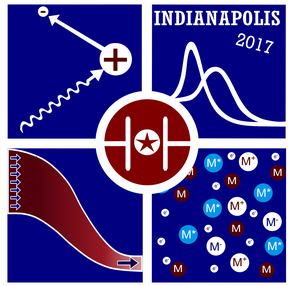

Fast space charge simulations: Simulation of ion – ion and background gas interaction in a linear quadrupole

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Introduction

The dynamics of molecular ions in transfer- and pressure reduction stages of atmospheric pressure mass spectrometers (MS) are governed by the present electric fields, their interaction with the flowing background gas, their chemical reactions and the coulombic interactions between the ions, generally referred to as "space charge".

Thus, a comprehensive numerical model of an ion transfer system must incorporate all those interactions, which renders such a numerical calculation rather complex. Particularly, the calculation of coulombic particle-particle interactions requires computational acceleration via fast approximation techniques, e.g. Barnes-Hut Tree calculations [1] or Fast Multipole Methods [2].

We present numerical simulations of ion dynamics in a transfer quadrupole of a commercial instrument, incorporating background gas interaction and space charge.

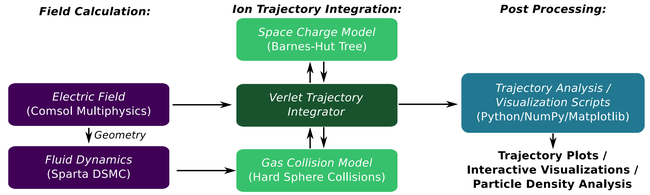
Methods / Simulation Overview

Field / Trajectory Calculation:

- Simplified quad geometry was generated with Comsol Multiphysics (version 4.4)
- Electric field calculation: Comsol Multiphysics
- Fluid dynamic simulation of the background gas flow: SPARTA Direct Simulation Monte-Carlo (DSMC) (version 21 Mar 2016) [3]
- Ion trajectory calculation: Custom developed Verlet ion trajectory integrator, space charge calculation with Barnes-Hut method

Post Processing / Field Translation:

- Custom-developed data analysis / transformation scripts utilizing NumPy / Matplotlib

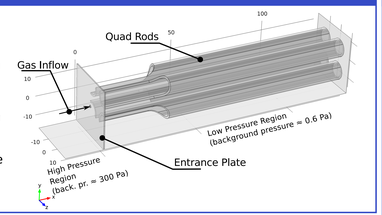


Simulation Domain

The simulation domain consists of the quadrupole rods in an rectangular chamber.

A gas flow enters a high pressure region, which is separated from the quad region by an entrance plate with an orifice (diam. 1.4 mm). Background gas and ions enter the quad region through the orifice.

In addition to the quadrupole field between the rod pairs, a variable potential offset between the entrance plate and the rods was assumed.



Outlook

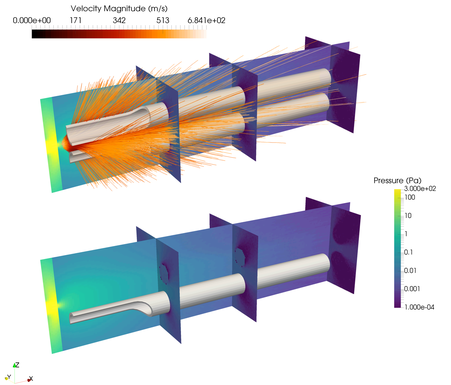
The presented results are a first step into the comprehensive simulation of ion transfer stages. Planned future work will include:

- Optimization and integration of additional space charge calculation methods (e.g. Fast Multipole Methods) and hardware platforms (GPGPUs) to increase the number of simulated particles
- Refining the DSMC model of the background gas flow, particularly the boundary conditions in the low pressure region
- Integration of chemical reactions between ions and neutrals and between ions considering the increased effective ion temperatures
- Modeling of internal states of molecules, enabling advanced ion temperature and reaction models

Quad Gas Dynamics

Flow Field:

below: Results of the DSMC calculation of the background gas flow. As indicated by the flow lines (top panel), starting at the entrance plate orifice, the gas expands rapidly through the gaps between the quad rods.

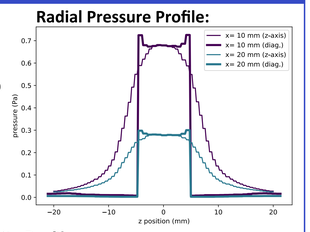


Flow Profiles:

right: Pressure profiles along the z-axis and diagonally (cross section through a quad rod pair) in 10 and 20 mm distance to the entrance plate.

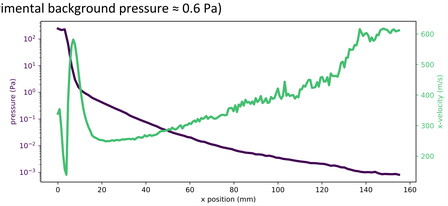
The outflowing gas creates a radial pressure gradient in the rod gaps, while a small pressure increase near the quad rods is visible from the gas impinging the rod walls.

Radial Pressure Profile:



Axial Pressure and Velocity Profile:

below: Axial profiles along the x-axis for gas pressure and axial velocity. Note that the assumption of ideally-pumped simulation boundaries leads to an underestimation of the background pressure in the DSMC simulation (experimental background pressure ≈ 0.6 Pa)



Space Charge Limitation of Radial Focusing

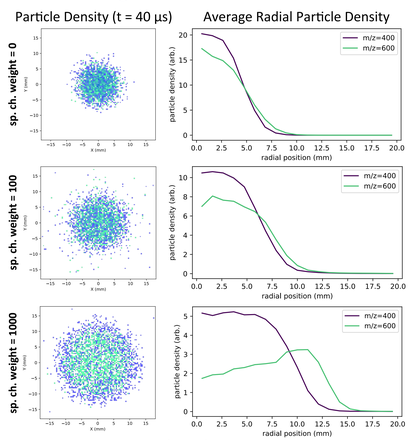
Space Charge Effect:

Space charge leads to a repulsive force between ions, which limits the capacity of ion focusing elements such as quadrupoles [4].

Two dimensional simulations in an idealized quadrupole potential (ignoring ion motion in the axial direction of the quadrupole) allow to estimate the effects space charge and background gas particle collisions have on ion trajectories.

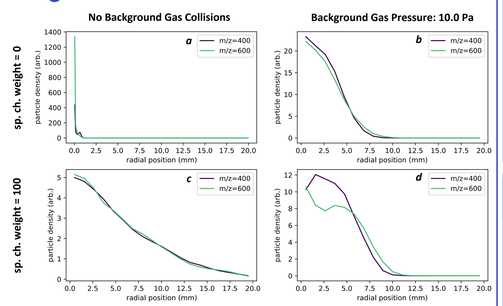
right:
Results of two dimensional simulations in an idealized quadrupole field.

The ion cloud expands with increasing charge weight in the space charge calculation. In addition, a significant separation of ion species with different m/z ratio occurs with increasing space charge intensity (m/z=400 in light blue in the particle density plots).



(collision gas: N_2, 3000 simulated particles)

Background Gas Collisions:



top:
Variation of the background gas pressure reveals the interactions between ions and background gas particles: without gas and space charge, all repulsive forces are vanishing and the ion ensemble is sharply focused (a), while gas addition leads to dispersion (b).

With strong space charge, collisions with background gas particles lead to cooling of the radial ion motion (c and d).

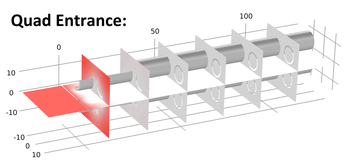
Conclusions

- A code for the integration of ion trajectories considering space charge was developed and coupled to fluid dynamic simulations with a DSMC method and a solver for electric fields
- A transfer quadrupole in a commercial mass spectrometer was successfully modeled
- Ion transport in the quadrupole is highly sensitive to the background gas flow
- The quality of the fluid dynamic simulation of the gas flow in the quadrupole region is critical. The currently available solution underestimates the background pressure in the quad region
- Space charge has only a minor effect on axial transport of ions into / through the quadrupole, and is thus most likely not limiting the transfer through the quadrupole
- Ions reach very high effective temperatures

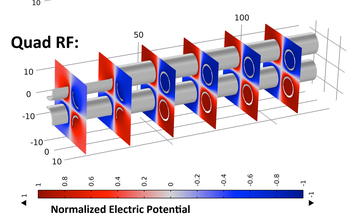
Axial Charge Transport: Field, Space Charge and Gas Dynamics

Electric Field:

Quad Entrance:



Quad RF:



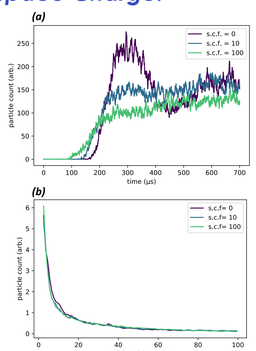
top: Normalized electrical fields between the quad rods and the entrance plate ("Quad Entrance") and between the quad rod pairs ("Quad RF").

Axial Transport with Space Charge:

The axial transport of ions through the quadrupole is the result of the forces created by electrical fields, the background gas flow and space charge.

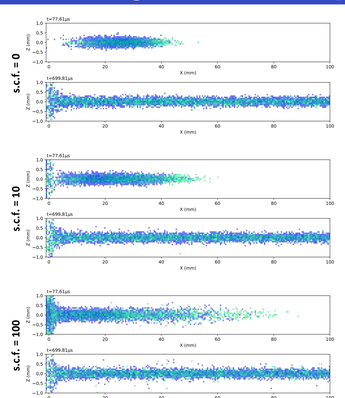
Three dimensional simulations of the ion transport in the transfer quadrupole were conducted with inputs from SPARTA and Comsol Multiphysics. An initial ion pulse was started at the entrance plate orifice. Ions leaving the simulation domain were restarted at the entrance plate orifice. This eventually leads to steady state conditions.

The simulations were performed with 8000 simulated particles of m/z= 400 (light blue in density plots) and 600 (dark blue in density plots).



(a): Time resolved particle intensity at the exit of the quadrupole geometry with different charge weights in the space charge calculation (space charge factor - s.c.f.). Strong space charge effects are observed.

(b): Average steady state axial particle density. Despite the strong space charge effects in (a), the axial particle density is not sensitive to space charge.



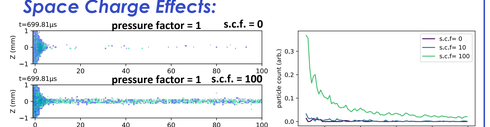
top: Particle density in the initial (t=77.6µs) and the steady state phase (t=699.8µs).

Strong space charge leads to strong axial dispersion of the initial ion pulse, while the steady state distribution is not affected significantly.

Simulations with Retention Potential:

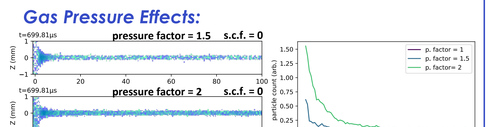
To estimate the relative effects of space charge forces and background gas interactions, a retention potential of -2 V was assumed. This potential was sufficient to balance the forward force resulting from the background gas motion when space charge was ignored.

Space Charge Effects:



top: Without space charge (s.c.f. = 0) virtually no ions enter the quadrupole. With increasing space charge the retention potential is overcome by the repulsive force between particles.

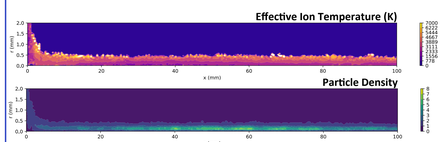
Gas Pressure Effects:



top: Even a moderate increase of the background gas pressure effectively overcomes the retention potential.

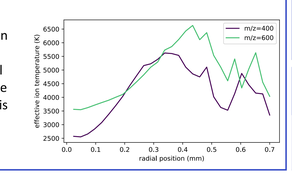
Ion Temperature

The acceleration of ions in an electrical field leads to increased kinetic energies and thus to increased energy transfer in collisions with background gas particles. When the acceleration is moderate, this can be treated as an increased effective ion temperature [5], which may strongly impact on the chemical dynamics of ionic species under such conditions. Analysis of simulated ion velocities allows an estimation of the effective ion temperatures in the transfer quadrupole under investigation.



top: Average effective ion temperature and average particle density (spatially resolved radial plot, s.c.f. = 0). Note that ions penetrating deep into the focusing field reach very high effective ion temperatures, up to several thousand Kelvin.

right: Average effective ion temperature. Even in the region close to the central axis of the quadrupole, the average ion temperature is significantly increased (> 2500 K).



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Acknowledgement

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