Simulating thermodynamics ensembles

what you simulate is what you would measure

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Intro

- system of classical particles interacting with potential V
  – deterministic system
- given initial conditions ($\vec{r}_0$ and $\vec{v}_0$),
  trajectory of the system ($\vec{r}(t)$ and $\vec{v}(t)$)
  is determined for all of the future $t \to \infty$
- for some systems – analytic solution
  e.g. harmonic oscillator:

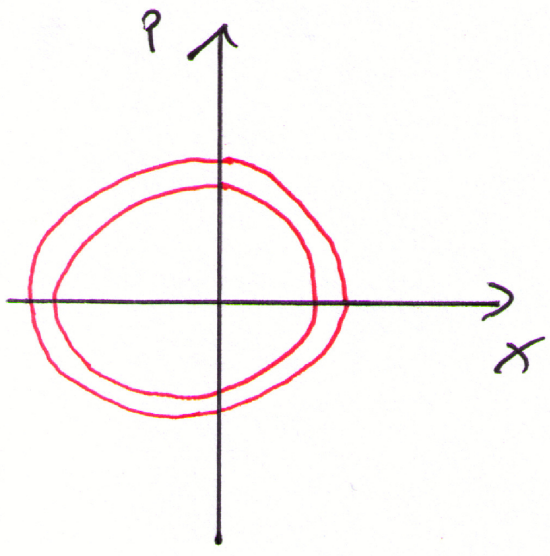
$$x(t) = x_0 \cdot \cos[\omega t] \qquad v(t) = -v_0 \cdot \sin[\omega t]$$

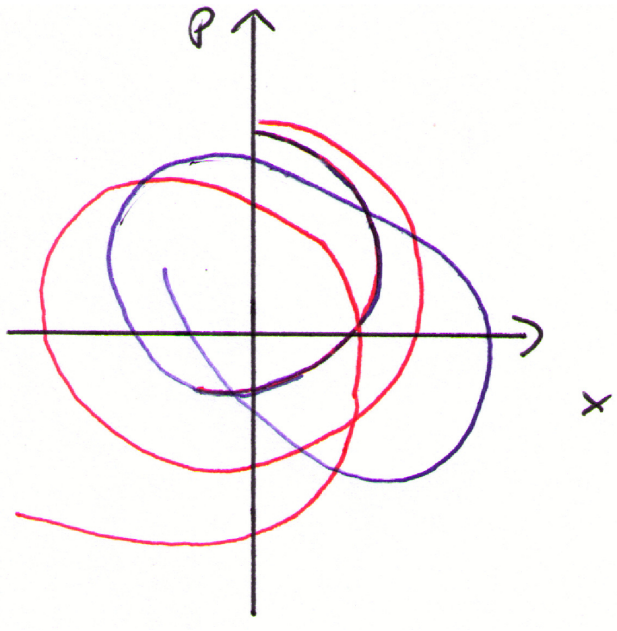
Intro

- for a complex system – trajectory is obtained numerically
- so-called chaotic systems – strictly deterministic, too
- chaos – two trajectories close in phase space initially will depart exponentially from each other (solution of the eqns of motion is unstable)

Intro

stable and unstable solutions of eqns of motion





Intro

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T – determines if a region of phase space shall be reached in MD
phase space – different sampling at high and at low temperatures – different ensembles will be generated

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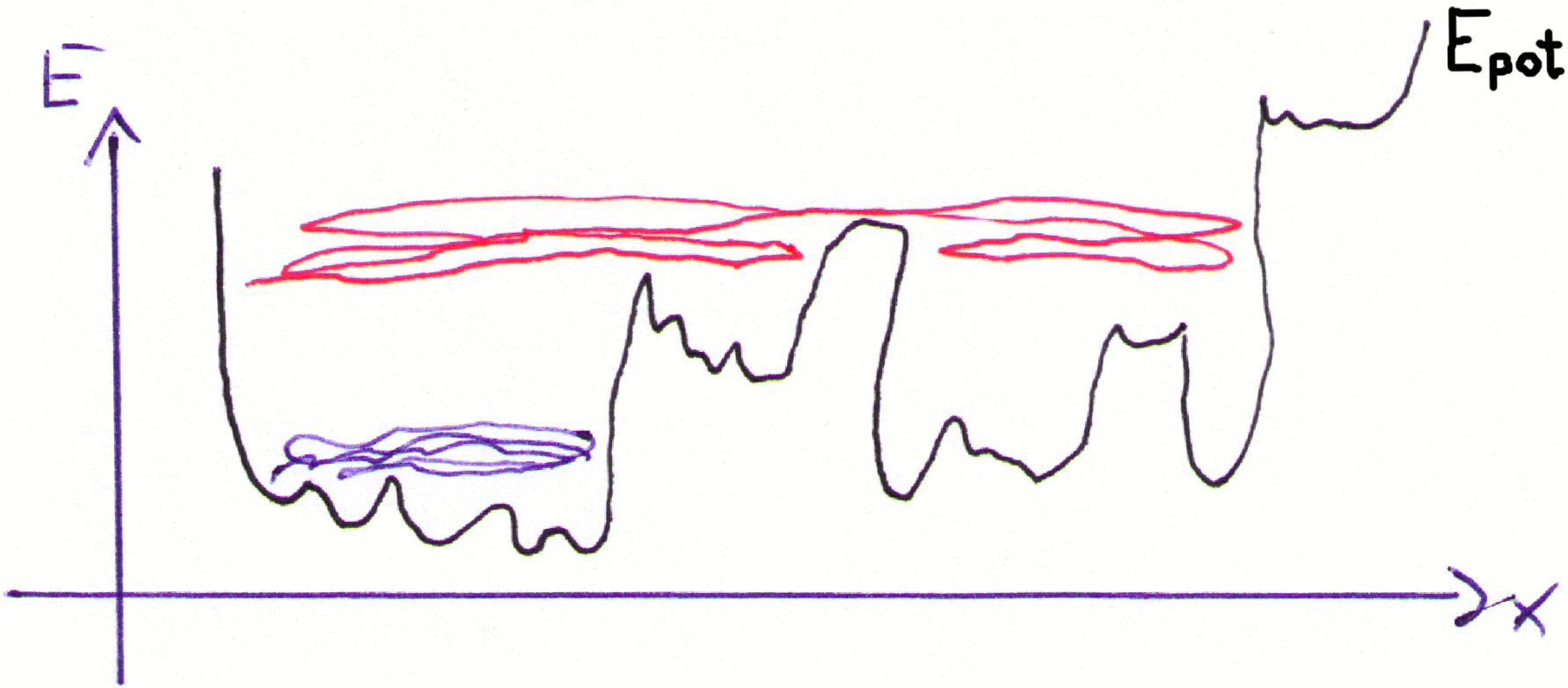
T – determines if a region of phase space shall be reached in MD
phase space – different sampling at high and at low temperatures – different ensembles will be generated

particularly important – to find a way to model the system, so that we obtain correct phase space density

Intro

high E – multiple different regions of the phase space are reached
low E – restricted available region of phase space



difference $E - E_{\text{pot}}$ corresponds to E_{kin} and temperature

Isolated system

- exchanges with surroundings neither energy (heat / work)
  nor matter (particles)
- total energy of system: $E = E_{\text{kin}} + E_{\text{pot}} = \text{const}$
- individually, E_{kin} and E_{pot} fluctuate in the course of time
  as they are being transformed into each other
- is what we get when using the Verlet method for a molecule
- trajectory in the microcanonical ensemble

Isolated system

kinetic theory of gases $\rightarrow$ relation of E_{kin} and temperature:

$$\begin{aligned} \langle E_{\text{kin}} \rangle &= \frac{3}{2} NkT \\ \text{where } \langle E_{\text{kin}} \rangle &= \frac{1}{2} \sum_i m_i \langle v_i^2 \rangle \\ \text{so } T &= \frac{\sum_i m_i \langle v_i^2 \rangle}{3Nk} \end{aligned}$$

'local' temperature

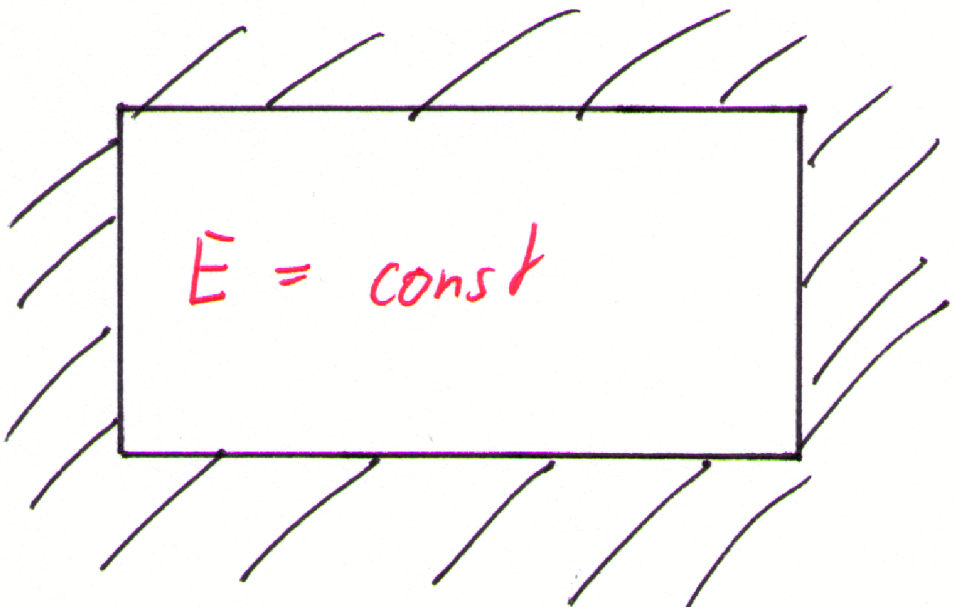
- fluctuates in time
- may differ between different parts of system

Isolated and closed system

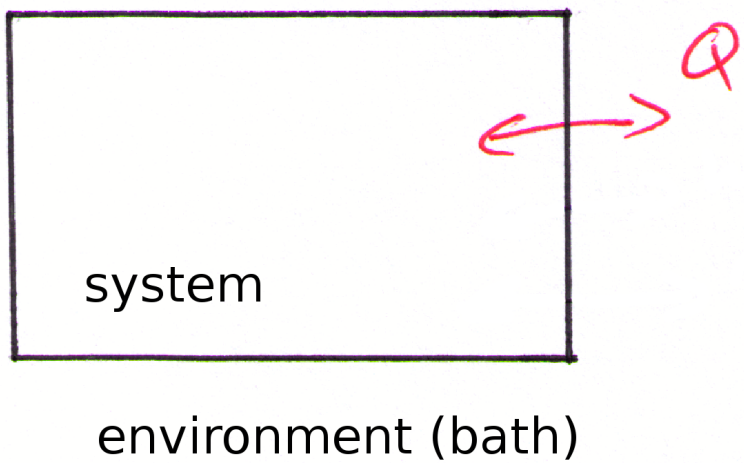
experimental setup (a test tube with a sample)

- usually in thermodynamic equilibrium with the surroundings
- temperature (and optionally pressure) equal as that of surr.

isolated system



closed system



Closed system

- thermal contact of system with surroundings
- exchange of energy in the form of heat
  until the temperature of surroundings is reached
- strictly speaking: T only defined with such thermal contact
  ($\rightarrow$ N/A in case of isolated system)
- trajectory in the canonical ensemble

Canonical ensemble

velocity / speed of atoms – Maxwell–Boltzmann distribution

$$p(v_{x,i}) = \sqrt{\frac{m_i}{2\pi kT}} \cdot \exp\left[-\frac{m_i v_{x,i}^2}{2kT}\right]$$

$$p(v_i) = 4\pi \left(\frac{m_i}{2\pi kT}\right)^{3/2} \cdot v_i^2 \cdot \exp\left[-\frac{m_i v_i^2}{2kT}\right]$$

Canonical ensemble

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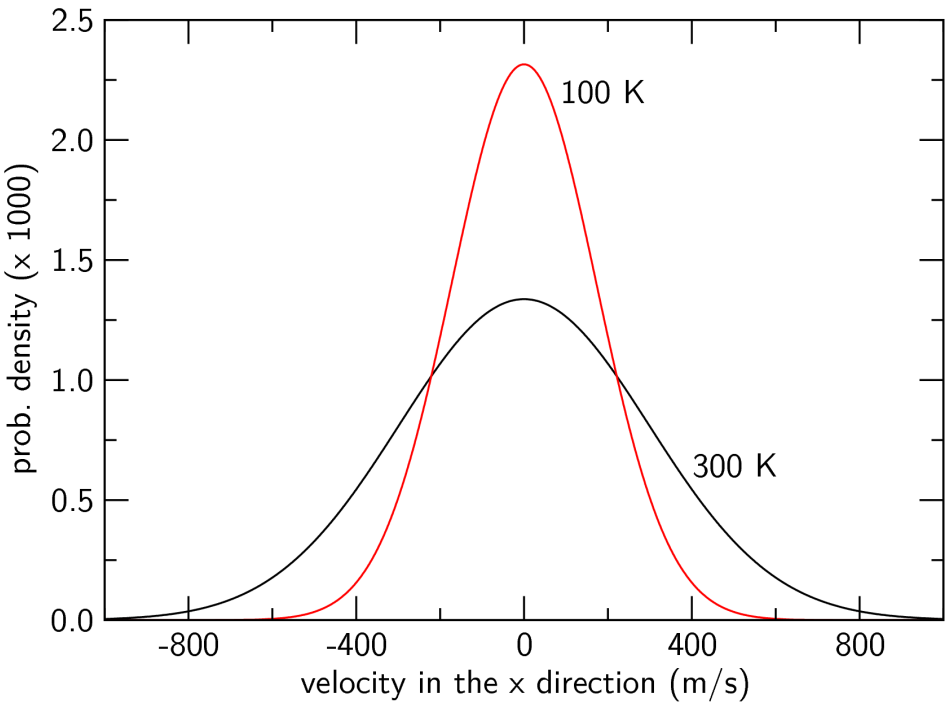

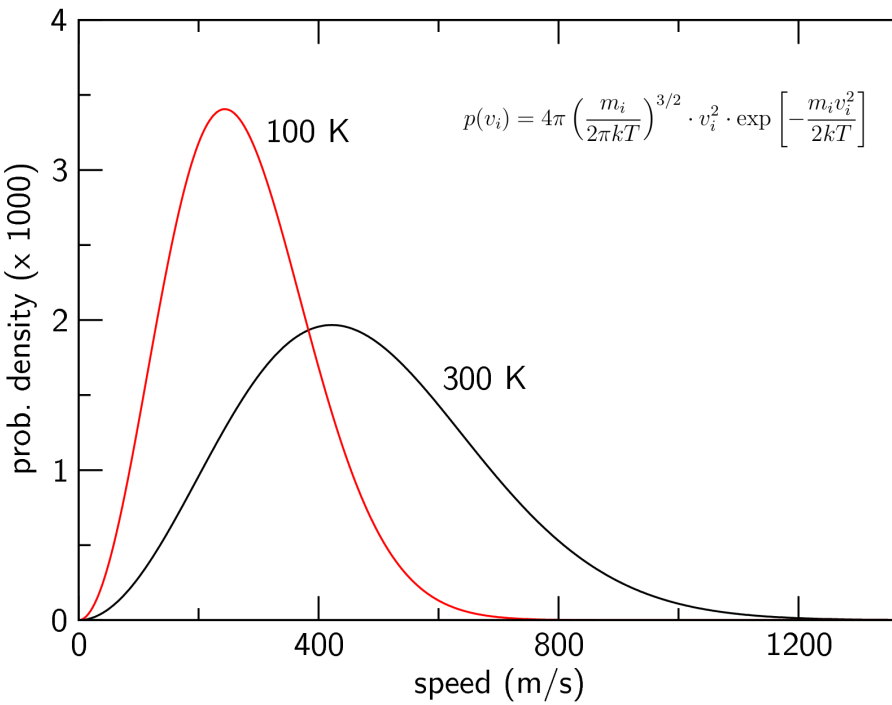

(for N_2 as IG)

Equipartition theorem

(Gleichverteilungssatz) (DOF = degree of freedom)
Every DOF contains the same average amount of kinetic energy of

$$\left\langle \frac{1}{2} m_i v_{x,i}^2 \right\rangle = \frac{1}{2} kT$$

Each atom i has 3 DOF x_i, y_i and z_i (and $v_i^2 = v_{x,i}^2 + v_{y,i}^2 + v_{z,i}^2$) $\rightarrow$

$$\langle E_{\text{kin}} \rangle = \left\langle \sum_i \frac{1}{2} m_i v_i^2 \right\rangle = \left\langle \sum_i \frac{1}{2} m_i v_{x,i}^2 + \frac{1}{2} m_i v_{y,i}^2 + \frac{1}{2} m_i v_{z,i}^2 \right\rangle = \frac{3}{2} NkT$$

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Such a distribution of velocity and kinetic energy is a property of systems in contact with heat bath (not of isolated system)

Question: How can we control the temperature in simulation?

Naïve thermostat – scaling of velocities

in a Verlet MD simulation – 'instantaneous temperature' T deviates from the target T_{ref} (of bath = the surroundings)

$$T(t) = \frac{2}{3}\frac{E_{\text{kin}}(t)}{Nk} \neq T_{\text{ref}}$$

$T(t)$ – another name for E_{kin} determined by velocities
simple idea – scale the velocities by a certain factor λ:

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$$\begin{aligned} T_{\text{ref}} &= \frac{1}{\frac{3}{2}Nk} \cdot \frac{1}{2}\sum_i m_i \left(\lambda \cdot v_i\right)^2 = \\ &= \lambda^2 \cdot \frac{1}{\frac{3}{2}Nk} \cdot \frac{1}{2}\sum_i m_i v_i^2 = \lambda^2 \cdot T \end{aligned}$$

scaling of all velocities by $\lambda = \sqrt{T_{\text{ref}}/T} \rightarrow T_{\text{ref}}$ reached exactly

Naïve thermostat – scaling of velocities

- very crude way of controlling the temperature
- rescaling the velocities affects the 'natural' way of evolution of the system
- velocities – not sure if the distribution is correct (M–B)
- importantly, system does not sample any canonical ensemble
  – phase space density is not that of a canonical ensemble
  – very important because everything is calculated as averages:

$$\langle A \rangle = \frac{1}{Z} \int \rho \cdot A \, \mathrm{d}\vec{r} \, \mathrm{d}\vec{p}$$

- possibly: wrong sampling $\rightarrow$ wrong averages

Naïve thermostat – scaling of velocities

How to avoid the drastic changes to the dynamics?

adjust velocities more smoothly, in the direction of T_{ref}, resigning on T_{ref} to be recovered in every step immediately

Berendsen thermostat

- system coupled to infinite bath with temperature T_{ref}
- temperature changes between two time steps according to

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{1}{\tau}\left(T_{\text{ref}} - T\right)$$

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- rate of change of T (due to the change of velocities) is proportional to the deviation of actual T from T_{ref}
- constant of proportionality – relaxation time τ
  – exponential decay of temperature towards T_{ref}:

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

Berendsen thermostat

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

- for that, velocities are scaled by λ as above:

$$\begin{aligned} T_{\text{new}} &= T + \Delta T = T + \frac{\Delta t}{\tau}\left(T_{\text{ref}} - T\right) \\ \lambda &= \sqrt{\frac{T_{\text{new}}}{T}} = \sqrt{1 + \frac{\Delta t}{\tau}\left(\frac{T_{\text{ref}}}{T} - 1\right)} \end{aligned}$$

- usually: $\tau = 0.1 - 10$ ps
- T is still fluctuating – however around the desired value T_{ref}

Berendsen thermostat

fluctuation of temperature – desired property
for canonical ensemble – variance of 'inst. temperature' T:

$$\sigma_T^2 = \left\langle (T - \langle T \rangle)^2 \right\rangle = \left\langle T^2 \right\rangle - \langle T \rangle^2$$

and relative variance

$$\frac{\sigma_T^2}{\langle T \rangle^2} = \frac{2}{3N}$$

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large number of atoms N: fluctuations $\to 0$
finite-sized systems: visible fluctuation of temperature
- feature of the canonical ensemble
- we would not obtain this with the simple velocity scaling

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- various parts of the system (different individual molecules, or solute × solvent) may exhibit different temperatures, while the temperature of the entire system is 'correct'
  – may remain like that for extended periods of time
- gradually moves the energy from the fastest modes of motion to the slowest/weakest ones, violating the equipartition

the fastest – bond stretching and angle bending
loss of energy → 'freezing' of the molecules

the slowest – 3 transl'ns (+ 3 rot'ns) of the entire system
energy gain → 'flying (+ spinning) ice cube'

Andersen thermostat

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this algorithm has a certain stochastic character:

- start MD with a standard integrator (Verlet. . .)
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advantage – generates canonical ensemble (if implemented right)
rate of collisions must be neither too low (inefficient) nor too high (collisions would dominate the dynamics over eqns of motion)

Nosé–Hoover thermostat

- conceptionally and mathematically $>$ difficult to understand
- heat bath is treated not as an external element
  rather as an integral part of the system
- the bath – an additional DOF s with fictitious mass Q
  may be understood as time-scaling parameter:

$$\mathrm{d}t' = s \cdot \mathrm{d}t$$

- eqns of motion will be propagated for this extended system,
  for which an energy-like quantity will be conserved
- generates canonical NVT ensemble of the molecular system

Nosé–Hoover thermostat

expression for the energy of the system involves the bath:

$$E_{\text{pot}} = U(r) + g \cdot kT_{\text{ref}} \cdot \log s$$

- g – number of DOF of the system $= 3N + 1$
- T_{ref} – reference temperature

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$$E_{\text{kin}} = \sum_i \frac{1}{2} m_i s^2 \dot{r}_i'^2 + \frac{1}{2} Q s'^2$$

- attention needed – derivatives w.r.t. the modified time:

$$\mathrm{d}t' \neq \mathrm{d}t \rightarrow \dot{r}_i' \neq \dot{r}_i$$

Nosé–Hoover thermostat

- eqns of motion for the extended system ($3N + 1$ DOF) derived with the Hamiltonian formalism:

$$H(r', \dot{r}', s, \dot{s}') \quad = \quad E_{\text{pot}} + E_{\text{kin}}$$

- eqns for the molecular DOF:

$$\frac{\mathrm{d}r_i}{\mathrm{d}t'} = \frac{1}{m_i} \cdot \frac{\partial H}{\partial \dot{r}_i'} \qquad \frac{\mathrm{d}\dot{r}_i'}{\mathrm{d}t'} = -\frac{1}{m_i} \cdot \frac{\partial H}{\partial r_i'}$$

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- eqns for the additional DOF:

$$\frac{\mathrm{d}s}{\mathrm{d}t'} = \frac{1}{Q} \cdot \frac{\partial H}{\partial \dot{s}'} \qquad \frac{\mathrm{d}\dot{s}'}{\mathrm{d}t'} = -\frac{1}{Q} \cdot \frac{\partial H}{\partial s'}$$

Nosé–Hoover thermostat

- we obtain these eqns of motion:

$$\ddot{r}'_i = \frac{F_i}{m_i} \cdot \frac{1}{s^2} - \frac{2\dot{s}'}{s} \cdot \dot{r}'_i$$

black – usual Newtonian eqns of motion
red – bath s integrated into the propagation,
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- one more eqn of motion – for the bath coordinate s:

$$\ddot{s}' = \frac{1}{Qs}\left(\sum_i m_i s^2 \dot{r}_i^2 - g \cdot kT_{\text{ref}}\right)$$

Nosé–Hoover thermostat

such eqns are impractical because

- they work with transformed velocities $\dot{r}'$ and accelerations $\ddot{r}'$
- time steps are not equally long ($\Delta t' = s \cdot \Delta t$)

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to make things clearer, we

- return from the modified time scale t' to the usual t
- transform the eqns to the usual vaiables $\dot{r}$, $\ddot{r}$
- for the 'velocity of bath': pass from $\dot{s}$ to $\gamma = \frac{\dot{s}}{s}$

Nosé–Hoover thermostat

final form of the eqns of motion:

$$\ddot{r}_i = \frac{F_i}{m_i} - \gamma \cdot \dot{r}_i$$

2nd term: formally – a kind of 'friction' (bath)

$$\dot{\gamma} = \frac{1}{Q}\left(T - T_{\text{ref}}\right)$$

note: $\sum_i \frac{1}{2} m_i \dot{r}_i^2 = 3N \cdot \frac{1}{2} kT$

Nosé–Hoover thermostat

- strength of coupling controlled by Q – more intuitively time τ:

$$Q = \frac{\tau^2 \cdot T_{\text{ref}}}{4\pi^2}$$

  – meaning of period of oscillation of the kinetic energy between the real system and the bath

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  Berendsen – exponential damping of ΔT with τ
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- thermostat – incorporated in eqns of motion – inseparable part of the integrator, rather than a posteriori correction
- generates canonical phase-space density, used frequently

Introducing pressure

chemical reality – constant pressure rather than constant volume
goal – implement such conditions in simulations, too

How to calculate pressure? – first, calculate virial of force

$$\Xi = -\frac{1}{2}\sum_{i<j} \vec{r}_{ij} \cdot \vec{F}_{ij}$$

($\vec{r}_{ij}$ distance of atoms i and j, $\vec{F}_{ij}$ – pairwise force between them)

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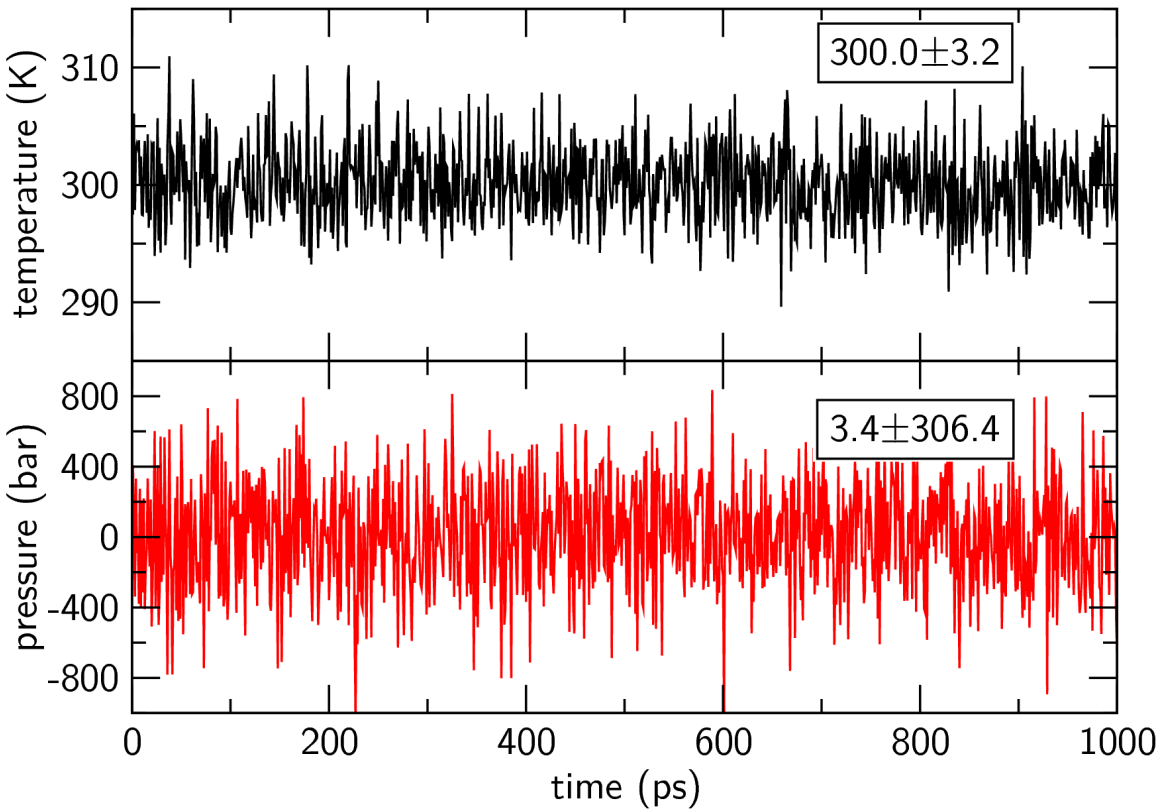
$$P = \frac{2}{3V} \cdot (E_{\text{kin}} - \Xi) = \frac{2}{3V} \cdot \left(\frac{1}{2}\sum_{i} m_i \cdot |\vec{v}_i|^2 + \frac{1}{2}\sum_{i<j} \vec{r}_{ij} \cdot \vec{F}_{ij} \right)$$

note – no mention of the idea of particles colliding with the wall
also, virial pressure fluctuates greatly and may even be negative

Measuring pressure

T and P in an NPT simulation of a DNA oligomer in water
($T_{\text{ref}} = 300$ K, $P_{\text{ref}} = 1.0$ bar)



Controlling pressure

we can calculate the pressure
– so how do we maintain it at a constant value?
barostat – algorithm that is equivalent of a thermostat,
just that it varies volume of the box instead of velocities

the scaling of the volume is usually isotropic,
except for special systems (e.g. membranes)
it shall be semi-isotropic (xy+z) for such geometries

several options are available:

Berendsen barostat

- equivalent to the Berendsen thermostat
- molecular system coupled to a 'force / pressure bath' – piston
- direct rescaling of box lengths and atom coordinates:

$$\begin{aligned} \mu &= 1 - \frac{\beta}{3}\frac{\Delta t}{\tau}\left(P_{\text{ref}} - P\right) \\ \vec{r}_i' &= \mu \cdot \vec{r}_i \end{aligned}$$

- β – compressibility; $\beta = 0.000045$ bar^{-1} for H_2O

Parrinello–Rahman barostat

- extended-ensemble barostat – much like Nosé–Hoover algo.
- eqns of motion contain box lengths b as additional DOFs:

$$\ddot{r}_i = \frac{F_i}{m_i} - \frac{\dot{b}}{b} \cdot \dot{r}_i$$

- additional eqn of motion for the dimensions of the box:

$$\ddot{b} = \frac{V}{b} \cdot W^{-1} \cdot (P - P_{\text{ref}})$$

- strength of coupling – due to mass parameter W^{-1}:

$$W^{-1} = \frac{4\pi^2}{3} \frac{\beta}{\tau^2} \frac{1}{L}$$

τ – relaxation time (parameter)

Note: these equations have been oversimplified...