

SIMULATIONS WITH CLASSICAL PARTICLES

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Computational Nanotechnology
2011 Gdansk, Poland
Lecture 4

1 Statistical ensembles

- What is the ensemble of molecular dynamics simulations
- MD in different ensembles

2 Molecular dynamics at constant temperature

- Different approaches to thermostating the system

- Real, physical systems consist of vast number of particles (Avogadro's number).
- Even if we could solve given equations of motion exactly, the mere number of them makes the problem intractable.
- Fortunately, we are not interested in such detailed information.

- Despite **micro**scopic „chaos”, **macro**scopic parameters (e.g. pressure, temperature) of physical systems behave in orderly, predictable fashion.
- In a consequence the macroscopic parameters are the outcome of averaging

Probabilistic approach

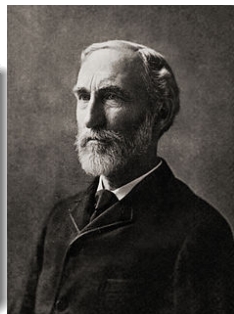
From solitaire game to probabilistic methods



- Instead single instance of a system, we focus on a very large set of *identical* systems – an **ensemble**.
- The systems are in different **microscopic** states, but external (known) parameters are the same for each system.
- We are asking about probability of finding a system at some particular state

DEFINITION

STATISTICAL ENSEMBLE is an idealisation consisting of a large number of copies (even infinitely many) of a system, that are considered *all at once*. Each of the copies represents a *possible state* that the real system might find is self in. The concept of an ensemble was introduced in 1878 by J. Willard Gibbs



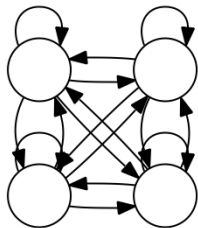
J. Willard Gibbs
1839–1903
physicist and chemist

The concept of an ensemble formalises the notation of physicist repeating an experiment again and again under the same macroscopic conditions, but being unable to control microscopic details, may expect to observe a range of different outcomes.

Ergodicity

In statistical physics, average of a quantity A is taken over an **ensemble**

$$\langle A \rangle_{\text{ens}} = \frac{\int A(\mathbf{q}^N, \mathbf{p}^N) f(\mathbf{q}^N, \mathbf{p}^N) d\mathbf{q}^N d\mathbf{p}^N}{\int f(\mathbf{q}^N, \mathbf{p}^N) d\mathbf{q}^N d\mathbf{p}^N}$$



Ergodic

During MD simulation A is averaged over the **time**

$$\bar{A} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T A(t) dt$$

IF, AND ONLY IF the system is **ergodic**, then:

$$\bar{A} = \langle A \rangle_{\text{ens}}$$

The *NVE* Ensemble

THE MICROCANONICAL ENSEMBLE describes a system for which all *microstates* (possible states of the system in phase space) are constrained to fix number of particles (N), a fixed volume (V), and fixed energy (E).

This ensemble (denoted as *NVE*) is the native ensemble for Molecular Dynamics simulations.

The *NVT* Ensemble

THE CANONICAL ENSEMBLE describes a system for which all *microstates* are constrained to fix number of particles (N), a fixed volume (V), and fixed temperature (T). The microstates of this ensemble may take only discrete values of energy, and the probability of finding the system in a particular microscopic state i with energy level E_i is given by the Boltzmann distribution

$$p_i = \frac{1}{Z} \exp\left(-\frac{E_i}{kT}\right) = \exp\left(\frac{-E_i - A}{kT}\right)$$

where $Z = \exp\left(-\frac{A}{kT}\right)$, and A is the Helmholtz free energy.

This *NVT* ensemble is the native ensemble for Monte Carlo simulations.

THE GRAND CANONICAL ENSEMBLE

Conserved quantities: volume (V), temperature (T)

ISOTHERMAL–ISOBARIC ENSEMBLE

Conserved quantities: Number of particles (N), pressure(p), temperature (T)

ISOENTHALPIC–ISOBARIC ENSEMBLE

Conserved quantities: Number of particles (N), pressure(p), temperature (H)

In MD simulations number of particles N , volume V , and total energy E are conserved. This implies that MD simulation are performed in microcanonical ensemble (NVE).

This is unfortunate situation because:

- 1 Total energy is hardly ever fixed in real experiments. Usually, pressure, temperature, etc. is controlled.
- 2 Monte Carlo simulations are performed in different ensembles (NVT , NpT). Results cannot be directly compared.

At first sight, it would seem that it is impossible to perform MD simulations in the ensemble other than microcanonical.

Two solutions were proposed to make this idea possible:

- 1 One idea is to mix the Newtonian MD with certain Monte Carlo moves.
- 2 The second approach (purely dynamical) is based on the reformulation of the Lagrangian equations of motion of the system.

Molecular Dynamics at $T=\text{const}$

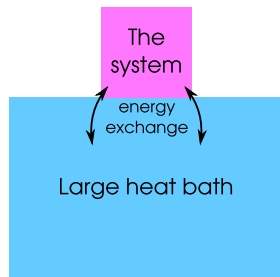
First lets define the system at constant temperature:

The probability to find a system in a given energy state (for classical systems) is given by the Maxwell–Boltzmann velocity distribution:

$$\mathcal{P}(p) = \left(\frac{\beta}{2\pi m} \right)^{2/3} \exp(-\beta p^2 / (2m))$$

we obtain a simple relation between the imposed temperature T and the kinetic energy per particle

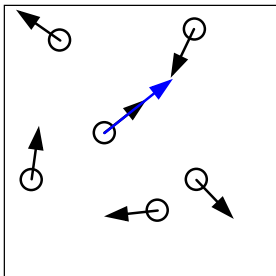
$$k_B T = m \langle v_\alpha^2 \rangle$$



Andersen's concept

The Andersen's idea to the heat bath and the system coupling is represented by *stochastic impulsive forces* that act occasionally on *randomly selected* particles.

The stochastic collisions ensure that all accessible constant-energy shells are visited according to their Boltzmann weight.



The heat bath–system coupling strength is determined by the frequency of stochastic collisions (ν). If successive collisions are uncorrelated then the distribution of time interval between stochastic collisions is of the Poisson's form:

$$P(t, \nu) = \nu \exp(-\nu t)$$

Andersen's concept

The Andersen's algorithm

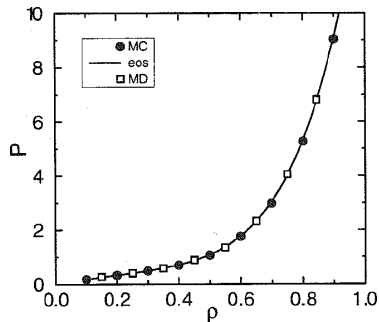
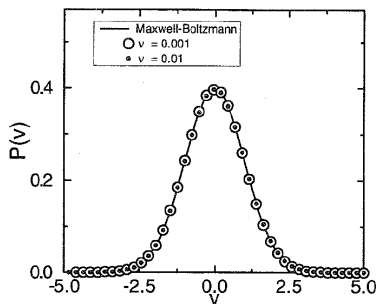
- 1 Start with initial set of positions and momenta $\mathbf{r}^N(0), \mathbf{p}^N(0)$ and integrate the equations of motion.
- 2 The probability that the particle undergoes a stochastic collision in a time Δt is $\nu \Delta t$.
- 3 If particle has been selected for a collision, its new velocity will be drawn from a Maxwell–Boltzmann distribution, corresponding to the desired T . All other particles are *unaffected* by the collision.

The above procedure turns MD simulation into a Markov process. Combined with the fact that Markov chain is also irreducible and aperiodic, this implies that the above indeed generates a *canonical distribution*.

Andersen's concept

Now, let's verify whether the Andersen's thermostat indeed produces the canonical distribution.

The velocity distribution of Andersen's thermostat should match exactly the Maxwell-Boltzmann distribution.



Nosé approach – the idea

To construct isothermal MD, Nosé introduced **additional coordinate** in the Lagrangian of classical N -body system:

$$\mathcal{L} = \sum_{i=1}^N \frac{1}{2} m_i s^2 \dot{\mathbf{r}}_i^2 - U(\mathbf{r}^N) + \frac{1}{2} Q \dot{s}^2 - \frac{L}{\beta} \ln s$$

where Q is an effective „mass”, L is a constant related to number of system degrees of freedom.

Calculating momenta conjugate to \mathbf{r}_i and s

$$\mathbf{p}_i = \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}_i} = m_i s^2 \dot{\mathbf{r}}_i, \quad p_s = \frac{\partial \mathcal{L}}{\partial \dot{s}} = Q \dot{s}$$

gives Hamiltonian of the **extended** system (N particles plus s):

$$\mathcal{H} = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i s^2} + U(\mathbf{r}^N) + \frac{p_s^2}{2Q} + \frac{L}{\beta} \ln s$$

Nosé approach – key points

- 1 Adding s introduces **time scaling**, thus distinction between real and „virtual” variables is necessary. The **real** and **virtual** variables are related as follows:

$$\begin{aligned}r' &= r, \\p' &= p/s, \\s' &= s, \\\Delta t' &= \Delta t/s.\end{aligned}$$

- 2 Extended system still generates a **microcanonical** ensemble. However, it can be shown that

$$\langle A(\mathbf{p}/s, r) \rangle_{\text{Nosé}} = \langle A(\mathbf{p}', r') \rangle_{NVT}$$

Nosé approach – features

- Extended approach was a real breakthrough in demonstrating possibility of making MD simulation in ensembles different than *NVE*.
- Yet, time scaling was very inconvenient from the practical point of view.

Nosé-Hoover approach

Hoover simplified original Nosé's equations to the form:

$$\begin{aligned}\dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m_i}, \\ \dot{\mathbf{p}}_i &= \frac{\partial U(\mathbf{r}^N)}{\partial \mathbf{r}_i} - \zeta \mathbf{p}_i, \\ \dot{\zeta} &= \frac{1}{Q} \left(\sum_{i=1}^N \frac{p_i^2}{m_i} - \frac{L}{\beta} \right), \\ \frac{\dot{s}}{s} &= \frac{d}{dt} \ln s = \zeta.\end{aligned}$$

Attention

No more time scaling. Variables \mathbf{r}_i , \mathbf{p}_i are **real**.

1 Quantity

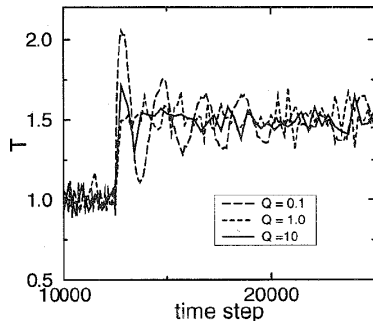
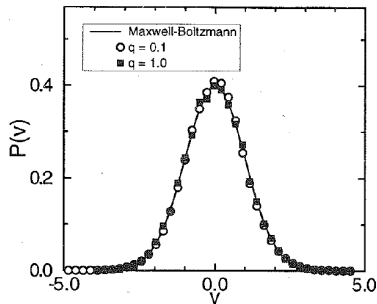
$$\mathcal{H}_{\text{NH}} = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} + U(\mathbf{r}^N) + \frac{1}{2}Q\zeta^2 + \frac{L}{\beta} \ln s$$

is conserved and can be treated as **constant of motion**.

2 It is **not** a Hamiltonian, i.e. one cannot obtain equation of motion from it.

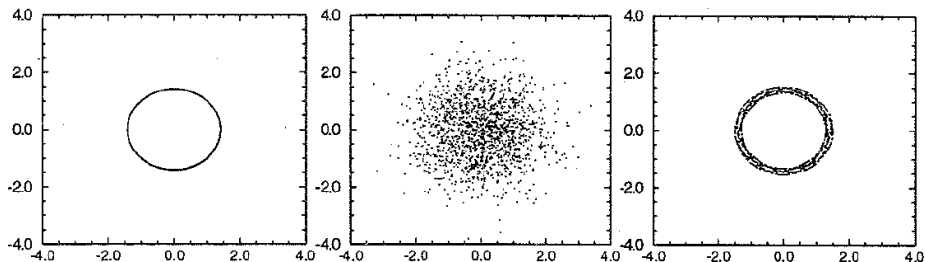
Application of Nosé-Hoover thermostat

It is clear that Nosé-Hoover method reproduces the behaviour of a system at constant N, V, T . In can be seen that the velocity distribution is indeed independent of the value chosen for coupling constant Q .



Phase trajectory comparison

The phase trajectory of harmonic oscillator (left), Andersen thermostat (middle), Nosé-Hoover thermostat (right)



THANK YOU FOR YOUR ATTENTION.