BERGISCHE UNIVERSITÄT WUPPERTAL

Physical & Theoretical Chemistry
University of Wuppertal

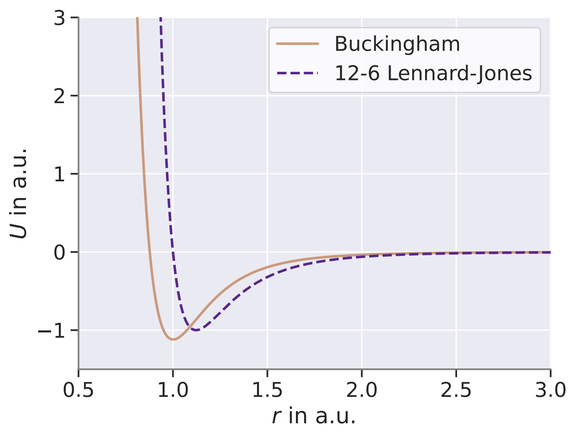
Study of molecular dynamics methods for prediction of ion mobilities at high and low fields of small molecular ions

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

Introduction

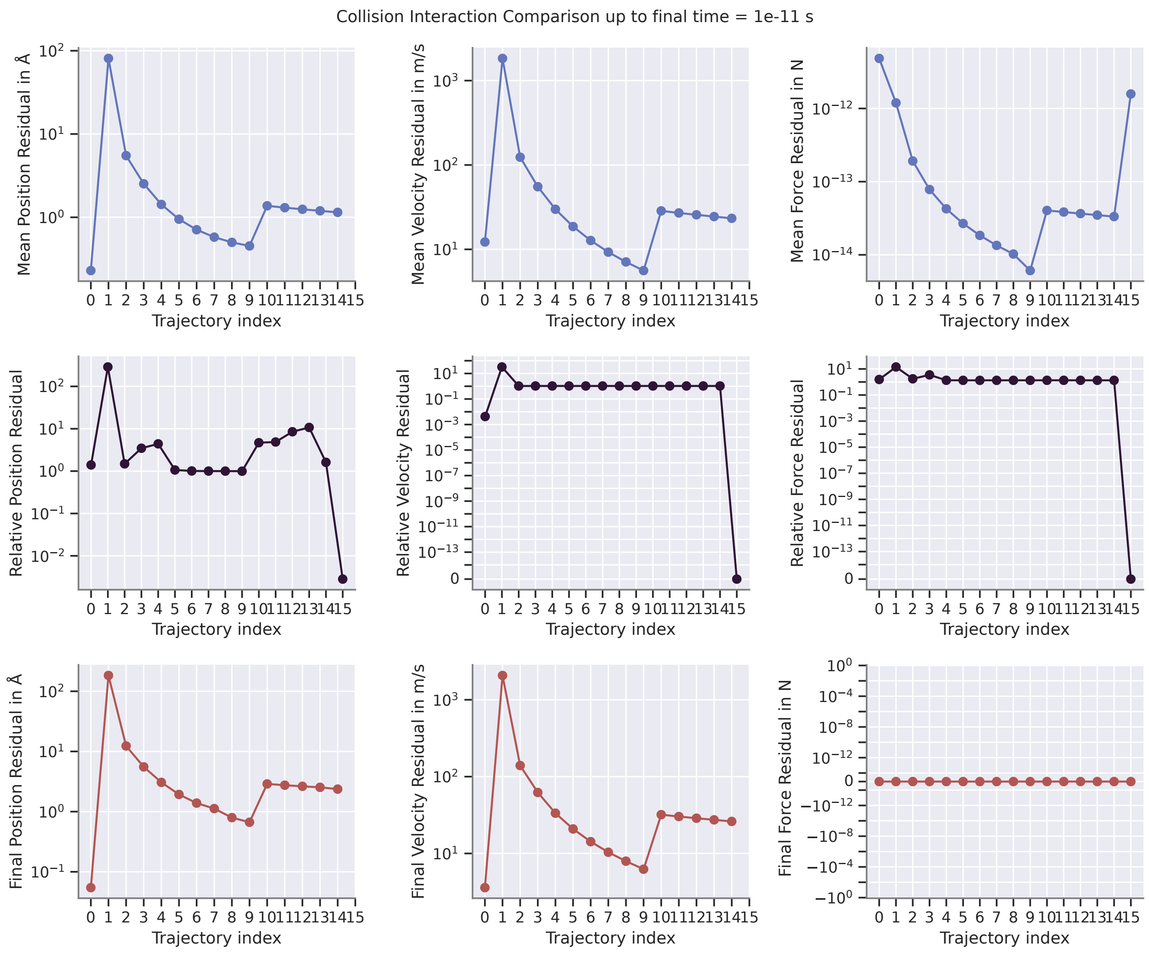
Gas phase ions can be separated by their ion mobility with drift tube ion-mobility spectrometry (DT-IMS). In DT-IMS, ions are accelerated in a buffer gas filled drift tube by a constant electric field. The ion species can be differentiated by their characteristic electric mobility in this field. For electric field strengths above the low field limit ($\approx$ 2 Td), several collision induced processes take place which lead to a complex change in ion mobilities (high field effects). There are several software packages available (MOBCAL, IMoS [2]), which can estimate ion mobilities at vanishing electric field conditions. Recently, the MobCal-MPI [1] version has been updated to include calculation of ion mobilities at high field. Additionally, the Ion Dynamics Simulation Framework (IDSimF) [3] is an open-source software, which allows to simulate non-equilibrium ion trajectories of high and low field drift-tube IMS with a molecular dynamics based (MD) collision model similar to that of MOBCAL to model ion-neutral collisions.

Trajectory comparisons



Potential comparison of modified Buckingham and 12-6 Lennard-Jones potential

- modified Buckingham potential is in first approximation a damped Lennard-Jones potential
- repulsion of particles at lower distances if Buckingham is used
- numerical instabilities for strongly attractive systems (Buckingham potential becomes attractive again for low r)



Comparison of integration of identical collisions between IDSimF and MobCal-MPI

Methods

Ion trajectories are calculated with a molecular dynamics based approach in both programs, IDSimF and MobCal-MPI.

MobCal-MPI

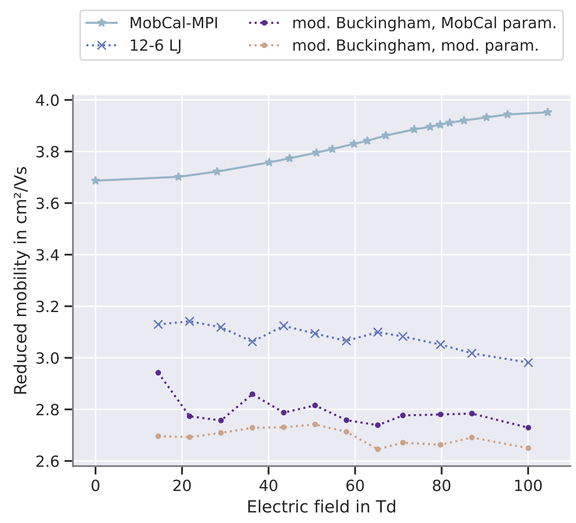
- solves the momentum transfer integral
- averaging over multiple collision events with varying velocities and relative geometries
- trajectory solving with Predictor-Corrector scheme
- uses two-temperature theory (2TT) for high field effects

IDSimF

- simulates whole trajectories of ions through an IMS
- background gas collisions are described with a MD collision model
- direct calculation of high field mobilities
- ion-neutral collisions are integrated by an adaptive Runge-Kutta method

Both programs use a combination of van der Waals interactions, ion-induced potentials and additionally quadrupole interaction if necessary. The van der Waals interactions are modeled through the modified Buckingham (MB) potential in MobCal-MPI.
Up to now, IDSimF used the classical 12-6 Lennard-Jones potential but was extended to also include the modified Buckingham potential as previous MobCal studies showed improved mobility predictions with the MB potential.

Ion mobilities



Simulated ion mobilities of protonated acetone

- simulated ion mobilities of protonated acetone at 420 K with MobCal-MPI and IDSimF (20 mbar)
- the 12-6 Lennard-Jones curves are obtained with a different set of parameters
- the mod. Buckingham mobility curves are obtained with both, the same parameters as MobCal and slightly altered parameters
- K_0 values of acetone have been reported at 1.91 cm^2/V s [4]

- even though good agreements of trajectories have been observed, ion mobilities show differences of about 20–25% between MobCal-MPI and IDSimF values for identical parameter sets
- more classical 12-6 Lennard-Jones potential shows marginal better agreement
- potential parameter variation can however alter absolute deviations
- possible divergence could arise from: approximations of 2TT, empirical corrections in MobCal, sensitivity of IDSimF simulations to pressure and temperature, sampling inaccuracies

References

[1] https://github.com/HopkinsLaboratory/MobCal-MPI

[2] C. Larriba, C.J. Hogan. *Ion mobilities in diatomic gases: measurement versus prediction with non-specular scattering models*. J. Phys. Chem. A 117, 3887-3901 (2013).

[3] M. Rajkovic et al. *IDSimF: An Open-Source Framework for the Simulation of Molecular Ion Dynamics in Mass Spectrometry and Ion Mobility Spectrometry*, Journal of the American Society for Mass Spectrometry 2024 35 (7), 1451-1460

[4] J. Langejuergen et al. *High Kinetic Energy Ion Mobility Spectrometer: Quantitative Analysis of Gas Mixtures with Ion Mobility Spectrometry*, Analytical Chemistry 2014 86 (14), 7023-7032

Conclusion

- mostly good agreement for single trajectories between both frameworks
- deviations in ion mobilities for protonated acetone
- origin of those deviations currently unclear
- non-equilibrium simulations can be directly calculated with IDSimF, allowing for further interesting research