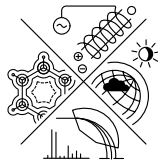




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MOLECULAR DYNAMICS STUDIES OF ION-NEUTRAL AND SURFACE COLLISIONS

FROM MOLECULAR IONS IN ION MOBILITY TO ESI DROPLETS

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"Ich versichere, die Arbeit selbstständig verfasst zu haben, nur die in der Dissertation angegebenen Hilfsmittel benutzt und alle wörtlich und inhaltlich übernommenen Stellen als solche gekennzeichnet zu haben, und dass die Dissertation in der gegenwärtigen oder einer anderen Fassung noch keiner anderen Fakultät, keiner Gesamthochschule und keiner anderen wissenschaftlichen Hochschule vorgelegen hat."

Wuppertal, den 26.04.2026

Michelle Rajkovic

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”

*“If you can dream—and not make dreams your master;
If you can think—and not make thoughts your aim;
If you can meet with Triumph and Disaster
And treat those two impostors just the same;”*

— Rudyard Kipling, *If*—

ABSTRACT

This work focuses on the establishment of methods and models for multi-scale simulations of electrospray ionization (ESI) droplet dynamics, from the ion source to the detector, in mass spectrometry. It consists of two main parts: modeling of ion-neutral collisions in drift tube ion mobility spectrometry (DT-IMS) with an advanced molecular dynamics (MD) based approach and classical molecular dynamics simulations of surface-induced dissociation (SID) events of ESI droplets.

A MD based collision model was integrated into the IDSimF ion trajectory simulation framework and used for DT-IMS simulations as a benchmark system. Good agreement with experimental ion mobilities was achieved for monoatomic background gases, while molecular nitrogen introduced additional complexity due to clustering artifacts and numerically demanding force fields. A variable hard-sphere (VHS) collision model with internal energy tracking was also implemented as a faster, though less accurate, alternative. Both models lay a foundation for further, more elaborate ion trajectory simulations of ESI droplets.

For the SID study, LAMMPS was used to simulate ESI droplet collisions with an idealized aluminum surface. Key findings include the predominant ejection of pure solvent clusters, the rare emission of charged clusters through high energy collisions, and the reduced cluster ejection for larger droplets. A proof-of-concept SID model in SIMION is further implemented and can be used to combine trajectory simulations with hard-sphere collisions and surface dissociation.

Additional work in the future should focus on improved clustering handling for ion-neutral collisions in IDSimF, refined force field parametrization, coarse-grained droplet models, and more realistic surface conditions to advance toward a more complete simulation of ESI droplet trajectories in vacuum systems of MS instruments.

ZUSAMMENFASSUNG

Diese Arbeit konzentriert sich auf die Entwicklung von Methoden und Modellen für die Simulation von geladenen Flüssigkeitstropfen die bei der Elektrospray-Ionisation (ESI) in der Massenspektrometrie entstehen. Diese Tropfen gelangen in die Vakuum-Systeme verbreiteter ESI-Massenspektrometer wo sie schlagartigen Veränderungen der Umgebungsbedingungen (Druck, Temperatur, elektrische Felder) ausgesetzt sind. Daher soll auf lange Sicht ein vollständiges, dynamisches Modell derartiger Tropfen von der Ionenquelle bis zum Detektor entwickelt werden. In dieser Arbeit werden zwei dafür grundlegende Teilaspekte beleuchtet: die stark verbesserte Modellierung von Ion-Neutral-Kollisionen mit einem auf klassischer Molekulardynamik (MD) basierenden Ansatz sowie Molekulardynamik Simulationen von oberflächeninduzierten Dissoziationen (SID) von ESI Tropfen.

Ein MD basiertes Kollisionsmodell wurde in IDSimF, ein offenes System zur Simulation von Iontrajektorien, integriert und für die Simulation eines Driftröhren-Ionenmobilitäts-Spektrometers (DT-IMS) verwendet, das als Benchmark-System benutzt wurde. Für monoatomare Hintergrundgase wurde eine gute Übereinstimmung mit experimentellen Ionenmobilitäten erzielt. Molekularer Stickstoff hingegen führte aufgrund der Ausbildung molekularer Cluster zwischen Ionen und Hintergrundgas und den anspruchsvollen Kraftfeldern zusätzliche Komplexität ein. Als schneller zu berechnende, wenn auch weniger präzise Alternative wurde außerdem ein Variable Hard-Sphere (VHS) Kollisionsmodell implementiert, welches zusätzlich interne Energien der modellierten Ionen verfolgen kann. Beide Modelle bilden dabei die Grundlage für weiterführende Ionentrajektorien Simulationen von ESI Tropfen.

Für die SID Simulationen wurde LAMMPS verwendet. LAMMPS ist ein klassischer MD Simulationscode zur Berechnung von atomaren Molekülsystemen. Typische ESI Tropfen wurden in diesen Simulationen mit einer idealisierten Aluminiumoberfläche zur Kollision gebracht. Zu den wesentlichen Ergebnissen zählen: die vorwiegend Freisetzung reiner Lösungsmittelcluster, die seltene Freisetzung geladener Cluster durch hochenergetische Kollisionen sowie die reduzierte Clusterfreisetzung bei größeren Tropfen. Darüber hinaus wurde ein erstes SID-Modell in das kommerzielle Simulationsprogramm SIMION

integriert. Dieses kombiniert Trajektorien Simulationen mit harten Kugelstößen zwischen den Tropfen und dem Hintergrundgas sowie die Dissoziation der Tropfen durch Oberflächenkollisionen.

Zukünftige Arbeiten sollten versuchen die Ion-Neutral-Kollisionen in IDSimF für die Cluster-Bildung anzupassen sowie eine umfängliche Kraftfeld Parametrisierung durchzuführen. Auch sollten in den SID Simulationen realistischere und komplexere Oberflächen simuliert werden und ein Ansatz zur effizienteren Berechnung von großen Tropfen etabliert werden (coarse-graining).

CONTENTS

List of Figures	xv
Listings	xxi
1 Background	1
2 Introduction to molecular dynamics simulations	3
2.1 Underlying principles	3
2.2 Numerical integration	5
2.2.1 Numerical requirements for molecular dynamics simulations . .	5
2.2.2 Explicit Euler	11
2.2.3 Leapfrog	11
2.2.4 Velocity Verlet	12
2.2.5 Runge-Kutta methods	12
2.2.6 Predictor-Corrector	14
2.3 System ensembles	15
2.3.1 Microcanonical ensemble	16
2.3.2 Canonical ensemble	16
2.3.3 Isothermal-isobaric ensemble	17
2.4 Boundary conditions	17
2.4.1 Periodic boundary conditions	18
2.5 Force fields	19
2.5.1 Pair potentials	19
2.5.2 Many-body potentials	23
2.5.3 Bonded potentials	24
2.5.4 Generation of force fields and limitations	26
3 Modeling of ion mobility	29
3.1 Ion mobility	29
3.2 Field dependence	30

3.3	Collision models	32
3.3.1	Hard-Sphere	32
3.3.2	Variable Hard-Sphere	34
3.3.3	Molecular dynamics based trajectory method	35
3.4	Inelastic collisions with Borgnakke-Larsen method	36
4	Dynamics of the electrospray process	39
4.1	Overview of working principle	39
4.2	Droplet formation	40
4.3	Droplet shrinkage and ion release	41
4.4	Observed discrepancies with ESI models and consequences	41
4.5	Potential fragmentation processes	44
4.5.1	Collision-induced dissociation	45
4.5.2	Surface-induced dissociation	46
5	Simulation software	47
5.1	LAMMPS	47
5.2	SIMION	49
5.3	IDSimF	49
5.4	MobCal / MobCal-MPI	50
5.5	Other libraries / software	50
5.5.1	AmberTools	50
5.5.2	Avogadro	51
5.5.3	Ovito	51
5.5.4	moltemplate	52
5.5.5	PACKMOL	53
6	Simulation of gas-phase ion-neutral collisions of molecular ions	55
6.1	Motivation	55
6.2	Molecular dynamics based trajectory method	56
6.2.1	Input parameters and usage	60
6.2.2	Comparison of integration methods	64
6.3	Ion-neutral collisions with monoatomic neutral gas	69
6.3.1	Standard simulation run	69
6.3.2	General trajectory characteristics	70
6.3.3	Collision radius scaling dependence	74
6.3.4	Collision cross section dependence	76
6.3.5	Pressure dependence	77
6.3.6	Temperature dependence	79
6.3.7	Force field parameter sensitivity	85
6.3.8	Prediction of ion mobilities	88
6.3.9	Parallelization efficiency	94

6.4	Introduction of nitrogen as neutral gas	98
6.4.1	Force field adaption	98
6.4.2	Numerical instabilities	100
6.4.3	Ion mobility dependencies	111
6.4.4	Prediction of ion mobilities	115
6.4.5	Rotations	120
6.5	Variable hard sphere model	131
6.5.1	Implementation	131
6.5.2	Tracking of internal energy	132
6.5.3	Comparison to hard-sphere and MD model	139
6.6	Summary	143
7	Simulation of electrospray droplets in surface collisions in vacuum	145
7.1	Droplet construction	147
7.2	SID LAMMPS model	150
7.2.1	Interatomic potentials	152
7.2.2	Processing of LAMMPS output	153
7.3	Simulations of frontal wall collisions	153
7.4	Simulations of slanted wall collisions	158
7.5	Droplet size variation	162
7.6	Force field sensitivity analysis	166
7.7	SID model for SIMION	169
8	Conclusion and Outlook	175
	Bibliography	179
	Appendices	
A	Force field parameters	197
B	Mathematical derivations and formulas	205
B.1	Parameter conversion between 12-6 Lennard-Jones and mod. Buckingham	205
B.2	High field mobilities from 2TT	205
B.3	Total potential function	206
B.4	Force field functions	206
B.4.1	12-6 Lennard-Jones	206
B.4.2	Mod. Buckingham	207
B.4.3	Ion-induced dipole	207
B.4.4	Quadrupole-ion	208
B.5	Borgnakke-Larsen energy transfer function	208
C	Graphics	211

LIST OF FIGURES

2.1	Example of MD lattice	4
2.2	Example of MD flow smulation domain	4
2.3	Simplified sequence of the standard MD algorithm	5
2.4	Comparison of solution trajectories of (non-)symplectic methods	7
2.5	Phase-space and energy of a simple pendulum	8
2.6	Numerical solution of a stiff system	10
2.7	Symbolic representation of thermodynamic ensembles	16
2.8	Example of periodic boundary conditions	18
2.9	12-6 Lennard-Jones potential energy function	20
2.10	Comparison of modified Buckingham and 12-6 Lennard-Jones potential energy function	22
2.11	Coulomb potential function	22
2.12	Ion-induced dipole potential function	23
2.13	Quadrupole-ion potential energy function for nitrogen	24
2.14	Bond potential example	25
2.15	Example molecule for proper dihedral angles	25
2.16	Example molecule for improper dihedrals	26
3.1	Schematic of DT-IMS device	30
3.2	Exemplary α -curves	31
3.3	Collision cross section	32
3.4	Two dimensional collision in HS	34
3.5	VHS diameter dependence on collisional energy	35
4.1	Scheme of ESI capillary	40
4.2	Droplet fragment spectra for two solvent systems in a quadrupole ion trap system	43
4.3	Oscillogram of ion burst signal	43
4.4	Scheme of ion source and simplified transfer stage of an ESI mass spectrometer system	45

4.5	Low-energy CID fragmentation pathways	46
4.6	SID fragmentation pathways	46
5.1	Graphical user interface of Avogadro	51
5.2	Graphical user interface of Ovito	52
6.1	MD collision model integration	57
6.2	Two dimensional initialization of MD collision	59
6.3	Head-on collision velocity example for vdW potential	65
6.4	Integrator residuals with van der Waals interaction	65
6.5	Head-on collision velocity example for II potential	66
6.6	Integrator residuals with van der Waals and ion-induced interaction	67
6.7	Wall times of benchmark application for varying integrators	68
6.8	Example MD collisions at 10 Td	71
6.9	Example MD collisions at 10 Td for two different background gases	72
6.10	Example MD collisions at 70 Td for two different background gases	72
6.11	Closest distances for MD example trajectories for different electric fields	73
6.12	Drift velocity at varying electric fields for example IMS simulations	74
6.13	Scaling parameter variation for O_2^+ in He	75
6.14	Scaling parameter variation for O_2^+ in Ar	76
6.15	Collision diameter variation in IMS simulation	77
6.16	Pressure variation for IMS simulation for He gas	78
6.17	Pressure variation for IMS simulation with smaller time step for He gas	79
6.18	Comparison of pressure dependence for varied time steps with different background gas	80
6.19	Temperature variation for IMS simulation for He gas	80
6.20	Collision velocity and mean-free-path distribution at 7 Td for O_2^+ in helium	81
6.21	Simulated closest distance in dependence of the predicted geometric closest distance for O_2^+ in He at 100 K	82
6.22	Simulated closest distance in dependence of the predicted geometric closest distance for O_2^+ in He at 400 K	82
6.23	Histogram of simulated closest distance in dependence of the predicted geometric closest distance for O_2^+ in He at 100 K	83
6.24	Histogram of simulated closest distance in dependence of the predicted geometric closest distance for O_2^+ in He at 400 K	84
6.25	Ion mobilities for different temperatures for CO^+ in helium	85
6.26	Ion mobilities in dependence of vdW parameters for O_2^+ in helium	86
6.27	Abs. differences in mobilities to experimental values at 10 and 70 Td for O_2^+ in helium	87
6.28	Combined abs. differences for 10 and 70 Td for O_2^+ in helium	88

6.29	Predicted ion mobilities for various ions in helium compared to literature mobilities	89
6.30	Predicted ion mobilities for various ions in argon compared to literature mobilities	90
6.31	Ion mobilities for Ar^+ in Ar with resonant charge transfer	91
6.32	Optimized structure of EtO	93
6.33	Comparison of ion mobilities between IDSimF, MobCal-MPI and experimental for EtO in helium	93
6.34	Speedup of benchmark simulation	95
6.35	Speedup of benchmark simulation with different scheduling types and sample / particle counts	96
6.36	Strong scaling of IMS simulation	98
6.37	Variants for computation of ion-induced dipole moment for molecular nitrogen	99
6.38	Numerical evaluation of force components for a lithium ion in nitrogen	101
6.39	Orbiting and detaching collisions with molecular nitrogen	103
6.40	Comparison of force and force residual between IDSimF and MobCal-MPI for an exemplary collision with only vdW interactions	104
6.41	Comparison of force and force residual between IDSimF and MobCal-MPI for an exemplary collision with only II interactions	105
6.42	Comparison of force and force residual between IDSimF and MobCal-MPI for an exemplary collision with only ion-quadrupole interactions	106
6.43	Comparison of force and force residual between IDSimF and MobCal-MPI for an exemplary collision with all force components active with only y -components	107
6.44	Comparison of force and force residual between IDSimF and MobCal-MPI for an exemplary collision with all force components active with x - and y -components	108
6.45	Comparison of position, velocity and force differences between MobCal-MPI and IDSimF for the same trajectories	109
6.46	Comparison of position, velocity and force differences between MobCal-MPI and IDSimF for the same trajectories in dependence of relative starting velocity	110
6.47	Ion mobility dependence on the two modes for ion-induced dipole moment calculation	111
6.48	Ion mobility dependence on the vdW force function	113
6.49	Ion mobility dependence on ion-induced dipole mode with mod. Buckingham as vdW function	113
6.50	Ion mobility dependence on the ion-quadrupole moment with 12-6 LJ as vdW function	114
6.51	Predicted ion mobilities for Li^+ in molecular nitrogen	116
6.52	Predicted ion mobilities for Na^+ in molecular nitrogen	117

6.53	Predicted ion mobilities for varying force field parameters for Cl^- in molecular nitrogen	118
6.54	Best matching simulated ion mobilities for Cl^- in N_2 in comparison to literature mobilities	119
6.55	Ion mobility comparison for prot. acetone and its carbon isotope in N_2 with MobCal-MPI, IDSimF and experimental values	120
6.56	Scheme of MD collision integration considering rigid body rotation	124
6.57	Trajectory snapshots of O_2^+ in N_2 with active rotations	126
6.58	Trajectory snapshots of AcH^+ in N_2 with active rotations	127
6.59	Ion mobility comparison with / without rotations for O_2^+ in He	128
6.60	Ion mobility comparison with / without rotations for Li^+ in N_2	129
6.61	Orbiting trajectories of the AcH^+ / N_2 system	130
6.62	VHS/BL simulation run for O_2^+ in O_2 with standard parameters	139
6.63	VHS/BL simulation run for O_2^+ in O_2 with mod. parameters	140
6.64	Ion mobility comparison between HS, VHS and MD for Li^+ in molecular nitrogen	141
6.65	Comparison of ion mobilities for various systems between HS, VHS and MD collision models	142
7.1	Average kinetic energies of the droplet halves	146
7.2	Summed kinetic energy of the model ESI droplet over six MD impacts . . .	147
7.3	Summed collision energy of an ensemble of model ESI droplets	148
7.4	Model ESI droplet before relaxation	148
7.5	Software tool-chain scheme for the preparation process of MD ESI droplets	149
7.6	Simulation system set-up of a SID event	151
7.7	Cross-section of the aluminum wall	151
7.8	Small model ESI droplet	153
7.9	Kinetic energy evolution of the droplet in a SID simulation	154
7.10	Visualization of frontal collision of the droplet with the aluminum wall for different voltages	155
7.11	Average number of observed cluster after the frontal collision of the small droplet with the aluminum wall for varying voltages	155
7.12	Composition of ejected clusters from small ESI droplet	156
7.13	Composition of an exemplary ejected charged cluster	157
7.14	Splatter pattern of the ESI droplet molecules on the aluminum wall	158
7.15	Visualization of slanted wall collisions of the droplet with the aluminum wall for varying angles	159
7.16	Visualization of slanted wall collisions of the droplet with the aluminum wall for varying angles	160
7.17	Kinetic energy evolution of the droplet in a slanted wall collision	161
7.18	ESI droplet impact comparison for angled walls	161

7.19	ESI droplet surface contact area comparison for angled walls	162
7.20	Composition of ejected clusters from small ESI droplet in slanted collision and comparison to frontal impact	163
7.21	Comparison of small and large ESI model droplet	164
7.22	Average number of observed cluster after the frontal collision of the large droplet with the aluminum wall for varying voltages	164
7.23	Kinetic energy evolution of the large droplet for 10 and 100 V	165
7.24	Composition of ejected clusters from large ESI droplet in frontal collisions for 50 and 100 V	165
7.25	Comparison of the two tested potential functions of the aluminum atoms in OPLS-AA	167
7.26	Comparison of the temporal ejected cluster evolution for both potential functions at 100 V	168
7.27	Cluster composition and occurrence comparison between the high interaction potential and standard potential by Heinz et al. at 100 V	168
7.28	SID modeling approach for SIMION	169
7.29	Comparison of ion trajectories in an exemplary collision cell at 940 kHz RF frequency with varied acceleration voltages in SIMION	172
7.30	Comparison of ion trajectories in an exemplary collision cell at 1.23 MHz RF frequency with varied acceleration voltages in SIMION	173
C.1	Reduced ion mobilities obtained in dependence of the electric field strength for varying 12-6 Lennard-Jones parameters σ and ϵ for O_2^+ in argon	211
C.2	Comparison of force and force residual in all three spatial directions between IDSimF and MobCal-MPI for one exemplary collision constructed by MobCal-MPI with all force field components	212

LISTINGS

5.1	LAMMPS input file example	48
6.1	RS configuration file example	62
6.2	MD force field configuration file example	63
6.3	Pseudo implementation code for the VHS collision cross section	132
6.4	Pseudo implementation code for internal energy initialization	133
6.5	Pseudo implementation code for transfer between translational and internal mode	133
6.6	Pseudo implementation code for transfer between two rotational modes	135
D.1	Example input script for PACKMOL	213
D.2	Example input script for moltemplate	213
D.3	SID model LAMMPS input	214

BACKGROUND

Electrospray ionization (ESI) is one of the most important ionization methods in molecular mass spectrometry (MS) [2]. A mass spectrometer is essentially any instrument, which allows the separation of particles based on their mass-to-charge (m/z) ratio to record a *mass spectrum*, which is the abundance of a m/z ratio in a sample.

In ESI-MS, a charged solution of the substance of interest (the *analyte*) is sprayed into an electric field which creates charged liquid droplets. These droplets contain the analyte and a large number of solvent molecules. Due to complex charge separation processes and electrochemical interactions in the ion source, the dynamics of the solvent/analyte droplets generated by the electrospray emitter are largely unexplained. Experiments have shown that the lifetimes of ESI droplets are much longer than typically anticipated in the ESI-MS literature. Thus, droplets can traverse the ion source stage and reach the high vacuum system and even the detector region of an MS instrument [3, 4]. This leads to adverse operational effects in the instrument like contamination of instrument parts, increased signal-to-noise ratio and complex chemical interferences in the mass spectrum. Ion trajectory as well as molecular dynamics (MD) simulations are two commonly employed simulation methods to study ion dynamics in a wide array of instruments and under varying external conditions. MD simulations are especially suitable for studies of internal dynamics of large molecular aggregates, where a wide variety of potential interactions between individual atoms as well as long-range interactions are of high importance. Due to the resolution of classical atomistic MD methods, the simulations are severely limited in terms of the size of the modeled system. Entire ion traversals through transfer stages or multipole assemblies in an actual MS instrument are not possible to be computed with such MD methods. This limitation gives rise to dedicated ion trajectory simulation methods, where larger aggregates are simplified to one monolithic particle, which then interact with their surroundings by more simplified models trying to approximate the results of MD level interaction modeling.

To improve instrument design and to gain a more fundamental understanding of droplet dynamics in ESI-MS instruments, a complete numerical / simulation model of the droplet traversal from ion source to the detector is necessary. As a result of the different time and

length scales, this becomes a multi-scale problem, requiring the use of multiple different simulation approaches and models.

In an effort to close the knowledge gaps in regard to the droplet dynamics, this work aims to implement and develop new methods as well as first simulation models for different processes taking place in ESI-MS instruments. Thereby, this work is split into two main areas of research. Two of the main ways in which droplets can interact within / with the instruments are by ion-neutral collisions (collision-induced dissociation) or surface impacts with electrodes (surface-induced dissociation).

The first part of this work thus revolves around the development and validation of an MD based collision approach to more accurately model the collisions between medium to smaller sized droplet aggregates and bare molecular ions with neutral gas particles, especially in collisions cells and other collision-dominated regions of mass spectrometers. The collision model is then used in combination with ion trajectory simulations, with a primary focus on the simulation of ion mobility spectrometers (IMS) as a first benchmark. Ion mobility simulations are particularly useful as a benchmark system, as the ion mobility requires very accurate simulation of ion dynamics primarily dependent on the mentioned ion-neutral collisions. In addition to the MD based collision model, a variable hard-sphere (VHS) collision model with internal energy tracking is also implemented. This is a first step to later combine the MD based collision model with internal energy tracking, as this allows to still include an approximation of the internal energy state even if no complete MD simulations can be used.

The second part of this work focuses on the establishment of an MD simulation system for SID events between larger ESI droplets and idealized surfaces. Especially in mass spectrometers with multiple transfer stages, where the background gas pressure is low, the droplets primarily interact with electrodes, lenses or other orifices. Since energetic surface collisions of highly charged ESI droplets are very complex and largely unknown molecular events, MD simulations are especially suitable in those regimens. Further, combinations of the SID and CID processes are likely to be possible in transitions zones in the instruments. As such, also an ion trajectory simulation based SID model was developed and used for a first simulation of an exemplary collision cell.

In total, various methods could be established and applied to simulations of ESI droplets and related processes, facilitating more complex combinations of all described models / methods in simulations of ESI droplet dynamics in major parts of typical MS instruments.

INTRODUCTION TO MOLECULAR DYNAMICS SIMULATIONS

MD is a numerical molecular modeling method in which the movement of a particle ensemble is described over a given temporal evolution. The movement alteration is calculated iteratively and the particle interactions are defined by classical potential functions, so called *force fields* (classical MD). Common areas of research in which MD simulations are applied include materials science and (bio-)physics. In cases where the concrete dynamics of a molecular system cannot be observed directly, e.g. thin film growth, numerical simulations are often carried out by use of MD. Also, molecular structure predictions and drug design are aided by molecular dynamics modelling.

2.1 Underlying principles

In its core a molecular dynamics simulation is a stochastic numerical method. MD creates stochastic paths sampled from thermodynamic particle ensembles (see section 2.3) to determine a valid prediction of configurations of a particle system in a fixed amount of time. The system itself is defined by a bounding simulation box with appropriate boundary conditions (see section 2.4) and the ensemble of particles, i.e. atoms or molecules. Figure 2.1 shows a simple three dimensional MD simulation system of a NaCl crystal lattice visualized by Ovito [5] (left panel: 3D perspective view, right panel: top view). The boundary is given by the black lines. The simulated particle ensemble consists of two types of atoms, potassium and chlorine, in interaction with each other. An additional molecular dynamics example of a two dimensional atomistic flow around two obstacles is given in Figure 2.2.

After the initial system set-up has been carried out and the boundary conditions are chosen, a MD simulation solves Newton's equation of motion for the particles to obtain their trajectories. The differential equations to be solved for an N particle system are

$$\begin{aligned} F(X) &= -\Delta U(R) = MA = M\dot{V}(t) \\ V(t) &= \dot{R}(t) \quad . \end{aligned} \tag{2.1}$$

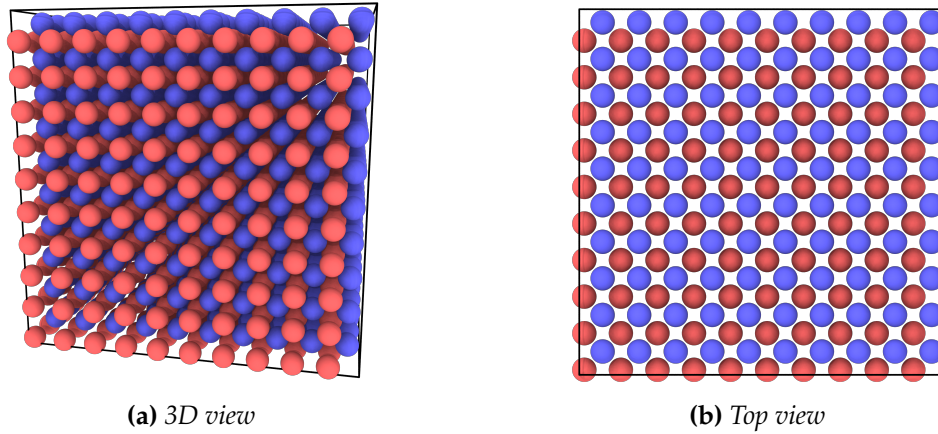


Figure 2.1: MD simulation system of a 3D NaCl lattice. The simulation boundary is given by the black lines. Since this is an atomistic set-up, the two different colored elements represent the two different atoms Na and Cl.

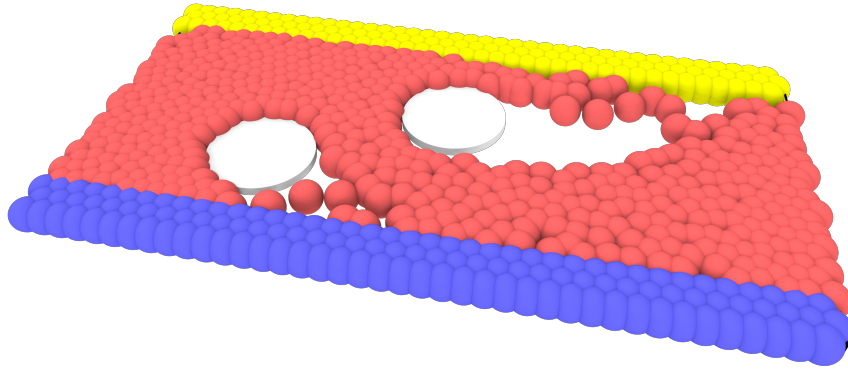


Figure 2.2: Atomistic flow MD simulation in two dimensions. The red particles are guided in a channel by the blue/yellow particles. Two obstacles (white circles) lie in the flow path, disrupting the normal red particle flow.

F is the force acting on each particle in dependency of the particle positions R . The force is the negative gradient of the potential energy function U , also as a function of R . This potential energy function is referred to as *force field*. Based on Newton's second law, the force equates to the masses M of the particles multiplied by their accelerations A which are the derivatives of the time-dependent velocities V . In turn, the velocities can be obtained by the derivative of the positions R . Through recurring calculation of an updated force, the particle positions R and the velocities V can be calculated iteratively in every time step of the simulation by a numerical integrator.

Figure 2.3 illustrates a simplified molecular dynamics algorithm with all necessary steps. The updating of positions and velocities can be repeated as long as required, generating the entire trajectories of the particles.

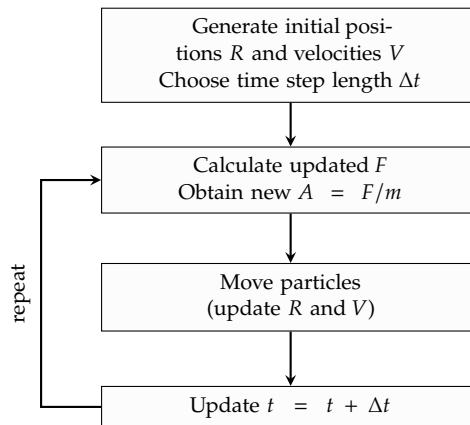


Figure 2.3: Simplified sequence of the standard MD algorithm.

2.2 Numerical integration

Approximate solutions to ordinary differential equations (ODE) and partial differential equations (PDE), which cannot be solved analytically, can be obtained by numerical integration methods. A general first-order ordinary differential equation given as an initial value problem (IVP) is denoted as follows [6, p. 24]:

$$y'(t) = f(t, y(t)) \quad \text{with} \quad y(t_0) = y_0 \quad (2.2)$$

and $f : [t_0, \infty) \times \mathbb{R} \rightarrow \mathbb{R}^d$ and $y_0 \in \mathbb{R}^d$.

Ordinary differential equations describe the rate of change of given quantities, e.g. the velocities of particles. The order of an ordinary differential equation is determined by the degree of the highest derivative. In the case of an ODE of higher order, it is first necessary to transform the equation into a system of first-order equations, in order to apply common methods to generate a solution [7, p. 221].

Equation 2.1 represents such a first-order system that is generated from Newton's equation of motion

$$\mathbf{F} = m \cdot \frac{d^2 \mathbf{r}}{dt^2} \quad (2.3)$$

Several different methods for solving of first-order systems exist. Not all of these methods are suitable in the context of molecular dynamics modelling.

The following sections give an overview of numerical constraints in MD, relevant mathematical concepts, and several different integrator methods.

2.2.1 Numerical requirements for molecular dynamics simulations

Molecular dynamics simulations can become quite complex and numerically expensive. There are various integrator method parameters and further system properties that have a significant impact on the simulation efficiency and accuracy. Most important is an appropriate choice of the *total simulation time*, *time step* and *simulation size* (i.e. number of particles) to accurately represent the modeled temporal dynamics of the studied process.

In molecular dynamics modelling, the total simulation time can vary strongly: some systems studied with MD only require a few hundred picoseconds, e.g. collisional activation of small molecules, while other processes can necessitate simulation times in ranges of nanoseconds to microseconds (e.g. MD modelling of DNA confinement [8]). The total time that can be simulated is thus a careful balancing of available compute power and necessary simulation time to reproduce the dynamics of the studied process.

The time step length also determines the numerical cost of a specific simulation. The force evaluation of the integrator is called more often with smaller time steps. How long each time step takes depends on the chosen integration method, as the integration methods vary in how often the force has to be re-calculated per time step. Overall, the force evaluation is the most costly part of the integration procedure and should be done as little as possible. However, based on the nature of the systems to be simulated, very small time steps have to be chosen to avoid discretization errors of the underlying dynamics. In molecular dynamics simulations with classical dynamics, typical time steps are about 1 femtosecond long.

There are two further properties of differential equations resp. their integration methods that have an impact on how large the time steps can be chosen: I) symplecticity and II) stiffness.

2.2.1.1 Symplecticity

It is often not required to obtain the most accurate single trajectories of the particles in MD simulations. Instead, interest lies in an efficient and statistically accurate sampling of thermodynamic ensembles.

Therefore, symplectic integrators are generally preferred over non-symplectic schemes. A symplectic integrator is volume-preserving [9, p. 184–185, p. 227]: it computes a perturbed trajectory, which lies on a symplectic manifold¹, while the exact solution to the symplectic system lies on a non-perturbed trajectory on the symplectic manifold [9, p. 184–185, p. 240–242], as is pictured in figure 2.4. The resulting drift of non-symplectic methods is therefore much higher and these methods tend to have difficulty with long-term integration of symplectic systems.

A common symplectic problem is the pendulum equation. The pendulum equation can be expressed through a Hamiltonian system

$$H = \frac{p^2}{2m\ell^2} + mg\ell(1 - \cos \theta) \quad , \quad (2.4)$$

which naturally is symplectic. To show the effects of non-symplectic as well as symplectic integrators, phase-space solutions and the energies of the pendulum system are computed

¹A manifold is a space which is locally described by an Euclidean space or in less abstract terms: a manifold of a specific dimension can be viewed as a reduced Euclidean space, e.g. an infinitesimal part of a 2D sphere is actually a 2D Euclidean plane. Now, a symplectic manifold is a manifold which holds the symplectic form (it is volume-preserving). This can be simplified to the following statement: a symplectic manifold is a generalized phase space of a system.

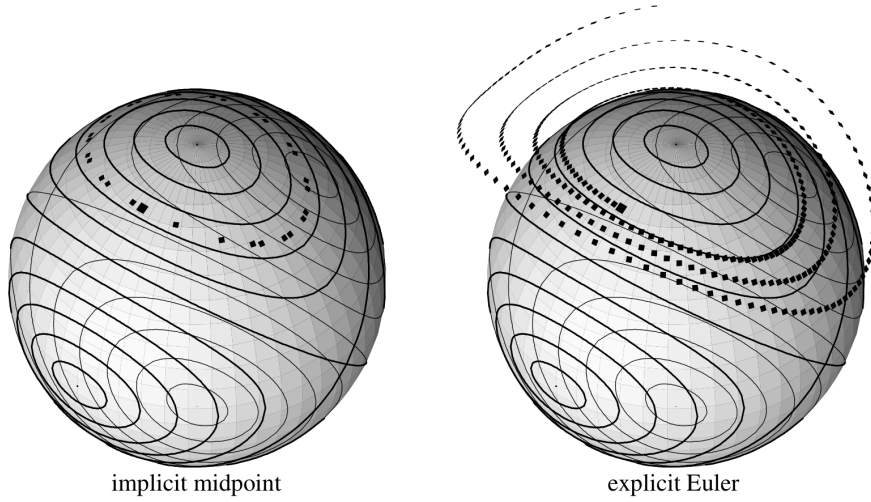


Figure 2.4: Solution trajectories for a symplectic (implicit midpoint, left side) and a non-symplectic (explicit Euler, right side) method. The solid black closed curves show the correct analytical solution. The symplectic method generates perturbed curves lying on the manifold. The non-symplectic method exhibits significant drift of the numerical solution, as it does not lie on the manifold. Reproduced from [9, p. 100] with permission.

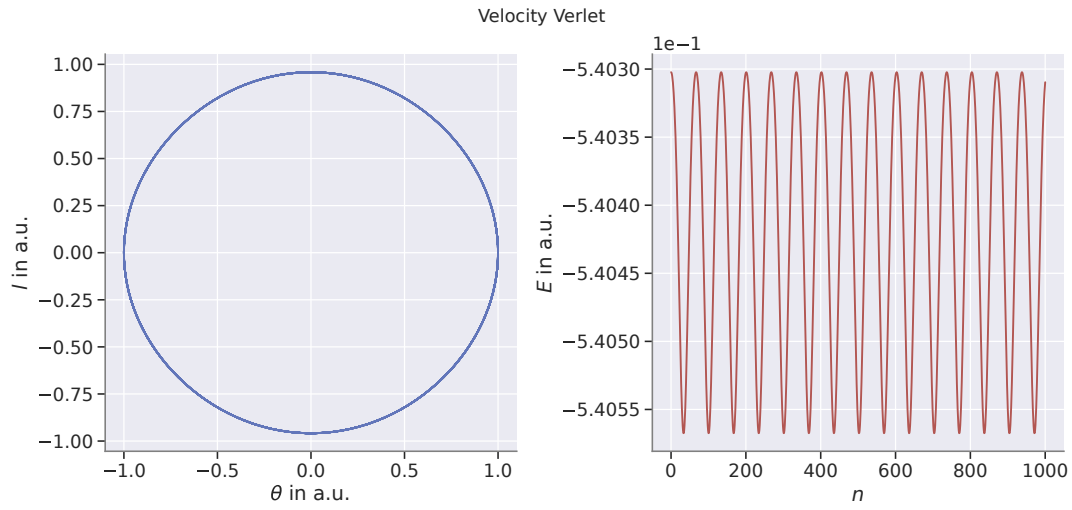
by three different methods. The correct ("true") Hamiltonian solution is constant in energy and has no drift in the phase-space orbit. Figure 2.5 illustrates the phase-space solution as well as the energy of an exemplary pendulum system integrated by (a) velocity Verlet, (b) explicit Euler and, (c) Runge-Kutta (RK) 45 for 50 time units.

The velocity Verlet method, which is symplectic, exhibits essentially no drift of the phase-space because it is simply a perturbed trajectory on the manifold. Consequentially, the energy is almost constant with periodic movements. The non-symplectic explicit Euler method instead shows a strong drift of the phase-space and significant energy gain. It becomes apparent that long-term integration of Hamiltonian systems are more accurate with use of a symplectic method.

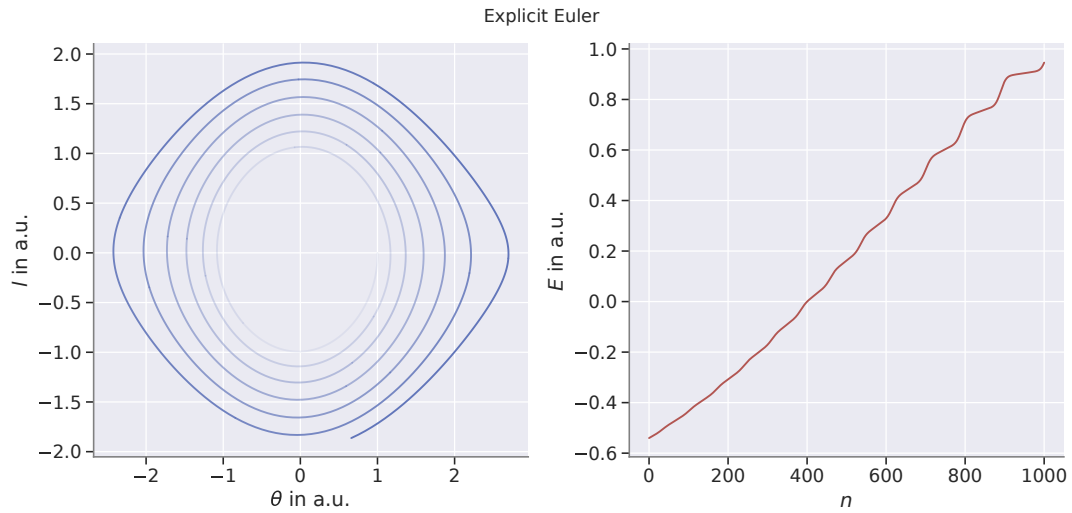
While symplectic methods are more suitable for Hamiltonian systems, there are also non-symplectic integrators which can give good results. The Runge-Kutta 45 method shows a relatively stable phase-space evolution even though a slight energy drift is observable. More importantly, the RK45 method requires much fewer integration steps (around 50 instead of 1000) for acceptable results because of non-constant time steps².

Overall, the exact performance of different integrators is dependent on the actually studied system and its constraints. For computational efficiency reasons it often is more suitable to choose a higher order adaptive method instead of a low order symplectic method. More details on specific integration methods are given in subsection 2.2.2 to subsection 2.2.6 with a focus on symplectic as well as adaptive step methods.

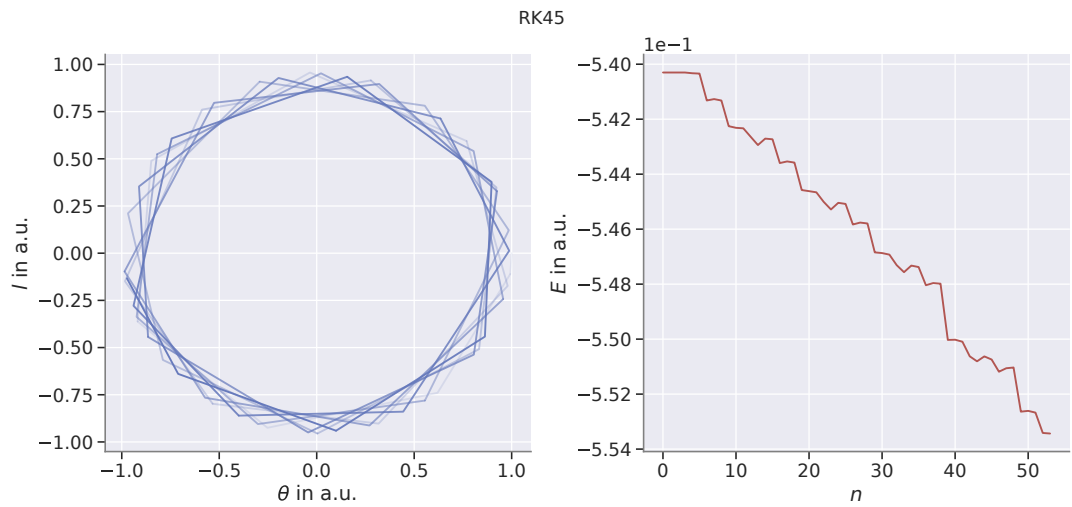
²Most symplectic methods cannot use non-constant time steps, as the symplectic property would otherwise be lost or other instabilities arise [10].



(a) Velocity Verlet method



(b) explicit Euler method



(c) RK45 method from SciPy

Figure 2.5: Phase-space solution of the simple pendulum ordinary differential equation (left). Earlier time steps are shown with reduced transparency. The energy evolution over the time steps n of the system is given in the right panel.

As already mentioned, to profit from symplectic integrators it is necessary for the MD system to also be symplectic, i.e. a Hamiltonian for this system exists.

Both the MD study of surface collisions (see chapter 7) and ion-neutral collisions (see chapter 6) use Newton's equations of motion (cf. Equation 2.1). It can be shown that the equations of motion are symplectic if the potential energy function is only position dependent and not also time dependent.

The Lagrangian equation of motion with generalized coordinates $\mathbf{q}_i$ is [7, p. 270]

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{\mathbf{q}}_i} \right) - \frac{\partial L}{\partial \mathbf{q}_i} = 0 \quad , \quad (2.5)$$

with $L = T - U$, where T is the kinetic energy and U the potential energy [9, p. 181]. In cartesian coordinates $\mathbf{r}_i$, the kinetic energy is given by [11, p. 10]

$$T = \frac{1}{2} \sum_i m_i \dot{\mathbf{r}}_i^2 \quad (2.6)$$

and the forces $\mathbf{F}_i$ are given by [11, p. 19]

$$\mathbf{F}_i = \nabla_{\mathbf{r}_i} L = \nabla_{\mathbf{r}_i} (T - U) \quad . \quad (2.7)$$

Newton's equations of motion are then obtained from the Lagrangian representation [11, p. 11]

$$m_i \ddot{\mathbf{r}}_i - \mathbf{F}_i = 0 \quad . \quad (2.8)$$

The Hamiltonian of a system is $H = \sum_i \mathbf{q}_i \mathbf{p}_i - L$ [11, p. 161] with p_i as generalized momenta and the canonical form of Hamiltonian equations of motion are

$$\begin{aligned} \dot{\mathbf{q}}_i &= \frac{\partial H}{\partial \mathbf{p}_i} \\ \dot{\mathbf{p}}_i &= - \frac{\partial H}{\partial \mathbf{q}_i} \quad . \end{aligned} \quad (2.9)$$

Transforming this back into cartesian coordinates

$$\begin{aligned} \dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m_i} \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i \quad , \end{aligned} \quad (2.10)$$

Newton's equations of motion are restored [9, p. 182][7, p. 271], providing a valid Hamiltonian description of the system, i.e. it is symplectic.

2.2.1.2 Stiff equations

Stiff equations pose a problem for numerical integration, as some numerical methods become unstable when applied to such equations. A rigorous, exact mathematical definition of *stiffness* is not possible, however stiffness occurs if a sought solution (i.e. a specific initial value problem) to a system is slowly varying (the solution curve is flat) while further

solutions in the neighborhood (i.e. other initial values producing solution curves close to the sought initial value) are rapidly varying [12]. If this is the case, the step size has to be very small to obtain good solutions [12]. Common explicit numerical solvers often fail at reliably integrating stiff systems and many integration methods for solving of stiff equations have thus been invented [12–14].

An IVP showing stiff behavior is

$$y'(t) = -15 \cdot y(t), \quad y(0) = 1 \quad , \quad (2.11)$$

with the exact solution $y(t) = e^{-15t}$.

Figure 2.6 illustrates the effect of stiffness for Equation 2.11 on the explicit Euler method. Both explicit Euler solutions with step size $h = \frac{1}{4}$ and $h = \frac{1}{8}$ show oscillating solutions. With a smaller step size the solution is fluctuating around the analytical solution, while the bigger step size solution becomes completely unstable. Implicit methods³ are the most common method to solve stiff equations [12–14], one of which is the trapezoidal method. The trapezoidal method is indeed able to compute a good approximation to the exact solution with the same time step length as the unstable explicit Euler.

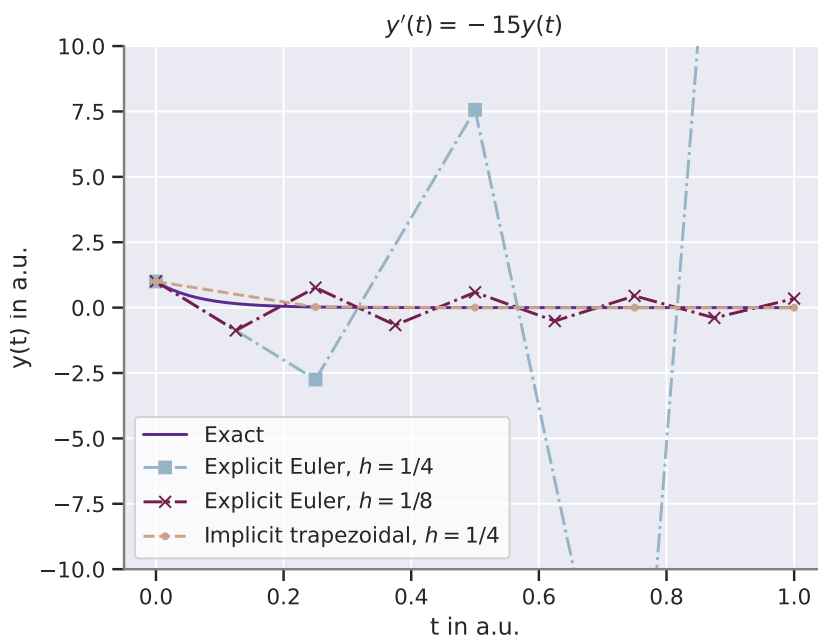


Figure 2.6: Exact solution and numerical solutions of the explicit Euler and the trapezoidal method for $y'(t) = -15y(t)$. The stiffness of the system becomes apparent by the unstable integration behavior of the explicit Euler method.

Typical stiff problems include kinetics and chemical reaction systems with at least one fast changing component. Additionally, interatomic forces can pose stiff problems and resulting instabilities or step size constraints need to be considered for MD systems. It

³Implicit methods find a solution by solving an ODE or PDE involving both the current and future system states.

often becomes less efficient to use adaptive step size methods over symplectic methods due to such step size constraints, as the possible proportional step size increase is lost.

Conclusion

Symplecticity and stiffness both have a high impact on which numerical integration method is suitable given the step size constraints. Subtle differences in sought solutions and underlying differential equations can quickly warrant for integration with a different method to guarantee *stability*, *accuracy* and *efficiency*. The following sections therefore give a short overview of standard algorithms and more sophisticated methods, which are implemented in the software described in chapter 5.

2.2.2 Explicit Euler

The explicit Euler method constitutes the most elementary integration technique, which can be utilized to integrate ordinary differential equations. Taylor expansion of a function y around x_0 yields the following equation for the approximate value at a place $x_0 + h$:

$$y(x_0 + h) = y(x_0) + h \cdot y'(x_0) + \frac{1}{2}h^2 \cdot y''(x_0) + O(h^3) \quad . \quad (2.12)$$

The Euler method is then produced by dropping the terms of order two and higher [7, p. 222]:

$$y(x_0 + h) = y(x_0) + h \cdot f(x_0) \quad (2.13)$$

Truncation errors accrued by an integration method give a bound on the possible accuracy of the method. Two types of truncation errors exist - local and global [7, p. 225]. The local error refers to the error made in one step of the integration scheme and is of order two here⁴, while the global error is the error made over all steps of the integration. Thus, for a total integration time of T and a step size of h , the global error is given by $T/h \cdot O(h^2) = O(h)$ for the explicit Euler method [7, p. 225].

The solution to a system with Newton's equations of motion can be obtained by

$$\begin{aligned} \mathbf{v}_i(t + \Delta t) &= \mathbf{v}_i(t) + \Delta t \cdot \frac{\sum_j \mathbf{F}_{ji}(\mathbf{r}_i(t))}{m_i} \\ \mathbf{r}_i(t + \Delta t) &= \mathbf{r}_i(t) + \Delta t \cdot \mathbf{v}_i(t) \quad , \end{aligned} \quad (2.14)$$

where the forces F_{ji} over all interactions between the monitored particle i and all other particles j need to be calculated and summed.

2.2.3 Leapfrog

The leapfrog method is a numerical integration scheme for ordinary differential equations of the form

$$\frac{d^2 \mathbf{r}}{dt^2} = \mathbf{F}(\mathbf{r}).$$

⁴Since the Taylor expansion is stopped after the first term.

The global error of this method is of order two. Additionally, the method is symplectic and can conserve the Hamiltonian of a system. The leapfrog method calculates the position and velocity alternately at different time steps, which are displaced by $1/2$ ("leap").

For Newton's equations of motion the update formulas are given by [15, p. 45]

$$\begin{aligned} \mathbf{v}_i(t + \frac{1}{2}\Delta t) &= \mathbf{v}_i(t - \frac{1}{2}\Delta t) + \Delta t \cdot \frac{\sum_j \mathbf{F}_{ji}(\mathbf{r}_i(t))}{m_i} \\ \mathbf{r}_i(t + \Delta t) &= \mathbf{r}_i(t) + \Delta t \cdot \mathbf{v}_i(t + \frac{1}{2}\Delta t) \end{aligned} \quad (2.15)$$

Since the velocity and position are not computed for the same time, an interpolation can be carried out to generate fitting velocity/position pairs [15].

2.2.4 Velocity Verlet

In contrast to the Leapfrog method, the velocity Verlet method allows to directly compute position and velocity for the same time step, while also providing an order two global error and symplecticity [15]. Newton's equation of motion can be solved in this scheme by [16]

$$\begin{aligned} \mathbf{r}_i(t + \Delta t) &= \mathbf{r}_i(t) + \Delta t \cdot \mathbf{v}_i(t) + \frac{1}{2}\Delta t^2 \cdot \frac{\sum_j \mathbf{F}_{ji}(\mathbf{r}_i(t))}{m_i} \\ \mathbf{v}_i(t + \Delta t) &= \mathbf{v}_i(t) + \frac{1}{2}\Delta t \left(\frac{\sum_j \mathbf{F}_{ji}(\mathbf{r}_i(t + \Delta t))}{m_i} + \frac{\sum_j \mathbf{F}_{ji}(\mathbf{r}_i(t))}{m_i} \right) \end{aligned} \quad (2.16)$$

2.2.5 Runge-Kutta methods

General s -stage Runge-Kutta methods (RK) are a class of algorithms with global errors of $O(h^s)$ [7, p. 231]. The general integration formula is derived from a combination of Taylor expansions and is defined as [9, p. 29]

$$\begin{aligned} y(t + h) &= y(t) + h \sum_{i=1}^s b_i k_i \\ k_i &= f(t + hc_i, y(t) + \sum_{j=1}^s a_{ij} k_j) \end{aligned} \quad (2.17)$$

with weights b_i , c_i and a_{ij} characteristic to the chosen specific method and most often arranged in a corresponding Butcher tableau [9, p. 29], as seen below:

c_1	a_{11}	a_{12}	$\dots$	a_{1s}
c_2	a_{21}	a_{22}	$\dots$	a_{2s}
$\vdots$	$\vdots$	$\vdots$	$\ddots$	$\vdots$
c_s	a_{s1}	a_{s2}	$\dots$	a_{ss}
	b_1	b_2	$\dots$	b_s

The explicit Euler method as discussed earlier in sec. 2.2.2 is also a Runge-Kutta method with the Butcher tableau

$$\begin{array}{c|c} 0 & 0 \\ \hline & 1 \end{array}$$

2.2.5.1 Runge-Kutta 4

One member of the Runge-Kutta family is the popular Runge-Kutta 4 (RK4), which is often imprecisely called *the* Runge-Kutta method. This is a method with a fourth order global truncation error and no symplecticity. The coefficients of the method are [9, p. 30][7, p. 237]:

$$\begin{array}{c|cccc} 0 & & & & \\ 1/2 & 1/2 & & & \\ 1/2 & 0 & 1/2 & & \\ 1 & 0 & 0 & 1 & \\ \hline & 1/6 & 1/3 & 1/3 & 1/6 \end{array}$$

2.2.5.2 Runge-Kutta-Fehlberg

In the absence of any information regarding an estimate of the "exact" local truncation error to the desired solution when employing a straightforward s -stage RK method, the construction of so called *embedded* RK methods is a viable solution. Construction of an embedded method requires two RK methods, where the b_i coefficients belong to a method of order P while the b_i^* coefficients are of an order $P + 1$ method. The resulting error e_{t+1} can be determined by:

$$e_{t+1} = y_{t+1} - y_{t+1}^* = h \sum_{i=1}^s (b_i - b_i^*) k_i, \text{ with } y_{t+1}^* = y(t) + h \sum_{i=1}^s b_i^* k_i \quad (2.18)$$

and the following Butcher tableau

$$\begin{array}{c|cccc} c_1 & a_{11} & a_{12} & \dots & a_{1s} \\ c_2 & a_{21} & a_{22} & \dots & a_{2s} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ c_s & a_{s1} & a_{s2} & \dots & a_{ss} \\ \hline & b_1 & b_2 & \dots & b_s \\ & b_1^* & b_2^* & \dots & b_s^* \end{array}$$

The calculated error gives a bound on the accuracy of the approximated solution. If the error is smaller than the desired tolerance, the step size can be increased. If it is exceeded,

the step size is reduced. Consequently, the computational cost in regions where a fine time discretization is not essential (e.g., flat segments of a potential curve) is substantially reduced. The intermediate steps in an embedded method are shared, resulting in a negligible increase in computational cost when calculating the error compared to the higher-order method.

One of those embedded RK methods is the Runge-Kutta-Fehlberg (RKF45) method, which uses a Runge-Kutta method of fourth order to integrate the function and an RK method of fifth order to give an error estimate. The Butcher tableau of this method is [17] [7, p. 245]:

0						
1/4	1/4					
3/8	3/32	9/32				
12/13	1932/2197	-7200/2197	7296/2197			
1	439/216	-8	3680/513	-845/4104		
1/2	-8/27	2	-3544/2565	1859/4104	-11/40	
	16/135	0	6656/12825	28561/56430	-9/50	2/55
	25/216	0	1408/2565	2197/4104	-1/5	0

The maximum relative error estimate over all components δ [7, p. 245] is used to control the step size:

$$\delta = \max_i \left| \frac{e_{i,t+1}}{y_{i,t+1}^*} \right| \quad (2.19)$$

The new step size is then generated by (here: $P = 4$, as the lower order method is of order 4)

$$\Delta t_{\text{new}} = \Delta t_{\text{old}} \cdot \left(\frac{\text{tol}}{\delta} \right)^{\frac{1}{P}} \cdot 0.84 \quad , \quad (2.20)$$

where Δt_{old} is the old step size, tol is the user defined error threshold (*tolerance*) and 0.84 is a security factor, guaranteeing success on the next integration step [7, p. 245].

2.2.6 Predictor-Corrector

Predictor-Corrector schemes are another family of numerical integrators for solving of ODEs. All algorithms in this class are built upon two basic steps [18]:

- Prediction step: extrapolate the next function value based on prior values
- Corrector step: improve on the predicted value by interpolation between the predicted value and an approximate value obtained with another method for the same point

Generally, for the prediction step an explicit method is used, while the corrector step is carried out with an implicit scheme. After the initial prediction step, the correction step can be repeated multiple times up to convergence. This process guarantees the stability and other favorable properties of pure implicit methods [18].

An example of a simple Predictor-Corrector scheme is the combination of the explicit Euler as the predictor method and the trapezoidal method as corrector, called Heun's method (2nd order accurate) [19]. The first predictor step, by the explicit Euler method, is

$$\hat{y}(t + h) = y(t) + h \cdot f(t, y(t)) \quad , \quad (2.21)$$

calculating the initial approximated value $\hat{y}(t + h)$. Then the corrector step is applied by

$$y(t + h) = y(t) + \frac{1}{2}h (f(t, y(t)) + f(t + h, \hat{y}(t + h))) \quad , \quad (2.22)$$

improving the initial guess.

2.3 System ensembles

Based on the physical requirements of the studied MD system (e.g. isolated, possible heat exchange with its surrounding), an ensemble fulfilling particular statistical characteristics has to be used. *Ensemble* thereby refers to a set of systems of particles with equivalent properties, which themselves are in thermodynamic equilibrium [20, p. 31]. Stochastic predictions for the real MD system can be made with ensemble averages (see *ergodicity* [21]).

Depending on which ensembles have to be chosen to represent a physical, real-world system, the modeling of this ensemble might necessitate solving of specialized versions of the equations of motion. Three of the most important types of ensembles are discussed in subsection 2.3.1 up to subsection 2.3.3. The important primary macroscopic variables for these ensembles are

- N : number of particles
- V : volume of the system
- E : energy of the system
- T : temperature of the system
- P : pressure of the system

A symbolic representation of the three discussed ensembles is given in Figure 2.7.

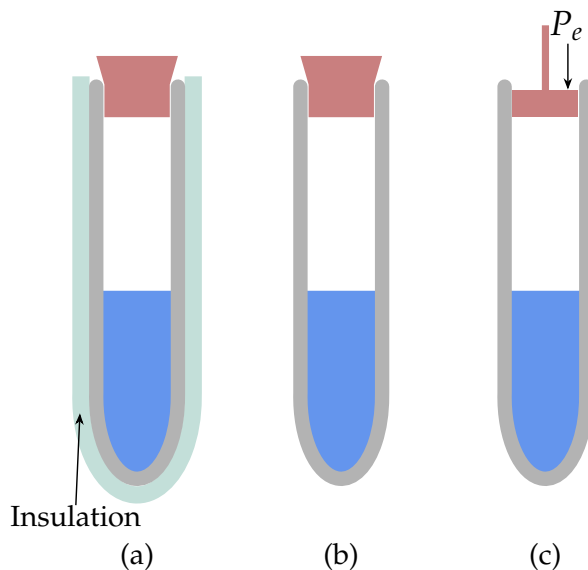


Figure 2.7: Symbolic representation of thermodynamic ensembles. (a) is a microcanonical ensemble, equivalent to a closed test tube completely isolated from its surroundings. (b) is a canonical ensemble represented by a closed test tube. (c) is an isothermal-isobaric ensemble, which can be seen as a test tube where a piston exerts external pressure P_e onto the volume in the test tube.

2.3.1 Microcanonical ensemble

The microcanonical ensemble (NVE) describes a completely isolated system without exchange of any particles N , volume V or energy E with the surrounding environment. In an NVE ensemble the energy thus stays constant. If the NVE ensemble is applicable to a real-world physical problem depends on the relevance of energy fluctuations and the system size. For the microcanonical ensemble no modifications to Equation 2.1 have to be made.

2.3.2 Canonical ensemble

In a system with the canonical ensemble (NVT) the temperature T instead of the energy E stays constant, allowing exchange of energy with a heat bath. Numerically this is realized by introduction of a thermostat function. Commonly known numerical thermostats are developed by Andersen [22] or Nosé and Hoover [23, 24].

The main idea of a thermostat function is to modify the particle velocity distribution within the system by either explicitly scaling the particle velocities according to the desired temperature or by including a friction term in the equation of motion. The modified equations are then

$$\begin{aligned} \dot{\mathbf{r}}_i &= \mathbf{v}_i \\ m_i \dot{\mathbf{v}}_i &= \mathbf{F}_i - \xi m \mathbf{v}_i \end{aligned} \quad (2.23)$$

where ξ is the friction term, which can also be dependent on the time t [15, p. 94–95]. Different types of friction functions can be applied – when the net value of ξ is positive,

energy is taken from the system, while a negative value leads to a deposition of energy. In the case of the Nosé-Hoover thermostat the heat bath is taken as an explicit part of the simulation and a second differential equation for ξ needs to be integrated [15, p. 96]:

$$\frac{d\xi}{dt} = \left(\sum_{i=1}^N m_i \mathbf{v}_i^2 - 3Nk_b T \right) / M \quad , \quad (2.24)$$

with M expressing the coupling of the heat bath to the system. An explicit technique to integrate the Nosé-Hoover thermostat with the velocity Verlet is given in [15, p. 97–98].

2.3.3 Isothermal-isobaric ensemble

The isothermal-isobaric ensemble (NPT) maintains constant temperature T and constant pressure P . It is especially useful for chemical reaction systems as these often have constant pressure or water simulations at ambient conditions [25].

Similar to the thermostat for a NVT ensemble, a barostat is introduced. For example, the Berendsen barostat rescales the positions of the particles to simulate the change in volume [26]. Analogous to the Nosé-Hoover thermostat, the Andersen barostat also couples a modified equation of motion with a second differential equation describing a notional piston with mass Q and an experienced external pressure P_e deforming the volume V . Particle positions and velocities are rescaled beforehand, akin to the Berendsen barostat. A modified differential equation system is inferred [22, 27]

$$\begin{aligned} \mathbf{r}_i &= V^{1/3} \mathbf{s}_i & \mathbf{v}_i &= V^{1/3} \dot{\mathbf{s}}_i \\ \dot{\mathbf{s}}_i &= \frac{\mathbf{F}_i}{m_i V^{1/3}} - \frac{2\dot{\mathbf{s}}_i \dot{V}}{3V} \\ \ddot{V} &= \frac{P - P_e}{Q} \quad . \end{aligned} \quad (2.25)$$

2.4 Boundary conditions

To model a realistic bulk gas/liquid/solid, a small, representative part of the system can be used as the MD system inside a simulation box. The conditions at the boundaries of the simulation box then need to be defined explicitly, providing a way to treat particles getting into contact with any of the boundary sides. Furthermore control of the temperature, pressure and particle density can be exerted by those boundary conditions.

One way to treat the boundaries is by applying so called *fixed* boundary conditions. If a particle would cross a fixed boundary it would normally be removed from the simulation domain. Additionally, shrink-wrapping can be applied. If shrink-wrapped boundaries are used, all particles are always inside the simulation box, i.e. the boundaries are dynamically increased to the lowest possible size to encompass all particles in the simulation. Those types of non-periodic boundaries are essentially a description of an isolated system in "vacuum". Such a simplification can lead to severe simulation artifacts and is often

inappropriate for the actual simulation case. In MD simulations it is thus common to use periodic boundary conditions (PBC).

2.4.1 Periodic boundary conditions

Periodic boundary conditions are used to approximate an "infinite" system through a small *unit cell*. This main cell is surrounded by infinite, translated copies of this cell and all particles also interact with generated copies across the boundaries. Particles that leave through one side of the simulation domain then re-enter on the other end, as illustrated in Figure 2.8.

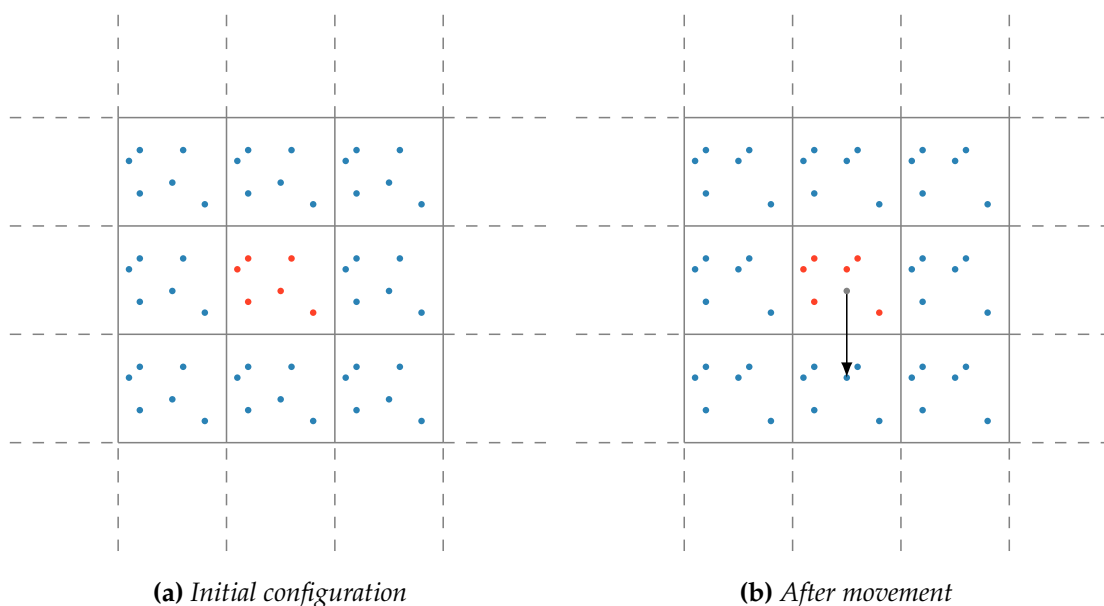


Figure 2.8: Example of periodic boundary conditions. (a) shows the initial configuration of the system, with the box in the center (red dots) as the main image and surrounding boxes as the periodic copies (blue dots). Further images are indicated by the dashed lines. (b) illustrates changes in the images through particle movement. The grey dot (old/initial position) moves to the new position as given by the arrow and enters the main image from "above" due to the periodicity.

However, PBC also introduce specific types of artifacts, which are often less pronounced than with fixed boundaries:

- Simulation of non-zero net charge systems: electrostatic interactions are frequently evaluated with methods of the *Ewald summation* type [28–31], which acts in reciprocal space also called *k*-space. Conventionally, Ewald summations require a vanishing net charge of the system, as the energy of a lattice with charge is infinite in reciprocal space. In actual implementations, charged systems can be calculated by introduction of an implicit background charge distribution neutralizing the net charge [32]. While this allows use of Ewald summation for charged systems, this approximation introduces its own artifacts [32].

- Self-image interaction: in a small simulation box particles may interact with their own copy in a surrounding box, introducing artifacts due to the nonphysical nature of the interactions. The appropriate box size is dependent on the size/interaction of the simulated particles and thus varies for each problem.

2.5 Force fields

To solve Newton's equations of motion as given in Equation 2.1, an evaluation of the forces acting on the particles in the MD simulation are required. The total potential energy is given by interatomic (nonbonded) as well as intramolecular (bonded) potentials

$$U_{\text{tot}} = \underbrace{U_{\text{coul}} + U_{\text{vdW}}}_{U_{\text{nonbonded}}} + \underbrace{U_{\text{bond}} + U_{\text{angle}} + U_{\text{dihedral}} + U_{\text{improper}}}_{U_{\text{bonded}}} \quad , \quad (2.26)$$

where the nonbonded potential energies contain long-range Coulomb U_{coul} and van der Waals U_{vdW} interactions and the bonded potential energies consist of bond (U_{bond}), angle (U_{angle}), dihedral (U_{dihedral}) and improper (U_{improper}) interactions.

The force for atom j can then be obtained by differentiation of the potential energies with respect to atom positions $\mathbf{r}_{ij}$

$$\mathbf{F}_j = -\nabla_{\mathbf{r}_{ij}} U_{\text{tot}} \quad , \quad (2.27)$$

which simplifies to

$$\mathbf{F}_j = -\sum_i \frac{\partial U_{ij}(r_{ij})}{\partial \mathbf{r}_{ij}} = -\sum_i \frac{dU_{ij}(r)}{dr_{ij}} \cdot \frac{\mathbf{r}_{ij}}{r_{ij}} \quad (2.28)$$

for two-body potentials due to symmetry in the potential function.

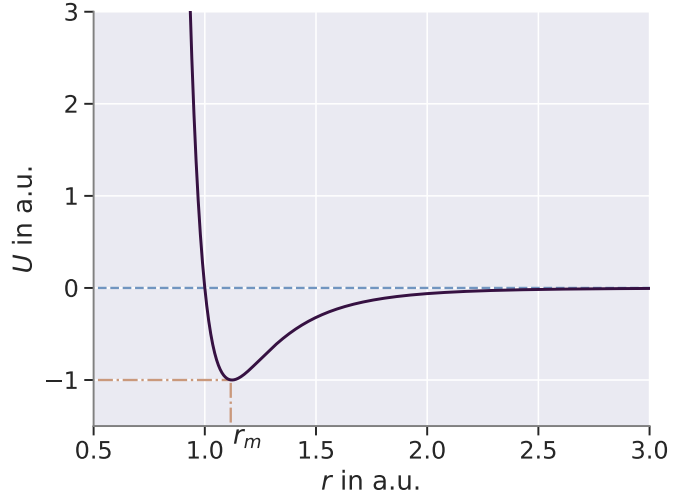
A *force field* is a combination of different potential energy functions and their used parameter sets to calculate the potential energy of atomistic particles of a MD system. Many, varying types of force fields exist and depend on the studied real-world system. Based on the physical constraints not all force components of Equation 2.26 are required and might be removed. Further, some other forces not discussed here could be included.

The utilized nonbonded potential energy functions are further divided into different subcategories of *pair* or *many-body* potentials. Pair potentials are calculated as the sum of energies between pairs of atoms, while many-body potentials include terms of higher order for three or more atoms interacting with each other. A few explicit examples of potential energy functions are given in the following sections and will be used as force field components for the simulations carried out in chapter 6 and chapter 7.

2.5.1 Pair potentials

To simplify the theoretical description of the pair potentials, the outer summation over all atom pairs is dropped from the mathematical formulations in the following section. The MD collision model later described in chapter 6, however, is based on an all-atom method,

Figure 2.9: *Dimensionless 12-6 Lennard-Jones potential energy function. The blue dashed line gives the zero point of the potential, i.e. the crossing of the potential and this line is σ . The potential minimum is found at r_m .*



e.g. for every pair of atoms the 12-6 Lennard-Jones force is computed and then summed as in Equation 2.28 to obtain the total LJ force acting on the molecules (see Equation B.3).

2.5.1.1 12-6 Lennard-Jones potential

The most widely used interatomic pair potential is the 12-6 Lennard-Jones potential [33, 34], as depicted in Figure 2.9. The general form of the potential function is

$$U_{\text{LJ}}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (2.29)$$

with r as the pair distance between two identical atoms as well as σ and ε as potential parameters. The potential well depth is given by ε and the distance at which the potential function crosses zero is given by σ . At $r_m = 2^{1/6}\sigma$ the potential function has its minimum. The potential itself is not entirely based on observation of physical phenomena: the attractive part of the potential function, i.e. the term $\propto (1/r)^6$, represent the long-range dispersion energies as observed by London [35]. However, the representation of the strong Pauli repulsion through the term $\propto (1/r)^{12}$ was then a simple fit Lennard-Jones found to describe experimental data of noble gases [34, 36]. Additionally, it simplifies the numerical computation immensely as the attractive term can be easily squared to obtain the repulsive forces. As such, the 12-6 Lennard-Jones potential form might not be suitable for many use cases but its simplicity paired with optimized parameters often warrants its use as a basic potential function for van der Waals interactions.

To allow use of differing atoms i, j with this potential, combined atom parameters can be generated by the Lorentz-Berthelot combination rule [37, 38]

$$\begin{aligned} \sigma_{ij} &= \frac{\sigma_{ii} + \sigma_{jj}}{2} \\ \varepsilon_{ij} &= \sqrt{\varepsilon_{ii} \cdot \varepsilon_{jj}} \end{aligned} \quad (2.30)$$

2.5.1.2 Modified Buckingham potential

The modified Buckingham potential is also used to describe van der Waals interactions. It is derived from the general Buckingham potential [39]

$$U_B(r_{ij}) = Ae^{-Br_{ij}} - \frac{C}{r_{ij}^6} \quad (2.31)$$

with general constants A , B and C , based on the collision theory of Chapman and Cowling [40]. An explicit form is given by the Merck Molecular Force Field 93 (MMFF93) as [41]

$$U_{MB}(r_{ij}) = \varepsilon \cdot \left[1.84 \cdot 10^5 \cdot e^{\frac{-12r_{ij}}{\sigma}} - 2.25 \cdot \left(\frac{\sigma}{r_{ij}} \right)^6 \right] . \quad (2.32)$$

A direct comparison between the 12-6 Lennard-Jones and the modified Buckingham potential is illustrated in Figure 2.10. It is apparent that both potential functions share a similar behavior for the area of the potential well, with the modified Buckingham potential being damped, i.e. the repulsion of particles begins at smaller distances. Most notably, however, is the maximum of the modified Buckingham potential and the subsequent flip back to attractive interactions for very small pair distances. In context of atomistic particle interactions this behavior is completely non-physical. Therefore, the potential is numerically often set to some value (e.g. infinity) if r is smaller than the point of the maximum $r_{\max}$.

2.5.1.3 Coulomb potential

The Coulomb potential represents the electrostatic interaction of two charged particles through Coulomb's law [42]

$$U_{\text{coul}}(r_{ij}) = \frac{1}{4\pi\epsilon} \frac{q_i q_j}{r_{ij}} , \quad (2.33)$$

with q_i , q_j being the charges of the two atoms, r_{ij} being the pair distance and ϵ being the electric permittivity of the medium. The Coulomb potential energy is a significant long-range contribution to the total potential energy for ionic and polar particles due to the $1/r$ dependence. Figure 2.11 depicts the Coulomb potential for identically (repulsive) and oppositely (attractive) charged particles.

2.5.1.4 Ion-induced potential

If an ion interacts with a non-polar particle, an ion-induced dipole moment forms inside the non-polar particle through rearrangement of electron distribution by polarization of the ion. In total, this leads to bent trajectories because of the fully attractive nature of the potential energy function. The potential energy function is given as [43]

$$U_{\text{ind}}(r_{ij}) = -\frac{\alpha}{8\pi\epsilon_0} \cdot \frac{q_i^2}{r_{ij}^4} \quad (2.34)$$

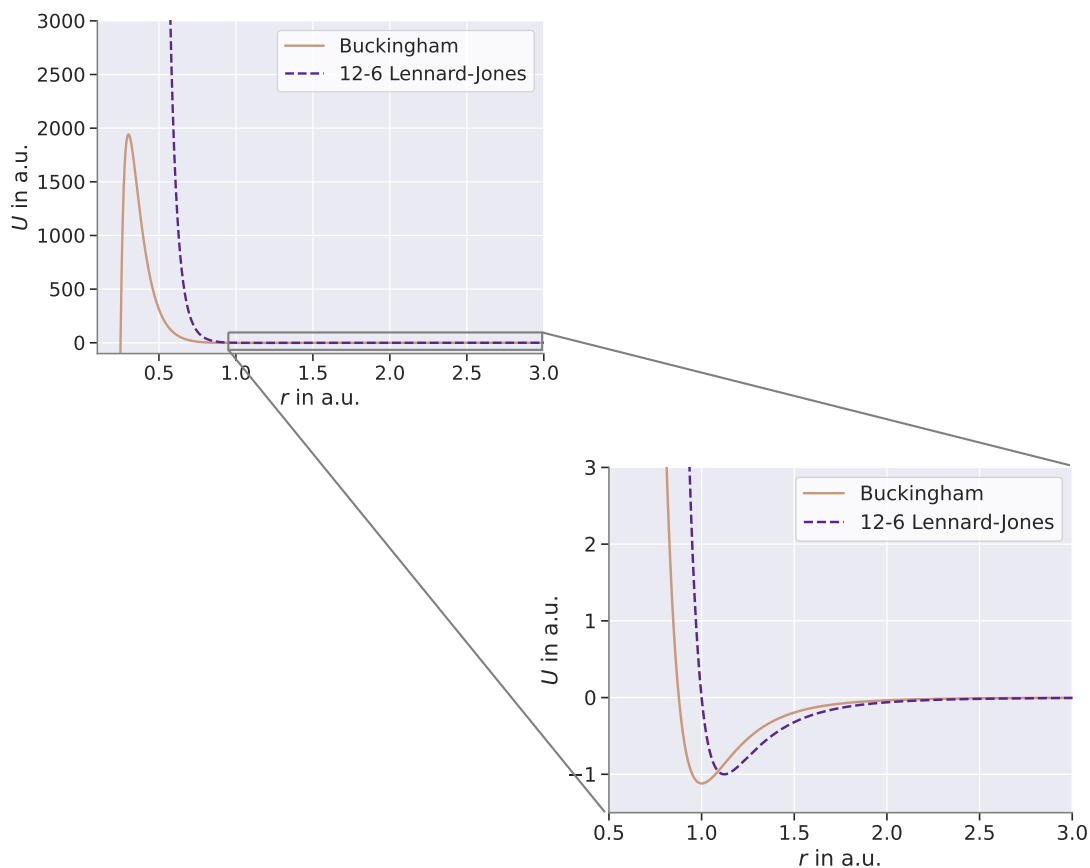


Figure 2.10: Comparison of modified Buckingham and 12-6 Lennard-Jones potential energy function. The upper left figure shows the overall shape of both functions, emphasizing the maximum of the modified Buckingham potential with subsequent drop to $-\infty$. A magnification of the area marked in gray, which includes the potential wells, is shown in the lower right figure.

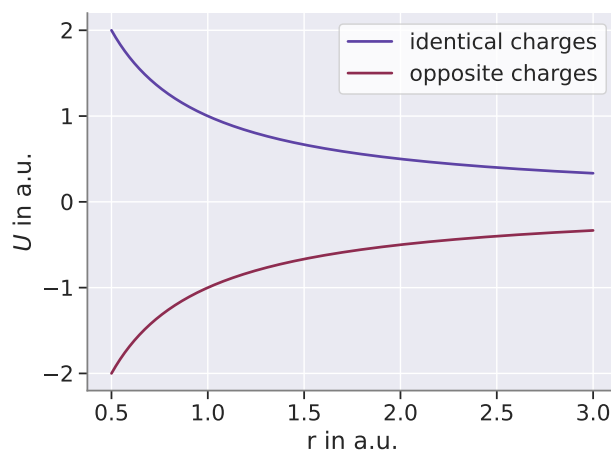


Figure 2.11: Dimensionless Coulomb potential function for either identical or opposite pair charges. The potential is either acting fully attractive or repulsive dependent on the charge.

with α as the polarizability volume of the non-polar particle, ϵ_0 as the permittivity of free space and q_i as the charge of the ion. A depiction of the ion-induced energy potential function is given in Figure 2.12. Since the potential energy scales with $1/r^4$ the long-range effects are much weaker than for the Coulomb interaction, but are high at close distances.

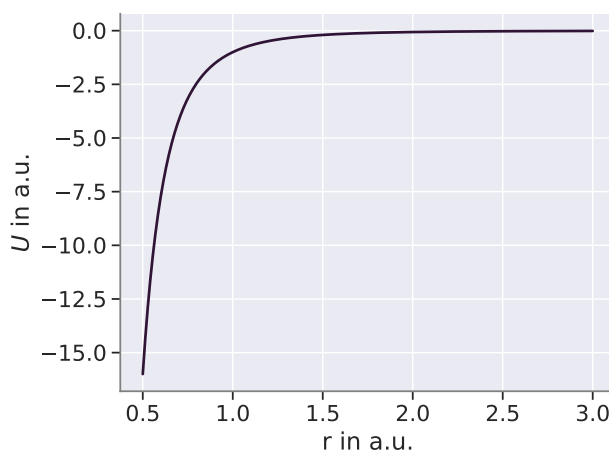


Figure 2.12: *Dimensionless ion-induced dipole potential function.*

2.5.1.5 Quadrupole potential

For some molecules it becomes a necessity to also consider the quadrupole-ion potential energy, e.g. in the case of N_2 . One way to describe the quadrupole moment of molecular nitrogen is the three-charge model [44, p. 13] where both nitrogen atoms have $-0.4825e$ charge and a dummy atom is introduced in the center-of-mass to balance those charges with $0.965e$. Calculation of the potential energy is then possible by [45]

$$U_{\text{quad}}(r_{ij}) = \frac{1}{4\pi\epsilon_0} \sum_{j=1}^3 \frac{q_i q_j}{r_{ij}} \quad . \quad (2.35)$$

The sum thereby iterates over the three atoms (including the dummy atom) of nitrogen, where q_i is the charge of the ion and q_j the charge of the specific nitrogen atom. Depending on the orientation of nitrogen in space and the relative position to the ion, the potential can become attractive or repulsive, as exemplified in Figure 2.13.

2.5.2 Many-body potentials

Many-body potentials are potentials in which some parts of the potential are calculated over the sum of more than two atoms. Many-body potential descriptions are necessary for large structures of interacting particles, where the pair-wise interactions of one particle change based on the electronic structure of surrounding particles.

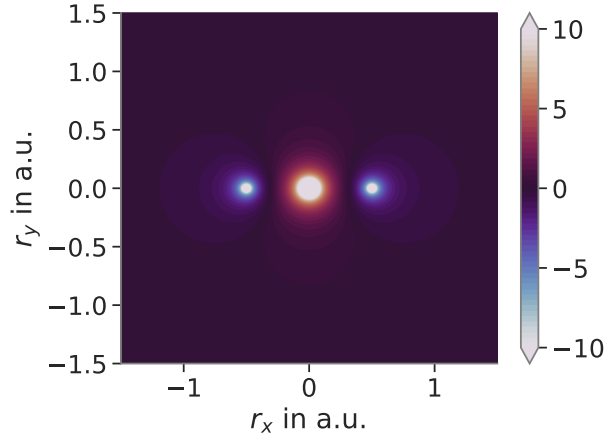


Figure 2.13: *Quadrupole-ion potential energy function for nitrogen. The colors represent the strength of the attractive or repulsive potential.*

2.5.2.1 Embedded-atom method

The embedded-atom method (EAM) is related to the second moment tight binding approximation and is a many-body potential, where the electron charge density is a summation over many atoms [46, 47]. The functional form is given by

$$U_{\text{eam},i}(r_{ij}) = F_{\alpha} \left(\sum_{j \neq i} \rho_{\beta}(r_{ij}) \right) + \frac{1}{2} \sum_{j \neq i} \phi_{\alpha\beta}(r_{ij}) \quad (2.36)$$

with F_{α} being the embedding function (energy required for atom i to be put into the electron cloud), ρ_{β} being the electron charge density of atom j (type β) at the position of atom i and $\phi_{\alpha\beta}$ being a pair-wise potential function. EAM is especially used for metallic compounds [47].

2.5.3 Bonded potentials

2.5.3.1 Bond potential

The bond potential describes the interaction of an actual covalent bond between two particles by approximation of a harmonic spring (see Figure 2.14) as [48]

$$U_{\text{bond}}(r_{ij}) = k(r_{ij} - r_0)^2, \quad (2.37)$$

where k is the spring constant and r_0 is the equilibrium distance. This approximation is valid for small deviations of the bond from its equilibrium position. Bond breakage and higher accuracy can be obtained with different models, e.g. Morse potentials or other higher order functions.

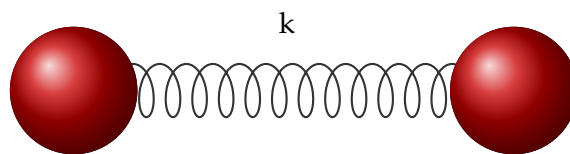


Figure 2.14: Harmonic spring with spring constant k between two particles to model covalent bond.

2.5.3.2 Angle potential

Similarly to the bond potential, the angular bond potential can be described as a 3-body harmonic covalent interaction in the form of [48, 49]

$$U_{\text{angle}}(\theta) = k_{\theta}(\theta - \theta_0)^2 \quad , \quad (2.38)$$

with θ being the angle between $\mathbf{r}_{ij}$ and $\mathbf{r}_{kj}$, θ_0 being the equilibrium angle and k_{θ} being the angle constant.

2.5.3.3 Dihedral potential

The dihedral potential is a 4-body potential energy between the four bonded atoms (i – j – k – l) and describes the torsion angle between the two planes spanned by the first three bonded atoms (i, j, k) and the last three bonded atoms (j, k, l). Particularly in the case of proteins/hydrocarbons this energy contribution is necessary to correctly describe local structures. In the case of butane, as seen in Figure 2.15, the two planes can be defined with the torsion angle of the jk bond along the center of the molecules. The common, most often used form of the dihedral potential is set to [49, 50]

$$U_{\text{dihedral}}(\phi) = K(1 + \cos(n\phi - \psi)) \quad , \quad (2.39)$$

where K is an energy constant, n is a non-negative integer number for periodicity, ϕ is the torsion angle between the two planes and ψ is a phase shift.

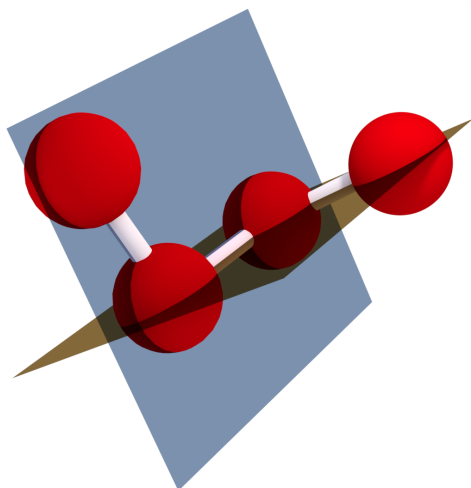
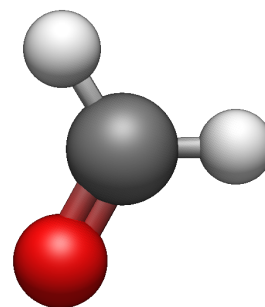


Figure 2.15: Butane molecule with the two ijk and jkl planes visualizing a proper dihedral angle.

2.5.3.4 Improper potential

Improper potentials are a special case of dihedral angle potentials, where not all four atoms are bonded in a row instead any four atoms can be taken with one central atom where the other three atoms are connected to. Improper dihedrals are necessary to correctly reproduce the structure of some molecules which are planar but do not have a proper dihedral torsion angle like formaldehyde, as pictured in Figure 2.16.

Figure 2.16: Formaldehyde molecule, where all atoms are in the same plane. This shows improper dihedrals, as the four atoms are not bonded in a row, but connected to one central atom.



Usually, the improper dihedral energy is also given as a harmonic function as

$$U_{\text{improper}}(\chi) = k_{\chi}(\chi - \chi_0)^2, \quad (2.40)$$

with χ being the improper angle, χ_0 being the equilibrium improper angle and k_{χ} being the improper energy constant. The improper angle is the angle between the plane the planar particle would lie in and any of the atoms position outside of this plane.

2.5.4 Generation of force fields and limitations

The research behind force fields and their generation is often complex. While the main idea behind development of a force field is simple, namely *fitting of potentials to some parameters of the systems*, actual parametrization is hard and can take years to work out [51]. Fitting of parameters first of all requires reference values for the atoms/molecules/structures to be described. Those reference values can be obtained by either "top-down" or "bottom-up" methods, i.e. by experimentally determined features of the structures or by ab initio methods. Reference values often include lattice constants for crystal structures, enthalpy of vaporization, heat capacity, entropies or binding energies [52–54]. Molecular dynamic simulations are carried out with first initial parameters and iteratively improve the parameter based on the agreement between MD simulations and reference values. How this step of improvement is actually carried out differs between force fields and is dependent on the molecular space to be fit. Exceptional force fields require extensive sets of reference values with large amounts of molecules in the domain of interest, e.g. proteins or specific kinds of crystals.

While empirical force fields often work well, there are some limitations:

- huge conformational space of protein structures beyond what is computational feasible to calculate for accurate predictions

- varying accuracy depending on the reference values, as not all structures can be computed ab initio to guarantee high accuracy
- limited simulation size and length if high accuracy quantum mechanic approaches are chosen in combination with classical force fields

Recent advances in force field generation focus on machine-learning (ML) based force fields as a way to bridge the efficiency of classical force fields and the accuracy of ab initio methods [55–57]. For ML force fields chemical descriptors of a very large set of input molecules (training data) are functionally connected to properties of structures in this data. Thereby, no physical formulas or laws have to be solved. If the training data set is well chosen for the molecular space and large enough, the ML force field is able to predict the behavior of molecules not in the training data set.

MODELING OF ION MOBILITY

In the field of spectrometric analysis techniques, ion mobility spectrometry (IMS) is an important tool for separation and identification of ions by their individual electric mobility [58]. It is often used complementary to mass spectrometry or other separation techniques like gas chromatography [59–61]. Ion mobility devices are used extensively in military and security applications [62] because they are relatively sensitive, easy to use, have exceptionally fast separation capabilities and can be compactly designed [58]. The use cases for IMS devices are vast and ion mobility is a key property of ions, which has an impact on ion behavior across many different devices utilizing electric fields and gas interactions. Correct modeling of ion mobility, or rather correct reproduction of ion movement, thus is relevant in numerous numeric studies. Since ion mobility is dependent on complex mechanisms, numeric modeling is non trivial and requires advanced methods to accurately describe [63, 64].

3.1 Ion mobility

In an electric field, a charged particle contained in a gas is accelerated up to a constant velocity, called drift velocity [58]. The ion mobility K is defined as the fraction of the drift velocity of the ion v_d and the magnitude of the applied electric field E [58, 65]:

$$K = \frac{v_d}{E} \quad (3.1)$$

There are several different ways to incorporate ion mobility as a separation property in spectrometric devices. The most simple device is a drift-tube ion mobility spectrometer (DT-IMS). In a DT-IMS (see Figure 3.1) a drift tube is filled with a buffer gas, where ions are periodically pushed into. A constant, uniform electric field is applied to this drift tube, pulling the ions through the buffer gas based on their individual mobilities [58]. The time taken for the ions to reach the end of the drift tube can then be used to effectively calculate the ion mobility. Actual drift times obtained by IMS devices are naturally pressure and temperature dependent, as such a reduced mobility is introduced to allow for comparison

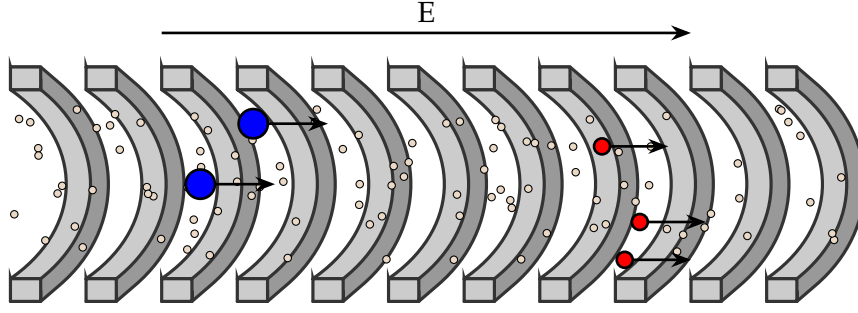


Figure 3.1: Schematic of DT-IMS device, showing the drift tube electrodes. The drift region is filled with buffer gas and ions are pushed through this gas by the applied electrical field E .

across different experiments [66]:

$$K_0 = K \cdot \frac{T_0}{T} \cdot \frac{p}{p_0} \quad , \quad (3.2)$$

where T , p are the variable temperature and pressure, while T_0 , p_0 are reference temperature and pressure. Conventionally, the reference temperature is taken as 273.15 K and the reference pressure is set to 760 Torr [66]. A complete independence from the temperature, however, is not possible even if using the reduced mobility [67]. Ion structure, especially for larger particles, is strongly influenced by the temperature and has an impact on collisional interactions with the buffer gas [67].

3.2 Field dependence

Alongside the dependence on the buffer gas properties comes the additional change in measured ion mobility based on the applied electric field in the instrument [68]. For cases in which the electric field is small enough, such that the ion and collision gas have roughly the same energy, the ion mobility is constant. If the ions gain considerable energy by the electric field between collisions, which starts to happen at around 2 to 10 Td [69], the strength of the electric field has a significant impact on the measured values of the ion mobility. In the context of ion mobility the electric field is most often given as the reduced electric field E/N , with E as the electric field and N as the buffer gas density. It is measured in Townsend (Td), with 1 Td equal to 10^{-21} Vm^2 [68]. The α -function is introduced as an empirical measure of the ion mobility change with the reduced electric field strength [68, 70]

$$\alpha \left(\frac{E}{N} \right) = \frac{K \left(\frac{E}{N} \right) - K(0)}{K(0)} \quad , \quad (3.3)$$

where $K(E/N)$ gives the ion mobility in dependence of the reduced electric field (*high field conditions*) and $K(0)$ is the ion mobility at *low field conditions*. Different classifications can be made based on the α -curve behavior, as illustrated in Figure 3.2. Three types exist: i) Type A - increasing values of α over the whole field range, ii) Type B - first increase then a decrease in α values and iii) Type C - decreasing α values over the whole range [71].

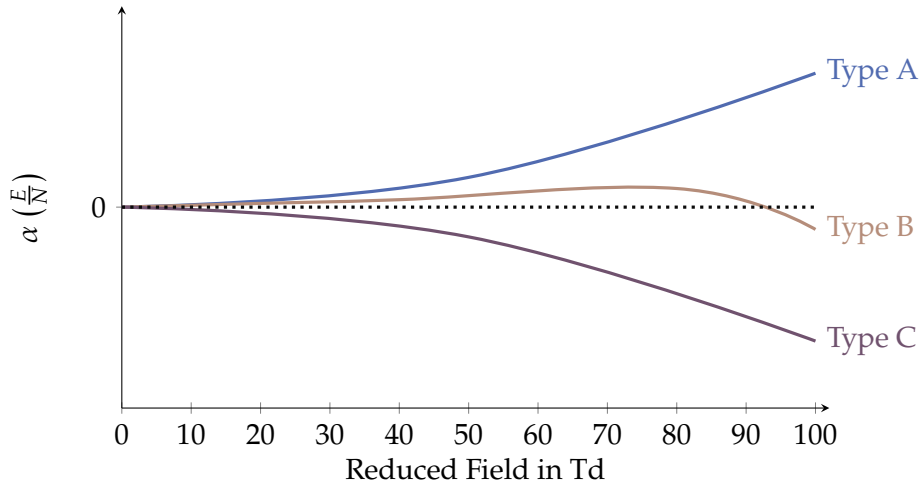
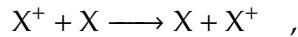


Figure 3.2: Three exemplary α -curves showing the different types of behavior.

As the reduced electric field increases, the ion-neutral collisions begin to change as different interaction mechanisms prevail at high field conditions in contrast to low field conditions. Possible collisional interaction effects are:

1. **Hard-sphere effect:** For high collision energies, i.e. a high reduced electric field, especially short-range repulsive interactions between the ion and neutral buffer gas take place [68]. Those short-range repulsive interactions are approximated well by a hard-sphere approach (elastic collisions with the particles acting like billiard balls, see subsection 3.3.1). The hard-sphere effect leads to a decrease of the ion mobility with higher field strengths as ion-neutral collisions become frontal and "harsh" in nature [68].
2. **Polarization:** Through ion-induced polarization of the neutral buffer gas, attractive forces between the ion and buffer gas particle form [68]. For low relative velocities between the collision partners, the long-range attraction results in trajectories of grazing collisions being bent. The interaction sphere basically becomes larger. With higher field strengths, this effect starts to diminish and the ion mobility thus increases [68].
3. **Clustering:** For specific ion-neutral pairs actual chemical molecular clustering is possible. The collision cross section of the clustered ion is larger, leading to a decrease of the ion mobility. With increased average collision energies, possible through higher electric field strengths, the clustered species begin to (partly) decluster [68]. For high field conditions the ions then have an increased ion mobility [68].
4. **Resonant charge transfer:** A resonant charge transfer process is a reaction of type



where the total internal energy stays constant [72–74]. In collisions with charge transfer, the ions lose almost all of their velocity with subsequent gain of velocity

from the electric field [74]. In principle, this results in an overall slowdown of the ions and therefore to a decrease of the ion mobility.

For all of these effects, various ideas and models have been discussed in literature to obtain accurate predictions of ion mobilities in low and high field conditions. This work has a primary focus on modeling of hard-sphere and polarization effects with different collision models varying in accuracy, computational effort and scope of possible ion-neutral pairs. The following sections 3.3 through 3.4 thus give a theoretical overview of modeling approaches for ion mobility predictions.

3.3 Collision models

3.3.1 Hard-Sphere

In the hard-sphere model, particles which undergo a collision are assumed to act analogously to hard, elastic billiard balls ("spheres") [75]. This leads to a model in which energy and momentum will be conserved and "clear"¹ cross sections can be defined.

The cross section of two non-penetrable particles a and b is defined by

$$\sigma_{ab} = \pi(r_a + r_b)^2 = \pi r_{\text{sum}}^2 \quad (3.4)$$

with their respective radius r_a and r_b , as illustrated in Figure 3.3. In the hard-sphere model collisions can only take place if the particles are spatially within the collision cross section. Since, e.g. in ion trajectory simulations using neutral background gas, the background gas is often only modeled implicitly (given as the pressure of the system), no actual penetration of a particle into any interaction sphere can be determined.

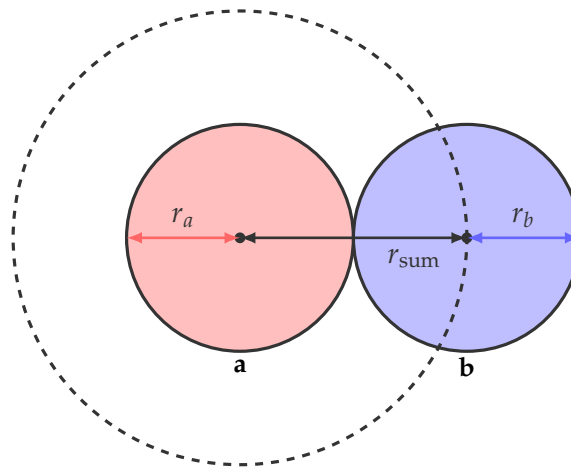


Figure 3.3: Two particles a and b with their interaction sphere given by their radii r_a and r_b . The collision cross section is given by the sphere with radius r_{sum} .

¹Clear in comparison to other models like the molecular dynamics based model, where collision cross-sections do not have a rigid value, due to attractive polarization effects, and are only numerically limited to decreased computational workload.

However, based on the collision cross section and the particles parameters an effective collision probability within each time step of an ion trajectory simulation can be calculated, essentially creating a statistical accurate sample [76, 77]. The estimation of a collision probability requires the mean-free-path of an ion inside the neutral background gas given as

$$\ell = kT \cdot \frac{v_{\text{ion, rel}}}{\bar{v}_{\text{rel}} \cdot p \cdot \sigma_{\text{ion/gas}}} , \quad (3.5)$$

with T as the background gas temperature, $v_{\text{ion, rel}} = v_{\text{ion}} - \bar{v}_{\text{gas}}$ as the relative ion velocity in respect to the mean gas velocity, $\bar{v}_{\text{rel}}$ as the mean relative velocity between ion and gas, p as the background gas pressure and $\sigma_{\text{ion/gas}}$ as the collision cross section between ion and background gas. The mean relative velocity between ion and gas can be computed by [78]

$$\bar{v}_{\text{rel}} = \bar{v}_{\text{gas}} \cdot \left[\left(s + \frac{1}{2s} \right) \cdot \frac{\sqrt{\pi}}{2} \cdot \text{erf}(s) + 0.5e^{-s^2} \right] \quad \text{with} \quad (3.6)$$

$$s = \frac{v_{\text{ion, rel}}}{v_{\text{gas}}^*} \quad (3.7)$$

$$\bar{v}_{\text{gas}} = \sqrt{\frac{8kT}{\pi m}} \quad (\text{mean gas velocity}) \quad (3.8)$$

$$v_{\text{gas}}^* = \sqrt{\frac{2kT}{m}} \quad (\text{median gas velocity}) \quad (3.9)$$

Then the effective collision probability can be calculated by [76, 77]

$$P = 1 - \exp\left(-\frac{v_{\text{ion, rel}} \cdot \Delta t}{\ell}\right) , \quad (3.10)$$

where Δt is the numerical time step length of the ion trajectory simulation. Thus, in each time step of the simulation for each ion a random number r (between 0 and 1) is computed and if $r \leq P$ a collision is evaluated for this ion.

If a collision takes place for an ion (red particle) in a specific time step, an updated ion velocity vector has to be computed. For this, the 3D problem is simplified to a 2D problem, as shown in Figure 3.4, and the entry ion velocity is shifted as $v_{\text{ion}} = v_{\text{ion, rel}} - v_{\text{gas}}$ [76, 77]. This creates a reference frame in which the explicit background gas particle (blue particle) is stationary (with the background gas velocity sampled from the Maxwell-Boltzmann distribution). An impact offset $d \in [0, 1]$ is drawn from a uniform distribution and the impact angle is then computed by $\phi = \arcsin(d)$. The ion velocity is separated into two velocity components v_t and v_r . Thereby, component v_t is orthogonal to the ion-gas axis and v_r is parallel to that axis. The force exerted by the collision only affects the radial component of the velocity, as such a further simplification to a 1D problem can be made, using the ion-gas axis as the principle axis.

The radial velocity v_r is calculated as

$$\frac{v_r}{v_{\text{ion}}} = \cos(\phi) \Leftrightarrow v_r = \cos(\phi) \cdot v_{\text{ion}} . \quad (3.11)$$

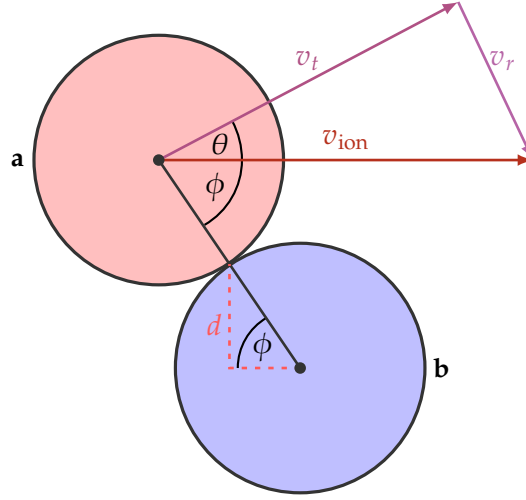


Figure 3.4: Collisional interaction of an ion (red) with a background gas particle (blue) as a two dimensional problem. The ion enters the collision with a relative velocity v_b , which can be split up into v_t (orthogonal to the ion-gas axis) and v_r (parallel to the ion-gas axis).

The momentum and energy of the collision are conserved (elastic billiard like collision) and with consideration of the stationary background gas, the following statements are obtained:

$$m_{\text{ion}} v_r = m_{\text{ion}} v_{\text{ion, s.}} + m_{\text{gas}} v_{\text{gas, s.}} \quad (\text{momentum cons.}) \quad (3.12)$$

$$\frac{1}{2} m_{\text{ion}} v_r^2 = \frac{1}{2} m_{\text{ion}} v_{\text{ion, s.}}^2 + \frac{1}{2} m_{\text{gas}} v_{\text{gas, s.}}^2 \quad (\text{energy cons.}) \quad (3.13)$$

The masses of ion and background gas are given by m_{ion} and m_{gas} respectively, while the velocities denoted by "s." give the velocities of ion and gas succeeding the collision event. Using both statements a formula for the ion velocity in the radial axis after the collision is found

$$v_{\text{ion, s.}} = \frac{m_{\text{ion}} v_r - m_{\text{gas}} v_r}{m_{\text{ion}} + m_{\text{gas}}} \quad (3.14)$$

The new radial velocity then needs to be corrected by the normal component $v_t = \sin(\phi) \cdot v_{\text{ion}}$ that was excluded from consideration in the one dimensional problem. Through this correction the final new ion velocity is obtained by

$$v_{\text{ion, } \hat{x}} = v_{\text{ion, s.}, x} + v_{t, x} = v_{\text{ion, s.}} \cdot \cos(\phi) + v_t \cdot \sin(\phi) \quad (3.15)$$

$$v_{\text{ion, } \hat{y}} = v_{\text{ion, s.}, y} + v_{t, y} = v_{\text{ion, s.}} \cdot \sin(\phi) + v_t \cdot \cos(\phi) \quad (3.16)$$

Lastly, the collision event is transformed back to three dimensions through rotation of the collision plane in x by a random angle, which is uniformly distributed.

3.3.2 Variable Hard-Sphere

The variable hard-sphere (VHS) model is a modification of the hard-sphere model [75, 79]. In the hard-sphere model the collision cross-section of a particle pair is constant, however

the interaction sphere of two particles is strongly dependent on their relative speed resp. the collision energy [75, 79]. Faster traveling particles lead to a reduction of the interaction sphere, as fewer time is spent in "direct" exchange. As such, the VHS model aims to correct for this phenomenon by converting the collision cross-section to a function, that is [75, 79]

$$\sigma_{\text{VHS}} = \sigma(v_{\text{rel}}) \quad . \quad (3.17)$$

The actual expression for the VHS diameter of a particle pair is given by [80]

$$d_{ab} = d_{\text{ref},ab} \cdot \left[\left(\frac{2k_b T_{\text{ref.}}}{\frac{m_a m_b}{m_a + m_b} |v_a - v_b|} \right)^{\omega_{ab}-0.5} \cdot \frac{1}{\Gamma(2.5 - \omega_{ab})} \right]^{0.5} , \quad (3.18)$$

where $d_{\text{ref},ab}$ and $T_{\text{ref.}}$ are the reference diameter and temperature for the particle pair, m_a , m_b are the particle masses, v_a , v_b are the particle velocities, ω_{ab} is the viscosity index and Γ is the Gamma function. For $\omega = 0.5$ the hard-sphere model is restored, i.e. the function is temperature independent.

Overall, the VHS model is an improvement over the HS model, as the viscosity of single species gas flow is taken into consideration through the viscosity index ω_{ab} . Further discussion of this collision model is carried out in a later chapter, see chapter 6.

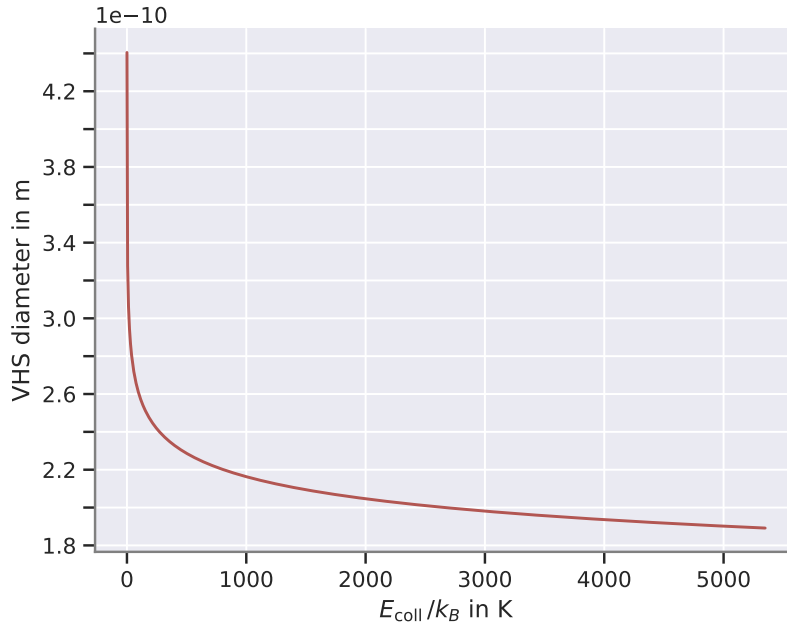


Figure 3.5: Change of VHS diameter with collisional energy for a He-He pair using the reference parameters in [81].

3.3.3 Molecular dynamics based trajectory method

Both the HS and the VHS model are based on the same principle: modification of the velocity of the collision partners through billiard-like collisions. This limits their

application context, as many physical problems exist where a more sophisticated treatment of collisional interactions has to be carried out.

One further model is a so called *molecular dynamics based trajectory* collision model [82]. As with the VHS model, the concrete implementation will be given in chapter 6, instead a short outline of the concept is given here.

The molecular dynamics collision model is reproduced from programs such as MobCal [83], Collidoscope [84] and in parts IMoS [85] and is comprised of the following steps:

1. Collision random sampling: a collision probability is calculated and it is determined if an ion has a collision with a background gas particle
2. Construction of collision: initialization of ion and background gas position/velocities and geometries, the background gas is an **explicit** collision partner in this model
3. Integration of trajectories: ion and background gas movement is calculated given by the MD process (see chapter 2) with appropriate force fields

This approach is a lot more flexible, as also attractive interaction potentials like the ion-induced dipole moment can be taken into consideration [82], which is a key property to correctly model high-field ion mobilities. However, the increased accuracy comes with a much higher computational cost for the numerical simulation procedure as one collision is a complete MD simulation instead of only a few values calculated by analytical formulas.

3.4 Inelastic collisions with Borgnakke-Larsen method

All discussed models are in their basic form completely elastic, i.e. no translational energy can be redistributed into the internal degrees of freedom (rotations or vibrations).

The phenomenological Borgnakke-Larsen (BL) model, originating from its use in Direct Simulation Monte Carlo (DSMC), makes it possible to simulate the relaxation of internal energy modes [86, 87]. In equilibrium, all energy modes follow their equilibrium energy distribution function and take a specific amount of collisions to relax to this state, namely [75]

$$Z = \frac{\tau}{\tau_{\text{coll}}} \quad (3.19)$$

with τ as the relaxation time of the energy mode and τ_{coll} as the mean collision time. It holds that $Z_{\text{tr}} = 1 < Z_{\text{rot}} < Z_{\text{vib}}$ [75]. The Borgnakke-Larsen model aims to exactly conserve the equilibrium energy distribution functions while replicating the correct relaxation number Z for each internal mode [75]. For this, it is assumed that a fraction of all collisions in a time step undergo an inelastic collision either in vibrational and/or rotational degrees with a probability of $\frac{\Delta t}{\tau_{\text{coll}}} p_i$, where p_i is either the rotational or vibrational base probability given as [75]

$$p_i = \frac{\zeta_{\text{tr}} + \zeta_i}{\zeta_{\text{tr}}} \cdot \frac{1}{Z_i} \quad (3.20)$$

This probability is defined by the degrees of freedom of the translational mode ζ_{tr} and the internal mode ζ_i as well as the relaxation collision number Z_i . If any of the collisions are then decided to be inelastic in any mode, the post-collisional energies are sampled from the joint equilibrium distribution of all modes by an acceptance-rejection method. Afterwards, the internal energy is split between the collision pair [75]. The translational energy distribution function is given by [75]

$$f(\epsilon_{\text{tr}}) = \frac{\sqrt{2/m_r}}{\Gamma(5/2 - \omega)} \left(\frac{1}{k_B T} \right)^{5/2 - \omega} \epsilon_{\text{tr}}^{3/2 - \omega} e^{-\frac{\epsilon_{\text{tr}}}{k_B T}} \quad (3.21)$$

and the internal energy distribution function is [75]

$$f(\epsilon_i) = \frac{1}{\Gamma(\zeta_i/2)} \left(\frac{\epsilon_i}{k_B T} \right)^{\zeta_i/2 - 1} e^{-\frac{\epsilon_i}{k_B T}}. \quad (3.22)$$

The joint distribution function is thus

$$f(\epsilon_i, \epsilon_{\text{tr}}) \propto \epsilon_i^{\zeta_i/2 - 1} \epsilon_{\text{tr}}^{3/2 - \omega} e^{-\frac{(\epsilon_i + \epsilon_{\text{tr}})}{k_B T}}. \quad (3.23)$$

The updated post-collision translational energy is used to determine a new relative velocity for the subsequent integration. Further details specific to the actual implementation are also presented in chapter 6.

DYNAMICS OF THE ELECTROSPRAY PROCESS

Electrospray ionization (ESI) is one of the most important techniques for *ionization* of analytes in a liquid solution for subsequent analysis in atmospheric pressure mass spectrometry. ESI is a so called "soft" ionization method, which allows the fragmented ionization of labile analytes. Additionally, ESI leads to multiply charged ions allowing larger biomolecules (peptides and proteins) to be analyzed as well.

The method itself builds upon generation of charged droplets containing analyte ions, which will then eventually be liberated from these droplets. Recent publications have shown discrepancies between hitherto existing theoretical concepts of electrospray ionization and experimental observations. The following chapter thus aims to illustrate the general ESI process as depicted in textbook literature as well as more advanced insight into the complex nature of final ion release.

4.1 Overview of working principle

Electrospray ionization works by placing a spray capillary (metal or glass) in front of a counter electrode, as pictured in Figure 4.1. Either one of those elements is put onto a high voltage (typically few kV), while the other element stays on ground potential. This leads to the formation of a strong electric field between the capillary and counter electrode. A liquid solution, containing the analyte ions and solvent molecules, is sprayed through the capillary into the ESI source. Thereby, the ions experience the electric field at the open capillary end. Ions of one polarity begin to move downfield toward the counter electrode, creating an electrospray plume [88]. The droplets are then guided to the mass spectrometer entrance by the present electric field, while heated gas is additionally used to desolvate these droplets [89]. It is often implicitly assumed in literature, that the solvent evaporation process is completely finished in the ion source chamber and only bare gas-phase ions enter the vacuum system of the mass spectrometer.

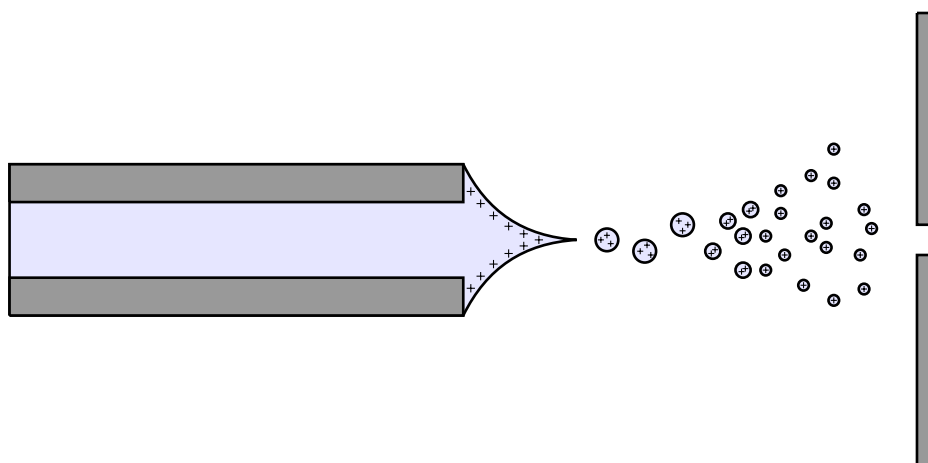


Figure 4.1: Scheme of ESI capillary showing the formation of an electrospray plume with subsequent droplet shrinkage.

4.2 Droplet formation

Charged droplets which form the electrospray spray plume originate from the so called *Taylor cone*: growing charge density at the liquid meniscus due to the displacement of homogeneous charges by the electric field leads to a deformation of the liquid into a cone shape. If the surface tension of the liquid is overcome, a fine jet is formed at the tip of the cone [88]. Such a jet is unstable due to the Coulomb repulsion of the high amount of charges and breaks apart into droplets.

The initial droplet size is dependent on the Taylor cone radius. Theoretical studies estimated the initial droplet size to not be larger than $2\text{ }\mu\text{m}$ [2, 4, 89–91]. However, several experimental studies, as illustrated in an overview by Markert et al. [3] given in Table 4.1, show widely varying initial droplet sizes much larger than the prediction.

Table 4.1: Experimentally observed initial ESI droplet sizes as compiled in [3].

analyte/solvent	observed droplet size	references
Pure solvents (water, acetonitrile, n-heptane, n-octane, p-xylene)	25–35 μm	[92, 93]
Heptane	Up to 100 μm with 466 $\mu\text{L}/\text{min}$ liquid flow rate, 5 μm with 4 $\mu\text{L}/\text{min}$ liquid flow rate	[94]
Fluorescent dyes in acetonitrile	6 μm in pos. mode, 20 μm in neg. mode	[95]
Water/methanol solution with desorption electrospray ionization emitter	Up to 10 μm with 2 $\mu\text{L}/\text{min}$ liquid flow rate	[96]
Fluorescent dye in 20% methanol/water mixture	2 μm with 50 $\mu\text{L}/\text{min}$ liquid flow rate	[97]

4.3 Droplet shrinkage and ion release

After the release of relatively large droplets from the formed jet, these droplets begin to shrink owing to natural as well as gas assisted solvent evaporation. The number of charges contained in the droplet/on the droplets surface stay constant during the evaporation, as such the intensity of charge repulsion at the surface of the droplets begins to increase. When the droplets reach the *Rayleigh limit*, i.e. the point at which the charge repulsion is equal to the surface tension, Coulomb fission events take place, where smaller, charged droplets are ejected from the parent droplet. The amount of elementary charges contained in the droplets at the Rayleigh limits is given by [98, 99]

$$z_R = \frac{8\pi}{e} \cdot \sqrt{\epsilon_0 \gamma R^3} \quad , \quad (4.1)$$

with ϵ_0 as the vacuum permittivity, γ as the surface tension and R as the droplet radius. These fission events continually repeat until the progeny droplets are small enough to release bare gas-phase ions. Several theoretical models exist for the final ion release:

- **Charge Residue Model (CRM):** The charge residue model propose that gas-phase ions are liberated by final solvent evaporation of very small, charged droplets containing only a single analyte molecule, with charge transfer to this molecule [100, 101]. This model is often used to describe ion formation for large analyte molecules.
- **Ion Evaporation Model (IEM):** The ion evaporation model assumes that the electrical field at the surface of charged droplets at their Rayleigh limit is so strong that ions are directly ejected from droplets with only few solvent molecules [4, 99]. In contrast to the CRM, this model is used to explain ion formation for small analytes.
- **Chain Ejection Model (CEM):** This model is primarily used for ion formation description of unfolded proteins [99]. Unfolded proteins initially reside in the interior of the highly charged droplets. When such droplets reach the Rayleigh limit, the proteins move to the surface with subsequent sequential ejection of the protein chain [99].

4.4 Observed discrepancies with ESI models and consequences

As already stated in section 4.2, discrepancies in the ESI droplet formation between experimental and theoretical studies have been observed, especially for initial droplet size and as a result also for droplet lifetime. Textbook literature assumes the complete evaporation of solvent molecules and thus liberation of bare gas-phase ions still inside the electrospray ion source. Therefore, no droplets should penetrate into the mass spectrometer vacuum system situated behind the ion source.

However, recent experimental results reveal that ion evaporation does not completely finish inside the ion source in most cases. Already in 1997, Thomson [102] showed first indication that "heavily clustered monomers and possibly dimers and multimers are present

in the expansion from ion source into vacuum", while in 2017 Kang et al. [103] also observed aspiration of large droplets in the vacuum system of a modern mass spectrometer. Several experiments were performed by Kang et al., one of which used a custom scan mode on a triple quadrupole system: the first quadrupole (Q1) in the mass analyzer system was set to RF-only mode, turning Q1 essentially into a high-pass filter. In the collision cell (q2), fragmentation of the ions passing the filter with collision-induced dissociation was carried out while the third quadrupole (Q3) was used for the mass-to-charge scan. In the case of low collision energies no analyte signal is observed, with only slight chemical noise found above the filter limit. With increased collision energies analyte signal is detected, indicating that the analyte had to be situated in some form of droplet with its m/z higher than the filter limit and was then liberated by collisions in the fragmentation stage after the high-pass Q1.

This custom scan mode and similar measurement methods were also used by Markert et al. [3] (2021) in three different atmospheric pressure ionization (API) instruments, also showing liberation of analytes from large, charged droplets in the mass spectrum. Further research carried out by Itzenhäuser et al. [104] in 2024 was able to show droplet fragment signatures using analytical conditions with an LC-ESI-MS setup, as pictured in Figure 4.2. Extremely different fragment spectra are visible for two different solvent systems in isolation and fragmentation experiments in an quadrupole ion trap (QIT) instrument. Here, the strongest difference is observed in the region above the isolation window of 2000 ± 50 m/z . The signals in this area are also strongly dependent on the applied dry gas¹ temperature of the ion source. The existence of signals above the isolation window also strongly suggests that this signal has to arise from fragmented, multiply charged droplets. Reserpine ($m/z = 609$) was used here as the analyte, and can additionally be seen to be liberated from the droplets for lower dry gas temperatures, i.e. a higher frequency of droplets entering the vacuum region. Another observation of droplets in high-vacuum regions of a mass analyzer was realized by Heintz et al. [105–107] (2024–2025) in the form of ion bursts, detected by an secondary electron multiplier (SEM) detector behind the orthogonal acceleration stage in a Bruker micrOTOF instrument. Figure 4.3 illustrates such an ion burst (intense signal) as an oscillogram of the SEM signal. The signal burst is cut by the pusher accelerating ions orthogonally into the mass analyzer region. Additionally, the results obtained with an ESI ionization source were compared to APCI measurements. The key results of those experiments can be summarized as follows: i) the burst signals show cut-out regions from the pusher, as such the signal can be attributed to a highly correlated cloud of ions and not a single monolithic droplet, ii) most of the analyte signal in a mass spectrum is generated by high intense spectra probably resulting from ion bursts and iii) droplet signatures / ion bursts are exclusive to ESI and do not show with APCI. Overall, multiple measurements and different research methods up until now have established that highly charged droplets are aspirated deeply into the vacuum mass analyzer

¹This gas flow is used to support further evaporation of the droplet generated by ESI.

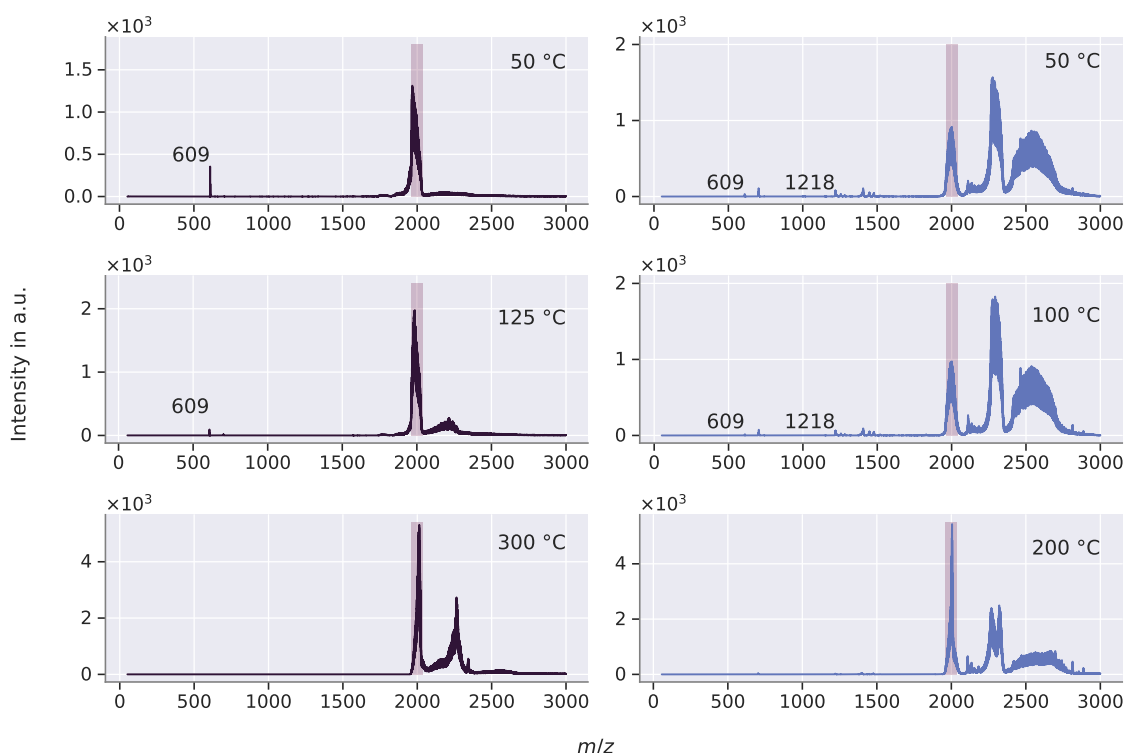


Figure 4.2: Droplet fragment spectra for two solvent systems in a quadrupole ion trap system: (left) acetonitrile/water and (right) ethanol/water. An isolation window of $m/z = 2000 \pm 50$ was used (red box). Different dry gas temperatures were set for both solvent systems. A strong dependency of the fragment spectra on the solvents and the dry gas temperature is observed. Reproduced from [104] with original data.

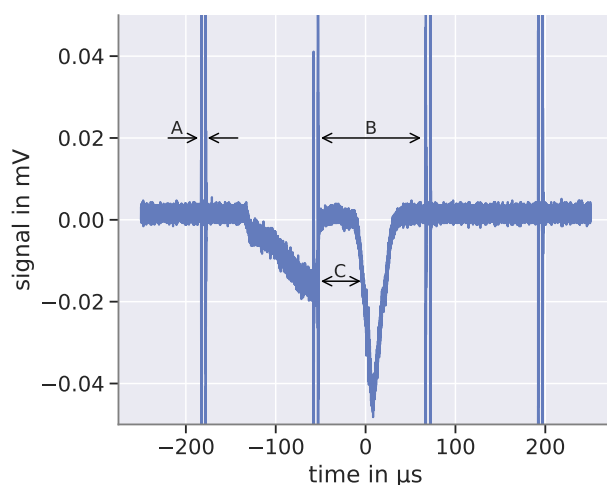


Figure 4.3: Oscilloscope of ion burst signal. (A) is the time of the pusher switched to high potential, while (B) shows the length of one push. Before the second pusher event, a strong increase in signal is noticeable which is then promptly interrupted by the pusher, showing a cut-out region (C). After this cut-out, the signal suddenly returns. Original data kindly provided by C. Heintz.

region and this has adverse effects on the operation of ESI mass spectrometers. The time between maintenance cycles and the maximal possible productive operation time of the instrument is reduced by contamination of surfaces inside the vacuum system, e.g. electrode surfaces, through droplet fragments. As cleaning a mass spectrometer is costly, end users are interested in reducing the number of maintenance cycles. Additionally, the gas phase composition in the inlet system of the instrument is subject to significant influence by entry/deposition of droplets. Chemical interference can be caused by solvents accumulating and interacting chemically with other compounds, especially the analytes. This can lead to changes in the observed mass signals and increase the complexity of interpretation of mass spectra. The large amount of charge carried by the droplets can also disrupt the system, as the performance of individual components of an instrument can be affected by charging and space charge effects.

4.5 Potential fragmentation processes

Further evaluation of the droplet dynamics require knowledge about possible ways for droplet fragments to be created along the flight path of those droplets inside the instruments. Multiple, different instruments were used for the measurements discussed in section 4.4, like triple quadrupole systems, Q-TOFs or quadrupole ion traps. Naturally, these instruments completely differ in their internal structure and thus also a manifold of processes could be responsible for the observed fragment spectra and other droplet signatures. Nevertheless, the overall construction principle stays the same for all instruments and includes the ion source, followed by the transfer stage, which then leads to the mass analyzer and ion detector. To allow further discussion of possible processes, a short sketch of an exemplary electrospray ionization mass spectrometer up to the mass analyzer region (i.e. the ion source and transfer stage) is given in Figure 4.4. After the droplets are sprayed from the ESI needle by help of the electric field between the needle and spray shield, the droplets are transferred into the first vacuum stage through the inlet capillary. Additional ion guiding is then carried out in the transfer stage which is given by the quadrupole and Einzel lens, in this example.

Now, several mechanisms can be responsible for fragmentation of the large, charged droplets. Two of those processes involve either fragmentation/dissociation by collisions with background gas particles or surfaces. Several experimental results² indicate that one or both of these processes are involved in effecting the generation of the observed droplet fragment spectra and will therefore be discussed in the following sections.

²Existence of droplet fragment spectra in a triple quadrupole system induced by increased collision energy in the collision cell might lead to the hypothesis that collision-induced dissociation is in effect. In contrast the ion bursts change their shape with the amplitude of the guiding RF hexapole in the micrOTOF, supporting surface interactions.

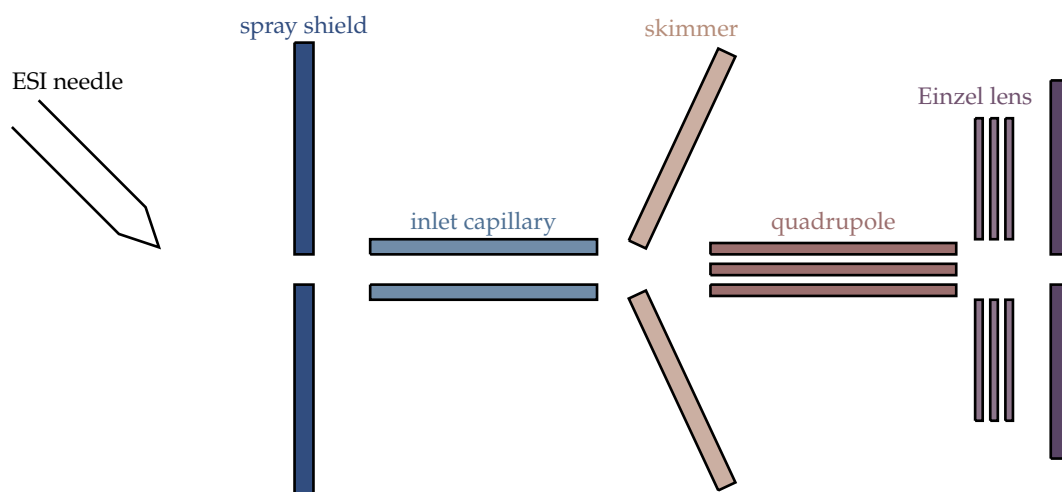
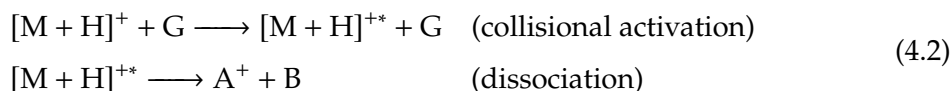


Figure 4.4: Scheme of ion source and simplified transfer stage of an ESI mass spectrometer system.

4.5.1 Collision-induced dissociation

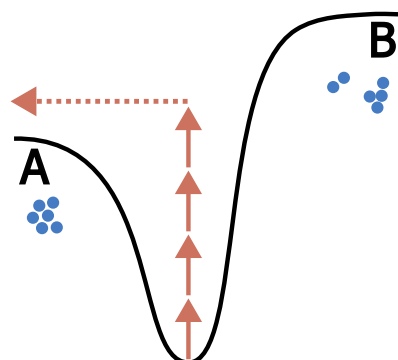
In collision-induced dissociation (CID), a particle is fragmented by accelerating it through a gas, where it collides with neutral background gas particles [108, 109]. In modern mass spectrometers, this is typically achieved by subjecting the particle to multiple low-energy collisions (*low-energy CID*, kinetic energies of < 100 eV) as seen in Figure 4.5, where after each collision a bit of impact energy is redistributed into internal degrees of freedom. *High-energy CID* (with a few keV collision energy), where only few collision take place but with much higher impact energy, is also rarely carried out, but is not the main mechanism used for CID [110–112]. After enough energy is acquired in the internal degrees, the particle can dissociate along a low-energy fragmentation pathway. The CID for a exemplary protonated molecular analyte takes place in two separate steps [113]



with the energy transfer of the activation step happening within 10^{-15} to 10^{-14} s. Collision-induced dissociation is most often done explicitly in a collision cell (e.g. in a triple quadrupole system), where a comparably high background gas pressure (≈ 10 mTorr) is introduced to induce a higher amount of collisions. In some instruments additional potential gradients are applied to lens' and other electrode elements to facilitate higher energy collisions in transition to the transfer stage region [114, 115]. Also in some instruments so called fragmentor voltages can be applied to additional electrodes placed in the ion source region, leading to early in-source CID fragmentation [116].

However, CID is still predominately found in dedicated collision cells or used in ion traps and droplet fragments might be created by intensive CID if one of these components is used in an instrument.

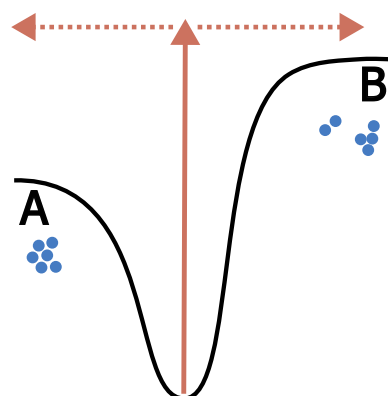
Figure 4.5: *Low-energy CID fragmentation pathways. As multiple low energy collisions are undergone, eventually enough internal energy is available for dissociation.*



4.5.2 Surface-induced dissociation

Surface-induced dissociation (SID) as an explicit method for particle fragmentation uses intentionally placed surfaces inside an instrument, where the collision of a particle with the surface leads to dissociation [117]. Such surface collisions lead to a large amount of energy being suddenly deposited into the particle (see Figure 4.6), which also allows to access diverse high-energy fragmentation pathways in contrast to CID. The high conversion rate between kinetic and internal energy of about 12–23% enables utilization of much lower kinetic energies in the range of 10–200 eV [118] to obtain various different fragmentation pathways. How effective a surface collision is and what fragmentation is possible is thereby not solely dependent on the kinetic energy but also on the impact angle between surface and particle [117, 118].

Figure 4.6: *SID fragmentation pathways. One, intense surface collision leads to fast dissociation with a possible high-energy fragmentation pathway.*



It is possible that droplets can collide with individual components (lenses, multipoles, etc.) on their way through the transfer stage (ref. Figure 4.4), as the droplets follow different trajectories depending on their actual size and internal energy state, not all of which lead stably through the transfer stage.

SIMULATION SOFTWARE

Several different frameworks and software packages were used for the numerical simulations performed in this work. The most notable programs are briefly described in this chapter.

5.1 LAMMPS

LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) [119] is the simulation framework employed for the molecular dynamics studies of charged droplet surface collisions (ref. chapter 7). It is a command-line classical molecular dynamics simulation code with a primary focus on material modeling. The code models particle ensembles on an atomistic level, but also supplies support and force fields for mesoscopic and coarse-grained systems. Furthermore, it is parallelized with MPI (Message Passing Interface) and is completely open-source under GPLv2¹.

LAMMPS allows to combine multiple simulation features in a modular way within one single input script with its own, relatively simple syntax. The main way to modify a molecular simulation is by pairing so called *fixes* and *computes*. Additionally, there are commands for changing of global simulation settings, general I/O operations, creating molecule/particle groups as well as for starting a simulation run. The input file is read line by line, with commands taking immediate effect. Listing 5.1 shows a simple input file for a LAMMPS simulation run. Each input file starts with an initialization step in which general parameters are set e.g. the unit system, the dimensionality or the boundary style (fixed, periodic, ...). After the initialization, the geometry of the simulation can be defined. With `create_atoms` atoms can be created inside a predefined area using e.g. `create_box` following a specific lattice geometry. The parameters of the placed atoms like the mass can then be adjusted. In the final steps before a simulation is actually run, styles, fixes and computes can be called: `pair_style` defines which force field to use, while `pair_coeff` sets the exact parameters; velocities of the particles can be fixed; the integrator style is chosen (`fix 1 all nve`) and additional other simulation modification can be introduced

¹<https://www.gnu.org/licenses/old-licenses/gpl-2.0.en.html>

like placing of a reflective wall. Finally, the simulation is simply run for a specified amount of time steps with `run`.

Overall, there is a wide variety of fixes and styles available, making it easy to create an appropriate numerical simulation system for many physical real-world problems. Yet, due to its modular source code nature, if a feature is currently not implemented, it is also straightforward to extend LAMMPS. LAMMPS does, however, not offer a built-in way to analyze or visualize any results produced by it. For post-processing other software is employed like Ovito and Python scripts.

Listing 5.1: LAMMPS input file example

```
1 # Initialization
2
3 units      metal
4 dimension  3
5 boundary   p f p
6
7 atom_style atomic
8 neighbor   2.0 bin
9
10 # Create geometry
11
12 lattice    sc 10
13 region     box block 0 10 0 10 0 10
14 create_box 1 box
15 create_atoms 1 box
16
17 mass       1 39.95
18
19 # Simulation settings
20
21 pair_style  lj/cut 8.5
22 pair_coeff   * * 0.01 3.4 8.5
23
24 velocity    all create 300 482748
25 fix         1 all nve
26 fix         ywalls all wall/reflect ylo EDGE yhi EDGE
27
28 thermo      1000
29
30 # Run
31
32 run         10000
```

5.2 SIMION

SIMION [120] is a software package for charged particle optics, focusing on the calculation of electric fields for a given electrode geometry and the simulation of charged particle trajectories through those fields. The system of interest's underlying geometry and starting conditions can be defined using the various interfaces provided by the software package. A geometry modeling language is provided, allowing to mathematically define complex electrode geometries [121]. User programs, written in Lua, can alter the particles' traversal through the system. This allows for example for further interactions of ions with electrodes. Implementation of background gas collision models is also possible. Examples of these include the hard-sphere collision model (HS) [78] and viscous damping through Stokes' Law with molecular diffusion modeling (SDS) [122]. Electrostatic fields are solved by solving of the partial differential Laplace Equation via finite difference methods (ref. [123]), which are confined to a regular grid (coined *potential array* in SIMION). Actual ion trajectories in those fields are then calculated by integration of Newton's equations of motion with a Runge-Kutta 4 [121]. A complete geometry with its solved electrostatic mesh and user programs is encapsulated in an "*ion workbench*". While SIMION is restricted to regular grids as potential arrays (PA), multiple PAs can be combined within one ion workbench to allow for varying mesh resolution and symmetries when simulating a large structure.

SIMION is widely used for simulation of lens elements, mass spectrometric devices and ion sources.

5.3 IDSimF

The Ion Dynamics Simulation Framework (IDSimF) [124, 125] is a command-line, open-source tool for the simulation of non-relativistic dynamics of molecular ions in mass spectrometry and ion mobility applications by calculation of ion trajectories in given electric fields. Ion trajectories can be integrated either by the velocity Verlet or Runge-Kutta 4 method. The electric fields are thereby not solved by IDSimF, but can either be analytically described or imported from SIMION or COMSOL [126]. IDSimF is implemented in C++ and partly parallelized with the OpenMP [127] library. Data structures and algorithms are compartmentalized in modules, i.e. specialized libraries, and can be combined into an application to solve a specific simulation task, which is then compiled into a separate C++ executable. Available features include: i) space charge simulation either with a Barnes-Hut tree [128] or via external FFM libraries [129–131], ii) various collision models including HS, SDS, VHS and molecular dynamics based, iii) chemical reaction kinetics. Additionally, there are already numerous pre-implemented applications provided for simulation of RF-only quadrupole cells, TWIMS, DT-IMS and ion traps.

Input files are given in the JSON format, which is a human-readable key-value list format and output of the ion trajectories is saved in HDF5 [132] files. IDSimPy [133] can be used

as a post-processing library for analysis and visualization of those HDF5 files.

5.4 MobCal / MobCal-MPI

MobCal [83] is a software framework, written in Fortran, for the prediction of ion collision cross sections resp. ion mobilities under low-field conditions. The ion mobility in the low-field limit can be described by the Mason-Schamp equation [134]

$$K(0) = \frac{3}{16} \left(\frac{2\pi}{\mu k_b T} \right)^{0.5} \frac{ze}{N\Omega(T)} \quad , \quad (5.1)$$

where μ is the reduced mass of the ion and neutral particle pair, k_b is the Boltzmann constant, ze is the ion charge, T is the temperature of the collision gas, N is the gas density and $\Omega(T)$ is the collision cross section at that specific temperature. The collision cross section is approximated by calculating multiple collisions between ion and background gas using a molecular dynamics trajectory method [83] and solving the momentum transfer integral, averaging over all possible velocities and geometries of the ion / neutral pair [83, 135]

$$\Omega(T) = \frac{1}{8\pi^2} \int_0^{2\pi} d\theta \int_0^\pi \sin(\varphi) d\varphi \int_0^{2\pi} \frac{\pi}{8} \left(\frac{\mu}{k_b T} \right)^3 d\gamma \int_0^\infty g^5 e^{-\frac{\mu g^2}{2k_b T}} dg \int_0^\infty 2b[1 - \cos(\chi(\theta, \varphi, \gamma, g, b))] db \quad (5.2)$$

with θ, φ and γ giving the orientation of the ion with respect to the ion-collision gas center-of-mass axis, g as the relative velocity between the two particles, b as the impact parameter and χ as the scattering angle of the collision gas after collision with the ion. This scattering angle is evaluated numerically through the trajectory integration following the concepts presented in chapter 2. The force field uses the 12-6 Lennard-Jones potential and only has potential parameters for helium as background gas.

In 2012, MobCal was extended by the introduction of molecular nitrogen as a background gas [45]. MobCal-MPI [135, 136], then published in 2019, consequently updated the used force field potential functions, swapping the 12-6 Lennard Jones for the modified Buckingham potential, and the force field parameters. Additionally, MobCal was parallelized with MPI, offering a speed increase of up to 64-fold [135]. Recent updates of the MobCal-MPI suite also implemented the calculation of high-field ion mobilities using the two temperature theory (2TT) [137].

5.5 Other libraries / software

5.5.1 AmberTools

The AmberTools [138] suite is a collection of mostly open-source programs and scripts for creation of force fields, ab initio calculations, molecular dynamics simulation, free energy

analysis and similar tasks. It allows to prepare molecular structures, assign force fields and carry out molecular dynamics simulation for energy minimization and conformational searching. In this work, primarily the antechamber script is used for molecular format conversion.

5.5.2 Avogadro

Avogadro [139] is an open-source molecular visualization and editing tool. Figure 5.1 shows the user interface and an exemplary DNA fragment, which was built with the automatic DNA build function. It also allows to build molecules by importing by name, PDB files, SMILES codes and by manual construction. Moreover, structures like supercells, slabs and crystal cells can be generated. Avogadro also has several force fields implemented and allows for geometry optimization. Molecules can be saved in many different file formats, supported by Open Babel [140] integration.

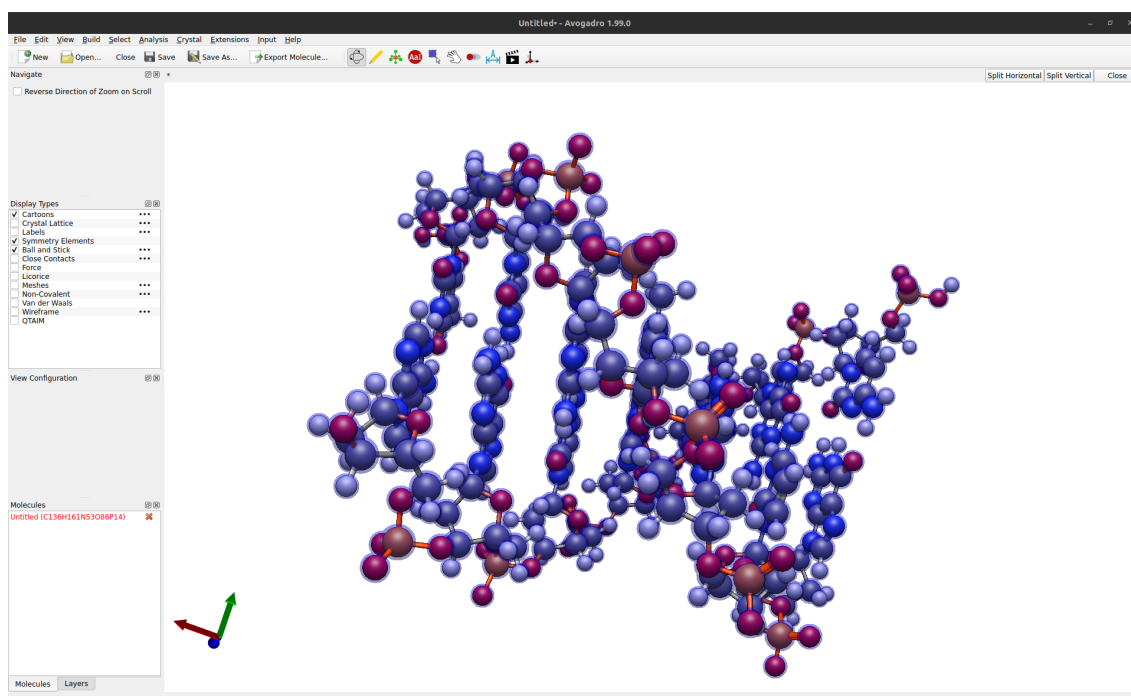


Figure 5.1: *Graphical user interface of Avogadro.*

5.5.3 Ovito

Ovito [141] is a visualization and analysis tool for particle simulations made by other software. It has built-in support for Gromacs [142], VTK [143], LAMMPS and many more input formats. The graphical user interface (see Figure 5.2) allows for data exploration of particle trajectories in real-time. Additionally, Ovito has an extensive pipeline-based analysis workflow, where multiple operations/modifiers are applied in sequence to the imported particle data. Modifiers include coloring of specific elements, plotting of a

parameter over time, deleting elements, coordination analysis as well as cluster analysis. Moreover, a high-quality rendering pipeline is attached offering RayTracing support and video creation of whole trajectories. In addition, Ovito offers a Python API to automate analysis of the data and to integrate visualization and processing functions into already existing custom software. Pipelines built in Ovito can be automatically transformed to Python code, reducing the need for complex programming tasks.

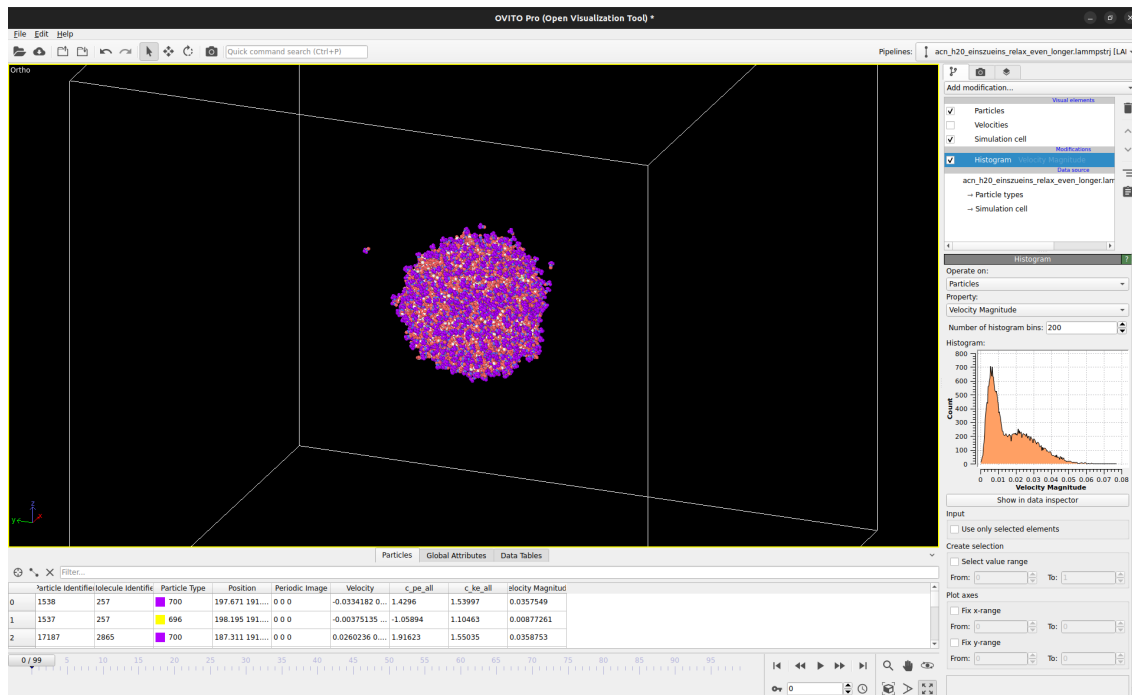


Figure 5.2: Graphical user interface of Ovito.

5.5.4 moltemplate

Moltemplate [144] is a command-line script for text-based molecular building for LAMMPS. With it, all-atom molecular simulation systems can be prepared and force field parameters from supported force fields like AMBER [145] and OPLS-AA [52] can be assigned. However, assignment is done manually as no automatic atom typing is possible. Moltemplate offers support for coarse-grained models and for combination of different representations of all-atom / coarse-grained. Running the moltemplate script on a valid input file produces a data file (containing all information about the atoms of the system) and input file for LAMMPS, which can be used as is for running a simulation in LAMMPS. The moltemplate input file is a LT file, which includes coordinates, bond topology, angles, force-field parameters and further constraints of a molecule. In the LT file, this molecule can then be further customized and used as a building block for the complete simulation system.

5.5.5 PACKMOL

PACKMOL [146] is a script allowing for packing of molecules in regions of space under user chosen spatial constraints. Given the types and coordinates of each molecule in a MD system, in an iterative process the whole system is relaxed towards the state where all constraints are honored. With this, ordered systems like layers and spheres can be generated. PACKMOL offers support for PDB, XYZ and TINKER input files.

SIMULATION OF GAS-PHASE ION-NEUTRAL COLLISIONS OF MOLECULAR IONS

In this chapter the molecular dynamics trajectory method as well as the variable hard sphere model are presented and used for ion mobility predictions. In addition, characteristics of the field dependent ion mobility resulting from the MD model are discussed. Moreover, the process of implementing molecular nitrogen as a neutral gas collision partner and the ensuing difficulties and possible mitigations are highlighted.

6.1 Motivation

Several processes found in mass spectrometric and ion mobility devices are complex in nature and require advanced modeling of ion-neutral collision effects acting on ions / analytes in those devices. Often ion trajectory simulation tools like SIMION are used to study ion traversal through mass spectrometry / ion mobility instruments. However, those programs often have limited accuracy for more complex systems as the common collision models employed in those programs, like HS and SDS, are simple and do not consider many physical aspects of actual collisions. In the context of electrospray ionization, the generated droplets are involved in complex molecular dynamic interactions. In a long-term effort to eventually simulate, using a wide array of simulation tools, whole trajectories of the droplets from ion source to detector more elaborate collision models are necessary.

Research has shown that more detailed collision models are needed to obtain good accuracy of ion mobility predictions. At the time, there are about three very well established ion mobility resp. collision cross section prediction software frameworks: MobCal [83], IMoS [85] and Collidoscope [84]. All three programs share a common general approach for collision cross section calculation. In the so called *trajectory method*, many individual collisions between an ion and a neutral background gas particle are computed. Each collision is thereby randomized in starting velocity and relative position/geometry, spanning the whole geometric space. The collisional interaction is approximated with a molecular

dynamics approach in which a defined classical force field potential function is evaluated at each time step. Through averaging over all input parameters, an approximation of the collision cross section using the momentum transfer integral is acquired [83]. Low-field mobilities are then calculated via the Mason-Schamp equation. Based on accessible software and ongoing research in the field, ion mobility predictions emerged as a good benchmark problem for method development, suitable for transfer to the ESI droplet modeling problem. Essentially all three programs (except IMoS) are exclusively used for prediction of low field mobilities and optimized for very large protein and peptide structures. In an effort to also provide a module capable of computing mobilities for low and high field as well as for small, molecular ions, IDSimF is extended by a molecular dynamics trajectory method based on the working principles of MobCal, IMoS and Collidoscope. Using smaller ions also allows for more stringent validation of this trajectory method, to ensure known limits for its final application to the ESI droplet trajectory modeling. As already mentioned in section 5.4, MobCal-MPI is an enhancement of the MobCal suite which, in contrast to MobCal and Collidoscope, is able to calculate high-field mobilities and is open-source (unlike IMoS). As such, MobCal-MPI is used as the reference / comparison framework in this work.

Overall, this work aims to

- establish a molecular dynamics trajectory method in the open-source software IDSimF
- validate and illustrate limits of the model
- predict ion mobilities for the benchmark problem of a DT-IMS simulation
- also implement a simpler VHS model which is, however, capable of tracking internal energy (inelastic collisions) as a first step to eventually simulate MD collisions with simple inelasticity

6.2 Molecular dynamics based trajectory method

A molecular dynamics based trajectory method following the ideas of MobCal, IMoS and Collidoscope was implemented in IDSimF [82]. In each potential collision carried out with the MD trajectory method several steps have to be carried out, which are

1. determination of collision event
2. initialization of the collision
3. integration of the collision

and will be described in detail in the following sections. In Figure 6.1 the general process of one time step of the ion trajectory integration with MD collisions is sketched.

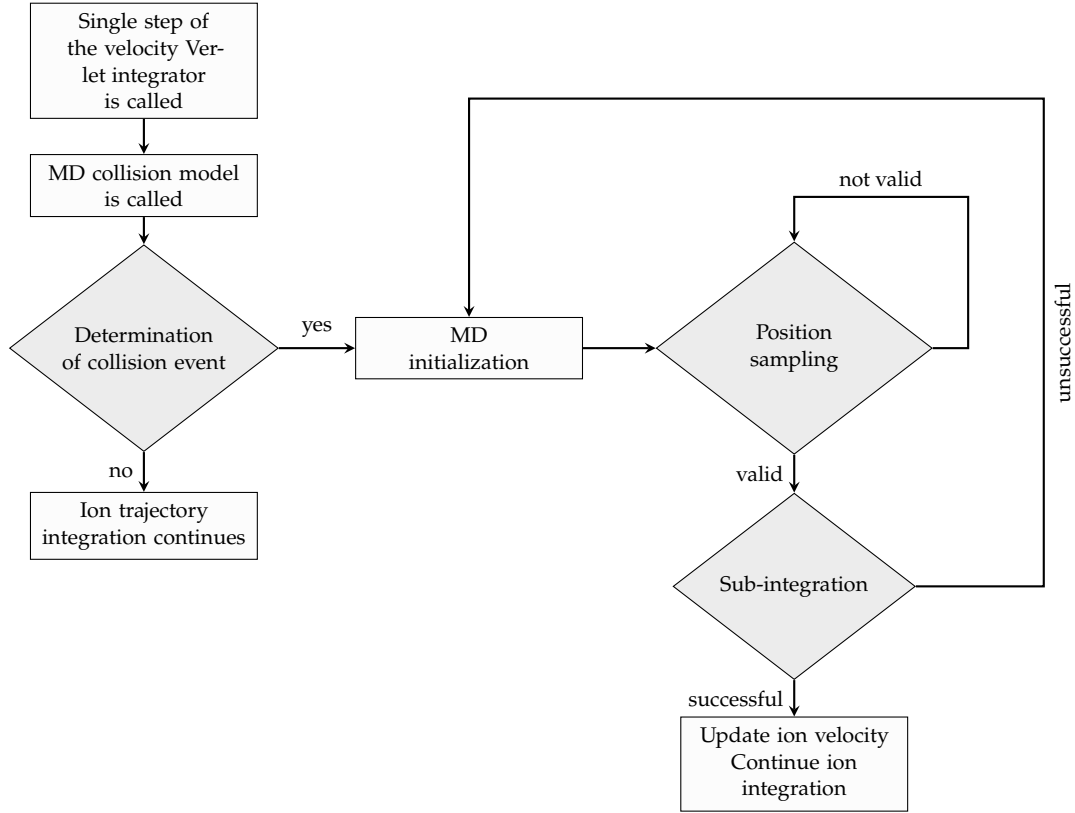


Figure 6.1: Sketch of the integration of the MD collision model steps into a single ion trajectory integration step.

Determination of collision event

The ion trajectories are integrated with the velocity Verlet or Runge-Kutta 4 method in IDSimF (here only the velocity Verlet method is used). By applying a continuous background gas pressure in the simulation domain, it becomes possible for the ion to collide with a background gas particle in any time step of the simulation. For the HS model (ref. subsection 3.3.1), a simple equation defines the collision probability of an ion in a time step in dependence of the collision cross section, temperature, time step length and pressure. As a first approximation, this simple equation can be transferred to the MD model without any changes. Even though technically the collision cross section of MD particles is much larger (or rather in a sense infinite) than for HS particles, this approximation is valid with a slight correction of the collision cross section by scaling the CCS by a factor β .

Overall, this means that in each time step for each ion, a collision probability following the HS approach is calculated and a random number is computed. If this random number is below this probability, a collision takes place meaning the normal ion integration with a velocity Verlet (*overarching simulation*) switches to the collision integration using molecular dynamics approaches (*sub-integration*).

Initialization of the collision

In a collision event, the start configuration of the collision has to be correctly initialized. First, this requires the construction of actual molecular structures for the ions and also for the background gas particle as rigid bodies. Thereby, each atom of the particle is defined by coordinates relative to the center-of-mass of the particle, the mass, the (partial) charge as well as the force field parameters. Both rigid particles / molecules are then initially rotated randomly and kept fixed over the whole collision integration. Molecular rotation as well as vibrations are not considered in this approach yet.

In a second step, a relative collision geometry with a "valid" trajectory has to be found by position sampling. For this, the frame of the collision is shifted such that the ion velocity is zero, as the motion in the laboratory frame is irrelevant for the collisional interaction. The laboratory frame background gas particle velocity $\mathbf{v}$ is randomly sampled from a 1D Maxwell-Boltzmann distribution in each component and then also shifted to the stationary ion reference frame. As a last preparation step before the position sampling, the ion's position is set to the coordinate origin (laboratory frame movement is irrelevant). Finally, the position sampling of the background gas particle is carried out:

1. define a spawn sphere for the background gas particle with radius r_{spawn} . The background gas particle is placed on a randomly drawn point $\mathbf{p}$ on this sphere. The sphere needs to be sufficiently large to minimize the initially experienced force between ion and background gas particle (ideally it should be zero), since otherwise the collision would not be energy conserving.
2. sample point $\mathbf{p}$ by generating three uniformly distributed numbers between -1 and 1. If the magnitude of the vector, constructed by those three values, is less than 1, it is acceptable to take this vector. In the other case, a new vector is generated until this condition is fulfilled. The result vector is then scaled by $r_{\text{spawn}}/|\mathbf{p}|$. This process guarantees a uniform distribution of position vectors on the spawn sphere [147].
3. before the position sampling, a random velocity vector was chosen for the background gas particle. While the position is correctly set on the spawn sphere, the velocity vector could point in any direction and might not even point towards the ion in the coordinate origin. Ideally, only collisions which have a "direct" interaction between both particles should be integrated. This means only collisions which penetrate the collision cross section, a sphere with radius $r_{\text{collision}}$, are valid. As such, not all sampled positions / velocity combinations should be used and need to be filtered again. For this purpose, α is defined as the angle between the background gas velocity vector $\mathbf{v}$ and the vector connecting point $\mathbf{p}$ and the coordinate origin (*midpoint vector*). Additionally, θ is the angle between the midpoint vector and the vector connecting $\mathbf{p}$ and the collision sphere in a right angle.

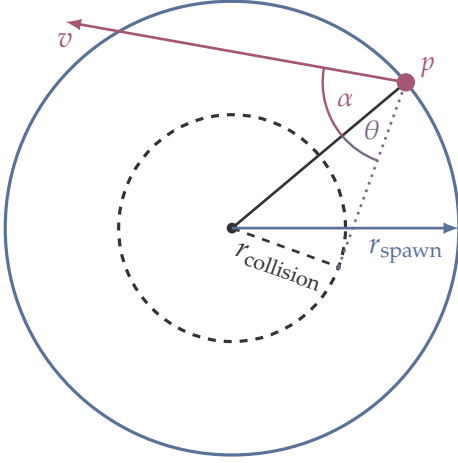


Figure 6.2: Two dimensional example of the initialization sampling step in a molecular dynamics collision. A particle with position $\mathbf{p}$ and velocity $\mathbf{v}$ would need to enter the collision sphere for the starting conditions to be considered. A crude approximation of a successful "hit" can be gained by comparing the two angles α and θ .

Mathematically, these two angles can be computed as

$$\begin{aligned}\alpha &= \arccos \left(\frac{-\mathbf{p} \cdot \mathbf{v}}{r_{\text{spawn}} \|\mathbf{v}\|} \right) \\ \theta &= \arcsin \left(\frac{r_{\text{collision}}}{r_{\text{spawn}}} \right)\end{aligned}\tag{6.1}$$

Valid collisions are those for which angle $\alpha \leq \theta$, as otherwise geometrically the background gas particle will never enter the collision sphere. Therefore, the position sampling continues until a point $\mathbf{p}$ is uniformly distributed on the sphere and fulfills the condition necessary for collision sphere penetration. Figure 6.2 illustrates the computed angles for a two dimensional case in which a resampling is necessary as $\alpha \leq \theta$ does not hold.

4. since the molecular dynamics approach is based on evaluation of force fields, which typically include long-range attractive forces (e.g. the ion-induced dipole potential), the collision cross section would technically be as large as necessary for the force to become essentially zero. Numerically, this is not feasible and the collision cross section is therefore simply enlarged by a user set factor dependent on the supplied force field. The effective collision cross section was already corrected for the collision probability calculation in the collision determination step by such a user set factor called β . This, overall, ensures that sufficiently many different collisions are integrated including grazing collisions of the two particles.

Integration of the collision

After successful initialization of the collision the sub-integration starts. Available numerical integration methods are Leapfrog, Runge-Kutta 4 and adaptive step-size Runge-Kutta-Fehlberg (RKF45). However, only the RKF45 is used for productive simulations, as it has by far the best computational performance (see subsection 6.2.2). The forces are evaluated in an atomistic MD like set-up with a combination of different force field functions as

described in section B.4, i.e for each pair of atoms of the different molecules all force functions are evaluated and then summed up.

The trajectory integration additionally includes a few checks to ensure correctness/validity. Over the course of the integration, if the particles enter the defined (scaled) collision sphere, the collision is marked as *hit*. Only collisions which "hit" are valid, as otherwise the consistency between collision probability calculation and actual integrated collision would be lost. Additionally, the collision integration is stopped as soon as the distance between both particles exceeds r_{spawn} , as no further relevant interaction takes place after this point (assuming a sensible choice for the spawn sphere was made; however otherwise the energy would not be conserved either way).

Energy conservation is checked after integration by comparison of input energy and output energy of the system. Since all collisions are elastic, kinetic energy cannot be deposited into internal energy and except from some numerical inaccuracies both energies should be identical. Currently, energy differences up to 10 % are allowed but this value can be freely changed. If energy is not conserved, a new trajectory is sampled (re-construct position and velocity of the background gas). Overall, an individual collision event is retried for up to 100 times after which the whole collision event is discarded, issuing a warning to the user. If the integration is successful the ion velocity is updated and the ion trajectory integration continues.

6.2.1 Input parameters and usage

A DT-IMS simulation uses a human-readable .json file, which is in key-value pair format. This file defines important parameters of the simulation and additionally sets values for the parameters of the MD model. The following table summarizes all parameters that need to be set. In the idealized drift tube ion mobility (DT-IMS) application an analytical electric field in x -direction is assumed over a specified length, modeling an ideal drift tube. After reaching the end of the drift tube the particles are terminated. The background gas is, as usual for IDSimF, given implicitly by a continuous pressure and temperature field, which defines the background gas density.

Table 6.1: All available input parameters of the drift tube IMS application in IDSimF and their function.

parameter	description
sim_time_steps	Number of time steps of the overarching ion trajectory simulation
dt_s	Time step length of the overarching ion trajectory simulation (s)

concentrations_write_interval	Interval between writing to the log file for the concentrations of the species (part of the reaction (RS) module)
trajectory_write_interval	Interval between writing to the standard output file in .h5 format which records the ion trajectories
trajectory_write_velocities	Flag to define if the ion velocities should also be written to the .h5 output file
space_charge_factor	Factor of the space charge calculation, if no space charge is needed the value needs to be set to zero
reaction_configuration	File path to the input file defining the RS configuration, which gives all reactions in the system
n_particles	Number of particles to simulate
electric_field_mag_Vm-1	Strength of the electric field that is applied in x -direction (V/m)
start_width_yz_mm	Size of the starting zone of the ions in y - and z -direction (mm)
start_width_x_mm	Size of the starting zone of the ions in x -direction (mm)
stop_position_x_mm	Position in x -direction at which the ions are terminated (mm)
transport_model_type	The type of collision model to use (HS, SDS, VHS, MD, ...)
background_temperature_K	The temperature in K of the background gases (multiple gases can be used)
background_partial_pressures_Pa	The pressure in Pa of the background gases (multiple gases can be used)
collision_gas_masses_amu	The masses in u of the particles of the used background gases
collision_gas_diameters_angstrom	The diameters in Å for the collision cross section for the background gas particles
collision_gas_polarizability_m3	The polarizability constants of the background gases in m^3
collision_gas_identifier	The unique identifier of the background gases to select the molecular structure for the MD model from the molecular structure file

CHAPTER 6. SIMULATION OF GAS-PHASE ION-NEUTRAL COLLISIONS OF MOLECULAR IONS

<code>particle_identifier</code>	The unique identifier of the ions to select the molecular structure for the MD model from the molecular structure file
<code>md_configuration</code>	File path to the MD model input file that defines all the molecular structures
<code>sub_integrator_integration_time_s</code>	Length of the MD sub-integration in s
<code>sub_integrator_step_size_s</code>	Time step length of the MD sub-integration in s
<code>force_field</code>	Different types of force field combinations of van der Waals, ion-induced and quadrupole moment
<code>potential_function</code>	Sets either 12-6 Lennard-Jones or mod. Buckingham as the van der Waals potential
<code>collision_radius_scaling</code>	Re-scaling parameter β
<code>spawn_radius_m</code>	Radius of the spawn sphere in m
<code>save_trajectory</code>	Flag to define if the individual MD collision trajectories are saved to a file
<code>trajectory_distance_m</code>	Distance at which the MD collision trajectories are written to the log file if they are saved
<code>trajectory_start_time_step</code>	Time step of the sub-integration at which the MD collision trajectories are written to the log file if they are saved

Since reaction modeling is also implemented in the DT-IMS application, a RS configuration file also needs to be supplied (currently even if no reactions are simulated). The following shows a standard reaction configuration file with no reactions (as reactions were not used here). The file (see Listing 6.1) declares the ions as well as the background gas. For the ion it is especially required to give the correct charge (here second numerical parameter in line 2). The mass (first parameter), the mobility constant (third parameter) and diameter (fourth parameter) are not actually used with the MD model as this is either computed or given elsewhere. For the background gas (isotropic particle, line 3) the neutral gas density is given, which is also only required if reactions are handled.

Listing 6.1: RS configuration file example

```

1 [SUBSTANCES]
2 O2 discrete 31.8 1 3.57e-4 3.1e-10
3 N2 isotropic 2.504e19
4
5 [REACTIONS]
```

The MD model itself is implemented as an additional collision model just like the HS or SDS model. In contrast to the other collision models an additional configuration file in .json format needs to be supplied. This configuration file defines the force field parameters of the individual molecules respectively the atoms contained within the molecules, as shown in Listing 6.2. Important parameters include diameters, relative positions, charges, masses and van der Waals potential parameters. Each molecule has a unique identifier (*name*) that is used in the application configuration to select ion and background gas molecules.

Listing 6.2: MD force field configuration file example

```

1  [
2  {
3      "name": "He",
4      "diameter": 2.8,
5      "atoms": [
6          {
7              "type": "He",
8              "posx": 0,
9              "posy": 0,
10             "posz": 0,
11             "mass": 4.003,
12             "charge": 0,
13             "partCharge": 0,
14             "LJsigma": 2.556,
15             "LJeps": 0.0836
16         }
17     ]
18 },
19 {
20     {
21         "name": "H2+",
22         "diameter": 2.89,
23         "atoms": [
24             {
25                 "type": "H",
26                 "posx": 0,
27                 "posy": 0.375,
28                 "posz": 0,
29                 "mass": 1.008,
30                 "charge": 1,
31                 "partCharge": 0,
32                 "LJsigma": 2.5,
33                 "LJeps": 0.249
34             },
35             {

```

```

36         "type": "H",
37         "posx": 0,
38         "posy": -0.375,
39         "posz": 0,
40         "mass": 1.008,
41         "charge": 0,
42         "partCharge": 0,
43         "LJsigma": 2.5,
44         "LJeps": 0.249
45     }
46
47 ]
48
49 }
50 ]

```

6.2.2 Comparison of integration methods

Several different integration methods as well as their respective properties were discussed in section 2.2. As already mentioned, three integration methods are implemented for the MD model in IDSimF: i) Leapfrog (LF), ii) Runge-Kutta 4 (RK4) and iii) Runge-Kutta-Fehlberg (RKF45).

In an effort to compare the behavior of the three integration methods, a test problem was constructed. A frontal head-on collision between two identical atoms (here: helium atoms) in the x -axis is generated, with one of the atoms initially at rest while the other atom starts with a predefined velocity of 1000 m/s solely in x -direction. Analytically, based on conservation of energy and momentum this results in a complete transfer of the momentum of the moving atom to the resting atom. After the collision, the initially moving atom should be at rest, i.e. zero velocity. Figure 6.3 shows the velocity during this test collision with the RKF45 method.

As already described, the velocity drops to zero and the collision event is "symmetrical", as right before the collision a small increase in velocity is noticeable and the same is seen in a decreasing manner right after the collision. This initial test only considers van der Waals interaction, here in the form of the 12-6 Lennard-Jones potential. All three integrators have one parameter which primarily determines the accuracy of the obtained solution. For both the Leapfrog and Runge-Kutta 4 method this parameter is the time step length Δt . The time step value defines in what spacing resp. resolution the trajectory is sampled. Smaller time steps give a higher resolution and better accuracy, while also having a higher computational cost as more force field evaluations have to be carried out. On the other hand, the RKF45 method has a tolerance parameter instead of a step size. This difference is due to the adaptive nature of the RKF45 integrator, as the step size is automatically changed based on a local error calculation (ref. subsection 2.2.5.2). The tolerance

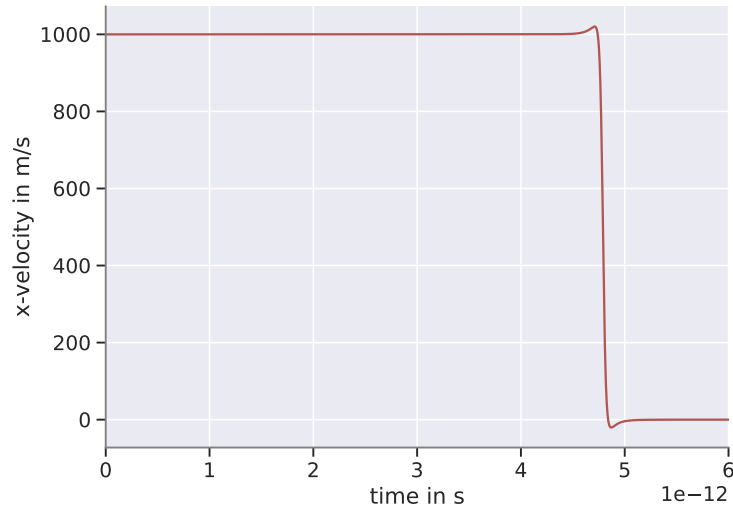


Figure 6.3: Velocity in x -direction in a head-on collision between two helium atoms, where one is at rest and one starts at 1000 m/s. Only the velocity of the initially moving particle is shown here.

defines how fast the step size adaption from one time step to the next is. Higher tolerance values lead to less change in step sizes, i.e. on average larger step sizes are used for a longer time span. For the test problem, each integration method was run for different step sizes or tolerance values. Figure 6.4 shows the residuals to the exact analytical solution for the various step sizes / tolerances for LF, RK4 and RKF45.

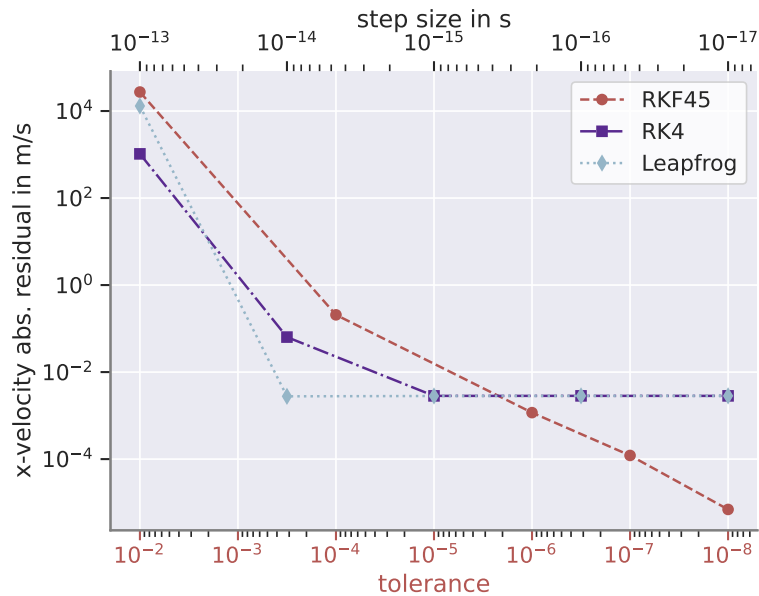


Figure 6.4: Absolute residual of the velocity in x -direction between obtained solutions by the integration methods and the analytical solution for van der Waals interactions. Integration methods were either varied in their step size length (LF and RK4) or tolerance (RKF45) based on provided parameter.

Overall, the lowest residual is obtained for the smallest tolerance value of 10^{-8} of the RKF45 method while both Leapfrog and RK4 plateau around the same values for step sizes between 10^{-15} and 10^{-17} seconds. Despite being a higher order method, RK4 does not give better results than the Leapfrog method, which is due to symplectic methods being more suitable for molecular dynamics systems.

The same procedure was then repeated with an extended force field supplemented by the ion-induced dipole moment. As the basic force field which will be used for prediction of ion mobilities always includes a van der Waals (vdW) component and also an ion-induced dipole moment component (II), the behavior of the integration methods for this case is most interesting. For this, the helium atom initially at rest has one elementary charge assigned, which allows the computation of a force between a neutral particle and a charged particle. In Figure 6.5 the velocity in dependence of time is pictured. Also, for the combination of vdW and II, the analytical end velocity is 0 m/s for the moving particle. The main difference is the much higher velocity increase before the impact as the attractive force is much larger due to the ion induced dipole effects.

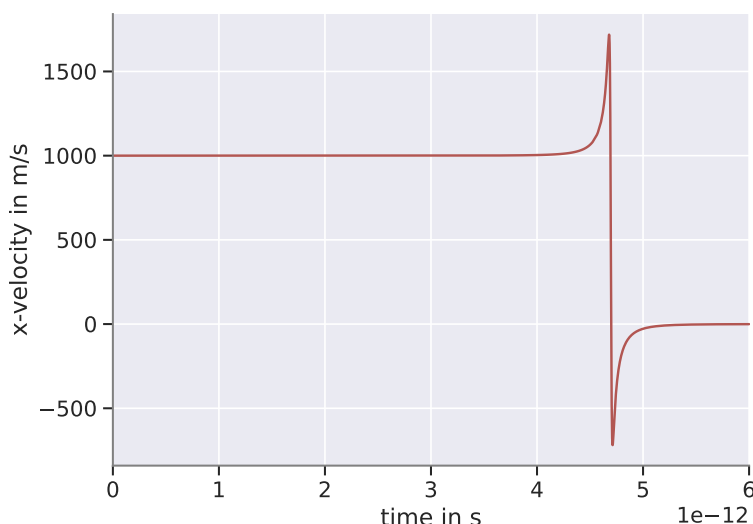


Figure 6.5: Velocity in x -direction in a head-on collision between two helium atoms, where one is at rest and one starts at 1000 m/s. The initially resting particle has a positive charge. Only the velocity of the initially moving particle is shown here.

Again the residual, as seen in Figure 6.6, is computed for all three integration methods using vdW+II. In contrast to the integration with van der Waals forces only, the Leapfrog method obtains the lowest residuals here. The Runge-Kutta 4 method gives worse results than Leapfrog for all used step sizes. Additionally, the RKF45 is initially the worst of all three methods and only returns equal residuals to the RK4 method for the two smallest tolerance levels. The strong integration differences between the two cases (vdW vs. vdW+II) primarily emerge from the larger forces present because of the ion-induced dipole moment. Due to the larger attractive forces in the beginning, the particles can even enter further into the repulsive potential, increasing the difficulty of accurate integration.

The extremely bad performance of the RKF45 for high tolerances is due to the too slow time step adaption, as higher errors are permitted and the integration methods basically oversteps the part of the force interaction, where the force is especially high. This is not happening for vdW only, as the attractive potential in this case is very small and the repulsion is very short ranged, while the ion-induced dipole potential is a long-range force.

Altogether, the Leapfrog method mostly likely performs better in this case since the symplecticity is a much favorable property for molecular dynamics systems compared to the higher-order integration.

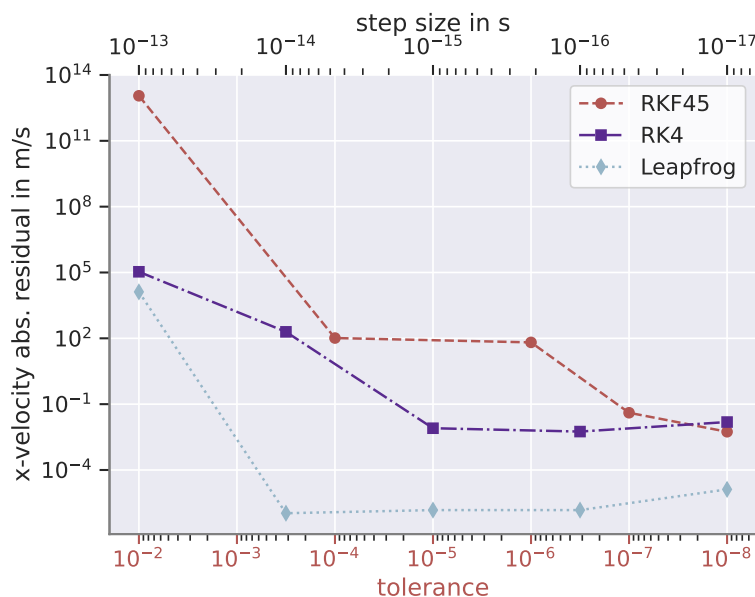


Figure 6.6: Absolute residual of the velocity in x -direction between obtained solutions by the integration methods and the analytical solution for vdW+II. Integration methods were either varied in their step size length (LF and RK4) or tolerance (RKF45) based on provided parameter.

In a further step of the integrator evaluation, the computational performance of all three integration methods is compared. For this, a benchmark application is implemented in which a standalone MD model is constructed, without any overarching simulation processes involved, i.e. no velocity Verlet is used. A particle count (" p ") and a sample amount (" s ") is given as user input to the benchmark program. For each particle, a MD collision process is called and this is in total repeated s times. The time it takes for the benchmark application to go through the sample / particle loop is recorded. The wall time of each integration method is then compared for three different particle / sample combinations and illustrated in Figure 6.7. Each combinations is repeated six times. The standard deviation of the simulation runs is given by the error bars. Collisions between Ar^+ and He at 10000 Pa were carried out as benchmark problem. The collision radius was scaled by $\beta = 2$ and the radius of the spawn sphere was 25 Å. A step size of 10^{-16} s is used for both fixed step size integrators and a tolerance of 10^{-8} for the adaptive step size

method. The top panel shows the measured wall time on a linear scale, while the bottom panel gives the wall time on a logarithmic scale. A logarithmic scale allows to see even the very small times, while the top panel illustrates the actual performance ratio between the integration methods much better. The actual absolute values of the observed wall time are dependent on the used architecture / CPU and are not discussed further. Relevant is only the performance of the methods relative to each other. There is a clear difference between the Leapfrog and Runge-Kutta 4 methods, as the RK4 is a factor of four slower. This is expected, since the Leapfrog method only evaluates the force function once while the RK4 carries out four force calculations per step. Compared to Leapfrog and RK4, RKF45 is by far the fastest method available due to the adaptive step size capability.

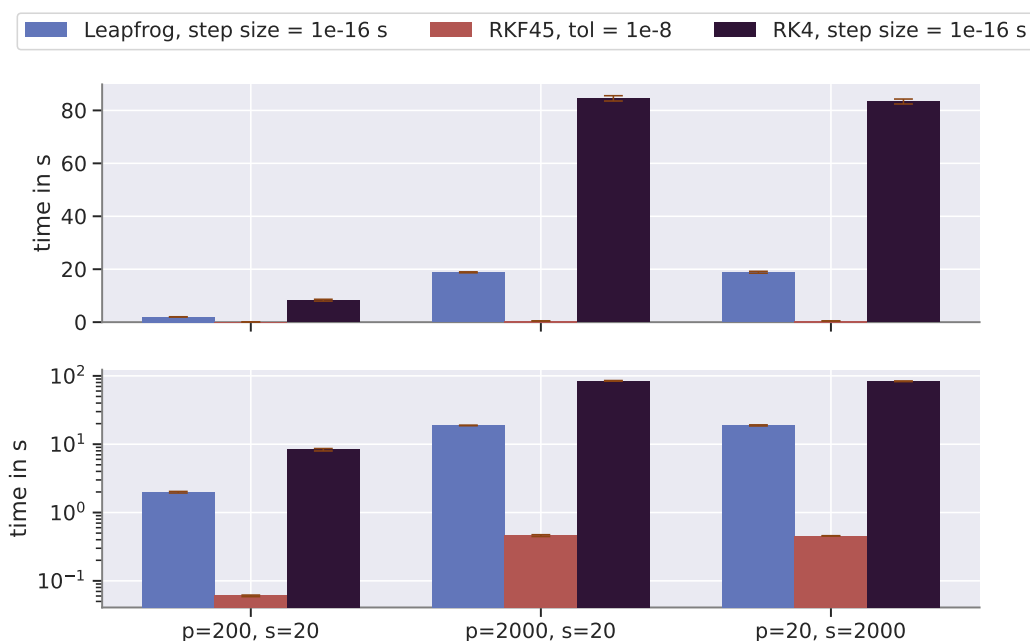


Figure 6.7: Measured wall time of the benchmark application with varied particle / sample configurations for all three integration methods. Each configuration was repeated six times and the standard deviation is given by the error bars. The bottom panel shows the wall time on a logarithmic scale to better visualize the wall times.

For slightly larger problem sizes ($p=2000$ and $s=20$ or the inverse) the Runge-Kutta-Fehlberg method only takes a small fraction of the Leapfrog run time. The RKF45 is almost 20-fold faster than the LF and in turn 80-fold faster than the RK4 method. A major advantage of the adaptive step sizing lies in basically “skipping” a large part of each integration where the potential is still close to zero, before reducing step sizes in the interesting part of the trajectory integration (essentially the actual collisional interaction). In the case of the benchmark problem, a spawn sphere of only 25 Å was necessary to guarantee energy conservation / accurate integration, as helium does not have strong, long-range interaction potentials. If stronger polarizing gases or gases with quadrupole moment are integrated (e.g. argon or nitrogen) a much larger spawn sphere would be required and the adaptive

step size method would perform even better in comparison.

Overall, while the Leapfrog method computes more accurate collision trajectories compared to the Runge-Kutta-Fehlberg integrator due to symplecticity, the RKF45 becomes the method of choice. The computational time required to simulate a whole collision event is so much shorter that it becomes desirable to rather repeat a handful of collisions over the course of a complete ion trajectory simulation than to slowdown the simulation by a factor of 20.

6.3 Ion-neutral collisions with monoatomic neutral gas

Initial validation and parameter sensitivity studies were conducted for monoatomic neutral gas particles with the objective of reducing computational effort for the test cases and simplifying the interpretation of characteristics and parameter dependencies of the MD method. Moreover, there is a large amount experimental ion mobilities for small systems like O_2^+ in helium or argon accessible in the literature, allowing for comparison between numerical predictions and experimental data.

6.3.1 Standard simulation run

As the standard application of choice the drift tube ion mobility spectrometry simulation implemented in IDSimF is chosen. The DT-IMS simulation was then expanded by the inclusion of the MD collision model. An analytically defined constant electric field in x -direction moves the ions forward, while the ions can collide with background gas particles on their way. For most simulations presented in this chapter the same simulation input parameters were chosen. They are given below in Table 6.2. Deviations from the standard parameter set are mentioned if necessary. Force field parameters of all used atoms and for all different force field functions are documented in Appendix A.

Table 6.2: *Input parameter values for a standard simulation run of the DT-IMS simulation application in IDSimF.*

input parameter	value
Total simulation time	3 μs
Step size for velocity Verlet (overarching simulation)	10^{-11} s (simulations done until subsection 6.3.5) and 10^{-12} s (for simulations after subsection 6.3.5)
Number of ions	2000
Space charge	no
Starting position	randomly placed in 3D box of size $1 \times 1 \times 1$ mm ³
Drift region length	10 cm

Electric field strength	varies, reduced electric field is kept between 5 to 100 Td
Background gas pressure	2000 Pa resp. 20 mbar
Background gas temperature	298 K
Maximum integration time of collisions	10^{-10} s
Integration method	RKF45
Tolerance / Step size	10^{-8} with initial step size of 10^{-16} s
Spawn radius collision	30 Å for helium, 50 Å for argon
Force field function	12-6 Lennard-Jones + ion-induced dipole potential
Polarizability	$0.205 \cdot 10^{-30} \text{ m}^3$ (helium), $1.664 \cdot 10^{-30} \text{ m}^3$ (argon)

6.3.2 General trajectory characteristics

In a first step, the general behavior of the MD trajectories is discussed. Each collisional interaction can be classified by one of the three possible collision types:

- *Head-on collisions* or also called frontal or reflective collisions. The scattering angles here lie between 180° and 90° .
- *Grazing collisions*. A slight attractive, long-range potential is experienced by the particles but no direct interaction with the repulsive potential of the van der Waals potential takes place. The particles thus never enter the interaction sphere defined by the σ parameter of the 12-6 Lennard-Jones potential.
- *Slightly scattered collisions*. The scattering angles are between 90° and 0° . The particles interact with the repulsive potential but not quite as intensive as in head-on collisions. Those collisions are often promoted by the long-range attractive interactions.

A visual representation of all three types of collision is given in Figure 6.8. The black dot gives the position of the ion, with the movement over the course of the integration not shown, i.e. the trajectories shown are the background gas trajectories (with the red dot indicating the end position). The green trajectory shows a head-on collision, the blue collisions show grazing collisions and the red trajectories visualize slightly scattered collisions. These trajectories were simulated for Ar^+ in helium at 10 Td, hence frontal collisions are the most rare.

Additionally, it is interesting to observe the effects of the electric field strength as well as the ion-induced dipole potential. For this, Ar^+ in He as well as Ar was simulated and the trajectories recorded. The reduced electric field was thereby either at 10 Td or at 70 Td. In Figure 6.9 trajectories at 10 Td are shown for both systems.

A few collisions are shown as examples after final equilibration to the drift velocity. Both systems show similarities at 10 Td, as most collisions are distributed over the whole spawn

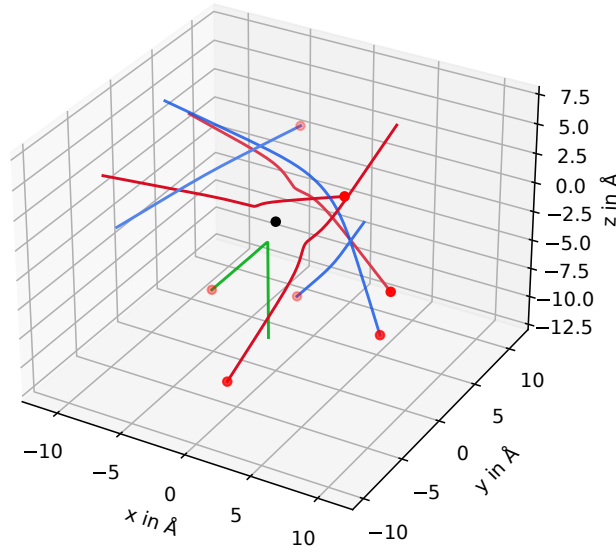


Figure 6.8: Exemplary collisions of Ar^+ in helium at 10 Td. Green collisions are head-on, blue collisions are grazing and red collisions are slightly scattered collisions.

sphere ($30 \text{ \AA}$ for helium and $50 \text{ \AA}$ for argon). The initial relative velocities in helium are higher compared to argon, still in helium more intense grazing collisions take place. At first glance this seems counter-intuitive as argon has the higher α value (polarizability constant) of $1.664 \text{ \AA}^3$ compared to $0.205 \text{ \AA}^3$ for helium. However, due to the larger mass difference between argon and helium, the momentum transfer over time in the Ar^+ -He collisions is higher leading to higher initial relative velocities. Additionally, the nonexistent mass difference for argon cations in argon makes grazing collisions less likely and less intense. The trajectories were then also simulated for 70 Td in both systems as illustrated in Figure 6.10.

In this case a much clearer difference becomes apparent: for collisions in helium the initial velocities are now much larger relative to the argon system, i.e. the argon system has only gained a small amount of additional initial velocity. Even more prominent is the change in collision type. The collisions become frontal in nature for helium and shift to a preferred direction coming from the direction of the electrical field. In the case of Ar^+ in Ar the collision distribution is significantly more spherical.

The closest approach distance over multiple collisions is shown in Figure 6.11 for both systems at 10 and 70 Td each. Closest approach distance thereby refers to the minimal distance between the two particles in a collision. Without any ion-induced potential effects or high field acceleration the closest approach distance should roughly cut-off at the 12-6 Lennard-Jones σ parameter. This would be $3.4 \text{ \AA}$ for Ar^+ in argon and $2.98 \text{ \AA}$ in helium. Comparing both distributions for 10 Td, a peak is visible below both cut-off values. With the small initial velocities, the ion-induced potential is capable of significantly accelerating the particles close to each other and press into the repulsive potential part slightly. This goes in hand with a dip in the distribution right before the peak structure (see: between

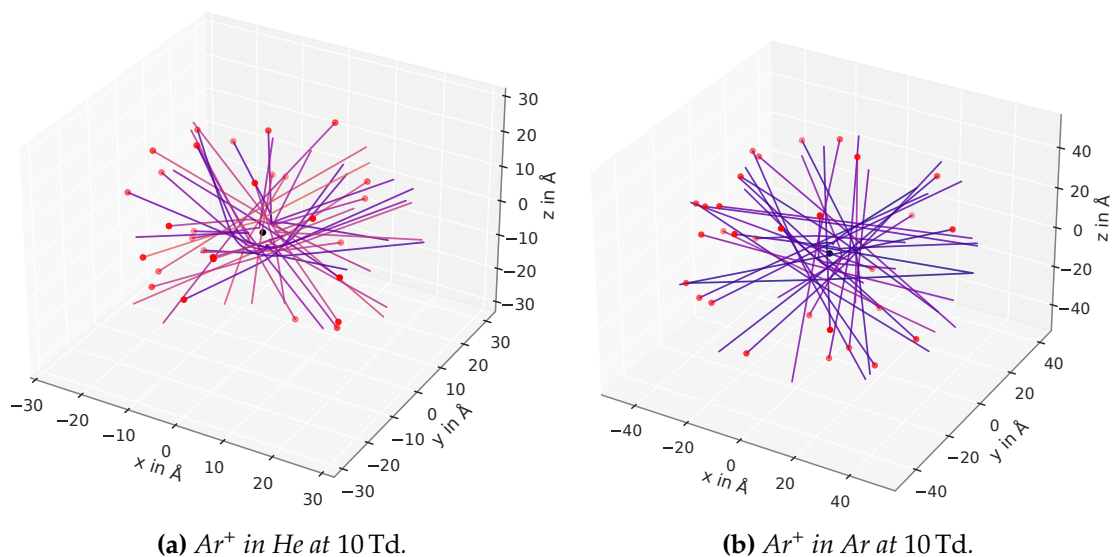


Figure 6.9: Collisions are colored by their relative initial velocity and the ion position at the start of the collision is given as a black dot. Only the background gas trajectories are shown.

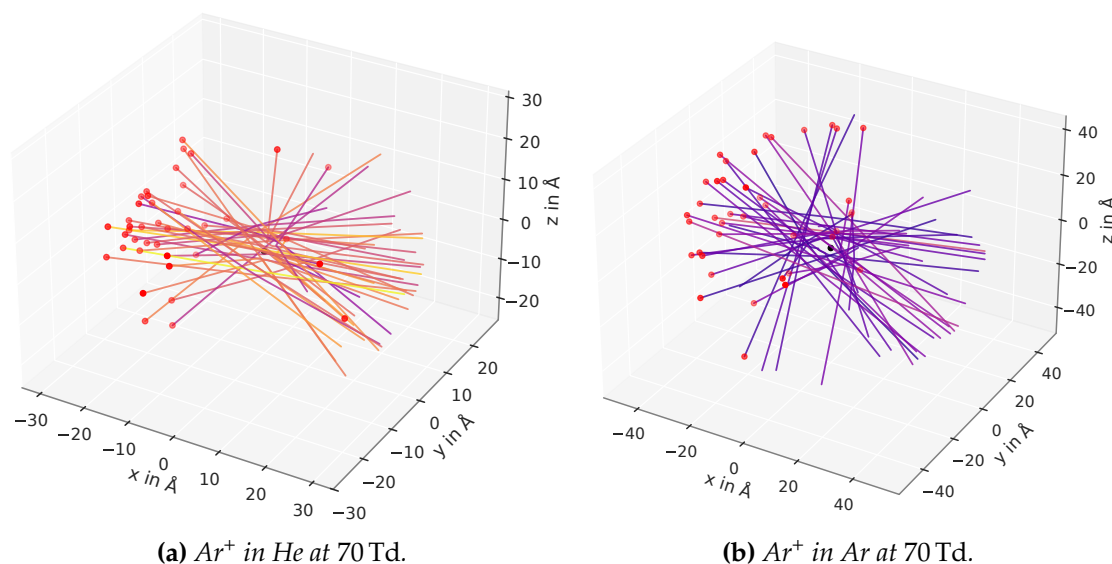
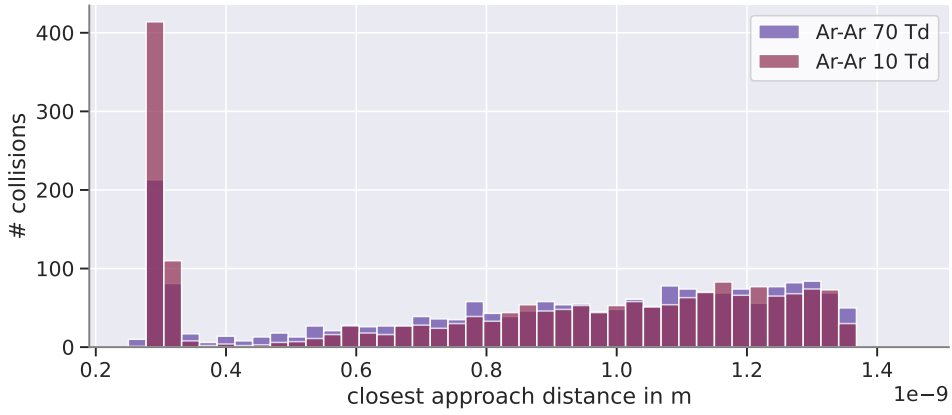


Figure 6.10: Collisions are colored by their relative initial velocity and the ion position at the start of the collision is given as a black dot. Only the background gas trajectories are shown.

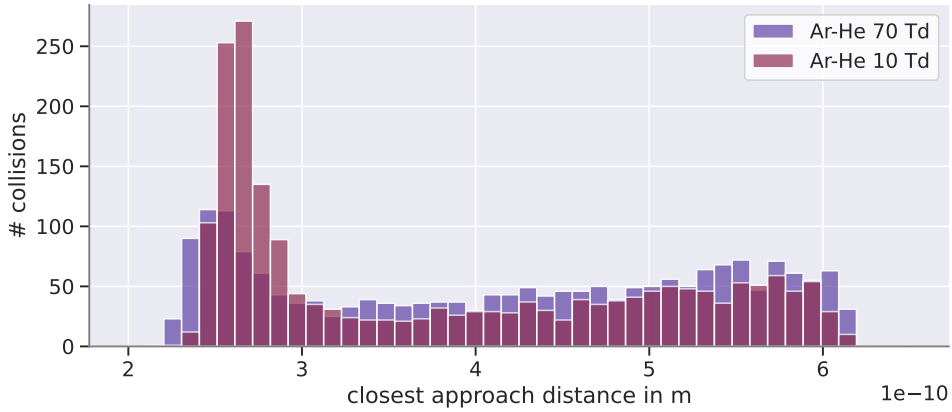
3.5 and 4.5 Å for argon and between 3.2 and 3.8 Å for helium), which is not visible in the 70 Td distributions. For argon between 3.5 Å and 4.5 Å almost no collisions are recorded at all.

The 70 Td curves show even smaller closest approach distances in both cases, even though the effect is small. However, as already mentioned, the small dip in the distribution is not visible which is plausible given that this closer distance is probably solely an effect of the higher field strength (higher initial velocity).

In addition, all distributions show an increasing probability of longer approach distances, which is more noticeable for the argon system (which is primarily a side effect of the larger spawn sphere radius). Because the volume of a sphere increases cubically, a proportionally greater number of trajectories can be found in the outer regions of the sphere where little attractive forces exist.



(a) Ar^+ in Ar at 10 and 70 Td.



(b) Ar^+ in He at 10 and 70 Td.

Figure 6.11: Closest distances between both collisions partners for several simulated collisions at the given electrical field strength.

Overall, the trajectory behavior is matching expectations and shows strong dependence on the field strength and polarizability effects. This dependence also changes based on the observed system, but follows similar trends. Lastly, the drift velocity evolution is

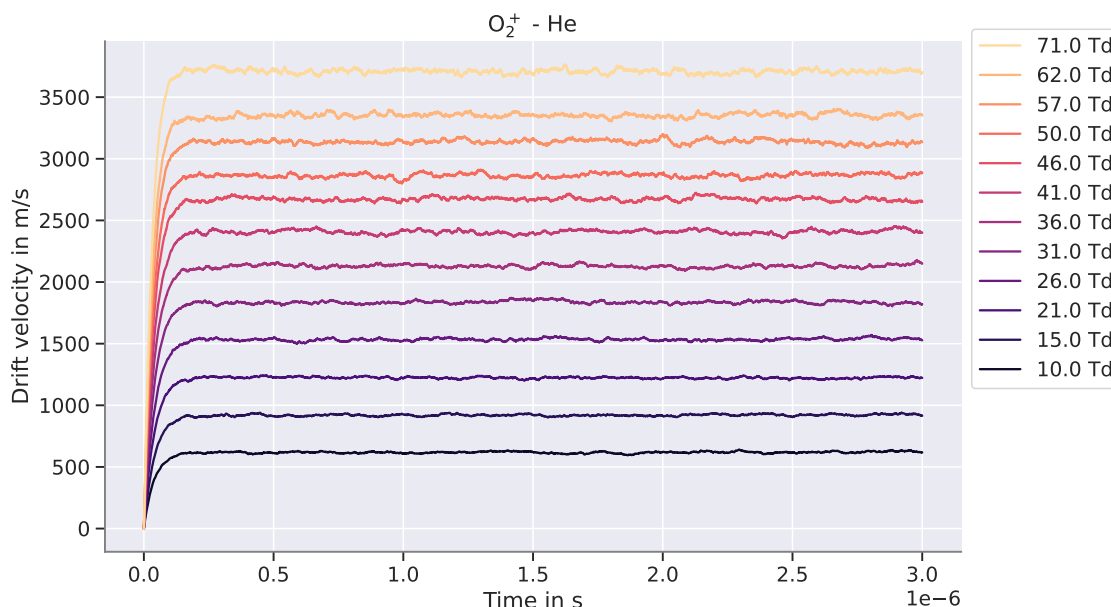


Figure 6.12: *Drift velocity evolution over time for O_2^+ in helium at various reduced electrical field strengths.*

studied and shown in Figure 6.12 for O_2^+ in He at different electric field strengths. The drift velocities are calculated by averaging over all ion velocities in field direction (i.e. x -direction) along the time dimension. For all field strengths, a very fast stabilization to the drift velocity is found, which is only a small fraction of the complete simulation time. The stabilization becomes faster with higher field strength, even though this effect is barely noticeable. Due to the randomness of collision events, visible noise exists and as such ion mobilities need to be calculated by also averaging over the drift velocity in a specific range.

Long simulation times are therefore essential for good averaging, however the simulation time could be shortened and in turn the simulated particles be increased to also decrease the numerical noise.

6.3.3 Collision radius scaling dependence

The scaling factor β is used in the MD model to artificially enlarge the collision sphere to guarantee all relevant collisions are integrated. A small collision sphere would otherwise result in mostly frontal, hard collisions disadvantaging grazing collisions and collisions with slight scattering. This approach of collision radius re-scaling is verified and the convergence of the results with higher scaling parameter values is checked. Since the collision sphere which is used in the integration process resembles the collision cross-section of the particle pair, re-scaling must also be transferred to the collision cross section to ensure conformity between collision sampling and integration.

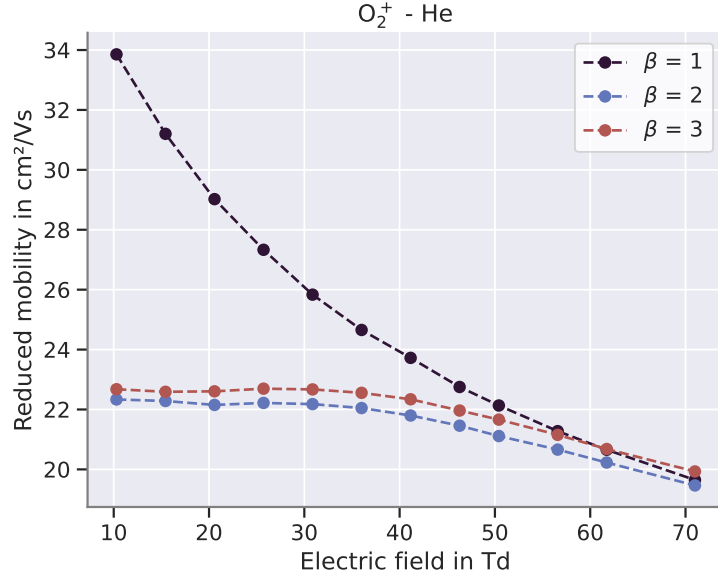


Figure 6.13: Reduced ion mobilities in dependence of the reduced electric field for O_2^+ in He for different values of the scaling parameter β .

The collision cross section is then computed as

$$\begin{aligned} r_{ab} &= \beta \cdot (r_a + r_b) \\ \sigma_{ab} &= \pi \cdot r_{ab}^2 \end{aligned} \tag{6.2}$$

and the collision sphere is then defined by the enlarged pair radius r_{ab} .

To show the effect of an inadequately chosen scaling parameter and to additionally prove convergence, ion mobilities for O_2^+ in helium as well as argon are computed for different β and shown in Figure 6.13 and Figure 6.14 respectively. In both cases for $\beta = 1$ a hard-sphere curve shape is found, i.e. the reduced ion mobility is constantly decreasing for higher field strengths. When increasing the scaling to values of two and higher, the curves begin to change their shape, leading to partly or steadily increasing ion mobilities as an effect of the ion-induced dipole interactions.

In addition, the curves approximately converge and lead to the same mobility values up to some uncertainties. Even though argon has much further reaching ion-induced forces due to higher polarizability, it is apparently not necessary to increase β higher than two. It should also be ensured that β is not set to be too large as the collision probability rises as well and could create undesirable side effects for the dynamic of the ion trajectory. Overall, a re-scaling is necessary to capture effects of grazing collisions but should be kept to a minimum to ensure good collision dynamics. A scaling value of two seems to be sufficient for monoatomic background gases, as both low and high polarizable gases react in the same way.

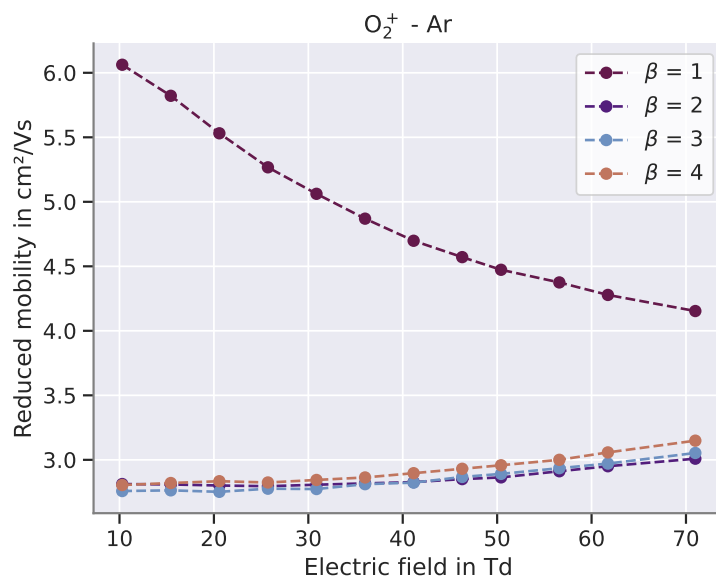


Figure 6.14: Reduced ion mobilities in dependence of the reduced electric field for O_2^+ in Ar for different values of the scaling parameter β .

6.3.4 Collision cross section dependence

The collision cross section is usually a very important parameter for the prediction of the collision probability when using a hard-sphere based collision model. As the CCS is the primary, unknown input parameter in the HS model, changes in CCS have a high impact on the actual simulated ion dynamics and the resulting ion mobility. In contrast, the impact of the CCS parameter in MD collision simulations is less important. Besides the determination of the radius of the collision sphere, it is used here to determine the probability to switch into an MD collision integration. Therefore, the collision cross section used in the MD model can in principle be set to "infinite" without leading to any significant changes in the simulated properties besides a much higher numerical effort and consequently unfeasible run times of the simulation. As such, similar to the re-scaling parameter β , it has to be ensured that the CCS is set not too low, which would lead to an unphysical bias towards harsh, head on collisions. Since β just rescales the CCS calculated from the effective collision diameter of the particles (cf. Equation 6.2), increasing the CCS and increasing β by the same factor has the same effect on the simulation results.

To verify this property, the reduced ion mobilities in dependence of the electric field strength are computed for O_2^+ in helium, where the collision cross section is varied for the different simulation runs by change of the collision diameter of O_2^+ . The collision diameter for helium is $2.8 \text{ \AA}$ and the default collision diameter for O_2^+ is $3.1 \text{ \AA}$, with variation to either $1.1 \text{ \AA}$ or $5.1 \text{ \AA}$.

Figure 6.15 shows the three different results for the altered collision cross section. As expected, for a combined diameter of $2.95 \text{ \AA}$ and $3.95 \text{ \AA}$ only small differences can be found with matching curve shapes. In contrast, the $1.95 \text{ \AA}$ curve shows distinctly different

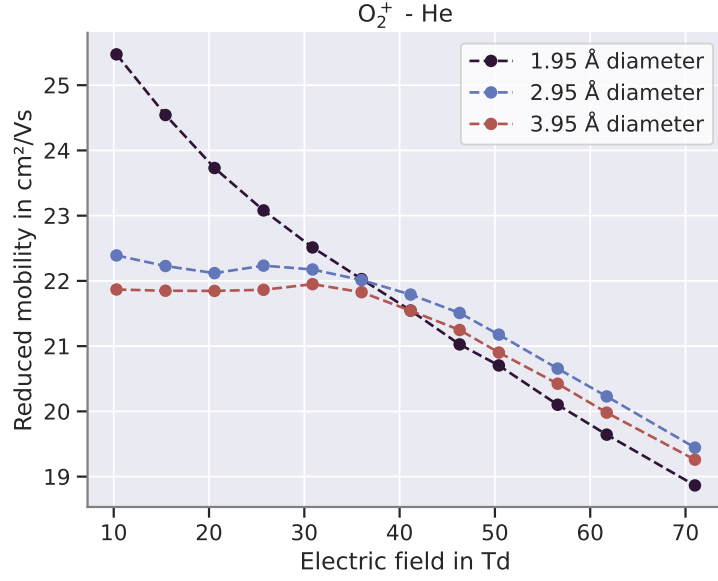


Figure 6.15: Variation of the combined collision diameter used in the collision cross section calculation for O_2^+ in helium and change of reduced ion mobilities for different field strengths.

behavior: while the curve is also close to the other two curves in the high field region (> 40 Td), the first half lies much higher. The whole curve shape is changed to a typical hard-sphere model result, without any type A or B effects. The other two curves increase slightly in ion mobility, hinting to the existence of the effect of long-range attractive forces. Based on the results shown in subsection 6.3.3, an insufficiently small collision cross section leads to the same characteristics in ion mobility curves as a too small collision radius scaling, which is the expected behavior.

6.3.5 Pressure dependence

An additional important input parameter is the pressure of the background gas in the drift region. The pressure is directly proportional to the neutral gas number density

$$n = \frac{p}{k_B \cdot T} \quad . \quad (6.3)$$

Ideally, the reduced electric field and the subsequently calculated reduced ion mobility should correct for varying neutral pressure as given in section 3.1. As such when varying the neutral gas pressure, the reduced ion mobilities obtained for a system should not change. In Figure 6.16 reduced ion mobility curves for three different background gas pressures are shown, which are calculated for a system of O_2^+ in He for reduced electric fields between 10 and ≈ 70 Td. Despite the expected pressure independence of the reduced ion mobility, a clear dependency of the ion mobilities on the pressure is visible. Here, higher pressures lead to higher reduced mobilities. However, the general shape of the ion mobility curves remain similar.

The semblance of all three curves seems to indicate a dependence on another parameter

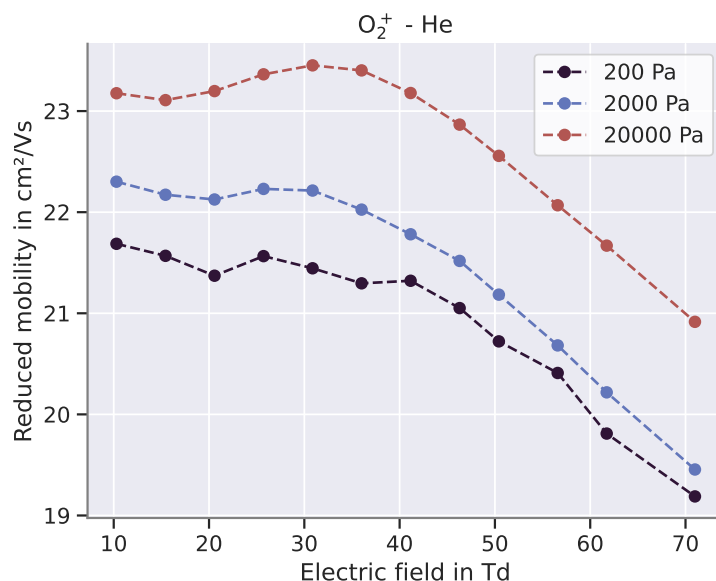


Figure 6.16: Reduced ion mobility in dependence of the reduced electric field for O_2^+ in helium. The pressure was varied between 200 to 20 000 Pa for the three different curves.

which likely has changed by an increase / decrease of the background gas pressure. In addition to the number density, the calculated collision probability for an ion in each time step changes drastically with increasing pressure (ref. Equation 3.10), as the mean-free-path has a direct inverse dependence on the pressure (a higher pressure decreases the mean-free-path, i.e. a higher collision probability). Therefore, the simulation runs were repeated with 10^{-12} s step size length of the velocity Verlet and an increase to 3 million total steps to keep the same simulation time of 3 μ s. As the high pressure curve (20 000 Pa) showed the most deviation relative to the two other curves, a reduction in step size length was carried out as it was assumed that a too large collision probability in the individual integration steps could lead to inaccurate ion mobilities. Figure 6.17 shows the same ion mobility curves for the reduced step size length / collision probability. Only marginal differences between the three curves are observed now, with a good convergence between all three curves for high field strengths. For the lowest pressure of 200 Pa in the low field region some stronger variance is observed which is an effect of the very low collision probability with this pressure. Since so few collisions take place, higher numerical noise on the averaged ion mobilities is noticeable. This effect decreases for the high field mobilities as the relative ion velocity rises and more simulated collisions take place.

To verify the pressure dependence as a general characteristic of the MD model, a secondary system of O_2^+ in argon is simulated. The same procedure was thereby repeated and in Figure 6.18 the simulated ion mobilities for all three pressures and the differing step size lengths are shown. The left panel, which shows the results with larger step size, clearly exhibits a strong divergence between the 20 000 Pa curve and the other two curves. While

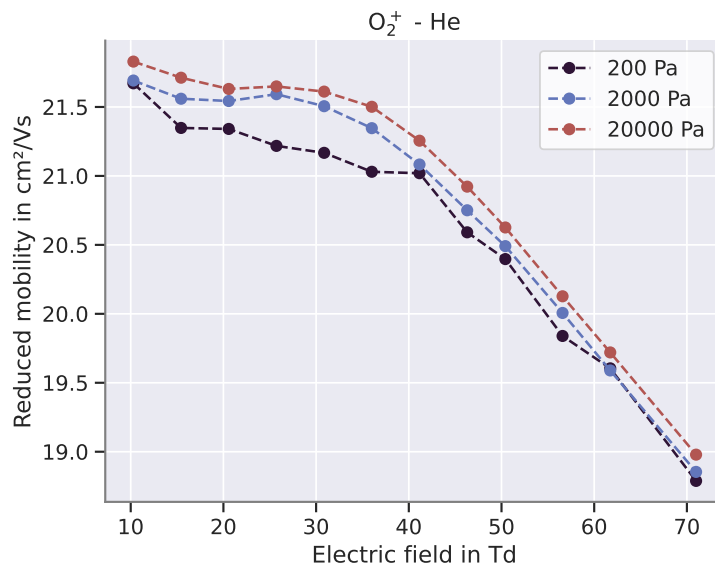


Figure 6.17: Reduced ion mobility in dependence of the reduced electric field for O_2^+ in helium. The pressure was varied between 200 to 20 000 Pa for the three different curves. A smaller step size of the ion trajectory simulation of 10^{-12} s was set and thereby increasing the amount of simulation steps to 3 million to keep $3 \mu\text{s}$ total simulation time.

the curve shapes match in the case of O_2^+ in helium, the curve shape marginally deviates for higher field strengths with the O_2^+ -Ar system. A decrease of the step size by one magnitude (and subsequent increase of the total time steps by one magnitude) reveals, again, a good convergence between all three curves as the collision probability per time step is sufficiently low. Taking a closer look, a higher noise level for the 200 Pa curve is noticeable here too. Thus, in this instance 2000 Pa appears as the optimum between collision probability value and noise level to obtain good ion mobility predictions. As such, a pressure of 2000 Pa but for a step size length of 10^{-12} s is set for all following ion mobility simulations showing the best convergence with the lowest noise level.

6.3.6 Temperature dependence

In the same way the pressure has an effect on the neutral gas density (ref. Equation 6.3), the background gas temperature also has a direct effect on this quantity. In section 3.1 it was discussed that the reduced ion mobility is not completely independent of the temperature of the system, because of structural changes in the analyte geometry. However, this influence on the ion mobility is not considered in the MD model as there is no relative geometry change based on supplied temperature implemented, i.e. all molecular geometries are static. In turn, even though this would probably not be an outcome of real-life experiments, it is initially expected that in the simulations carried out no dependence on the background gas temperature should be found. However, besides the structural changes, the velocity distribution of background gas particles exhibits a strong temperature dependence. As such, it should still be expected that the ion-neutral dynamics change

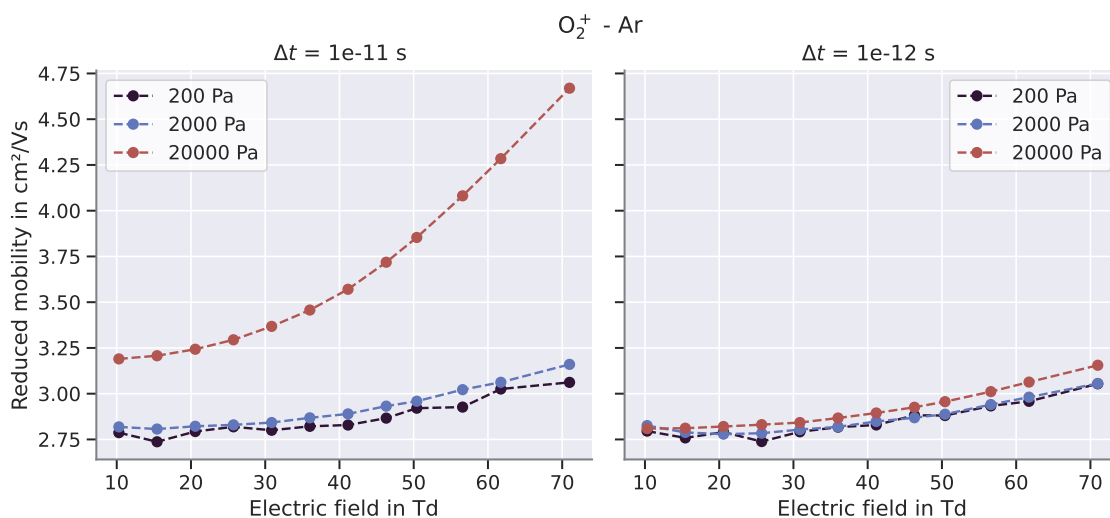


Figure 6.18: Reduced ion mobility in dependence of the reduced electric field for O_2^+ in argon. The pressure was varied between 200 to 20 000 Pa for the three different curves. The left panel shows the simulated mobilities for a step size of 10^{-11} s, while the right panel is done with $\Delta t = 10^{-12}$ s (3 million time steps).

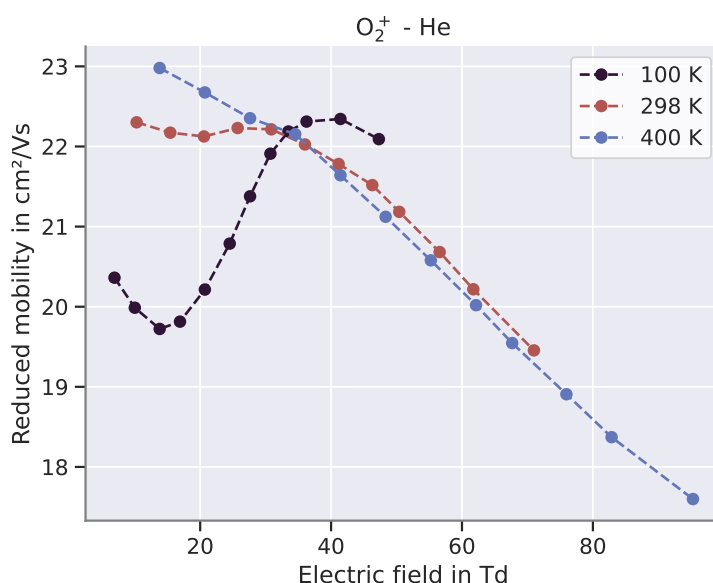


Figure 6.19: Reduced ion mobilities for O_2^+ in helium at different reduced field strengths under variation of the temperature of the background gas.

significantly especially for lower temperatures. A study of the ion mobility change with varied temperature of the background gas is shown in Figure 6.19. The region between 5 to 42Td supplies important information about the temperature dependence: there is a stark difference between the 100 K curve and the other two curves at 298 K and 400 K. The simulations with 298 K and 400 K follow the same curve for higher reduced field strengths and have some slight deviation for the low field region. However the 100 K curve has a completely different shape which looks roughly like an "S"-shape.

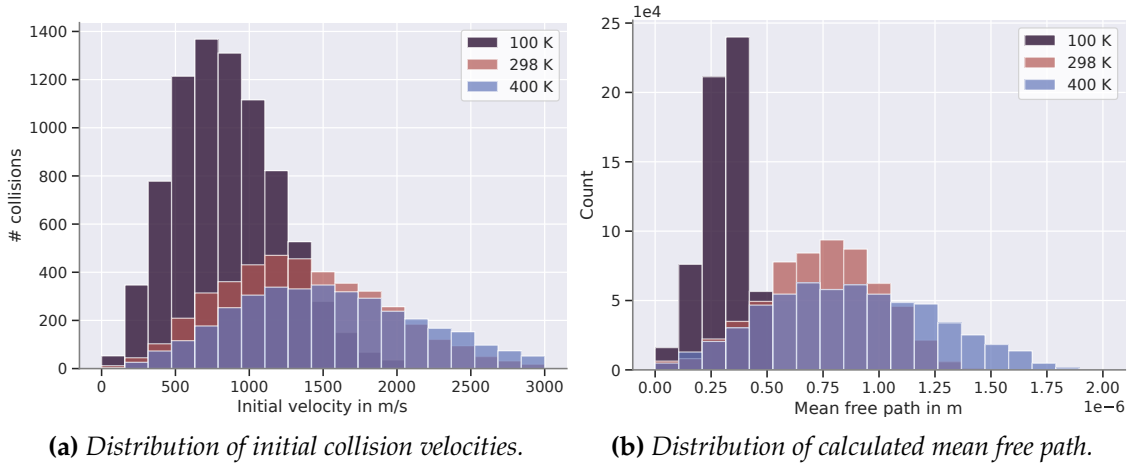


Figure 6.20: A system of O_2^+ in helium was simulated at 7 Td, where the initial velocity in carried out collisions as well as the computed mean free path for all possible collisions was recorded. The temperature was thereby varied between 100 K, 298 K and 400 K, changing the applied electric field so that all simulations are at 7 Td.

Further studies of the collision dynamics were then carried out to verify if this temperature dependence is indeed an effect of the changed neutral gas velocity distributions. In Figure 6.20 the distributions of the initial relative velocity in each collision as well as the computed mean free path for any possible collision were recorded for all three temperatures at 7 Td¹. Both 298 K and 400 K distributions are similar for the mean free path as well as the initial velocities, which is in accordance to the quite comparable ion mobility curves. At 100 K a significant change in the distributions is observed: the initial relative velocity distribution becomes relatively narrow with a maximum at only roughly 700 m/s. The mean free path distribution is even narrower and is generally much smaller than for the higher temperatures. This signifies overall more collisions for low temperatures due to the small average mean free path as well as background gas particle velocities which are very close or even faster than the ion drift velocity (comp. drift velocity at 10 Td in Figure 6.12). The resulting ion mobility at 100 K and low fields is primarily controlled by the low temperature thermal collisions while the electric field has little effect on the collisions dynamics. Additionally, the actual distribution of collision types is illustrated in Figure 6.21 and Figure 6.22 for 100 K and 400 K, respectively. The collision type can be evaluated by visualizing the relationship between the *geometric closest distance* and the *simulated closest distance*. Geometric closest distance refers to the minimal distance between the background gas and ion in the MD collision which can be predicted by following the "ray" (i.e. the direction of movement) used to initialize the background gas particle at the beginning of the collision process. In contrast, the simulated closest distance is the minimal distance between both particles that was actually achieved over the course of the MD trajectory simulation. If only minor forces play a role, the simulated distance should be approximately equal to the distance predicted by the ray. Those kinds of collisions can

¹Highest divergence is found for low field mobilities, as such a small reduced field was chosen.

Figure 6.21: Simulated closest distance in dependence of the predicted geometric closest distance for O_2^+ in He at 7 Td for 100 K. The geometric distance is the distance computed in the collision initialization to determine if a collision is valid / can in theory "hit". The simulated distance is the actual closest distance found during the collision trajectory integration. Each collision is colored by its initial relative velocity.

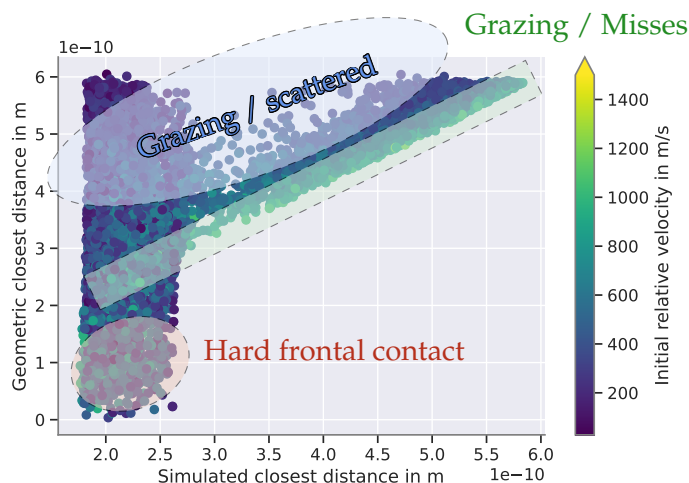
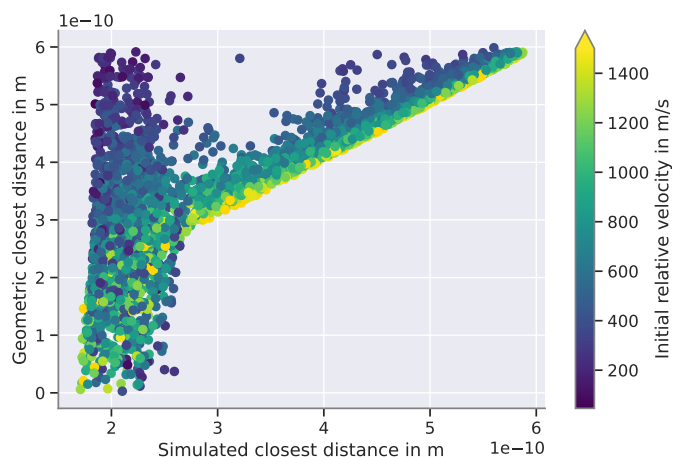


Figure 6.22: Simulated closest distance in dependence of the predicted geometric closest distance for O_2^+ in He at 7 Td for 400 K. Each collision is colored by its initial relative velocity.



surely be found and are marked by the green box in Figure 6.21. This linear behavior can be found for grazing type collisions which are not actually experiencing relevant attractive forces and thus basically fly-by / miss any interaction sphere. Especially particles which have a high relative initial velocity are able to do fly-by's, as seen in Figure 6.22. In the case of head-on, reflective collisions the geometric distance is often underestimated as the simulated closest distance is limited by the repulsive potential well and cannot be as small as predicted geometrically. Those collisions can be found in the region marked by the red ellipse, lying below the linear relationship area.

Lastly, the area found above the linear relationship region is populated by grazing as well as slightly scattered collisions. The left hand part of this region, meaning the collisions that lie in alignment (above) the head-on collisions, are the slightly scattered trajectories as here the geometric distance was predicted to be large but the simulated distances were very small and in the region of the 12-6 Lennard-Jones σ value. To the right hand side of this region is a small thinning before another trajectory group becomes visible. There, the simulated minimal distances were only slightly smaller than the geometric predictions and the collision in this area can therefore be attributed to grazing collisions, which do not miss the attractive potential (in contrast to the "grazing" fly-by's).

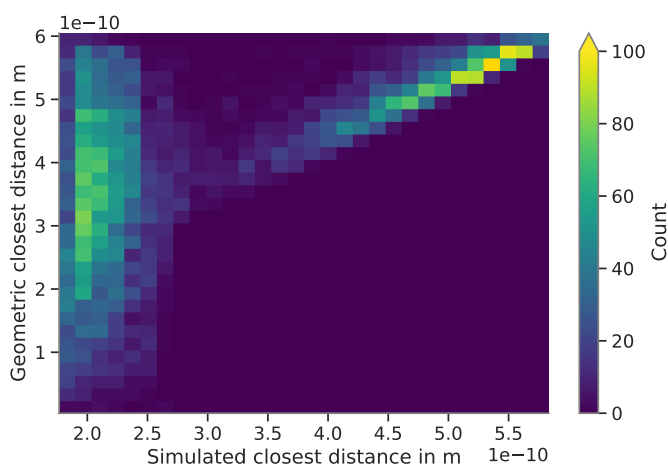
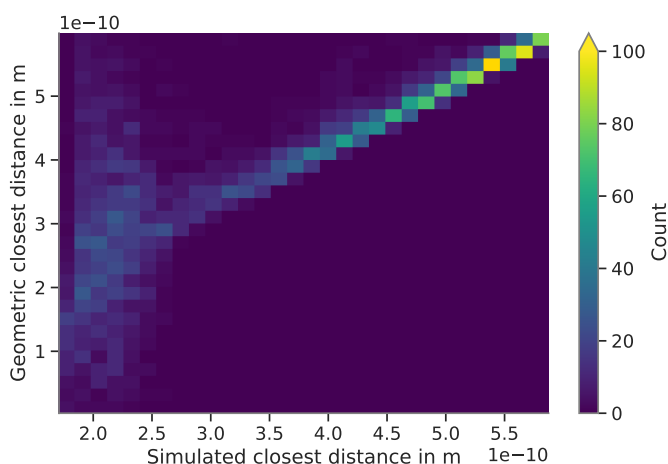


Figure 6.23: Simulated closest distance in dependence of the predicted geometric closest distance for O_2^+ in He at 7 Td for 100 K in a two-dimensional histogram.

Both temperatures show similar trends on first glance: i) all three different regions are populated and ii) the grazing fly-by's have on average higher initial velocities. However, the grazing / scattered region is apparently much more occupied in the 100 K case while the grazing / misses region has much higher initial relative velocity at 400 K in accordance with Figure 6.21. To put the density difference into perspective the same data is visualized with a 2D histogram as presented in Figure 6.23 and Figure 6.24. This allows to obtain a relative density profile of the population of the individual areas as data points lying close by one another are grouped into the same bin. Now, comparing both distributions it can be verified that for 100 K indeed more² collisions occupy the grazing / scattering region than for 400 K. Especially the slightly scattered collisions are predominately occurring for 100 K which is primarily due to the on average very low initial velocity of the collisions. Overall, the primary reason for the changed curve shape at 100 K and subsequent mobility differences lies in the altered collision dynamics in a cold, collision dominated environment. While the reduced mobility is temperature corrected and the neutral buffer gas number density is inversely proportional to the temperature, the changed temperature has a strong non-linear effect on the background gas velocity distribution and hence on the initial collision velocity as well as the free path distribution. The reduced velocities then in turn change the interaction dynamics. Much different forces are experienced and a greater share of grazing collisions take place, ultimately leading to a lowered K_0 . Finally, a second reference system of CO^+ in helium is evaluated as in this case literature mobilities are published for the two strongly different temperatures of 300 K and 4.35 K. In addition, also ion mobility predictions using the 2TT have been carried out with MobCal-MPI to further verify if the temperature dependence can be reproduced by other mobility prediction methods. To have MobCal-MPI and IDSimF as similar as possible, the force field potential function for the van der Waals interaction in IDSimF was switched from

²Relative to the distribution itself, i.e. the ratio / share within all collisions at the same temperature is higher.

Figure 6.24: *Simulated closest distance in dependence of the predicted geometric closest distance for O_2^+ in He at 7 Td for 400 K in a two-dimensional histogram.*



12-6 Lennard-Jones to the modified Buckingham potential³ and the parameter values were taken from MobCal-MPI as well. Usually, MobCal-MPI uses the MMFF94 force field parameter set with parameters N , G , A and α . These parameters can be converted to σ and ϵ values, with the conversion equations given in section B.1. The process in which the 2TT is used to generate high field mobilities in MobCal-MPI is explained in section B.2 as well.

Figure 6.25 visualizes the ion mobilities for IDSimF, MobCal-MPI as well as experimental references from literature at different field strength and at two temperatures. For 300 K both, MobCal-MPI and IDSimF, lay within the uncertainty band, while only IDSimF is not within the uncertainties for lower field strengths below 20 Td. Consequently, both predictions follow the literature mobility curve well, with MobCal-MPI giving slightly better lower field mobilities and IDSimF converging much better to the high field experimental mobilities. In the case of 4.35 K the curve shape changes drastically and also turns into some kind of "S"-shape as was noticeable for O_2^+ in helium. The mobility decrease at low field strength and low temperature due to stronger effect of attractive interactions is in qualitative accordance with other experimental and theoretical results [148]. Both simulation frameworks also obtain a matching curve shape, with IDSimF having one outlier for the lowest field strength. However, MobCal-MPI values are entirely outside of the uncertainty band of the experimental values. Mobilities predicted by IDSimF converge for higher field strengths to the experimental values.

The temperature dependence is visible in experimental observations and in another reference simulation framework. For small temperature differences or for temperatures closer or slightly higher than room temperature, the mobility curves converge. At low temperatures the ion mobility apparently is dominated by the low temperature thermal collision dynamics, at least in the two systems studied here.

³This potential / force function was implemented in the course of the integration of N_2 and will be explained in more detail in the relevant sections.

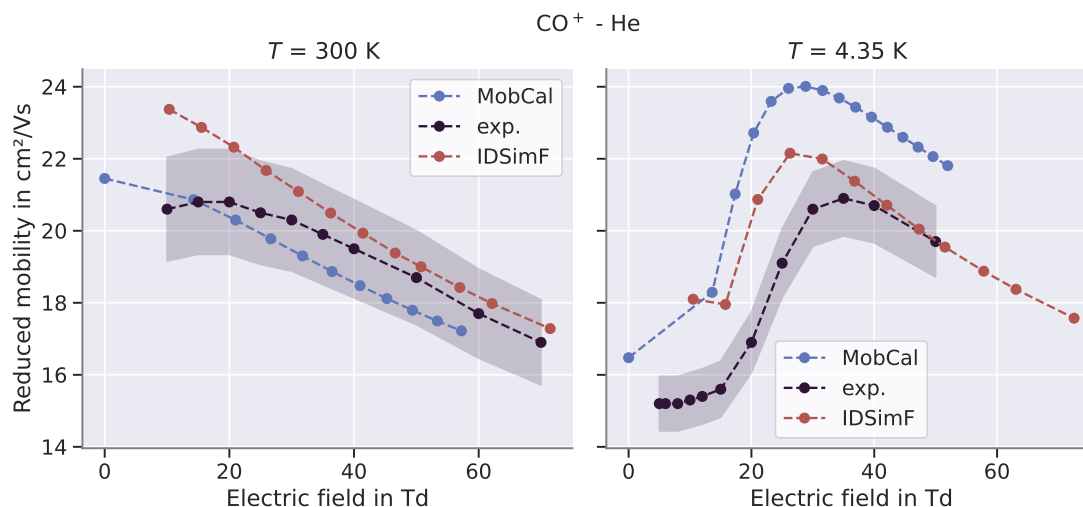


Figure 6.25: Reduced ion mobilities for CO^+ in helium at different reduced field strengths for 300 K (left panel) and 4.35 K (right panel). Literature values are given with their respective uncertainties [149, 150]. MobCal-MPI simulations were also carried out as a secondary reference.

6.3.7 Force field parameter sensitivity

Up until now some fixed set of parameters for the van der Waals component of the force field, namely the 12-6 Lennard-Jones potential, has been used. The 12-6 Lennard-Jones potential has two parameters σ and ϵ , defining the repulsion distance and the potential well depth respectively (see subsubsection 2.5.1.1). Actual values of the parameters for each atom of a molecular structure depend on multiple factors:

- molecular structure: differences in optimized molecular geometries can naturally change any of the parameter values as different bond lengths and relative positions have a strong impact on the calculated forces.
- charge distribution: if any charge-dependent force field component is used, the repulsiveness of individual atoms is different based on the applied charge on that atom even though the charge is not a parameter of the van der Waals potential. With higher charge density, further penetration into the repulsive potential part occurs leading to different scattering behavior.
- neighborhood: atoms can change their interaction dynamics based on their molecular neighborhood and hybridization. As an example, one of the O atoms in O_2^+ might have completely different interaction spheres than an O atom in a C–O–H bond.
- collision partner: van der Waals parameters additionally change based on the collision partner as the parameters are *pair* parameters.
- other force field components: including / excluding other force field components might require correction of the van der Waals parameters.

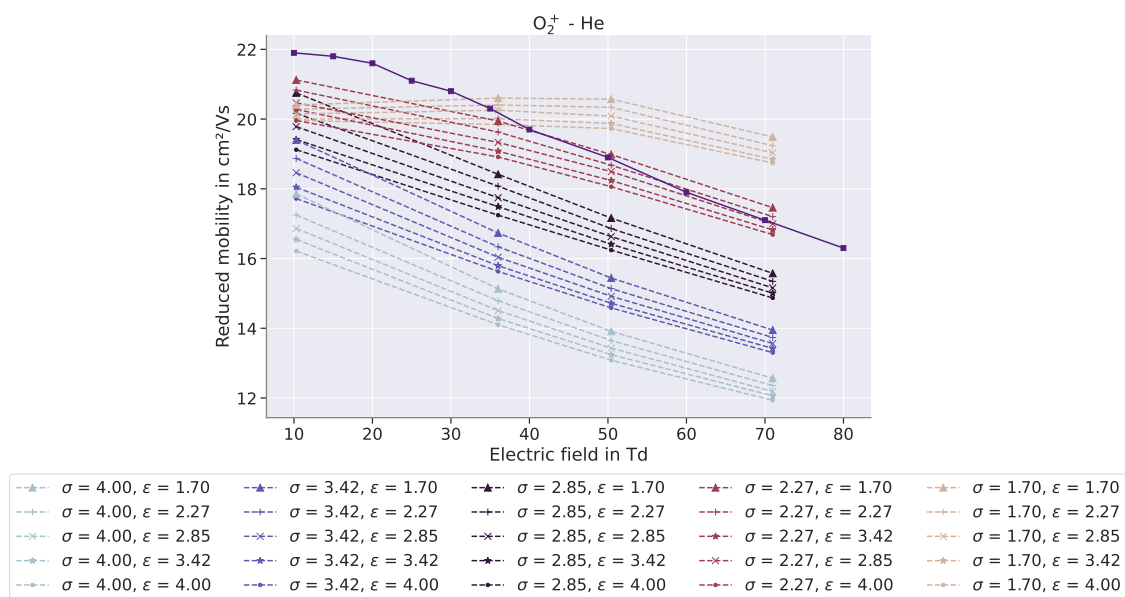


Figure 6.26: Reduced ion mobilities obtained in dependence of the electric field strength for varying 12-6 Lennard-Jones parameters σ (in Å) and ϵ (in kcal/mol) for O_2^+ in helium. The solid, purple line with square markers shows the experimental data given in [149].

Figure 6.26 shows reduced mobility curves for the test system of O_2^+ in He. Thereby, the σ as well as the ϵ values of both oxygen atoms were modified between the same, five values each. This sensitivity study does not aim to find "good" parameters but rather just show trends in mobility curves obtained through certain values for this test system. As such, experimental values from the literature are given but simply as a reference and to calculate absolute differences for easier visualization.

The first observation is a grouping of ion mobility curves into five regions defined by the value of the σ parameter. Particularly for high field strengths every curve for the same σ value is close by each other, which intuitively can be rationalized by the overall very hard-sphere like behavior for high Townsend values. For lower field strengths also grouping is visible, but, dependent on the well depth strength ϵ , overlap between the different groups is observable. Therefore, the group boundaries cannot be distinguished clearly anymore, e.g. at 10 Td. For the lowest σ value of 1.7 Å a change in mobility curve shape is noticeable, indicating that different parameter sets in the van der Waals potential, at least in the case of He with a low polarizability, still have significant impact. Apparently, lower σ values increase ion mobility and make the system more susceptible to ion-induced effects. Also lower ϵ values increase the ion mobility slightly, but the curve shape stays relatively constant for all ϵ values. Additionally, in Figure C.1 the same parameter variation was done for O_2^+ in argon instead, showing similar behavior for the ϵ values. However, no clear grouping is observed and curve shapes are almost identical, revealing a potentially stronger dependence on the ion-induced dipole potential.

A stable simulation requires that small changes in the parameter set do not lead to strongly different mobility results. For such systems there is an optimal parameter set,

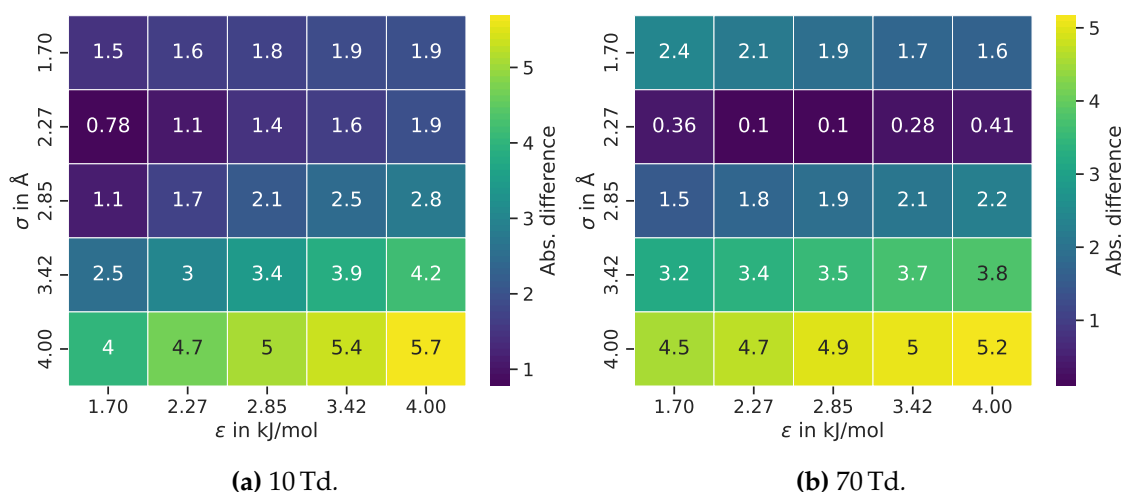


Figure 6.27: Absolute differences of the computed mobilities and experimental mobilities at the denoted reduced electric field strength for different Lennard-Jones parameter combinations.

which produces results closest to the experimental data. It is then possible to find such optimal parameters by systematic parameter variation / minimization of the residual between experiments and simulations. While this work does not aim to systematically fit general potential parameters, a reduced parameter fitting is shown for the described test system. In this case, the absolute error of the potential parameter set is given by

$$\Delta = |K_{10} - \hat{K}_{10}| + |K_{70} - \hat{K}_{70}| \quad , \quad (6.4)$$

with K_{10}, K_{70} being the mobility obtained by simulations at 10 and 70 Td and $\hat{K}_{10}, \hat{K}_{70}$ being the experimental values. The error for both individual reduced electric fields is given in Figure 6.27 and the absolute comb. error Δ is shown in Figure 6.28.

The absolute difference to the respective experimental value is computed and color-coded for each σ and ϵ value combination. Generally, at both field strengths it is apparent that higher values in any of the parameters leads to a stronger deviation from experimental values. The parameter set showing the smallest difference between experiment and simulation at 70 Td, i.e. $\sigma = 2.27$ Å and $\epsilon = 2.27$ kJ/mol, are not the best fitting parameters at 10 Td. Therefore, the combined differences shown in Figure 6.28 are better suited to assess the global optimum.

When extensively fitting for a optimal parameter set, this study should be extended to include more field strengths in the combined error as well as increasing the parameter range to find a more optimal parameter set. This process then needs to be repeated for many more molecules to either find one good parameter value set of an atom for all possible molecules, which potentially introduces high errors in some sub-classes of molecules, or to identify multiple parameter values depending on the molecule the atom is part of. As an example, old versions of MobCal only had one parameter set for each available atom, while MobCal-MPI supplies already optimized parameters for e.g. carbon atoms in different neighborhoods. Additionally, also generic parameters for sp² hybridized carbon

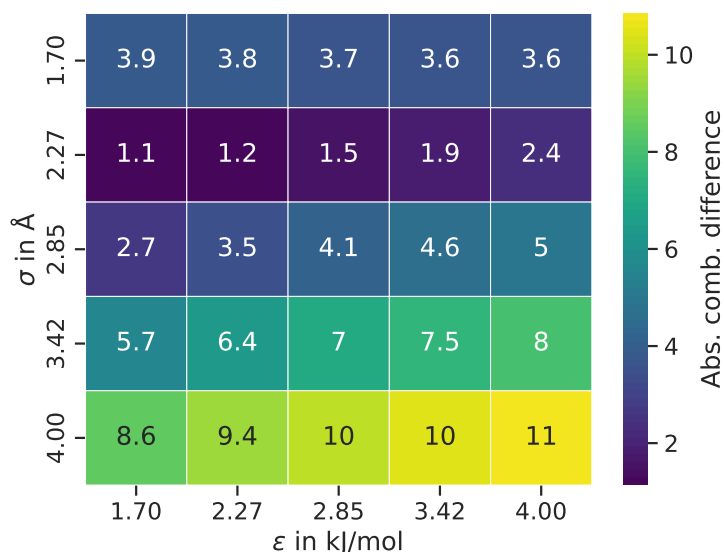


Figure 6.28: Absolute combined differences of 10 Td and 70 Td of the computed mobilities and experimental mobilities for different Lennard-Jones parameter combinations.

atoms are supplied, for example. Similar to MobCal-MPI, each atom in each molecule / particle has its individual parameters in IDSimF, which can freely be set by the user. This of course requires custom fitting of parameters by the user or transferring parameter sets available from other sources as e.g. MobCal-MPI or other similar force fields.

Overall, predicted ion mobilities can only be as good as the used parameter set and further work needs to be done to find optimal, or rather sufficiently good, parameter values for different molecules.

6.3.8 Prediction of ion mobilities

To finally evaluate the predictive capabilities of the MD model for ion mobilities, several small sized systems (i.e. monoatomic and diatomic) are simulated in helium as well as argon and compared to published literature values. Figure 6.29 shows ion mobilities obtained in IDSimF for O_2^+ , Li^+ , Ar^+ and Cl^- in helium, which are compared to experimental literature values. For the case of O_2^+ , agreeing low field mobilities between simulation and experimental are found with stronger deviations starting above 20 Td. For the very high field region the simulated curve starts to follow the experimental curve with its slope but stays outside of the uncertainty band of the experiments. O_2^+ in helium presents itself as a type C system in the experimental data range measured, while the simulation shows slight type B behavior noticeable in the lower field region. However, the curves are both similar overall.

For Li^+ in He the simulated ion mobility curves does not lie within the uncertainty of the experiment at all except for the 15 Td data point. Important to note is that there is a good reproduction of the curve shape between simulation and experiment and type A is correctly predicted. While there are large discrepancies between the actual mobility values,

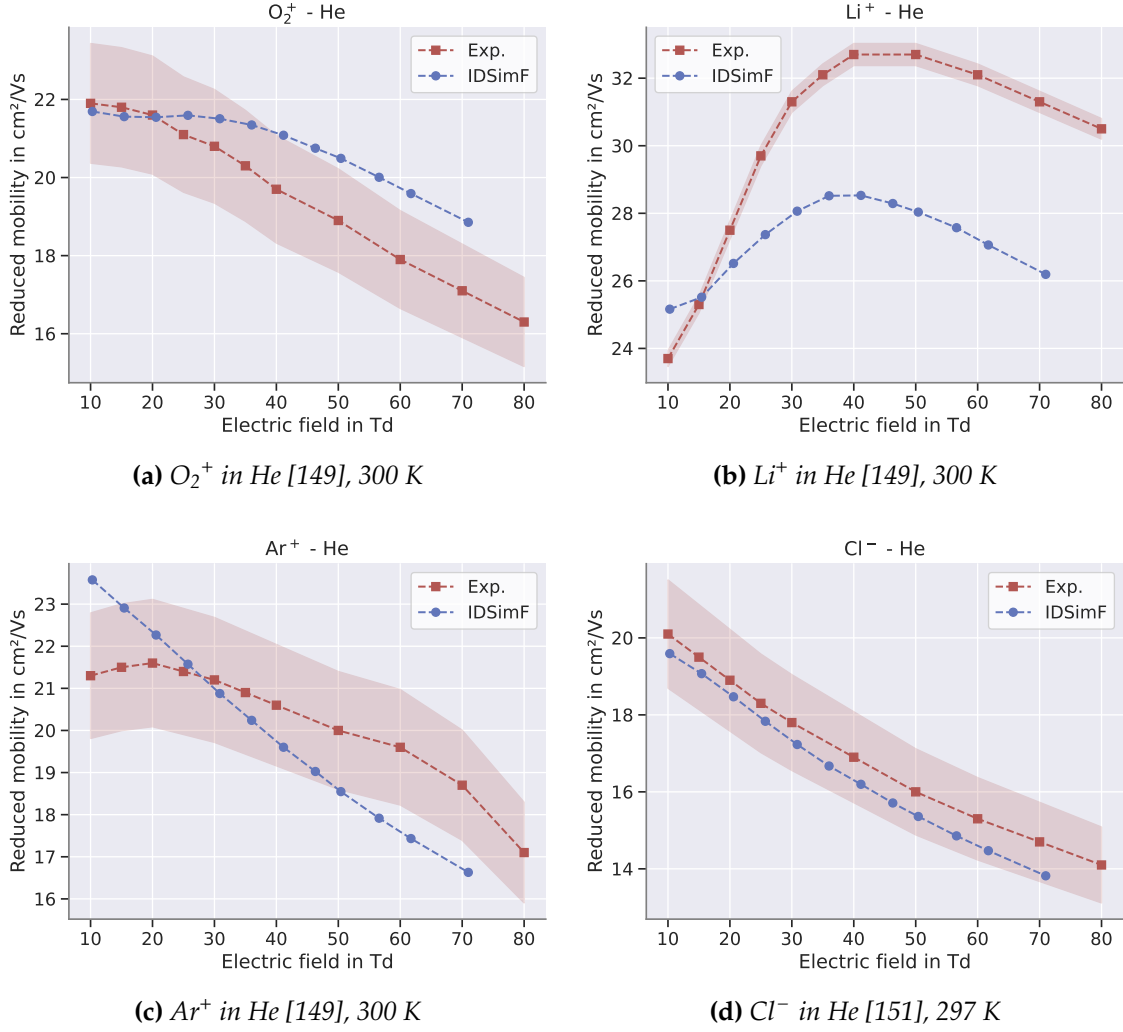


Figure 6.29: Predicted reduced ion mobilities in dependence of the reduced electric field for various ions in helium. Simulations were carried out with a step size length of 10^{-12} s. Experimental values are given with their respective uncertainty band.

generation of a type A curve is e.g. not possible with a HS or VHS approach as this requires attractive forces like the ion-induced dipole moment. In that regard, the MD model allows to simulate systems not possible with other collision approaches. Additionally, Ar^+ in helium was simulated where a type C curve is predicted. The experimental data suggests for the curve to likely be of type B instead. In this case, the curve shape and slope does not quite match but many of the data points still are within the uncertainty of the experimental data. Finally, Cl^- shows a very good match between experimental and simulated data in helium. All data points are within the uncertainty, follow the experimental curve closely with a nicely fitting slope and correctly exhibits type C behavior.

The same simulations were repeated using argon as the collision gas, which is shown in Figure 6.30. Across the board, expect for Ar^+ in argon, all systems studied here show type A properties, which the MD model is mostly able to reproduce. In the cases of Li^+ and O_2^+ low field mobilities show stronger deviation from the experimental data with slight

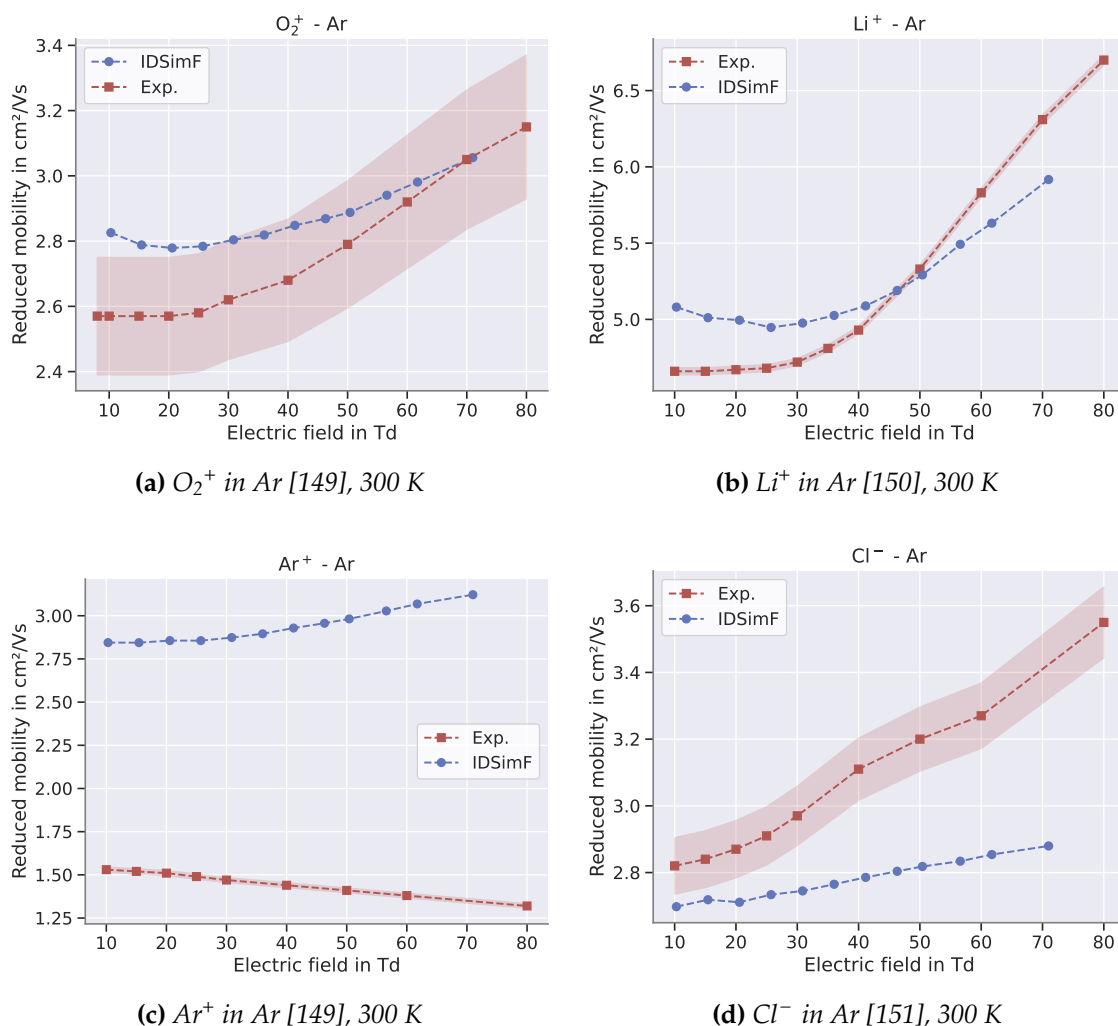


Figure 6.30: Predicted reduced ion mobilities in dependence of the reduced electric field for various ions in argon. Simulations were carried out with a step size length of 10^{-12} s. Experimental values are given with their respective uncertainty band.

indication of type B behavior (increased mobilities for low field strengths). The simulated mobility of Cl^- deviates much stronger from experimental results in argon as in helium. This is most likely due to not quite adequate force field parameters as the same 12-6 Lennard-Jones parameter sets were used in both helium and argon. The ideal helium/argon parameters of course differ, since the Lennard-Jones parameters have a large impact on the obtained mobility for such small molecular systems and should thus be adjusted for the ions if the background gas is changed. Still, while the differences seem large on first glance, most of the data points deviate by a maximum of 9 % from the experimental values, which is a good agreement for simulated ion mobilities of these small, sensitive systems.

The Ar^+ -Ar system has a significantly larger deviation, with the simulations predicting type A while the experimental data indicate type C and much lower absolute mobility. The large discrepancies in this case are owed to resonant charge transfer effects. Resonant

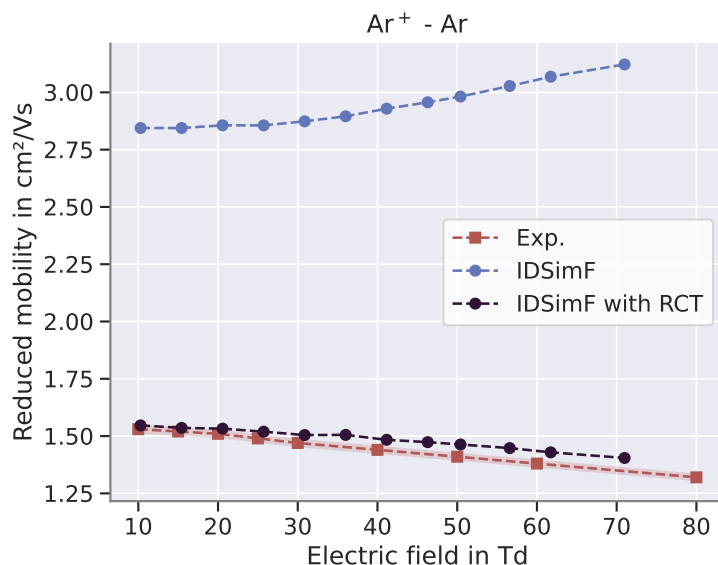


Figure 6.31: Predicted reduced ion mobilities in dependence of the reduced electric field for Ar^+ in argon at 300 K simulated with IDSimF as well as literature values [66]. Simulations in IDSimF were carried out with a step size length of 10^{-12} s. A second IDSimF simulation was carried out where the resonant charge transfer was considered by thermalizing reactions.

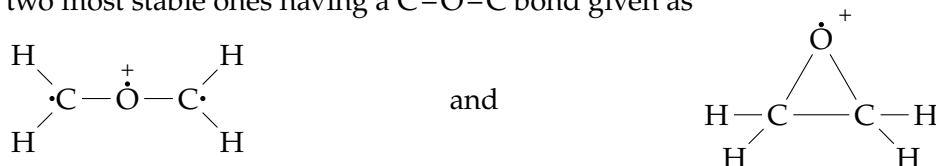
charge transfer (see section 3.2) takes place when two particles of the same type (with one being ionized) collide. The charge can then be transferred to the former neutral, and hence thermal, particle. As a result, the momentum gained from the electric field is lost. The ions are effectively "restarted" from a thermal state by the resonant charge transfer reaction and the effective ion mobility is reduced. Since such resonant charge transfer effect is not modeled by any explicit force field component, the correct ion mobility cannot be modeled by the MD model alone. By usage of the reaction simulation (RS) module of IDSimF it is possible to model / include resonant charge transfer effects. For this, a thermalizing reaction kind was implemented:

- the ion is thermalized by the reaction, i.e. the velocity vector of the reacting ion is set to a random velocity drawn from a Maxwell-Boltzmann distribution of the respective background gas temperature
- this thermalizing reaction happens with a probability estimated analogous to the hard-sphere approach with a reaction diameter σ

As mentioned, resonant charge transfer (RCT) leads to a transfer of charge from an accelerated ion to a thermal neutral particle. The thermalizing reaction can replicate this by returning the ions velocity back to a thermal state since the neutral background gas particles are not explicitly simulated. Figure 6.31 shows the experimental as well as simulated reduced ion mobility of Ar^+ in argon. The IDSimF curve (blue dots) and the experimental curve (orange squares) were already discussed in Figure 6.30c and given as a reference here. The black curve shows updated ion mobility values under consideration of RCT

with a reaction diameter σ of $7.4 \cdot 10^{-10}$ m (estimated from a parameterization presented in [72] neglecting a dependence of the rate constant on the ion velocity, since the change is small). As expected, the ion mobility is reduced significantly and the type changes from A to C. The overall curve with RCT has a very good agreement with the experimental curve, which only has 1 % uncertainty also. The deviations between both curves increase slightly for higher field strengths, possibly due to the velocity dependence of the cross section. Overall, the combination of the MD module and the RS module allow for good predictions of complex dynamic molecular interactions, which also cannot be modeled by other ion mobility prediction frameworks like MobCal-MPI, IMoS or Collidoscope.

Lastly, a larger ion was chosen to also test ion mobility predictions in helium (no experimental data is available in argon). Ions with a much larger number of atoms are often easier to predict, as force field inaccuracies on individual atoms “average” out. As an ion the $\text{CH}_2\text{OCH}_2^+$, shortened to EtO, is used. Experimental data is available in [150] for this system. Based on [152] there are several structures in which this ion can be present, with the two most stable ones having a C–O–C bond given as



Exact molecular structures with partial charge distribution were not readily available for EtO, therefore the ab-initio quantum chemistry code ORCA [153] was utilized to calculate a possible molecular structure. A base starting structure was constructed in Avogadro. The open-ring structure was used as initial starting point, since [152] indicates that this structure has lower energy levels. This also agrees well with the already unstable nature of the three-ring in the case of the neutral molecule. This initially linear structure was then structure optimized at the $\omega\text{B97X-V/DEF2-TZVP}$ level of theory using density functional theory. On first optimization it was unclear if the open-ring structure has the three unpaired electrons each in spin up with multiplicity $S = 4$ or if the unpaired electron located by the O atom has one spin down electron with total multiplicity of $S = 2$. As such, both multiplicities were structure optimized and subsequently vibrational frequencies (of numerical form, i.e. not as an analytical differentiation) were calculated. In the case of $S = 4$, negative vibrational frequencies are obtained indicating that the optimized structure found is not in a minimum state but on a saddle-point on the potential energy surface. For $S = 2$ instead only positive vibrational frequencies are found where all values lie in plausible ranges. Those results indicate, that the correct structure has indeed a multiplicity of 2. The fact that multiplicity states usually do not change in ring opening reactions further supports this notion. As the linear structure is most likely a result of the ring opening of the meta-stable, higher energy three-ring structure, only a multiplicity of $S = 2$ would be possible since the ring only has one unpaired electron. The final structure is thus shown in Figure 6.32. Using the Buckingham potential for the van der Waals interactions, ion mobilities are computed for EtO in helium in IDSimF

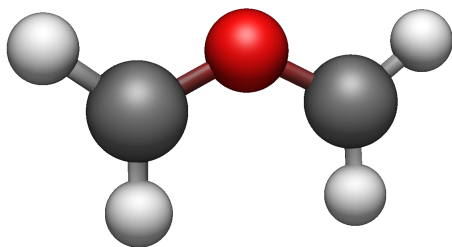


Figure 6.32: Optimized structure in $S = 2$ state of $\text{CH}_2\text{OCH}_2^{+\bullet}$.

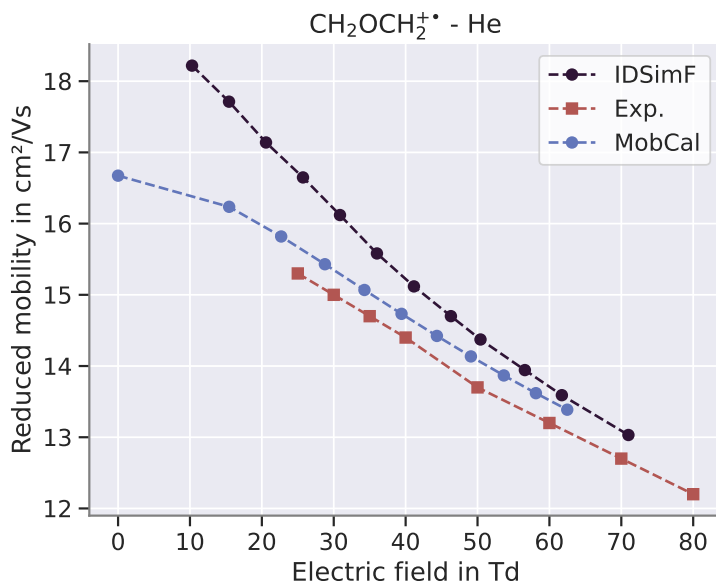


Figure 6.33: Predicted reduced ion mobilities in dependence of the reduced electric field for EtO in helium for IDSimF, MobCal-MPI as well as literature values [150] at 293 K. Simulations in IDSimF were carried out with a step size length of 10^{-12} s.

as well as in MobCal-MPI and compared to experimental values in Figure 6.33. Force field parameters for IDSimF were thereby taken from MobCal-MPI, i.e. both programs employ the same force field in this simulation. MobCal-MPI shows overall a slightly better agreement with the experimental curve, which is especially present for lower field strengths with diminishing effect at the very high field end. Below 25 Td no experimental values are given, as such it is unclear if the curve will follow MobCal's prediction or not. Deviations between IDSimF and literature values are, however, still only in the region of 7%. The differing results of both simulation programs are probably a result of diverging approaches and integration methods, as the force field was kept identical.

6.3.9 Parallelization efficiency

In an effort to improve the runtime of the DT-IMS application, a closer look at the OpenMP parallelization is carried out. First, the benchmark application used in subsection 6.2.2 is evaluated for its parallel performance. As a reminder, in this benchmark application a number of particles are defined at a specific background gas pressure which defines the collision probability. For each particle, the collision model is called and a collision can potentially happen. This whole process is repeated multiple times. The actual code segment of the benchmark application which is parallelized is shown in the following:

```

1  for(size_t j = 0; j<nSamples; j++) {
2      #pragma omp for schedule(static , 1)
3      for(i = 0; i<nParticles; ++i) {
4          mdSim.modifyVelocity(*particlesPtrs[i], 1e-11);
5      }
6  }
```

Thereby, the `modfiyVelocity` function is the call to the individual MD collisions and `#pragma omp for schedule(static, 1)` defines how the particle loop itself is parallelized. As each of the MD collisions is independent of each other, ideal scaling for the benchmark application should be observed since each thread can work on its allocated chunk of data without having to synchronize between threads. In Figure 6.34 the strong-scaling behavior of the benchmark application is shown. The strong-scaling behavior, also called speedup, is the change of the required run time / wall time with number of threads relative to the time taken with one thread while keeping the total problem size constant (number of samples / particles). For the ideal speedup a linear relationship with a slope of one is obtained, as e.g. four threads decrease the wall time to 1/4. This speedup here was computed for 200 Ar^+ in helium at 10000 Pa, such that the collision probability is larger than 99 %, with one sample / loop. An almost ideal speedup up-to 64 threads is visible. At 64 threads the problem size of 200 particles simply becomes too small for ideal scaling.

Since the workload of the individual threads is strongly varying in each time step of the actual DT-IMS application, a further evaluation of how the parallelization is technically done is performed. The workload per thread in the DT-IMS application is primarily determined by the pressure, i.e. the collision probability, and how long the individual collisions take. Each collision requires a different amount of wall time to be integrated dependent on the initial collision configuration (particle positions and velocities). Low relative velocities often lead to stronger attractive forces which result in collisions having a longer interaction time until the particles separate. This uneven distribution of workload per thread would especially stand out if fixed step size methods would be used, as the workload for such methods is much higher. Individual collisions with RKF45 often only vary by 50 time steps total and not thousands of time steps. Because of this potential inequality of the threads, a dynamic allocation of the particles to the threads was initially

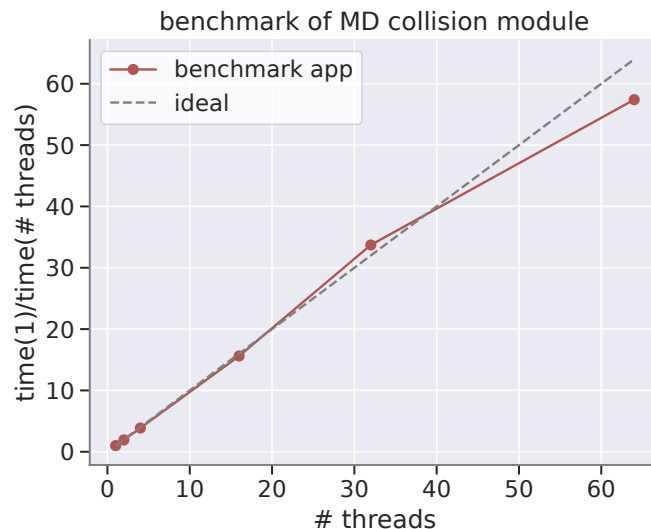


Figure 6.34: Speedup of the benchmark application for MD collisions of 200 Ar^+ in helium at 10 000 Pa. The ideal speedup is shown in gray.

chosen using the dynamic scheduling keyword of the OpenMP library. With dynamic scheduling a portion of the work (in this case here: ions) called `chunk_size` (in this code segment: 1) is dynamically distributed to the threads in no specific order until all work is allocated ("first come, first serve"). There is also the static scheduling type where also a `chunk_size` amount of ions will be distributed to the threads, however this happens in circular order of thread ID ("round-robin style"). Figure 6.35 visualizes the speedup of the benchmark application for different combinations of sample / particle numbers as well as the scheduling type. The top left panel additionally shows the already discussed speedup behavior from Figure 6.34 as reference. Comparing the first panel *a* with the second panel *b* a slight difference is observed. It was expected, that the right panel should also exert ideal speedup as only one sample is done, however there is large divergence from the ideal speedup. In the case of the left panel *a*, benchmark simulations with static scheduling and a 99 % collision rate per particle were carried out. For the right panel *b*, 400 workload allocations with dynamic scheduling are done instead, which becomes especially costly for higher thread counts. This is the case, as threads frequently need to communicate with the scheduler to obtain new chunks. With way more chunk allocations possible than threads available, this communication needs to be done more often which induces additional synchronization costs. Larger chunk sizes in relation to the total particle number would reduce the scheduling overhead, returning to a more ideal speedup. As such, in this case the overhead produced by dynamic scheduling can significantly disrupt the speedup. Additionally, with a collision rate of only about 33 %, the workload is further unbalanced. Additionally, panel *c* and panel *d* show the same particle / sample size for the dynamic scheduling. In *c* the speedup is shown for a chunk size of 1000 while in *d* a chunk size of 100 is used. Since only 4000 particles are used, the chunk size of 1000 only allows for four

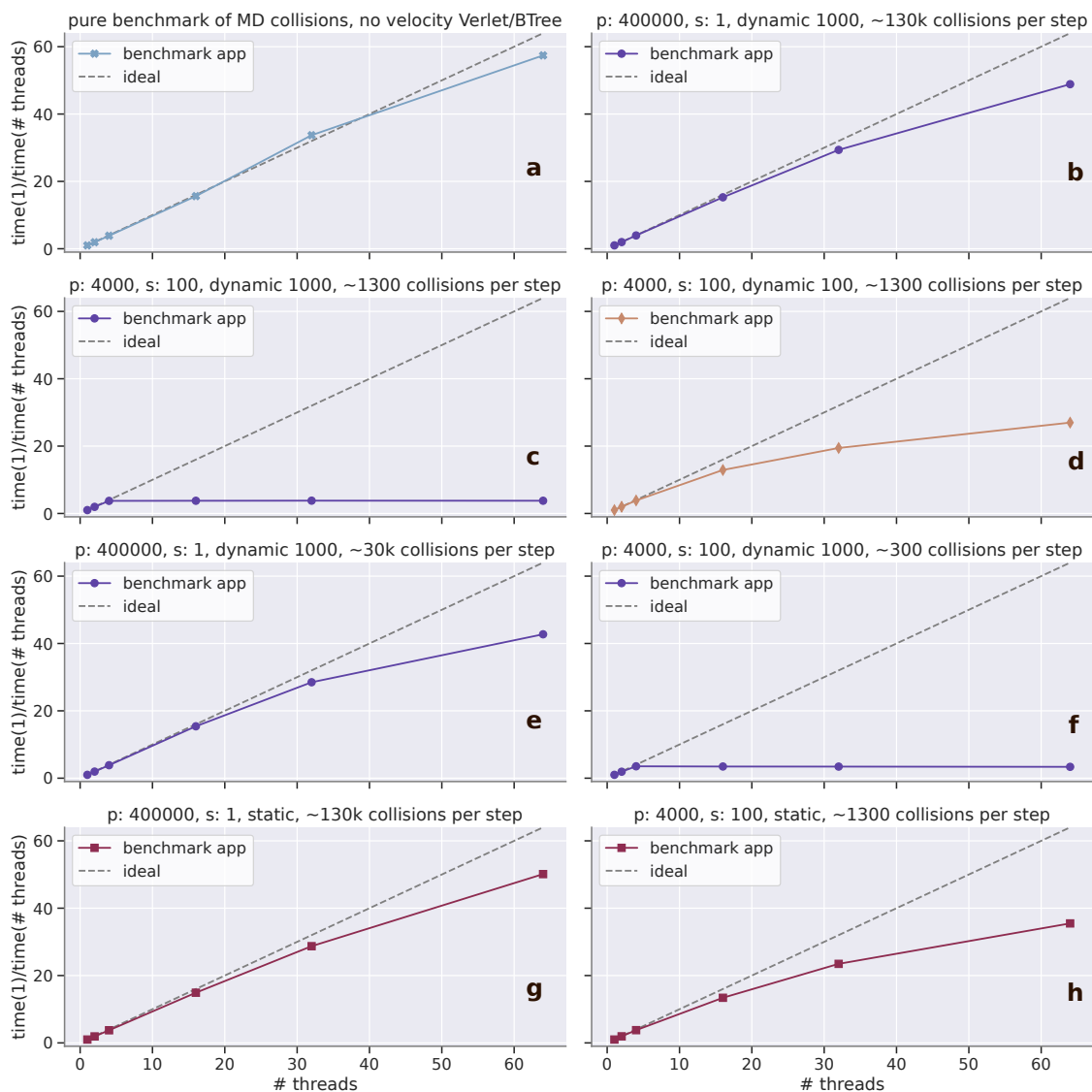


Figure 6.35: Speedup of the benchmark application for a different combination of samples (s) and particle numbers (p) as well as static and dynamic scheduling. The speedup curves are color coded by the scheduling type (blue dots: dynamic 1000, beige diamond: dynamic 100, red squares: static).

allocation chunks. As such, the scaling cannot be greater than four, which is apparent by the complete scaling breakdown after four threads in the left panel. For a chunk size of 100 it instead scales moderately well up to 32 threads.

In panel *e* and *f* for dynamic scheduling with chunk size 1000, the speedup was computed for only one sample but with 400000 particles (so conditions under which ideal scaling is possible) in *e* and 4000 particles in 100 samples in *f*. Individually, each of those particle / sample combinations was already computed, however the pressure was varied for both panels. In both cases, the collisional count (i.e. the computational workload) was reduced significantly. Comparing panel *e* to panel *b* with identical particle / sample count, for higher thread counts a decrease in scaling for a thread count of 64 is noticeable. For the smaller simulation (panel *f*) no further decrease is visible, which also shows the hard computational blockage due to the too large dynamic chunk size.

Lastly, the last row of panels (panel *g* and *h*) show the strong scaling behavior for static scheduling for a system with a high and a low particle count each. In the high particle count simulations, a worse scaling compared to panel *a* is visible, which is due to the decreased collision rate and thus uneven work distribution. The simulation in panel *h* shows a slight increase in scaling compared to the reference in panel *d*, which has the same workload distribution but uses dynamic scheduling instead. As the simulations in panel *d* cannot scale better than 40 threads, the static scheduling performs much better here.

Overall, for small systems resp. particle sizes, the static scheduling seems to be marginally superior. The scheduling overhead is much lower and in addition the dynamic scheduling seems very sensitive to inadequate chunk sizes in relation to the problem size / particle count. For larger systems⁴, dynamic scheduling with appropriate chunk sizes might prove to be better. However, as this scheduling would be a modification to the overall ion trajectory integration method (the velocity Verlet) for all possible applications of IDSimF and not only the DT-IMS application, it was still chosen to use a dynamic type scheduling. To keep the scheduling overhead low, a chunk size that scales with the particle number is set.

For this modification a full, productive DT-IMS run was carried out. Figure 6.36 visualizes the scaling behavior of IMS simulation for the Ar^+ in helium system at two different pressure values leading to either 1.5 or 15 collisions on average per time step. For low pressure values (left panel), the scaling cannot be larger than 1.5 as a further increase in thread number only increases the overhead while not being able to further divide any notable work to the threads. With larger collision numbers (right panel) a stronger scaling is observed up to 16 threads. However, while some scaling is existent at 16 threads, it is far from ideal. This is simply a result from the further overhead of the surrounding non-parallelized workload in the velocity Verlet time step. Additionally, particles are moved in a collective ensemble, meaning the overarching trajectory integration needs to

⁴The particle count in the DT-IMS simulations is normally set to 2000 (i.e. a small system), as the MD model takes too long in total wall time for higher counts in productive use.

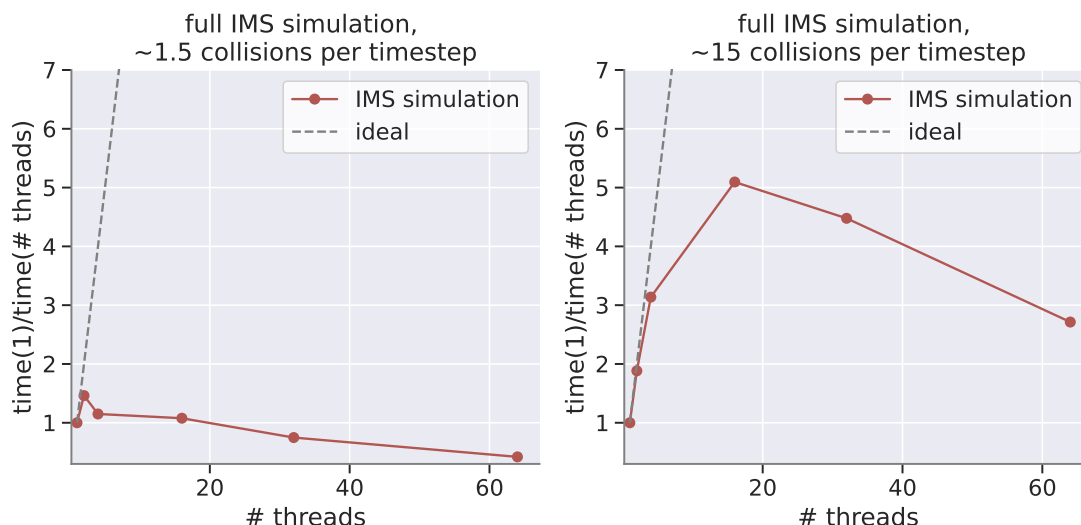


Figure 6.36: Strong scaling of full IMS simulation runs for 200 Ar^+ in helium at 20 mbar (left panel) and 200 mbar (right panel).

wait for synchronization after each time step. If space-charge is not relevant, the loop can be re-written to be parallel along the time axis instead (specific particles are always on the same thread without any synchronization), however this was not done yet.

6.4 Introduction of nitrogen as neutral gas

Many of the earlier versions of well-known ion mobility prediction programs used to be limited to simulations carried out in helium alone. As nitrogen gained significantly higher importance as a drift gas in IMS applications, a lot of effort was put into including as well as optimizing for nitrogen in those frameworks [84, 85, 135, 154]. Certain complexities arise when using nitrogen as the drift gas in simulations. In contrast to helium and argon, the diatomic nature of nitrogen leads to new types of potential interaction between ion and gas and possible effects of molecular rotation.

The following section therefore focuses on necessary adaptations of the IDSimF MD model implementation to allow molecular nitrogen simulations and outlines numerical obstacles, their effect on ion mobility predictions and possible mitigation techniques.

6.4.1 Force field adaption

Owed to the step from monoatomic to diatomic collision gas, the force field function requires the inclusion of the quadrupole moment potential as described in subsubsection 2.5.1.5. The quadrupole-ion potential is not only dependent on the distance between a nitrogen particle and the ion, but also on the angle of attack / rotation of the nitrogen itself as this potential can be either attractive or repulsive and is not spherical symmetric. On first instance this rotational effect is considered in a simplified manner: each collision

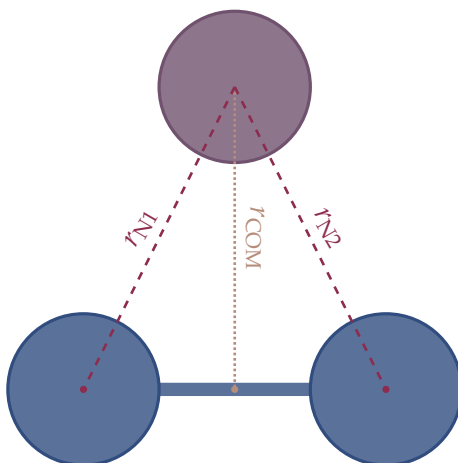


Figure 6.37: Two versions of how to compute the ion-induced dipole moment. The center-of-mass (r_{COM}) version takes the full potential from each atom of an ion (simplified by red circle) to the center-of-mass of nitrogen (blue circles: nitrogen atoms), i.e. the center of the bond. The splitted version (r_{N1} and r_{N2}) takes half of the polarizability force but calculates it to each of the center points of the N atoms (essentially averaging the force value).

is initialized with a randomly rotated configuration of the ion and the background gas and the rotation is kept fixed over the collision integration.

Additionally, the ion-induced dipole moment can be implemented in two different ways by either calculating the share of this force between the atoms of the ions and the center-of-mass of N_2 or by splitting half of the induced potential to the two N atoms, as illustrated in Figure 6.37.

The complete force field potential function with nitrogen as background gas partner is thus the sum of van der Waals interaction, ion-induced dipole moment and ion-quadrupole moment given as

$$U_{\text{N}_2}(r_{ij}) = U_{\text{vdW}}(r_{ij}) + U_{\text{ind}}(r_{ij}) + U_{\text{quad}}(r_{ij}) \quad . \quad (6.5)$$

In [155] three force field functions are compared, two of which are the 12-6 Lennard-Jones and the modified Buckingham potential. The study showed that the most accurate collision cross-sections are obtained when using the modified Buckingham potential function, which was a basis for the implementation of this potential form in MobCal-MPI. In an effort to test this statement in the context of smaller ions and to also easier compare MobCal-MPI with IDSimF (see e.g. Figure 6.25 and Figure 6.33), the modified Buckingham potential was also implemented into IDSimF. Initial tests of the implementation were performed with Li^+ , but quickly proved to be unstable. These instabilities initiated extensive studies of integration and methodological differences between MobCal-MPI and IDSimF, which will be discussed in condensed form in subsubsection 6.4.2.2. However, the observed instabilities and the mitigation for both van der Waals potentials are presented at first.

6.4.2 Numerical instabilities

6.4.2.1 Modified Buckingham and 12-6 Lennard-Jones potential

Initially, the modified Buckingham potential respectively the force function was simply implemented as is described by subsection 2.5.1.2. As already mentioned, the first test system chosen was Li^+ , which proved to be a simple and reliable ion in the cases of helium and argon as background gas. Ion mobility simulations were carried out for low field strengths with the mod. Buckingham potential, but resulted in most of the collisions not being energy conserving (energy was gained). This effect was already seen for some collisions with the 12-6 Lennard-Jones potential as well, prior to the implementation of the modified Buckingham potential. Besides enabling better comparisons between MobCal-MPI and IDSimF due to an identical force field function, another reason for the implementation of the mod. Buckingham potential was in the hopes of reducing collision trajectories which are unstable (i.e. not energy conserving). Studies had shown better ion mobility results with the mod. Buckingham potential. On closer look, it is intuitive as to why the mod. Buckingham severely increased the amount of unstable trajectories: the mod. Buckingham has a similar potential well as the 12-6 Lennard-Jones potential, but with a later onset (i.e. it is basically like a damped 12-6 Lennard-Jones) and more importantly it has a maximum in its potential curve after which the interaction between the ion and background gas becomes attractive again. This is in stark contrast to the 12-6 Lennard-Jones potential, which has a potential wall going to infinity. Due to this, the mentioned energy gain effect is notably exacerbated. Figure 6.38 illustrates the differences between the 12-6 Lennard-Jones and mod. Buckingham potential by showing the total force as well as the individual force components (the quadrupole force is neglected here for reasons of simplicity) on a logarithmic scale. As a test collision a frontal collision in x -direction was used and computed in IDSimF. Thereby, values above zero are a repulsive force and values below zero are an attractive force. It is unambiguously visible that the repulsive part of the mod. Buckingham force starts much later and is weaker than the 12-6 Lennard-Jones force. Additionally, it becomes easy to see that at close distances of around 1 Å in the model system shown here the interaction becomes attractive again which is amplified by the ion-induced dipole moment. Exactly this part of the force function seemingly leads to many invalid / non energy conserving collision integrations. It becomes possible for small systems like Li^+ to overcome the repulsive hill and for the atom centers to get very close to each other, leading to numerical integration errors⁵.

To mitigate the occurrence of critical collisions, the mod. Buckingham force function is split into two parts. The first part is just the unmodified force calculation defined by subsection B.4.2 for all positions between the maximum of the potential function and

⁵When the distances between two atoms get very small, the integration can become numerically unstable. This is due to the fact that the distance is used as a divisor in the force function calculation and division by values close to zero are numerically difficult. Often forces are overestimated and the involved particles gain a significant amount of energy, resulting in a kind of "catapulting" effect with high exit velocities.

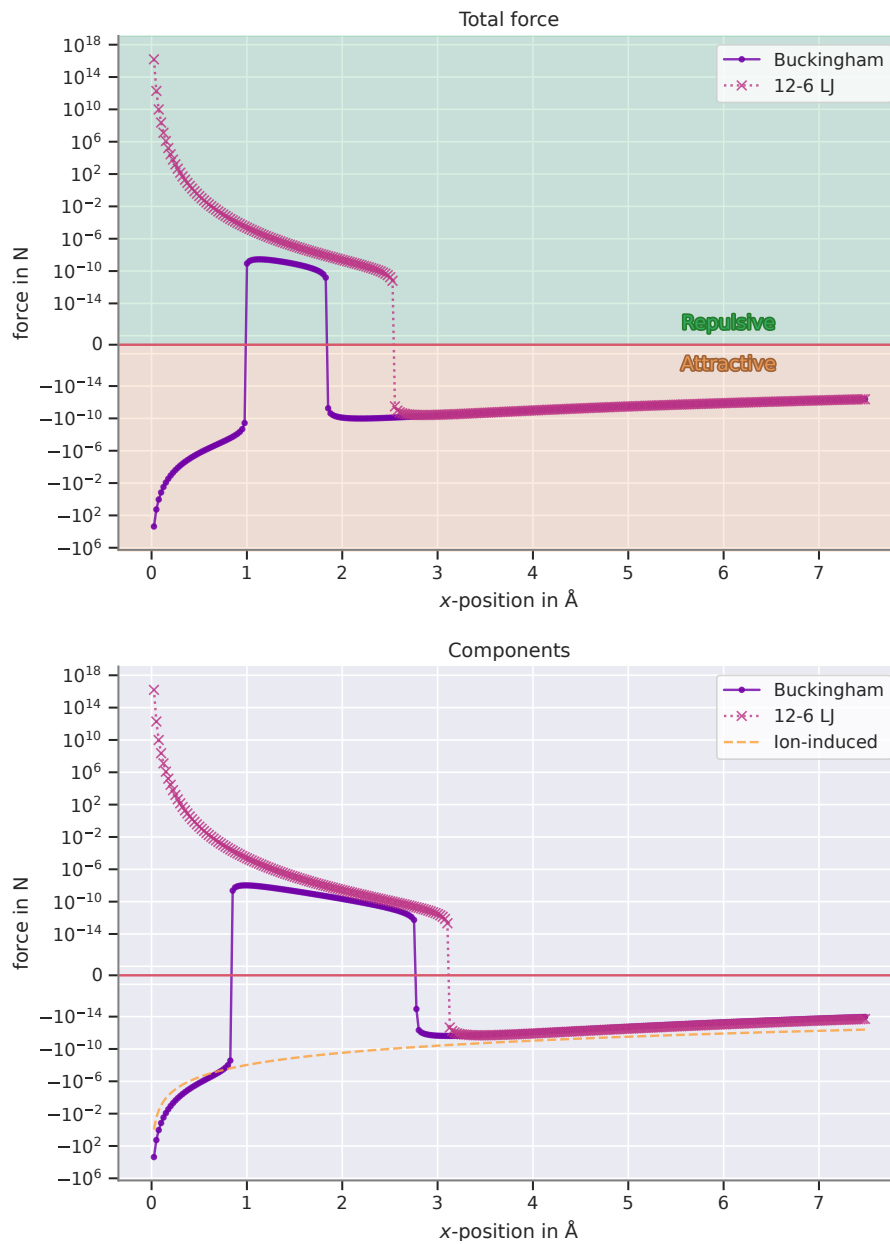


Figure 6.38: Numerical calculation of the force as well as its individual components based on x -distance between nitrogen and a lithium ion in a head-on collision (i.e. the positions were sampled on the x -axis and for each position just the force was calculated; no actual integration was done). The force is shown on a logarithmic scale.

infinity. In Figure 6.38 the maximum of the potential function is the left zero crossing of the force function at approximately $0.9 \text{ \AA}$, since the force is the negative derivative of the potential. For positions below the maximum an infinitely increasing potential similar to the 12-6 Lennard-Jones force is implemented. Since the exact position of the maximum is dependent on the force field parameters and thus varies for each different atom pair, the maximum position needs to be numerically evaluated at the beginning of an IMS simulation resp. at the point of the MD model initialization in the application code. The evaluation is carried out by a golden-section search, which is an algorithm to find either the minimum or maximum of a unimodal function. More information can be found in [156]. The method is robust but slow, however since for each atom pair the position of the maximum r_{max} stays constant for the whole simulation, each value has to be computed only once hence the computational speed is not as important.

The function which is applied below the boundary of r_{max} is

$$F_{\text{MB, cutoff}} = -10 \cdot \epsilon \cdot \frac{1.85 \cdot 10^5 \cdot 12}{r \cdot \sigma} \cdot \exp\left(\frac{-12 \cdot r}{\sigma}\right) \cdot \vec{r} \quad , \quad (6.6)$$

which is simply the repulsive part of the mod. Buckingham force function scaled by 10-fold (see subsection B.4.2) to allow for a significant potential wall without directly applying an infinite force (this could potentially also lead to numerical errors). Several scaling factors were tested, with a scaling of 10 found to offer the best transition between the normal mod. Buckingham force function and the fully repulsive force. The step-function like switch between repulsive and attractive force did not lead to any additional instabilities in the tested systems.

Even after correcting of the non-physicality of the mod. Buckingham potential still many collisions ended up gaining energy. As a reminder this is also the case for collisions computed with the 12-6 Lennard-Jones potential, hence there is a further factor resulting in energy gain when nitrogen is used as the background gas particle. Individual collisions were then examined and it was recognized that particularly collisions with slow relative velocities lead to energy gain. Further visual examination of the gas trajectories showed that the trajectories were not yet complete when the integration was terminated, i.e., the termination of the trajectories was caused by the maximum integration time and not by the desired distance (the set starting distance) between the two particles being reached. Figure 6.39 illustrates the difference between collisions terminated by the integration time limitation and regular collisions. In regular, i.e. energy conserving, trajectories, as shown in Figure 6.39b, the particles interact with each other but "relatively" quickly detach again and leave the interaction sphere (of course dependent on velocity, entrance angle, rotation, etc.). The collisions which reach the maximum integration time behave much different (Figure 6.39a): the particles continuously orbit around each other and form a kind of meta-stable cluster state. Since these particles require many orbiting cycles to detach, the maximum integration time would often be reached. Initially⁶, the

⁶Meaning in the first steps of the nitrogen implementation and first published results [82], as there was never an apparent problem with a slightly lower integration time.

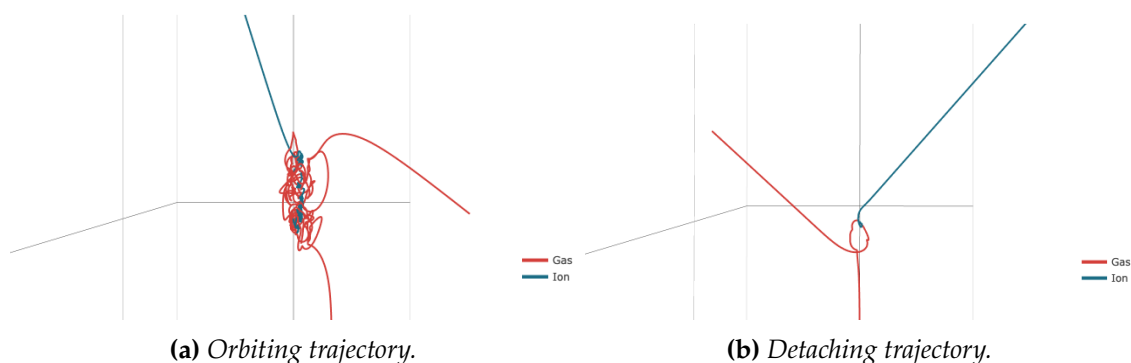


Figure 6.39: Example collisions showing orbiting as well as detaching trajectories.

maximum integration time was set to 10^{-11} s to match the step size of the overarching velocity Verlet integration (which was later also reduced to 10^{-12} s for more stable ion mobility predictions). Prevention of many energy gaining collisions was then reached by increasing the maximum integration time to 10^{-10} s. Even though the maximum collision integration time is larger than the velocity Verlet time steps, auxiliary simulations showed no adverse effects. However, energy gain collisions are not completely prevented by this change. Not only termination of the integration during close interaction of the particles leads to incorrect energy distribution but also longer integration times, since induced numerical integration errors start to add up.

6.4.2.2 Comparison to MobCal-MPI

First computed ion mobility curves for low and high field showed large discrepancies from experimental values and the instabilities encountered in the collision integration prompted a more in-depth study of differences between MobCal-MPI and IDSimF, as seemingly MobCal-MPI did not show as many stability problems (at least in cases of larger ions). The idea was thus to simulate several collisions in MobCal-MPI for Li^+ in nitrogen first, as this was the "simplest" system available, and to simulate exactly the same collisions in IDSimF for direct comparison. The ability to simulate monoatomic ions in MobCal-MPI required changes to the code. Using a MobCal input file with one atom for the ion results in an abnormal program termination due to memory protection violation (segmentation fault). This is a result of an unset variable in the calculation of the maximum extent and orientation along the x -axis, which is used among other things to check for error calculation in ion mobility calculation. A special case was introduced which sets this variable if only one atom was read in. As this is basically only a workaround and has some implications for the ion mobility predictions in MobCal-MPI, ion mobilities obtained with this modified program version should not be used as reference value as correct calculation and usage of values inside the outer simulation loop (i.e. grid construction, error calculation, scattering angle determination) cannot be guaranteed. Fortunately, besides potentially changing the starting grid of the simulated background gas particles, this modification has no further effect on the actual trajectory integration loop and trajectories between both programs can

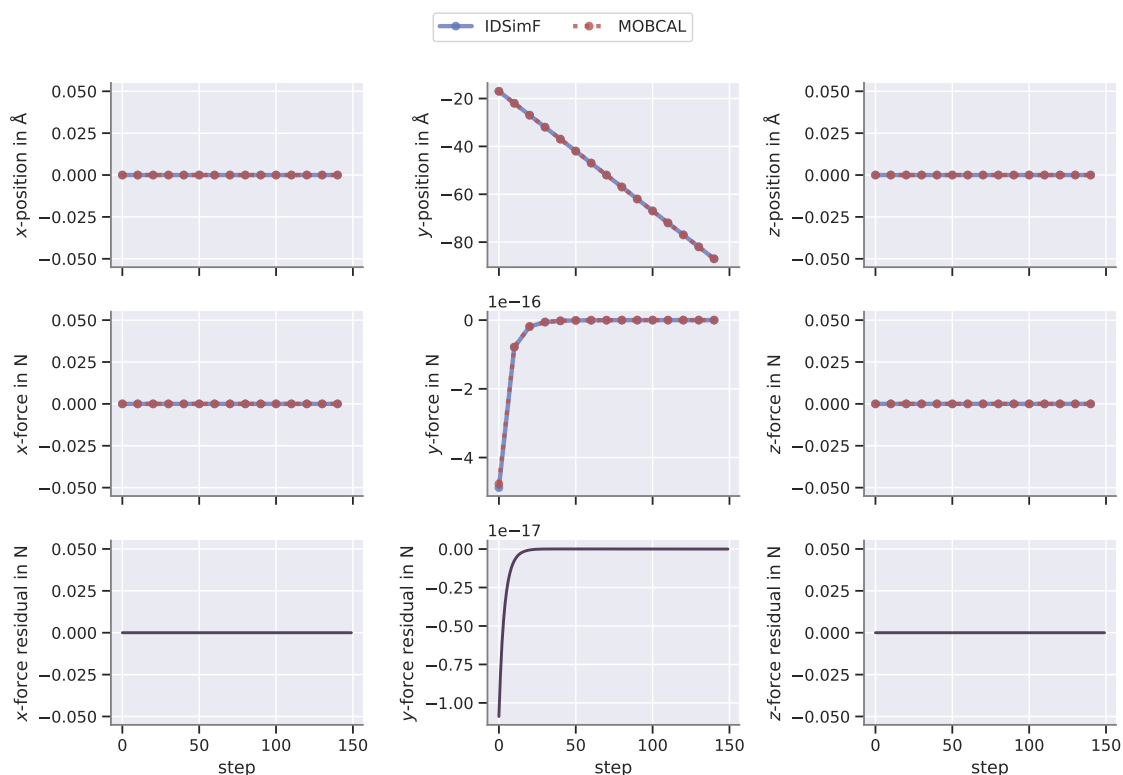


Figure 6.40: Comparison of force and force residual in all three spatial directions between IDSimF and MobCal-MPI for one exemplary collision, with initial conditions constructed by MobCal-MPI. Only every tenth time step is plotted for the positions and forces to better visualize agreement between both curves. The force residual is shown for all time steps. In this case, only *van der Waals interactions* with the mod. Buckingham potential were active.

be safely compared. Additionally, since MobCal-MPI does not support the recording of individual trajectories, trajectory logging has been added with writing of position, force, time and velocity data in each time step of a trajectory to an output file.

Before actual trajectories are compared with each other, some trajectories are calculated in MobCal-MPI and the background gas positions are extracted. The position values of one whole trajectory are then used in IDSimF to evaluate only the force at those positions which is compared to the calculated force in MobCal-MPI. Positions of trajectories calculated by MobCal-MPI instead of predefined, arbitrary test positions were used for the force field comparison. The reason for this approach was the significant required effort to implement the functionality to use externally defined positions in MobCal-MPI. As a consequence of this procedure, modifications of the force field to isolate individual force field contributions, as shown in the following section, result in changed MobCal-MPI trajectories and therefore in changed test positions.

When using the exact same force field parameters and the same force field function, the computed forces should be essentially identical in both programs. As a first step, each force field function component was compared individually (i.e. mod. Buckingham, ion-induced and quadrupole potential). The quadrupole-ion potential is a special case

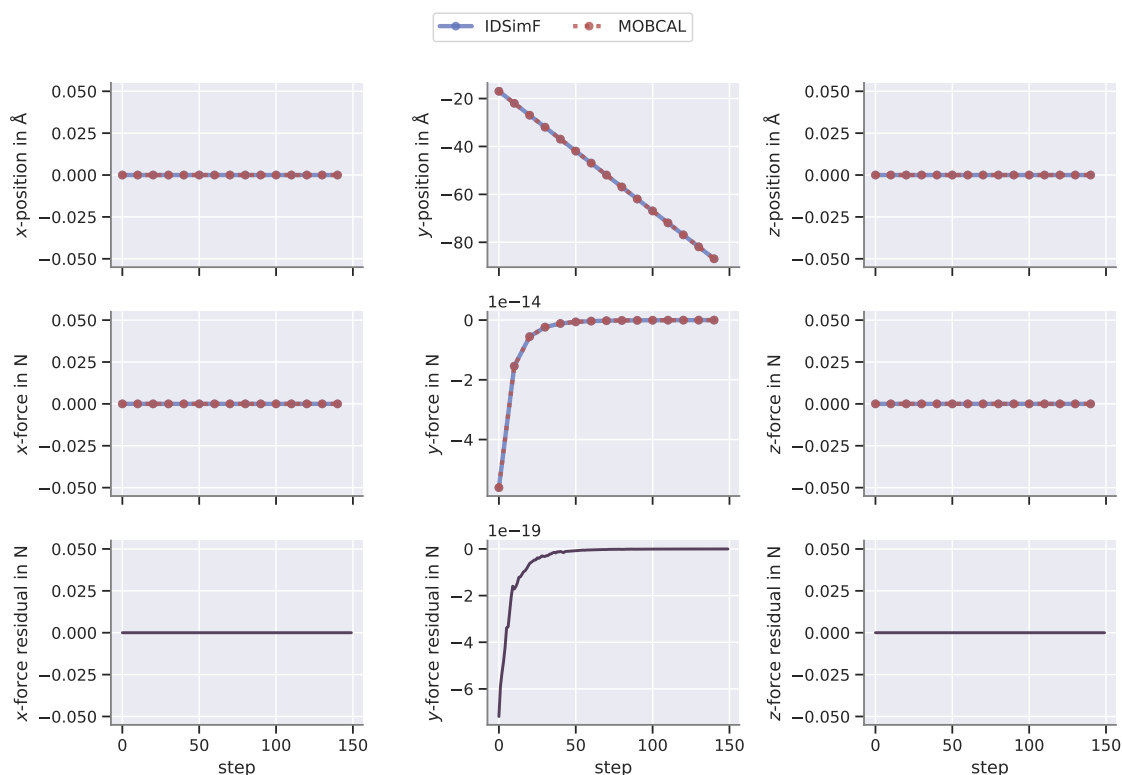


Figure 6.41: Comparison of force and force residual in all three spatial directions between IDSimF and MobCal-MPI for one exemplary collision constructed by MobCal-MPI. Only every tenth time step is plotted for the positions and forces to better visualize agreement between both curves. The force residual is shown for all time steps. In this case, only **ion-induced dipole interactions** were active.

in MobCal-MPI as the quadrupole force is computed as a weighted average of the force with nitrogen positioned in all three spatial directions to approximate a rotating nitrogen molecule. In IDSimF, the initial rotation is randomly determined and then fixed over the integration of a single trajectory and no weighted average is calculated. Therefore, the weighted averaging is disabled in MobCal-MPI to allow for exact comparison between both programs and the nitrogen bond is fixed in the y -direction in both programs. Figure 6.40 shows a comparison of the force for a collision with only van der Waals forces defined by the mod. Buckingham interaction between Li^+ and N_2 .

Since the collisions completely takes place in the y -direction no differences between x - and z -direction exist. Additionally, as the position values from an exemplary MobCal-MPI trajectory are used for the force calculation in both programs, the positions are naturally always identical. For the y -direction overall forces are in the ranges of 10^{-16} N, with the residuals being on the order of 10^{-17} N (i.e. differences are on the first decimal place). The same procedure was then repeated for a force field only containing the ion-induced dipole force. The results are shown in Figure 6.41. In this case the ion-induced dipole force is about two magnitudes larger than the mod. Buckingham force, with values around 10^{-14} N. The residuals in this case are about 10^{-19} N, i.e. the difference between

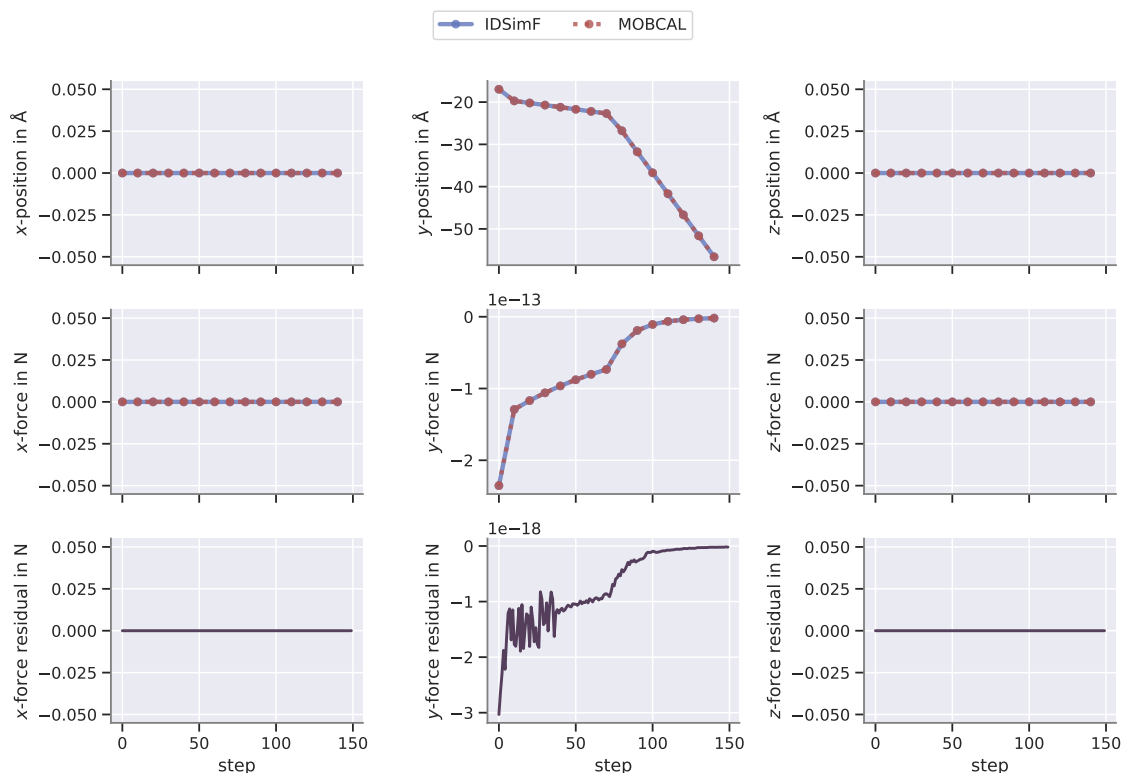


Figure 6.42: Comparison of force and force residual in all three spatial directions between IDSimF and MobCal-MPI for one exemplary collision constructed by MobCal-MPI. Only every tenth time step is plotted for the positions and forces to better visualize agreement between both curves. The force residual is shown for all time steps. In this case, only **ion-quadrupole interactions** were active.

both programs is much smaller. This behavior is slightly unexpected as similar or less accuracy for the ion-induced dipole moment was expected as this is the numerically more complex function to evaluate which was expected to be more sensitive to rounding errors. Lastly, the force field was modified to only contain the quadrupole-ion interaction with the resulting computed forces given in Figure 6.42. With forces on the order of 10^{-13} N, the interaction is even stronger than for the ion-induced dipole moment. The residual resides at about 10^{-18} N, with more noticeable noise on the residual curve.

Overall, there is a good agreement between the computed forces between both programs at the same position values with the van der Waals forces showing the largest difference. When combining all three force components of the force field which is normally used for all ion mobility simulations, a slightly different behavior is visible. In Figure 6.43 the force comparison with all three forces is shown. While the largest difference was about 10^{-16} N with the van der Waals forces only, for this trajectory the residual is on the order of 10^{-13} N. Noticeable disagreement between both programs is thus found for the force in y -direction, with divergence being the largest for the positions in the beginning where the calculated force is the highest. A second trajectory was then extracted as shown in Figure 6.44. In this case, the trajectory also has a component in x -direction with similar

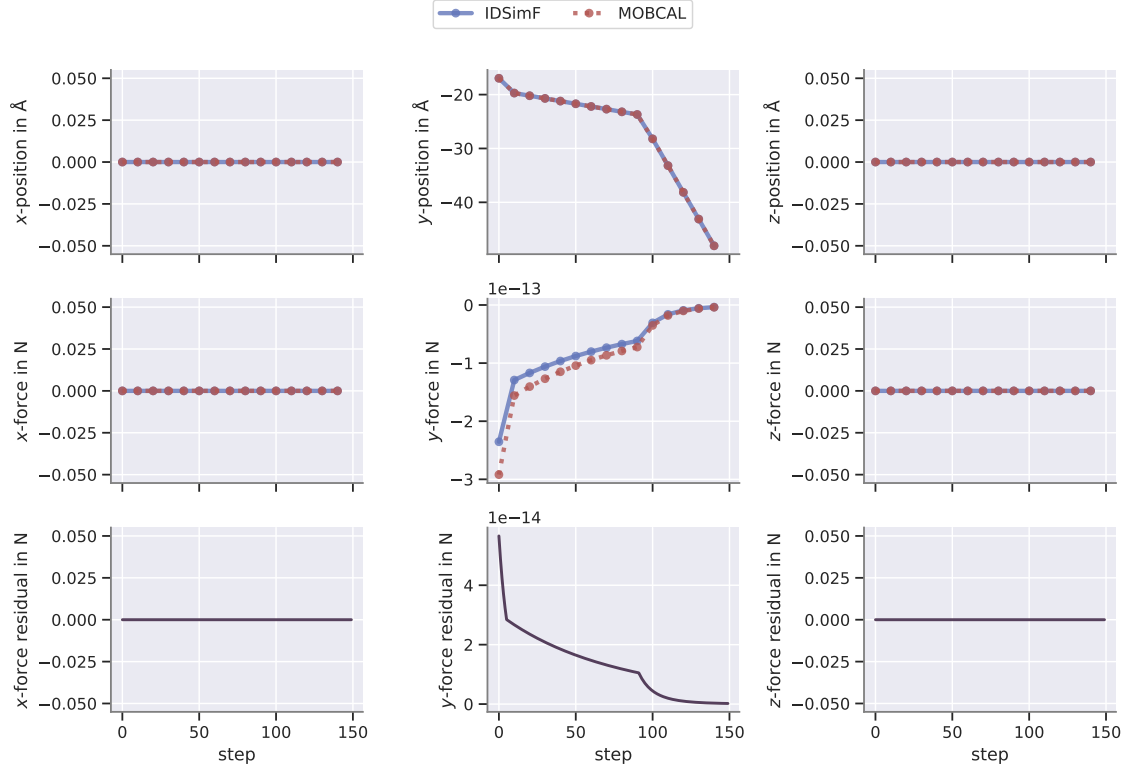


Figure 6.43: Comparison of force and force residual in all three spatial directions between IDSimF and MobCal-MPI for one exemplary collision constructed by MobCal-MPI. Only every tenth time step is plotted for the positions and forces to better visualize agreement between both curves. The force residual is shown for all time steps. All force field components were active.

force components in y -direction. For this trajectory, much smaller residuals are obtained and there is no apparent visible difference between calculated forces. Another trajectory with components in x - as well as y -direction, as given in Figure C.2 shows identical patterns with very small residuals. Seemingly, the larger deviations in Figure 6.43 result from a specific trajectory configuration as the two other compared trajectories have much smaller deviations.

Further comparison was done by actually integrating several collisions in both programs, with the starting positions and velocities defined by MobCal-MPI to verify the similarity of integrated trajectories despite some (numerical) differences in the force calculation. Seventeen different trajectories were sampled in both programs and the mean as well as final values of the position, velocity and force vector were compared. The mean residuals are used for a better comparison of the average of the whole trajectory integration, while the residuals at the final integration point also need to be low as the end change in the velocity is propagated back to the ion trajectory simulation. The results are visualized in Figure 6.45 for trajectories up to an integration time of $3 \cdot 10^{-12}$ s, as this was the stop point for the integration in IDSimF (given by the maximum interaction sphere). In general, the differences were much smaller than anticipated due to the large differences in forces as

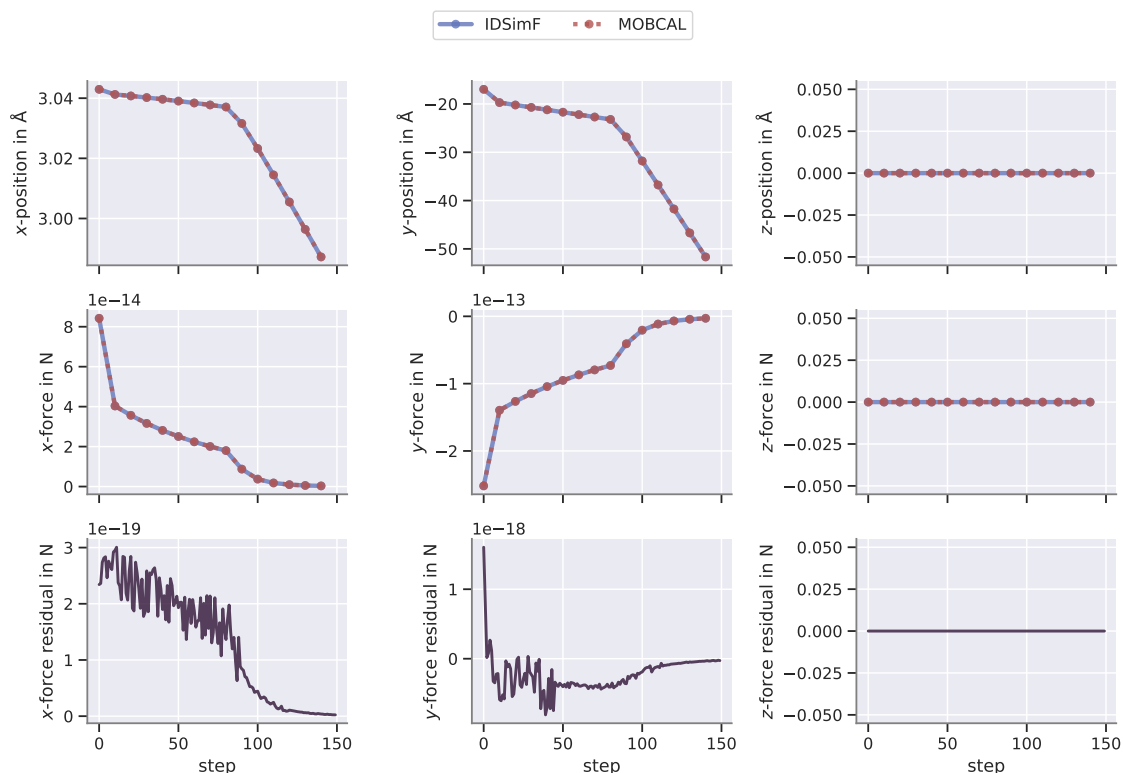


Figure 6.44: Comparison of force and force residual in all three spatial directions between IDSimF and MobCal-MPI for one exemplary collision constructed by MobCal-MPI. Only every tenth time step is plotted for the positions and forces to better visualize agreement between both curves. The force residual is shown for all time steps. All force field components were active.

shown in Figure 6.43 and are more inline with the behavior visible in Figure 6.44 and Figure C.2.

Final positions differ by less than 1 Å and final velocities by less than 10 m/s. Interesting are the mean residuals of the velocity and force compared to the mean residual of the position: both mean velocity and mean force residual are strongly correlated while the mean position residual completely differs. As such, there seems to be no direct one to one relationship between velocity and position even though the positions are calculated from the velocity vectors in Newton’s equations of motion. The reason for this is unclear at the moment.

To make the comparison more representative, a larger set of trajectories was then also compared, where only the final residuals for position, velocity and force are calculated, which is visualized in Figure 6.46. For these trajectories the starting velocity of the background gas particle is also given. The amount of sampled trajectories was increased significantly and the cycle count in MobCal-MPI was increased from one to two also. The starting velocity vector is thus completely repeated besides the initial start-up phase. Starting positions are thereby slightly randomized between the cycles. The repetition of the velocity samples can be clearly seen in the panel of the starting velocity (bottom)

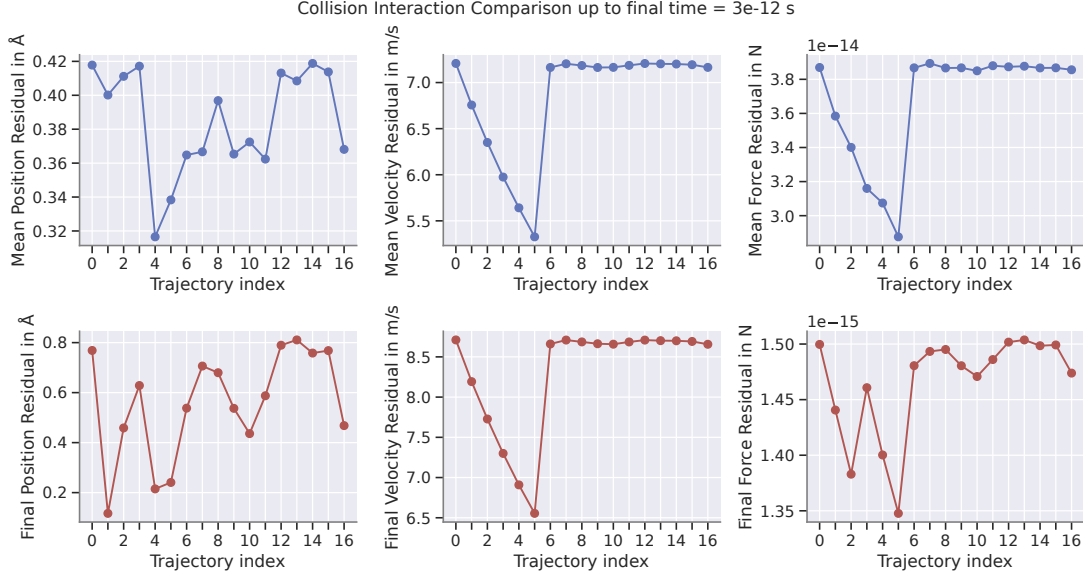


Figure 6.45: Comparison of trajectories with the full force field between MobCal-MPI and IDSimF for starting conditions generated by MobCal-MPI. Position, velocity and force differences are shown as a mean value over all trajectory points as well as for the final position (i.e. the point at which IDSimF stops integrating) at an end time of $3 \cdot 10^{-12}$ s.

where everything is carried out identically two times except besides the first approx. 70 trajectories.

This larger data set also confirms that final force and velocity residuals follow the same pattern, while the final position residual is largely uncorrelated. Again, larger residuals in position do not directly correlate with high residuals in the force / velocity. In the position residuals it can further be seen that the cycles do not lead to an exact repetition of position residuals for the same velocity point. This becomes obvious by comparing the group of trajectories with high position residual between 998 and the next tick and the group around trajectory index 1997 and later. Comparison of the starting velocity with the final velocity residual reveals another interesting observation: with lower starting velocity the final velocity residual increases systematically. This effect was already noticed in single trajectories in IDSimF and was described as *energy gaining* behavior. As starting velocities decrease, the integration takes longer over all and the particles start to orbit because of longer close contact. Seemingly, exactly those trajectories have larger divergence between both programs and are harder to integrate. It is unclear if MobCal-MPI or IDSimF has the more physically valid result as analytical solutions cannot be obtained. Since MobCal-MPI uses an Adams-Moulton Predictor-Corrector integrator scheme, which is in parts an implicit method, it might be able to handle the slight stiffness of the force field better. In summary, there is a high agreement between MobCal-MPI and IDSimF for the investigated trajectories, with average differences of around $1 \text{ \AA}$ in the position and around 10 m/s in the velocity. Since the same force field parameters were applied and overall handling of the forces were congruent between both programs using the modified MobCal-MPI

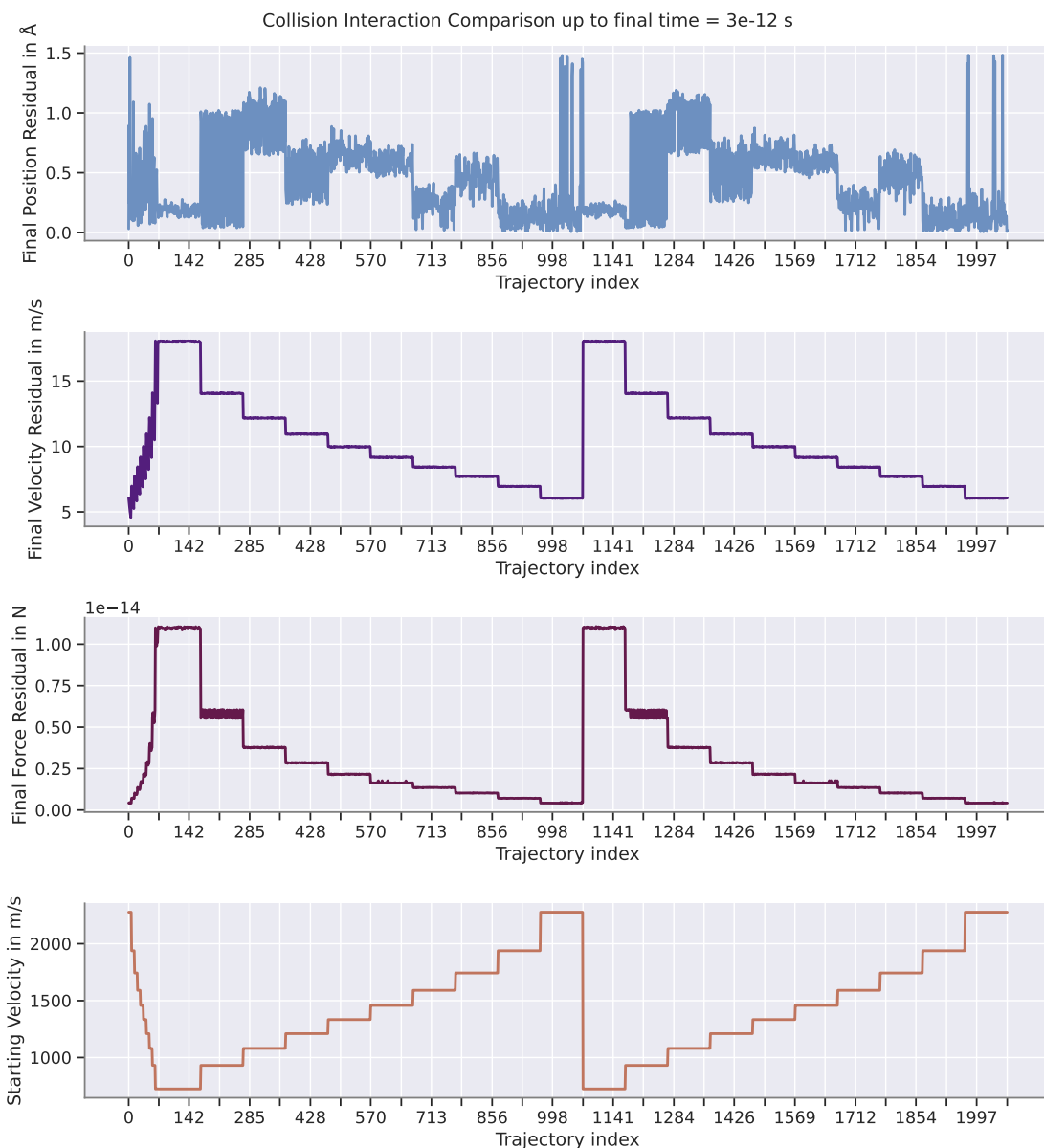


Figure 6.46: Comparison of trajectories with the full force field between MobCal-MPI and IDSimF for starting conditions generated by MobCal-MPI. Position, velocity and force differences are shown for the final position (i.e. the point at which IDSimF stops integrating) at an end time of $3 \cdot 10^{-12}$ s. Additionally, the starting velocity of the background gas particle is given.

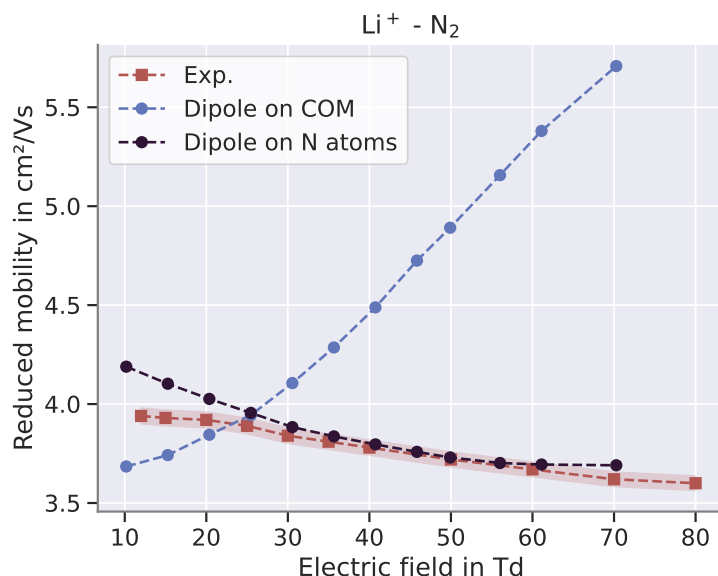


Figure 6.47: Predicted reduced ion mobilities in dependence of the reduced electric field for Li^+ in molecular nitrogen at 295 K for IDSimF as well as literature values [150]. Simulations in IDSimF were carried out with a step size length of 10^{-12} s. The mobilities were determined by either averaging of the ion induced dipole forces or by COM position.

program, the observed differences probably originate from the different integrators used (RKF45 in IDSimF vs. Adams-Moulton predictor-corrector in MobCal-MPI) and numerical rounding differences / errors.

6.4.3 Ion mobility dependencies

In the following section the effect of several forces and special cases arising for molecular nitrogen as the background gas on the obtained ion mobilities are studied. For all shown simulations it has to be kept in mind that changes in the force field parameters can alter the dynamics for each discussed effect, but due to time constraints an extensive force field optimization was not carried out. If force field parameters were available for an atom in MobCal-MPI, the values would initially be adopted for the force field in IDSimF independent of employed van der Waals force function if not noted otherwise.

6.4.3.1 Ion-induced dipole moment

In a first step the two different ways to implement the ion-induced dipole moment were compared in their effect on the ion mobility. As a test system still Li^+ in N_2 with the standard 12-6 Lennard-Jones as van der Waals component is used. As a reminder, the ion-induced dipole moment can either be calculated between the atoms of the ion and the center-of-mass of nitrogen (COM) or be summed over the two N atoms, where each atom has only half of the dipole moment as its contribution (*averaging*).

The changes in ion mobility in dependence on the different force modeling is shown in

Figure 6.47. Calculation of the ion-induced dipole to the COM leads to a drastic divergence of the ion mobility to the experimental literature values, particularly in the higher field regions with errors in the range of 20 to 50 %. In contrast, the averaging of the ion-induced dipole force results in a way better convergence to the experimental data, with very good matches between 30 to 60 Td. There are, however, still larger deviations for lower field strengths below 15 Td. The averaged force model appears to be favorable for small ion systems as this severely reduces the possibility of alignment of the ion around the center-of-mass of the nitrogen molecules. The COM can act as an effective singularity, since it is implemented as a dummy atom with no van der Waals parameters, i.e. no attractive and, more importantly, no repulsive forces. By interaction with this singularity, energy gaining collisions can be produced and overall the velocity can be overestimated (while keeping in the energy threshold).

6.4.3.2 Buckingham potential

Despite the Buckingham potential being able to approximate systems involving helium as background gas reasonably well (see e.g. Figure 6.25 and Figure 6.33), multiple simulations combining the Buckingham potential with N_2 as the neutral collision gas often failed. This was especially a problem when excluding the ion-quadrupole moment from the force field which lead to collisions not being energy conserving. Figure 6.48 shows exactly this effect for Li^+ in N_2 : below roughly 40 Td no simulation data points are available if the ion-quadrupole force is turned off. Presumably most, at some point in the simulations even all, of the collisions cannot be integrated below this electric field strength while conserving energy. This is also influenced by the force field parameter set used. As a result of the softer repulsive interaction of the Buckingham potential, much harsher force field parameters need to be set. It can thus be concluded that the Buckingham potential is marginally more fragile in handling such small ion systems and might not be suited well for them. Additionally, when taking into account the results illustrated in Figure 6.47, it becomes apparent that including the ion-quadrupole force in the force field is obligatory to compute ion mobilities in agreement with experimental data as otherwise errors of 20 % are possible for a curve which matched well including the ion-quadrupole force (compare the no ion-quad. curve in Figure 6.48 with the averaged curve in Figure 6.47).

Also the effect of the two varying treatments of the ion-induced dipole potential were studied using the mod. Buckingham potential instead of the 12-6 LJ potential for the same system. Figure 6.49 demonstrates that both implementations strongly differ from the experimental values when the mod. Buckingham force is used, even though the force field parameters are taken from MobCal-MPI (and thus are optimized for the mod. Buckingham potential). Seemingly, either of two possible explanations for this result seem plausible: i) the force field parameters optimized for MobCal-MPI only work well for the ion mobility calculation approach with Mason-Schamp / 2TT or what is more likely ii) the force field parameters are simply optimized for much larger molecules structures since

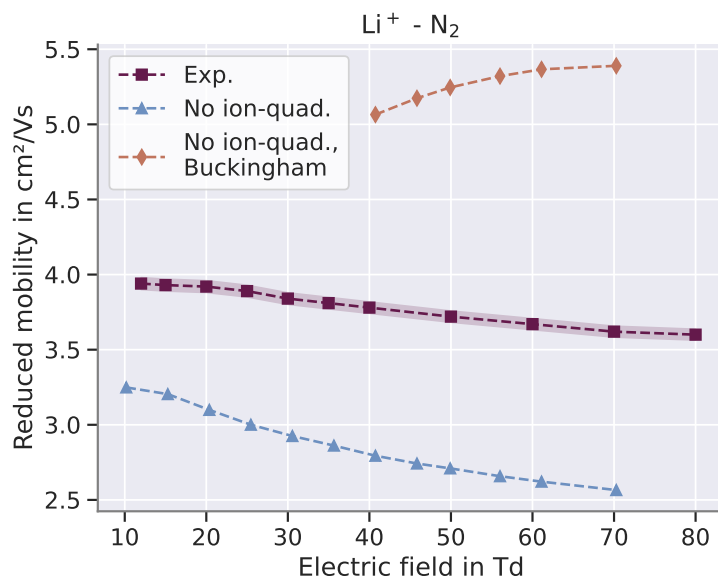


Figure 6.48: Predicted reduced ion mobilities in dependence of the reduced electric field for Li^+ in molecular nitrogen at 295 K for IDSimF as well as literature values [150]. Simulations in IDSimF were carried out with a step size length of 10^{-12} s. The mobilities were determined by exclusion of the ion-quadrupole potential.

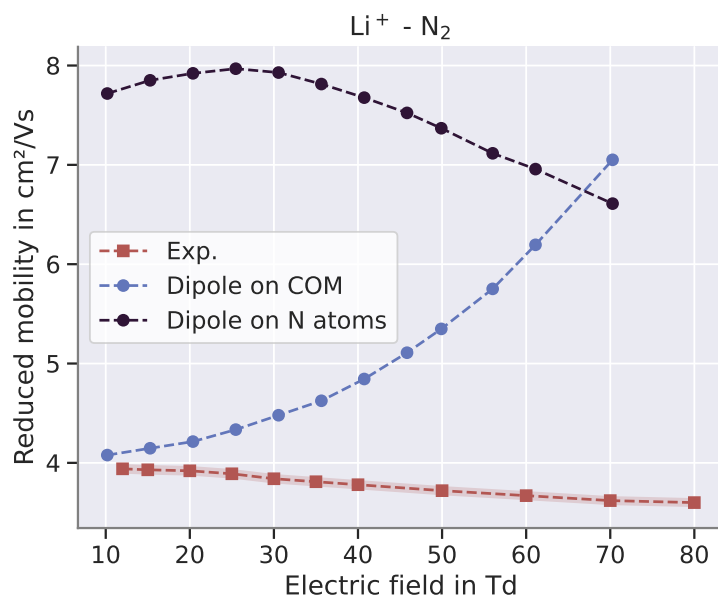


Figure 6.49: Predicted reduced ion mobilities in dependence of the reduced electric field for Li^+ in molecular nitrogen at 295 K for IDSimF as well as literature values [150]. Simulations in IDSimF were carried out with a step size length of 10^{-12} s. The mobilities were determined by either averaging of the forces or by COM position. The van der Waals component is given by the mod. Buckingham potential.

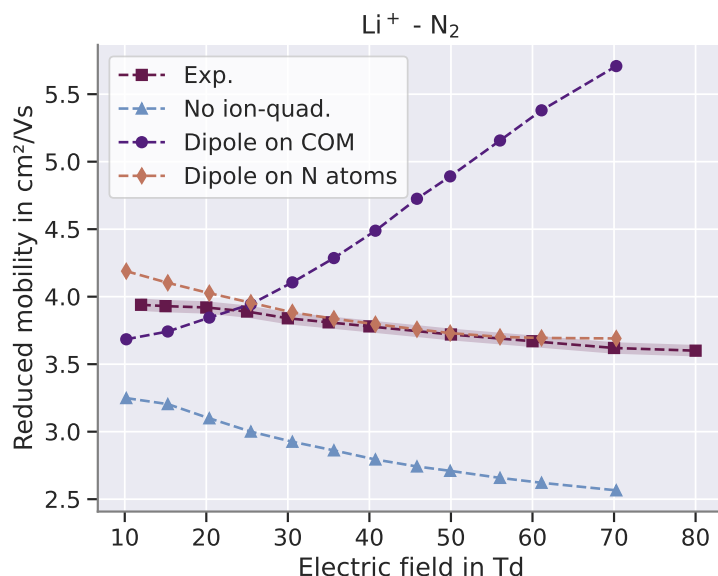


Figure 6.50: Predicted reduced ion mobilities in dependence of the reduced electric field for Li^+ in molecular nitrogen at 295 K for IDSimF as well as literature values [150]. Simulations in IDSimF were carried out with a step size length of 10^{-12} s. The mobilities were determined by simulations with either averaging of the forces, by COM position or by excluding the ion-quadrupole potential. The van der Waals component is given by the 12-6 Lennard-Jones potential.

MobCal-MPI is focused on molecules scales of smaller biomolecules up to peptides. In that regard, monoatomic / diatomic ions have not been attempted before (MobCal-MPI cannot even calculate monoatomic ion mobilities without modification, see subsection 6.4.2.2). Usage of the mod. Buckingham potential would thus require re-optimization of the force field parameters found in the MobCal-MPI suite to approximate the much harsher conditions that arise from the "hard" point charges found in monoatomic ion systems.

6.4.3.3 Ion-quadrupole moment

Taking into account all the information gained in the study of the ion-induced dipole potential and the mod. Buckingham potential, Figure 6.50 compiles all already presented data computed for the 12-6 LJ potential as van der Waals component into one figure. This concisely shows the need for the inclusion of the ion-quadrupole moment since this is also the strongest force for the nitrogen background gas (cf. Figure 6.40 to Figure 6.42). Neglecting the ion-quadrupole moment produces simulated mobilities that are too small compared to the experimental data. It is also possible to mimic / approximate the effect of the ion-quadrupole force with the van der Waals force only. For this, a suitable vdW parameter set has to be determined. However, this modification does not guarantee to work equally well over all field strength ranges. Thus, it is overall to be preferred to calculate those effects directly as the computational cost of the ion-quadrupole force function is not very high.

Additionally, the ion-quadrupole potential is dependent on the orientation of the nitrogen

molecule with respect to the ion. Therefore, rotational effects should receive further consideration and will be discussed in the following subsection 6.4.5.

6.4.4 Prediction of ion mobilities

Similar to helium / argon as background gas, ion mobilities with several small as well as one slightly larger (i.e. not only 1–3 atoms) ion were also computed for nitrogen. The standard input parameter values for the DT-IMS simulations with N₂ are given in the following Table 6.3 and are always used if not noted otherwise. Unfortunately, the amount of reliable experimental IMS data with molecular nitrogen as background gas is far more limited compared to helium or argon. As such only four systems will be directly compared here, with one reference system being theoretically computed and not experimentally measured.

Table 6.3: *Input parameter values for a standard simulation run of the DT-IMS simulation application in IDSimF for N₂ as background gas.*

input parameter	value
Total simulation time	3 000 000 steps equaling 3 μ s
Step size for velocity Verlet (overarching simulation)	10^{-12} s
Number of ions	2000
Space charge	no
Starting position	randomly placed in 3D box of size $1 \times 1 \times 1$ mm ³
Drift region length	10 cm
Electric field strength	varies, reduced electric field is kept between 5 to 80 Td
Background gas pressure	2000 Pa resp. 20 mbar
Background gas temperature	298 K
Maximum integration time of collisions	10^{-10} s
Integration method	RKF45
Tolerance / Step size	10^{-8} with initial step size of 10^{-16} s
Spawn radius collision	50 Å
Collision radius scaling	3
Force field function	vdW (12-6 LJ or MB) + ion-induced dipole potential + ion-quadrupole moment
Polarizability constant	$1.7 \cdot 10^{-30}$ m ³

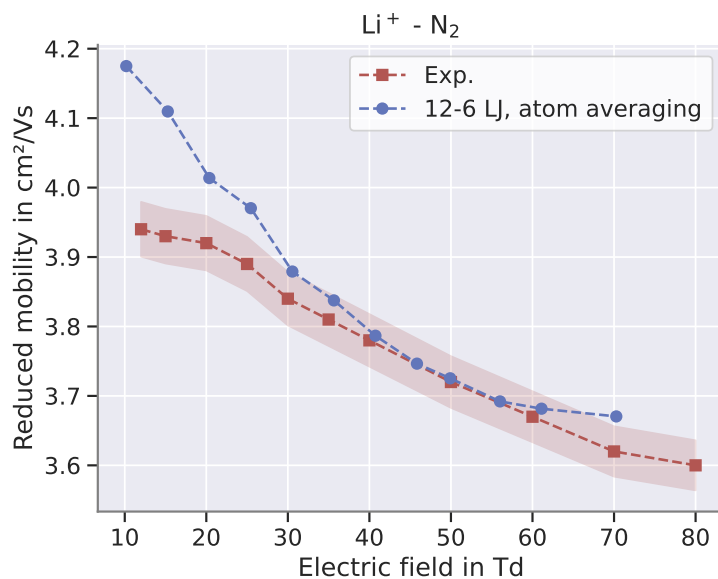


Figure 6.51: Predicted reduced ion mobilities in dependence of the reduced electric field for Li^+ in N_2 at 295 K. Experimental values [150] are given with their respective uncertainty band.

6.4.4.1 Small ions: Li^+

For simplicity of evaluating the capability of the program to predict ion mobilities for N_2 , the system used for the study of the ion mobility dependencies in subsection 6.4.3 is shown here once more with the best fit obtained as presented in Figure 6.51. The best fitting curve is reproduced using the 12-6 Lennard-Jones potential with an averaging of the ion-induced dipole moment over both nitrogen atoms. Overall, the curve shape is roughly in agreement between simulation and literature experimental values (type C) with some values for the electric field ranges right in the middle of the chosen interval lying within the uncertainty of the experiment. The highest divergence is found for low electric fields with a maximum deviation of approx. 6 %.

6.4.4.2 Small ions: Na^+ and comparison between differing force fields

Thompson et al. [157] reported ab-initio potential energy surface data for $\text{Na}^+ - \text{N}_2$ in a rigid rotor approximation at the MP4SDTQ/6-311+G(2df) level of theory, which could then be utilized to approximate ion mobility by evaluating transport cross-sections and integrating over collision impact parameters. The aforementioned calculations were done similarly to another theoretical study of $\text{Li}^+ - \text{N}_2$, which provide theoretical values in good agreement to the experimental values reported by Viehland et al. [158]. Based on this good agreement and accuracy studies, the authors proclaimed certainty in the high confidence of the calculated theoretical values with experimental values being very hard to obtain for Na in N_2 . As such, those theoretical values are then used as reference values for the predictions obtained by IDSimF. Initial simulation runs were carried out for all four combinations of vdW components (12-6 LJ or MB, dashed vs dotted lines) and

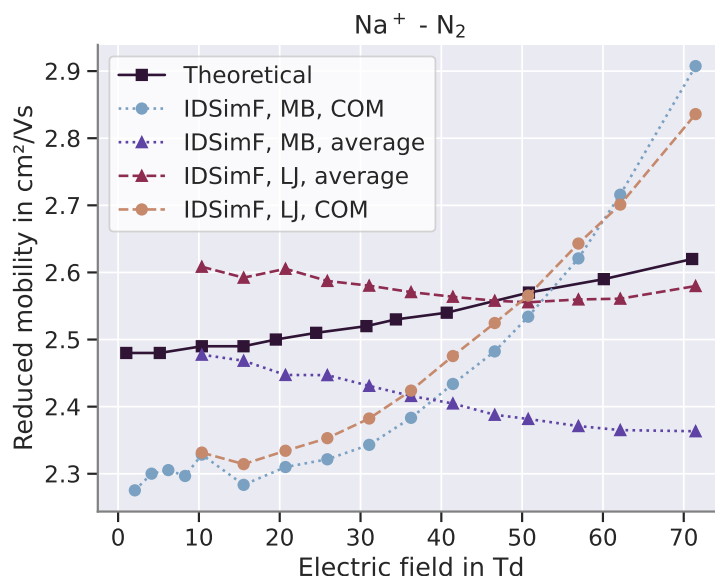


Figure 6.52: Predicted reduced ion mobilities in dependence of the reduced electric field for Na^+ in N_2 for several force field descriptions. Reference values are given in the form of theoretical predictions obtained from [157] (300 K).

ion-induced dipole treatment (COM or average, circle vs triangle marker) as shown in Figure 6.52. In first instance for all combinations the same force field parameter values are used and are initially approximated from the mod. Buckingham parameters supplied with MobCal-MPI. All four simulation runs exhibit problems with reproducing the desired theoretical values. Both results using the center-of-mass for the ion-induced potential follow the same type A behavior as the reference data but massively overestimate the slope. The averaged curves exhibit better matching slopes but with type B or C behavior instead. Using the COM treatment, both van der Waals potentials are very close in their respective prediction. Larger differences are found for the averaging mode (approx 9 % for averaging to 2 % and less for COM). For this system here, with the specific force field parameters, the 12-6 Lennard Jones potential for the most part (i.e. every data point except for the last two for the COM mode) always leads to higher ion mobilities even though the 12-6 Lennard-Jones potential is the "harsher" potential. Overall, no very good agreement to the reference data could be obtained for this system. Some supplementary force field parameter variations also returned no results better than the averaged 12-6 Lennard-Jones curve as shown in Figure 6.52.

6.4.4.3 Small ions: Cl^- with sensitivity analysis

For the $\text{Cl}^- - \text{N}_2$ system a sensitivity analysis of the force field parameters for the mod. Buckingham component was carried out, analogous to the sensitivity analysis done for helium / argon in subsection 6.3.7. Figure 6.53 visualizes the results for variation of $\sigma = \{2.4, 3.1, 3.8, 4.5\}$ given in Å and $\epsilon = \{0.05, 1.04, 2.02, 3.01, 4.00\}$ given in kcal/mol with

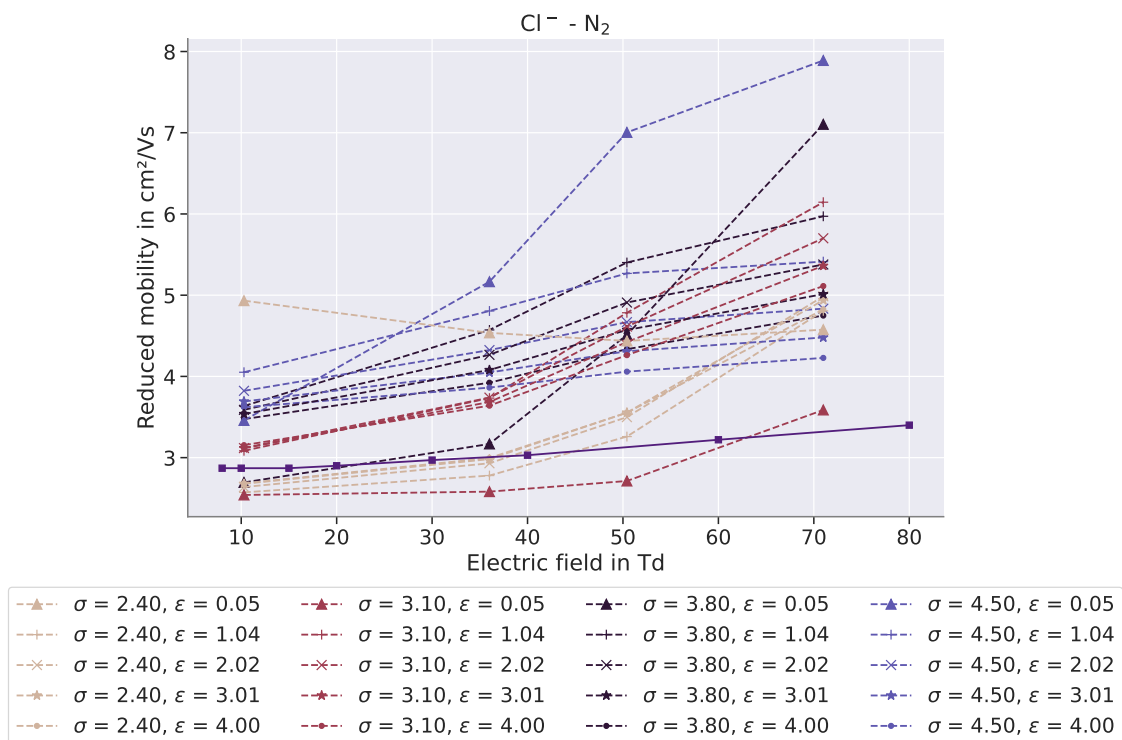


Figure 6.53: Reduced ion mobilities obtained in dependence of the electric field strength for varying 12-6 Lennard-Jones parameters σ (in Å) and ϵ (in kcal/mol) for Cl^- in nitrogen. The solid, purple line with square markers gives the experimental data given in [66] at 300 K.

the experimental values depicted by the solid line with square markers. Compared to Figure 6.26 and Figure C.1 the results cannot be grouped as easily and have much larger overlap, especially the two highest σ value groups have a large spread. In general, despite the additional influence of the ion-quadrupole potential on this system in contrast to monatomic background gases, the van der Waals parameters still have a major effect on ion mobility, which is the desired behavior. However, the exact position and shape of the curves in dependence on the applied parameters is less clear and predictable than e.g. for helium. In this case here smaller σ values across the board also lead to smaller ion mobility across the whole ϵ range (cf. $\sigma = 2.4$ Å and $\sigma = 4.5$ Å).

As no curve seemed to match very well initially, a few parameter values outside of the shown values in Figure 6.53 were evaluated. The best fitting curve, using the mod. Buckingham potential, is shown in Figure 6.54.

This curves matches the slope and curve shape exceptionally well, even reproducing the flattening at the lower electric field values, yet the actual values differ strongly. The deviations are in the range of 20 %, which is much too high for reliable dynamics simulations with this systems.

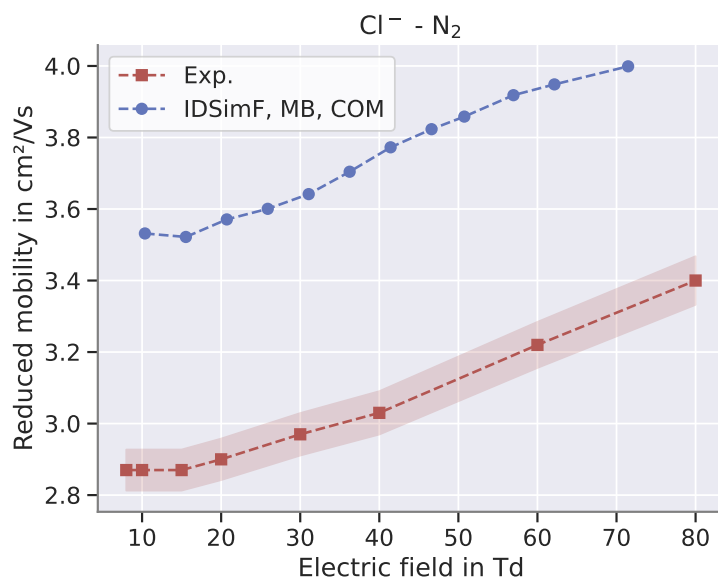


Figure 6.54: Predicted reduced ion mobilities in dependence of the reduced electric field for Cl^- in N_2 at 300 K. Experimental values [66] are given with their respective uncertainty band.

6.4.4.4 Protonated acetone and isotope effect

Finally, a larger system of protonated acetone in N_2 was simulated. As this system includes more than one atom for the ion, it is also possible to simulate this system with MobCal-MPI to provide additional reference values. To be able to compare between IDSimF and MobCal-MPI, IDSimF again uses the mod. Buckingham potential for the vdW component. Experimental data was provided by [159] for field strengths above roughly 70 Td, with a range of these values extracted by graph based extraction methods (as the data was not tabulated and only given as a graphical figure) to include them for easier comparison in one single figure. Schaefer et al. further measured ion mobility values for the ^{13}C isotope of the protonated acetone, allowing to study this effect on both IDSimF and MobCal-MPI results. The MobCal-MPI force field uses the values provided with the program itself and IDSimF uses slightly modified force field values for nitrogen (the atoms of the prot. acetone have the same force field parameters as in MobCal-MPI). Additionally, MobCal-MPI simulations are carried out with the program in its initial state, i.e. the weighted rotation of N_2 is included and all other code changes were reverted. For the sake of accuracy, a fresh version was downloaded from GitHub⁷ and compiled. Figure 6.55 shows the results for all simulations and the experimental data. The IDSimF simulations were repeated three times each to establish that the isotope effect is not simply numerical noise due to the randomness of each simulation run.

For higher field strengths MobCal-MPI and IDSimF roughly follow the same curve, with exact curve shape of MobCal-MPI fitting better to the experimental data, as the leveling off begins much earlier and the curvature is greater. For lower field strengths the curves

⁷<https://github.com/HopkinsLaboratory/MobCal-MPI>

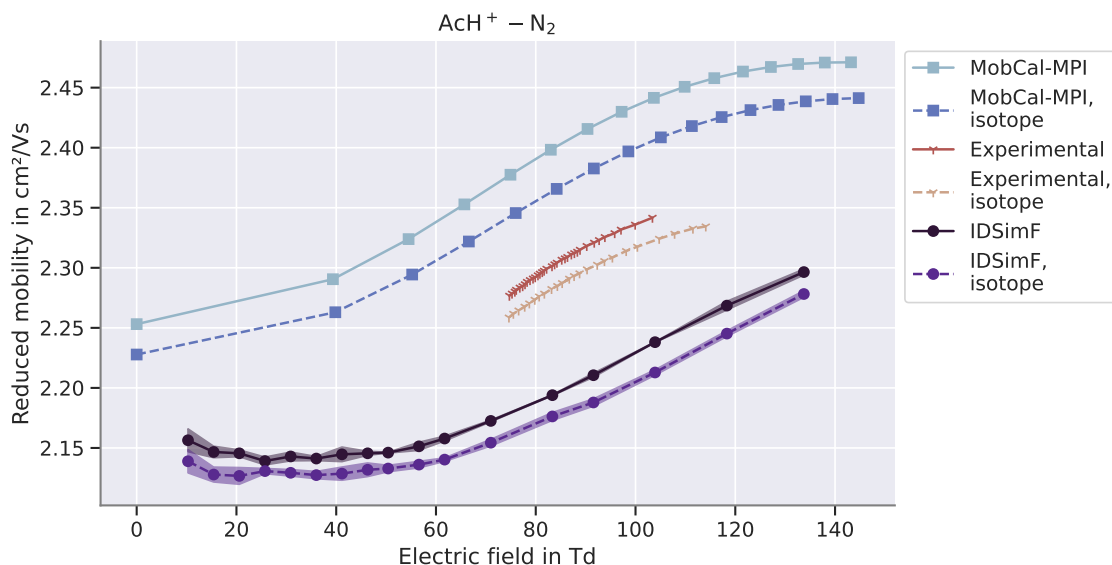


Figure 6.55: Reduced ion mobilities obtained in dependence of the electric field strength for MobCal-MPI and IDSimF for protonated acetone as well as its ^{13}C isotope in N_2 . Experimental references are taken from [159].

have diverging type behavior, where MobCal-MPI values are continuing to lower and IDSimF values begin to rise. Since no experimental data is available for the low fields, it is unclear which result is more physically valid.

Comparing the isotope mobility curves, both MobCal-MPI and IDSimF show the expected behavior: the ion mobility curve simply lies lower than the non isotope one and has the same shape as the non isotope curve. In this case, the IDSimF curve seems to better represent the differences between both curves though. The value difference between both curves is small and MobCal-MPI overestimates the separation slightly. Interesting to note is also that the the uncertainty of the IDSimF simulations is neither constant or directly tied to the reduced electric field. Across the board the uncertainties are higher for lower fields, but at specific electric fields the uncertainties increase again. This effect might be a result of only using three samples. Overall, the uncertainties are very small though, as such in general one simulation run is sufficient.

6.4.5 Rotations

One of the largest differences between MobCal-MPI and IDSimF is the consideration of rotational effects of molecular nitrogen. As the ion-quadrupole moment induced by nitrogen as a background gas is a major part of the applied force between the two molecules, it is important to include a better approximation of this force component by taking into account how nitrogen is oriented in space during the collisional interaction. In MobCal-MPI a simplified approach is taken: in each time step of the integration the force between the atoms of the ion and the nitrogen molecule is a weighted average of three different orientations of nitrogen. For this, nitrogen is oriented with its bond axis in

each of the three cartesian axes, the forces are the computed for each orientation and then summed with a weight dependent on the bath gas temperature.

In a final step to improve the N₂ background gas model in IDSimF, also rotations should be considered. However, the rotation of the ion should also be taken into account such that the acting force can change the rotation and angular momentum of both molecules. In this first attempt, the particles are still considered as rigid bodies, i.e. vibrational degrees are not opened.

This requires the introduction of Euler's equations which describe the rotation of a rigid body in a rotating reference frame fixed to the body. The general form is given as [160, 161]

$$\mathbf{I}\dot{\boldsymbol{\omega}} + \boldsymbol{\omega} \times (\mathbf{I}\boldsymbol{\omega}) = \boldsymbol{\tau} \quad , \quad (6.7)$$

with $\mathbf{I}$ as the inertia matrix, $\boldsymbol{\omega}$ as the angular velocity and $\boldsymbol{\tau}$ as the applied torques. Using an orthonormal, center-of-mass body frame, the equations can be reduced to [160, 161]

$$\begin{aligned} I_1\dot{\omega}_1 + (I_3 - I_2)\omega_2\omega_3 &= \tau_1 \\ I_2\dot{\omega}_2 + (I_1 - I_3)\omega_1\omega_3 &= \tau_2 \\ I_3\dot{\omega}_3 + (I_2 - I_1)\omega_1\omega_2 &= \tau_3 \quad . \end{aligned} \quad (6.8)$$

Thereby, ω_i and τ_i each are the components of the angular velocity and torque, while I_i are the principal moments of inertia. Principal moments of inertia are those moments of inertia obtained when the coordinate system is orthonormal and goes through the center-of-mass of the rigid body (i.e. principal axes). The inertia matrix obtained using principle axes is diagonal, i.e. the products of inertia (off-diagonal entries) are zero [161]. The inertia matrix thus is given by

$$\mathbf{I}_{\text{RB}} = \begin{pmatrix} I_1 & 0 & 0 \\ 0 & I_2 & 0 \\ 0 & 0 & I_3 \end{pmatrix} \quad . \quad (6.9)$$

The integration of rotation can be done in body frame (i.e. the frame changes with the body) in this way, but trajectory simulations in IDSimF are carried out in world frame. For this reason, a description of the rotation as a mapping that can be applied to the Euler equations to transform them into world frame is needed. Given the molecular structure coordinates of a particle in center-of-mass body frame, a *rotation matrix* $\mathbf{R}$ can be used to define the orientation of this body in world frame [162]. The world frame location of any body frame point p (here: atom) of the particle is described by [162]

$$\mathbf{r} = \mathbf{R}\mathbf{p} + \mathbf{r}_{\text{cm}} \quad , \quad (6.10)$$

meaning the world location is the rotated body location about the origin translated by the center-of-mass position $\mathbf{r}_{\text{cm}}$ of the particle in the world frame. Consequently, the columns of the rotation matrix give the directions of the x , y and z axes of the rigid body in world frame.

A rotation of a rigid body is simply the spinning of each point of the body about some axis through the center-of-mass over time. In the context of rigid body rotations this spin is the angular velocity $\omega(t)$. The analogous quantity for translation motion would be the velocity of a particle which is defined by $\mathbf{v}(t) = \frac{d}{dt}\mathbf{x}(t)$ (recall Newton's equations of motion). Similarly, in some way the angular velocity propagates forward a change in the rotation matrix to map the new orientation in world frame. However, as one quantity is a matrix and the other a vector, the relationship cannot just be described by a derivative. The rate of change of a vector due to rotation is

$$\dot{\mathbf{r}}(t) = \omega(t) \times \mathbf{r}(t) \quad , \quad (6.11)$$

which then can be applied to the rotation matrix by using the change rate expression individually on each column of the rotation matrix [162]. Using the simplification [162, 163]

$$\mathbf{a} \times \mathbf{b} = \begin{pmatrix} a_2b_3 - a_3b_2 \\ a_3b_1 - a_1b_3 \\ a_1b_2 - b_1a_2 \end{pmatrix} = \begin{pmatrix} 0 & -a_3 & a_2 \\ a_3 & 0 & -a_1 \\ -a_2 & a_1 & 0 \end{pmatrix} \begin{pmatrix} b_1 \\ b_2 \\ b_3 \end{pmatrix} = \mathbf{a}^* \mathbf{b} \quad (6.12)$$

the rate of the change of the rotation matrix can be calculated in matrix form by column-wise application of the $*$ operator to the matrix (the derivation of which is found in [162])

$$\dot{\mathbf{R}}(t) = \omega(t)^* \mathbf{R}(t) \quad . \quad (6.13)$$

To allow the forces applied by the force field function to induce rotational changes, the total external torque needs to be computed. The torque acting on an atom i is dependent on the relative distance to the center-of-mass position of the particle and is analogously also a rate of change (i.e. the moment of force). Hence, the torque acting on atom i becomes [162]

$$\tau_i(t) = (\mathbf{r}_i(t) - \mathbf{r}_{\text{cm}}(t)) \times \mathbf{F}_i(t) \quad (6.14)$$

and the total torque of the rigid body / particle is defined by the sum over all acting torques for each atom [164]

$$\tau = \sum_i (\mathbf{r}_i(t) - \mathbf{r}_{\text{cm}}) \times \mathbf{F}_i(t) \quad . \quad (6.15)$$

Finally, a way to compute an updated angular velocity from the currently acting torque is required.

Equivalently to $\dot{\mathbf{p}}(t) = \mathbf{F}(t)$ and $\mathbf{p}(t) = m\mathbf{v}(t)$ for linear / translational movement, the following identities for the angular momentum $\mathbf{L}$ hold [164]:

$$\begin{aligned} \mathbf{L}(t) &= \mathbf{I}(t)\omega(t) \\ \dot{\mathbf{L}}(t) &= \tau(t) \end{aligned} \quad (6.16)$$

Combining all equations given above, a system of four first-order ordinary differential equations can be established, called the Newton-Euler equations [165]

$$\frac{d}{dt} \begin{pmatrix} \mathbf{r}(t) \\ \mathbf{R}(t) \\ \mathbf{v}(t) \\ \mathbf{L}(t) \end{pmatrix} = \begin{pmatrix} \mathbf{v}(t) \\ \boldsymbol{\omega}(t)^* \mathbf{R}(t) \\ \frac{\mathbf{F}(t)}{m} \\ \boldsymbol{\tau}(t) \end{pmatrix} . \quad (6.17)$$

To solve the Newton-Euler equations numerically, the world frame inverse inertia matrix $\mathbf{I}^{-1}(t)$ needs to be generated as it is necessary to re-compute the angular velocity when the angular momentum is altered by $\boldsymbol{\omega}(t) = \mathbf{I}^{-1}(t)\mathbf{L}(t)$. The world frame inertia matrix can be computed with (a derivation of this can be found in [162])

$$\mathbf{I}(t) = \mathbf{R}(t)\mathbf{I}_{\text{RB}}\mathbf{R}(t)^T . \quad (6.18)$$

In essence this equation is the connection between world and body frame and enables a computation of the forces in world frame instead of the body frame as Euler's equations become

$$\begin{aligned} \mathbf{I}\dot{\boldsymbol{\omega}} + \boldsymbol{\omega} \times (\mathbf{I}\boldsymbol{\omega}) &= \boldsymbol{\tau} \\ \Leftrightarrow \left(\mathbf{R}(t)\mathbf{I}_{\text{RB}}\mathbf{R}(t)^T \right) \dot{\boldsymbol{\omega}} + \boldsymbol{\omega} \times \left(\left(\mathbf{R}(t)\mathbf{I}_{\text{RB}}\mathbf{R}(t)^T \right) \boldsymbol{\omega} \right) &= \boldsymbol{\tau} . \end{aligned} \quad (6.19)$$

The inverse of the world frame inertia matrix then is

$$\mathbf{I}^{-1}(t) = \mathbf{R}(t)\mathbf{I}_{\text{RB}}^{-1}\mathbf{R}(t)^T \quad (6.20)$$

due to rotation matrices being orthogonal, i.e. $\mathbf{R}^T = \mathbf{R}^{-1}$. As neither $\mathbf{I}_{\text{RB}}$ nor $\mathbf{I}_{\text{RB}}^{-1}$ are time-dependent⁸, both quantities can be computed at the beginning of a simulation run for all involved molecules once.

Diatomic molecules represent a special case for the inertia matrix calculation, as one of the rotational degrees of freedom is lost because rotations about the bond axis have no effect. As a result, one of the diagonal entries of $\mathbf{I}_{\text{RB}}$ becomes zero. Mathematically, the inverse of $\mathbf{I}_{\text{RB}}$ cannot be determined anymore in this case as it becomes singular (the determinant is zero). Since this approach of rotation integration should be possible for any molecule and particularly for molecular nitrogen, the inertia matrix and algorithm need to be modified slightly: when the initial, constant inertia body matrix is generated, it is checked if any component of the diagonal of the matrix is zero (so either I_1 , I_2 or I_3). If that is the case, this component is also set to zero in the corresponding inverted matrix. Additionally, for reasons of stability, the matching $\boldsymbol{\omega}$ component (also either ω_1 , ω_2 or ω_3) is restricted to zero during the simulation. Both changes together guarantee that diatomic molecules can be integrated without any undefined behavior.

Various data structures and program modules in IDSimF like *molecules*, *force fields* and

⁸Remember $\mathbf{I}_{\text{RB}}$ is the principle axes inertia matrix in the body-fixed rotating frame, thus the orientation is "fixed" as it moves with the body.

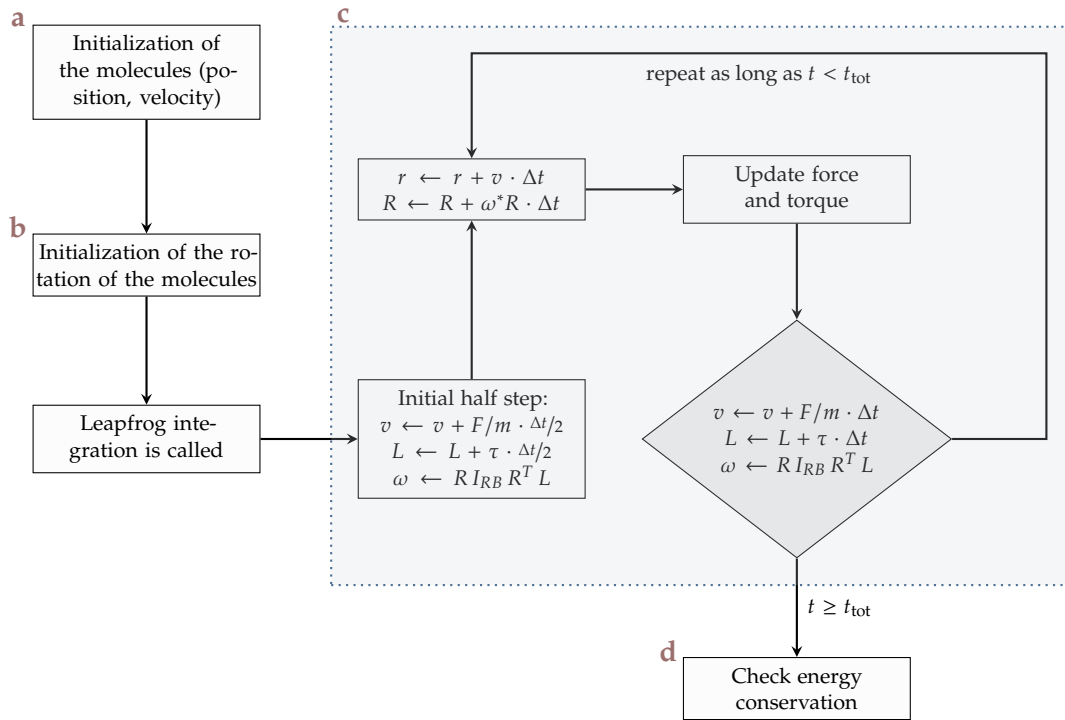


Figure 6.56: Scheme of the steps of a MD collision considering rigid body rotation with the Leapfrog integration steps highlighted by a blue box.

logging were altered such that they support all necessary structures and variables required for rotation integration. This also required the extension of IDSimF by a 3×3 matrix class, which has the * ("star") operator implemented.

The Newton-Euler equations are implemented for the Leapfrog and RKF45 integration methods in the MD model. With the Leapfrog method as an example, the following flowchart in Figure 6.56 shows the general procedure for integration of collisions of rotating rigid molecules. The individual steps of the process are summarized below:

- Initialization of the molecules:** The initialization of the molecules follows the same procedure already explained for the general MD model. Position and velocity of the background gas particle is sampled to construct initial conditions for a collision in which both particles will interact with each other.
- Initialization of rotation:** The orientation of the simulated molecules is switched to a representation using the rotation matrix. The rotation matrix is initialized by three random angles, which therefore randomizes the orientation of the molecule. The rotation matrix is given by

$$\mathbf{R} = \begin{pmatrix} \cos(\beta) \cdot \cos(\gamma) & \sin(\alpha) \cdot \sin(\beta) \cdot \cos(\gamma) + \cos(\alpha) \cdot \sin(\gamma) & \sin(\alpha) \cdot \sin(\gamma) - \cos(\alpha) \cdot \sin(\beta) \cdot \cos(\gamma) \\ -\cos(\beta) \cdot \sin(\gamma) & \cos(\alpha) \cdot \cos(\gamma) - \sin(\alpha) \cdot \sin(\beta) \cdot \sin(\gamma) & \cos(\alpha) \cdot \sin(\beta) \cdot \sin(\gamma) + \sin(\alpha) \cdot \cos(\gamma) \\ \sin(\beta) & -\sin(\alpha) \cdot \cos(\beta) & \cos(\alpha) \cdot \cos(\beta) \end{pmatrix} \quad (6.21)$$

and rotates about the world frame x -, y - and z -axis with angles α , β and γ , respectively. Additionally, the available rotational energy is computed for each molecule. Each

rotational degree of freedom contributes $1/2k_B T$ energy, as such for each $I_i \neq 0$ the rotational energy is increased by that amount. Under the assumption that all angular velocity components are equal⁹, one angular velocity component can be computed by $\omega_1 = \sqrt{\frac{2 \cdot E_{\text{rot}}}{I_1 + I_2 + I_3}}$ and setting each component of ω that does not belong to a zero inertia matrix entry to ω_1 . Finally, the angular momentum is set according to $\mathbf{L}(t) = \mathbf{I}(t)\omega(t)$.

- c. Trajectory integration: The trajectory is then integrated using either the Leapfrog or RKF45 method. For simplicity reasons, the flowchart shows the Leapfrog method only as this method does not use weighted increments. Instead of the normal Newton's equations now the Newton-Euler equations need to be solved as presented in Equation 6.17. This requires, in addition to the update steps for $\mathbf{R}$ and $\mathbf{L}$, continuously updating ω each time a new angular momentum is available.
- d. Energy check: After the trajectory is finished, $E_{\text{tot, end}}$ is compared with $E_{\text{tot, start}}$ for energy convergence up to 10 %. The total energy is given by the sum of the kinetic and rotational energy. Due to force / torque transfer neither the kinetic nor the rotational energy itself need to be conserved, but the total energy available to the system should stay the same.

As an initial validation step of the implementation, a few collisions with activated rotations are visually evaluated to check for consistency. This included collisions with only constant rotation, i.e. without consideration of rotation change due to torque, as well as collisions with consideration of torque but no initial rotation of the molecules. Each of those collisions behaved as expected, and the constant rotation collision also returned the expected number of revolutions, based on integrated time and angular velocity, correctly. However, for collisions with many time steps, or "orbiting" collisions (see Figure 6.39), it became apparent that the bonds within the molecules begin to stretch and at some point the molecule structure entirely dissolves into a severely distorted state. This stretching behavior is due to the numerical instability of the rotation matrix. With longer integration time, the rotation matrix starts to lose the properties of a rotation matrix, namely the orthonormality of the column vectors. As soon as the rotation matrix is not orthonormal anymore, bond distances can start to change and this distortion usually accumulates over time. To mitigate this, the modified Gram-Schmidt (MGS) method is implemented. The MGS methods re-orthonormalizes the rotation matrix in every other time step, preventing the drift of the rotation matrix. The standard Gram-Schmidt cannot be used here, as it is itself unstable in finite-precision arithmetic [166].

An example interaction with initial rotation and activated torque for O_2^+ in N_2 and

⁹This is an approximation, ideally the ω_i values would need to be sampled by an acceptance-rejection method fulfilling the equation $E_{\text{rot}} = 0.5\omega^T \mathbf{I} \omega$. For the proof-of-concept simulations presented here, this detail is skipped due to time restrictions. For more precise simulations, it needs to be implemented in the future.

integrated with the RKF45 is presented in Figure 6.57 through several snapshots of the trajectory shortly before and after the "collision point". The first three snapshots

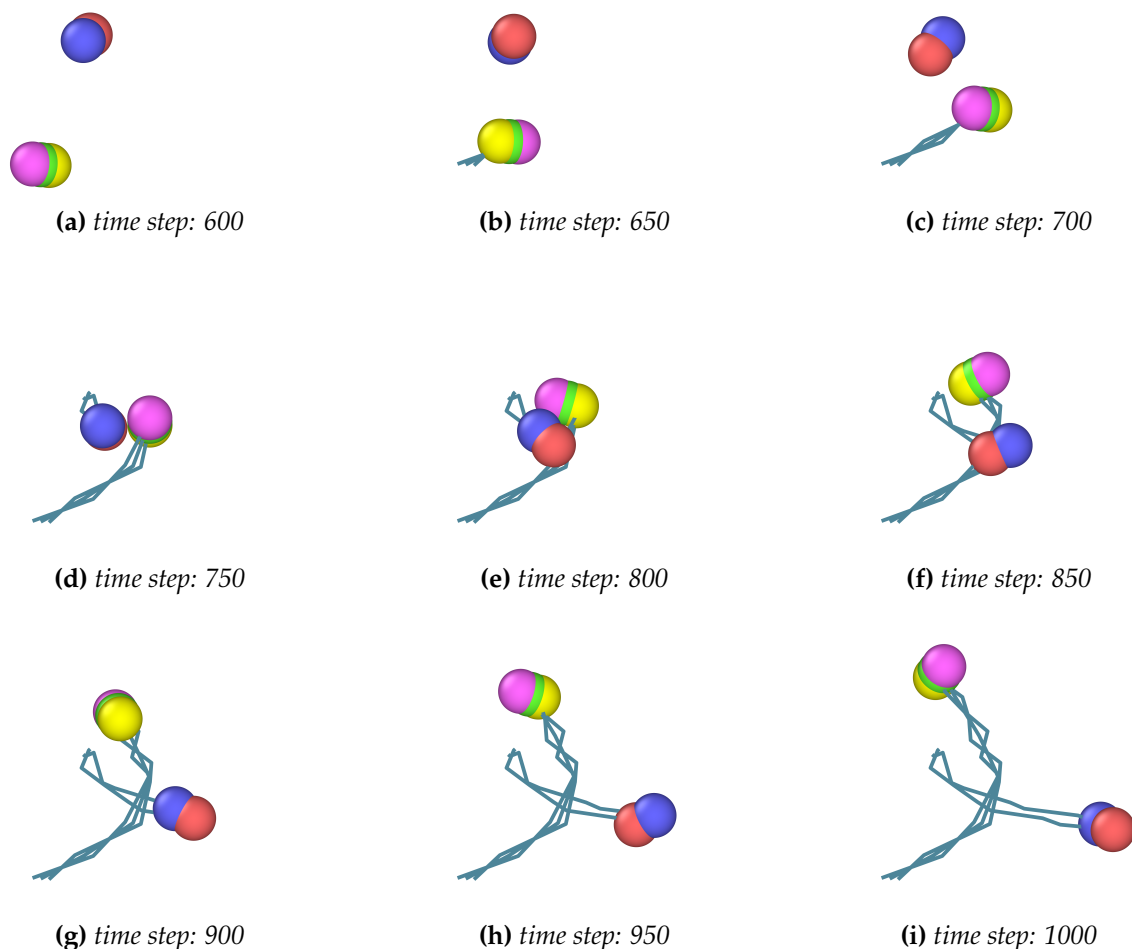


Figure 6.57: Trajectory snapshots of O_2^+ in N_2 , also showing the center-of-mass positioned dummy atom of molecular nitrogen for calculation of the ion-quadrupole moment. The blue lines visualize the trajectories of each atom, which supports visual assessment of the rotational behavior.

Figure 6.57a to Figure 6.57c clearly show both molecules rotating around themselves, as otherwise each snapshot would show all atoms still in the same relative position to each other. It is also apparent that both molecules rotate with varying angular velocities (nitrogen is basically exactly flipping in each snapshot, while snapshot one and three for O_2^+ are very different), as the inertia matrices are slightly different due to different bond distances. Snapshots Figure 6.57d to Figure 6.57f then very nicely visualize the collisional interaction, where both molecules begin to orient about each other and both change their orientation completely. Additionally, it has to be kept in mind that in time step 600 up to 700 much more "actual" time has passed compared to time step 750 up to 850, as the adaptive RKF45 method reduced the time step length drastically around this point for more precise integration of e.g. the close-range repulsion. The final snapshots Figure 6.57g

to Figure 6.57i highlight the changed rotation due to the collision compared to the initially randomly sampled rotational orientation. To also show the integration with rotations for a larger system, protonated acetone in N_2 was also simulated. The trajectories over a few snapshots of the simulation are presented in Figure 6.58. The blue trajectory lines of nitrogen show the stable rotation over time, with a change in rotation pattern after time step 1000, i.e. the actual "collision". In contrast to O_2^+ and N_2 , protonated acetone has non-zero moments of inertia in all directions. The visual examination shows that the implemented integration can calculate rotations in all three dimensions as well as for the special case of diatomic molecules.

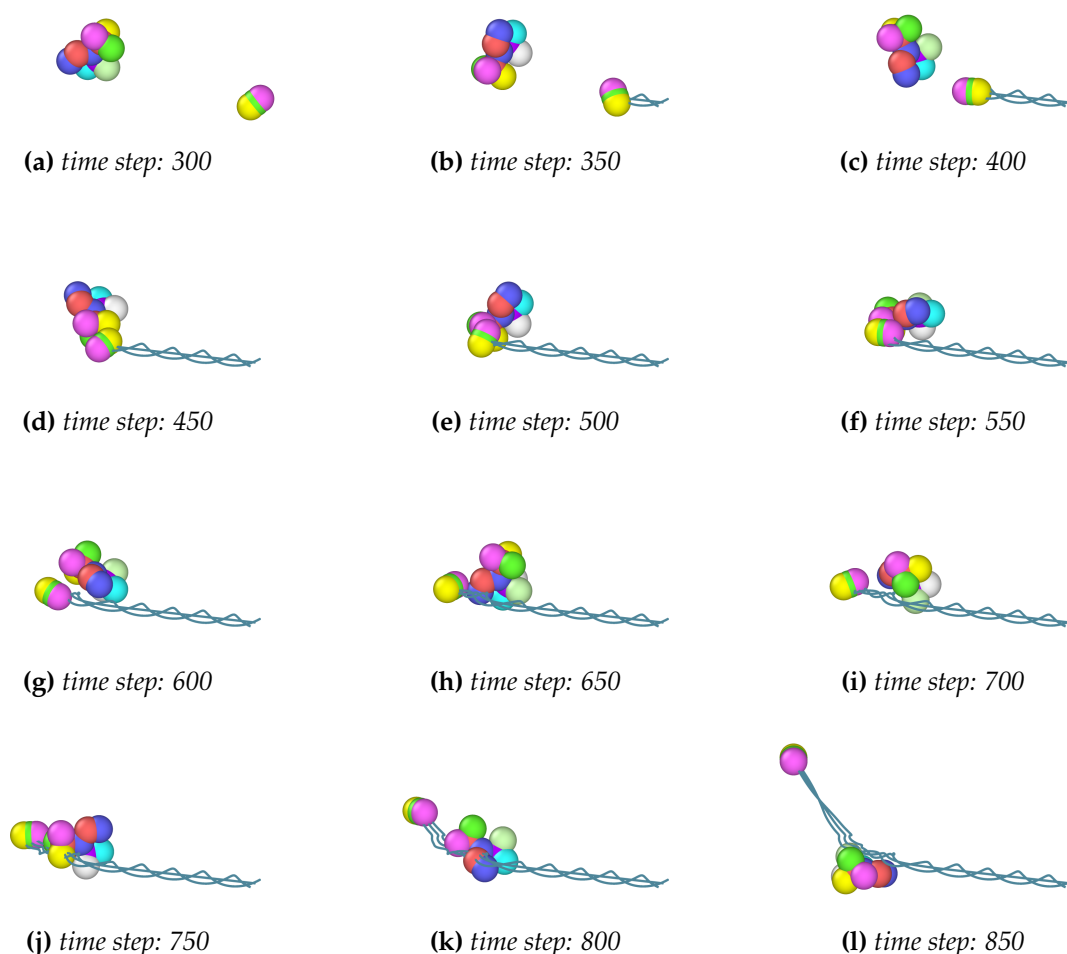


Figure 6.58: Trajectory snapshots of protonated acetone in N_2 , also showing the center-of-mass positioned dummy atom of molecular nitrogen for calculation of the ion-quadrupole moment. The blue lines visualize the trajectories of each atom, which supports visual assessment of the rotational behavior.

After the visual examination, ion mobilities were computed for the two systems of O_2^+ in helium and in molecular nitrogen with the standard simulation parameters with 12-6 Lennard-Jones as the vdW force. Figure 6.59 shows the ion mobilities obtained for O_2^+ in helium for the IMS simulation run with rotations off and on as well as the experimental

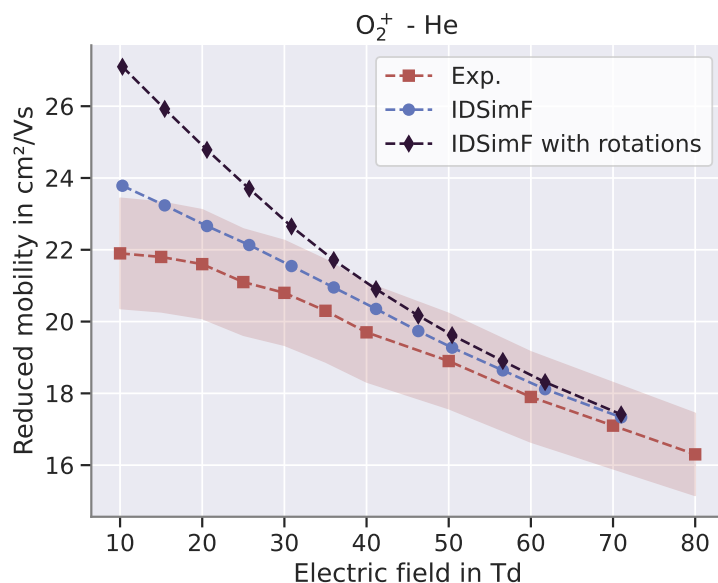


Figure 6.59: Predicted ion mobilities over changes in reduced field strength for O_2^+ in He at 300 K with / without rotations compared to the experimental data [149].

data (as presented beforehand). For high electric field strengths a convergence between all three curves to the same values is observed, as the rotations become less important with higher relative velocities (less rotations in a collision as well as less interaction time). As such, the hard-sphere behavior still stays dominant even with active rotations. For lower field strengths, however, the activated rotations lead to less agreement between simulated and experimental curves. In total, the simulations considering rotation lead to a complete change of the curve to type C in this case. Additionally, auxiliary simulation showed that changes in the 12-6 Lennard-Jones parameters lead to a movement of the curve along the y -axis, but did not change the curve shape.

In Figure 6.60 IMS simulation results for Li^+ in N_2 are given. In this case, the maximum relative deviations between the simulation result considering molecular rotations and the experimental curve are on roughly the same order of magnitude as for O_2^+ in He. However, there is no convergence between the Li^+ in N_2 curves for high field strengths. In return, the actual curve shape of rotational simulation is a much better fit here than without active rotations, just severely shifted to too high ion mobility values. Especially the flattening of the curve towards lower field strength is more accurately described by the simulations with activated rotations. Finally, a simulation of the ion mobility curves for protonated acetone in N_2 with the mod. Buckingham potential was attempted to compare those results to MobCal-MPI as well. Quickly, though, it was noticed that the simulations did not finish within a feasible run-time and would take up to 70 days with the currently employed force field parameter set. This phenomenon was then investigated using a dedicated application for sampling and inspection of collision trajectories with pre-determined initialization parameters, e.g. velocity, angular velocity, orientation and

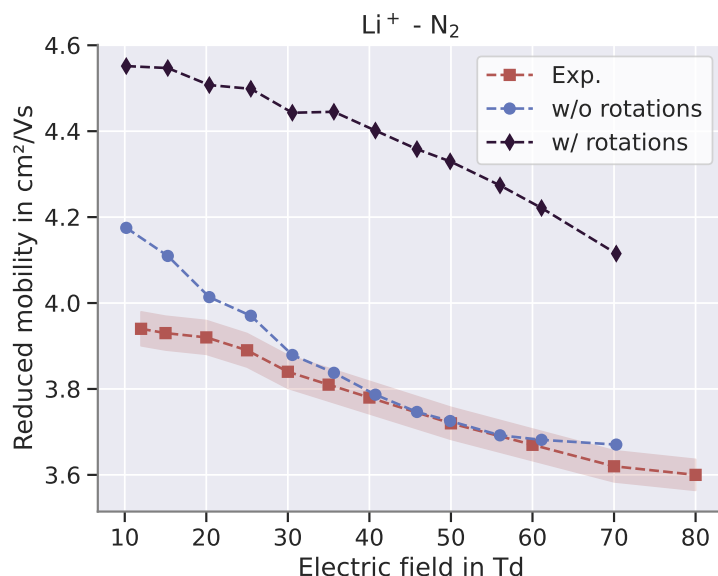


Figure 6.60: Predicted ion mobilities over changes in reduced field strength for Li^+ in N_2 at 295 K with and without rotations compared to the experimental data [150].

Table 6.4: Runtime of 100 sampled trajectories for varying systems with / without rotations.

system	run time in s	
	w/o rotations	w/ rotations
O_2^+ / He	0.15	0.36
$\text{O}_2^+ / \text{N}_2$	0.22	0.63
$\text{AcH}^+ / \text{N}_2$	0.57	22

position. The initial configuration is a head-on collision between the ion and background gas. Starting from this collision axis between the center of masses of both collision partners, in each direction in the y -axis a new initial position with a spacing of $0.1 \text{ \AA}$ is chosen for 100 trajectories total. All trajectories were initialized with no angular velocity and no initial rotation, while the relative (collision) velocity was set to 1000 m/s . The wall time taken for the integration of all trajectories was then measured. This process was performed for three different molecular systems with and without rotation integration. The run times obtained for each system are presented in Table 6.4. The first two systems with O_2^+ as the ion have their run times doubled resp. tripled when rotations are turned on depending on the background gas, as N_2 is slightly more expensive to compute than the non-rotating He.

A notable increase of the run times is expected as a second set of differential equations needs to be solved, which involve computation of expensive matrix-matrix and matrix-vector products. Comparing the times obtained for the protonated acetone / nitrogen system, a much larger discrepancy between the two modes is observed as the rotation

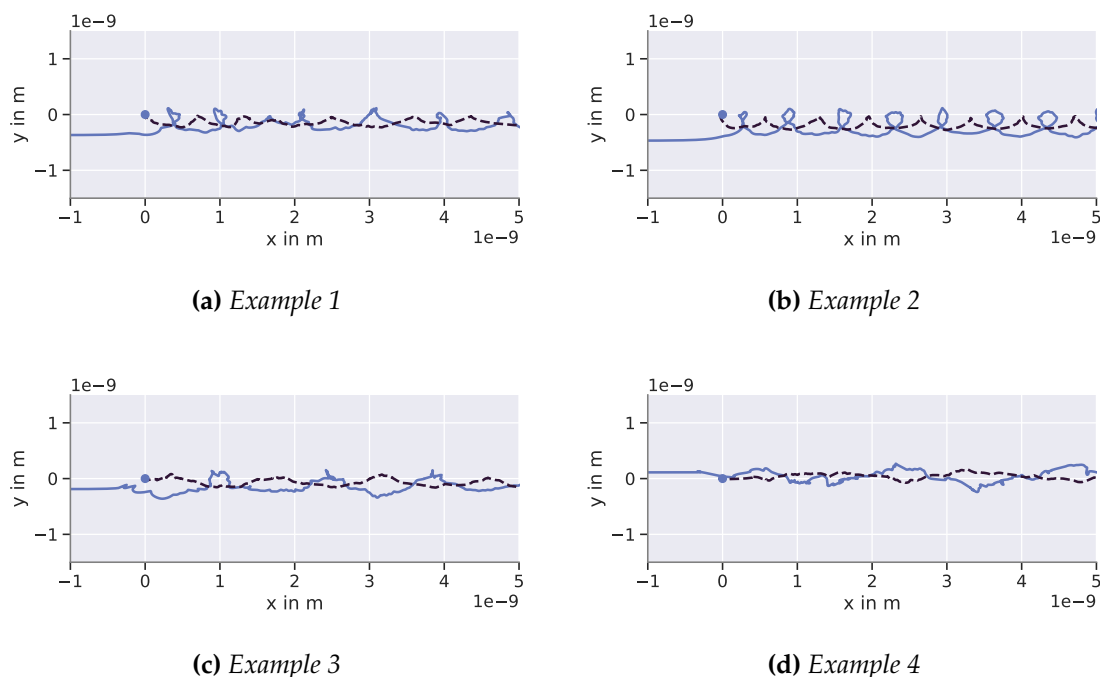


Figure 6.61: Example orbiting trajectories of the AcH^+ / N_2 system for a starting velocity of 1000 m/s. The solid line is the trajectory of nitrogen and the dashed line the trajectory of protonated acetone. The blue dot marks the ion origin. The trajectories are cut-off at the right side, but would continue in a similar pattern.

integration leads to an increase of the run time by almost 40-fold. Due to this large increase it becomes clear why the standard IMS simulations would take up to 70 days. The time increase cannot be a sole consequence of the higher atom count of AcH^+ , since the consideration of rotation does not introduce a non linearly increasing numerical burden. Rather, a phenomenon already discussed in the implementation section for nitrogen as a background gas is the cause for the run time increase: The orbiting trajectories, observed if nitrogen as a background gas is used, increase by a large amount in this specific system. The rotation leads to a kind of "compass needle" effect: one of the nitrogen atoms starts to align to the protonated acetone molecule, completely stopping the rotation, leading to subsequent fairly long-lived clustering. The nitrogen molecule wanders around the protonated acetone in a circle-like motion and does not experience sufficient repulsive force to detach from the temporary cluster as it is constantly realigned on account of the open rotation. Figure 6.61 presents several examples for those kinds of orbiting trajectories. The blue and black lines represent the trajectory lines of N_2 respectively protonated acetone. As already explained, the background gas particle starts to the left of the ion along the y -axis and is shot with 1000 m/s towards the ion, whose origin is marked by the blue dot. All examples show that initially one or multiple initial impingements between the ion and background gas particle take place. Example 3 (cf. Figure 6.61c) illustrates this clearly by the blue trajectory line before / around the ion origin. After those first hits, the nitrogen molecule is then captured due to the compass needle effect. A direct result of

those cluster collisions is that the energy of the system is not conserved anymore. The collision integration would be stopped after the defined maximum time of 10^{-10} s while they are still intertwined with each other. A first rough estimation of the likelihood of such "orbiting trajectories" was carried out with about 33 % of all $\text{AcH}^+ / \text{N}_2$ collisions observed to be in this category. It was also found that even for the smaller systems about 6 % to 10 % of all collisions are orbiting. As such, the IMS simulation effectively discriminates against those cluster-like collisions as these collisions would all be discarded in the current implementation of the IMS simulation application. Exactly those collisions are, however, probably very important to lower the ion mobility as the velocity of the ion would be altered significantly after the collisions. Based on this, it is assumed that the simulated too high ion mobilities are most likely a result of the failure to take such orbiting trajectories into account.

At this stage it is unclear, if those clustering collisions are indeed physically possible or if quantum mechanic effects would inhibit this compass needle effect. Further effort should be made to evaluate example systems by DFT or with semi-empirical methods. If clustering is found to be possible, the program would need to be changed to allow for those clustering effects by use of the RS module.

6.5 Variable hard sphere model

In the following chapter the implementation of the variable hard sphere model as well as the combination with internal energy tracking with Borgnakke-Larsen is presented. The theoretical / mathematical background is briefly explained, but the focus lies on the code implementation and a cursory comparison to the hard-sphere and MD model.

6.5.1 Implementation

In Equation 3.18 the mathematical formulation of the VHS model is shown, which then needs to be implemented into IDSimF's C++ code. The HS model code in which a collision cross section is already computed as detailed in subsection 3.3.1 is used as a basis for the VHS model. This HS collision cross section needs to be corrected by the factor defined in Equation 3.18 to incorporate the effects of the VHS diameter. Additionally, an explicit background gas particle needs to be constructed much earlier in the program code compared to the HS model. In the case of the HS model, it is sufficient to compute an explicit background gas particle velocity after determination of a possible collision. This velocity is not required before, since the mean and median bulk gas velocity can be used as the reference (cf. Equation 3.6). In contrast, the VHS model instead requires the actual relative velocity between ion and gas particle for the correction factor. A pseudo C++-styled code segment for the calculation of the VHS collision cross section is shown in Listing 6.3, without the procedure to construct a gas particle as this is identical to

the pre-existing HS model. After the calculation of the VHS collision cross section the collision probability can be computed as described before (ref. Equation 3.10).

Listing 6.3: Pseudo implementation code for the VHS collision cross section.

```

1 vRelIonToGas = vRestingIon - vGasParticle;
2
3 averagedViscosity = (viscosityGas + viscosityIon)/2;
4 correctionFactor = ( (2 * K_BOLTZMANN * tempRef/
5                     (reducedMass * vRelIonToGas * vRelIonToGas))
6                     ^ (averagedViscosity - 0.5)
7                     * 1/gammaFunc(2.5-averagedViscosity) )^0.5;
8
9 sigma = PI * (diameterIon + diameterGas)/2^2
10        * correctionFactor^(2*(averagedViscosity-0.5));

```

6.5.2 Tracking of internal energy

When a collision then finally takes place, the Borgnakke-Larsen procedure can be used to redistribute energy from elastic collisions into internal modes to allow inelasticity.

Each ion and gas particle needs to be initialized with a value for the internal energy (for each: *vibration* and *rotation*) before the simulation can continue. In the case of the ion, its initial internal energy is calculated at the beginning in the main driver code for the DT-IMS application and is tracked over the course of the simulation. The background gas particle internal energy can be computed in the actual VHS code segment, as the background gas particles do not keep their internal energy over the course of the simulation as they are normally only implicitly given as idealized thermal background gas particle ensemble¹⁰. Thereby, the energy value needs to be sampled from the internal energy distribution function which is defined in Equation 3.22.

In cases where $\zeta_i = 2$ (degrees of freedom in internal modes) this distribution simplifies and the energy can be initialized by [75]

$$\varepsilon_i = -kT \cdot \ln(R) \quad , \quad (6.22)$$

where k is Boltzmann's constant, T is the temperature of the particle and R is a uniform random number $\in [0, 1]$. If $\zeta_i > 2$ an acceptance-rejection sampling needs to be carried out instead. An energy value is randomly computed, according to the distribution probability, and only accepted if a second randomly determined probability is smaller or equal. If the probability is higher, a new energy and its probability need to be computed. The following pseudo code gives a possible way to sample from this distribution similar to the procedure reported in [75, 167].

¹⁰This simplification is fine as much more background gas particles than ions exist and the background gas particles are each re-initialized with energy from the Maxwell-Boltzmann distribution function.

Listing 6.4: Pseudo implementation code for internal energy initialization for degrees of freedom > 2 [75, 167].

```

1 cMax = nof/2 - 1 # nof = number degrees of freedom
2 fMax = cMax^cMax * exp(-cMax)
3
4 while True:
5     c = rnd(0, nof+10) # rnd(a,b) returns a uniform random number
        between a and b
6     f = c^cMax * exp(-c)
7     p = f/fMax # probability for this energy
8
9     if rnd(0,1) <= p:
10         return K_BOLTZMANN * temperature * c

```

The energy transfer between translational and internal modes is implemented with multiple relaxation permitted, i.e. a translational-vibrational transfer for particle A with probability $p_{v,A}$ and particle B with probability $p_{v,B}$ as well as a combined translational-rotational transfer with probability $p_{r,AB}$ can be carried out independently. Before the internal energy transfer can take place, a few auxiliary parameters have to be computed as

$$\begin{aligned}
 \zeta_{t,IG} &= 5 - 2 \cdot \omega_{IG} \\
 p_{r,IG} &= \frac{\zeta_{t,IG} + (\zeta_{r,I} + \zeta_{r,G})}{\zeta_{t,IG} \cdot (Z_{r,I} + Z_{r,G})} \\
 p_{v,I} &= \frac{\zeta_{t,I} + \zeta_{v,I}}{\zeta_{t,I} \cdot Z_{v,I}} \\
 p_{v,G} &= \frac{\zeta_{t,G} + \zeta_{v,G}}{\zeta_{t,G} \cdot Z_{v,G}} \\
 \epsilon_{tr} &= \frac{1}{2} \cdot m_r \cdot g^2
 \end{aligned} \tag{6.23}$$

with $\zeta_{t,IG}$ as the combined translational degrees of freedom for the particle pair [75], ω_{IG} as the averaged viscosity parameter of both particles, ϵ_{tr} as the translational energy, m_r as the reduced mass, g as the relative velocity and $\zeta_{x,y}$, $Z_{x,y}$ each as the degrees of freedom and relaxation collision number of I as ion, G as background gas and t, r, v as translational, rotational or vibrational, respectively.

In a first step each particle undergoes its internal energy transfer for the vibrational mode with a probability of $\frac{\Delta t}{\tau_{coll}} \cdot p_{v,*}$ (with $*$ being either I or G). For this the following function (Listing 6.5) calculates updated values for the translational and any internal energy with an acceptance-rejection algorithm due to the BL-transfer [75] (first return argument is trans. energy, second is internal energy). Section B.5 shows the derivation of this function. For the independent vib. modes, only the degrees of freedom of the considered particle are relevant and the other is assumed as zero.

Listing 6.5: Pseudo implementation code for transfer between translational and internal mode [75].

```

1  nofAveraged = (nofIon + nofGas)/2; # internal degrees of freedom
2
3  if nofAveraged == 0: return totalEnergy, 0; # no internal modes,
    internal energy is zero
4
5  if nofAveraged == 1:
6      while True:
7
8          transferFraction = rnd(); # returns a uniform random number in
            [0,1)
9          transferProbability = transferFraction^(1.5 - viscosityOmega);
10         if transferProbability >= rnd():
11
12             translationEnergy = totalEnergy * transferFraction;
13             internalEnergy = totalEnergy - translationEnergy;
14             return translationEnergy, internalEnergy;
15
16     else:
17         a = nofAveraged + 0.5 - viscosityOmega;
18         b = 1.5 - viscosityOmega;
19         c = nofAveraged - 1;
20
21         while True:
22
23             transferFraction = rnd();
24             transferProbability = a^a * b^-b * c^-c * transferFraction^a *
                (1-transferFraction)^c;
25             if transferProbability >= rnd():
26
27                 translationEnergy = totalEnergy * transferFraction;
28                 internalEnergy = totalEnergy - translationEnergy;
29                 return translationEnergy, internalEnergy;

```

After both particles potentially carried out vibrational transfers, the multiple relaxation scheme then computes the rotational transfer for both particles as a pair. This can also be carried out with the code in Listing 6.5 with consideration of the degrees of freedom for both particles.

Since the rotational mode is done for the pair, the calculated internal energy also needs to be correctly deposited between the two particles. Listing 6.6 shows an algorithm for the transfer between two identical rotational modes of two different particles¹¹ [75]. Again, the background gas is not an explicit simulation particle in IDSimF and therefore the

¹¹Of course this can be expanded to also work for vibrational modes.

rotational energy of the background gas particle is dropped. The rotational energy of the ion needs to be properly tracked though.

Listing 6.6: Pseudo implementation code for transfer between two rotational modes [75].

```

1 checkTransfer = 0; # the rotational energy is set as a parameter
  directly and not as a return value, as such the last case should
  only happen if no other did
2 if nofRotIon == 0: # ion has no rotational degrees, energy is zero
3     ion.setRot(0); # sets rotational energy of the ion
4     checkTransfer += 1;
5
6 if nofRotGas == 0 && nofRotIon != 0: # gas has no rotational degrees,
  all energy into ion
7     checkTransfer += 1;
8
9 if nofRotGas == 2 && nofRotIon == 2: # same degrees of freedom, energy
  is randomly redistributed
10     energy_ion = ion.getRot() * rnd(); # getRot returns the current
      rotational energy of the ion
11     ion.setRot(energy_ion);
12     checkTransfer += 1;
13
14 if nofRotIon == 2 && nofRotGas != 2: # simplified redistributions if
  either of the two particles has exactly two rotational degrees of
  freedom
15     while True:
16         fraction = rnd();
17         probabilityRatio = fraction^(nofRotGas/2 - 1);
18
19         if probabilityRatio >= rnd():
20             energy_ion = fraction * ion.getRot();
21             ion.setRot(energy_ion);
22             checkTransfer += 1;
23             break;
24
25 if nofRotGas == 2 && nofRotIon != 2: # see above
26     while True:
27         fraction = rnd();
28         probabilityRatio = fraction^(nofRotIon/2 - 1);
29
30         if probabilityRatio >= rnd():
31             energy_ion = fraction * ion.getRot();
32             ion.setRot(energy_ion);
33
34             checkTransfer += 1;
35             break;

```

```

36
37 if checkTransfer == 0: # no simplifications can be made
38     max_frac = (1 - nofRotIon/2) /
39         (2 - nofRotIon/2 - nofRotGas/2);
40     max_prob = (1 - max_frac)^(nofRotIon/2 - 1)
41         * max_frac^(nofRotGas/2 - 1);
42     while True:
43         fraction = rnd();
44         probability = (1-fraction)^(nofRotIon/2 - 1) * fraction^(
45             nofRotGas/2 - 1);
46         probabilityRatio = probability/max_prob;
47         if probabilityRatio >= rnd():
48             energy_ion = fraction * ion.getRot();
49             ion.setRot(energy_ion);
50             checkTransfer += 1;
51             break;

```

As a final step, the velocity of the ion needs to be re-scaled to accommodate changes in the kinetic energy ϵ_{tr} due to transfer into internal modes for the subsequent HS-like collision calculation. The new velocity magnitude is computed as

$$v_{\text{new}} = \sqrt{\frac{2 \cdot \epsilon_{tr}}{m_r}} \quad (6.24)$$

and the direction of the velocity is kept as beforehand.

The VHS model in combination with the Borgnakke-Larsen model should reproduce the correctly distributed values for the velocity as well as values for the energies in rotational and vibrational mode for a thermal gas. The velocities thereby follow the Maxwell-Boltzmann distribution for the defined temperature and the internal modes follow the Boltzmann distribution. As a test system O_2^+ was thermalized in O_2 bath gas at 10000 Pa using the DT-IMS application. The ion was initialized with 2000 m/s in arbitrary directions with no deposited energy in any internal modes. The following table introduces all application input parameters necessary to run a DT-IMS simulation in IDSimF with the VHS/BL collision model and the values set for the test system.

Table 6.5: Input parameter values for the VHS/BL test system and description for the general parameters.

input parameter	description	value
sim_time_steps	see Table 6.1	150 000
dt_s	see Table 6.1	10^{-10}
concentrations_write_interval	see Table 6.1	10
trajectory_write_interval	see Table 6.1	400

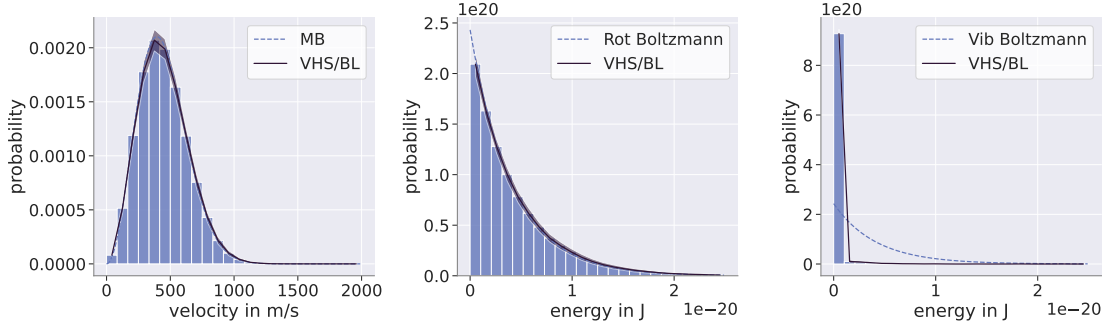
trajectory_write_velocities	see Table 6.1	true	
space_charge_factor	see Table 6.1	0	
reaction_configuration	see Table 6.1	gen.	file-name
n_particles	see Table 6.1	2000	
electric_field_mag_Vm-1	see Table 6.1	0	
start_width_yz_mm	see Table 6.1	1	
start_width_x_mm	see Table 6.1	1	
stop_position_x_mm	see Table 6.1	100	
transport_model_type	see Table 6.1	btree_VHS	
background_temperature_K	see Table 6.1	298	
background_partial_pressures_Pa	see Table 6.1	10 000	
collision_gas_masses_amu	see Table 6.1	31.8	
collision_gas_diameters_angstrom	VHS collision gas reference diameter	4.07 [81]	
vhs_viscosity_omega	VHS ω for the collision gas	0.77 [81]	
vhs_viscosity_omega_ion	VHS ω for the ion	0.77 [81]	
vhs_reference_temperature	VHS reference temperature	273 [81]	
rot_degress_freedom_collision_gas	Number of degrees of freedom ζ in rotational mode for the gas	2	
vib_degress_freedom_collision_gas	Number of degrees of freedom ζ in vibrational mode for the gas	2	
z_rot_collision_gas	Relaxation collision number Z in rotational mode for the gas	5 [81]	
z_vib_collision_gas	Relaxation collision number Z in vibrational mode for the gas	24 000 [79]	
rot_degress_freedom_ion	Number of degrees of freedom ζ in rotational mode for the ion	2	
vib_degress_freedom_ion	Number of degrees of freedom ζ in vibrational mode for the ion	2	
z_rot_ion	Relaxation collision number Z in rotational mode for the ion	5 [81]	

z_vib_ion	Relaxation collision number	24 000 [79]
	Z in vibrational mode for the	ion

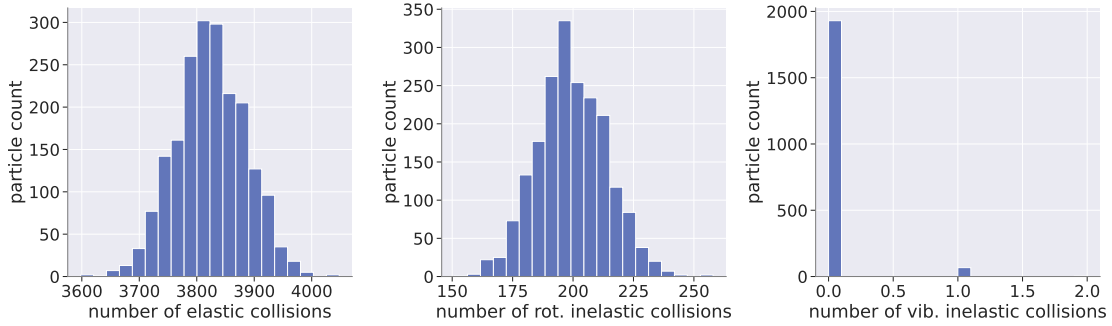
Even though O_2^+ has only one vibrational *mode*, it has two *effective vibrational degrees of freedom* due to the vibrational mode contributing kinetic (moving atoms) as well as potential (spring-like bonds) energy¹². Based on data available in [79], a relaxation collision number can be estimated. In the future, a more stable and accurate implementation would use a discretized vibrational model [169], where vibrational modes are applied based on their characteristic temperature and allows for ζ_{vib} to vary during the simulation. The rotational relaxation collision number is typically between 2 and 10 and thus simply just set to 5 for testing purposes.

Figure 6.62a shows the obtained averaged energy distributions for each mode across all recorded frames (every 400th time step) with its uncertainty as a result of the averaging process. The solid black line is the extrapolated curve based on the simulated values, shown as the blue histogram, while the dashed blue line gives the theoretical expectation of the respective distribution at the set temperature and degrees of freedom. For the velocity distribution (Maxwell-Boltzmann) and the rotational energy distribution (Boltzmann) a very good agreement between simulation and analytical / theoretical curves are found. The simulated, vibrational curve instead does not fit at all as almost all (i.e. all except one) ions still have zero energy in their vibrational mode (initial energy value). As the collision relaxation number amounts to the average collisions necessary to transfer energy between translational and internal, this is expected as a high vibrational collision relaxation number of 24 000 is set. The high relaxation number for O_2^+ results from the fact that almost all O_2^+ atoms are in its ground vibrational state at room temperature [170]. In Figure 6.62b this behavior is additionally confirmed as essentially all ions had no kinetic-vibrational energy transfer. Overall, elastic collisions should be the most prominent, with rotational transfer taking place more often than vibrational energy transfer (dependent on the temperature), which is exactly the result of the test simulation. Like any other collision model also the VHS/BL model thus needs a certain time to equilibrate based on the set parameters. To verify if the vibrational mode can also reach thermal equilibrium, the relaxation collision number for the vibrational mode was arbitrarily reduced from 24 000 to 2. As the relaxation number is now much smaller and even smaller than the rotational relaxation number, the vibrational mode now thermalizes with higher numbers of vibrational collisions than rotational collisions. Since nothing changed for the kinetic or rotational mode, the distributions and counts stayed essentially the same. These simulations show that the

¹²The equipartition theorem states that every quadratic degree of freedom contributes $1/2kT$ to the equilibrium internal energy. Using a harmonic oscillator approximation for the vibrational energy (which is the case for Borgnakke-Larsen) this yields $\epsilon_{\text{vib}} = 0.5kx^2 + 0.5mv^2$, i.e. two quadratic terms. The Borgnakke-Larsen method can also be combined with a discretized vibrational model (which would be more accurate) [168], which is not part of this work.



(a) Energy distributions of kinetic and internal (rotation and vibration) of O_2^+ in O_2 using the VHS/BL collision model during a thermalization run (no electric field). The simulation parameters are given in Table 6.5. The ions had a starting velocity of 2000 m/s. A frame is extracted every 400th time step and the energy distribution is averaged over all frames, with the uncertainty given by the error band.



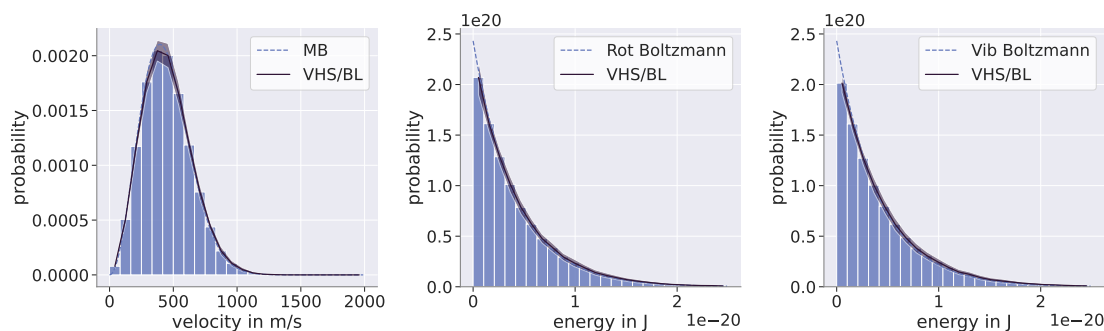
(b) Distribution of collision numbers of the ions for each collision type for the simulation shown in Figure 6.62a.

Figure 6.62: VHS/BL simulation run with parameters as in Table 6.5.

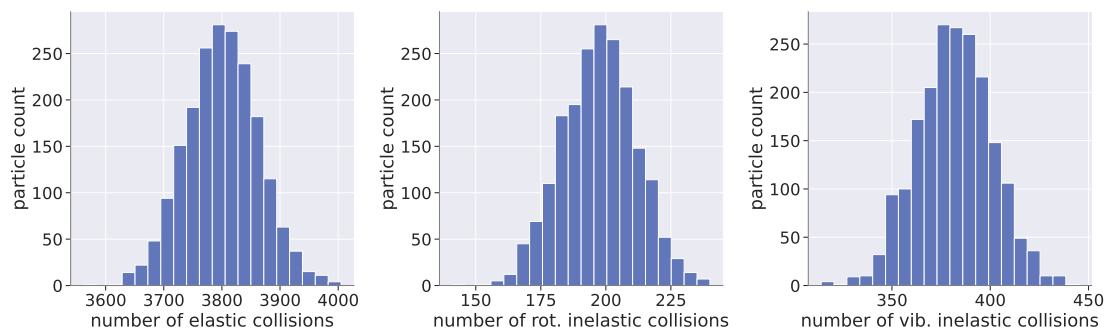
model works as expected. However, as usual special care must be taken to set correct or at least sufficiently valid approximated values for the model parameters to ensure correct ion behavior.

6.5.3 Comparison to hard-sphere and MD model

In a last step a few of the systems simulated for the MD model are compared to the VHS/BL model, additionally also showing results obtained for the HS model. First, the ion mobility values obtained for Li^+ in N_2 are shown in Figure 6.64. References values (experimental) and MD model values are given as in Figure 6.51. A simulation run with the HS model was carried out and additionally four VHS/BL simulations. The VHS/BL runs vary in the applied collision diameter the viscosity parameter ω for Li^+ as no reference VHS data is available. Notably, to further validate the VHS/BL model, one run was carried out with $\omega = 0.5$ (and no deposition in rotational degrees) as this should result in a temperature independent VHS model, i.e. the HS behavior is restored. This is indeed the case, as both curves of the HS and VHS(HS) run lie exactly on top of each other. With rotational relaxation turned on (molecular nitrogen has two degrees of rotational freedom



(a) Energy distributions of kinetic and internal (rotation and vibration) of O_2^+ in O_2 using the VHS/BL collision model during a thermalization run (no electric field). The ions had a starting velocity of 2000 m/s. A frame is extracted every 400th time step and the energy distribution is averaged over all frames, with the uncertainty given by the error band.



(b) Distribution of collision numbers of the ions for each collision type for the simulation shown in Figure 6.63a.

Figure 6.63: VHS/BL simulation run with parameters as in Table 6.5 with the ζ_{vib} parameter changed from 24 000 to 2.

and essentially zero vibrational modes at room temperature, like O_2^+), increasing the ω value of the ion leads to higher mobilities with the same behavior found for a decreasing diameter. Despite various changes in the "unknown" VHS parameter for Li^+ , the shape of all VHS curves is very similar. The curve is essentially just moved up or down on the ion mobility range by the parameter variation.

Neither VHS or HS can accurately predict the ion mobilities for Li^+ in molecular nitrogen, as both approaches are simply too hard-sphere like. Even though the system exhibits a type C curve, which is hard-sphere behavior, the ion mobility curve is much flatter than possible with HS or VHS. While the Borgnakke-Larsen model introduces inelasticity, the main influences on the ion mobility in this system are the attractive forces between nitrogen and lithium, i.e. ion-induced dipole and ion-quadrupole forces. However, only the MD collision approach models these effects with the help of a fitting force field function while (V)HS just considers repulsive, (but dampened) billiard-like collisions. As expected, the MD model thus gives much better predictions of the ion mobilities in this system. On the other hand, the VHS model can integrate almost twice the simulated time of the MD

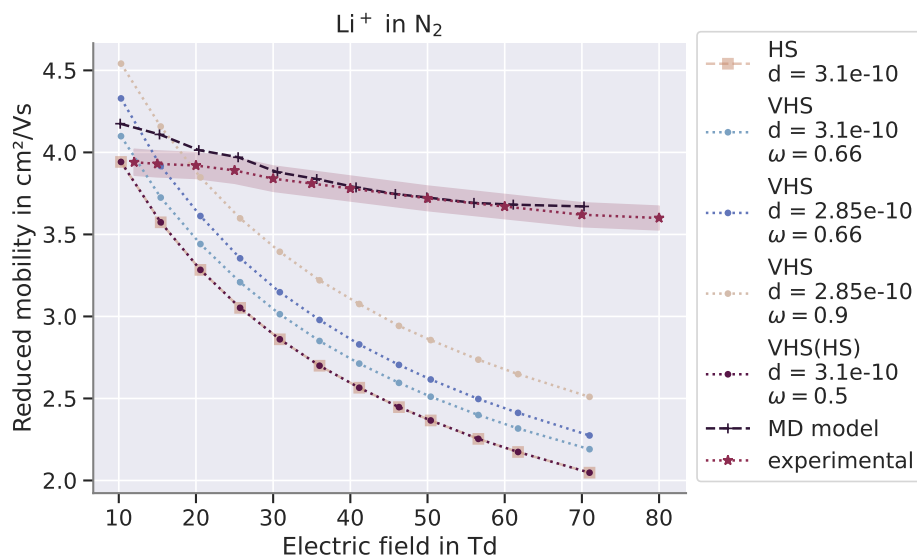


Figure 6.64: Reduced ion mobility for varied reduced electric fields for Li^+ in molecular nitrogen at 295 K using different collision models compared to experimental data [150]. The collision models used are the HS, MD and VHS model, where for the VHS model various collision diameters for lithium as well as different ω values are used.

model simulations with the particle count increased by an order of magnitude in only three hours instead of in 14 up to 48 hours¹³. For systems assumed to be closer to strong hard-sphere behavior or in simulations where the very accurate description of ion-neutral collision dynamics is not necessary (e.g. rarefied gas dynamics), the VHS model is a good alternative for fast and stable ion trajectory simulations.

For three additional systems with known VHS parameters, as given in [81], the ion mobilities were simulated and compared to literature, experimental ion mobilities as well as to the HS and MD model. Figure 6.65 shows the ion mobility curves for O_2^+ in helium and argon along with CO_2^+ in nitrogen (no MD data for this system). In an identical fashion to the VHS characteristics as shown for Li in N_2 , the VHS curves only show type C behavior. Across the board the VHS model always results in ion mobilities higher than for the HS model. This is likely the result of the decrease of the collision cross section with higher collision energies in the VHS model. The same diameter as for the VHS model was also applied for the HS model, which is then probably slightly too large without energy correction. From the three systems only O_2^+ in helium exhibits a type C curve in experiments, as such the VHS model could in theory be a good fit there. However, the ion mobilities of the VHS, or HS, model are much lower than the data from literature for this system. The curve slope for higher reduced electric fields has ample agreement with the experimental data, though. In the case of O_2^+ in argon and CO_2^+ in nitrogen neither the VHS nor the HS model can reproduce the experimental ion mobility values as the systems

¹³Heavily depending on pressure and force field parameters and the resulting possible parallelization efficiency.

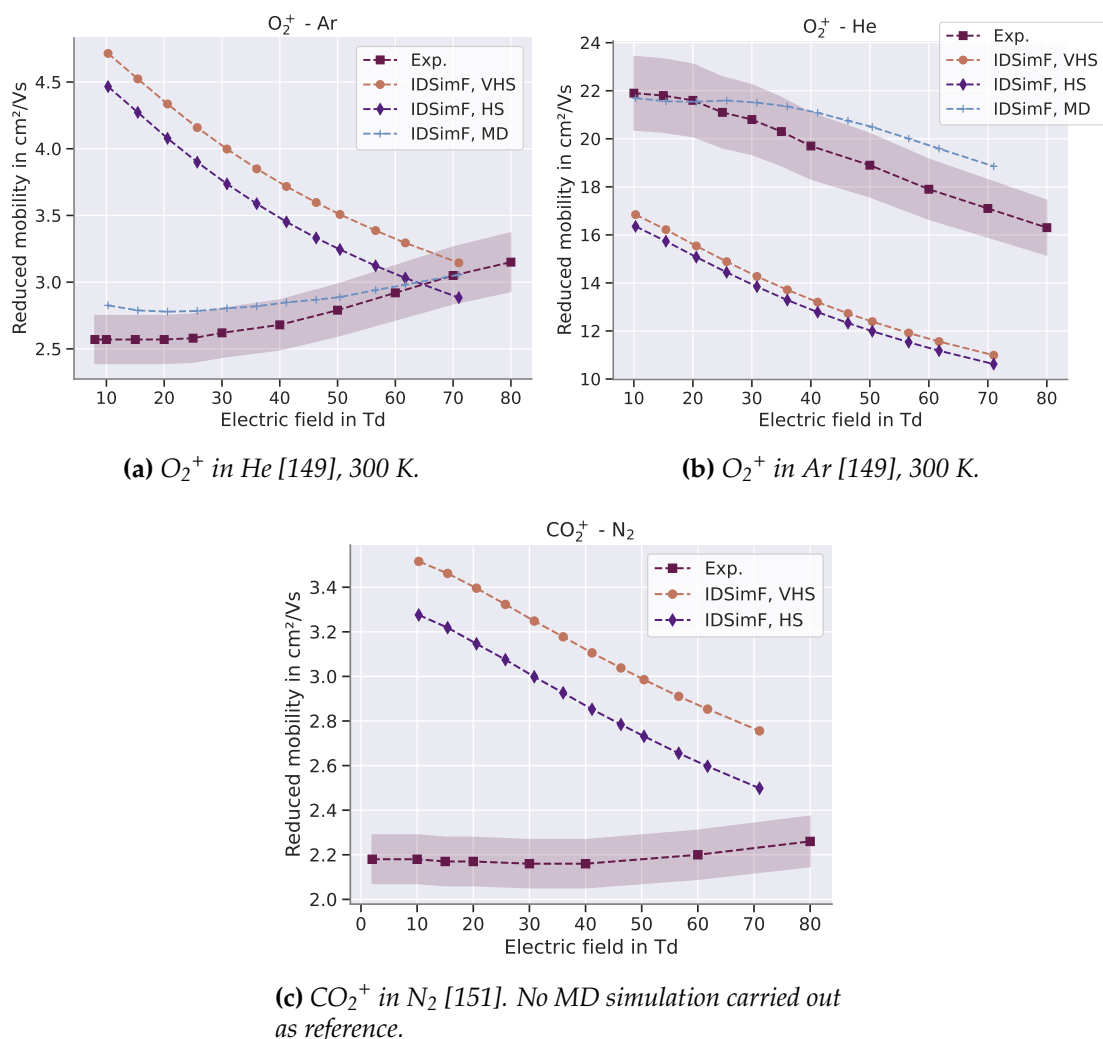


Figure 6.65: Comparison of the reduced ion mobility over varied electric fields for the VHS, HS, MD model (if available) and literature experimental data.

are either type A or type B.

As such, the MD model has a much higher accuracy in ion mobility predictions at the price of much higher computational costs. The VHS/BL model can, however, be improved further by three ideas:

- **Diffusion:** The VHS model in its nature cannot simulate both, correct viscosity and diffusion of a mixture [75]. Therefore, correction in either direction leads to a loss of accuracy in the other parameter. A very important improvement over the VHS model with minimal implementation effort is the variable soft sphere (VSS) model [171], which allows to better reproduce viscosity and diffusion at the same time. The VSS model changes the impact parameter $b = d \cdot \cos(\chi/2)$ of the VHS model to $b = d \cdot \cos^\alpha(\chi/2)$ [171] with an energy-dependent parameter α so that the scattering angle is also subject to the collision energy. Compared to the VHS model, the scattering angle in the VSS model is always smaller [171]. Therefore, the VSS

model has the potential to better approximate effects produced by attractive forces as those primarily lead to small scattering angles.

- **Simple Harmonic Oscillator:** The current employed VHS/BL model uses a continuum approximation for the energy levels of translational and internal modes. This approximation is adequate for translational energy and rotational energy at large temperature ranges [81], however a quantum model is required for vibrational modes. An approximation for the vibrational energy levels i is given by a simple harmonic oscillator with $\varepsilon_{v,i} = ik\theta_v$, where θ_v is the characteristic vibrational temperature.
- **Vibrational relaxation rate corrections:** The collision numbers and thus the relaxation rates are a function of the temperature [81]. The Millikan-White theory [172] shows a dependence of the vibrational collision time on $T^{-1/3}$, which leads to a vibrational collision approximation of $Z_v = \frac{C}{T^\omega} \exp(S \cdot T^{-1/3})$ with C, S as constants fitted to experimental data [79]. This approximation leads to a better equipartition and equilibration [81].

In further works, an effort should be made to improve the current version of the VHS/BL model by the aforementioned modifications, especially in preparation for the implementation of internal energy tracking for the MD model.

6.6 Summary

This chapter aimed to establish the MD based as well as the VHS/BL collision model for ion trajectory simulations in IDSimF. A short summary of the main takeaways is given below:

- the MD model could be successfully established for helium and argon as background gas. Even without extensive parameter fitting, matching ion mobilities in low and high field with deviations in the ranges of 4 % to 10 % are observed.
- the MD collision model was combined with a resonant charge transfer reaction model and returned very good results for an argon / argon system. This is currently not possible in e.g. MobCal-MPI or IMoS.
- the MD model was extended by nitrogen as a background gas. MobCal-MPI and IDSimF thereby return similar trajectories under same starting conditions.
- the ion mobility results for nitrogen systems are of mixed quality with larger discrepancies than for helium/argon for most simulated system but with some systems being a good fit though, e.g. protonated acetone.
- rigid-body rotations were implemented. This introduced a "compass needle" effect currently inhibiting good ion mobility predictions.

- the VHS/BL model was incorporated. Ion mobilities did not have as high of an accuracy as for the MD model, which is expected. This model, however, allows for internal energy transfer and can be further developed in following works.

All in all, the results of this chapter show that ion mobility predictions work well even in a combination with direct ion trajectory simulation in contrast to standalone ion collision cross section simulation programs. There are still some discrepancies using molecular nitrogen as background gas, which need to be further evaluated. On account of continued development, this work lays the groundwork necessary to simulate non-equilibrium systems with internal energy tracking / inelastic collisions.

SIMULATION OF ELECTROSPRAY DROPLETS IN SURFACE COLLISIONS IN VACUUM

This chapter focuses on the study of gas-phase behavior and surface collision events of electrospray droplets in an effort to gain better insight into possible fragmentation processes in MS instruments. As discussed in section 4.4 and section 4.5, fragment spectra recorded with a triple quadrupole instrument suggest that the CID mechanism plays an important role in the fragmentation and dynamics of ESI droplets. To verify this initial hypothesis, molecular dynamics simulations of droplet-neutral collision events were performed with LAMMPS instead of IDSimF. LAMMPS is a comprehensive MD framework, which allows for a lot more flexibility and construction of more complex molecular systems. However, both programs, IDSimF and LAMMPS, share a similar fundamental approach, namely the simulation of atomistic systems with defined classical (non quantum) force fields. The MD model in IDSimF is basically a small, selected subset of the possibilities LAMMPS offers: each MD simulation in IDSimF is limited to a two particle system with closed boundaries. In that way, actual fragmentation processes of the ESI droplets currently cannot be modeled with IDSimF and LAMMPS is used instead.

MD simulations of collisions between ESI droplets and neutral gas particles were initially done by C. Markert [173]. In those calculations, a stationary model ESI droplet, consisting of hundreds of individual molecules (ref. Figure 7.8), was constructed¹ and an argon particle (*impactor*) is fired onto the droplet with a defined kinetic energy of 20 eV. Figure 7.1 shows the average kinetic energy of each half of a droplet over the simulated time steps. The impactor is shot at the droplet from the left side, as such this is the half where the initial impact takes place. The impact shows as the sharp transient in average kinetic energy at a time step of around 105. The energy is then distributed over the whole droplet by internal interactions of the molecules in the droplet and equilibrium of both droplet halves is reached quickly. To investigate the effect of multiple successive impact events (which is exactly the process in a collision cell, i.e. many, low-energy collisions), the simulation was repeated with six impactors with 20 eV each.

¹The process for the setup of an ESI droplet for the simulation is explained in a later section, as this is just for demonstration purposes of the discrepancies in energy.

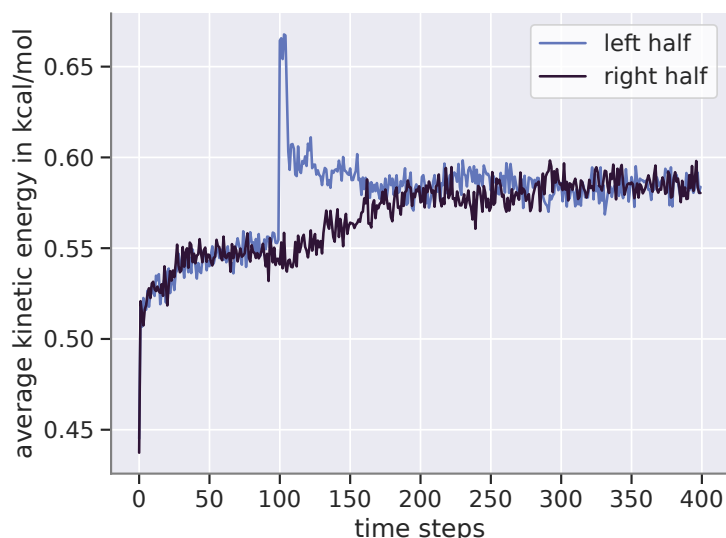


Figure 7.1: Average kinetic energy of the left half and right half of the model ESI droplet. Time step 105 shows a sharp energy increase from the impact of an argon atom with 20 eV kinetic energy. The energy is quickly redistributed in the droplet and an equilibrium is reached. Reproduced from [173].

The average kinetic energy of the droplet particles shows six stepwise increases corresponding to each of the impacts with argon. After each impact the obtained energy is quickly redistributed internally in the droplet and the energy plateaus again. At the end of the simulation, the droplet has gained a total of about 247 eV of kinetic energy. The MD simulation was also visually evaluated in Ovito. Even after all six collisions, no significant fragmentation was noticed, instead the droplet just heated up and acted as a kind of kinetic energy "sponge". Only a few clusters of particles separated themselves from the droplet, which is however expected in a heating event.

After those observations, ion trajectory simulations in SIMION were carried out to more accurately replicate the path of a charged droplet in a collision cell [174]. A geometry representative of the SCIEX 6500 collision cell² was constructed in SIMION and a hard-sphere collision approach was used to model CID events in ESI droplet trajectory simulations. The large ESI droplets were mostly unaffected by the RF-field of the RF-only quadrupole collision cell. As a consequence, since this particular collision cell is bent by 180°, no charged droplets reached the end of the collision cell. Nonetheless, the estimated accumulated energy of the modeled droplets by CID events can still be computed. Figure 7.3 visualizes the distribution of summed collision energy for an ensemble of ESI model droplets for varying acceleration voltages³ of the droplets at 298 K background gas temperature. Even for the highest acceleration voltage of 50 V only a mean summed collision energy of roughly 153 eV is accumulated. Comparing this to the value of 247 eV

²Remember the SCIEX 6500 was one of the instruments where fragment spectra of droplets could be produced experimentally.

³The acceleration voltage changes the velocity resp. kinetic energy of the droplets when entering the quadrupole of the collision cell.

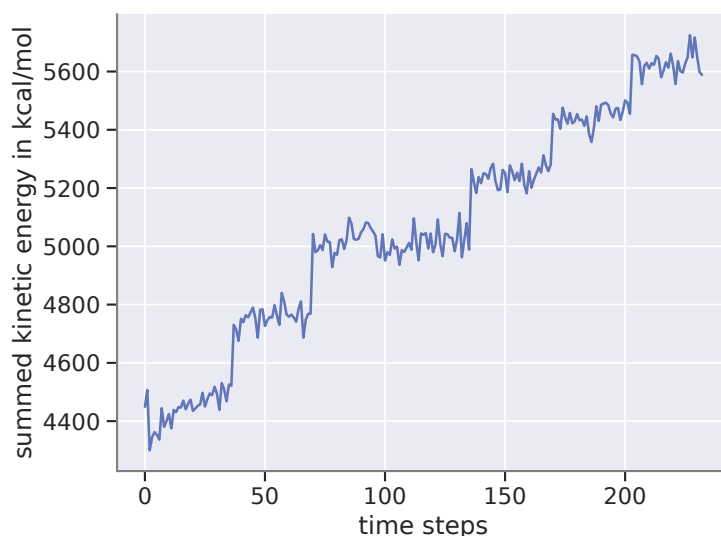


Figure 7.2: Summed kinetic energy of the model ESI droplet over six MD impacts with 20 eV argon impactors. A total kinetic energy of 5700 kcal/mol (247 eV) is reached. Reproduced from [173].

calculated for the MD simulations, the summed collision energy is still about 100 eV lower. Since the MD simulation did not show strong fragmentation, it is to be expected that the energy gathered by normal CID processes in the collision cell might not be sufficient to result in the fragmentation patterns visible in the mass spectra of such an instrument.

As such it is proposed that the fragmentation spectra might be a result of other collision mechanisms or a combination of multiple processes. Another relevant collision process is the surface-induced dissociation (ref. subsection 4.5.2), which can potentially produce higher fragment counts with less available kinetic energy. Results by C. Heintz showed that the ion bursts seen in a micrOTOF change their shape with the RF amplitude of a focusing hexapole, which is in a low pressure and hence low collision region, additionally supporting the notion of surface processes taking place.

Based on the results of the MD collision simulations and the ion trajectory simulations, and due to further support by experimental results, the surface-induced dissociation process is evaluated in MD surface collision simulations in this chapter. This allows to assess the possibility of SID to be a primary contributor to the experimental fragment spectra.

7.1 Droplet construction

The simulation of collisions of charged droplets with surfaces resp. walls requires an established preparation method, that allows to generate reliable ESI droplet descriptions of different sizes and compositions. An example of such a droplet is visualized in Figure 7.4. Based on the works of C. Markert, which used a simplified approach of building LAMMPS compliant droplets, a new and much more reliable method was established and will be described in the following section. The text-based molecular builder *moltemplate* (see

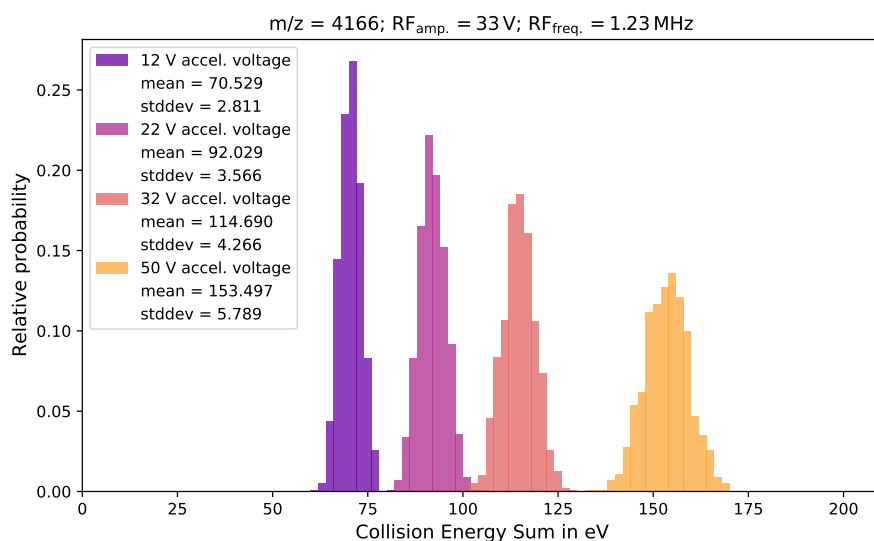
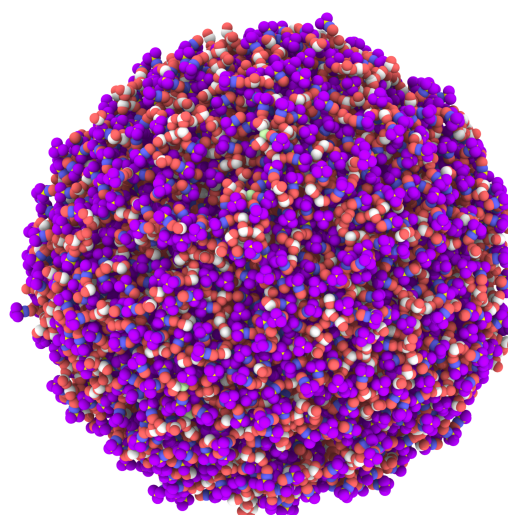


Figure 7.3: Summed collision energy of an ensemble of model ESI droplets with $m/z = 4166$ accumulated along the flight paths of a SCIEX 6500 collision cell. Collisions were modeled by a simple hard-sphere approach at a background gas temperature of 298 K. Different acceleration voltages were applied to the charged particles before entering the collision cell. Taken from [174].

Figure 7.4: Model ESI droplet containing water, acetonitrile and lithium ions generated by the droplet construction workflow and visualized with Ovito. Final position equilibration has not been carried out in LAMMPS at this stage, as such the droplet is unnaturally spherical.



Water



Li^+



Acetonitrile

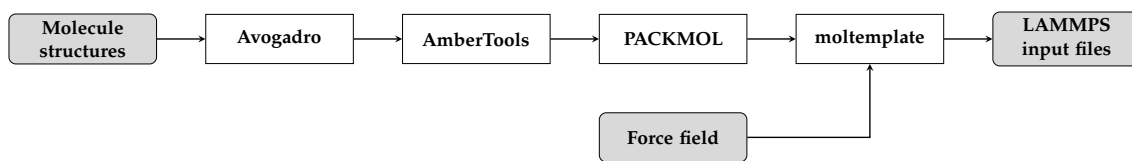


Figure 7.5: Scheme of the software tool-chain for the preparation process of MD ESI droplets.

subsection 5.5.4) is used as the main building block of the droplet preparation process. This script allows to generate all necessary files to run a LAMMPS simulation from a model description in a specialized scripting language. Further auxiliary programs and scripts are then used to guarantee good stability of the generated droplet, with only minimal re-configuration of the scripts necessary if different droplet size / molecules should be used.

Before a droplet can be constructed, the type of atoms or molecules included in the droplet need to be defined. For all simulations here solely droplets consisting of water and acetonitrile are used, as this is a common solvent composition of ESI droplets. Additionally, lithium ions are used to represent the charges found in the non-neutral ESI droplets. To reduce complexity of the first simulations considering surface collisions of ESI droplets, no explicit analyte ions are simulated in this work.

An overview of the build process is shown in Figure 7.5 and outlined below:

1. Avogadro [139]: Individual molecules of the different species to be simulated are defined in Avogadro with information of the molecular structure (bond distance, angles and elements present). An initial geometry optimization with Open Babel [140], also through a molecular mechanics methods, is carried out at this step (included in Avogadro). The optimized molecular structures are then exported in the *pdb* and *xyz* file formats.
2. AmberTools (2023) [138]: The *antechamber* script packaged with AmberTools is used to convert the molecule *pdb* files, generated by the first step, to *mol2* files needed by the *moltemplate* script. The following command-line can be used for successful generation:

```
# ./antechamber -i <input>.pdb -fi pdb -o <output>.mol2 -fo mol2
```
3. PACKMOL [146]: The spherical geometry of the droplet is constructed by PACKMOL. A defined sphere is randomly filled in an iterative process with the given number of molecules (defined by *xyz* files produced in step one), honoring a limiting bond distance (here: 2 Å). The output of PACKMOL is a *xyz* file again, containing the positions of all atoms in the droplet. An example script is shown in Listing D.1.
4. mol22lt.py: The *mol2* molecule files and the desired force field file⁴ in *lt* format (e.g. OPLS-AA) are combined with the *mol22lt.py* script (also a part of *moltemplate*) to

⁴The force field file gives information about charges, masses and interaction parameters on a per atom type basis.

build molecule files in the *lt* format required by moltemplate in the next step. The following command-line can be used to obtain *lt* files:

```
# mol22lt.py -in <input>.mol2 -out <output>.lt -ff OPLSAA -ff-file "oplsaa.lt"
```

To correctly set atom types for the force field in the output file, the atom types also need to be set in the *mol2* file beforehand.

5. moltemplate [144]: As a last step, a simulation box is defined in a moltemplate input file (again as *lt* file) and molecular structure files are included. An example moltemplate system configuration file is listed in Listing D.2. The PACKMOL droplet *xyz* file is additionally required to let moltemplate know of the correct positions of each atom. With the following moltemplate script call

```
# moltemplate.sh -xyz <system>.xyz <system>.lt
```

finally all LAMMPS input files are produced (information on atom positions, atom type numbers, charges, bonds, angles, force field configuration, simulation box size, etc.).

After the droplet has been generated it needs to be energy minimized by iteratively adjusting atom coordinates, based on the potential function, to correct for overlapping atoms⁵ in LAMMPS. Furthermore, a full MD trajectory simulation employing a Nosé-Hoover thermostat at 298 K (`fix nvt` command) is carried out to bring the droplet into quasi-equilibrium, as the droplet otherwise is too unnaturally shaped (PACKMOL simply fills a simple geometric sphere). This simulation is done for a few 10 000 time steps and stopped then as longer simulation would eventually lead to complete evaporation of the droplet due to the constant energy input by the heat bath.

7.2 SID LAMMPS model

To simulate the dynamics of surface collisions of an ESI droplet, a MD system as shown in Figure 7.6 is built. The simulation box has dimensions of $550 \times 200 \times 200 \text{ \AA}$ in a *xyz* coordinate system and is visualized by the bold black lines. Inside the simulation box the two main components are contained: i) a droplet and ii) a wall.

The wall consists of individual aluminum atoms ordered in a fcc crystal structure. The outer "shell" of the aluminum grid is rigid, while the atoms inside the shell can freely vibrate. Figure 7.7 illustrates a cross-section of this aluminum wall, with two aluminum layers which are in contact with the simulation box boundary colored in orange. Exactly those atoms are kept rigid and make up the shell. Without the shell, the aluminum wall is not stable due to its small thickness and often rips apart in the minimization step. In all simulations the wall is always at the left-hand boundary of the long side of the simulation box (i.e. $x = 0$). The droplet is then placed in the center of the simulation box.

Before the MD simulation can integrate the atom trajectories by solving Newton's equations

⁵Any actual MD simulations carried out with overlapping atoms leads to simulation crash in LAMMPS.

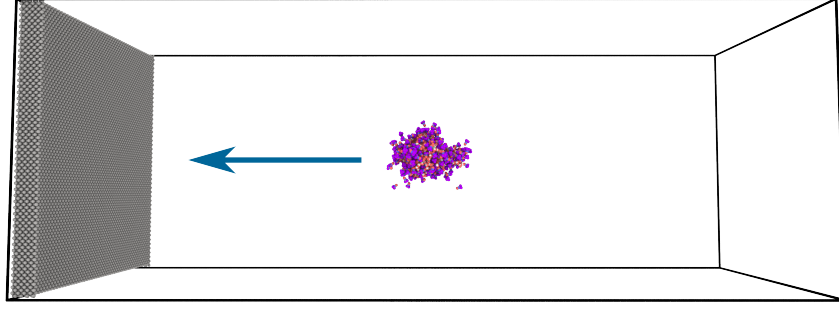


Figure 7.6: Simulation system set-up of a SID event. The blue arrow shows the velocity direction of the droplet.

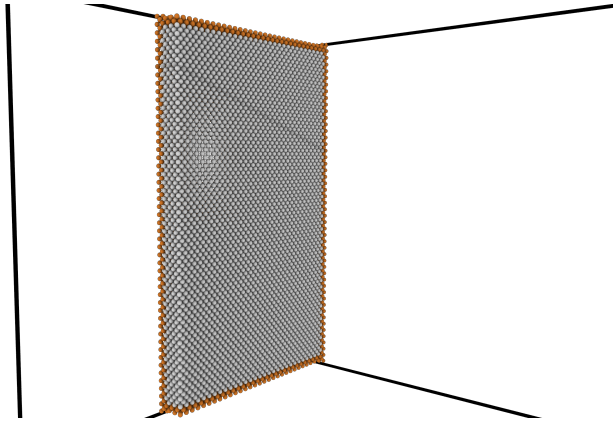


Figure 7.7: Cross-section of the aluminum wall. Rigid aluminum atoms are colored in orange.

of motion with the velocity Verlet integrator, the system needs to be energy minimized a second time. An energy minimization of the droplet was already carried out in the droplet construction, however the wall is only initialized in the combined, complete model and thus also needs to be corrected for overlapping atoms in the wall segment. Furthermore the temperature resp. velocities of all atoms need to be adjusted. All atoms of the wall are put at 298 K without a thermostat. Additionally, randomized starting velocities following a thermal distribution at 298 K are initially assigned to the droplet atoms. The droplet is intended to hit the wall with a defined kinetic energy. Therefore, a secondary velocity component directed towards the wall is superimposed on the 298 K distribution. Analogously to the different acceleration voltages with which a droplet can enter a collision cell in e.g. the SCIEX 6500 instrument, the droplet in the SID simulation should also have varying initial "acceleration" / starting voltages. The velocity in downfield x -direction can be computed from the droplet charges q_d , droplet mass m_d and the starting voltage U_s by

$$v_x = \sqrt{\frac{2 \cdot q_d \cdot U_s}{m_d}} . \quad (7.1)$$

As such, the droplet is already fully accelerated at the start of the simulation and moves with v_x towards the wall, with the internal temperature being 298 K. No thermostat is applied for the droplet, i.e. the full simulation is integrated as a microcanonical system (fix nve command). If not otherwise noted, all simulations run for a total of

10^5 time steps with a step size of 1 fs, resulting in 100 ps total simulation time. This simulation length is chosen to ensure that the droplet and its fragments can experience the complete dissociation/recombination process without evaporation playing a significant role. Available experimental data and estimations of the interaction time between small ions and surfaces suggest that dissociation processes may occur either temporarily close to the direct surface interaction or instead well after surface ejection [175–178], thus 100 ps is estimated to be good compromise to observe all relevant processes. An input file example containing the system set-up is listed in Listing D.3.

7.2.1 Interatomic potentials

Since this MD model contains organic particles as well as metal particles, a hybrid force field approach is chosen. Based on which groups of particles interact with each other, a different force field should be used. This ensures a good approximation of the interaction dynamics for the metal wall as typical force fields designed for organic molecules and bio-molecules are not well suited to describe metal crystal structures (ref. subsection 2.5.2.1). There are three different cases in the used hybrid force field:

- Droplet ↔ Droplet: For the interaction potential between droplet atoms the OPLS-AA force field [52], as given by moltemplate [179], is utilized. OPLS-AA is based on a 12-6 Lennard-Jones approach and is combined with a long-range Coulomb interaction

$$U_{\text{coul}} = \frac{C q_i q_j}{\epsilon \cdot r} \quad , \quad (7.2)$$

where C is a LAMMPS internal energy conversion constant (unit system dependent) and ϵ is the vacuum permittivity. The simulation is configured so that the pairwise Coulomb interaction is evaluated directly below a cut-off of 20 Å. Above this cut-off, forces of the Coulomb interaction are instead calculated in reciprocal space by a Particle-Particle Particle-Mesh algorithm (PPPM), which is a Ewald summation type computation for accurate calculation of Coulomb interactions [28].

- Wall ↔ Wall: Interactions within the aluminum wall are characterized by an eam/alloy LAMMPS potential, which uses an EAM potential as its basis. Force field parameters used for the SID MD simulations are taken from Mishin et al. [180].
- Droplet ↔ Wall: Atom pair interactions with atoms of different groups, i.e. one atom is located in the droplet and the other in the wall, are also modeled by a 12-6 Lennard-Jones approach. The standard OPLS-AA force field parameter set did not include aluminum parameters, but Heinz et al. [181] produced LJ parameters for fcc aluminum compatible with OPLS-AA. As the aluminum wall does not have any partial charges assigned, no Coulomb interaction between the droplet and wall take place. Mirror charge effects are therefore excluded.

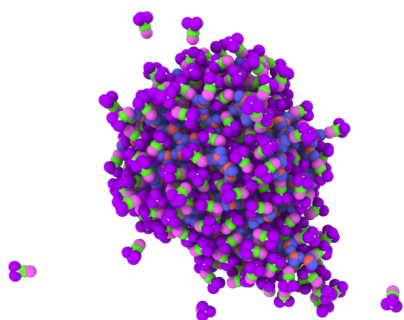


Figure 7.8: *Small model ESI droplet consisting of 7 charges (lithium ions), 334 acetonitrile molecules and 440 water molecules.*

The precise parameters employed for the Lennard-Jones potential are documented in Table A.24. The TIP3P water model is utilized in this context. It has been observed that TIP3P water exhibits insufficient surface tension [182], which may result in diminished stability of the simulated droplets in comparison to other water models, such as SPC/E and TIP4P/Ew [182].

7.2.2 Processing of LAMMPS output

All data produced by LAMMPS is further processed in Ovito. This includes a visual evaluation as well as cluster analysis. The cluster analysis is used to compute the number of fragments and their composition after a surface collision. A Python script for Ovito evaluates for every atom of the simulation if any neighboring atoms are present within a defined cut-off distance (here: 4 Å). The term *cluster* (or fragment) thus describes a group of atoms / particles, where each particle is not further apart than the cut-off distance to its nearest neighbor. The cluster analysis then returns, for each time step, all atom data (position, velocity, mass and numerical atom type) as well as the cluster identifier. With additional Python scripts this data can be analyzed to determine the cluster sizes and composition over time.

7.3 Simulations of frontal wall collisions

Initial simulations focused on a small model droplet containing 7 charges (lithium ions), 334 acetonitrile molecules and 440 water molecules (the fully equilibrated droplet is shown in Figure 7.8) shot in a frontal collision at a wall oriented perpendicularly with respect to the droplet motion direction.

For each frontal collision a different starting voltage was set which was between 10 V and 100 V (in 10 V steps). A first interesting observation can be made by visualizing the total kinetic energy evolution of the droplet over time for the smallest and largest voltages respectively, as seen in Figure 7.9. Both surface collisions behave similar: the kinetic energy

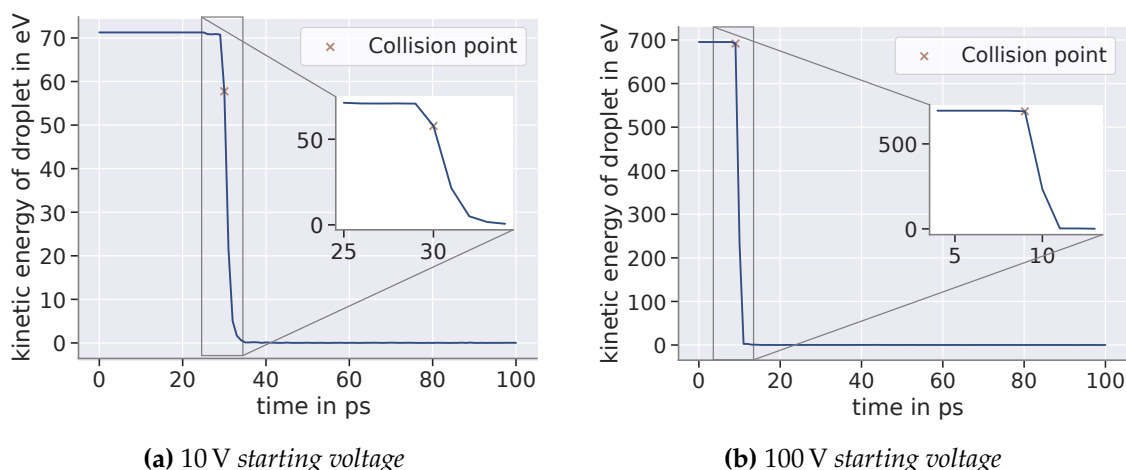


Figure 7.9: Kinetic energy evolution of the droplet over the complete simulation. A collision point is numerically approximated by a Gaussian kernel fitted to the time evolution.

stays constant while the droplet is moving through vacuum until parts of the droplet come into contact with the wall and rapid energy loss over a few ps takes places. After the energy loss, the droplet formally has zero kinetic energy as the entity is now connected to the wall with large portions of the energy transfer to the wall atoms. The generated fragments also take a part of the collision energy with them. The main difference between the two voltages is in how fast the energy is deposited into the wall and the generated fragments. The collision event takes roughly half the time with the 100 V droplet.

In addition, with this energy curve an estimated collision time (the exact time at which the droplet comes fully in contact with the wall) can be computed. This is done by numerically fitting a Gaussian kernel / filter to the energy curve to smooth the curve and computing the time for the inflection point of the smoothed curve, as the inflection point is a good estimate for the central point of the collision process. This collision time estimation can then be used in further analysis to describe processes that take place "after the collision with the surface". A visual examination of MD simulations, as seen in Figure 7.10, shows the droplet-surface collision for three different voltages of 10 V, 50 V and 100 V at a time of 75 ps⁶. For low voltages the droplet essentially stays intact and with higher voltages the droplet begins to disintegrate due to the surface hit, with several clusters generated. Carrying out a complete cluster analysis after the numerically defined collision time, the average number of ejected clusters originating from the surface collision can be determined and is shown in Figure 7.11.

Each simulation run was repeated 10 times with a different random seed to obtain uncertainty information in terms of estimated standard deviations. The obtained standard deviations are relatively small and do not show a direct correlation with the starting voltage. Most likely the variations in deviations are a result of the slight uncertainty of the

⁶Due to the different velocities of the droplets, the collision is captured at different states. The visualized time is chosen such that the slowest moving droplet has hit the wall.

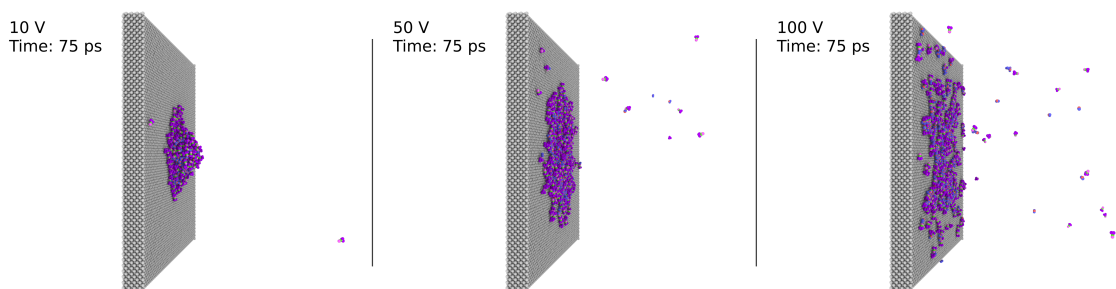


Figure 7.10: Frontal collision of the droplet with the aluminum wall at 10 V, 50 V and 100 V each at the same time stamp of 75 ps.

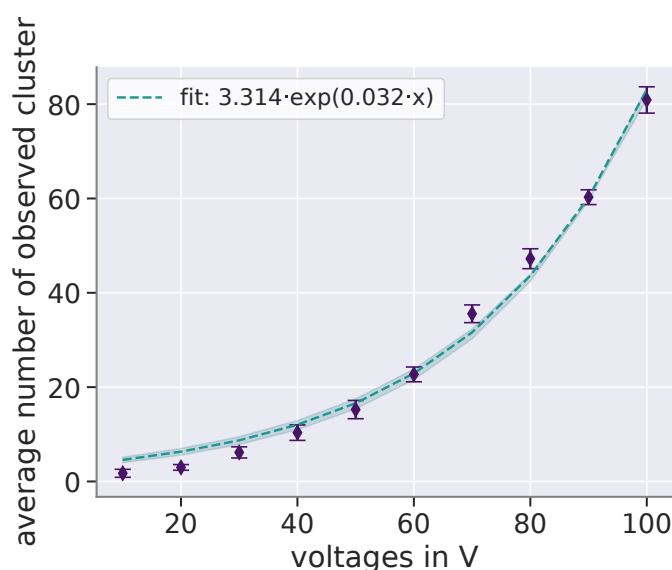


Figure 7.11: Average number of observed cluster after the frontal collision of the small droplet with the aluminum wall. The starting voltage is varied and each simulation is reproduced 10 times, with the error bars being the standard deviation of the reproductions. Additionally, a best fit with an exponential function and its corresponding uncertainty band is given.

exact collision point due to automatic / numerical determination. The average number of liberated clusters after the collision time is dependent on the acceleration voltages. More clusters are ejected with higher voltages, as is expected since more collision energy is available. The observed proportionality for the small droplet is best fit with an exponential function, which is shown by the dashed line in Figure 7.11. A fit with a quadratic function was also proposed, but returned worse agreement with the observed data.

The simulation provides interesting insights not only into the number but also into the composition of the released clusters. An analysis of the cluster composition is illustrated in Figure 7.12. Two starting velocities, namely 50 and 100 V, are selected and all 10 repetition runs are summed to obtain the total occurrence of the cluster species for a specific acceleration voltage. Acetonitrile (C_2H_3N) and water are ejected predominately for both voltages. Most of the other liberated clusters then either consist of multiple water

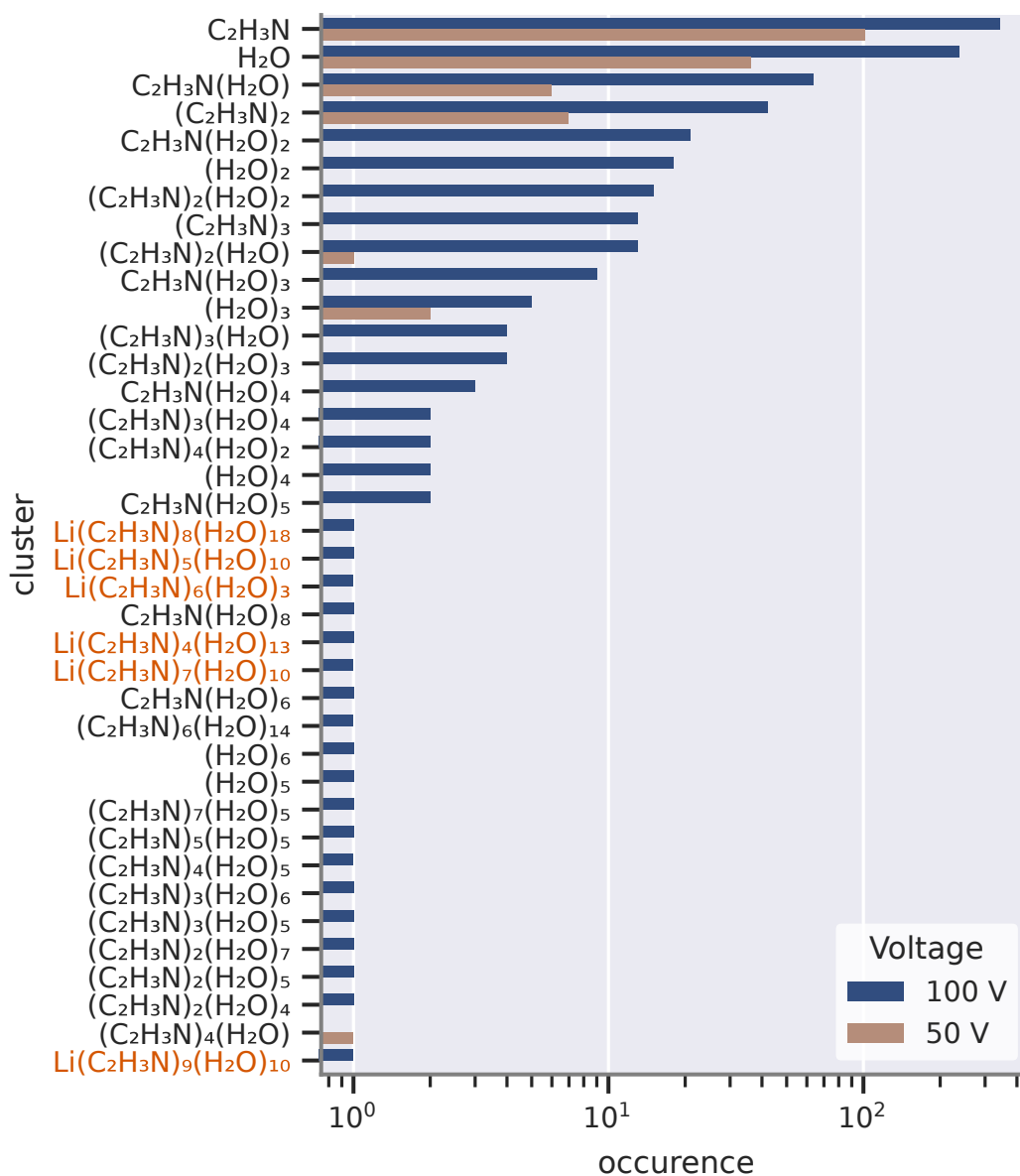


Figure 7.12: Composition and count of ejected cluster for a total of 10 frontal collision simulation runs of the small ESI droplet for 50 and 100 V starting voltage. The occurrence is displayed on a logarithmic axis and cluster containing charges (Li^+) are colored in orange.

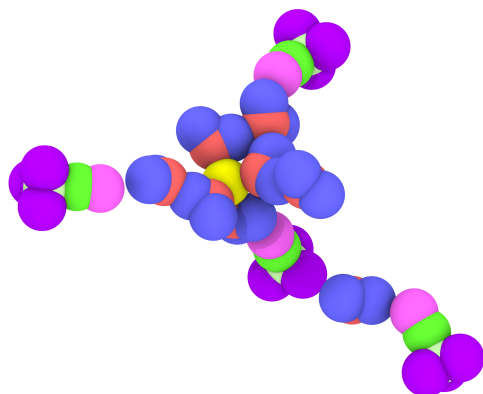


Figure 7.13: *Composition of an exemplary ejected charged cluster.*

molecules, multiple acetonitrile molecules or a mix of both. The maximum amount of acetonitrile contained in any cluster is limited to 9 for 100 V and 4 for 50 V. At 100 V acceleration voltage, larger clusters mostly are composed of water molecules, while at 50 V the size of the ejected clusters is also very limited with $(\text{C}_2\text{H}_3\text{N})_4(\text{H}_2\text{O})$ being the largest. Overall, the cluster species diversity for 50 V is small. However, the distribution of charged clusters (those that contain Li^+) is particularly noteworthy as only collisions with 100 V starting voltage produce any amount of ejected *charged* clusters. Even then the occurrence is small with only 6 charged clusters across ten collisions. If charged clusters are ejected, the charges seem to primarily be situated in clusters with larger amounts of water molecules.

Figure 7.13 shows exactly such a charged cluster with the lithium ion colored in yellow with several water molecules directly coordinated around the charged center. The acetonitrile molecules are positioned at the partially positively charged H atoms of the water molecules instead. As such, most charges remain on the wall after the collision in some way.

In Figure 7.14 the splatter pattern of an ESI droplet on the wall is visualized. Lithium ions are thereby colored in black to improve the immediate visibility and the aluminum wall itself is not shown. The line of sight originates from the droplet origin and the viewing direction is in downfield x -direction onto the wall. Similar to the ejected charged clusters, mostly water molecules orientate around the lithium ion with acetonitrile molecules located around the outer "layers" and acting like bridges between larger groups of water molecules. A maximum of 4 water molecules are directly in contact with the ion itself. Due to the strong interaction potential between the water (more accurately: the O atom of water) and the aluminum wall the charges are mostly likely "trapped" in the O atom cages and stick to the wall. Large collision energies are thus necessary to ablate those water accumulations from the wall or to prevent the sticking from happening. Below 100 V the energies appear as insufficient to release any charged clusters.

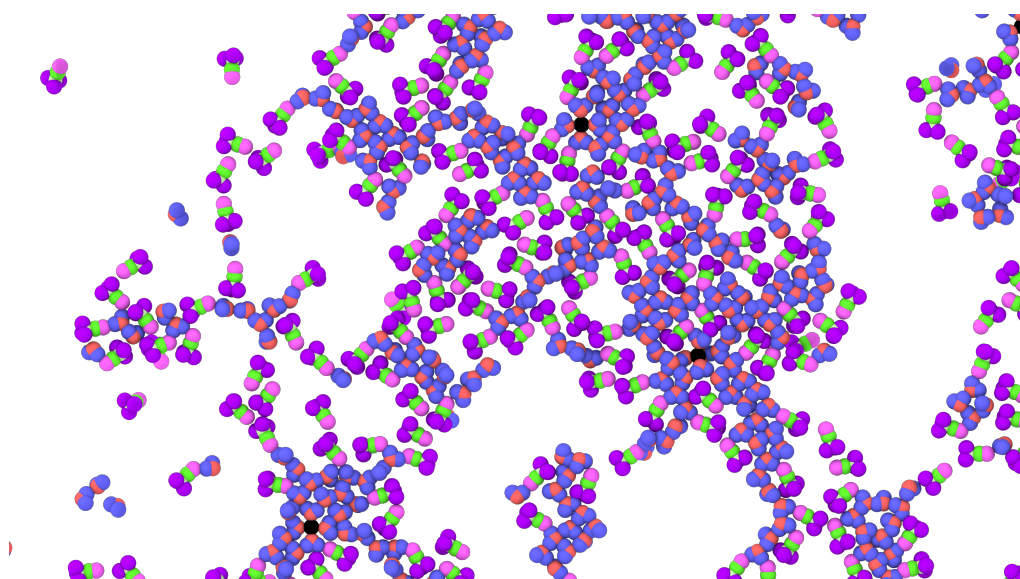


Figure 7.14: Exemplary "splatter" pattern of the ESI droplet molecules on the aluminum wall. Lithium ions are colored in black.

7.4 Simulations of slanted wall collisions

Frontal collisions of droplets would mostly originate from collisions with lens elements while collisions with multipoles are probably grazing and lead to slanted impacts. Since multipole segments are a large part of MS instruments, simulations with slanted / angled walls are also carried out. Again, wall collisions with varying starting voltages are simulated, but the wall now is rotated around its y -axis by angles between 10° and 60° (from here on denoted as *rotation angles*). Figure 7.15 shows exemplary collisions for all six different angles with a starting voltage of 100 V after 25 ps have passed. An initial visual examination reveals that steeper angles seem to lead to stronger smearing of the droplet and a change in cluster ejection angles.

This observation is confirmed by Figure 7.16, which illustrates the cluster ejection angles from the wall collision at 100 V in dependence of the rotation angle of the wall. Thereby, the ejection angles are the angles between the wall and the velocity directions of the clusters shortly after (about 1–2 time steps) the collision. The bin "height" of each angle bin is not normalized between different wall rotation angles, as such the height only gives an estimate of the relative abundance per wall angle.

The smaller wall rotation angles, i.e. 10° and 20° , still show a strong uniform scattering angle distribution of the clusters with a slight preference for the downward direction (260°). With further rotation angle increase, the ejection angle distribution severely shifts towards the downward direction with the main ejection axis parallel to the wall axis. This behavior is the observable (cf. 60° in Figure 7.15) smearing of the droplet along the wall. Additionally, the kinetic energy evolution for two different rotation angles of 10° and 60° at 100 V is illustrated in Figure 7.17. The two angles exhibit roughly the same point

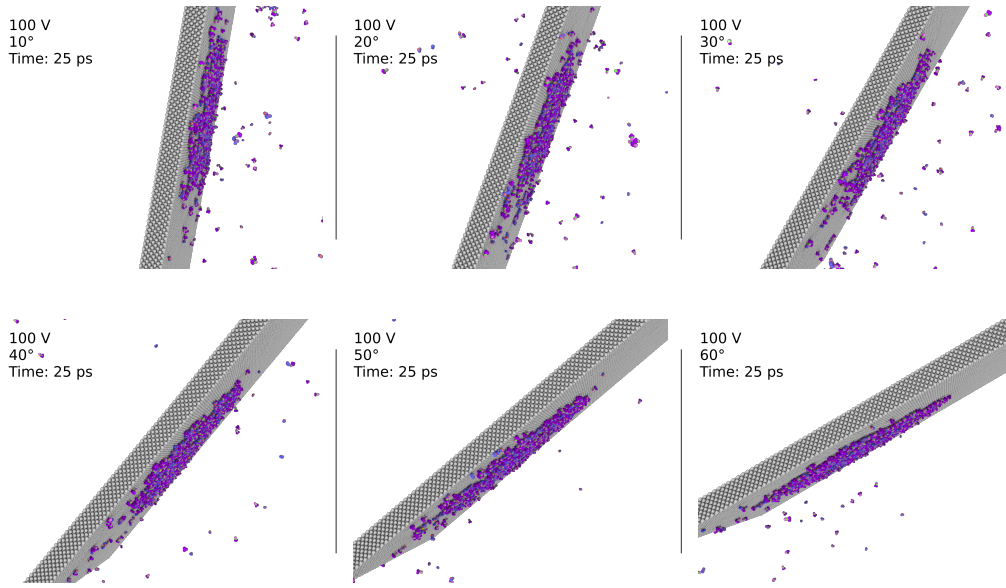


Figure 7.15: Visualization of slanted wall collisions of the ESI droplet with the aluminum wall for varying angles at 100 V starting voltage after 25 ps simulation time.

of collision at around 10 ps. The most noticeable difference is, however, the prolonged energy transfer for the steeper rotation angle. The energy transfer takes about 3 ps at 10° rotation angle and 8 ps for 60° rotation angle. The initial area available for the droplet to transfer energy (first contact point) is roughly the same for 60° and 10° . However, the impact velocity vector component is different for two impact angles. Figure 7.18 illustrates this effect quite clearly. In frontal collisions the impact velocity component (in direction of the surface normal) is the same magnitude as the droplet velocity. For slanted collisions the impact velocity is instead lower in relation to the droplet velocity. Overall, this leads to a slower propagation of the energy transfer.

For the angled collisions also the average ejected cluster count is determined and presented in Figure 7.19 for 50 and 100 V acceleration voltage. For both voltages a clear trend is visible: a steeper rotation angle leads to less liberated clusters. This effect is much less pronounced for the lower acceleration voltage, but is clearly apparent for 100 V.

At this point the two mutually influencing effects described earlier, namely the smearing and changed impact velocity, are unambiguously responsible for the reduction of ejected clusters with larger rotation angles. Consequently, this changes the cluster composition and diversity significantly.

A cluster composition analysis was carried out for the steepest rotation angle and compared to a frontal collision in Figure 7.20. Similarly to lower acceleration voltages the slanted impact leads to a much less diverse cluster spectrum with no charged clusters ejected. With that it becomes quite clear that the ejection count and composition is not only simply dependent on the total available kinetic / collision energy but also on how fast this energy is transferred / deposited into internal degrees of freedom.

Overall, frontal collisions have a much higher probability to actually lead to charged

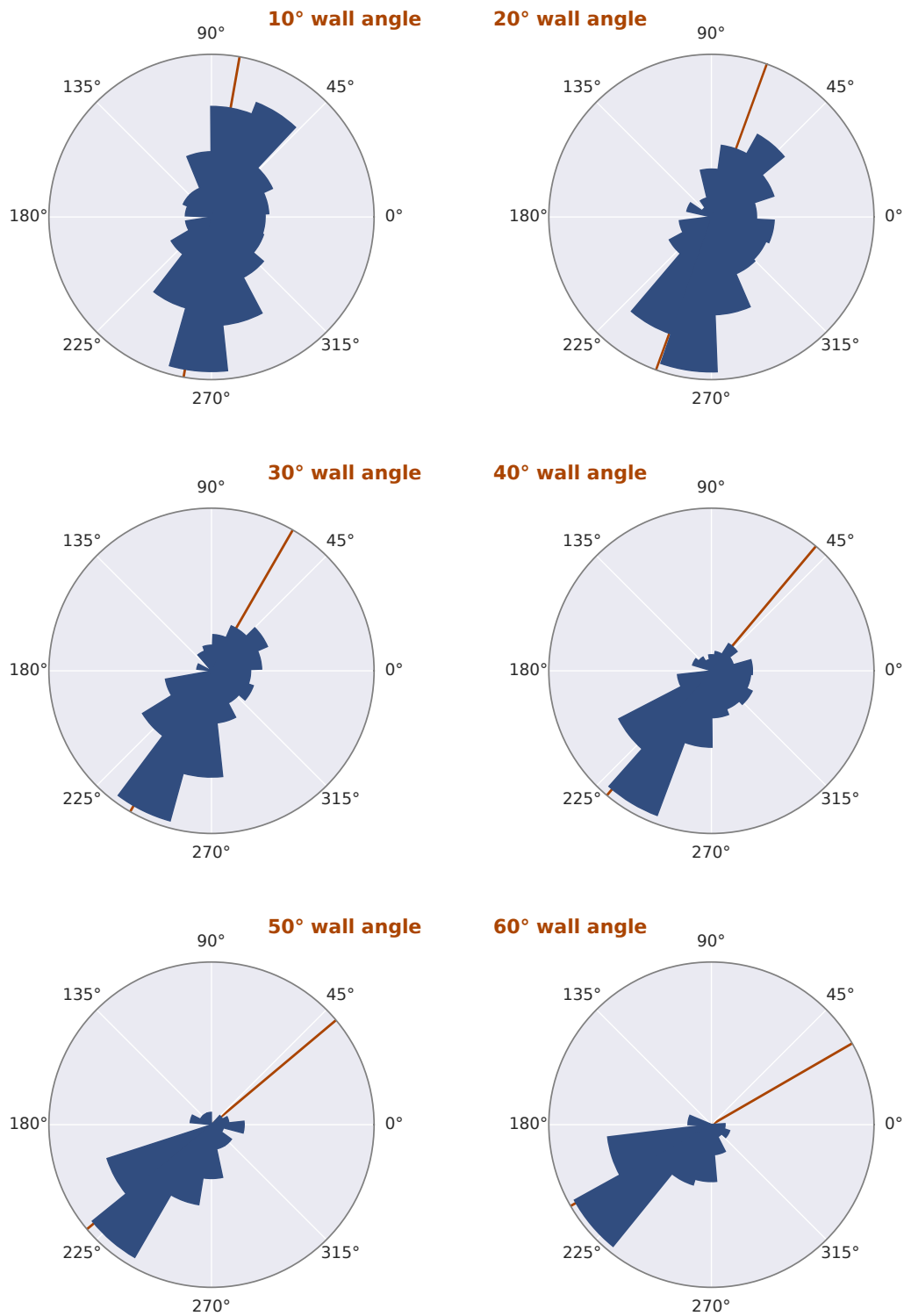


Figure 7.16: Scattering / ejection angles of clusters after the surface collision for varying wall rotation angles. An acceleration voltage of 100 V was applied. The orange line schematically represents the wall, with wall angles relative to the 90° frontal configuration.

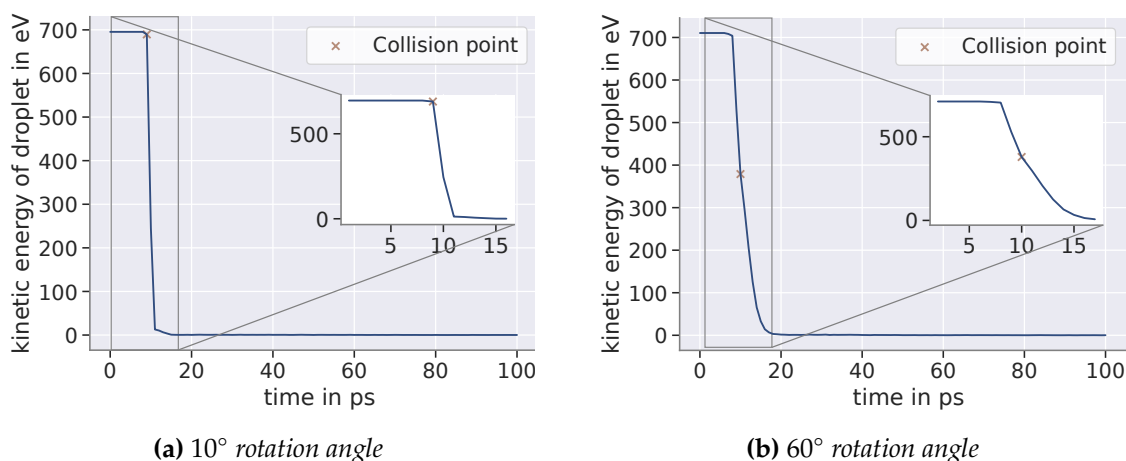


Figure 7.17: Kinetic energy evolution of the droplet over the complete simulation in a slanted collision at 100 V acceleration voltage. A collision point is numerically approximated by a Gaussian kernel fitted to the time evolution.

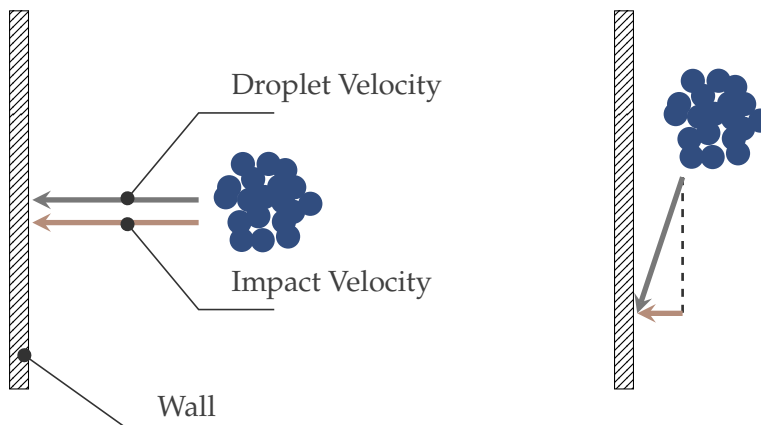


Figure 7.18: ESI droplet before impact for two impact angles. In this case the wall is not rotated but instead the droplet comes at an angle. This shows the impact velocity component is much smaller component for a slanted impact.

cluster ejection. It is particularly intriguing to understand the dynamics of charged clusters generated by such collisions as those clusters would be visible in the mass spectrum of the MS instruments. In that sense these first results show that the slanted collisions, even though these are probably the more frequently occurring impacts, might not solely lead to those experimentally observed spectra with liberated charged analyte from ESI droplets.

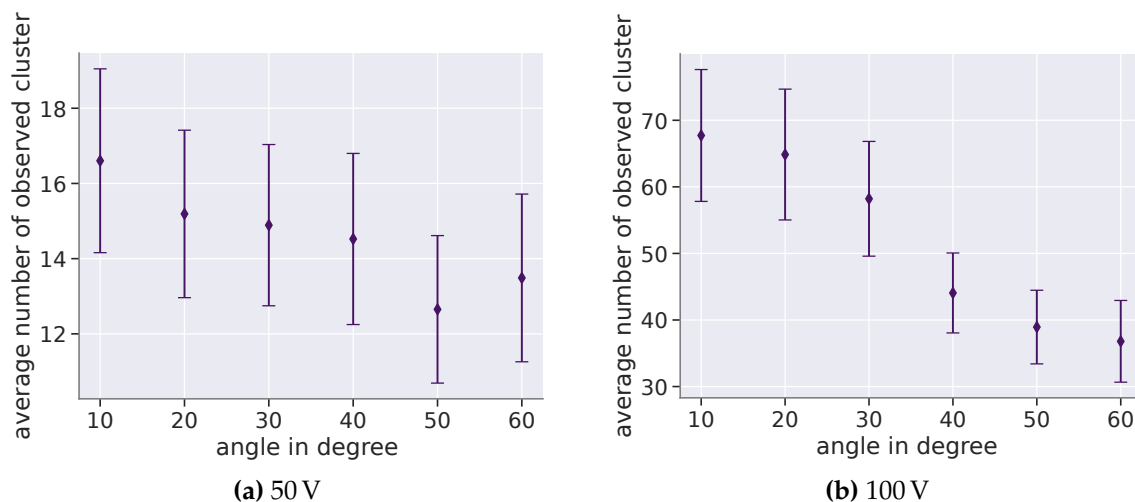


Figure 7.19: Average number of observed cluster after angled collisions of the small droplet with the aluminum wall for various rotation angles. The starting voltage is varied in the left / right panel and each simulation is reproduced 10 times. The error bars indicate the standard deviation of the reproductions.

7.5 Droplet size variation

A larger ESI droplet was designed as the small ESI droplet investigated so far is one of the smallest droplets estimated at the very end of the ESI process. This larger droplet contains 18 charges, 2385 acetonitrile, and 2919 water molecules, respectively. Figure 7.21 shows a comparison of the small and large droplet. As such, the total molecule count is roughly 7 times the amount of the small droplet simulated before.

For this larger droplet the same frontal SID collisions were repeated. Since the droplet is much larger in diameter, the aluminum wall is increased in size in y - and z -dimension accordingly. The total number of atom layers is the same as before.

A cluster analysis was carried out for frontal collisions of the large droplet at varying acceleration voltages, with the average ejected cluster count shown in Figure 7.22. Due to the significantly higher atom count, the simulation run / wall time is increased noticeably. As each simulation run now takes about 17 hours (before: 2–3 hours), only five reproduction runs are carried out and the total simulation time was reduced from 100 ps to 85 ps, which is still ample time for recombination / dissociation effects.

A comparison of the evolution of ejected clusters of the large and small droplet indicates that a significantly higher collision energy is required to cause substantial fragmentation of the large droplet. At an approximate acceleration voltage of 50 V, the droplet initiates the production of significant quantities of clusters, subsequently displaying a trend analogous to that observed in the smaller droplet. The larger droplet produces, on average, fewer clusters as compared to the small ESI droplet.

One of the reasons for the late dissociation onset of the large droplet is the vast number of internal degrees of freedom available, which dampen the energy transfer and act kind

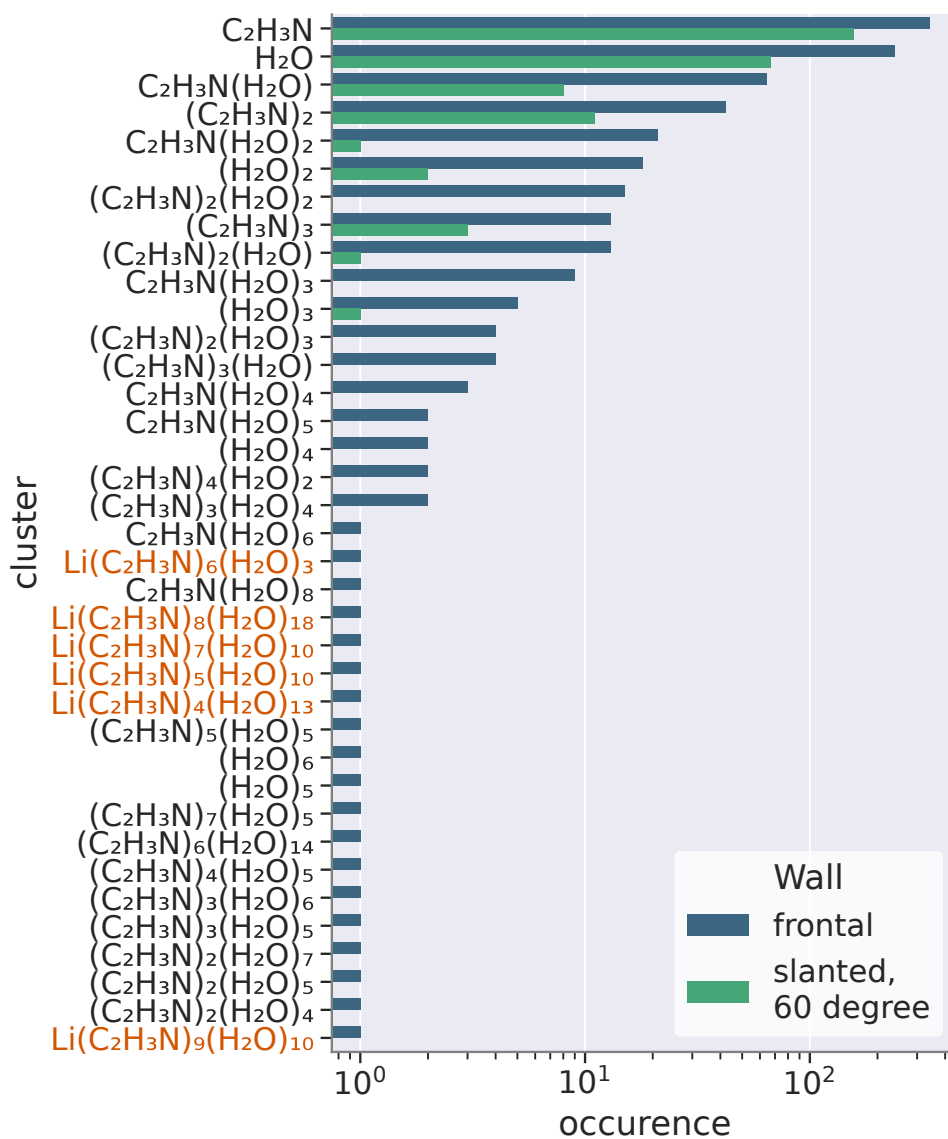


Figure 7.20: Composition and count of ejected cluster for a total of 10 frontal collision simulation runs of the small ESI droplet for 100 V starting voltage in a frontal and 60° slanted impact. The occurrence is displayed on a logarithmic axis and cluster containing charges (Li^+) are colored in orange.

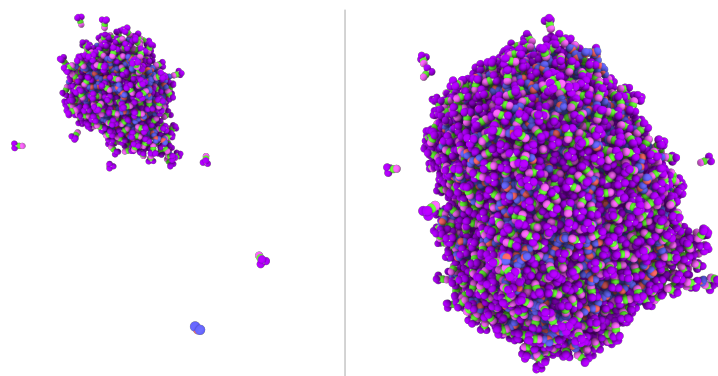


Figure 7.21: Comparison of the small and large model ESI droplet. The large droplet (right side) is about 7 times larger in terms of number of molecules in the droplet.

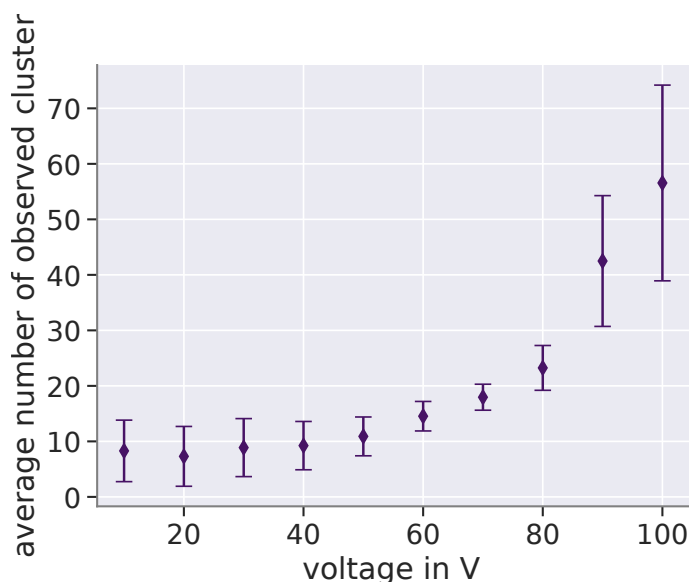


Figure 7.22: Average number of observed cluster after the frontal collision of the large droplet with the aluminum wall. The starting voltage is varied and each simulation is reproduced 5 times, with the error bars being the standard deviation of the reproductions.

of like a sponge absorbing the initial impact.

Consequently, the kinetic energy evolution as presented in Figure 7.23 shows this effect quite clearly. For 10 V acceleration voltage of the droplet, where essentially no cluster ejection takes place, the energy change is comparably slow. In total about 12 ps pass, before the droplet is completely stuck to the wall. In direct comparison, at 100 V clusters are ejected and the energy transfer takes less than 4 ps.

While this effect is quite analogous for the small and large droplet, the composition of the ejected clusters is quite different. Figure 7.24 shows the ejected cluster composition and the corresponding count for 50 and 100 V of the large droplet. Since only five reproduction runs have been carried out instead of ten, the total occurrence between small and large droplet can not be compared at this point.

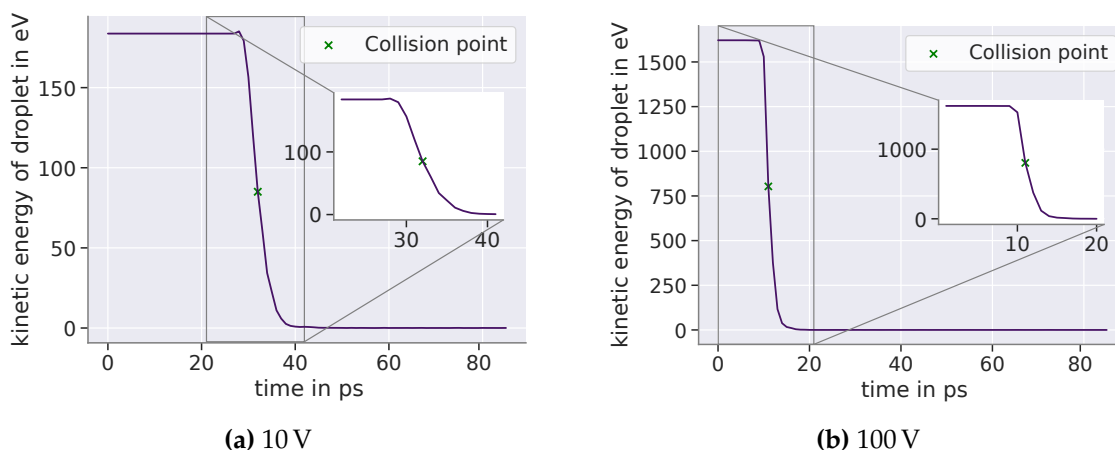


Figure 7.23: Kinetic energy evolution of the large droplet over the complete simulation in a frontal collision at varying acceleration voltages. A collision point is numerically approximated by a Gaussian kernel fitted to the time evolution.

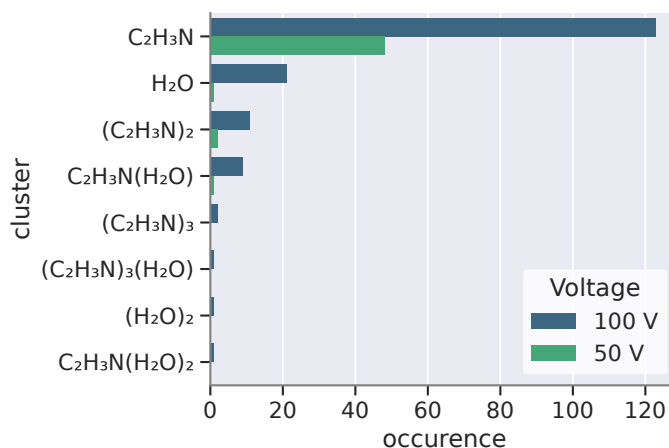


Figure 7.24: Comparison of cluster composition and count after the collision point of the large droplet at 50 and 100 V for five summed reproduction runs.

At first glance, the diversity of the cluster spectra for both voltages is much lower than for the small droplet in frontal collisions (cf. Figure 7.12). However, this can be in part a consequence of the fewer reproduction runs as those occurrences are total, summed numbers. The numbers of simulation runs was limited due to the high computational effort for the large droplet simulations.

Despite the reduced diversity, there is a noticeable change in the relative occurrence of water and acetonitrile molecules. For the small droplet the counts of liberated water and acetonitrile molecules were more in the range of 1:2, while for the large droplet this relation is around 1:6. The large droplet seems to primarily eject acetonitrile molecules while water stays in the droplet. Also, no charged cluster are ejected for any voltage for the large droplet. This might also be in part a result of the lower reproduction count as the smaller droplet also only showed single counts of different charged clusters. When directly comparing 100 V frontal collisions for the small and large droplet, both exhibit

the same order of liberated clusters (60–70 vs 80) with the small droplet ejecting 37 (19 of those occur only once) different species over all simulations while the large droplet only has 8 (3 of those occur only once) ejected cluster types over all reruns. As such, we have an effective cluster type range of 18 for the small and 5 for the large cluster. Even assuming the same amount of individual cluster types would further be liberated by an additional 5 reruns, the diversity would most likely still be notably smaller.

As such, these first estimations suggest that the cluster ejection dynamics can vary for larger droplet aggregates. In further studies, droplets should be made even larger to verify this behavior. As this size of droplet already requires significant computational resources, methods to reduce the number of simulated particles would need to be introduced. *Coarse-graining* is the process of reducing the particle count by combining several individual atoms into pseudo-atoms, which approximate specific atom groups, i.e. the two H and one O could be combined to a water pseudo-atom. These pseudo-atoms then have interaction parameters mapping the behavior of this abstract, simplified water molecule. This type of method severely reduces the total degrees of freedom in the system as structures containing multiple individual atoms can be shrunk to just one smoothed particle. Overall, this allows the computation of mesoscale MD simulations with μm sized ESI droplets, which are more inline with experimentally observed droplet sizes in MS instruments. Examples for coarse-grained force field and potentials include MARTINI [183] and DPD (Dissipative Particle Dynamics) [184].

7.6 Force field sensitivity analysis

Similar to the MD based ion-neutral collisions in IDSimF, the SID MD simulations carried out in LAMMPS are strongly dependent on the applied force field parameters.

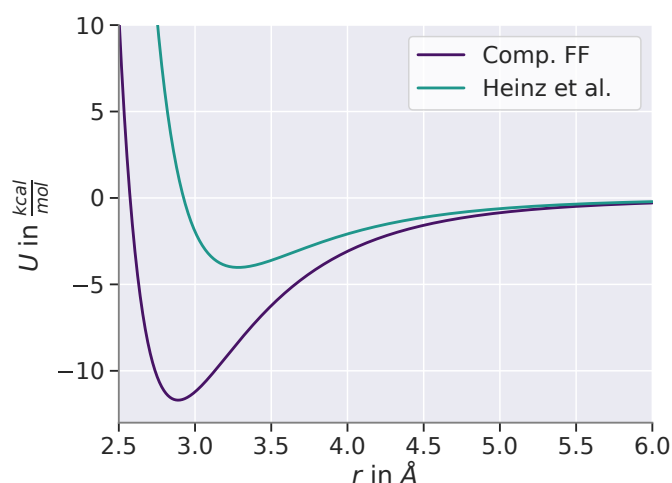
The eam/alloy aluminum parameters as well as the parameters of the OPLS-AA force field for interactions between water, acetonitrile and lithium are well tested and commonly used in research. In auxiliary simulations, the aluminum wall cohesion and correct reproduction of the fcc lattice constant was successfully reproduced.

The SID simulation primarily stems from the interaction of droplet molecules and the metal surface, as OPLS-AA does not contain parametrization for metal / organic molecular interactions by default. To estimate the sensitivity of the system to parameter changes a second Lennard-Jones parameter set for aluminum in OPLS-AA is generated and the dynamics compared to the parameter set used in all simulations presented here. The secondary / comparison force field is explicitly constructed as a high interaction potential (see Table 7.1). The exact values of the two parameters are not of any physical relevance. They are simply parameters with a stronger / deeper interaction potential well with later starting repulsion. Figure 7.25 shows the differences between the two potential functions, with the higher interaction potential immediately visible.

The frontal wall collisions of the small ESI droplet were repeated for both interaction potentials. The acceleration voltage was varied as usual, but since the overall behavior

Table 7.1: Lennard-Jones parameters of aluminum atoms used in OPLS-AA for the standard and comparison force field. Pair interactions are generated with geometric mixing rules.

Force field	σ in Å	ϵ in kcal/mol
Heinz et al. [181]	2.925	4.02
High interaction comparison	2.574	11.697

**Figure 7.25:** Comparison of the two tested potential functions for the 12-6 Lennard-Jones interaction of the aluminum atoms in OPLS-AA.

for all simulations is the same for all voltages only the 100 V simulations are shown and compared here.

A temporal evolution of the ejected cluster count is given in Figure 7.26. The collision event with the wall takes place at around 12 ps. Up until that collision point, the evolution is almost identical with slight changes only due to different random seeds. At the collision point, the number of ejected clusters rises drastically and immediately in both cases. After the impact, the high interaction potential naturally leads to more ejected clusters (about 120) compared to the actually employed potential in the productive simulations (about 80). The general trend, however, is quite similar with a slight loss of clusters over time noticeable for the high interaction potential while the other potential being stable around 80 counts. This effect might be due to higher likelihood of recombination events (reducing the cluster count) since more clusters are present in the simulation box. Lastly, the cluster composition and the occurrence of each cluster is compared in Figure 7.27. At first glance, the cluster spectra look alike with some variations in the clusters with single occurrence, where some larger clusters are found for the high interaction potential. A more interesting observation is the swap in the acetonitrile and water cluster ratio: for the high interaction potential more water clusters are liberated while the potential by Heinz et al. leads to a higher ejection of acetonitrile compared to water. The high interaction potential also is

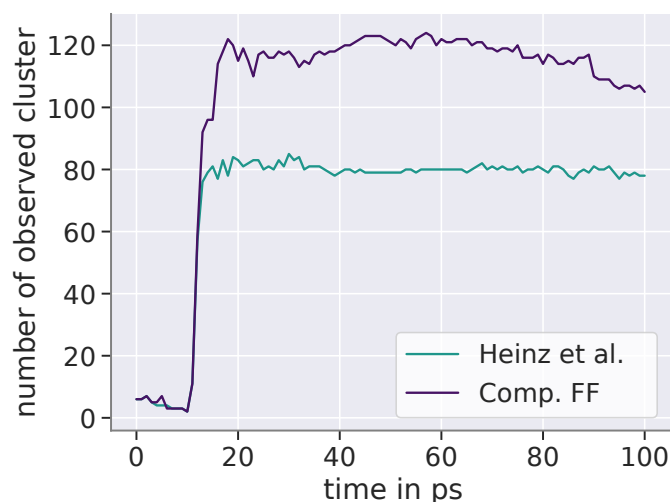


Figure 7.26: Comparison of the temporal ejected cluster evolution for both potential functions at 100 V starting voltage using the small ESI droplet model.

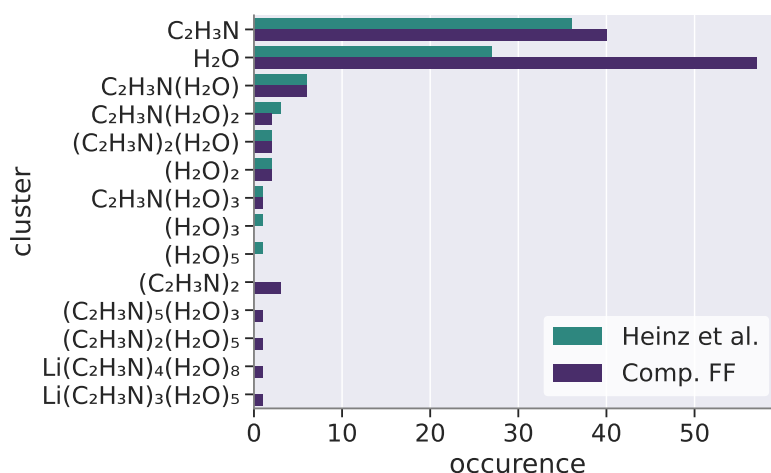


Figure 7.27: Cluster composition and occurrence comparison for the high interaction potential and standard potential by Heinz et al. at 100 V acceleration voltage for the small ESI droplet model. The cluster composition is captured directly after the collision point at 25 ps. Only one simulation was done for each potential.

able to liberate charged clusters, while the standard potential used here has no charged clusters ejected. Since only one collision is done for each parameter set, both described changes could be an effect of statistical noise.

Overall, the potential parameter set can change the amount and type of ejected clusters strongly as expected.

7.7 SID model for SIMION

The exact circumstances under which surface collisions might take place in an instrument are unclear and cannot be obtained by MD simulations alone. The long term goal of the study of ESI droplet collisions is to fully map the flight path and dynamics from ion source to detector.

As a supplementary step to reach this final objective, a SID model is implemented into the ion trajectory simulation program SIMION. The aim of this model is to enable SID simulations of droplet aggregates in larger elements of an MS instruments, e.g. transfer multipoles or collisions cells, and to study the combination of SID and CID effects.

Danell et al. [185] presented a modeling approach for SID processes in SIMION, which is used in the following as the basic groundwork to implement a standalone module for SID simulation in SIMION. The idea is to model the surface-induced dissociation event as a simple reflection from the impact surface, meaning the reflection angle r of the parent particle is equal to the incident angle i of the product particle. Two different energy terms can be identified: i) the total kinetic energy and ii) the impact energy. The total kinetic energy T_{parent} is the energy along the parent particle's direction of movement. An impact energy T_{impact} can then be defined as the energy in the direction perpendicular to the impact surface (collision surface normal). A schematic sketch is shown in Figure 7.28.

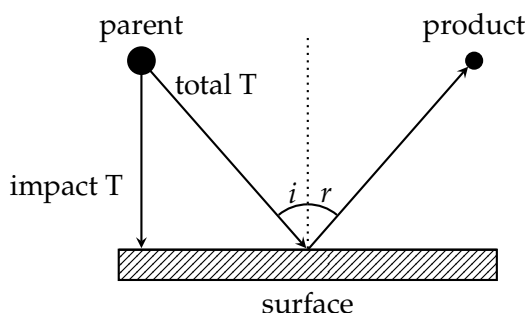


Figure 7.28: SID modeling approach via reflective collisions. Reproduced from [185].

The reflection angle is further randomized by $\pm 20^\circ$, since regular surfaces do not lead to perfect specular reflections. The parent particle is converted due to the surface collision to a product particle with reduced masses by one of the randomly chosen fractions $\{1/4, 1/2, 3/4\}$. Further tracking of the "original" parent particle is dropped, i.e. the surface collision transforms the one parent particle to a sole product particle. Analogously to the mass change, the product particle total kinetic energy is reduced by the same fraction x and additionally modified by the internal energy conversion efficiency [185]. The studies in [117] and [118] have observed conversion rates between 10 % to 20 %, thus in agreement with [185] a conversion factor c of 15 % is chosen.

As a result, the total kinetic energy of the product ion is given by [185]

$$T_{\text{product}} = x(1 - c)T_{\text{parent}} \quad . \quad (7.3)$$

The new kinetic energy of the product ion as well as its mass is then used to compute an updated velocity along the slightly randomized, reflected angle r . This basic idea is implemented into a user program written in Lua to be used in SIMION simulations. The user program sequence is as follows:

1. The impact surface normal $\mathbf{n}$ is computed, with the normal direction opposite to the impact velocity vector $\mathbf{v}$. As SIMION does not "know" how any of the electrode points are orientated in space, the electric field is used as a workaround. The ideal electric field lines very close to a electrode surface are parallel to that surface, as such the voltage gradient $\mathbf{e}$ at the impact point can be used as an approximate proxy for the the surface normal. To ensure that the normal is definitely oriented in the opposite direction of the impact vector, the dot product between $\mathbf{v}$ and $\mathbf{e}$ is calculated. If it is > 0 , the sign of $\mathbf{e}$ is switched. Afterwards, $\mathbf{e}$ is normalized to obtain $\mathbf{n}$.

2. The reflection vector $\mathbf{r}$ can then be calculated. The dot product between $\mathbf{n}$ and $\mathbf{v}$ is employed to obtain $\mathbf{r}$ by

$$\mathbf{r} = \mathbf{v} - 2 \cdot \langle \mathbf{v}, \mathbf{n} \rangle \cdot \mathbf{n} \quad , \quad (7.4)$$

which needs to be normalized thereafter. It is then randomly modified by up to $\pm 20^\circ$.

3. In a final step the product / child particle is generated in SIMION. One of three possible fragment sizes is chosen and the mass and the kinetic energy is changed accordingly (ref. Equation 7.3). As the SID model is supposed to be compatible with a HS CID model, the collision cross section also needs to be changed in accordance with the mass loss. Valid actual parameter values have to be found in further studies, but as a first approximation the parent CCS is multiplied by $\{0.7, 0.8, 0.9\}$ (matching the fractions x in that order) to generate the product CCS. The velocity vector after the impact is computed by multiplying the new velocity magnitude by the normalized reflection vector r .
4. This process is repeated for further possible surface impacts. However, if the child particle mass would end below 40 amu, the child particle creation is omitted and the particle is instead terminated. In a first instance this is a stopping mechanism for infinite dissociation processes that would eventually lead to a particle mass of zero.

A plate capacitor electrode system was modeled in SIMION and used as an initial test bench to verify the correct behavior of the modeling approach. Individual impacts were reviewed by hand and matched with the expected behavior.

Additionally, a more complex system was then used to use both CID and SID models simultaneously. For this, a bent collision cell, used in other works already, was extended by this SID model. The main components of the collision cell model are:

- An acceleration stage: The particles are started in front of an electrode with a counter electrode on a user-defined acceleration voltage.

- A linear quadrupole: A short transfer region. This quadrupole has the same applied parameters as the actual collision cell bent quadrupole.
- The bent quadrupole: A RF-only bent quadrupole with 33 V peak-to-peak amplitude and either 940 kHz or 1.23 MHz RF frequency.
- An end plate: This electrode normally would include a pinhole as connection to the next region of an instrument, but is used as a plate for particle termination here.

Simulations were then carried out for 200 ions of an m/z of 4166, which represents a small model ESI droplet. The CID process takes place with 7 mTorr background gas pressure. The acceleration voltage as well as the RF frequency was varied in multiple simulation runs. For each parameter variation, one simulation is carried out with SID and one without SID, where SID events are marked by a red dot and product particles are shown as green trajectories. Figure 7.29 visualizes such trajectories for 940 kHz RF frequency of the bent quadrupole. The first row shows trajectories for an acceleration voltage of 50 V with SID turned off (left) and turned on (right). At 50 V there is not any noticeable difference between the simulation runs, as the large particles are too fast to be influenced by the quadrupole field much. The outer walls of the collision cell are omitted in the simulation. This simplification is most likely not a significant limitation of the model, since particles generated at the outer walls by SID events cannot enter the inner region of the quadrupole due to the field geometry. In the case of an acceleration voltage of 5 V, as seen in the second row of Figure 7.29, the ions are slow enough such that the quadrupole can actually have an effect on the trajectory. With the sole consideration of CID events, only two ions reach the end plate and would not be able to hit an appropriate transfer orifice there. With SID turned on, a noticeable amount of product ions are able to actually pass through the collision cell, since the generated product ions can be focused by the quadrupole again. Due to the surface dissociation events and subsequent reflection many ions are able to get pulled back into the actual quadrupole field and end up in slightly more stable trajectories. Still, most of the ions are lost inside the quadrupole.

The same simulations were repeated for 1.23 MHz RF frequency and are presented in Figure 7.30. The change in RF frequency leads to a very similar behavior as with the low RF frequency. There is a marginal focusing to the center of the quadrupole observable for the product ions produced in Figure 7.30d also, as the smaller weight ions are simply more affected by the faster changing quadrupole field in that case.

Overall, it is clear that the SID process itself could potentially allow for more ions to pass through complex elements of a mass spectrometric device. However, more in depth analysis and simulations have to be carried out encompassing multiple different geometries / instruments as well as parameter variations in those systems. Combining an SID and CID hybrid approach in SIMION can allow to get a better understanding of possible fragmentation pathways, which in turn could feed back information to the MD simulation side of the ESI study.

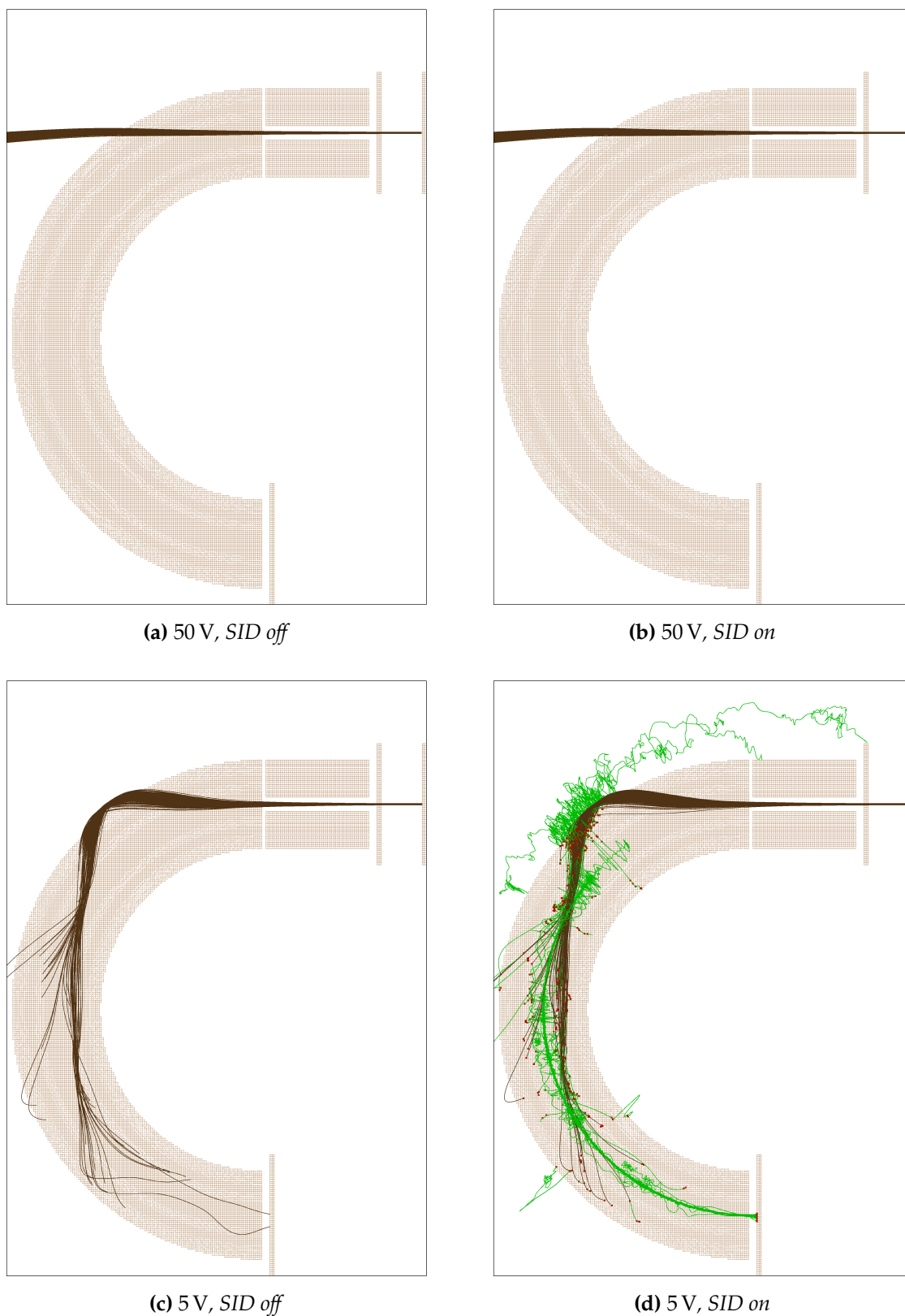


Figure 7.29: Comparison of ion trajectories in an exemplary collision cell at 940 kHz RF frequency with varied acceleration voltages. Product ion trajectories are shown in green. Red dots mark SID events, while CID events are not explicitly marked. The background gas pressure is 7 mTorr.

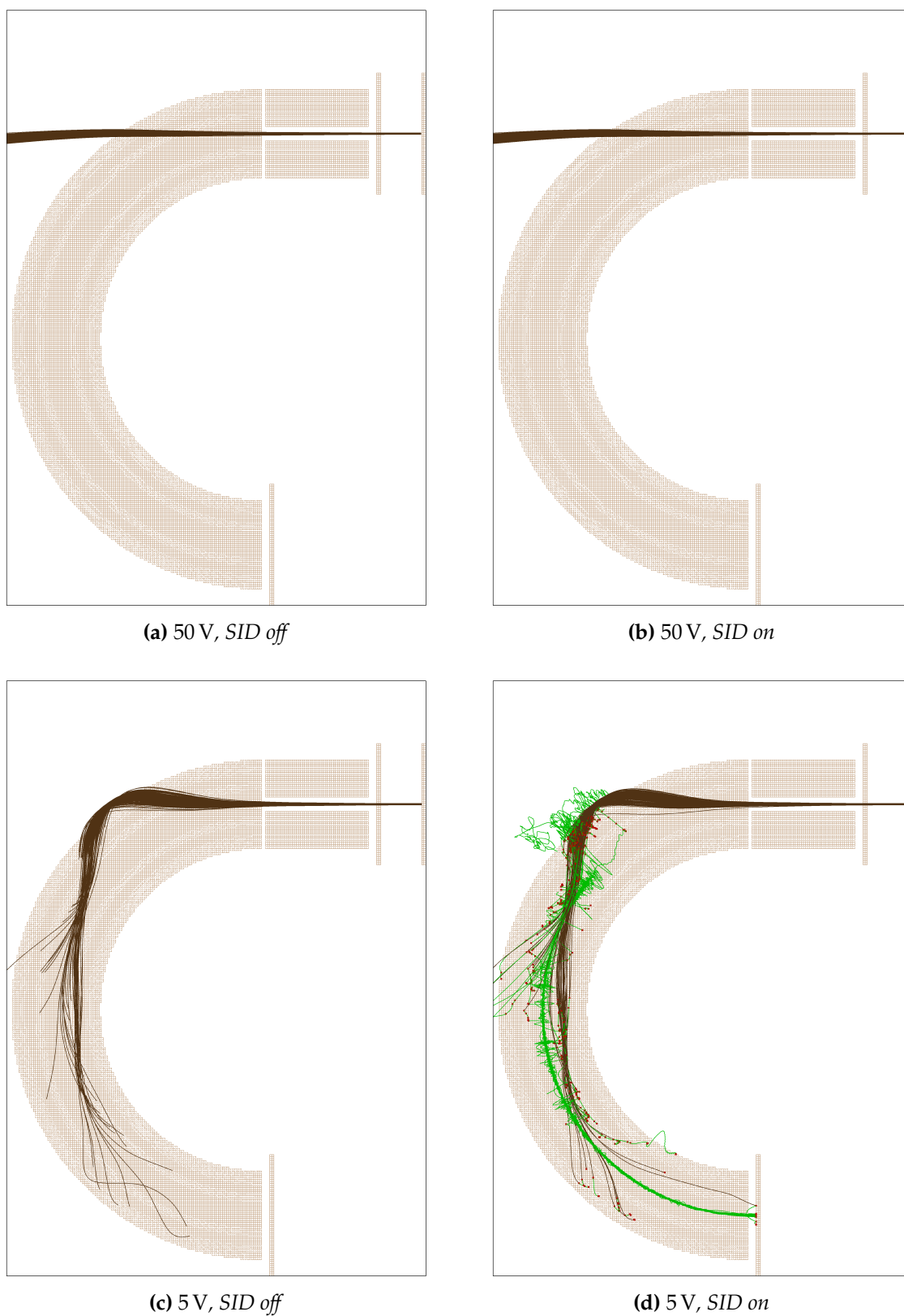


Figure 7.30: Comparison of ion trajectories in an exemplary collision cell at 1.23 MHz RF frequency with varied acceleration voltages. Product ion trajectories are shown in green. Red dots mark SID events, while CID events are not explicitly marked. The background gas pressure is 7 mTorr.

CONCLUSION AND OUTLOOK

There is a long term effort made to simulate a complete traversal of an ESI droplet from ion source up to the detector. This is a multi-scale problem on the time and spatial domain. Droplet / ion dynamics take place on multiple timescales (effect of the electric fields, ion-neutral collisions, ion-surface collisions) and instrument sizes are too large to be modeled with classical MD approaches alone.

In this work, two initially different topics, i.e. ion-neutral collision modeling in IMS and modeling of SID dynamics, were studied. However, the common ground of both studies is in enabling certain parts of the droplet flight path to be modeled across different simulation frameworks.

Thereby, one of the overarching goals of this work was to implement, refine and compare multiple collision modeling methods to simulate ion dynamics under complex ion-neutral interactions for smaller particle sizes. A focus was set on areas of the mass spectrometer where intensive ion-background gas interaction takes place (drift tube, collision cells, high pressure transfer stages). Typically, those areas cannot be simulated by classical MD approaches as surrounding parts like electrode surfaces or employed time-dependent electric fields cannot be simulated efficiently as MD time steps are too small.

The classical MD approach was thus combined with ion trajectory simulations in IDSimF to construct a more refined and accurate way to simulate complex ion-neutral interactions. The first steps in developing the MD based collision modeling method involved determining how collision dynamics change compared to a pure hard-sphere approach. Additionally, the dependence of the method on various input parameters like pressure, temperature and collision radius scaling was studied through DT-IMS simulations as a benchmark system.

The DT-IMS simulations were also used to establish the accuracy of the method by comparing simulated ion mobilities with experimental mobilities from literature, where for monoatomic background gases a very good agreement is found. However, mass spectrometric devices are commonly using other background gases, particularly molecular nitrogen. As such, molecular nitrogen was implemented for the MD collision model, which complicated the force field calculation drastically. Trajectories calculated by MobCal-MPI

were used as references to compare the IDSimF trajectories to, with the results being quite similar. Most of the differences are assumed to be related to the different numerical integration method used.

Actual ion mobilities computed for molecular nitrogen systems, however, returned mixed results, often with larger discrepancies than found for monoatomic background gases. Furthermore, rigid body rotations were implemented in an effort to increase the accuracy of the force field calculation, especially for the treatment of the ion-quadrupole potential. Proof-of-concept simulations were carried out, with the rotations working correctly in first instance. As a side effect of the rotations, the ion-neutral clustering, often also observed with non-rotating systems when N_2 is used, is immensely amplified. This currently leads to a decreased correctness of the ion mobility simulations, as clustering collisions are not energy conserving and discarded in the current implementation of the simulation method. Since specific ion-neutral collisions are discarded, especially those that would lead to decreased ion velocities after the collision, the ion mobilities obtained are too high in the present state of the MD model.

Moreover, a variable hard-sphere collision model with internal energy tracking was implemented. This model overall works as intended and lays a good foundation for implementation of internal energy tracking for MD based collision simulation. Mobilities obtained by VHS are generally worse than those computed by the MD approach, however much faster to calculate.

The second study surrounded the MD simulation of ESI droplets in surface collision events in vacuum. LAMMPS was employed for this and a model system was built combining two model droplets, altered in size, and an idealized aluminum wall. Droplets were then fired at this wall in different configurations with varied input parameters. The main results here include: i) most of the ejected clusters only consist of acetonitrile or water, ii) charged clusters are rarely ejected with high energies required, iii) slanted walls lead to less ejected clusters due to changes in energy transfer dynamics and iv) larger droplets dampen the collisions heavily leading to reduced cluster counts.

There was also a small SID model implemented in SIMION as a proof-of-concept, allowing for ion trajectory simulations to be combined with a simplified surface dissociation approach. Initial simulations showed the model to be working and having an impact in simplified collision cell simulations combining CID and SID.

Further effort has to be made in a few areas across both topics to gain a better understanding of the underlying droplet / ion dynamics. The main improvement for the MD collision model should focus on a good handling of the clustering interactions. The basic idea there could be to combine the MD model with the RS module to allow actual clustering to take place. For this, collisions would need to be parametrized such that it can be efficiently decided if a collision is an actual clustering reaction. The molecular structure can then be changed in a subsequent step to reflect the cluster formation across following collisions. Additionally, more detailed force field parameter fitting should be

carried out. Also, the VHS model should be extended to the VSS model and the tracking of internal energy should be transferred to the MD model. For the SID studies a multitude of additional system variations could be carried out. As a first step, the small ESI droplet could be simulated in a system with modified wall conditions, i.e. uneven / rough surfaces, surfaces with water layers as well as oxidized aluminum walls since the highly idealized surfaces used here are not found in actual instruments. Additionally, the charge distribution inside the droplet should be changed to resemble more accurate conditions by including negative charges as well instead of only the positive charge surplus. Actual analyte molecules could then also be introduced in a secondary step.

Another crucial step is an additional size increase of the model ESI droplet to ranges up to micrometer scales. This requires the transition from an all-atom MD to a coarse-grained model to keep the numerical effort in ranges possible with the available compute resources. All in all, this work serves as a good foundation for more sophisticated and detailed studies as well as method development in both simulation domains (ion trajectory simulation and classical MD simulations) in the hopes of forming a more complete image of droplet dynamics present in electrospray ionization mass spectrometry.

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FORCE FIELD PARAMETERS

Table A.1: Force field parameters used in Fig. 6.13

species	atom	x	y	z	mass	charge	part. charge	σ	ϵ
O2+	O	0	0.561	0	15.999	1	0	2.3	0.12
O2+	O	0	-0.561	0	15.999	0	0	2.3	0.12
Ar	Ar	0	0	0	39.948	0	0	3.401	0.9777

Table A.2: Force field parameters used in Fig. 6.14

species	atom	x	y	z	mass	charge	part. charge	σ	ϵ
O2+	O	0	0.561	0	15.999	1	0	2.3	0.12
O2+	O	0	-0.561	0	15.999	0	0	2.3	0.12
Ar	Ar	0	0	0	39.948	0	0	3.401	0.9777

Table A.3: Force field parameters used in Fig. 6.15

species	atom	x	y	z	mass	charge	part. charge	σ	ϵ
O2+	O	0	0.561	0	15.999	1	0	2.3	0.12
O2+	O	0	-0.561	0	15.999	0	0	2.3	0.12
He	He	0	0	0	4.003	0	0	2.556	0.0836

Table A.4: Force field parameters used in Fig. 6.16

species	atom	x	y	z	mass	charge	part. charge	σ	ϵ
O2+	O	0	0.561	0	15.999	1	0	2.3	0.12
O2+	O	0	-0.561	0	15.999	0	0	2.3	0.12
He	He	0	0	0	4.003	0	0	2.556	0.0836

APPENDIX A. FORCE FIELD PARAMETERS

Table A.5: Force field parameters used in Fig. 6.17

species	atom	x	y	z	mass	charge	part. charge	σ	ϵ
O2+	O	0	0.561	0	15.999	1	0	2.3	0.12
O2+	O	0	-0.561	0	15.999	0	0	2.3	0.12
He	He	0	0	0	4.003	0	0	2.556	0.0836

Table A.6: Force field parameters used in Fig. 6.18

species	atom	x	y	z	mass	charge	part. charge	σ	ϵ
O2+	O	0	0.561	0	15.999	1	0	2.3	0.12
O2+	O	0	-0.561	0	15.999	0	0	2.3	0.12
Ar	Ar	0	0	0	39.948	0	0	3.401	0.9777

Table A.7: Force field parameters used in Fig. 6.19

species	atom	x	y	z	mass	charge	part. charge	σ	ϵ
O2+	O	0	0.561	0	15.999	1	0	2.3	0.12
O2+	O	0	-0.561	0	15.999	0	0	2.3	0.12
He	He	0	0	0	4.003	0	0	2.556	0.0836

Table A.8: Force field parameters used in Fig. 6.25

species	atom	x	y	z	mass	charge	part. charge	σ	ϵ
CO+	C	0.56	0	0	12	0.732451	0	3.93	0.2895328
CO+	O	-0.56	0	0	15.995	0.267549	0	3.55	0.319
He	He	0	0	0	4.003	0	0	2.96	0.091

Table A.9: Force field parameters used in Fig. 6.28

species	atom	x	y	z	mass	charge	part. charge	σ	ϵ
O2+	O	0	0.561	0	15.999	1	0	2.3	0.12
O2+	O	0	-0.561	0	15.999	0	0	2.3	0.12
Li+	Li	0	0	0	6.941	1	0	2.12	0.0764
Ar+	Ar	0	0	0	39.948	1	0	3.401	0.977
Cl-	Cl	0	0	0	35.453	-1	0	4.02	3.06

Table A.10: Force field parameters used in Fig. 6.29

species	atom	x	y	z	mass	charge	part. charge	σ	ε
O2+	O	0	0.561	0	15.999	0.5	0	2.3	0.12
O2+	O	0	-0.561	0	15.999	0.5	0	2.3	0.12
Li+	Li	0	0	0	6.941	1	0	2.12	0.0764
Ar+	Ar	0	0	0	39.948	1	0	3.401	0.977
Cl-	Cl	0	0	0	35.453	-1	0	4.02	3.06

Table A.11: Force field parameters used in Fig. 6.31

species	atom	x	y	z	mass	charge	part. charge	σ	ε
Ar+	Ar	0	0	0	39.948	1	0	3.401	0.977
Ar	Ar	0	0	0	39.948	0	0	3.401	0.9777

Table A.13: Force field parameters used in Fig. 6.47

species	atom	x	y	z	mass	charge	part. charge	σ	ε
Li+	Li	0	0	0	6.941	1	0	2.12	0.0764
N2	N	0.54	0	0	14.0067	0	-0.4825	3.65	1.207
N2	N	-0.54	0	0	14.0067	0	-0.4825	3.65	1.207
N2	COM	0	0	0	0	0	0.965	0	0

Table A.14: Force field parameters used in Fig. 6.48

species	atom	x	y	z	mass	charge	part. charge	σ	ε
Li+	Li	0	0	0	6.941	1	0	2.12	0.0764
N2_noquad	N	0	0.54	0	14.0067	0	0	3.65	1.207
N2_noquad	N	0	-0.54	0	14.0067	0	0	3.65	1.207

Table A.15: Force field parameters used in Fig. 6.49

species	atom	x	y	z	mass	charge	part. charge	σ	ε
Li+	Li	0	0	0	6.941	1	0	2.12	0.0764
N2	N	0.54	0	0	14.0067	0	-0.4825	3.65	1.207
N2	N	-0.54	0	0	14.0067	0	-0.4825	3.65	1.207
N2	COM	0	0	0	0	0	0.965	0	0

Table A.12: Force field parameters used in Fig. 6.33

species	atom	x	y	z	mass	charge	part. charge	σ	ϵ
CH ₂ OCH ₂ +R	O	-0.061610937	0.39613938	-0.014989051	15.995	0.444643	0	3.55	0.319
CH ₂ OCH ₂ +R	H	1.9009769	0.7762199	0.22328043	1.008	0.15098	0	2.97	0.0904
CH ₂ OCH ₂ +R	C	1.1650786	-0.014547817	0.14149348	12	-0.014682	0	3.94	0.28
CH ₂ OCH ₂ +R	C	-1.1040983	-0.3775708	-0.12674612	12	-0.014649	0	3.94	0.28
CH ₂ OCH ₂ +R	H	-2.0444489	0.14453523	-0.2559158	1.008	0.15099	0	2.97	0.0904
CH ₂ OCH ₂ +R	H	1.375245	-1.0811828	0.18009982	1.008	0.141365	0	2.97	0.0904
CH ₂ OCH ₂ +R	H	-0.9800849	-1.4574554	-0.08518141	1.008	0.141353	0	2.97	0.0904
He	He	0	0	0	4.003	0	0	2.556	0.0836

Table A.16: Force field parameters used in Fig. 6.51

species	atom	x	y	z	mass	charge	part. charge	σ	ϵ
Li+	Li	0	0	0	6.941	1	0	2.12	0.0764
N2	N	0.54	0	0	14.0067	0	-0.4825	3.65	1.207
N2	N	-0.54	0	0	14.0067	0	-0.4825	3.65	1.207
N2	COM	0	0	0	0	0	0.965	0	0

Table A.17: Force field parameters used in Fig. 6.52

species	atom	x	y	z	mass	charge	part. charge	σ	ϵ
Na+	Na	0	0	0	22.99	1	0	3.18	0.29
N2	N	0.54	0	0	14.0067	0	-0.4825	3.65	1.207
N2	N	-0.54	0	0	14.0067	0	-0.4825	3.65	1.207
N2	COM	0	0	0	0	0	0.965	0	0

Table A.18: Force field parameters used in Fig. 6.54

species	atom	x	y	z	mass	charge	part. charge	σ	ϵ
Cl-	Cl	0	0	0	35.453	-1	0	4.5	1.5
N2	N	0.54	0	0	14.0067	0	-0.4825	3.65	1.207
N2	N	-0.54	0	0	14.0067	0	-0.4825	3.65	1.207
N2	COM	0	0	0	0	0	0.965	0	0

Table A.20: Force field parameters used in Fig. 6.59

species	atom	x	y	z	mass	charge	part. charge	σ	ϵ
O2+	O	0	0.561	0	15.999	0.5	0	2.3	0.12
O2+	O	0	-0.561	0	15.999	0.5	0	2.3	0.12
He	He	0	0	0	4.003	0	0	2.556	0.0836

Table A.21: Force field parameters used in Fig. 6.60

species	atom	x	y	z	mass	charge	part. charge	σ	ϵ
Li+	Li	0	0	0	6.941	1	0	2.12	0.0764
N2	N	0.54	0	0	14.0067	0	-0.4825	3.65	1.207
N2	N	-0.54	0	0	14.0067	0	-0.4825	3.65	1.207
N2	COM	0	0	0	0	0	0.965	0	0

Table A.19: Force field parameters used in Fig. 6.55

species	atom	x	y	z	mass	charge	part. charge	σ	ϵ
Acetone	C	-1.3483	0.5196	0.0017	12.011	-0.457492	0	3.93	0.2895328
Acetone	C	-0.0052	-0.0663	0.0056	12.011	0.624504	0	3.93	0.2895328
Acetone	H	-2.1237	-0.2386	0.0458	1.007	0.214081	0	2.97	0.0904
Acetone	H	-1.4362	1.2198	0.8362	1.007	0.200223	0	2.97	0.0904
Acetone	H	-1.4561	1.1224	-0.906	1.007	0.201423	0	2.97	0.0904
Acetone	H	1.2121	1.3632	-0.9096	1.007	0.235091	0	2.97	0.0904
Acetone	C	1.2121	0.7566	0.0015	12.011	-0.573511	0	3.93	0.2895328
Acetone	H	1.1659	1.4643	0.8326	1.007	0.23752	0	2.97	0.0904
Acetone	H	2.13	0.1749	0.0549	1.007	0.208219	0	2.97	0.0904
Acetone	O	0.0508	-1.3336	-0.0003	15.999	-0.347201	0	3.56	0.319
Acetone	H	0.9503	-1.696	-0.0034	1.007	0.457144	0	2.97	0.0904
N2	N	0.54	0	0	14.0067	0	-0.4825	1.5	2.711
N2	N	-0.54	0	0	14.0067	0	-0.4825	1.5	2.711
N2	COM	0	0	0	0	0	0.965	0	0

Table A.22: Force field parameters used in Fig. 6.64

species	atom	x	y	z	mass	charge	part. charge	σ	ϵ
Li+	Li	0	0	0	6.941	1	0	2.12	0.0764
N2	N	0.54	0	0	14.0067	0	-0.4825	3.65	1.207
N2	N	-0.54	0	0	14.0067	0	-0.4825	3.65	1.207
N2	COM	0	0	0	0	0	0.965	0	0

Table A.23: Force field parameters used in Fig. 6.65

species	atom	x	y	z	mass	charge	part. charge	σ	ϵ
O2+	O	0	0.561	0	15.999	0.5	0	2.3	0.12
O2+	O	0	-0.561	0	15.999	0.5	0	2.3	0.12
Ar	Ar	0	0	0	39.948	0	0	3.401	0.9777
He	He	0	0	0	4.003	0	0	2.556	0.0836

Table A.24: OPLS-AA force field parameters. Pair interactions are generated with geometric mixing rules.

Atom	σ in Å	ϵ in kcal/mol	partial charge in e
O (Water TIP3P)	3.15061	0.1521	-0.834
H (Water TIP3P)	0.0	0.0	0.417
Li	2.87	0.0005	1.0
N (acetonitrile)	3.2	0.17	-0.56
C ₁ (acetonitrile)	3.3	0.066	0.46
C ₂ (acetonitrile)	3.3	0.066	-0.08
H (acetonitrile)	2.5	0.015	0.06
Al	2.925	4.02	0

MATHEMATICAL DERIVATIONS AND FORMULAS

B.1 Parameter conversion between 12-6 Lennard-Jones and mod. Buckingham

$$\begin{aligned}\sigma &= A \cdot \alpha^{0.25} \\ \varepsilon &= 90.58 \cdot G^2 \cdot \frac{N^{0.5}}{A^6}\end{aligned}\tag{B.1}$$

B.2 High field mobilities from 2TT

High field mobilities are generated by choosing a bath gas temperature T and a range of higher temperatures, which will be the effective ion temperatures T_{eff} . This method will then also output the corresponding electric field strengths. Essentially, the lowest temperature T will be used to calculate the zero-field mobility and the higher temperatures allow to approximate a "heated" ion if the mobility is corrected by T_{eff} . This results in the following workflow:

1. Compute the zero-field and higher temperature ion mobility values K_{eff}
2. For each simulation of the effective ion temperatures
 - a) Correct the ion mobility by the neutral gas density with $K = K_{\text{eff}} \cdot \frac{T}{T_{\text{eff}}}$
 - b) Calculate the reduced ion mobility $K_0 = \frac{p}{101325 \text{ Pa}} \frac{273.15 \text{ K}}{T} \cdot K$. The pressure p can be any value here (which is consistent for all simulations)
 - c) Generate the reduced field strength with the corrected mobility and the effective temperature formula of the 2TT, that is $T_{\text{eff}} = T + \frac{mv_d^2}{3k_b}$, as

$$\frac{E}{n} = \frac{1}{K \cdot n} \cdot \left(\frac{3k_b(T_{\text{eff}} - T)}{m} \right)^{0.5}\tag{B.2}$$

with n as the ideal gas density

3. The zero-field simulation does not require correction ($T = T_{\text{eff}}$ in this case)

Using different zero-field bath gas temperatures thus result in different curves and care must be taken to choose the bath gas temperature such that it matches experimental conditions e.g. if comparisons are made.

This whole process is encapsulated inside MobCal-MPI, therefore the workflow does not need to be carried out in post-processing rather MobCal-MPI directly returns ion mobility values for varying field strengths if a temperature range is specified in the input file.

B.3 Total potential function

B.4 Force field functions

The following section gives the actual force functions implemented in IDSimF and not their general potential form. The distance r (the pair distance) is thereby split into its three dimensions r_x , r_y and r_z and is given as $r = \sqrt{r_x^2 + r_y^2 + r_z^2}$. Each force field function is only shown as the sole pair potential, but actual calculation in IDSimF requires the summation over all atoms, i.e. the total forces are given by

$$F_{\text{tot}} = \sum_{i \neq j} F_{\text{vdW}} + \sum_{i \neq j} F_{\text{ind}} + \sum_{i \neq j} F_{\text{quad}} \quad . \quad (\text{B.3})$$

B.4.1 12-6 Lennard-Jones

The 12-6 Lennard-Jones potential is

$$U_{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad . \quad (\text{B.4})$$

Taking into account only relevant variables, the form can be reduced to

$$U_{\text{LJ}}(r) = \left(\frac{1}{r} \right)^{12} - \left(\frac{1}{r} \right)^6 = \frac{1}{\sqrt{r_x^2 + r_y^2 + r_z^2}^{12}} - \frac{1}{\sqrt{r_x^2 + r_y^2 + r_z^2}^6} \quad . \quad (\text{B.5})$$

The force in x -direction is computed by taking the negative derivative:

$$\begin{aligned} -\frac{\partial U_{\text{LJ}}(r)}{\partial x} &= -6 \cdot 2r_x \cdot (r_x^2 + r_y^2 + r_z^2)^{-\frac{14}{2}} + 3 \cdot 2r_x \cdot (r_x^2 + r_y^2 + r_z^2)^{-\frac{8}{2}} \\ &= -12r_x \cdot \frac{1}{r^{14}} + 6r_x \cdot \frac{1}{r^8} \end{aligned} \quad (\text{B.6})$$

Then the parameters are reintroduced to give (i.e. the formula is multiplied by 4ϵ and σ is substituted back)

$$F_x = -24\epsilon \cdot r_x \cdot \left(2 \cdot \frac{\sigma^{12}}{r^{14}} - \frac{\sigma^6}{r^8} \right) \quad . \quad (\text{B.7})$$

The total force vector is then

$$\mathbf{F}_{\text{LJ}} = - \begin{pmatrix} \frac{\partial U_{\text{LJ}}}{\partial x} \\ \frac{\partial U_{\text{LJ}}}{\partial y} \\ \frac{\partial U_{\text{LJ}}}{\partial z} \end{pmatrix} = -24\varepsilon \cdot \frac{1}{r^8} \cdot \left(2 \cdot \frac{\sigma^{12}}{r^6} - \sigma^6 \right) \cdot \begin{pmatrix} r_x \\ r_y \\ r_z \end{pmatrix} . \quad (\text{B.8})$$

B.4.2 Mod. Buckingham

The general mod. Buckingham is defined as

$$U_{\text{MB}}(r) = \varepsilon \cdot \left[1.84 \cdot 10^5 \cdot e^{-\frac{12r}{\sigma}} - 2.25 \cdot \left(\frac{\sigma}{r} \right)^6 \right] . \quad (\text{B.9})$$

A simplified version can be constructed

$$U_{\text{MB}}(r) \propto e^{-12r} - \frac{1}{r^6} \quad (\text{B.10})$$

and then can be derived e.g. in x as

$$\frac{\partial U_{\text{MB}}}{\partial x} = -12 \cdot \frac{1}{r} \cdot r_x \cdot e^{-12r} + 6 \cdot r_x \cdot \frac{1}{r^8} . \quad (\text{B.11})$$

The exact force component in x then becomes

$$F_x = -\varepsilon \cdot \frac{1}{r} \left(-1.84 \cdot 10^5 \cdot 12 \cdot r_x \cdot e^{-\frac{12r}{\sigma}} \cdot \frac{1}{\sigma} + 2.25 \cdot 6 \cdot r_x \cdot \frac{\sigma^6}{r^7} \right) . \quad (\text{B.12})$$

Repeating the process for y and z , the complete force vector is

$$\mathbf{F}_{\text{MB}} = - \begin{pmatrix} \frac{\partial U_{\text{MB}}}{\partial x} \\ \frac{\partial U_{\text{MB}}}{\partial y} \\ \frac{\partial U_{\text{MB}}}{\partial z} \end{pmatrix} = -\varepsilon \cdot \frac{1}{r} \cdot \left(-1.84 \cdot 10^5 \cdot 12 \cdot e^{-\frac{12r}{\sigma}} \cdot \frac{1}{\sigma} + 2.25 \cdot 6 \cdot \frac{\sigma^6}{r^7} \right) \cdot \begin{pmatrix} r_x \\ r_y \\ r_z \end{pmatrix} . \quad (\text{B.13})$$

B.4.3 Ion-induced dipole

The ion-induced potential is given as

$$U_{\text{ind}}(r) = -\frac{\alpha}{8\pi\varepsilon_0} \cdot \frac{q_i^2}{r^4} \quad (\text{B.14})$$

and can be reformulated with split position components as

$$U_{\text{ind}}(r) = -\frac{\alpha}{8\pi\varepsilon_0} \left[\left(\frac{ze \cdot r_x}{\sqrt{r_x^2 + r_y^2 + r_z^2}^3} \right)^2 + \left(\frac{ze \cdot r_y}{\sqrt{r_x^2 + r_y^2 + r_z^2}^3} \right)^2 + \left(\frac{ze \cdot r_z}{\sqrt{r_x^2 + r_y^2 + r_z^2}^3} \right)^2 \right] \quad (\text{B.15})$$

since

$$\frac{1}{\sqrt{r_x^2 + r_y^2 + r_z^2}^4} = \frac{1}{(r_x^2 + r_y^2 + r_z^2)^2} = \frac{r_x^2 + r_y^2 + r_z^2}{(r_x^2 + r_y^2 + r_z^2)^3} . \quad (\text{B.16})$$

The force component in x can be derived as (all constants are dropped for simplicity first)

$$\begin{aligned} \frac{\partial U_{\text{ind}}}{\partial x} &\propto -\frac{2r_x}{(r_x^2 + r_y^2 + r_z^2)^3} + \frac{r_x^2 \cdot (-3) \cdot 2r_x}{(r_x^2 + r_y^2 + r_z^2)^4} + \frac{2r_x \cdot (-3) \cdot r_y^2}{(r_x^2 + r_y^2 + r_z^2)^4} + \frac{2r_x \cdot (-3) \cdot r_z^2}{(r_x^2 + r_y^2 + r_z^2)^4} \\ &= -\frac{2r_x}{(r_x^2 + r_y^2 + r_z^2)^3} - \frac{6r_x^3}{(r_x^2 + r_y^2 + r_z^2)^4} - \frac{6r_x r_y^2}{(r_x^2 + r_y^2 + r_z^2)^4} - \frac{6r_x r_z^2}{(r_x^2 + r_y^2 + r_z^2)^4} \end{aligned} \quad (\text{B.17})$$

Reintroducing the constants the following formula is obtained:

$$\frac{\partial U_{\text{ind}}}{\partial x} = -\frac{\alpha z^2 e^2}{4\pi\epsilon_0} \left[\frac{r_x}{(r_x^2 + r_y^2 + r_z^2)^3} - \frac{3r_x^3}{(r_x^2 + r_y^2 + r_z^2)^4} - \frac{3r_x r_y^2}{(r_x^2 + r_y^2 + r_z^2)^4} - \frac{3r_x r_z^2}{(r_x^2 + r_y^2 + r_z^2)^4} \right] \quad (\text{B.18})$$

Analogous to the x -derivative, the y - and z -derivative can be obtained for the complete potential gradient:

$$\mathbf{F}_{\text{ind}} = -\begin{pmatrix} \frac{\partial U_{\text{ind}}}{\partial x} \\ \frac{\partial U_{\text{ind}}}{\partial y} \\ \frac{\partial U_{\text{ind}}}{\partial z} \end{pmatrix} = \frac{\alpha z^2 e^2}{4\pi\epsilon_0} \cdot \begin{pmatrix} \frac{r_x}{(r_x^2 + r_y^2 + r_z^2)^3} - \frac{3r_x^3}{(r_x^2 + r_y^2 + r_z^2)^4} - \frac{3r_x r_y^2}{(r_x^2 + r_y^2 + r_z^2)^4} - \frac{3r_x r_z^2}{(r_x^2 + r_y^2 + r_z^2)^4} \\ \frac{r_y}{(r_x^2 + r_y^2 + r_z^2)^3} - \frac{3r_y^3}{(r_x^2 + r_y^2 + r_z^2)^4} - \frac{3r_y r_x^2}{(r_x^2 + r_y^2 + r_z^2)^4} - \frac{3r_y r_z^2}{(r_x^2 + r_y^2 + r_z^2)^4} \\ \frac{r_z}{(r_x^2 + r_y^2 + r_z^2)^3} - \frac{3r_z^3}{(r_x^2 + r_y^2 + r_z^2)^4} - \frac{3r_z r_x^2}{(r_x^2 + r_y^2 + r_z^2)^4} - \frac{3r_z r_y^2}{(r_x^2 + r_y^2 + r_z^2)^4} \end{pmatrix} \quad (\text{B.19})$$

B.4.4 Quadrupole-ion

The quadrupole-ion potential is described by

$$U_{\text{quad}}(r) = \frac{1}{4\pi\epsilon_0} \sum_{j=1}^3 \frac{q_i q_j}{r} \quad , \quad (\text{B.20})$$

where q_i and q_j are the charges of the atom of the ion and an atom of nitrogen respectively. The derivative in x without constants is

$$\frac{\partial U_{\text{quad}}(r)}{\partial x} = -0.5 \sum_{j=1}^3 q_i q_j \cdot (r_x^2 + r_y^2 + r_z^2)^{-3/2} \cdot 2r_x = -\sum_{j=1}^3 q_i q_j \cdot \frac{r_x}{r^3} \quad . \quad (\text{B.21})$$

The total force then is

$$\mathbf{F}_{\text{quad}} = -\begin{pmatrix} \frac{\partial U_{\text{quad}}}{\partial x} \\ \frac{\partial U_{\text{quad}}}{\partial y} \\ \frac{\partial U_{\text{quad}}}{\partial z} \end{pmatrix} = \frac{1}{4\pi\epsilon_0} \cdot \begin{pmatrix} \sum_{j=1}^3 q_i q_j \frac{r_x}{r^3} \\ \sum_{j=1}^3 q_i q_j \frac{r_y}{r^3} \\ \sum_{j=1}^3 q_i q_j \frac{r_z}{r^3} \end{pmatrix} \quad , \quad (\text{B.22})$$

where r is also dependent on i and j as it is the pair distance between each atom pair.

B.5 Borgnakke-Larsen energy transfer function

An acceptance-rejection algorithm is used to sample the energy transfer fraction $\frac{\epsilon_{\text{tr}}}{\epsilon_c}$ from its probability distribution, where ϵ_{tr} is the translational energy and ϵ_c the collision energy.

The joint probability distribution function in Equation 3.23 can be reduced (the exponential function is constant as T is dependent on $\epsilon_c = \epsilon_{tr} + \epsilon_i$) to

$$P = c \cdot \epsilon_{tr}^{3/2-\omega} (\epsilon_c - \epsilon_{tr})^{\bar{\zeta}-1} , \quad (B.23)$$

with $\bar{\zeta} = 0.5 \cdot (\zeta_1 + \zeta_2)$ as the average degrees of freedom over two modes.

This probability function has its maximum at [75]

$$\frac{\epsilon_{tr}}{\epsilon_c} = \frac{3/2 - \omega}{\bar{\zeta} + 1/2 - \omega} \quad (B.24)$$

with a maximum probability of [75]

$$P_{\max} = c \cdot \left(\frac{3}{2} - \omega \right)^{\frac{3}{2}-\omega} (\bar{\zeta} - 1)^{\bar{\zeta}-1} \left[\left(\bar{\zeta} + \frac{1}{2} - \omega \right) \epsilon_c \right]^{\bar{\zeta}+\frac{1}{2}-\omega} . \quad (B.25)$$

Setting $a = \bar{\zeta} + \frac{1}{2} - \omega$, $b = \frac{3}{2} - \omega$ and $c = \bar{\zeta} - 1$ the fraction of the probability to obtain a specific energy transfer fraction to its maximum probability is obtained

$$\begin{aligned} \frac{P}{P_{\max}} &= \left(\frac{a}{b} \cdot \frac{\epsilon_{tr}}{\epsilon_c} \right)^b \cdot \left(\frac{a}{c} \left(1 - \frac{\epsilon_{tr}}{\epsilon_c} \right) \right)^c \\ &= a^{b+c} \cdot c^{-c} \cdot b^{-b} \cdot \left(\frac{\epsilon_{tr}}{\epsilon_c} \right)^b \cdot \left(1 - \frac{\epsilon_{tr}}{\epsilon_c} \right)^c \\ &= a^a \cdot c^{-c} \cdot b^{-b} \cdot \left(\frac{\epsilon_{tr}}{\epsilon_c} \right)^b \cdot \left(1 - \frac{\epsilon_{tr}}{\epsilon_c} \right)^c , \end{aligned} \quad (B.26)$$

which is exactly the sampled transfer probability in Listing 6.5.

For $\bar{\zeta} = 1$ Equation 3.23 simplifies such that Equation B.26 becomes [75]

$$\frac{P}{P_{\max}} = \left(\frac{\epsilon_{tr}}{\epsilon_c} \right)^b \quad (B.27)$$

to allow for cases of $\bar{\zeta} = 1$ to also be sampled, as otherwise Equation B.26 is not defined.

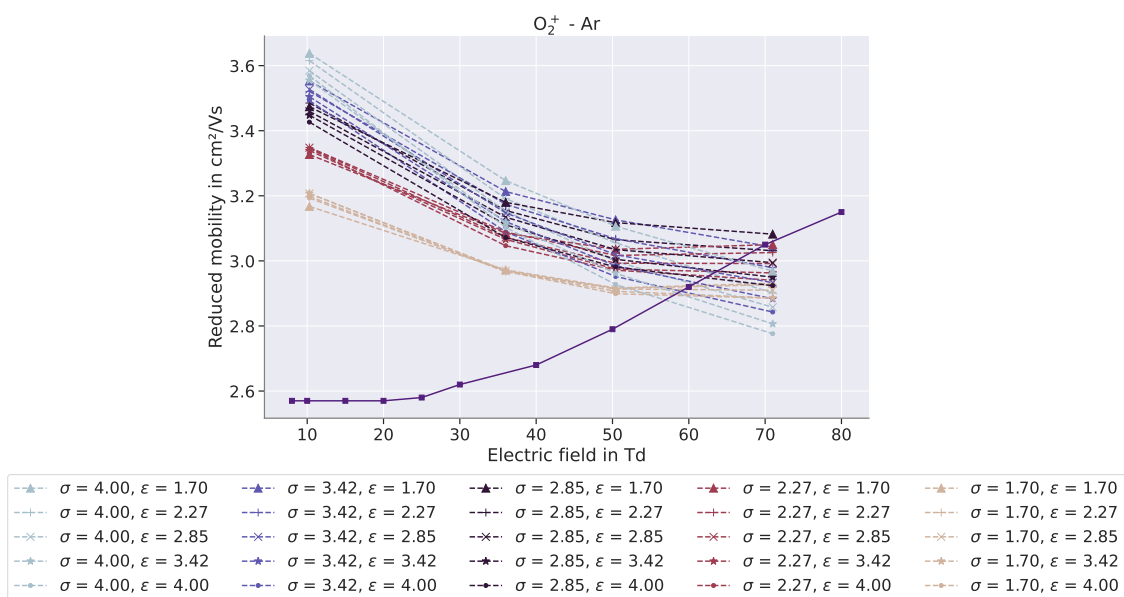


Figure C.1: Reduced ion mobilities obtained in dependence of the electric field strength for varying 12-6 Lennard-Jones parameters σ and ϵ for O_2^+ in argon. The solid, purple line with square markers gives the experimental data given in [149].

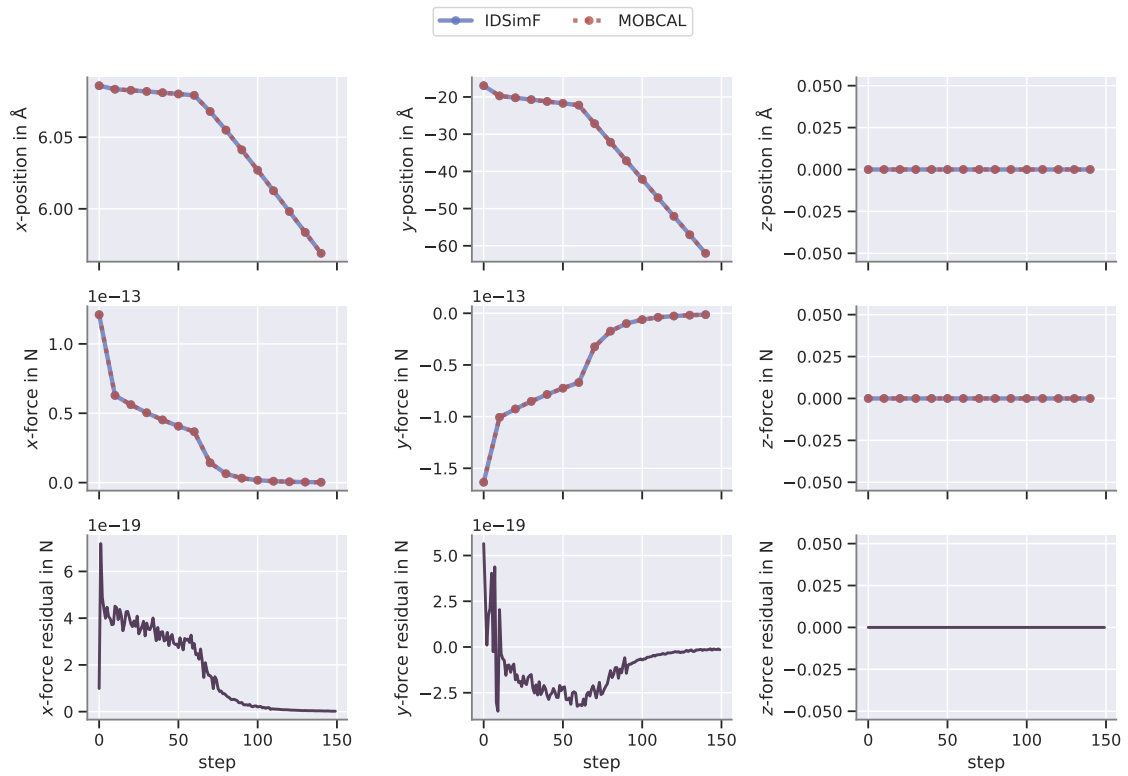


Figure C.2: Comparison of force and force residual in all three spatial directions between IDSimF and MobCal-MPI for one exemplary collision constructed by MobCal-MPI. Only every tenth time step is plotted for the positions and forces to better visualize agreement between both curves. The force residual is shown for all time steps. All force field components were active.

CODE SNIPPETS

Listing D.1: Example input script in *inp* format for PACKMOL to generate a model ESI droplet containing water, acetonitrile and lithium ions

```
1 tolerance 2.0
2
3 filetype xyz
4
5 structure acetonitril.xyz
6     number 3000
7     inside sphere 200. 200. 200. 50.
8 end structure
9
10 structure water.xyz
11     number 3000
12     inside sphere 200. 200. 200. 50.
13 end structure
14
15 structure lithium.xyz
16     number 21
17     inside sphere 200. 200. 200. 50.
18 end structure
19
20 output droplet.xyz
```

Listing D.2: Example input script in *lt* format for moltemplate.sh to generate the final system LAMMPS input file for a droplet containing water, acetonitrile and lithium ions

```
1 import "acetonitril.lt"
2 import "water.lt"
3 import "lithium.lt"
4
5
6 acn = new Acetonitril[3000]
7 water = new HOH[3000]
```

```
8 li = new lithium[21]
9
10
11 write_once("Data Boundary") {
12     0 400.0 xlo xhi
13     0 400.0 ylo yhi
14     0 400.0 zlo zhi
15 }
```

Listing D.3: SID model LAMMPS input

```
1 variable      a loop 10
2 variable      c loop 10 pad
3 label         loop
4 boundary      p p p
5 comm_style    tiled
6
7 # ----- Init Section -----
8
9 include        "system.in.init"
10
11 # ----- Atom Definition Section -----
12
13 read_data      "only_droplet_min.data" extra/atom/types 1
14 read_data      "wall.data" add append
15
16 # ----- Settings Section -----
17
18 include        "system.in.settings"
19
20 # ----- Charges Section -----
21
22 include        "system.in.charges"
23
24 # ----- Force field parameters Section -----
25
26 include        "mixed_coeffs_new.coeff"
27
28 # ----- Run Section -----
29
30 # Grouping of the atom types
31 group          tip3p type 1 2
32 group          lithium type 3
33 group          acetonitril type 4 5 6 7
34 group          droplet type 1 2 3 4 5 6 7
35 group          alwall type 8
36
```

```

37 # move droplet to center of the simulation box
38 displace_atoms droplet move $(-xcm(droplet,x)+0.5*lx+xlo) &
39                               $(-xcm(droplet,y)+0.5*ly+ylo) &
40                               $(-xcm(droplet,z)+0.5*lz+zlo) units box
41 variable                centerX equal $(0.5*lx+xlo)
42 variable                centerY equal $(0.5*ly+ylo)
43 variable                centerZ equal $(0.5*lz+zlo)
44
45 # neighbor list management
46 neigh_modify            every 1 delay 2 check yes one 10000 page 1000000
47 kspace_modify           gewald 0.1
48
49 # create wall
50
51 lattice                fcc 4.04 orient x 1 0 0 orient y 0 1 0 orient z 0 0 1
52 region                wallBack    block $(xlo+2) $(xlo+5) 0 INF 0 INF units
    box side in
53 region                wallLeft    block $(xlo+4) $(xlo+17) $(ylo+1) $(ylo+5)
    0 INF units box side in
54 region                wallRight    block $(xlo+4) $(xlo+17) $(yhi-4) $(yhi)
    0 INF units box side in
55 region                wallTop      block $(xlo+4) $(xlo+17) $(ylo+2) $(yhi-2)
    $(zhi-1-5) $(zhi-1) units box side in
56 region                wallBottom   block $(xlo+4) $(xlo+17) $(ylo+2) $(yhi-2)
    $(zlo+3) $(zlo+3+4) units box side in
57 region                wall        union 5 wallRight wallLeft wallTop
    wallBottom wallBack
58 region                crystal      block $(xlo+4) $(xlo+17) $(ylo+5) $(yhi-4)
    $(zlo+3+4) $(zhi-1-5) units box side in
59
60 create_atoms           8 region wall
61 delete_atoms           region crystal
62 create_atoms           8 region crystal
63 fix                    2    alwall    setforce 0 NULL NULL
64 lattice                none 1
65
66 delete_atoms           overlap 0.1 all all
67 reset_atom_ids
68 group                  swingAl region crystal
69
70 # output of system data
71 write_data              "droplet_wall.data"
72
73
74 # minimize and correct for overlapping atoms
75 minimize                1.0e-4 1.0e-5 1000 2000

```

```
76
77 # calculate velocity in x
78 region          drop_box block $(v_centerX-50) $(v_centerX+50) $(
    v_centerY-50) $(v_centerY+50) $(v_centerZ-50) $(v_centerZ+50) side
    in
79 variable        MassDroplet equal mass(all,drop_box)
80 print           "$(v_MassDroplet:%.6f)"
81 variable        ChargeDroplet equal charge(all,drop_box)
82 print           "$(v_ChargeDroplet:%.6f)"
83 variable        e equal 1.602*10^(-19)
84 variable        gmolToKg equal 1/(6.022*10^(23))*10^(-3)
85 variable        Voltage equal 10*${a} # a is used to ramp over varying
    voltages
86 variable        velocityX equal sqrt(2*${ChargeDroplet}*${e}*${Voltage
    }/(${MassDroplet}*${gmolToKg}))
87 print           "$(v_velocityX:%.6f)"
88 variable        velocityXAfs equal -1*${velocityX}*10^(-5)
89
90 # set up MD system
91 timestep        1.0
92 velocity        all create 298.0 4928459
93 velocity        droplet set v_velocityXAfs 0 0 sum yes # add x-
    velocity
94
95 # microcanonical ensemble, atoms not contained in droplet / swingAl do
    not move, i.e. the shell
96 fix            5      swingAl      nve
97 fix            1      droplet      nve
98
99 # compute energy parameters of the droplet
100 compute        pe_all droplet      pe/atom
101 compute        ke_all droplet      ke/atom
102 compute        pot_drop droplet    reduce sum c_pe_all
103 compute        kin_drop droplet    reduce sum c_ke_all
104 compute        myTemp droplet      temp/com # remove com velocity
105
106
107 thermo_modify   temp myTemp format 3 %15.8g
108 thermo         100
109
110 # output file
111 dump            $a      all          custom 1000 acn_h20_com_vel_alloy_${c.
    lammppstrj id mol type x y z ix iy iz vx vy vz c_pe_all c_ke_all
    mass
112 fix            4      all          balance 100 1.2 rcb
113 reset_timestep  0
```

```
114 run          1000000
115 next        a
```
