

VO Advanced Computational Physics

SS 2023

Lesson 1

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Computational and Soft Matter Physics
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■ Personnell

- 1 Main lecture: **Andreas Tröster**, PD. Dr.
- 2 Exercises: **Sebastian Falkner**, MSc

■ Topics

- 1 Monte Carlo simulations
- 2 Molecular Dynamics simulations
- 3 Long range interactions
- 4 if time allows: entropy and free energy, rare events

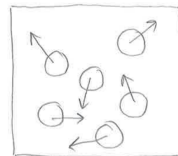
in *classical* lattice and off-lattice systems.

- **Emphasis** will be on understanding the thermodynamic foundations of algorithms rather than on learning to use big packages like LAMMPS or GROMACS as “black boxes”
- **Lecture notes and slides** will be written during the course of the lecture and will be made available for download on the Moodle page of the course.

■ Literature

- D.P. Landau and K. Binder, A Guide to Monte Carlo Simulations in Statistical Physic, Cambridge University Press, 2014
- M.P. Allen, D.J. Tildesley, Computer Simulation of Liquids, Clarendon Press, Oxford, 2017
- B. Leimkuhler and C. Matthews, Molecular Dynamics, Springer, 2014
- D. Frenkel, B. Smit, Understanding Molecular Simulation, Academic Press, San Diego, 2002
- D.C. Rapaport, The Art of Molecular Dynamics Simulation, Cambridge University Press, 1995
- M. E. Newman, G. T. Barkema, Monte Carlo Methods in Statistical Physics, Clarendon Press, Oxford, 1999
- M. E. Tuckerman, Statistical Mechanics: Theory and Molecular Simulation, Oxford University Press, 2010
- F. J. Vesely, "Computational Physics", WUV Universitätsverlag, 1993

- 1953: birth of **MC simulations** in statistical mechanics [Nicholas Metropolis, Arianna W. Rosenbluth, Marshall N. Rosenbluth, Augusta H. Teller and Edward Teller, *Equation of State Calculations by Fast Computing Machines*, J. Chem. Phys. **21**, 1087 (1953)].
- **Example: Equation of state (EOS) for hard disks.** Pressure $p = p(V, T)$ in a volume V at temperature T can be calculated analytically for ideal gas, but not for hard disks ($d=2$) or spheres ($d=3$).
- General formalism of statistical mechanics is known since Gibbs and Boltzmann, but **high-dimensional integrals** appearing in this formalism are difficult to compute analytically.
- Simulations provided an efficient way to evaluate these integrals.
- Simulations can provide “numerically exact” results. Using simulations, we can
 - test assumptions and predictions of simplified theories.
 - study realistic models under conditions not realizable in experiment.
- Simulations do not produce “new physics”, but can give insight into the **complex collective behavior** of systems consisting of many simple components (building blocks). In this sense, simulations *can* produce “new phenomena”.
- But further *analysis* usually required, e.g.
 - evaluation of observables
 - statistical error analysis
 - finite size corrections
 - assessment of effects due to model approximations
- In this course we discuss different particle-based simulation techniques applicable to
 - *atomistic* simulations
 - *mesoscopic* particles (colloids)
- We shall focus on **Monte Carlo (MC)** and **molecular dynamics (MD)** simulations.



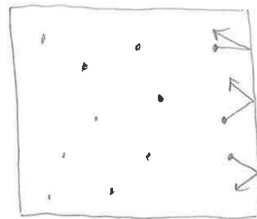
Statistical-Mechanical Averages

Goal of statistical mechanics: predict properties of system based on knowledge of intermolecular interactions.

- N-particle systems consisting of identical building blocks (atoms, molecules, colloids, spins, ...).
- time and length scales of macroscopic experiments much larger than molecular dimensions.

Example: pressure of gas or liquid

- instantaneous pressure is result of many collisions of atoms with container wall.
- pressure measured in macroscopic experiment is result of both temporal and spatial average.



- Knowledge of particle **microstates** = **snapshots of all coordinates and momenta**

$$\mathbf{r}^N \equiv \{\mathbf{r}_1, \dots, \mathbf{r}_N\}, \quad \mathbf{p}^N \equiv \{\mathbf{p}_1, \dots, \mathbf{p}_N\}$$

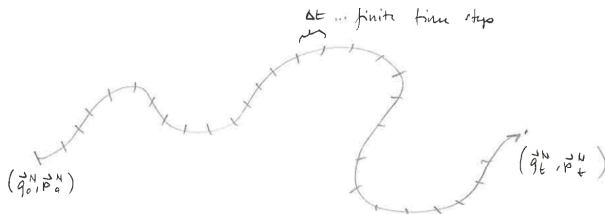
completely determines state of system, provides initial conditions for the solution of the EsOM at past and future times.

- In practice, however, one can never control all degrees of freedom but only **ensemble** of all microstates i.e. a collection of microstates compatible with the macroscopic states of the system parametrized by a **small number of macroscopic parameters** (V, N, T, p , magnetic field $H \dots$).

Statistical-Mechanical Averages

- In MD we integrate the equations of motion and determine time evolution in phase space spanned by all coordinates and momenta

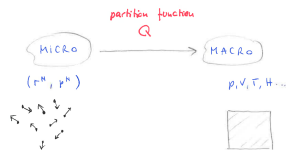
⇒ MD yields **trajectory**, i.e. series of such snapshots



- MC simulations also generate stochastic trajectories of samples of microstates according to probability distribution of the desired ensemble.
- statistical-mechanical expectation values of observables from averages over snapshots of this “movie”.
- In equilibrium (and for quantities that depend only on one time i.e. not on two or more times separately), temporal order of snapshots is unimportant; only occurrence **probabilities** of microstates occur matter.
- probability distribution of microstates defines **ensemble** compatible with prescribed macroscopic parameters
- **ensemble average**: knowledge of probability distribution of microstates allows averaging over the distribution rather than over a trajectory.

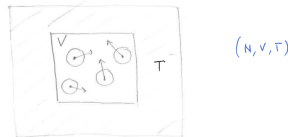
Classical Canonical(NVT) Ensemble: canonical partition function

- central quantity connecting microscopic and macroscopic world:
canonical partition function Q_{NVT}



- N identical point particles i.e. no internal degrees of freedom.
- microstates: collection (r^N, p^N) of all positions and momenta ($p_i = mv_i$).
- fixed volume V in contact with heat bath at fixed temperature T .
- **classical canonical partition function Q_{NVT} :**

$$Q_{NVT} = \frac{1}{N!(2\pi\hbar)^{3N}} \int d\mathbf{r}^N d\mathbf{p}^N e^{-\beta H(\mathbf{r}^N, \mathbf{p}^N)}$$



where

- integral taken over the entire phase space.
- factor $1/N!$ resolves notorious “Gibbs paradox” correcting the overcounting due to the fact that all permutations of identical particles over microstates result in the same physical microstate
- $h^3 = (2\pi\hbar)^3$ is measure of “cell size” in phase space and makes Q_{NVT} dimensionless.
- $\beta = 1/k_B T$ denotes reciprocal/inverse temperature.
- k_B is the Boltzmann constant.
- $H(r^N, p^N)$ is the classical Hamilton function
- **Boltzmann factor** $e^{-\beta H(r^N, p^N)}$ is proportional to probability of observing this microstate.

canonical partition function

- For $H(\mathbf{r}^N, \mathbf{p}^N) = \underbrace{\sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m}}_{\text{kinetic energy}} + \underbrace{U(\mathbf{r}^N)}_{\text{potential energy}}$, partition function factorizes into product of

separate integrals, one over configuration space and one over momentum space:

$$Q_{NVT} = \frac{1}{N!(2\pi\hbar)^{3N}} \left\{ \int d\mathbf{p}^N e^{-\beta \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m}} \right\} \left\{ \int_{V^N} d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N)} \right\}$$

- momentum space integral can be factorized further into product of Gaussian integrals

$$\int d\mathbf{p}^N e^{-\beta \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m}} = \left(\int_{-\infty}^{\infty} d\mathbf{p} e^{-\frac{1}{2} \frac{\mathbf{p}^2}{m/\beta}} \right)^{3N} = (2\pi m/\beta)^{3N/2}$$

- Therefore

$$Q_{NVT} = \frac{1}{N!} \frac{(2\pi m/\beta)^{3N/2}}{(2\pi\hbar)^{3N}} \int_{V^N} d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N)} = \frac{1}{N!} \left(\frac{m/\beta}{2\pi\hbar^2} \right)^{3N/2} \int_{V^N} d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N)}$$

i.e.

$$Q_{NVT} = \frac{1}{N!} \frac{1}{\Lambda^{3N}} \int_{V^N} d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N)} = \frac{Z}{N! \Lambda^{3N}}$$

with **configuration integral** $Z \equiv \int_{V^N} d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N)}$ and **thermal de Broglie wave length**

$$\Lambda = \sqrt{\frac{2\pi\hbar^2\beta}{m}}$$

- For the example of an **ideal gas** $U(\mathbf{r}^N) \equiv 0$, the above configuration integral is given by

$$\int_{V^N} d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N)} = \int_{V^N} d\mathbf{r}^N 1 = V^N$$

⇒ canonical partition function of the ideal gas is given by

$$Q_{NVT}^{(id)} = \frac{V^N}{N! \Lambda^{3N}}$$

- Rewrite partition function of interacting system

$$Q_{NVT} = \frac{1}{N!} \frac{V^N}{\Lambda^{3N}} \frac{1}{V^N} \int_{V^N} d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N)}$$

as a product

$$Q_{NVT} = Q_{NVT}^{(id)} \cdot Q_{NVT}^{(ex)}$$

of an **ideal part** $Q_{NVT}^{(id)}$ and an **excess part**

$$Q_{NVT}^{(ex)} = \frac{1}{V^N} \int_{V^N} d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N)} = \frac{Z}{V^N}$$

which contains all non-trivial effects due to the interactions.

A more interesting case: configurational averages

- canonical phase space density:

$$f(\mathbf{r}^N, \mathbf{p}^N) := \frac{1}{N!} \frac{1}{(2\pi\hbar)^{3N}} \frac{e^{-\beta \left[\sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + U(\mathbf{r}^N) \right]}}{Q_{NVT}}$$

- Suppose that $A = A(\mathbf{r}^N)$ depends only on the particle positions:

$$\begin{aligned} \langle A(\mathbf{r}^N) \rangle &= \int d\mathbf{r}^N d\mathbf{p}^N f(\mathbf{r}^N, \mathbf{p}^N) A(\mathbf{r}^N) \\ &= \frac{1}{Q_{NVT}} \frac{1}{N!} \frac{1}{(2\pi\hbar)^{3N}} \underbrace{\int d\mathbf{p}^N e^{-\beta \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m}}}_{Q_{NVT}^{(id)} / V^N} \int d\mathbf{r}^N A(\mathbf{r}^N) e^{-\beta U(\mathbf{r}^N)} \\ &= \frac{\cancel{Q_{NVT}^{(id)}}}{\cancel{Q_{NVT}^{(id)}} \underbrace{Q_{NVT}^{(ex)}}_{=Z} V^N} \int d\mathbf{r}^N A(\mathbf{r}^N) e^{-\beta U(\mathbf{r}^N)} = \frac{1}{Z} \int d\mathbf{r}^N A(\mathbf{r}^N) e^{-\beta U(\mathbf{r}^N)} \end{aligned}$$

- Such integrals are highly non-trivial and difficult (usually impossible) to compute analytically. **This is why we need MC simulations!**
- **Idea of Metropolis MC:** Replace expectation value with average over a large sample of configurations generated with the **Metropolis procedure**.
- big advantage: **no need to normalize probability density**, because in the acceptance step we only need the *ratio* of probabilities in which any constant factor cancels (Z can remain undetermined!)