

Integrated Ion Dynamics Simulations in OpenFOAM: Flow, Transport, Chemical Reactions, and Space-Charge

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Introduction

The chemical reactivity of analyte ions plays a paramount role for the understanding of API-MS and associated methods, e.g. ion mobility spectrometry (DMS / IMS). Thus, the numerical simulation of the ion dynamics in analytical instruments must incorporate a model of the chemical dynamics of analyte ions [1,2,3].

We presented an open source framework based on OpenFOAM for the simulation of ion trajectories under viscous conditions in 2014 [4]. This framework was extended with modules for the statistical simulation of chemical kinetics (RS), the calculation of the effective ion reaction temperature, and a low pressure collision model (hard sphere collisions). This approach paves the way for the simulation of highly dynamic processes under viscous and medium pressure conditions.

Methods

Software Tools / Frameworks:

Frameworks:

- OpenFOAM v2.2.3
- Palabos 1.5

Calculation Mesh Generation:

- Salome 6.3.0
- blockMesh

OpenFOAM Result Visualization: Paraview 4.1

Additional Result Analysis Generation:

- NumPy and Matplotlib
- Python libraries

CFD Codes:

- Palabos 1.5 (Lattice Boltzmann code)
- dsMCFoam

Ion Trajectory and Kinetics Simulation:

- Set of custom-built libraries and solvers ("ionFoam")

Hardware:

- Dell Precision T7400 Workstation (Xeon E5530)
- Apple iMac (Core i5)
- Custom-built cluster (Opteron 6282)

Reacting Ions: Reactant Ion Peak in Ion Mobility Spectrometry

The signal of *proton bound water clusters* in high pressure Ion Mobility Spectrometry (IMS), the so called *Reactant Ion Peak* (RIP), is an ideal benchmark problem for the simulation of the chemical dynamics of gas phase ions under viscous conditions.

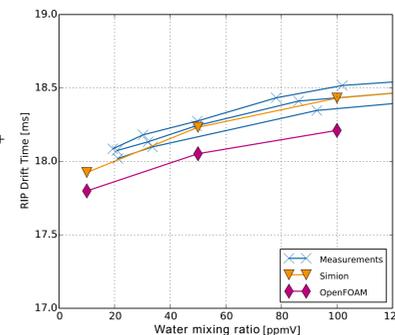
RIP = Signal of water cluster equilibrium
 $[H + (H_2O)_n]^+ + H_2O \rightleftharpoons [H + (H_2O)_{n+1}]^+$

The details of the chemical system and the basic simulation technique are presented elsewhere [2,3].

We have added a statistical model for the simulation of chemical kinetics ("reaction simulation" - RS) to the ionFoam framework and have applied the method to solve the water-cluster RIP benchmark case.

In contrast to the Simion / RS model, the OpenFOAM based calculations are distributable to multiple processors and can readily handle space charge effects in the simulation.

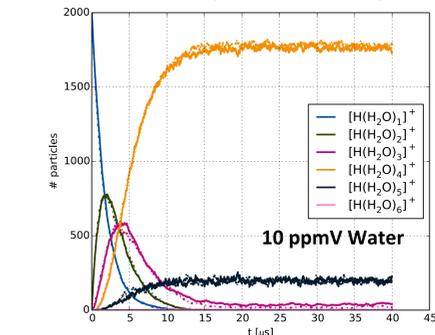
RIP Drift Times:



above: Simulated RIP drift times in an AP-IMS (ISAS-IMS)

The OpenFOAM based simulation reproduces the measured drift times with a systematic deviation of less than 1.5%, which is comparable to the observed experimental variation. Note that the uncertainty of the individual water cluster mobilities is well above 5%.

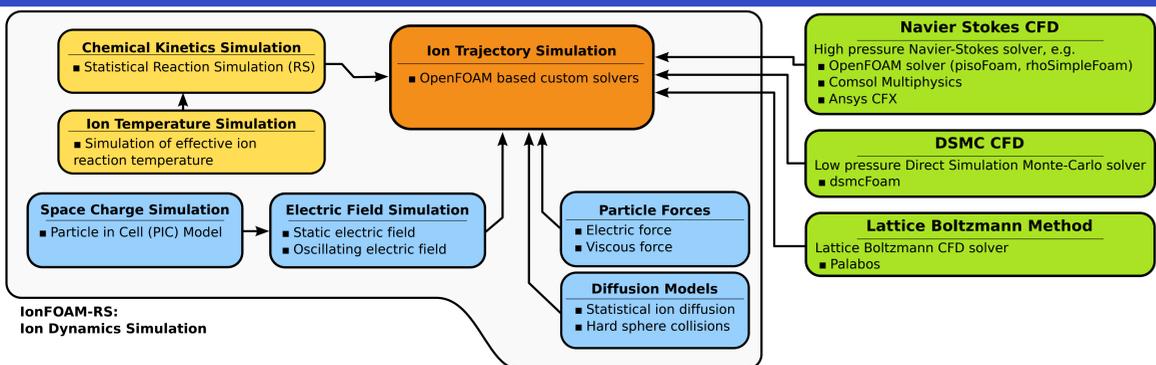
Chemical Kinetics: Equilibration of the System



above: Equilibration of the water cluster system

The results of the simulation of the water cluster system with Simion / RS (solid lines) and the OpenFOAM based model (dashed lines) agree well. The visible slight systematic deviation potentially contributes to the deviation of the simulated drift times shown on the left.

Simulation Methods Overview

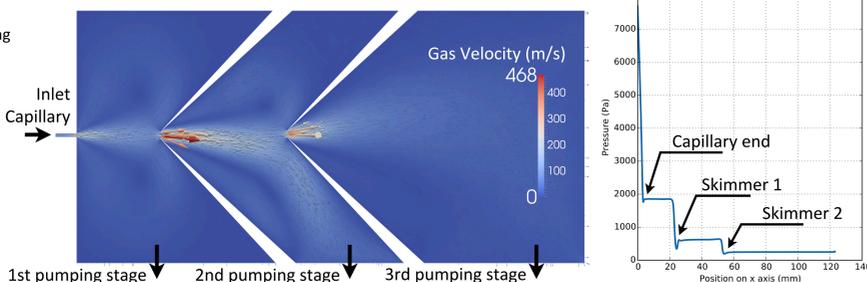


Reacting Ions: Medium Pressure Transfer Stage

At typical medium pressure conditions (approx. 1-10 mbar), even moderate electrical field strengths lead to a significant acceleration of gas phase ions due to their long mean free paths. A consequence of this electrical driven acceleration are increased ion collision energies and increased effective ion reaction temperatures.

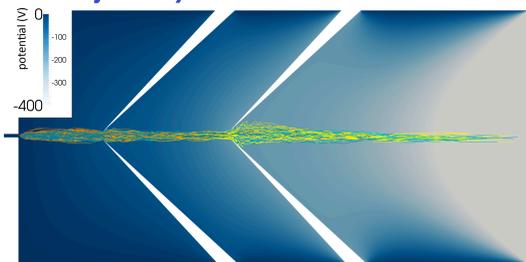
To demonstrate the applicability of the developed simulation framework under such conditions, we have simulated the gas flow and the trajectories of reacting ions in the resulting flow field of a generic pressure reduction stage with a double skimmer setup.

DSMC Gas Flow Simulation:



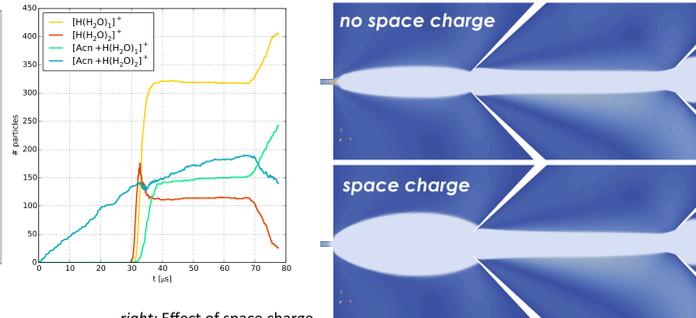
above: Simulation result (flow field) of the statistical (Direct Simulation Monte Carlo - DSMC) simulation of the flow in the pressure reduction stage

Ion Trajectory Simulation:



above: Ion trajectory simulations
 Ion trajectory simulations of proton-bound acetone-water- and water clusters. Declustering to cluster size one occurs due to the electrical acceleration of the ions (above right).

Space Charge:



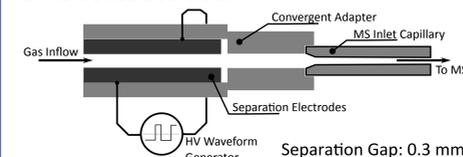
right: Effect of space charge
 Trajectory simulations of the cluster systems considering space charge reveal significant effects of the space charge, particularly in the regions with high ion densities. The shown simulations was performed with 1 million simulated particles on a consumer grade computer system. The velocity is shown in the background.

Reacting Ions: Differential Ion Mobility

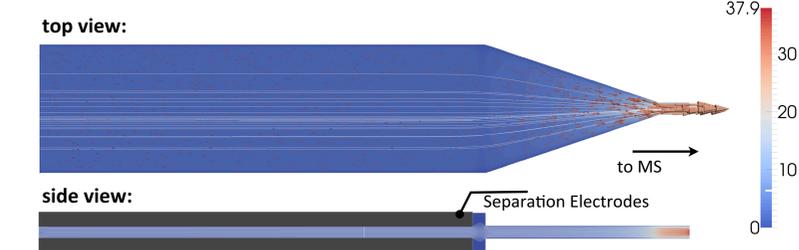
The differential mobility of reactive ions in the strong RF-field of a DIMS separation device at atmospheric pressure results primarily from the increased and oscillating effective ion temperature. This leads to oscillating mean cluster sizes in the high- and low-field phases of the dispersion field.

We have simulated gas flow and ion dynamics in a generic plate electrode DIMS device attached to the front end of a MS inlet capillary to demonstrate the applicability of the developed simulation framework.

DIMS Device Overview:



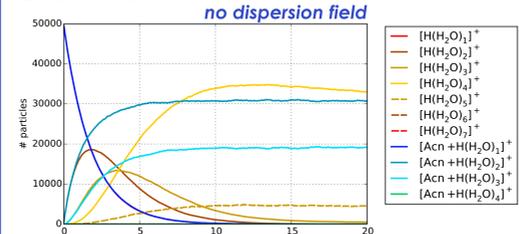
Lattice Boltzmann Gas Flow Simulation:



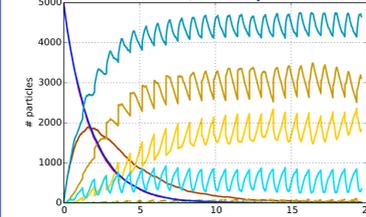
above: Lattice Boltzmann simulation of gas flow in the DIMS device

The simulated gas flow accelerates in the convergent adapter and reaches its highest velocity at the capillary inlet. Due to the small size of the gap between the separation electrodes and the adapter, the flow is not disturbed significantly.

Chemical Kinetics:

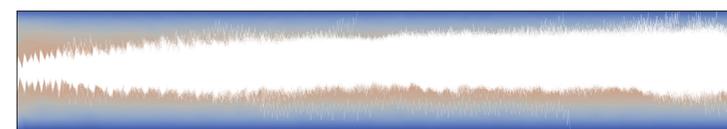


3.6 kV/cm dispersion field



left: Chemical kinetics of proton-bound water and acetone-water clusters, respectively, in the DIMS device
 The chemical oscillation and the shift of the mean cluster distribution due to the strong dispersion field is clearly observable.

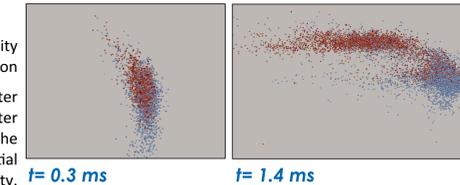
Ion Trajectories:



above: Simulated ion trajectories in the DIMS device
 The tracks diverge due to the differential mobility separation.

right: Differential mobility separation

The simulated water cluster (blue) and acetone water cluster system (red) separate due to the chemically induced differential ion mobility.



Conclusions

- A simulation framework ("ionFoam") based on OpenFOAM was developed.
- The framework can be coupled with a wide range of CFD methods. Particularly, methods suitable for the simulation of rarefied gas flows (Lattice Boltzmann methods and DSMC) can be combined with ionFoam.
- The framework incorporates models for chemical kinetics, the effective reaction temperature of reactive gas phase ions, and space charge.
- The calculations can be parallelized and run on cluster computer systems. Millions of particles can be simulated in a parallel calculation.
- Benchmark simulations of the chemical dynamics and drift time of the proton bound water cluster RIP in an AP-IMS reveal that the simulation of the chemical kinetics in ionFoam is valid with respect to SIMION/RS calculations as well as experimental results.
- The trajectories and reactions of proton bound water clusters in an rarefied gas flow through a double skimmer setup were successfully simulated.
- The chemical dynamics and separation of cluster ions in a differential mobility separation device were simulated.
- The modular design of OpenFOAM and ionFoam allows for integration of more complex collision and reaction models which e.g. consider the internal energies and degrees of freedom of the reacting particles.

Literature

- Klee, S.; Dierpman, V.; Wißdorf, W.; Klopotoski, S.; Kersten, H.; Brockmann, K. J.; Benter, T.; Albrecht, S.; Bruins, A. P.; Dousty, F.; Kauppila, T. J.; Kostianen, R.; O'Brien, R.; Robb, D. B.; Syage, J. A. Are Clusters Important in Understanding the Mechanisms in Atmospheric Pressure Ionization? Part 1: Reagent Ion Generation and Chemical Control of Ion Populations. *J. Am. Soc. Mass Spectrom.* 2014, 25, 1310-1325. DOI: 10.1007/s13361-014-0891-2.
- Wissdorf, W.; Seifert, L.; Dierpman, V.; Klee, S.; Vautz, W.; Benter, T., Monte Carlo Simulation of Ion Trajectories of Reacting Chemical Systems: Mobility of Small Water Clusters in Ion Mobility Spectrometry. *J. Am. Soc. Mass Spectrom.* 2013, 24, 632-641. DOI: 10.1007/s13361-012-0553-1.
- Wissdorf, W.; Dierpman, V.; Klee, S.; Kersten, H.; Benter, T.; Vautz, W., Numerical Simulation of Reacting Flows of Ions at Atmospheric Pressure - the Reactant Ion Peak in IMS; in Proceedings of the 60th ASMS Conference on Mass Spectrometry and Allied Topics; Vancouver, Canada, 2012.
- Wissdorf, W.; Benter, T., Integrated ion trajectory simulations in OpenFOAM, an open source framework for complex numerical simulations; in Proceedings of the 62th ASMS Conference on Mass Spectrometry and Allied Topics; Baltimore, MD, USA, 2014.

Acknowledgement

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