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 required 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 H_2O molecule is represented explicitly. Other molecules were simulated with the OPLS force field [3]. Argon with simple Lennard-Jones potentials was used as background gas. The text-based 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 most probably existing in a real ESI experiment
- The droplet is equilibrated over 10^5 timesteps (0.1 ns) with a Nosé-Hoover thermostat and barostat
- Background gas is argon
- Box length is approximately 40 nm

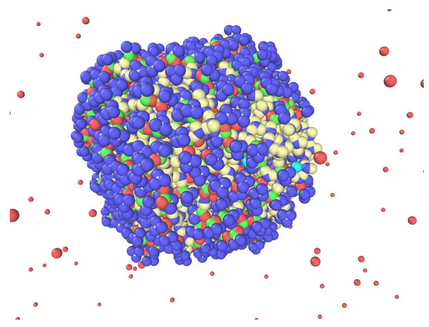

Fig. 1: Main droplet used as initial system

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

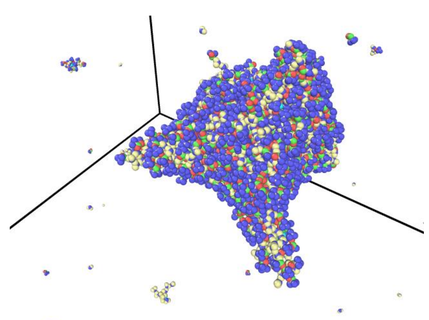

Fig. 2: Charge density 1.35 %, clustered ions surround the droplet

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 gar 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)

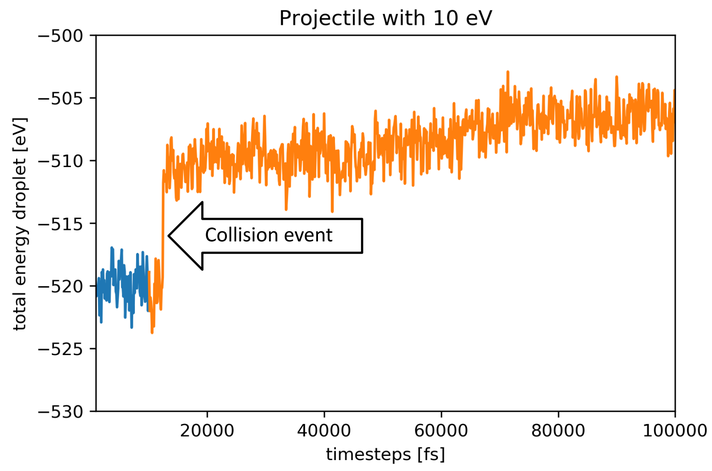

Fig. 3: Simple collision of charged droplet and an argon projectile

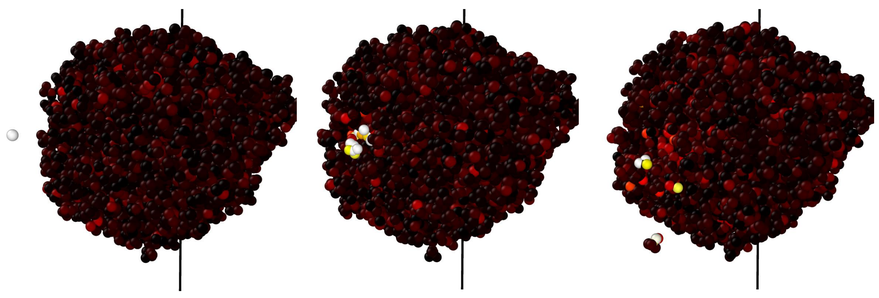

Fig. 4: Single collision with droplet. Colors depict kinetic energy of particles

The colors of the droplets represent the kinetic energy of the particles (dark = low, light = high) (Fig. 4):

- Energy is transferred into the droplet
- Projectile is reflected of the surface of the droplet
- Impact of projectile (10 eV) sputters molecules from the surface of the droplet

Collisions with a wall/surface (e.g. an electrode surface) were simulated (Fig. 5):

- This collision event represents a possible collision for example with a multipole rod in an instrument inlet stage
- The droplet disintegrates with a collision energy of 600 eV. Note that this energy is readily reachable in an experiment, due to the multiple charges in the droplet.
- After the collision, fragment of the droplet are forming different sized clusters

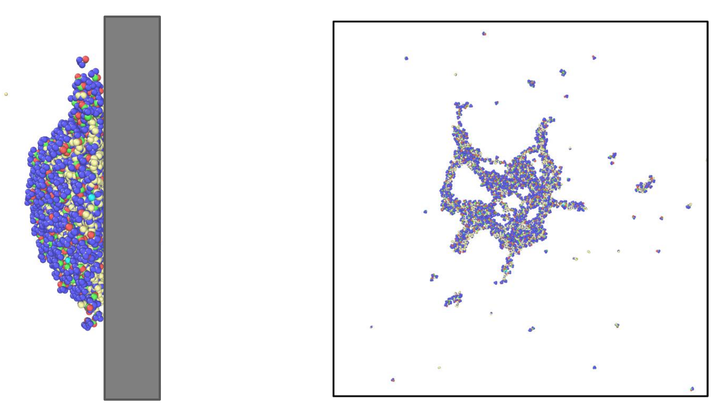

Fig. 5: Left: Side view of collision with wall; Right: Cluster forming after collision

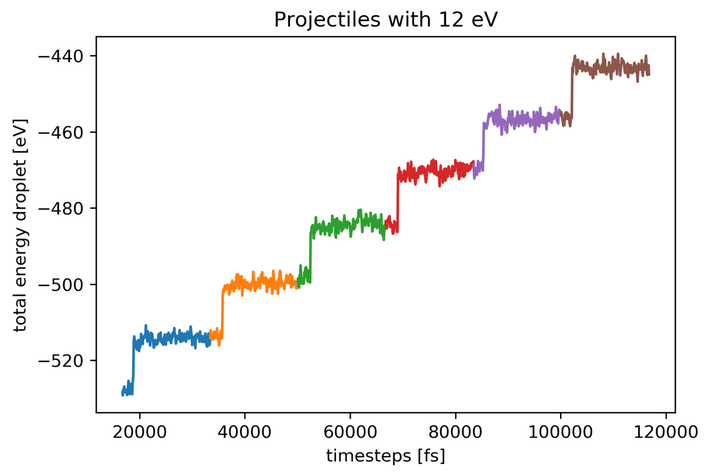

Fig. 6: Heating curves of the droplet with successive collisions

Simulations with multiple collisions of neutral particles (Fig. 6):

- Individual particles (single argon atoms) were started with a kinetic energy of 12 eV each
- Between the collisions was a waiting time of ca. 16 ps
- Droplet does not disintegrate in the time frame of 0.1 ns
- From the increasing internal energy, which corresponds to an increasing temperature in the droplet, parameters describing the heating and evaporation process of the droplets are extractable in future simulations

Conclusion / Outlook

Conclusion

- Rayleigh Limit is reproduced with LAMMPS
- 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
  → Solution: The droplet position is kept fixed and the background gas particles are used as projectiles
- Single high energetic collisions with background gas particles do not lead to prompt droplet disintegration
- Simulations of many (ca. 100) individual collisions is technically possible
  → Kinetic energy of collisions is distributed rapidly within the droplet

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

[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.
[4] A. Jewett, Moltemplate Manual, Jensen Lab (Caltech), 2016.
[5] A. Stukowski, Modelling and Simulation in Materials Science and Engineering 2010, 18(1).

Acknowledgement

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