\vec{E}_{rf} = \frac{2(\epsilon_{rf}-1)\sum_i \vec{\mu_i}}{(2\epsilon_{rf}+1)r_c^3}$$

$$V_{crf} = f\frac{q_i q_j}{\varepsilon_r r_{ij}}\left[1 + \frac{\varepsilon_{rf}-\varepsilon_r}{2\varepsilon_{rf}+\varepsilon_r}\frac{r_{ij}^3}{r_c^3}\right] - f\frac{q_i q_j}{\varepsilon_r r_c}\frac{3\varepsilon_{rf}}{2\varepsilon_{rf}+\varepsilon_r}$$

- Instantaneous response of the dielectric to the dipole in the sphere. Some variants of this method introduce a relaxation time.
- The method works well in isotropic systems with large electrostatic screening due to the presence of many ion pairs (high ionic strength → small Debye length).
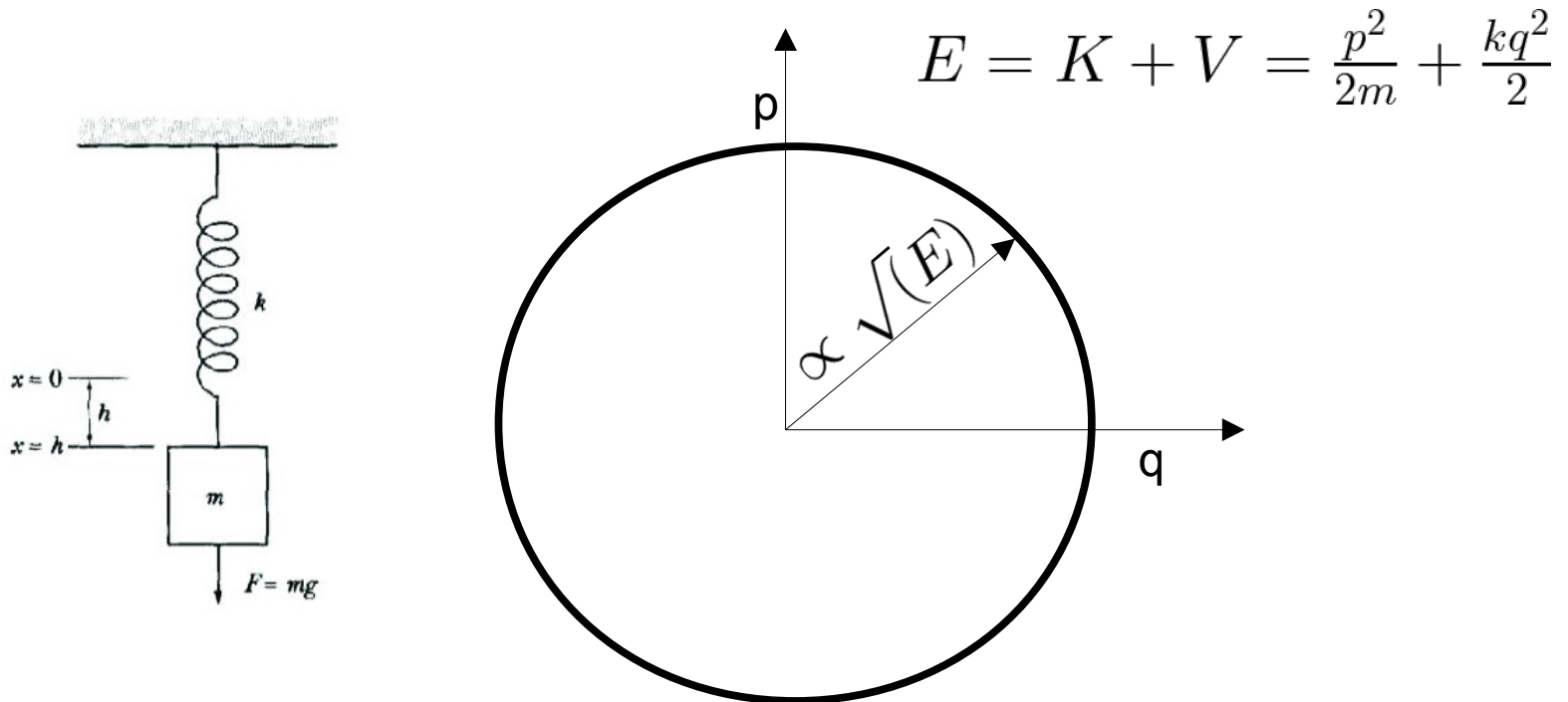
Fluctations in the canonical ensemble

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

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

Hamiltons equations of motion are energy conserving (NVE)

$$E = K + V = \frac{p^2}{2m} + \frac{kq^2}{2}$$

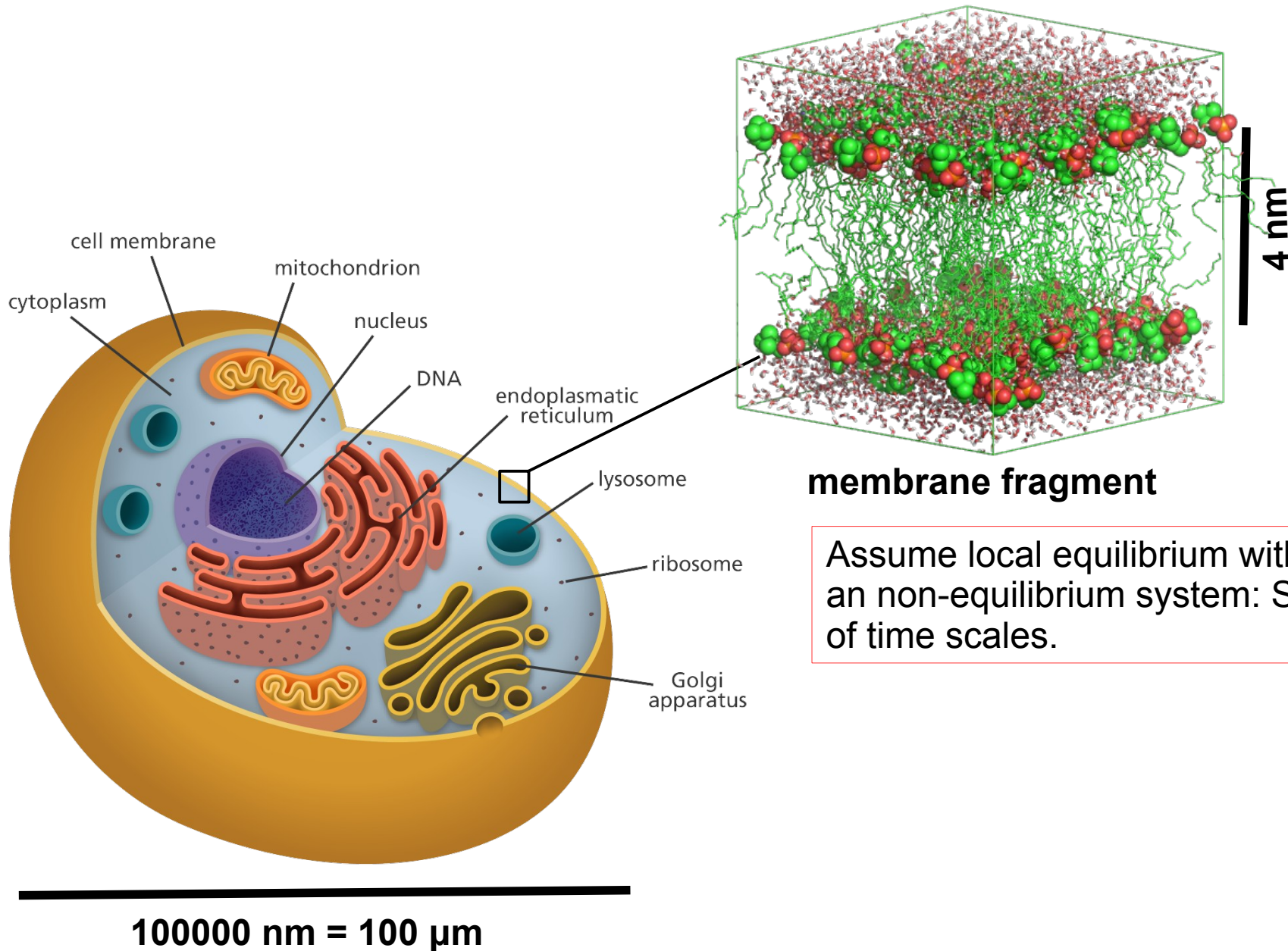# *Fluctations in the canonical ensemble*

The general proof:

$$dH(p,r) = \frac{\partial H}{\partial p} dp + \frac{\partial H}{\partial r} dr$$

$$\frac{\partial H}{\partial p} = \dot{r} \qquad \frac{\partial H}{\partial r} = -\dot{p}$$

$$\frac{dH(p,r)}{dt} = \frac{\partial H}{\partial p}\dot{p} + \frac{\partial H}{\partial r}\dot{r} = \dot{r}\dot{p} - \dot{p}\dot{r} = 0$$

Simulation of "living" biological systems?

membrane fragment

Assume local equilibrium within
an non-equilibrium system: Separation
of time scales.

4 nm

cell membrane
cytoplasm
mitochondrion
nucleus
DNA
endoplasmatic
reticulum
lysosome
ribosome
Golgi
apparatus

100000 nm = 100 μm

Constant temperature in finite systems

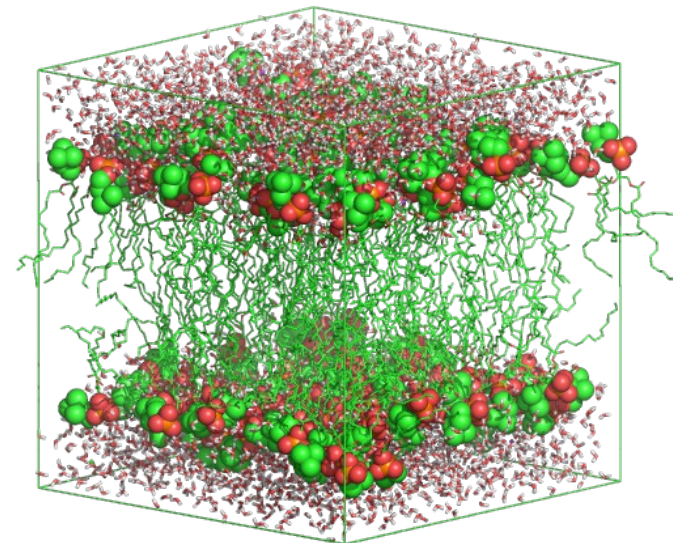The simulation system is coupled to a heath bath with a constant temperature and energy (infinite energy)!

heat bath T_c (constant energy)

4 nm
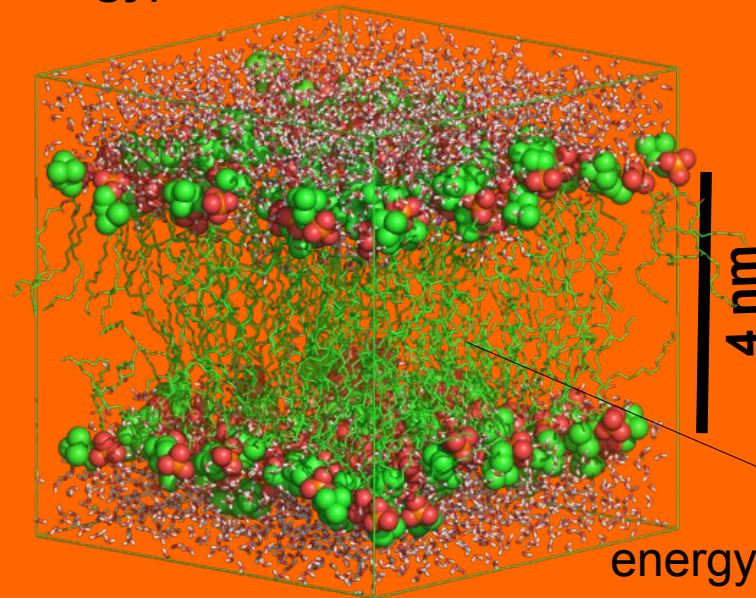
energy is not conserved!: NVT

membrane fragment

How large are energy fluctuations?

Energy (kcal/mol)

Legend:
- Potential energy (blue)
- Non-bond energy (green dashed)
- Kinetic energy (red)
- Total energy (blue/purple)
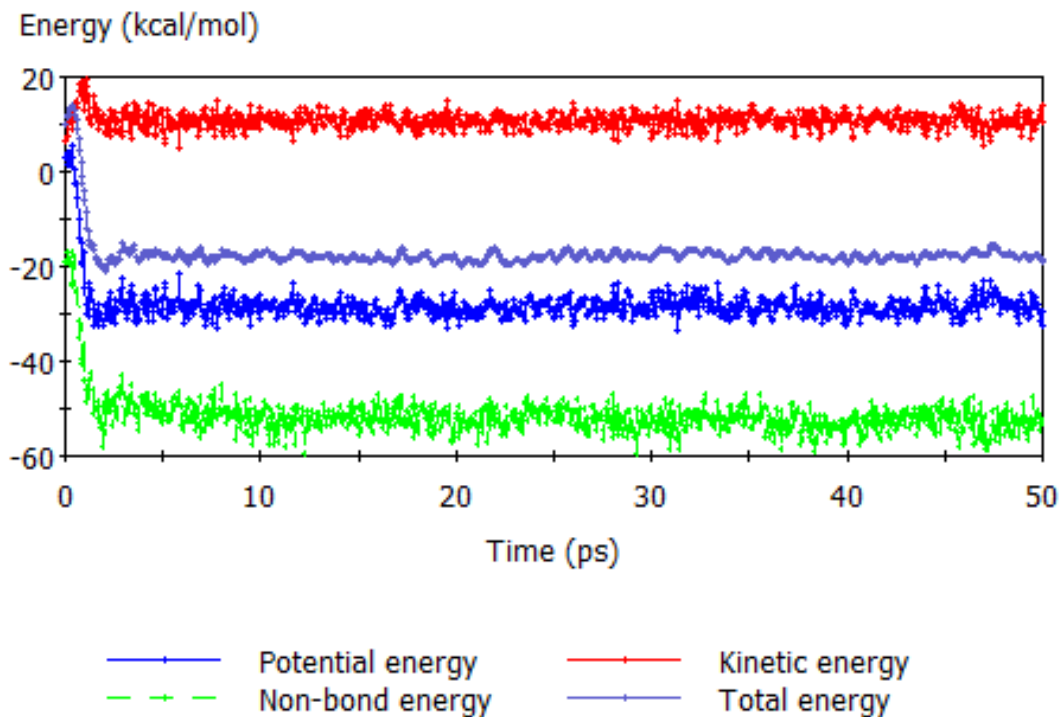
Note that the potential energy is typically negative!
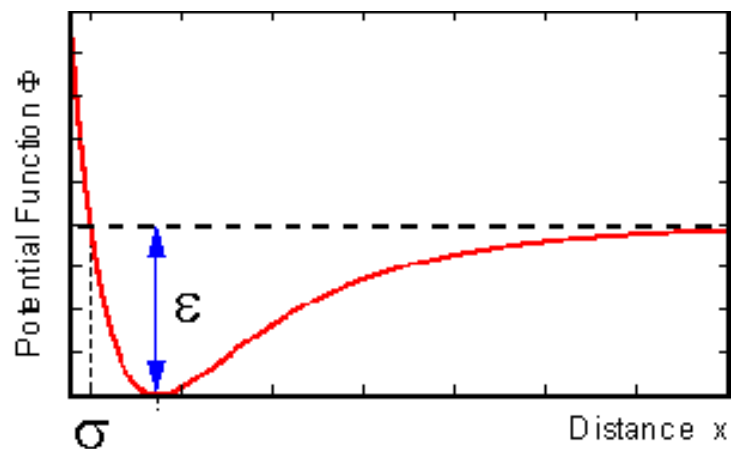
$$\phi\left(r_{ij}\right) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

How large are energy fluctuations?

Question: How large are energy fluctuations in the finite simulation system at equilibrium?

The average energy E and the average of E^2 are Boltzmann distributed:

$$\langle E \rangle = \frac{1}{Z} \sum_j E_j e^{\frac{-E_j}{kT}}$$

$$\langle E^2 \rangle = \frac{1}{Z} \sum_j E_j^2 e^{\frac{-E_j}{kT}},$$

How large are energy fluctuations?

$$\langle E \rangle = \frac{1}{Z} \sum_j E_j e^{\frac{-E_j}{kT}}$$

$$\langle E^2 \rangle = \frac{1}{Z} \sum_j E_j^2 e^{\frac{-E_j}{kT}},$$

Take the derivative with respect to the temperature T:

$$\frac{\partial \langle E \rangle}{\partial T} = \frac{1}{Z} \sum_j \frac{E_j^2}{kT^2} e^{\frac{-E_j}{kT}} + \left(\sum_j E_j e^{\frac{-E_j}{kT}} \right) \left(\frac{-1}{Z^2} \frac{\partial Z}{\partial T} \right)$$

$$= \frac{1}{kT^2} \langle E^2 \rangle - \langle E \rangle \frac{\partial \ln Z}{\partial T} = \frac{1}{kT^2} \left(\langle E^2 \rangle - \langle E \rangle^2 \right),$$

<E>/kT²

How large are energy fluctuations?

$$\frac{\partial \langle E \rangle}{\partial T} = \frac{1}{Z} \sum_j \frac{E_j^2}{kT^2} e^{\frac{-E_j}{kT}} + \left(\sum_j E_j e^{\frac{-E_j}{kT}} \right) \left(\frac{-1}{Z^2} \frac{\partial Z}{\partial T} \right)$$

$$= \frac{1}{kT^2} \langle E^2 \rangle - \langle E \rangle \frac{\partial \ln Z}{\partial T} = \frac{1}{kT^2} \left(\langle E^2 \rangle - \langle E \rangle^2 \right),$$

$$\langle E^2 \rangle - \langle E \rangle^2 = kT^2 \frac{\partial \langle E \rangle}{\partial T} = kT^2 C_V.$$

C_v is the heath capacity at constant volume

How large are energy fluctuations?

$$\langle E^2 \rangle - \langle E \rangle^2 = kT^2 \frac{\partial \langle E \rangle}{\partial T} = kT^2 C_V.$$

"random walk-like term"

Brownian displacement:
$$< \Delta R^2 > = 2Dt$$

$$(\Delta E)^2 = kT^2 C_V.$$ (fluctuation-dissipation theorem)

$$
\begin{aligned}
(\Delta E)^2 &= \langle E^2 - 2E\langle E \rangle + \langle E \rangle^2 \rangle = \langle E^2 \rangle - 2\langle E\langle E \rangle \rangle + \langle \langle E \rangle^2 \rangle \\
&= \langle E^2 \rangle - \langle E \rangle^2.
\end{aligned}
$$

$$(\Delta E)^2 = kT^2 C_V.$$ (fluctuation-dissipation theorem)

How does ΔE scale with the number of particles ΔN? Lets normalize E:

$$\frac{\Delta E}{\langle E \rangle} = \sqrt{kT^2} \frac{\sqrt{C_V}}{\langle E \rangle}.$$

$$C_V \propto N$$
$$<E> \propto N$$

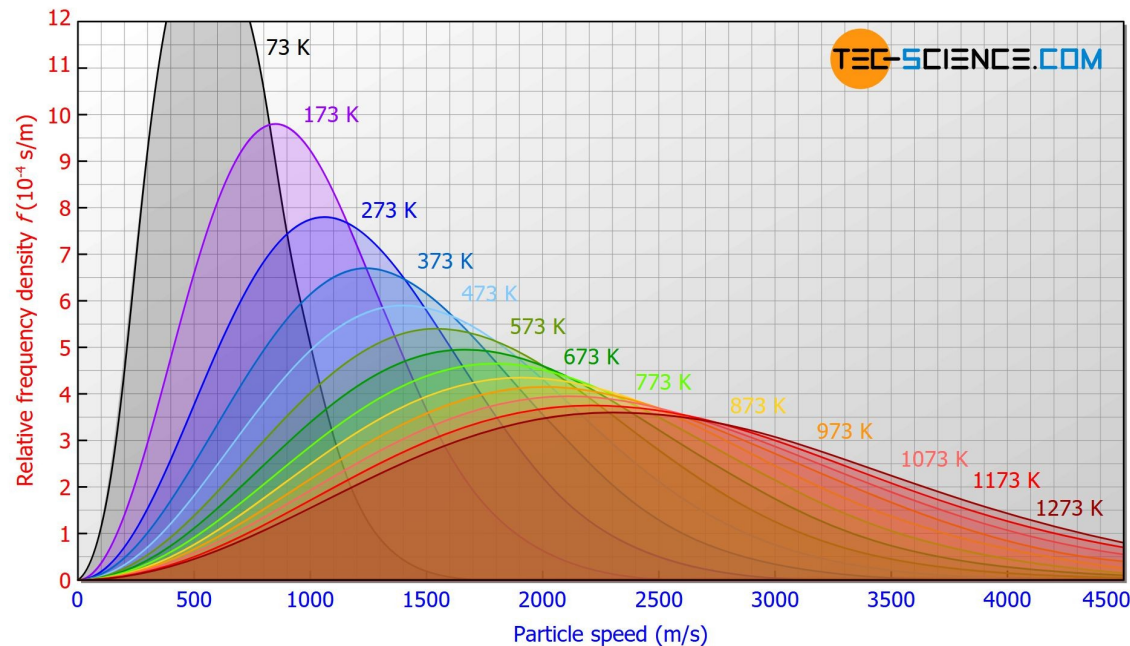$$\frac{\Delta E}{\langle E \rangle} \propto \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}},$$

Energy fluctuations scale with √(1/N). Fluctuations vanish if N approaches ∞

N is "countable" in simulations thus strong fluctuations.

$$\sum_{i=1}^{N} \frac{|\mathbf{p}_i|^2}{2m_i} = \frac{k_b T}{2}\left(3N - N_c\right) \quad \longrightarrow \quad T = \sum_{i=1}^{N} \frac{|\mathbf{p}_i|^2}{m_i k_{\mathrm{B}} N_{df}}$$

$$3N - N_c = N_{df}$$

- Individual velocities of particles follow the Maxwell-Boltzmann distribution!

- Initializing temperature T in a simulation: Assign the velocity of particles based the on the M-B distribution corresponding to T.

Controlling temperature: Velocity scaling

$$\Delta T = T_0 - T(t) \qquad T = \sum_{i=1}^{N} \frac{|\mathbf{p}_i|^2}{m_i k_{\mathrm{B}} N_{df}}$$

T_0 is the target temperature, $T(t)$ is the instantaneous temperature.

scaling parameter λ

$$\Delta T = \frac{1}{2} \sum_{i=1} 2 \frac{m_i (\lambda v_i)^2}{N_{df} k_B} - \frac{1}{2} \sum_{i=1} 2 \frac{m_i v_i^2}{N_{df} k_B}$$

$$\Delta T = (\lambda^2 - 1) T(t)$$

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

- Velocity-scaling suppresses the characteristic thermal fluctuations which are present in a finite ensemble

Controlling temperature: Langevin dynamics

$$m_i \mathbf{a}_i = \mathbf{F}_i - \gamma \mathbf{v}_i + \mathbf{R}_i(t)$$

Friction. Heat loss!   **Random force. Adds heat!**

The gain and loss of heat must be in balance (Fluctuation-dissipation theorem). This balance is temperature dependent and thus acts a thermostat.
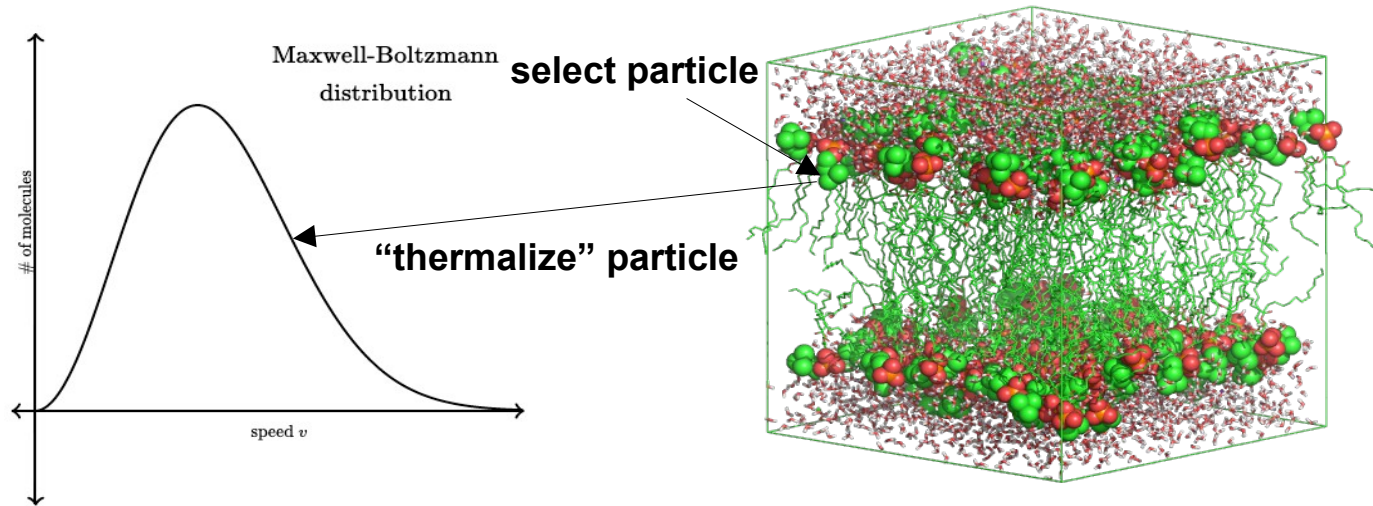
This balance is (only) satisfied when:

$$\langle \mathbf{R}_i(t) \rangle = 0$$

$$\langle \mathbf{R}_i(t)\mathbf{R}_i(t') \rangle = 2k_B T \gamma \delta(t - t') \qquad 1/\Delta t$$

- Explicit knowledge of the number of degrees of freedom in the system is not required to control the temperature.
- Sampling of phase-space is excellent.
- Canonical ensemble is well reproduced: $(\Delta E)^2 = kT^2 C_V$.
- Dynamics is (of course) not conserved!

Controlling temperature: Andersen-Thermostat

- Stochastic thermostat: Reassigns the velocities of randomly selected particles using the M-B distribution.
- The number of particles selected and frequency of the velocity reassignment determines the coupling strength with the heat bath.
- An Boltzmann distribution as input gives a Boltzmann distribution as output.
- This still does not conserve dynamics or properties related to dynamics (e.g., diffusion constants)!

Controlling temperature: Berendsen Thermostat

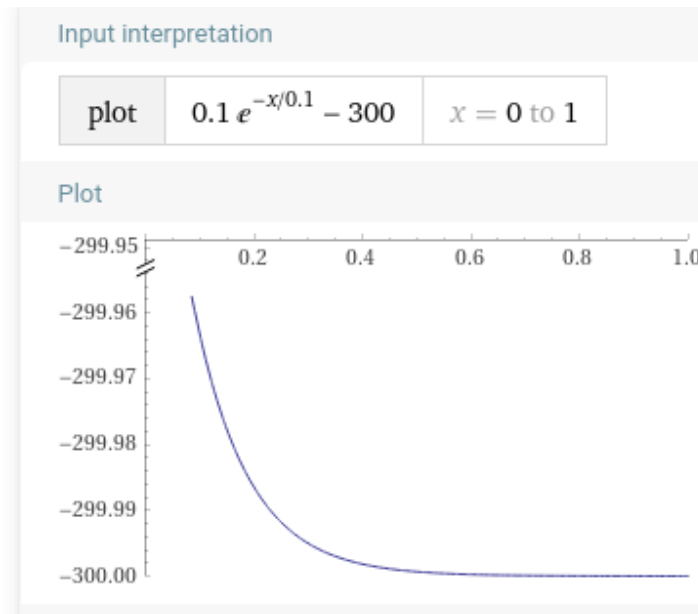**Main idea**: Model the change in T as a first order decay:

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

with τ being a coupling constant (1/time), T_0 the target temperature.
The solution is an exponential decay (weak coupling):

$$T(t) = \tau C e^{-t/\tau} + T_0$$

Herman Berendsen

Input interpretation

plot	$0.1\,e^{-x/0.1} - 300$	$x = 0$ to 1

Plot

Controlling temperature: Velocity scaling

$$\Delta T = T_0 - T(t) \qquad \boxed{T = \sum_{i=1}^{N} \frac{|\mathbf{p}_i|^2}{m_i k_{\mathrm{B}} N_{df}}}$$

T_0 is the target temperature, $T(t)$ is the instantaneous temperature.

scaling parameter λ

$$\Delta T = \frac{1}{2} \sum_{i=1} 2 \frac{m_i (\lambda v_i)^2}{N_{df} k_B} - \frac{1}{2} \sum_{i=1} 2 \frac{m_i v_i^2}{N_{df} k_B}$$

$$\Delta T = (\lambda^2 - 1) T(t)$$

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

- Velocity-scaling suppresses the characteristic thermal fluctuations which are present in a finite ensemble

Controlling temperature: Berendsen Thermostat

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

In discrete time this takes the form:

$$\Delta T = \frac{\Delta t}{\tau}(T_0 - T(t))$$

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

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Leap-frog scheme

$$\lambda^2 = 1 + \frac{\Delta t}{\tau}\left\{\frac{T_0}{T(t-\frac{\Delta t}{2})} - 1\right\}$$

If τ goes to infinity then the ensemble approaches NVE, if τ equal dt then velocity scaling is recovered. Typically τ is 0.1 ps.

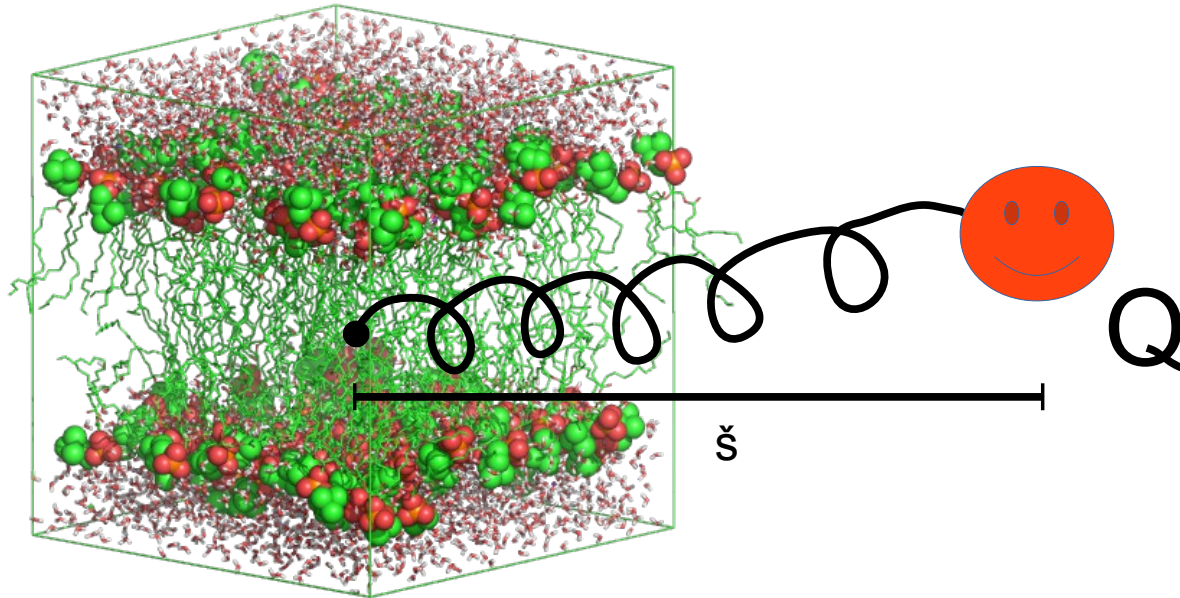# *Controlling temperature: Berendsen Thermostat*

The Berendsen thermostat (still) does not produce the canonical ensemble!!!!

(Though in Lennard-Jones fluids, it closely approaches it.)

$$(\Delta E)^2 = kT^2 C_V.$$

The main idea is to couple the heat bath and energy of the system by a spring with a virtual length š, a mass Q, and velocity dš/dt. This combined system is coined "the extended system":

Now let š act as an effective time-scaling parameter (š ~ 1):

$$d\tilde{t} = \tilde{s}dt$$

This yields the following set of extended variables:

$$\tilde{\mathbf{r}} = \mathbf{r}\,,\ \dot{\tilde{\mathbf{r}}} = \tilde{s}^{-1}\dot{\mathbf{r}}\,,\ \tilde{s} = s \text{ and } \dot{\tilde{s}} = \tilde{s}^{-1}\dot{s}$$

Controlling temperature: Nose-Hoover

$$\tilde{\mathbf{r}} = \mathbf{r} \, , \; \dot{\tilde{\mathbf{r}}} = \tilde{s}^{-1}\dot{\mathbf{r}} \, , \; \tilde{s} = s \text{ and } \dot{\tilde{s}} = \tilde{s}^{-1}\dot{s}$$

The Lagrangian of the extended ensemble is given by:

$$\mathcal{L} = \sum_i \frac{m_i}{2}\tilde{s}^2\dot{\tilde{\mathbf{r}}}_i^2 - U(\tilde{\mathbf{r}}) + \frac{1}{2}Q\dot{\tilde{s}}^2 - gk_bT_0\ln\tilde{s}$$

potential energy heat bath

kinetic energy heat bath

degrees of freedom

$$g = N_{df} + 1$$

$$\mathcal{L} = \sum_i \frac{m_i}{2} \tilde{s}^2 \dot{\tilde{\mathbf{r}}}_i^2 - U(\tilde{\mathbf{r}}) + \frac{1}{2} Q \dot{\tilde{s}}^2 - g k_b T_0 \ln \tilde{s}$$

$\tilde{r}$ $\tilde{s}$

Euler-Lagrange:

$$\frac{\partial}{\partial t} \frac{\partial L}{\partial \dot{q}} = \frac{\partial L}{\partial q}$$

$$\ddot{\tilde{\mathbf{r}}}_i = \frac{\tilde{\mathbf{F}}_i}{m_i \tilde{s}^2} - \frac{2 \dot{\tilde{s}} \dot{\tilde{\mathbf{r}}}_i}{\tilde{s}} \, ,$$

$$\ddot{\tilde{s}} = \frac{1}{Q \tilde{s}} \left(\sum_i m_i \tilde{s}^2 \dot{\tilde{\mathbf{r}}}_i^2 - g k_b T_0 \right)$$

- Although these equations sample a microcanonical ensemble (constant energy) in the extended system, the real system (r, dr/dt) samples a canonical esemble!

The real system is retrieved via the transformation:

$$s = \tilde{s}, \quad \dot{s} = \tilde{s}\dot{\tilde{s}}, \quad \ddot{s} = \tilde{s}^2\ddot{\tilde{s}} + \tilde{s}\dot{\tilde{s}}^2,$$

$$\mathbf{r} = \tilde{\mathbf{r}}, \quad \dot{\mathbf{r}} = \tilde{s}\dot{\tilde{\mathbf{r}}}, \quad \ddot{\mathbf{r}} = \tilde{s}^2\ddot{\tilde{\mathbf{r}}} + \tilde{s}\dot{\tilde{\mathbf{r}}}^2$$

$$\gamma = \frac{\dot{s}}{s}$$

$$\ddot{\mathbf{r}}_i = \frac{\mathbf{F}_i}{m_i} - \gamma\mathbf{r}_i,$$

$$\dot{\gamma} = \frac{-k_B N_{df}}{Q}T(t)\left(\frac{g}{N_{df}}\frac{T_0}{T(t)} - 1\right).$$

heat bath acceleration

- If Q goes to infinity the NVE ensemble is obtained. Small Q values (tight coupling) may result in high-frequency oscillations. Q should be large. If Q is large then the canonical ensemble is only obtained when the ensemble averaging occurs over longer time-scales.
- The main limitation of the NH thermostat is its oscillatory behavior: True energy fluctuations are stochastic in nature!

Controlling temperature: Nose-Hoover


Berk Hess (PhD thesis)
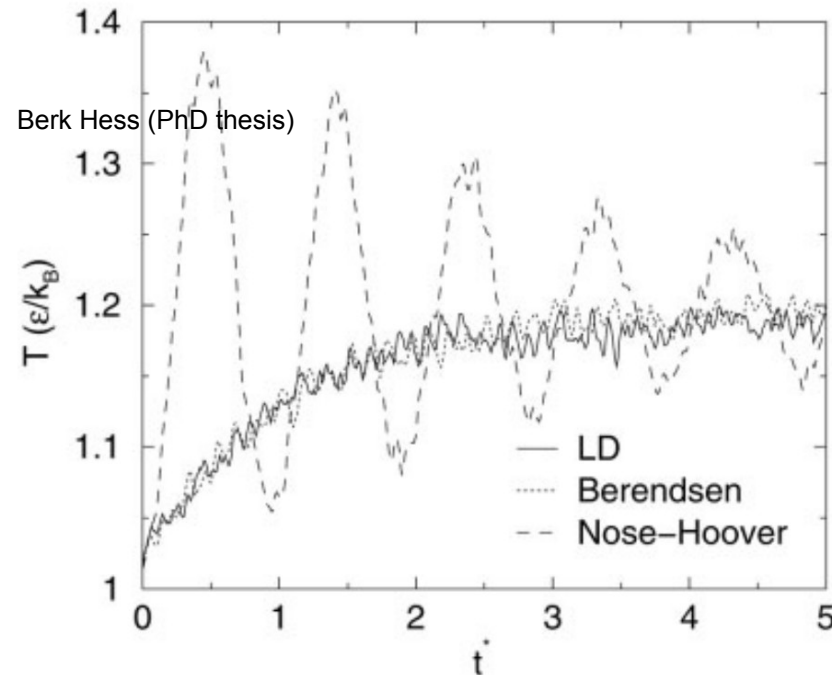
Figure 2. Response of three different thermostats to a temperature jump from 1 to 1.2 for a system of 8000 Lennard–Jones particles. Time and temperature are in reduced units (from Hess[61]).

- The Nose-Hoover thermostat has a very slow response! (e.g., Use Berendsen to first equilibrate system then switch to Nose-Hoover)
- The Nose-Hoover infact becomes nonergodic in small, solid systems (resonance with normal modes in the system).
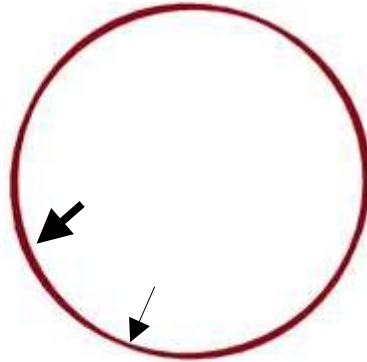
Controlling temperature: A summary

Phase-space of the harmonic oscillator:

Microcanonical   Nosé-Hoover   Andersen   Langevin
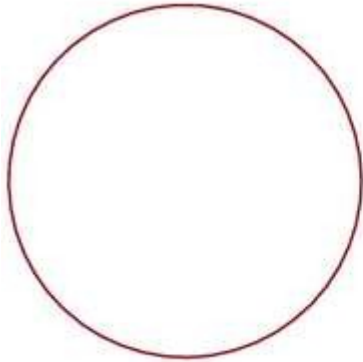
Energy is constant
Temperature is not.

Ergodicity problems
in small, stiff systems.
Excellent conservation
of dynamics.

Superior sampling.
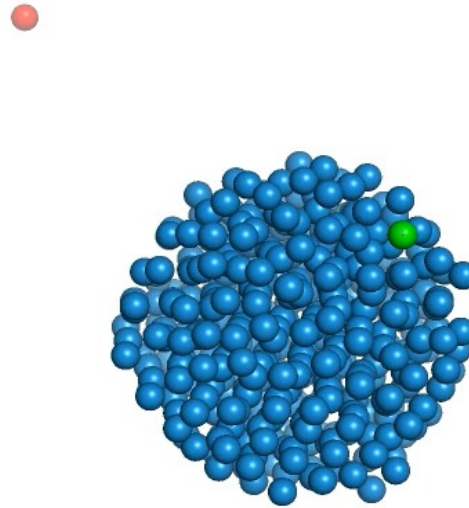Dynamics is lost.
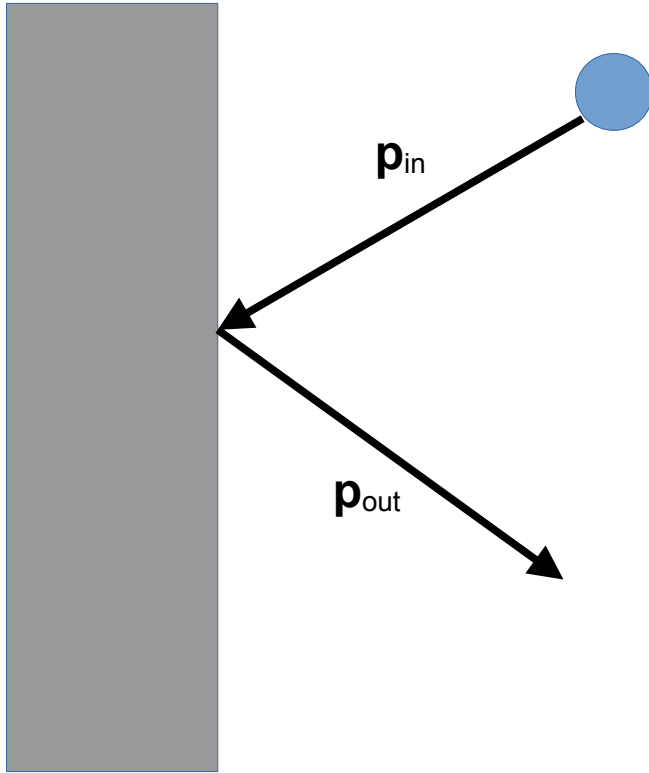
The sampling resembles a superposition
of multiple NVE ensembles.
Dynamics is distorted.

- **All thermostats come with pro's and con's. Picking the most suitable thermostat depends on the application**. Dynamics?: Nose-Hoover. Non-equilibrium? (weak-coupling schemes: Berendsen & co). Sampling efficiency only? Andersen and Langevin.
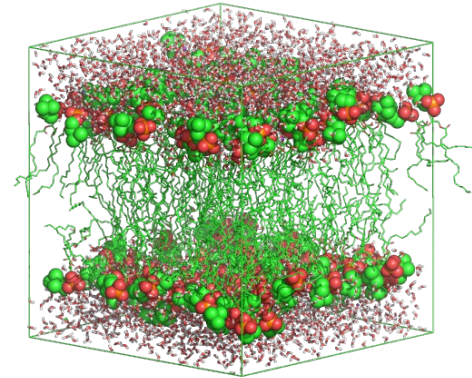
The famous "flying ice cube" artifact

$$\Delta\mathbf{p} = \mathbf{p}_{out} - \mathbf{p}_{in}$$

The force on the wall is:

$$\mathbf{F} = - \sum_{collisions} \frac{\Delta\mathbf{p}}{\Delta t}$$

The pressure on the wall is:

$$P = F/A$$

- This classic "wall definition" of pressure is ambiguous in periodic boundary conditions, though can be effective in the presence of an actual boundary potential. In that case, the force on the wall F is precisely known (local pressure).

Controlling pressure: Clausius virial theorem

Lets start with Newton again……………….

$$m\ddot{\mathbf{r}}_i = \mathbf{F}_i$$

multiply both sides by r$_i$

$$\mathbf{r}\ddot{\mathbf{r}} = \frac{d}{dt}\left(\mathbf{r}\dot{\mathbf{r}}\right) - \dot{\mathbf{r}}^2 \, ,$$

Substitution now yields

$$\frac{d}{dt}(m_i\mathbf{r}_i\dot{\mathbf{r}}_i) - m\dot{\mathbf{r}}_i^2 = \mathbf{F}_i\mathbf{r}_i$$

In this notation Fr is a scalar product: $F_x r_x + F_y r_y + F_z r_z$

Controlling pressure: Clausius virial theorem

$$\frac{d}{dt}(m_i \mathbf{r}_i \dot{\mathbf{r}}_i) - m \dot{\mathbf{r}}_i^2 = \mathbf{F}_i \mathbf{r}_i$$

angular momentum: dL/dt=0

For all N particles thus yields:

$$-2E_{kin} = \sum_{i=0}^{N} \mathbf{F}_i \mathbf{r}_r$$

2x kinetic energy!

This is the total virial W

Assume the system is under an externally applied pressure P. Then the total virial W is split into two contributions:

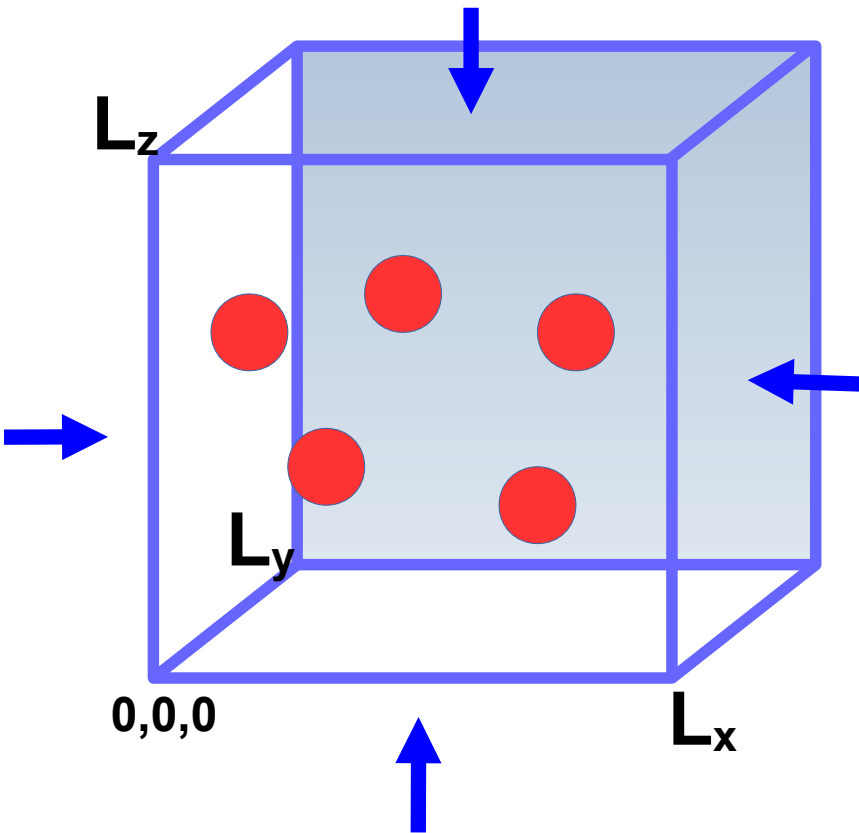$$\langle W \rangle = \langle W^{ext} \rangle + \langle W^{int} \rangle$$

particles not (!)
in contact with the wall

$$\langle W^{ext} \rangle = \sum_{Walls} r_i F_i \rightarrow r_{i,w} \sum_{Wall} F_i = r_w F_{wall}$$

average force
on the wall

average force
on the wall

$$\langle W^{ext} \rangle = -L_x(\overline{PL_y L_z}) + -L_y(PL_x L_z)$$
$$+ -L_z(PL_x L_y) = -3PV$$

L_z

L_y

0,0,0

L_x

Controlling pressure: Definition of pressure

$$\langle W^{int} \rangle := \Xi$$

Note that the average kinetic energy Ekin is 3/2NK$_B$T. Therefore, this yields:

$$PV = Nk_BT + \frac{1}{3}\Xi$$

ideal gas term

+interaction term

$$\sum_{k=1}^{N} \mathbf{F}_k \cdot \mathbf{r}_k = \sum_{k=1}^{N}\sum_{j=1}^{N} \mathbf{F}_{jk} \cdot \mathbf{r}_k = \sum_{k=2}^{N}\sum_{j=1}^{k-1} (\mathbf{F}_{jk} \cdot \mathbf{r}_k + \mathbf{F}_{kj} \cdot \mathbf{r}_j)$$

single sum

$$= \sum_{k=2}^{N}\sum_{j=1}^{k-1} (\mathbf{F}_{jk} \cdot \mathbf{r}_k - \mathbf{F}_{jk} \cdot \mathbf{r}_j) = \sum_{k=2}^{N}\sum_{j=1}^{k-1} \mathbf{F}_{jk} \cdot (\mathbf{r}_k - \mathbf{r}_j)$$

double sum

- Disclaimer: These derivations used the "single virial". In periodic boundary conditions the single virial requires additional corrections (no conservation of angular momentum), i.e., "book keeping" of force contributions that crossed the periodic boundaries.

Controlling pressure: Berendsen barostat

Main idea: Model the change in P as a first order decay:

$$\frac{dP}{dt} = \frac{P_0 - P(t)}{\tau_P}$$

with τ being a coupling constant (1/time), P_0 the target pressure.

Scale coordinates and box over Δt :

$$x \to \mu x$$

$$\Delta V / \Delta t = 3\mu V$$

The relation ship between change in pressure and volume is given by :

$$\frac{dP}{dt} = -\frac{1}{\kappa_T V}\frac{dV}{dt} = -\frac{3\mu}{\kappa_T}$$

κ_T isothermal compressibility Its dimension is 1/pressure.

Herman Berendsen

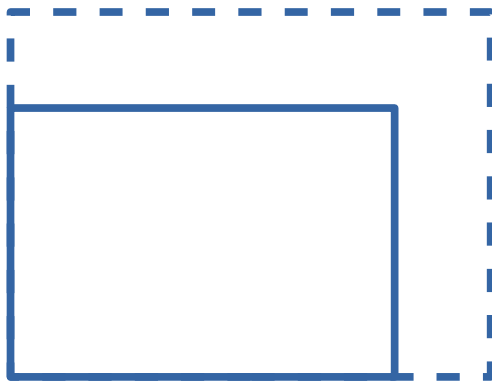Simulation box and coordinates are thus (isotropically) scaled as :

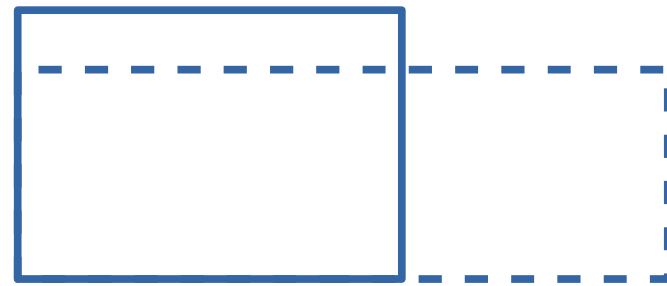$$\mu = 1 - \frac{\kappa_T \Delta t}{3\tau_P}(P_0 - P(t))$$

- Andersen Barostat. Note that this is an 'extended' barostat rather than a stochastic one like 'his' thermostat! It could be coined "Noose-Hover" barostat ;-):

$$\frac{d\mathbf{r}_i}{dt} = \frac{\mathbf{p}_i}{m_i} + \frac{1}{3}\mathbf{r}_i\frac{d\ln V}{dt},$$

$$\frac{d\mathbf{p}_i}{dt} = -\sum \hat{\mathbf{r}}_{ij}U'(\mathbf{r}_{ij}) - \frac{1}{3}\mathbf{p}_i\frac{d\ln V}{dt},$$

$$\frac{Md^2V}{dt^2} = p_0 + \left(\frac{2}{3}\sum \frac{\mathbf{p}_i^2}{2m_i} - \frac{1}{3}\sum \mathbf{r}_{ij}U'(r_{ij})\right)/V.$$

- The Parrinello-Rahman barostat is an anisotropic extension on the Anderson barostat.

isotropic   anisotropic