Tutorial: Raspberry Electrophoresis*

ESPResSo Basics

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1 Tutorial Outline

Welcome to the raspberry electrophoresis ESPResSo tutorial! This tutorial assumes some basic knowledge of ESPResSo. The first step is compiling ESPResSo with the appropriate flags, as listed in Sec. 2. The tutorial starts by discussing how to build a colloid out of a series of MD beads. These particles typically ressemble a raspberry as can be seen in Fig. 1. After covering the construction of a raspberry colloid, we then briefly discuss the inclusion of hydrodynamic interactions via a lattice-Boltzmann fluid. Finally we will cover including ions via the restrictive primitive model (hard sphere ions) and the addition of an electric field to measure the electrokinetic properties. A working TCl script is also provided in the file simulate_raspberry_electrophoresis.tcl. Running this script will run a raspberry electrophoresis simulation and write the time and position of the colloid out to a file named posVsTime.dat in the same directory. A sample set of data is included in the file posVsTime_sample.dat.

2 Compiling ESPResSo for this Tutorial

The first thing with any ESPResSo project is to compile ESPResSo with all of the necessary features. The following myconfig.hpp example contains all of the flags needed for running the accompanying tcl script. Please compile ESPResSo using this myconfig.hpp before starting this tutorial.

```
/* Necessary Flags for the ESPResSo Raspberry Tutorial */

#define ELECTROSTATICS
#define ROTATION
#define ROTATIONAL_INERTIA
#define EXTERNAL_FORCES
#define MASS
```

*For ESPResSo unknown

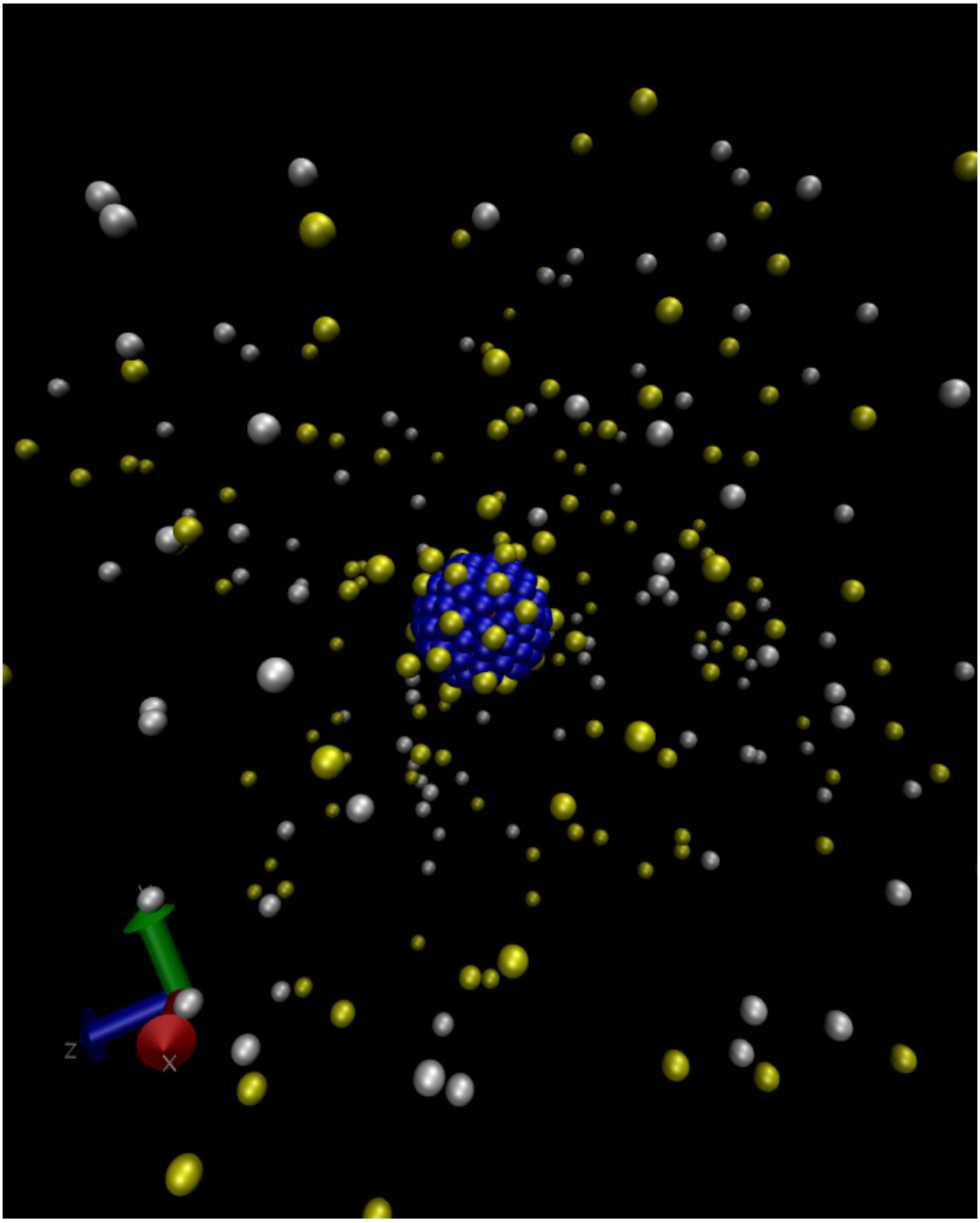


Figure 1: A snapshot of the simulation consisting of positive salt ions (yellow spheres), negative salt ions (grey spheres) and surface beads (blue spheres). There is also a central bead in the middle of the colloid bearing a large negative charge.

```
#define BOND_VIRTUAL
#define LB_GPU
#define LENNARD_JONES
}
```

3 Global MD Variables

The first thing in any ESPResSo simulation is to set a few global simulation parameters:

```
1 setmd box_l $box_length $box_length $box_length
```

The parameter *box_l* set the size of the simulation box. In general, one should check for finite size effects which can be surprisingly large in simulations using hydrodynamic interactions. They also generally scale as box_l^{-1} or box_l^{-3} depending on the transport mechanism which sometimes allows for the infinite box limit to be extrapolated to, instead of using an excessively large simulation box. As a rule of thumb, a box size five times greater than the characteristic length scale of the object.

```
setmd time_step $time_step
}
```

The parameter *time_step*, which represents the time step used in the Verlet integration, should generally be chosen to be as large as possible, while still producing the same numerical values of the physical properties being measured. In typical coarse-grained simulations as covered in this tutorial, this value turns out to be $time_step = 0.01$.

```
setmd skin 0.3
}
```

The skin is used for constructing the Verlet lists and is purely an optimization parameter. Whatever value provides the fastest integration speed should be used. For the type of simulations covered in this tutorial, this value turns out to be $skin \approx 0.3$.

```
setmd periodic 1 1 1
}
```

The *periodic* parameter indicates that the system is periodic in all three dimensions. Note that the lattice-Boltzmann algorithm requires periodicity in all three directions (although this can be modified using boundaries, a topic not covered in this tutorial).

```
set n_nodes [setmd n_nodes]
set start_node 1
set pid [pid]
for {set i 1} {$i <= $n_nodes} {incr i} {
    lappend seeds [expr $i + $n_nodes*$start_node*$pid]
eval t_random seed $seeds
}
```

The last part of this code snippet initiates *t_random* with a unique seed for each CPU core so that the same simulation does not always yield the same results.

4 Setting up the raspberry

The setting up of the raspberry is a non-trivial task. The main problem lies in creating a relatively uniform distribution of beads on the surface of the colloid. In general one should take about 1 bead per grid point on the surfaceto ensure no holes in the surface. The behavior of the colloid can be further improved by placing beads inside the colloid, though this is not done in this example script. In our example we first define a center of the colloid, a harmonic interaction causing the surface beads to be attracted to the center, and a Lennard-Jones interaction preventing the beads from entering the colloid. There is also a Lennard-Jones potential between the surface beads to get them to distribute evenly on the surface.

The beads are initialed at random positions on the surface of the colloid. The beads are then allowed to relax using an integration loop where the forces between the beads are capped. The best way to ensure a relatively uniform distribution of the beads on the surface is to simply take a look at a VMD snapshot of the system after this integration. As can be seen in Fig. 1.

In order to make the colloid perfectly round we now adjust the beads positions to be exactly *radius_col* away from the central bead. Now that the beads make are in the shape of a raspberry the surface beads are virtualized. The central bead is also given an appropriate mass and moment of inertia tensor (note that the off-diagonal elements are zero in ESPResSo's implementation). Lastly the central bead is given the total charge on the colloid. In principle one could also assign the charge to the surface beads, which might be more realistic, but would require more computational effort for calculating the electrostatic interactions.

5 Inserting Counterions and Salt Ions

Next we insert enough ions at random positions (outside the radius of the colloid) with opposite charge to the colloid such that the system is electro-neutral. In addition ions of both signs are added to represent the salt in the solution. Between all of the ions is the WCA potential, a purely repulsive version of the Lennard-Jones potential which approximates hard spheres or radius σ. The ions also have a WCA potential with the central bead of the colloid with an offset of around $radius_col - \sigma + a_{\mathrm{grid}}/2$. This make the colloid appear as a hard sphere of radius roughly $radius_col + a_{\mathrm{grid}}/2$ to the ions, which is roughly equal to the hydrodynamic radius of the colloid. After inserting the ions, a short integration is again performed with a force cap to prevent strong overlaps between the ions.

6 Electrostatics

Electrostatics are simulated using the Particle-Particle Particle-Mesh (P3M) algorithm. In ESPResSo this can be added to the simulation rather trivially:

```
set bjerrum 2
inter coulomb $bjerum p3m tunev2 accuracy 0.001
```

Generally a Bjerrum length of 2 is appropriate when using WCA interactions with $\sigma = 1$ since a typical ion has a radius of 0.35 nm, while the Bjerrum length in water is around 0.7 nm.

The external electric field is simulated by simply adding a constant force equal to the simulated field times the particle charge. Generally the electric field is set to 0.1 in MD units which is the maximum field before the response becomes nonlinear. Smaller fields are also possible, but the required simulation time is considerably larger. Green-Kubo methods are also sometimes used, but these are generally only feasible in cases where is either no salt or a very low salt concentration.

7 Lattice-Boltzmann

The lattice-Boltzmann (LB) fluid can be easily create in ESPResSo with the help of the lbfluid command. Before creating the LB fluid it is a good idea to set all of the particle velocities to zero via the *kill_particle_motion* command. This is necessary to set the total momentum of the system to zero. Failing to do so will lead to an unphysical drift of the system, which will change the values of the measured velocities.

The important parameters for the LB fluid are the density, the viscosity, the time step and the friction. The time step should generally be comparable to the MD time step. While large time steps are possible, a time step of 0.01 turns out to provide more reasonable values for the root mean squared particle velocities. The density, viscosity should be around 1, while the friction should be set around 20. The grid spacing should be comparable to the ions' size.

```
setmd time_step 0.01
#note that it is important to set all of the particle velocities to
  zero just before initializing the LB so that the total system
  momentum is zero
kill_particle_motion
lbfluid gpu dens 1 visc 3 agrid 1 tau 0.01 friction 20

#replace the Langevin thermostat with the lb thermostat
thermostat off
thermostat lb $kT
```

A logical way of picking a specific set of parameters is to choose them such that the hydrodynamic radius of an ion roughly matches its physical radius determined by the WCA potential ($R = 0.5\sigma$). Using the following equation:

$$\frac{1}{\Gamma} = \frac{1}{6\pi\eta R_{\mathrm{H0}}} = \frac{1}{\Gamma_0} + \frac{1}{g\eta a} \tag{1}$$

one can see that the set of parameters grid spacing $a = 1\sigma$, fluid density $\rho = 1$, a kinematic viscosity is $\gamma = 3$ and a friction of $\Gamma_0 = 50$ leads to a hydrodynamic radius of approximately 0.5σ.

The last step is to first turn off all other thermostats with the thermostat off command, followed by turning on the LB thermostat. The temperature is typically set to 1, which is equivalent to setting $k_{\mathrm{B}}T = 1$ in molecular dynamics units.

8 Simulating Electrophoresis

The main simulation can now begin! The only important thing is to make sure the system has enough time to equilibrate. There are two separate equilibration times: 1) The time for the ion distribution to stabilize, and 2) The time needed for the fluid flow profile to equilibrate. The ion distribution equilibration is generally fast, and so the needed warmup time is largely determined by the fluid relaxation time which can be calculated via $\tau_{\mathrm{relax}} = \$box_length^2/\nu$. This means for a box of size 48 with a kinematic viscosity of 3 as in our example script, the relaxation time is $\tau_{\mathrm{relax}} = 48^2/3 = 768\tau_{\mathrm{MD}}$, or 76800 interation steps. In general it is a good idea to run for many relaxation times before starting to use the simulation results for averaging observables, to be on the safe side 10^6 integration steps is a reasonable equilibration time. Please feel free to modify the provided script and try and get some interesting results!