Analysis of surface-induced dissociation of large droplets formed by ESI in wall collisions via molecular dynamics simulations

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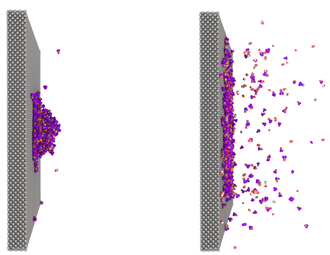
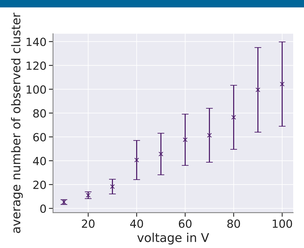
Introduction

The initial step of electrospray ionization (ESI) is the generation of large, charged droplets containing analyte ions. The lifetime of those droplets is often underestimated and the exact transfer dynamics trough the vacuum system of the mass spectrometer is unknown.
Experimental observations show that the droplets can penetrate deeply into the instrument vacuum system producing fragments visible in the mass spectra [1].
The formation of the fragments could possibly be attributed to collision-induced fragmentation (CID) of larger droplets aspirated into the vacuum system. Studies of ion trajectory and molecular dynamics (MD) simulations of charged droplets, show that larger droplets likely do not obtain sufficient energy by gas phase collisions to fragment significantly by CID.
Surface-induced dissociation (SID) is an alternative mechanism responsible for the fragment spectra as the available collision energy in an individual collision event is much higher compared to CID.

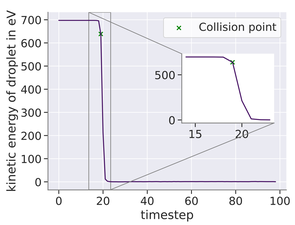
Frontal collisions



Wall collision for different initial droplet energies. (left: 10 V, right: 100 V)



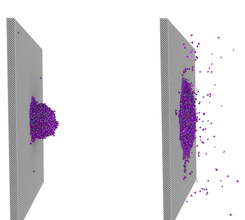
Average number of clusters (mean) with deviation for varying acceleration voltages.



Evolution of the kinetic energy of the droplet for 100 V acceleration voltage.

- small collision energies (voltage of 10 V): droplet mostly sticks to the wall
- energy is rapidly distributed into the wall
- higher collision energies (voltage of 100 V): droplet disintegrates, collision generates small fragments
- fragment count increases steadily with higher energies

Droplet size variation



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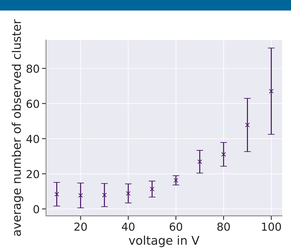

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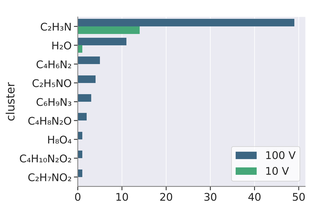


Comparison of fragments for varying acceleration voltages.

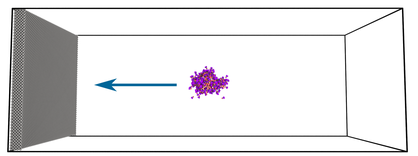
- larger droplet: 18 charges, 2919 water and 2385 acetonitrile molecules
- much higher energies are needed to produce similar number of fragments compared to the smaller droplet
- overall droplet behaviour similar, however fragments are ejected from the frontal collision site instead of a ”disintegration” of the droplet
- increase in cluster count is non-linear

Methods

The SID behavior of charged droplets is studied with molecular dynamics simulations of droplet-wall collisions using *LAMMPS* [2], a classical molecular dynamics code. The simulation set-up consists of

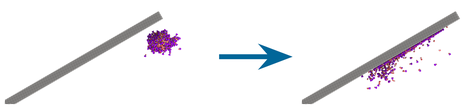
- a stable droplet, containing several ions (7 charges), acetonitrile (334 molecules) and water (440 molecules)
- the initial droplet is built with *moltemplate* [3] and *PACKMOL* [4] and then minimized in LAMMPS before the collision simulation is run
- a wall made up of aluminum atoms in a fcc structure
- the edges of the wall in contact with the simulation box are rigid, while the inner structure can freely vibrate

The droplet is placed in the center of the simulation box and launched towards the wall with varying pre-defined velocities reproducing electric accelerations commonly found in mass analyzer instruments.
The dynamics of the collision and the resulting molecular fragments are analyzed with custom analysis scripts (Python / SciPy and Ovito)

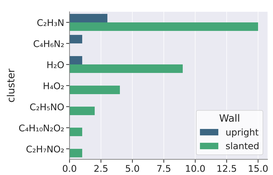


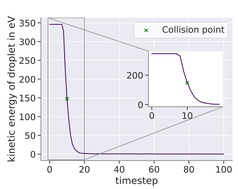
Simulation system set-up.

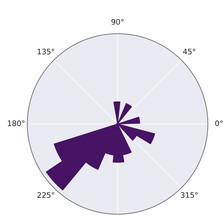
Slanted wall and fragmentation



- slanted walls with 50 V droplet acceleration voltage
- represent grazing collisions
- assumed to be dominant collision type in most analyzer systems
- for the same initial droplet energy: increased variety of fragments and larger fragments are ejected from the droplet on impact
- compared to the upright wall, the kinetic energy of the droplet is transferred to the wall more slowly
- fragments are mostly ejected downwards along the wall (cf. the radial fragment ejection distribution on the right)
- droplet is ”smearing” along the wall

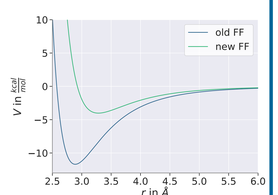


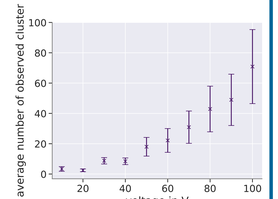


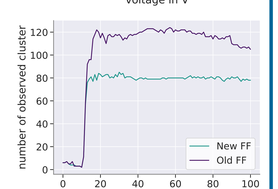


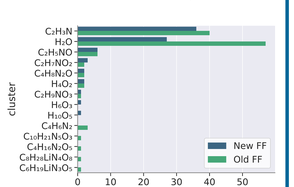
Force field variation

- the wall collision simulations are a combination of two force fields
  - the aluminum wall is described with an *eam/alloy* FF
  - the moelcules of the droplet interact via *OPLS-AA*
  - the interaction of the wall atoms with the droplet is additionally described via a *OPLS-AA* parameter set
- the interaction between the wall and droplet was varied
- with the new FF parameter set on average less fragments were ejected compared to the old parameters
- a direct comparison of 100 V accel. voltage collisions shows similar collision dynamics with the old FF generating more fragments
- old FF produces more diverse fragment spectra









Conclusions and outlook

- number of clusters ejected from droplet increases with higher energy
- kinetic energy is quickly transferred to the wall
- slanted walls change fragment cluster composition and occurrence
- droplet is smearing along the wall under low impact angles
- larger droplet system overall shows less fragments for the same acceleration voltages compared to small droplet
- system is sensitive to the force field parameters
- overall droplet ejection behaviour however remains similar
- ”old” parameter set generated larger and more diverse cluster

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- further increase of droplet size
- varying impact angle for bigger droplets
- change wall to aluminum oxide and introduce few layers of water on wall
- change over to dissipative particle dynamics (DPD) to be able to simulate much larger droplets, where individual atomistic interactions can be averaged out by molecule interactions

References

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[2] A. P. Thompson, H. M. Aktulga, R. Berger et al. *LAMMPS - a flexible simulation tool for particle-based materials modeling at the atomic, meso, and continuum scales*, Comp Phys Comm, 271 (2022) 10817.

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[4] L. Martínez, R. Andrade, E. G. Birgin, J. M. Martínez. *Packmol: A package for building initial configurations for molecular dynamics simulations*, Journal of Computational Chemistry, 30(13):2157-2164, 2009.

The authors declare no competing financial interest.