Implementation of a molecular dynamics collision model for determination of ion mobilities in the ion dynamics simulation framework (IDSimF)

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Introduction

In ion-mobility spectrometry (IMS) gas phase ions are seperated by their individual drift velocities inside a gas filled drift tube with an applied electric field. Several software packages (e.g. MOBCAL [1], IMoS [2]) can accurately predict ion mobilities. However, in these frameworks it is not possible to vary the electric field directly, or to simulate transient conditions.

The simulation framework IDSimF [3], allows to simulate ion trajectories in an IMS module for abitrary electric fields with interactions between the ions and background gas particles.
So far, the background gas collision models were limited to a hard-sphere (HS) approach and a statistical diffusion model. Both models are not well suited to predict ion mobilities for low pressure and high electric fields. This work presents a new collision model based on molecular dynamics (MD), similar to the approaches found in other frameworks.

Molecular dynamics collision model

The newly implemented collision model is based on a molecular dynamics (MD) approach using the trajectory method. It solves Newton's equations of motion using numerical integration (e.g. adaptive step size Runge-Kutta methods) for each individual collision between an ion and a background gas particle. Molecules are modeled as rigid bodies, internal degrees of freedom are currently not considered.
The acceleration experienced by both colliding particles is calculated from the force acting on each other, resulting from a molecular dynamics force field. The force field is a combination of the 12-6 Lennard-Jones potential, which models short range repulsion between two non-bonding particles, and an ion induced dipole moment potential, which represents long-range attraction.

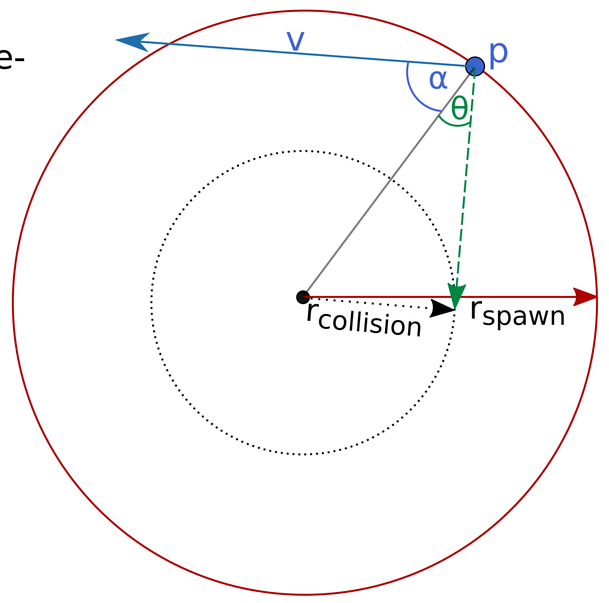

Fig. 1: Schematic representation of collision initialization

Initialization of each collision (Fig. 1):

- ion velocity known from overarching trajectory simulation, background gas is Maxwell-Boltzmann distributed
- set ion as coordinate system origin (black dot in Fig. 1)
- transform to stationary ion reference frame
- background gas particle randomly placed on sphere of radius r_{spawn}
- angle θ is the maximum angle under which the particle still hits the ion in a sphere of radius $r_{collision}$
- background gas particle hits the ion under angle α
  - if α ≤ θ: position is accepted
  - else: sample new positions until α ≤ θ fulfilled

Trajectories

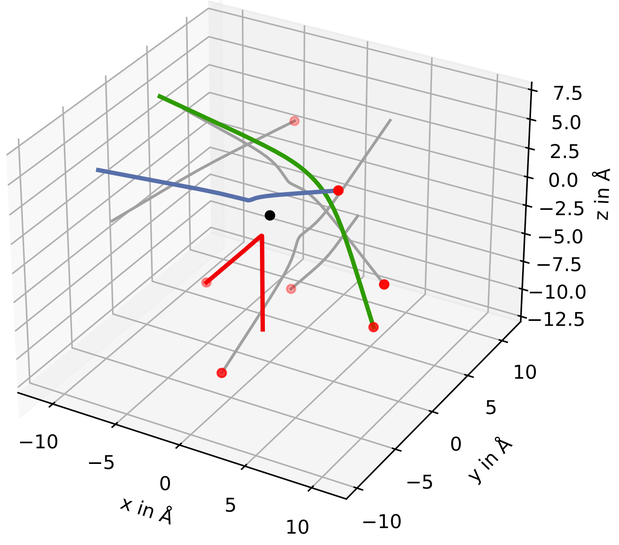

Fig. 2: Exemplary trajectories of background gas particles, Ar^+ is shown as a black dot

Simulated trajectories for Ar^+ in Helium at 10 Td:

- different types of trajectories of the background gas particle can be observed (**Fig. 2**):
  - "head-on" collision
  - trajectories which experience attractive force and then get repelled by the 12-6 LJ potential
  - grazing collisions
- ion induced dipole moment attracts background gas particle over a large distance
  - closest distance between two particles ("collision point") is closer than expected by pure geometric considerations (**Fig. 3**, orange ellipse)

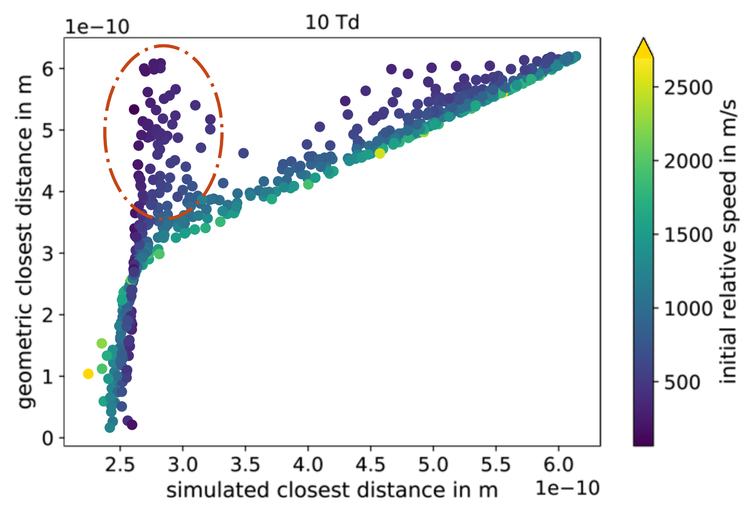

Fig. 3: Comparison of geometric closest distance to actual closest distance in simulation

Ion mobility

- ion mobility K: ratio of ion drift velocity to magnitude of electric field
- reduced ion mobility: allows to compare across different ion mobility devices

$$K_0 = K\frac{T_0}{T}\frac{p}{p_0}$$

Simulations in IMS drift tube for varying electric field (background gas p=20 mbar, T=298 K):

- MD collision model shows significant increase in accuracy of ion mobility predictions compared to the HS model
- **Fig. 4** additionally shows a good agreement with experimental measurements [4] within uncertainties
- accuracy of the ion mobility prediction can decrease for increasing field strengths (**Fig. 5**)

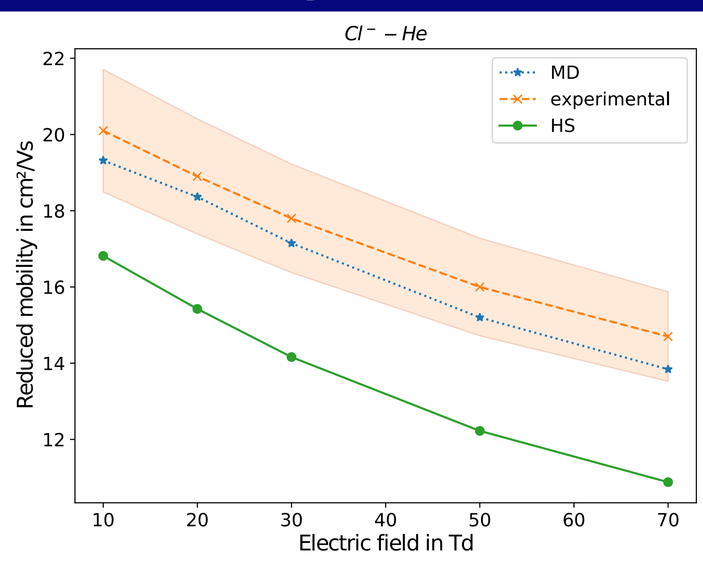

Fig. 4: Comparison of ion mobilities between MD, HS and experiment for Cl^- in He

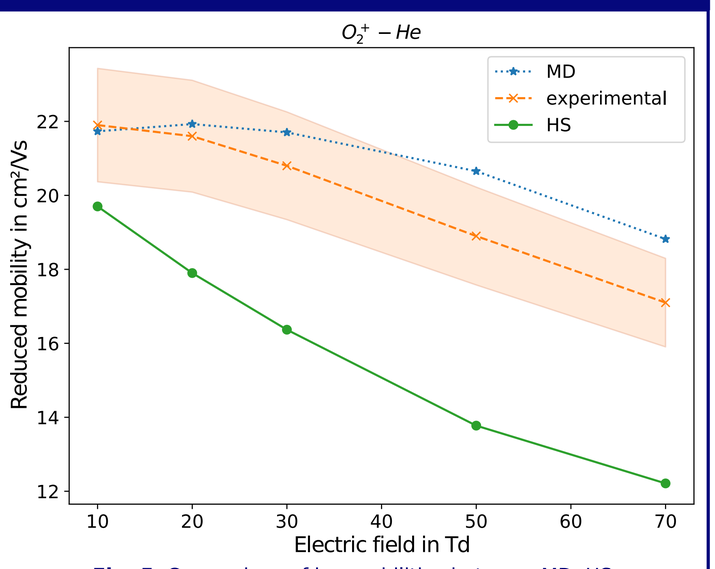

Fig. 5: Comparison of ion mobilities between MD, HS and experiment for O_2^+ in He

Conclusion & Outlook

Conclusion:

- all expected types of collisions are observed
- ion induced dipole moment potential has significant impact on ion mobility
- ion mobilities simulated more accurately with the MD model compared to the HS approach
- deviations to literature values generally increase with field strength

Outlook:

- simulate more complex molecules in different background gases (e.g. N_2)
- simulate different devices (e.g. DMS) and varying pressures using the MD collision model
- improve the force field/model to reduce systematic deviations for high field mobilities

Literature

[1] A. A. Shvartsburg, M. F. Jarrold: An exact hard-spheres scattering model for the mobilities of polyatomic ions. Chem. Phys. Lett., 1996, 261 , 86 —91.
[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] W. Wißdorf, D. Erdogdu, M. Thinius, T. Benter: Ion Dynamics Simulation Framework (IDSimF). ASMS 2020, Online reboot.
[4] H.W. Ellis, R.Y. Pai, E.W. McDaniel, E.A. Mason, L.A. Viehland: Transport properties of gaseous ions over a wide energy range. Atomic Data and Nuclear Data Tables, Volume 17, Issue 3, 1976, Pages 177-210.