# Simulations of Charged Nanodroplets in MS Transfer Stages

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## Introduction

Electrospray ionization (ESI) is the most common technique for polar substances. After spraying, the analyte is situated within a charged nanodroplet mostly comprised of solvent molecules. These nanodroplets within MS transfer stages can be described with different simulation approaches, e.g. classical molecular dynamics simulation. The simulation of the dynamics of the nanodroplets allow to investigate the evaporation and fragmentation processes of these charged aggregates in MS inlet stages. The stability of nanodroplets was studied in previous works, by simulating individual collision events. Because of the length of simulated time frames ad computational costs, a full droplet trajectory simulation with classical MD simulations is not feasible. However, parameters like the energy distribution within the droplet and heating curves can be extracted from a numerical model, which has thus to incorporate the complex interactions of the molecules in the nanodroplet. Due to the size of the designed simulated particle ensembles, a quantum-mechanical MD approach is excluded; instead a purely classical approach is used.

## Methods

The simulations are performed on a compute server with 64 AMD Opteron cores. 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 the H2O molecule is represented explicitly. Other molecules were simulated with the DPLS force field [3]. Argon with simple Lennard-Jones potentials was used as background gas. The text-atom molecule builder moltemplate [4] is used to generate LAMMPS input files. OVITO [5] is used for visualization and result data analysis.

## Initial System

The nanodroplets are comprised of 1000 water molecules, 1000 methanol molecules, and 12 ammonium ions

- Droplet diameter: ca. 50 Å (5 nm), droplet mass: 50 000 Da, charge density 0.6 %
- Droplets of this size are mostly probably existing in a real ESI experiment
- The droplet is equilibrated over 10^6 timesteps (0.1 ns) with a Nose-Hoover thermostat and barostat
- Background gas is argon
- Box length is approximately 40 nm

## Rayleigh Limit

One proposed ionization mechanism in ESI is based on the charge density of the droplets:

- When reaching a critical charge density, the so called “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 above the Rayleigh limit, the droplet deforms, and individual ions clustered with solvent molecules are ejected

## Simulated Collision Events

The achievable simulated time frame of classical MD simulations is too short to simulate the collision induced heating of charged droplets with the physical collision rate with background gas particles. Therefore, individual collision events are set up in the simulation. They are analyzed in detail to derive a parameterization of the collision induced heating.

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

- Kinetic energy of the projectile is 10 eV
- Projectile hit the droplet centrally
- The energy of the projectile is absorbed by the droplet (Fig. 3) and transferred like a shockwave through the droplet (Fig. 4)
  - Energy on y-axis = total energy (potential energy + kinetic energy)

## Conclusion

### Rayleigh Limit

- The internal structure of the droplet is not influenced by external electric fields
- The simulated time frame is too short to simulate the direct transfer of droplets through the MS

### Outlook

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

## Literature

5. A. Stukowski, Modelling and Simulation in Materials Science and Engineering 2010, 18(1).

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