Worksheet 6: Advanced MC/MD Widom Insertion Method

Solutions

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Contents

Remarks

The Solutions provided here show possible approaches to solve the tasks from the corresponding worksheet and may not be exhaustive.

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. However, 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, still leading to results with correct thermodynamic properties. However, no valuable information of the system's dynamics can be obtained. The combination of MD and MC moves allows us to mimic any ensemble.

In this tutorial, you will compute the chemical potential of a monovalent salt solution 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 a external reservoir, which is too large to be simulated explicitly, or between two subsystems.

2 Widom Insertion Method

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 trial particle insertions [1]. Implementation details can be found in [2], pp 173ff.

The chemical potential for species α is defined as

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

It corresponds to the difference in the Helmholtz free energy F or Gibbs free energy G for bringing 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

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

where V is the volume, $\Lambda = h/\sqrt{2\pi m k_B T}$ the thermal wavelength, n_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:

$$\mu = -k_B T \ln\left(\frac{Z(N+1, V, T)}{Z(N, V, T)}\right) \tag{3}$$

$$= \mu_{\text{ideal}} + \mu_{\text{ex}}$$

$$= -k_B T \ln\left(\frac{V}{\Lambda^{n_d} N}\right) + \mu_{\text{ex}},$$

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)

- Derive relation (3).

Solution

The Helmholtz free energy F can be obtained from the partition function Z with

$$F(N, V, T) = -k_B T \ln(Z(N, V, T)) \quad . \tag{4}$$

By expressing the derivative in equation (3) with a difference quotient, one obtains

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{VT} = \frac{F(N+1, V, T) - F(N, V, T)}{N+1-N} = F(N+1, V, T) - F(N, V, T)$$

in the limit of large N. Plugging in equation (4) yields

$$\mu = -k_B T \ln(Z(N+1, V, T)) + k_B T \ln(Z(N, V, T)) = \underline{\underline{-k_B T \ln\left(\frac{Z(N+1, V, T)}{Z(N, V, T)}\right)}} \quad .$$

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

$$\mu - \mu_{\text{ideal}} = \mu_{\text{ex}} = -k_B T \ln\left(\int_0^V \langle \exp(-\beta \Delta U)\rangle d\boldsymbol{r}^{N+1}\right) \quad . \tag{5}$$

ΔU is the energy difference of the system before and after the insertion of a test particle. The value of the integral in equation (5) can be computed by Metropolis sampling [2], which will be the main task of this tutorial.

2.1 Algorithm

The algorithm of the Widom insertion method to calculate the excess chemical potential can be described as follows:

- Perform an MD simulation
- Perform an MC simulation:
    - Calculate the 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
    - Remove the particle(s) again
    - Repeat
    - Calculate the excess chemical potential for the 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.

2.2 Chemical Potential - Debye-Hückel Approximation

The Debye-Hückel approximation (DHA) is valid for dilute salt solutions, where the particles are on average far away from each other and the long-range electrostatic interactions dominate the system so that short-range potentials can be neglected. The derivation can be found in [3], pp 164ff. The excess chemical potential for ion species α can be approximated by

$$\mu_{\text{ex}}^{\alpha} = -\frac{e^3 z_\alpha^2 \sqrt{N_A} \sqrt{\frac{1}{2} \sum_i c_i z_i^2}}{4\pi\sqrt{2} \left(\epsilon_r \epsilon_0 k_B T\right)^{\frac{3}{2}}} \quad , \tag{6}$$

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/l, ϵ_r the relative permittivity, ϵ_0 the vacuum permittivity, k_B Boltzmann's constant and T the absolute temperature.

Task (2 points)

- Convert equation (6) to the internal units used in ESPResSo (see sections 3.1 and 3.2).

Solution

The Bjerrum length is defined as

$$\lambda_b = \frac{e^2}{4\pi\epsilon_0\epsilon_r k_B T} \quad . \tag{7}$$

Plugging this definition into equation (6) together with the valencies $z_i = 1$ and the information that the concentrations $c_i \equiv c$ are the same for both species yields

$$\mu_{\text{ex}}^\alpha = -\lambda_b^{\frac{3}{2}}\sqrt{2\pi N_A c} \quad . \tag{8}$$

The concentration is $c = \frac{\varrho}{N_A}$, and with equation (12) one can express the density as

$$\varrho = \varrho^{sim}\frac{(\lambda_b^{sim})^3}{\lambda_b^3} \quad , \tag{9}$$

so that

$$c = \frac{\varrho^{sim}(\lambda_b^{sim})^3}{N_A\lambda_b^3} \quad . \tag{10}$$

Inserting (10) in (8) yields

$$\mu_{\text{ex}}^\alpha = -\frac{1}{2}\sqrt{\pi\varrho^{sim}} \quad . \tag{11}$$

3 Simulation

For this tutorial, you will need an ESPResSo installation with the features `LENNARD_JONES` and `ELECTROSTATICS` enabled. Download the Tcl script `template.tcl` from the course website and understand how it works.

3.1 System Setup

The system under consideration consists of N monovalent ion pairs. In order to avoid that particles overlap, the Weeks-Chandler-Andersen potential is used. In the simulations, the following parameters will be used:

$$\lambda_b = 0.5\,, \quad k_B T = 1.0\,, \quad z_i = 1.0\,, \quad N = N_i = 100$$

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

In the simulation, all parameters are already predefined except for the seed of the random number generator, the ion density, the number of ion pairs, and the number of integration steps between the MC parts (measurement cycles) of the simulation. Those parameters have to be passed as command line arguments, so that the similation has to be run with

```
./Espresso template.tcl SEED DENSITY N_ION_PAIRS STEPS_PER_CYCLE
```

To generate random integers within bash, use the bash built-in `$RANDOM`.

3.2 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:

$$\frac{\lambda_b^{\text{sim}}}{\langle r^{\text{sim}} \rangle} = \frac{\lambda_b}{\langle r \rangle} \quad . \tag{12}$$

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

3.3 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 an 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 correlations, the computed autocorrelation 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 should be between 0.2 and 0.3, which means that the integration time is 3 to 5 times larger than the correlation time.

For your convenience, these calculations are already implemented in the template script. The values are output at the end of the simulation. Thus, you only have to make sure that you *choose a large enough number* of integration steps per cycle, such that the correlation time lies below 0.3 cycles.

3.4 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 (5) can be computed.

Frenkel proposes the following implementation [2]:

```
proc widom_insertion
    E_old=potential_energy
    create_particle
    E_new=potential_energy
    delete_particle
    bf=exp(-beta*(E_new-E_old))
    return
```

The excess chemical potential is then $\beta\mu_{\mathrm{ex}} = -\ln\left(\langle\mathrm{bf}\rangle\right)$, where $\langle\mathrm{bf}\rangle$ is the mean value of `bf` after the test insertions.

Task (4 points)

- Complete the function `widom_insertion_step` in the template Tcl script.

- Run the script for different densities
  $\varrho \in \{0.00001, 0.00003, 0.0001, 0.0003, 0.001, 0.003, 0.01, 0.03, 0.1\}$
  and calculate the excess chemical potential. Make sure you choose a large enough number of integration steps per cycle! Supply the obtained autocorrelation times of the potential energy.

- 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.

- In the simulation, the measured excess chemical potential is independent of the sign of the test particles' charge. Explain why!

Hints

- For this task, the procedure `potential_energy` can be used, which computes the difference of the total energy and the kinetic energy, thus returning the potential energy of the system.

- A convenient way to implement the test particle insertion and removal is to use the procedures `create_test_particle` and `delete_test_particle` provided in the template script, which perform the creation and removal of a test particle.

- 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.

Solution

- A working example for the complete function looks as follows:

```
proc widom_insertion_step {E_pot} {
    global beta
    create_test_particle
    integrate 0
    set DeltaU [expr [potential_energy] - $E_pot]
    set exponent [expr -$beta * $DeltaU]
    # For the case that the energies become too large,
    # cut off what's numerically 0:
    if { $exponent > -30.0 } {
        set boltzmann_factor [expr exp($exponent)]
    } else {
        set boltzmann_factor 0.0
    }
    delete_test_particle
    return "$boltzmann_factor␣$DeltaU"
}
```

- The following table lists the number of integration steps per measurement cycle for the different densities as well as the resulting autocorrelation times of the potential energy:

ϱ	0.00001	0.00003	0.0001	0.0003	0.001	0.003	0.01	0.03	0.1
n_{cycle}	40000	20000	10000	8000	3000	1000	1000	1000	1000
$\tau_{E_{\mathrm{pot}}}$	0.249	0.242	0.174	0.063	0.148	0.151	0.166	0.088	0.151

Table 1: Number of integration steps n_{cycle} for different densities ϱ and corresponding autocorrelation times $\tau_{E_{\mathrm{pot}}}$ (in cycles) of the simulated system's potential energy.

The autocorrelation times lie always below 0.3, which is sufficient.

- The results of the simulations are plotted below:
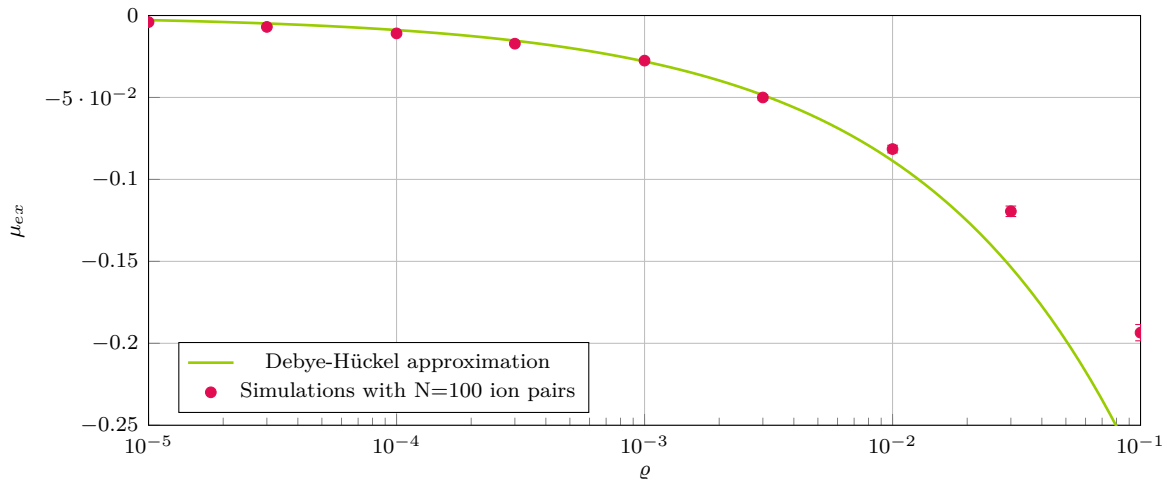
Figure 1: Excess chemical potential μ_{ex} as a function of density ϱ obtained from the simulations (●) and according to Debye-Hückel approximation (———).

For low densities, the curve obtained from the DHA matches the simulation very well. For densities higher than about 0.01, this is no longer the case. This is mostly due to excluded volume effects arising from the WCA potential, which is neglected. Also, for high densities, the mean field ansatz of the DHA breaks down, since it neglects correlation effects.

- Since in the simulated system, all particles are of the same size and the system is completely charge-symmetric, the values of the excess chemical potential is the same for both species.

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4 Short Questions – Short Answers

Task (2 points)

Answer the following questions:

- Is Widom insertion an applicable method to calculate the chemical potential in fluids or solids? Give reasons for your answer!

- What problems would you run into if you tried to use the Widom insertion method with molecules (species with several atoms) as test particles?

Solution

- In very dens systems such as fluids or solids, the Widom insertion method cannot be used. This is due to the fact that the MC integration would basically always end up sampling unphysical states with strongly overlapping particles, and the resulting Boltzmann factors would vanish.

- With species consisting of several atoms as test particles, the MC sampling of the Widom insertion would become very complicated. Then, not only many configurations of the rest of the system would have to be generated (MD runs), but also the conformations of the inserted molecule would have to be sampled. Since generally, the applicable conformations of the molecule in the system are not known *a priori*, this is hard to accomplish in an efficient way.

Bibliography

[1] B. Widom. Some topics in the theory of fluids. *Journal of Chemical Physics*, 39:2808, 1963.

[2] Daan Frenkel and Berend Smit. *Understanding Molecular Simulation.* Academic Press, San Diego, second edition, 2002.

[3] Peter Atkins and Julio de Paula. *Physical Chemistry.* Oxford University Press, 2006.