Simulation of charged Nanodroplets in MS-Transfer-Stage Ion-Guides

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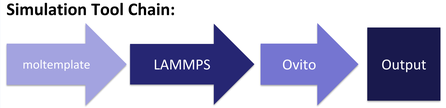
Introduction

Electrospray Ionization (ESI) is the most commonly used ionization technique for polar substances, particularly fragile macro-molecules. After spraying, the analyte is situated within a charged nanodroplet mostly comprised of solvent molecules. Dynamics of these droplets within MS transfer stages may be simulated with different approaches. One promising method is classical molecular dynamics simulation. A droplet is guided through the regions of the MS transfer stage in an experiment. Thus, it experiences drastically changing external parameters, e.g, temperature, electric field strength and/or collision frequency with the background gas. A numerical model has thus to incorporate complex interactions of the simulated particles matching these conditions. Due to the size of the simulated particle ensembles, a quantum-mechanical MD approach is excluded; instead a purely classical approach is used here. With such simulations, trends of evaporation processes and dynamics of energetic collisions of nanodroplets as they occur in MS transfer stages can be examined. Thus, these tools allow to investigate the motion of the droplets in the ion source and MS transfer stage.

Methods

The simulations are performed on amazon elastic-compute-cloud (EC2) nodes. The EC2-instances have 36 virtual-cores and run on Ubuntu-Linux. Less demanding calculations are simulated on a workstation computer (Dell Precision T7500) with eight physical cores on two Xeon E5530 CPUs. The classical open-source MD code LAMMPS [1] is used for the simulations. It is based on Newton's equations of motion, which are solved in the Verlet integration scheme. Water was modeled with the SPC/E-force field [2], in which every atom in H_2O is represented explicitly. Other molecules were simulated with the OPLS force field [3]. Ammonium ions were modeled in an united atoms approach. Background nitrogen was described by a custom force field, derived with QuickFF, which attains parameters from ab-initio calculations performed with the Gaussian09 program package. The text-based molecule builder moltemplate is used to generate LAMMPS input files. OVITO is used for visualization and result data analysis.

Simulation Tool Chain:



Initial System

Main Simulated Droplets:
Droplets are comprised of 1000 water molecules, 1000 methanol molecules, and 12 ammonium ions (ca. 50 Å and 50 000 Da, charge density 0.6 %)

- Droplets of this size are most probably existing in a real ESI experiment
- Droplet is equilibrated over 10^5 timesteps (0.1 ns) with Nosé-Hoover thermostat and barostat (Fig. 1)
- Background gas is simulated to mitigate possible interferences of periodic boundary conditions (pbc) and errors due to a not-charge-neutral particle ensemble

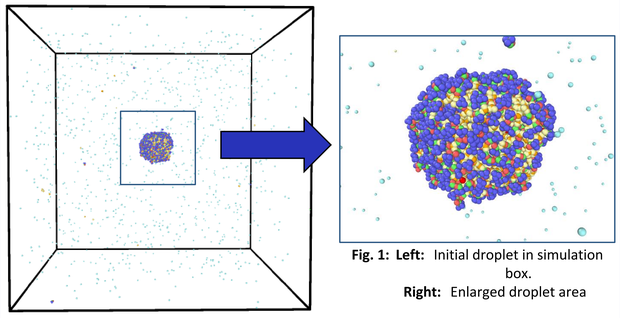


Fig. 1: Left: Initial droplet in simulation box.
Right: Enlarged droplet area

Particles in simulation: Argon = turquoise; methanol = blue, green, orange; water = yellow, light orange; ammonium ions = red

Rayleigh Limit

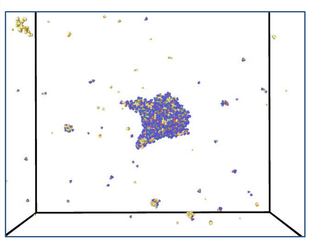


Fig. 2: Charge density 1.35 %, clustered ions surround the droplet

Rayleigh Limit:
One proposed ionization process in ESI depends on the Rayleigh limit of the droplets:

- When reaching the Rayleigh limit, electrostatic repulsion overcomes the surface tension of the droplet, a "Coulomb Explosion" forms
- This process is reproduced with LAMMPS (Fig. 2)
- When the charge density is increased even more, the droplet deforms and individual ions clustered with solvent molecules are ejected

Simulated External Effects

Increasing background gas temperature:
To investigate the droplet behavior in the presence of an external heat bath, the background gas temperature was raised

- Simple calculations of the collision frequency reveals that a droplet experiences only about 14 collisions in the current simulation time frame of 0.1 ns. Therefore, it is not feasible to directly simulate the temperature equilibration and thus the evaporation
- However, with an unrealistic high background temperature (50000 K) disintegration (via heating and evaporation) of the droplets is observed

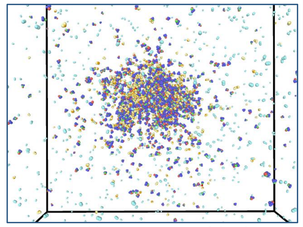


Fig. 3: Sudden evaporation of droplet as background temperature is increased

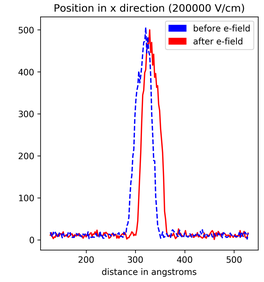


Fig. 4: Change in position of the droplet caused by the electric field

Applying external electric field:
Charged droplets are guided through the MS by external electric fields, which can be also considered in LAMMPS. A charged droplet should thus accelerate in the field

- Similarly to the thermal equilibrium, a significant motion of the charged droplet in an electric field is only observed with unrealistically high field strengths due to the short simulated timeframe (Fig. 4)
- The internal structure of the droplet is not affected significantly even by strong external electric fields, due to strong short-range forces between the particles (Fig. 5)

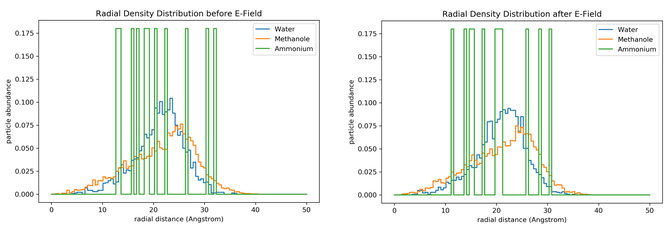


Fig. 5: Radial distribution of molecules within the droplet (**left:** before E-field, **right:** after: E-field) . The radial distribution is the average radial abundance of a particle species in the simulation measured from the center of mass.

Simulated time frame is too short to propel the droplet electrically through the background gas and to record thermal equilibration

Simulated Collision Events

Simple collision simulations:
Collisions of energetic single argon atom impactors with droplets are simulated to mimic the effects of accelerated droplets in a static gas

- Collision-trajectory was set to hit the droplet in the center, which is calculated as the center of mass
- The energy of the projectile is absorbed by the droplet (Fig. 6)
  - Energy on y-axis = total energy (potential energy + kinetic energy)
- The colliding atoms sputtered molecules from the surface of the droplet (Fig. 7)

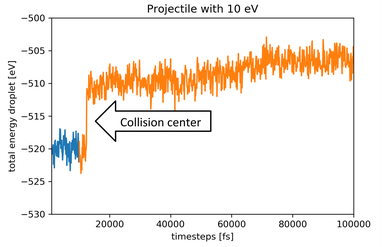


Fig. 6: Simple collision of droplet and an argon atom

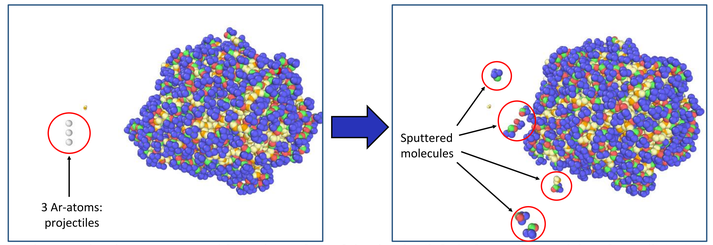


Fig. 7: Molecules are sputtered from the surface of the droplet (**left:** before collision, **right:** after collision)

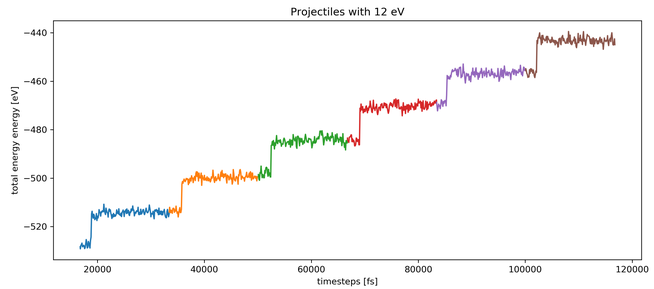


Fig. 8: Heating curve caused by multiple, successive collisions of Ar-atoms with the droplet

Successive collision simulations:
In another set of simulations the projectiles were impacting the droplet in multiple successive collisions from different angles

- Stability and shape of the droplet did not change → no disintegration caused by the collisions
- Kinetic energy of the droplet through the simulation represents a heating curve (Fig. 8) → from this curve the evaporation process of the droplet will be examined in further simulations

Conclusion/Outlook

Conclusion

- Rayleigh Limit is reproduced with LAMMPS
- The internal structure of the droplet is not influenced by high external electric fields
- The simulated time frame is too short to simulate the direct transfer of droplets through the MS
  → Solution: the droplet position is fixed and the background gas particles are used as projectiles
- High energetic collisions with background gas particles do not lead to droplet disintegration
  → Kinetic energy of collisions is distributed rapidly within the droplet

Outlook

- Investigating the performance of other open-source MD Codes
- Simulating analyte chemistry within the droplet to infer possible ionization pathways
- Simulation of droplet trajectories in MS transfer stages considering droplet evaporation processes
- Calculating collision cross sections with MD methods
- Investigate evaporation processes as observed in experiments with refined models
- Varying droplet sizes
- Investigate systems with kinetic Monte Carlo methods
- Develop a mathematical trajectory model

Literature

[1] S. Plimpton, Journal of Computational Physics 1995, 117, 1–19.
[2] H. J C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, J. Hermans, Intermolecular Forces 1981, 31, 331-342.
[3] W. L. Jorgensen, D. S. Maxwell, J. Tirado-Rives, Journal of the American Chemical Society 1996, 118, 11225-11236.

Acknowledgement

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