BERGISCHE UNIVERSITÄT WUPPERTAL

Physical & Theoretical Chemistry
University of Wuppertal

Investigation of Surface-Induced Dissociation: Molecular Dynamics Simulations of Wall Collisions of Large Droplets Formed by ESI

Michelle Rajkovic*, Walter Wißdorf, Thorsten Benter
*michelle.rajkovic@uni-wuppertal.de

Introduction

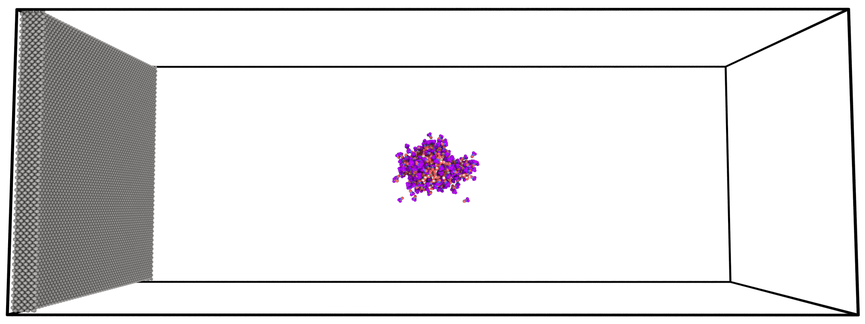
In electrospray ionization (ESI), large, charged droplets containing analyte ions are produced. The lifetime of those droplets is often underestimated and the exact transfer dynamics trough the vacuum system of the mass spectrometer is unknown. Experimental observations show that the droplets can penetrate 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 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.

Methods

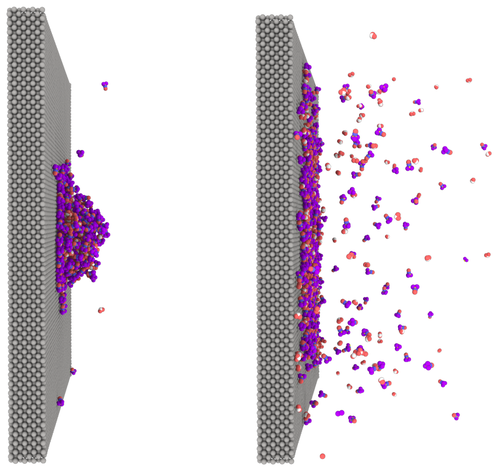
The SID behavior of charged droplets is studied with molecular dynamics simulations of droplet-wall collisions using *LAMMPS* [2], a classical molecular dynamics code. The simulation set-up consists of

- a stable droplet, containing several charges, acetonitrile and water (the initial droplet is built with *moltemplate* [3])
- 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 shot at the wall with varying pre-defined velocities reproducing electric accelerations commonly found in mass analyzer instruments.

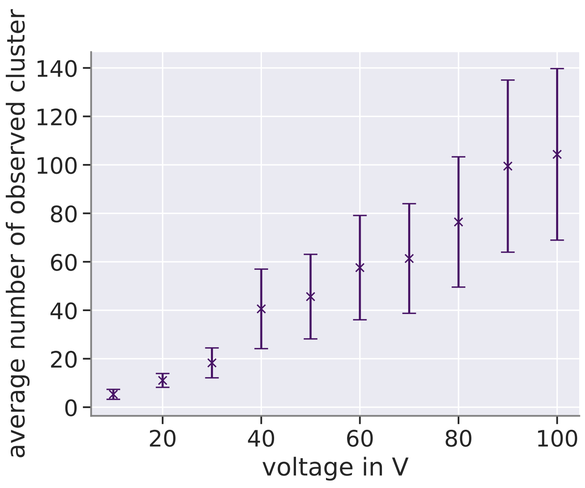


General collision behavior

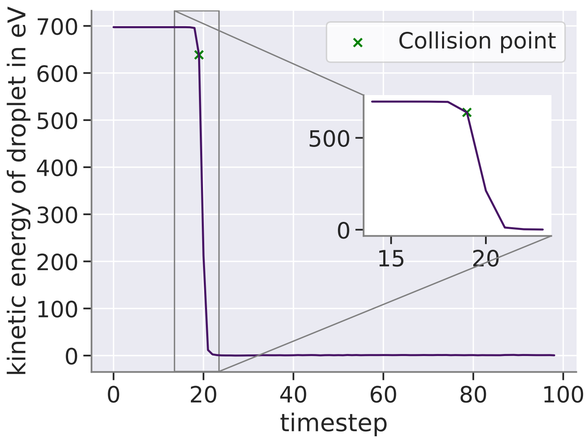


Wall collision for different initial droplet energies.

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

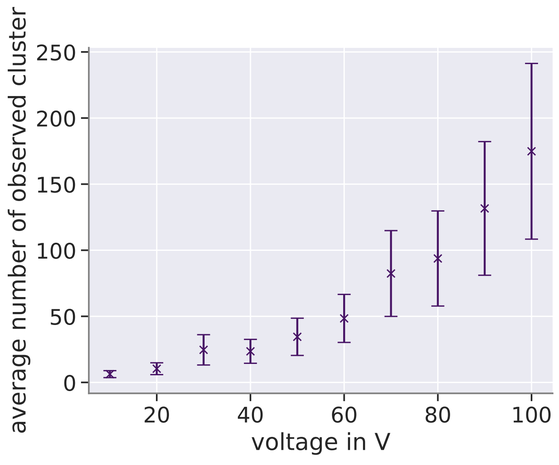


Average number of clusters (mean) with deviation for varying acceleration voltages.



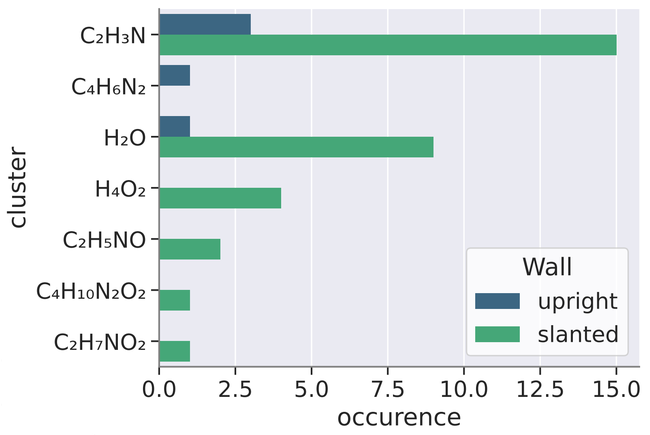
Evolution of the kinetic energy of the droplet for 100 V acceleration voltage.

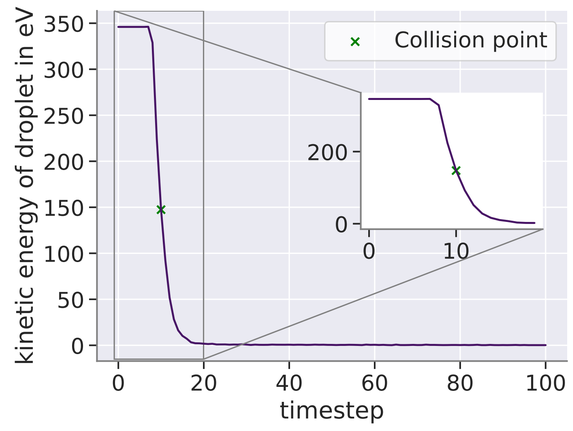
- different force field parameters for aluminum atoms
- aluminum has less attractive potential
- more clusters are ejected
- result comparably sensitive to force field variations



Slanted wall and fragmentation

- simulations with slanted walls
- 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





Conclusion

- number of clusters ejected from droplet increases with higher energy
- slanted walls change total cluster composition and frequency
- system is sensitive to the force field parameters, as such further sensitivity studies need to be carried out

References

[1] Markert, C., Thinius, M., Lehmann, L., Heintz, C., Stappert, F., Wissdorf, W., Kersten, H., Benter, T., Schneider, B. B., & Covey, T. R. (2021). *Observation of charged droplets from electrospray ionization (ESI) plumes in API mass spectrometers*, Analytical and bioanalytical chemistry, 413(22), 5587–5600. https://doi.org/10.1007/s00216-021-03452-y.

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