Simulating thermodynamics ensembles

what you simulate is what you would measure

Marcus Elstner and Tomáš Kubař

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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:

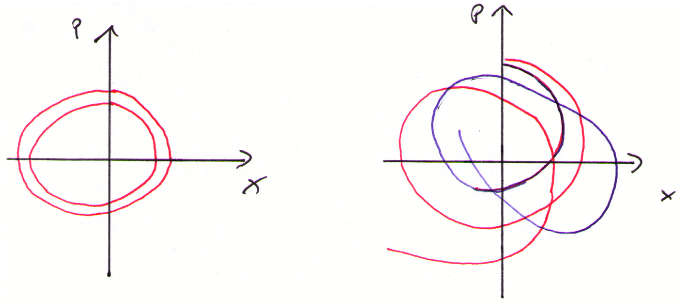
$$x(t) = x_0 \cdot \cos[\omega t] \qquad v(t) = -v_0 \cdot \sin[\omega t]$$

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

stochastic process – when we do not have sufficient information
about all of the degrees of freedom of the system
then, we have to describe the systems with statistical mechanics

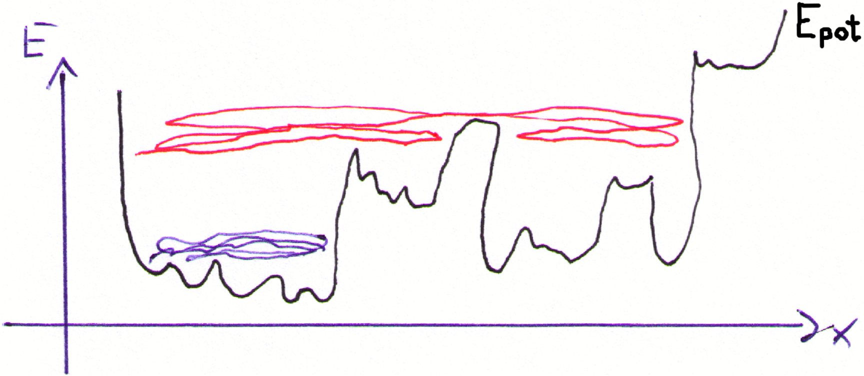
what we need – techniques to control basic simulation parameters
– temperature, possibly pressure etc.

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 at a given T

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 → relation of E_{kin} and temperature:

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

'local' / 'instantaneous' temperature

$$T = \frac{\sum_i m_i v_i^2}{3Nk}$$

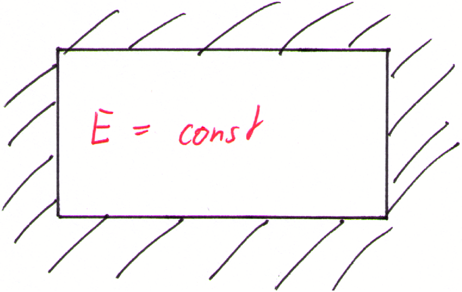
- fluctuates in time
- may differ between different parts of system

Isolated and closed system

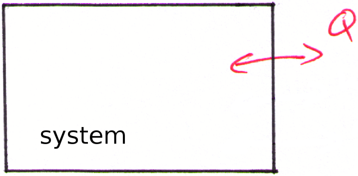
experimental setup (a test tube with a sample)

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

isolated system



closed system



system

environment (bath)

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
  (→ N/A in case of isolated system)
- MD simulation of such a system will provide
  a trajectory in the canonical ensemble

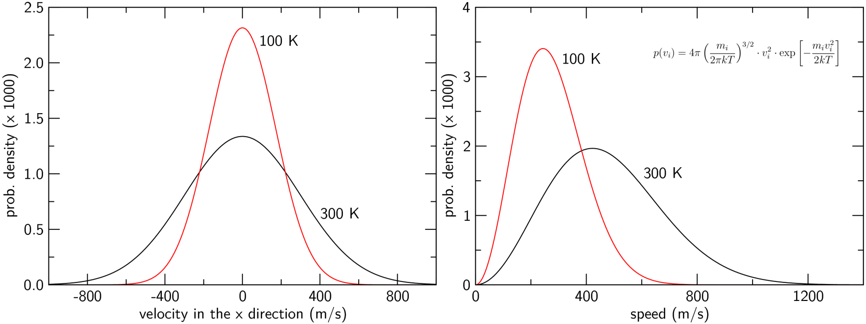
Canonical ensemble

velocity / speed of atoms – Maxwell–Boltzmann distribution

$$\begin{aligned} p(v_{x,i}) &= \sqrt{\frac{m_i}{2\pi kT}} \cdot \exp\left[-\frac{m_i v_{x,i}^2}{2kT}\right] \\ p(v_i) &= 4\pi \left(\frac{m_i}{2\pi kT}\right)^{3/2} \cdot v_i^2 \cdot \exp\left[-\frac{m_i v_i^2}{2kT}\right] \end{aligned}$$

Canonical ensemble

velocity / speed of atoms – Maxwell–Boltzmann distribution



(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 $v_i^2 = v_{x,i}^2 + v_{y,i}^2 + v_{z,i}^2$) →

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

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

Attention if constraints are being applied:
– reduced number of DoF $3N - N_c$ here and in all what follows!

Equipartition theorem

Virial theorem:

$$\left\langle \sum_k q_k \frac{\partial H}{\partial q_k} \right\rangle = \left\langle \sum_k p_k \frac{\partial H}{\partial p_k} \right\rangle = \left\langle \sum_k p_k \frac{dq_k}{dt} \right\rangle = -\left\langle \sum_k q_k \frac{dp_k}{dt} \right\rangle$$

(DoFs: generalized coordinates q_k, generalized momenta p_k)

Generalized equipartition theorem – extension of virial theorem:

$$\begin{aligned} \left\langle p_k \frac{\partial H}{\partial p_k} \right\rangle = kT \rightarrow \quad & \left\langle \frac{1}{m} p_k^2 \right\rangle &=& \quad \frac{1}{2} kT \\ \left\langle q_k \frac{\partial H}{\partial q_k} \right\rangle = kT \rightarrow \quad & \langle q_k \cdot F_k \rangle &=& \quad -kT \\ \rightarrow \quad & \left\langle \vec{r}_i \cdot \vec{F}_i \right\rangle &=& \quad -3kT \end{aligned}$$

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 designation for E_{kin} determined by velocities

a simple idea – scale the velocities by a certain factor λ:

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

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 of 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 → 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

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

  – exponential decay of temperature towards T_{ref}:
- 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
- change of temperature due to thermostat, during 1 time step:

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

Berendsen thermostat

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

- to achieve ΔT, 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

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

large number of atoms N: fluctuations $\rightarrow 0$
finite-sized systems: visible fluctuation of temperature

- – feature of the canonical ensemble
- – we would not obtain this with the simple velocity scaling

Berendsen thermostat

drawbacks:

- correct canonical ensemble is still not generated!
- 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'

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:

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

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

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

- 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:

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

- 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 incorporated into the propagation,
rather than correcting velocities a posteriori

- 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 $(\Delta t' = s \cdot \Delta t)$

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)

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

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
- difference between τ in Berendsen and in Nosé–Hoover:
  Berendsen – exponential damping of ΔT with τ
  Nosé–Hoover – oscillatory relaxation of T with period τ
- N–H thermostat – incorporated in eqns of motion
  – inseparable part of the integrator,
  rather than an a posteriori correction
- generates canonical phase-space density, used frequently

Andersen thermostat

from time to time, some particles (atoms) are selected randomly to undergo a ‘collision’ with the particles of a heat bath, which changes their velocities suddenly

this algorithm has a stochastic character:

- start MD with a standard integrator (Verlet. . .)
- select randomly the atoms that shall be hit by the bath
- for these atoms, draw new velocities from Maxwell–Boltzmann distribution, and keep all of the other atoms untouched

Andersen thermostat

advantage: generates canonical ensemble (if implemented right)
– rate of collisions must be neither too low (inefficient)
nor too high (collisions would dominate over eqns of motion)

disadvantage: no continuity of momentum
- dynamic properties incorrect (diffusion, viscosity. . .)

MD simulations of a molecule / molecular complex in vacuo
- Verlet integrator: no energy flow between modes of motion
  - equipartition of energy possibly violated
- Andersen thermostat is a viable solution
  (other stochastic algorithms applicable, see further on)

Langevin dynamics

a.k.a. stochastic dynamics
additional terms in the eqns of motion:

$$m_i \ddot{\vec{r}}_i = \vec{F}_i - m_i \gamma \dot{\vec{r}}_i + \sqrt{\frac{2 m_i \gamma k T}{\Delta t}} \vec{R}_i(t)$$

- velocity-dependent friction $m_i \gamma \dot{\vec{r}}_i$ (removes energy)
  - shall be $\gamma \Delta t \ll 1$, related to diffusivity: $D = kT/m\gamma$
  - frictional drag (like, of solvent imposed on a solute)
- random force or noise $\vec{R}_i$ (adds energy)
  - from a standard normal distribution, uncorrelated in time and across particles
  - if higher T desired → larger additional force required
  - random collisions (like, with solvent molecules)

modified eqns of motion → the integrator has to be modified

Brownian dynamics

overdamped Langevin dynamics, or dynamics without inertia

– no acceleration takes place, $\ddot{\vec{r}}_i = \vec{o}$:

$$\cancel{m_i \ddot{\vec{r}}_i} = \vec{F}_i - m_i \gamma \dot{\vec{r}}_i + \sqrt{\frac{2 m_i \gamma k T}{\Delta t}} \vec{R}_i(t)$$

$$\dot{\vec{r}}_i = \frac{\vec{F}_i}{m_i \gamma} + \sqrt{\frac{2kT}{m_i \gamma \Delta t}} \vec{R}_i(t)$$

- 1st order ODE – integration: $\vec{r}_i(t + \Delta t) = \vec{r}_i(t) + \dot{\vec{r}}_i(t) \Delta t$
- over-damped → long time step Δt possible
- very different from explicit all-atom MD simulation
- applications: large molecules without explicit solvent
  polymers, proteins, nucleic acid molecules, colloid systems

Controlling temperature

Summary

- scaling of velocities (Berendsen, v-rescale)
- extended Lagrangian (Nosé–Hoover)
- stochastic algorithms (Andersen, Langevin)

Introducing pressure

Chemical reality – constant pressure rather than constant volume

How to calculate pressure?

From the (generalized) equipartition theorem:

$$\frac{1}{3}\left\langle \sum_i \vec{r}_i \cdot \vec{F}_i^{\text{tot}} \right\rangle = \frac{1}{3}\left\langle \sum_i \vec{r}_i \left(\vec{F}_i + \vec{F}_i^{\text{ext}} \right) \right\rangle = -NkT$$

$\vec{F}_i^{\text{ext}}$ – force due to external pressure:

$$\frac{1}{3}\left\langle \sum_i \vec{r}_i \cdot \vec{F}_i^{\text{ext}} \right\rangle = -PV$$

$\vec{F}_i$ – force from interactions between atoms

introduce the virial of force:

$$\Xi = -\frac{1}{3} \sum_i \vec{r}_i \cdot \vec{F}_i$$

Introducing pressure

Adding the components of forces:

$$-NkT = -PV - \langle \Xi \rangle$$

Consider 'instantaneous' temperature and pressure from now on:

$$\begin{aligned} -NkT &= -PV - \Xi \\ P &= \frac{NkT}{V} - \frac{1}{V}\Xi = \frac{2}{3}E_{\text{kin}} - \frac{1}{V}\Xi \end{aligned}$$

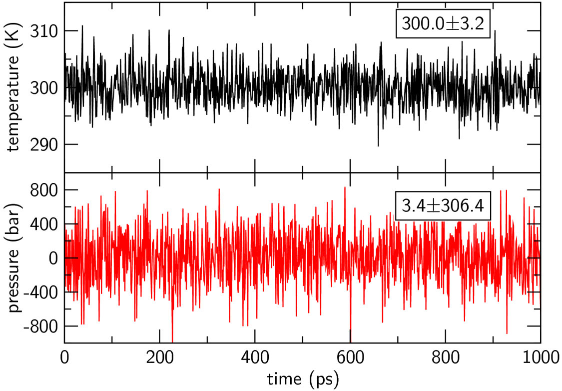
Pass to pairwise forces $\vec{F}_{ij}$ between atoms on distances $\vec{r}_{ij}$:

$$\Xi = -\frac{1}{3}\sum_i \vec{r}_i \vec{F}_i = -\frac{1}{3}\sum_{i<j} \vec{r}_{ij}\vec{F}_{ij}$$

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

Measuring pressure

- no mention of the idea of particles colliding with the wall
- virial pressure fluctuates greatly and may even be negative:



(DNA oligomer in water at $T_{\text{ref}} = 300$ 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:

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

- β – compressibility; $\beta = 0.000045\ \mathrm{bar}^{-1}$ 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. . .