Implementing a variable Soft Sphere Collision Model into the IDSimF Simulation Framework

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University of Wuppertal

Sanna Benter, Walter Wißdorf, Michelle Rajkovic, Hendrik Kersten, Thorsten Benter

Introduction

IMS Application

Ion mobility spectrometry (IMS) separates ions by their characteristic motion through a gas filled tube under the influence of a static electric field. In a preceding contribution[1] the Simulation Framework (Ion Dynamics Simulation Framework) **IDSimF** was presented. It allows ion trajectory simulations in electric fields with consideration of ion-ion interactions within large particle ensembles.

Former Implementation

IDSimF uses a Hard Sphere (HS) Collision Model to describe the direct collisional interaction between charged particles and neutral background gas.

New Implementation

This work presents the implementation of a variable Soft Sphere (VSS) Collision Model in IDSimF.

Motivation

The VSS Model introduces a softness parameter of the colliding spheres, as well as correcting the radii of the colliding particles based on the collision energy. Thus, the VSS Collision Model allows a significantly more accurate calculation of ion trajectories especially under high field conditions as compared to the simple HS Model.

Molecular Collision Models

Geometry of the collisional event

The colliding spheres have the pre-collision velocity vectors $\mathbf{v}_i$ and $\mathbf{v}_j$. The relative velocity vector $\mathbf{v}_{rel}$ is defined in a frame where the background gas particle **i** is stationary. The impact parameter b describes the offset of the colliding spheres in the range 0 (head-on collision) and 1 (grazing spheres). χ is the deflection angle and Θ is the angle of the collision plane round the collision axis. After the collisional event, **j** has the resulting relative viscosity vector $\mathbf{v}_{rel}^*$.

Variable Collision Models [2, 3]

The variable Collision Models VSS and VHS are based on the non variable Hard Sphere (HS) or Soft Sphere (SS) Collision Model. They calculate the particle diameter d based on the kinetic energy of the collision. With higher kinetic energies, the radii and thus the collision cross sections become smaller. Therefore, the collision probability is reduced, leading to different mobilities.
In the Monte Carlo simulation, the values of cos(χ) and Θ are derived from an assumed random distribution using the equations shown below, with R being a uniform random number in the range (0, 1).

$$b = d \cos^{\alpha}(\chi/2) \qquad \cos\chi = 2 \cdot R^{1/\alpha} - 1 \qquad \Theta = 2\pi R$$

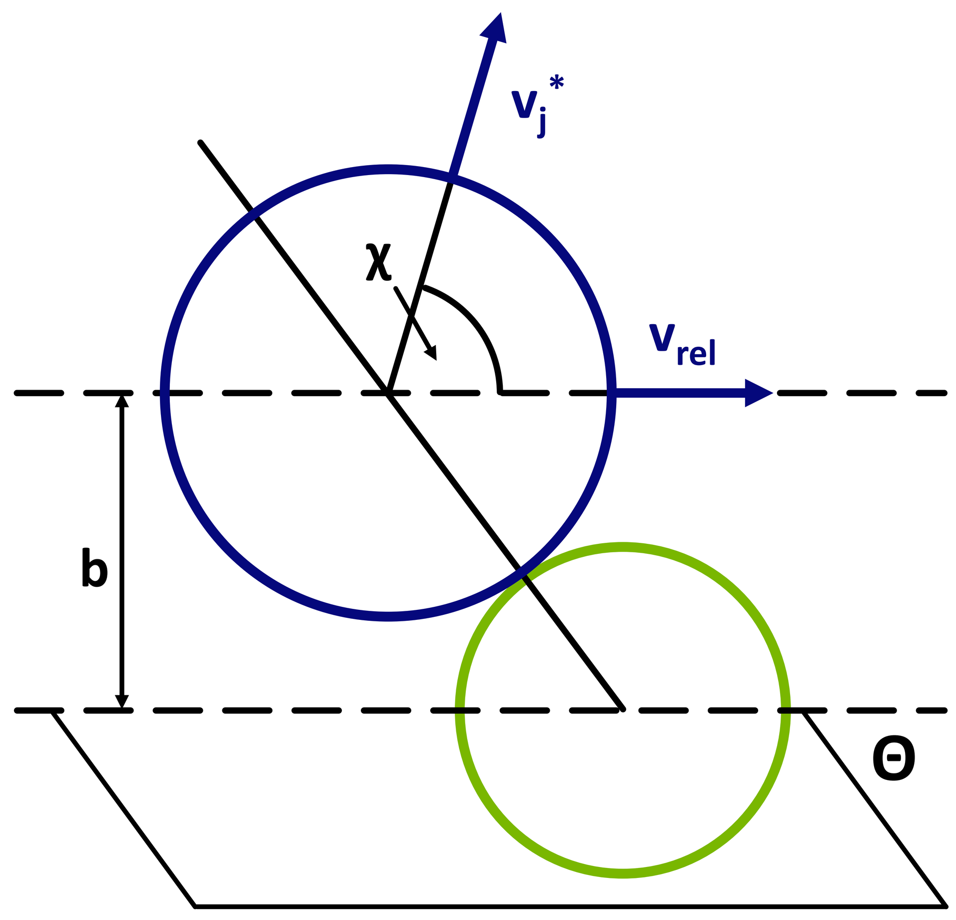

Fig. 1: Geometry of the Monte Carlo Collisions.

VSS introduces the scattering parameter α to describe the softness of the colliding spheres. It is easily convertible to the VHS Model by setting α = 1. As seen in the left equation, in the VSS model the maximum interaction distance b_{max} is not only determined by the diameter d but also the softness of the spheres. With values of α greater than 1.0, the distance between the spheres within in the collision is smaller; as well as the deflection angle χ being reduced in Soft Sphere collisions, influencing the scattering and the Ion Mobility (as shown below).

Scattering Probability

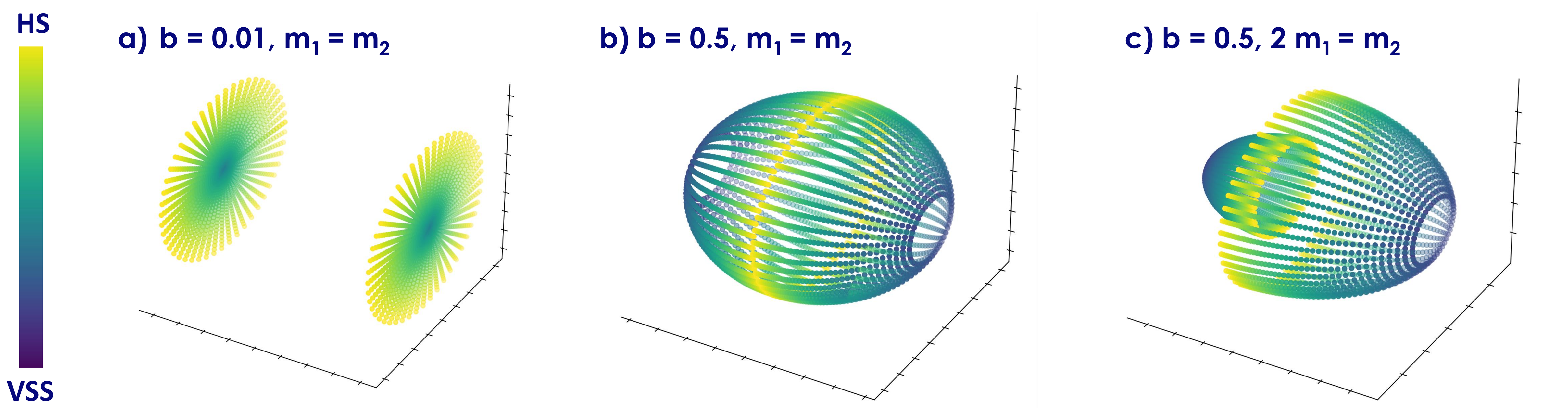

Fig. 2: Different scattering patterns for a) a small offset - almost head on collision, b) an increased offset (both for particles with the same mass) and c) increased offset and unequal masses; with alpha increasing from yellow (a=1, VHS) to purple (a=2, VSS).

The influence of α in combination with the impact parameter b is shown in **Fig. 2**, where the scattering of two colliding particles is calculated with the collision plane being rotated around 360°. With increasing b (takes values from 0 to 1), the particles are increasingly deflected. Thus, if the particles have the same mass and the same velocity, a bigger offset leads to a broader scattering in HS collision events. With an increasing softness of the particles, the resulting scatter distribution is less wide, leading to a less dramatic trajectory change. This difference in the scattering leads to different ion trajectories and therefore ion mobilities as in the HS model.

Ion Mobility

Charged particles move in gases under the influence of an electric field. The **Ion Mobility** describes the ratio of the ion drift to the magnitude of the electric field. The **reduced Ion Mobility** allows comparison across different ion mobility devices. To compare the accuracy of different Collision Models, the simulated Ion Mobilities are compared to experimental data (**Fig. 3**).

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

In low fields the accuracies of the Soft Models are higher than the accuracy of the HS Model. The HS Model underestimates the Mobility systematically, as due to the stiffness of the particles, the collision has a high impact in the scattering angle and the ions lose their original trajectory; rather than in the SS and VSS Model where the softness of the spheres lead to a smaller scattering angle and thus to a smaller change in the trajectory. In high fields, the SS model with static collision cross sections underestimates the mobility. With energy dependent collision cross sections, as in the VSS Model, the experimental results are much better reproduced.

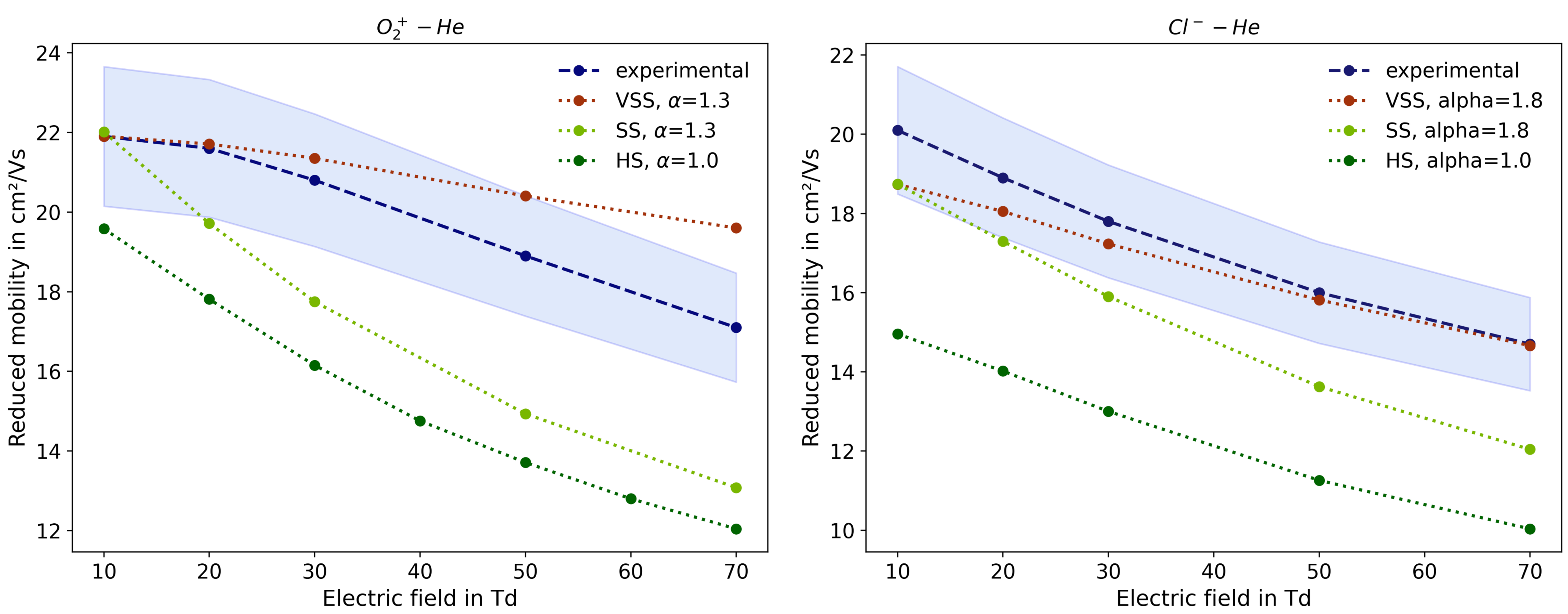

Fig. 3: Comparison of the Ion Mobilities of the HS and VSS Model with experimental results for a) O2+ in a Helium-Matrix and b) Cl- in a Helium Matrix.

Conclusion

- VSS Model was implemented and the ion trajectories of three different Collision Models (HS, SS, VSS) were simulated with IDSimF and compared to experimental results
- The implementation of the model is comparably straightforward
- The VSS Model generates significantly better results than the HS model, while the non variable Soft Sphere Model only achieves better results in low fields
- The results show a notable deviation at high field conditions and the kinetic correction factor of the cross section is only empirically derived and not yet determined from fundamental characteristics of the simulated particles

Outlook

- Kinetic Correction is not sufficient as the simulated results deviate from experimental results (esp. in high fields)
  → Calculate the kinetic correction factor of the diameter from the molecular properties of the species rather than determining it empirically
- Determine and document the softness parameter for different systems empirically
- Simulate different devices and more complex molecules in different background gases
- To counteract the deviation in high fields with the variable Models elasticity has to be added to the collisions as the mobility would be reduced due to higher deceleration within a collision

Literature

[1] W. Wißdorf, D. Erdogdu, M. Thinius, T. Benter: Ion Dynamics Simulation Framework (IDSimF). *ASMS 2020*, Online reboot. **[2] a)** K. Koura, H. Matsumoto *Phys. Fluids A* **3** (10), October 1991; **b)** K. Koura, H. Matsumoto *Phys. Fluids A* **4** (5), May 1992 **[3]** G. A. Bird (2013) *The DMSC Method* (Version 1.2).