

Tutorial 6

ESPResSo 3: Advanced MC/MD

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Contents

| | | |
|----------|---|----------|
| 1 | Introduction | 1 |
| 2 | Before you start | 2 |
| 3 | Widom test particle insertion | 2 |
| 3.1 | Algorithm | 2 |
| 3.2 | Chemical potential - Debye-Hückel approximation | 3 |
| 4 | System setup | 3 |
| 4.1 | Electrostatics in ESPRESSO | 4 |
| 4.2 | Mapping between ESPRESSO and SI units | 4 |
| 4.3 | Performance and correlation analysis | 4 |
| 4.4 | Sampling | 5 |

1 Introduction

The combination of Monte Carlo and Molecular Dynamic simulations offers many possibilities beyond using each technique solely on their own. In general MD simulations are restricted to relatively small time scales and, depending on the modeled interactions, to rather small particle numbers as well, but they have the advantage of computing collective particle movements with the correct dynamics. The time between two MD steps is bound by the fastest motion of the system of interest (for all atom MD, those are atomic vibrations). MC simulations on the other hand do not have such limitations. Even nonphysical moves can be considered and still lead to results with correct thermodynamic properties. However, no valuable information of the systems dynamics can be obtained. But the combination of MD and MC moves allows us to mimic any ensemble. In this tutorial the chemical potential of a salt solution will be computed by using a combination of MD and MC techniques. The chemical potential is important for simulating chemical equilibria and systems where particles can be exchanged with an external reservoir, which is too large to be simulated explicitly or between two subsystems.

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2 Before you start

Download the files from the tutorial web-page, unpack them and switch to the newly created directory `advanced_md_mc`. In the archive is a precompiled binary of Espresso with enabled **ELECTROSTATICS** and a `tel` script. But if you prefer you can compile an ESPRESSO binary on your own.

3 Widom test particle insertion

3.1 Algorithm

In a pure MD simulation there is no direct way to access the chemical potential. In 1963 Widom proposed a scheme to measure the chemical potential in a system using a trial particle insertion [2]. Implementation details can be found in Ref. [3], pages 173ff.

The chemical potential for species α is defined as:

$$\mu_\alpha = \left(\frac{\partial G}{\partial N_\alpha} \right)_{pTN_{\beta \neq \alpha}} = \left(\frac{\partial F}{\partial N_\alpha} \right)_{VTN_{\beta \neq \alpha}} . \quad (1)$$

It corresponds to the difference in the free (F) or Gibbs (G) energy for inserting a particle from infinity into the system, or equally for removing one particle, thus changing the particle number N_α .

The partition function is defined as:

$$Z(N, V, T) = \frac{V^N}{\Lambda^{dN} N!} \int_0^V d\vec{r}^N \exp(-\beta U(\vec{r}^N)) , \quad (2)$$

where V is the volume, $\Lambda = h/\sqrt{2\pi m k_B T}$ the thermal wavelength, d the dimension of the system, β the inverse thermal energy and U the interaction potential. The free energy F can be computed from the partition function: $F = -k_B T \ln(Z(N, V, T))$. For sufficiently large N the following relation approximates the chemical potential:

$$\begin{aligned} \mu &= -k_B T \ln \left(\frac{Z(N+1, V, T)}{Z(N, V, T)} \right) \\ &= \mu_{\text{ideal}} + \mu_{\text{ex}} . \\ &= -k_B T \ln \left(\frac{V}{\Lambda^d N} \right) + \mu_{\text{ex}} , \end{aligned} \quad (3)$$

where μ_{ideal} depends only on the density of the system, so it is a constant for systems with different interactions but the same particle density.

Task: (2 points)

1. Derive relation (3).

The interesting part is the excess chemical potential μ_{ex} :

$$\mu - \mu_{\text{ideal}} = \mu_{\text{ex}} = -k_B T \ln \left(\int_0^V d\vec{r}_{N+1} \langle \exp(-\beta \Delta U) \rangle \right) . \quad (4)$$

ΔU is the energy difference of the system before and after the insertion of a test particle. The value of the integral (4) can be computed by Metropolis sampling [3], which will be the main task of this tutorial. This means the algorithm to calculate the excess chemical potential is as follows:

- Perform a MD run
- Perform a MC simulation:
 - Calculate potential energy of the system
 - Generate a random position within the simulation box and add an ion pair
 - Calculate the potential energy of the new configuration
 - Delete the particle again
 - Repeat
 - calculate excess chemical potential for current MC part
- Repeat the whole process

In order to obtain reasonably many independent samples, several MD steps are performed between the trial particle insertions.

3.2 Chemical potential - Debye-Hückel approximation

The Debye-Hückel approximation is valid for dilute salt solutions, where the particles are on average far away from each other and the long ranged electrostatic interactions dominate the system and short ranged potentials can be neglected. The derivation can be found in Ref. [1], pages 164ff. The excess chemical potential for ion species α can be approximated by:

$$\mu_{\text{ex}}^{\alpha} = -\frac{e^3 z_{\alpha}^2 \sqrt{N_A} \sqrt{\frac{1}{2} \sum_i c_i z_i^2}}{4\pi\sqrt{2} (\epsilon_r \epsilon_0 k_B T)^{\frac{3}{2}}}, \quad (5)$$

where e is the elementary charge, z_{α} and z_i the valency of the ions, N_A Avogadro's number, c_i the concentration of ions of species i in mol/dm³, ϵ_r the relative permittivity, ϵ_0 the electric permittivity of the vacuum, k_B Boltzmann's constant and T the absolute temperature.

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| Task: (2 points) |
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| <ol style="list-style-type: none"> 1. Convert the equation (5) to the internal units used in ESPRESSO (see sections 4.1 and 4.2). |
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4 System setup

First of all you have to set the fundamental parameters of the simulation, like the time step, the temperature, the thermostat and so on. This already happened in the provided scripts. Furthermore you have to set the parameters crucial for the investigated system, i.e. the number of particles, the size of the simulation box and the interaction potentials in your system. In order to use the script conveniently the parameters you want to vary should be given as command line parameters to the tcl-script. For this task you can use the standard tcl variable **argv** and **argc**, the former one contains everything that was entered after the name of the tcl-script, whereas the latter is the number of given parameters (arbitrary strings separated by spaces).

```
$ ./Espresso <tcl-script> [<param1> <param2> ...]
```

To extract the values from **argv** the tcl built-in function **lindex** can be used:

```
set parameter1 [lindex $argv 0]
set parameter2 [lindex $argv 1]
```

In order to avoid that particles overlap, the Weeks-Chandler-Andersen potential is used. After those core parameters are set, the particles can be created. In the given scripts the particles are created as type 0 with charges +1 and -1 at random positions within the simulation box. After creation and before the electrostatic interactions are switched on the system should be relaxed in a warm-up procedure, so that no significant particle overlaps remain. After this, the coulomb interactions can be activated and the actual simulation can commence. There is still a small problem remaining: During the simulation the test particle is inserted at random positions, however, if it comes too close to another particle or even overlap then the energies cannot be computed in a reliable way or worse the simulation may even crash. In order to avoid such unlikely and nonphysical events, the minimal distance in the system is computed and if it is below a certain cutoff the particle will be placed at a different position. This effect becomes more and more important when the system becomes denser.

Task: (1 points)

1. *Decide which parameters have to be changed for different simulations and implement them as external parameters as explained above (see the last two tasks). Also write a short script (in bash for example), which performs the calling of Espresso with the corresponding parameters.*

4.1 Electrostatics in ESPResSo

To simulate charged systems in ESPRESSO the feature **ELECTROSTATICS** has to be activated. This enables the usage of the P³M algorithm for calculating the forces due to Coulomb interactions. The strength of the Coulomb interaction is set via the Bjerrum length:

$$\lambda_b = \frac{e^2}{4\pi\epsilon_0\epsilon_r k_B T}, \quad (6)$$

which gives a measure for the distance when Coulomb interactions become comparable to the thermal energy. In order to use the P³M algorithm it has to be switched on with:

```
inter coulomb $bjerrum_length p3m tune accuracy $accuracy
```

which auto-tunes all important parameters for the current simulation. So the system has to be set up beforehand. For the simulations of this tutorial a value of $\lambda_b = 0.5$ will be used (**bjerrum** in the script).

4.2 Mapping between ESPResSo and SI units

To compare the results obtained in ESPRESSO with real systems the ratio of characteristic time an length scales has to be the same. In the case of an equilibrium simulation the ratio of the mean distance between particles and the Bjerrum length has to be the same in order to obtain the excess chemical potential :

$$\frac{\lambda_b^{\text{sim}}}{\langle r^{\text{sim}} \rangle} = \frac{\lambda_b}{\langle r \rangle}. \quad (7)$$

The mean particle distance can be expressed as the cube root of the inverse particle density $\langle r \rangle = \rho^{-1/3}$.

In this tutorial the investigated system is a monovalent salt, so the concentrations of positive and negative ions are the same.

4.3 Performance and correlation analysis

A practical measure of performance for computer simulations is the cpu-time used to produce statistical independent samples. For the task at hand this is the time needed to obtain a energy difference

for one particle insertion. So obviously it would be preferable to do as much trial insertions as possible without performing MD steps at all. But as the system is limited in size and particle number one may produce correlated data, when the configuration doesn't change at all, *i.e.* no MD steps are performed or too few MD steps are used or, equally bad, just a fraction of the whole phase space is sampled. The evaluation of statistical independence is a difficult task, but a measure for statistical dependence, *i.e.* correlations, can be obtained directly during the simulation. For this task the ESPRESSO-function **uwerr** can be used, which calculates some statistical quantities for a given time series. For the analysis of correlation the computed auto correlation time of this function can be used. To be more specific the correlation time can be used to estimate whether the used integration time **\$int_steps*\$time_step** is long enough, to produce independent configurations after each integration cycle. To this end the computed correlation time must be around $0.2 \cdots 0.3$, which means the integration time is 3 to 5 times larger than the correlation time.

```
set data_uwerr [uwerr $data $number_of_samples $column]
```

This example illustrates the general usage of **uwerr**, where **\$data** is a matrix. But when using it only with a vector of data (a tcl list), the following variation is easier to use, where data is a string of values delimited by spaces:

```
set data_uwerr [uwerr $data [llength $data] 1]
```

uwerr will return a tcl-list with the mean value of the data, the error estimate for the mean value, an error estimate for the error itself and, for this task most important, the integrated autocorrelation time. The result of **uwerr** can be assigned to a variable and the single values can be accessed via the **lindex** command like the commandline parameters as explained above.

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| Task: (2 points) |
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| <ol style="list-style-type: none"> 1. <i>Perform a correlation analysis for the energies obtained after each MD integration (total, kinetic, potential and Coulomb energy). To this end rerun the simulation for one density and vary the number of integration steps performed between the trial insertions.</i> |
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4.4 Sampling

To calculate the excess chemical potential, we have to measure the energy differences before and after a test particle insertion at many randomly chosen positions, so that the integral (4) can be computed. For this task the procedure **potential_energy** can be used, which computes the difference of the total energy and the kinetic energy, thus returns the potential energy of the system. A convenient way to implement this algorithm is to write a procedure **particle_insert**, which performs the creation and removal of a test particle and returns the energy difference. Frenkel proposes the following implementation [3]:

```
proc Widom
  E_old=potential_energy
  create_particle
  E_new=potential_energy
  delete_particle
  wtest=exp(-beta*(E_new-E_old))
return
```

The excess chemical potential is then: $\beta\mu_{\text{ex}} = -\ln(\langle \text{wtest} \rangle)$, where $\langle \text{wtest} \rangle$ is the mean value of **wtest** after the test insertions. The temperature and β are available as tcl-variables **temperature**

and **beta**. For the correct energy calculation it is necessary to update the system with a call of the integrator. This means after the particles are created the command **integrate 0** has to be executed.

In the given tcl script is a function **create_particle** which takes the charge of the particle to be created as argument and returns its particle id. There is also a function for deleting particles which takes the particle id as argument:

```
set id [create_particle 1]
delete_particle $id
```

Task: (3 points)

1. Complete the function **try_particle_insert** in the script *widom_method.tcl*.
2. Run the script for the following densities: $\rho = 10^{-5}, 3 \times 10^{-5}, 10^{-4} \dots 10^{-1}$ and calculate the excess chemical potential.
3. Compare and plot those results with the Debye-Hückel approximation for the excess chemical potential for dilute salt solutions and discuss the agreement or disagreement, respectively.

References

- [1] Peter Atkins and Julio de Paula. *Physical Chemistry*. Oxford University Press, 2006.
- [2] B. Widom. Some topics in the theory of fluids. *Journal of Chemical Physics*, 39:2808, 1963.
- [3] Daan Frenkel and Berend Smit. *Understanding Molecular Simulation*. Academic Press, San Diego, second edition, 2002.