Simulations of Collision Induced Evaporation Processes of Nanodroplets in MS Inlet Stages

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Introduction

Electrospray Ionization (ESI) is a commonly used ionization technique for a wide range of substances. After spraying, the (ionized) analyte is situated in a charged droplet of solvent molecules. Different parameters of these droplets, e.g. size distribution, velocity, etc., were studied in works of numerous research groups. Principally all these works signify-cantly underestimate the lifetime of micro- and nanodroplets. The size distribution of these droplets depends strongly on the position of the spray-emitter and spans a range up to a few micro-meters.[1] In high flow ESI experiments a large fraction of the measured ion current is caused by intact droplets.[2] Based on the literature referenced below, the dynamics of nanodroplets in MS inlet and transfer stages remains unclear. Classical molecular dynamics (MD) simulations are thus used to describe the microscopic behavior of charged nanodroplets and the internal energy distribution after energetic collisions with the background gas. An energy profile and collision rate of these nanodroplets is given by trajectory simulations. Parameterization leads to higher level trajectory simulations with a better description of the evaporation process of the droplets.

Methods

Hardware:
- compute server (64 AMD Opteron cores)
- amazon elastic-compute-cloud (48 virtual cores)
- pre-processing/less demanding simulations: workstation computer (8 physical cores)

Software:
- trajectory simulations: SIMION (8.1.1.32-x32-2013-05-20) [3], custom suite IDSimF
- molecular dynamics simulations: LAMMPS [4]
  - force field: OPLSAA [5]
- pre-processing: moltemplate [6]
- post-processing: Ovito (visualization) [7], python-scripts (result data analysis)

Results/Discussion

Trajectory Simulations

SIMION Simulations:
- Geometry of a quadrupolar collision cell is simulated (Pressure: 7 mTorr, Voltage on end plate: -10 V)
- Aggregates of nanodroplets with a mass of 50000 Da and 12 ions (m/z = 4166) are simulated in the RF-field

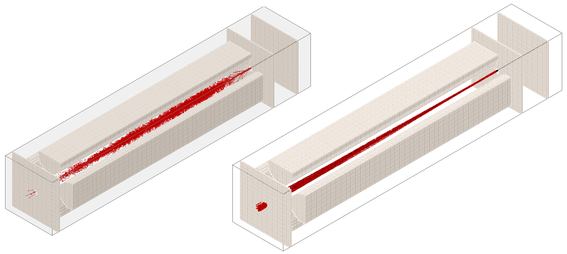

Fig. 1 (Left): Trajectory of Ions (m/z = 40) is influenced by the RF-frequency

Fig. 1 (Right): Trajectory of nanodroplets is not affected by the RF-field

Energy Profile of Nanodroplets:
- Nanodroplets (m/z = 4166) have a mean collision count at 500 – 600 per particle
- Mean collision energy in dependence of the probability of a collision event shown below (*Fig. 2*)
- Mean collision energy increases linear with the acceleration voltage simulated on the nanodroplets

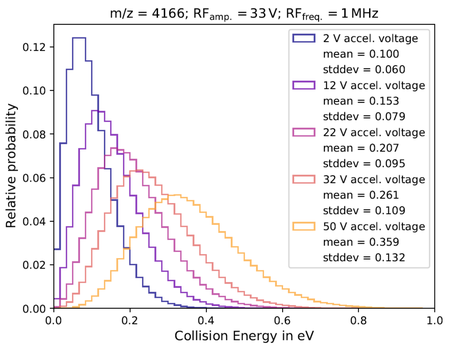

Fig 2: Collision energy in dependence of probability

Molecular Dynamics Simulations

Individual Collision Events:
- Simulated Nanodroplet = 1000 water, 1000 methanol molecules and 12 ammonium ions (nanodroplet diameter: 5 nm)
- Simulating individual collision events: argon particle with a given kinetic energy collides with the nanodroplets center of geometry as trajectory
- *Fig. 3:* Collision event results in an increase in total energy of the nanodroplet (approx. 20 eV)
  - Kinetic energy of the projectile is completely disseminated into the droplet

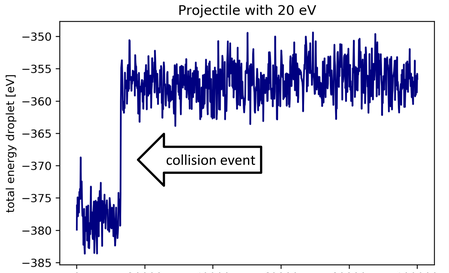

Fig 3: Indiviual collision event

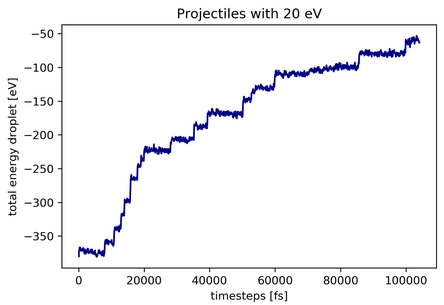

Fig 4: Limitation of energy intake due to collisions

Limitation of Energy Intake through Collisions:
- For testing the endurance of the energy intake of the nanodroplet, multiple collisions with argon particles from one side were simulated
- Results in *Fig. 4*: After an energy increase of 300 eV due to collisions the nanodroplet is still intact and does not disintegrate

Relaxation Time:
- To analyze the relaxation time the droplet is separated into halves *(Fig. 5)*
- Projectile is approaching from the left with a kinetic energy of 45 eV
- Collision event should mainly influence the energy distribution of the left half
- *Fig. 6:* Relaxation Time: energy levels of the two halves converge within 120 frames (60 ps)
- If the kinetic energy of the projectile is lower, the relaxation time decreases as well (20 eV ≈ 40 ps)
- Spike on impact: particles sputtered from the surface of the droplet with the projectile particle

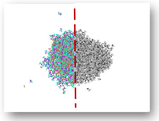

Fig. 5: Example of droplet half spheres

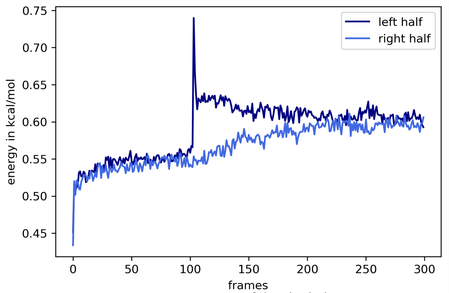

Fig 6: Examination of droplet halves

Conclusion/Outlook

Conclusion:
- As shown in the trajectory simulation performed with SIMION the flight paths of nanodroplets are hardly affected by the simulated RF-field
- The trajectories suggest that the nanodroplets are passing through a quadrupolar collision cell with a linear flight path
- Furthermore, the collision count with the probable mean collision energy indicates that the droplets can survive the conditions in a quadrupolar collision cell
- The energy dissemination in the simulated nanodrop-lets is within a time frame of picoseconds (range of vibrations)
  - This indicates that collisions with the background gas can be fully disseminated within the degrees of freedom and have no effect other than “heating” the nanodroplets
- The energy level of the aggregates is increasing after an individual collision event and the nanodroplets can survive an energy increase of 300 eV without disintegration

Outlook:
- Trajectory simulations with a more realistic geometry of a commercial collision cell
- Modelling the evaporation process of the nanodroplets with a higher level of trajectory simulations
- Experiments of droplet-detection in commercial instruments (first results on poster: TP 266)

Literature

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Acknowledgement

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