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Modeling of the plasma extraction efficiency of an inductively coupled plasma-mass spectrometer interface using the direct simulation Monte Carlo method

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ABSTRACT

The interface between the atmospheric pressure plasma ion source and the high vacuum mass spectrometer is a crucial part of an inductively coupled plasma-mass spectrometer. It influences the efficiency of the mass transfer into the mass spectrometer, it also contributes to the formation of interfering ions and to mass discrimination. This region was simulated using the Direct Simulation Monte Carlo method with respect to the formation of shock waves, mass transport and mass discrimination. The modeling results for shock waves and mass transport are in overall agreement with the literature. Insights into the effects and geometrical features causing mass discrimination could be gained. The overall observed collision based mass discrimination is lower than expected from measurements on real instruments, supporting the assumptions that inter-particle collisions play a minor role in this context published earlier. A full representation of the study, for two selected geometries, is given in form of a movie as supplementary data.

1. Introduction

From the beginning of the deployment of the inductively coupled plasma (ICP) as ion source for mass spectrometry [1], the vacuum interface was a key part and the main focus of instrument research and development. The initial single-stage pinhole interface, as proposed by Kantrowitz and Grey [2], posed several disadvantages, mainly the limited acceptance of high matrix containing samples and the formation of cluster ions [3]. This limitation was significantly mitigated by the introduction of a dual-stage setup, based on the early work of Campargue [4] and Beijerinck et al. [5] on molecular beams. A general improved performance was reported for such setups by Gray and Date [6] and Douglas et al. [7]. However, with the success of commercially available instruments, the focus of instrument development shifted towards application-oriented aspects. Just recently, the interface is receiving renewed attention, by the development of the Jet-interface [8], the triple cone setup [9] and 90° ion deflection designs [9–11] to improve sensitivity and/or reduce background and interferences. A side-effect of the Jet-interface is a substantial reduction in mass discrimination [12]. The underlying effects leading to this are unknown or at least unpublished.

The present paper describes a possibility to model the fluid flow through the entire interface into the mass spectrometer with the Direct Simulation Monte Carlo (DSMC) method developed by Bird [13]. This particle-based computational fluid dynamics (CFD) method is the dominant numerical approach for solving rarefied gas flows [14].

The rarefaction of a fluid is best described by the Knudsen number K_n. This dimensionless parameter is describing the ratio of the mean free path length of an atom or molecule λ and the critical dimension d – in this case the skimmer orifice diameter – according to Eq. (1).

$$K_n = \frac{\lambda}{d}. \quad (1)$$

For sufficiently rarefied fluids, the Navier–Stokes equation becomes inadequate; the threshold for validity is reported as $K_n \leq 0.1$–0.2 [15]. In the ICP-MS interface, the Knudsen number expected at the tip of the skimmer cone is in the range of $K_n \approx 0.3$ [16], thus rendering the Navier–Stokes equation invalid.

A further issue with the application of conventional CFD is the formation of shock waves in the process of establishing the flow field. The modeling is always starting with a predefined set of boundary conditions. In order to reduce the computation time, these are selected to be in the range of the equilibrium conditions for the observed system. For conventional CFD, this leads to the problem that the incident Ar plasma at ambient pressure is facing the intermediate interface void at about 100 Pa vacuum. The sudden drop in pressure causes a shock wave to form with rapid changes in thermophysical properties, namely pressure and temperature of the fluid. Those rapid changes eventually

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exceed the tabulated values of certain properties, causing a crash of the modeling software.

DSMC, however, does not rely on thermophysical data for the simulation. It is rather based on particles representing a large number of real gas molecules. The evolution of the fluid flow is tracked by the calculation of the collisions of particles with other particles, as well as with the walls of the simulation domain. By dividing the simulation regime into small time steps and subsequently performing the calculations mentioned above, the system is eventually reaching steady-state [13].

Typical DSMC applications vary from space vehicle re-entry [17] to micro- and nanoscale fluid flows [18]. So far, only the first vacuum stage of the ICP interface was modeled by DSMC [19–21]. Those studies were limited to the flow through the sample cone, whereas the present study is focused on the complete transport into the mass spectrometer. Furthermore, the ability of DSMC to support the design of new cones is evaluated and the possible contribution of collisions to the instrumental mass discrimination is investigated.

2. Modeling conditions

2.1. Simulation domain and boundary conditions

All simulations were carried out with *dsmcFoam*, which is part of the open source C++ CFD toolbox OpenFOAM v2.2 [22]. Most simulations were performed on a high performance computing cluster offering 360 cores operating Scientific Linux. Additionally, the Cray XE6, Monte Rosa of the CSCS Swiss National Supercomputing Center was utilized. A conventional dual processor hex-core Xeon PC running under Gentoo Linux was used for simple tasks and the post processing. The *dsmcFoam* code has been benchmarked against other DSMC codes, as well as conventional CFD and analytical solution to well described problems ranging from 1D to 3D as described by Scanlon et al. [23].

The ICP-MS interface set-up investigated here resembles that of the Neptune multi-collector ICP-mass spectrometer and Element 2 single-collection sector field ICP-mass spectrometer from Thermo Scientific [24]. Four different set-ups were modeled based on the two commercially available cone designs for sampler (Standard and Jet) and skimmer (H and X), respectively. Based on technical drawings and close-ups of the skimmer tip cross section by Taylor et al. [25], the geometry was digitized and a mesh was established. In Fig. 1, a schematic representation of the simulation domain for a Jet-sampler/X-skimmer configuration is given with the positions for quantitative geometry comparison (see Figs. 6–8). The simulation domain is filled with a structured mesh. Mesh size and shape of the individual cells have been checked for impact on the simulation results. No such impact was detected with mesh sizes in the range of 5–100 μm. Because the interface is axisymmetric, it was opted to perform the modeling in 2D with cylindrical symmetry. For this purpose a wedge-shaped piece representing 5° of the geometry was used. This, unfortunately results in poor statistics in the very central part of the domain caused by the wedge-shaped cells in axisymmetric meshes, as described by Spencer et al. [21].

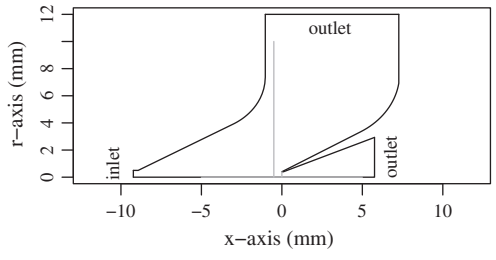

Fig. 1. Outline of the Jet-sampler/X-skimmer simulation domain with the gray lines indicating the positions used for the geometry comparison.

Table 1
Physical parameters for the DSMC simulation [26].

Gas	m (10^{-27} kg)	d_{ref} (10^{-10} m)	ω
Argon	66.3	4.17	0.81
Krypton	139.1	4.76	0.80
Xenon	218.0	5.74	0.85

The walls of the simulation domain were set to constant temperatures with the "Maxwellian-Thermal" wall interaction model. In this model, the particles bouncing off the walls are thermalized with according wall temperature. To mimic the temperature gradient from the tip of the cones towards the water-cooled base, the walls were sectioned into four segments. The segment representing the pipe-like part of the cones was set to 1500 K, the adjacent walls were kept at 1200 K, the following segment at 500 K and the base at 300 K. The Ar plasma is represented by Ar neutrals only. A temperature of 5400 K [20] and a pressure of 101,325 Pa were assigned to the inlet boundary. Since the real flow field at the inlet is not modeled in this work, a uniformly distributed velocity field was applied to the inlet with a gas velocity of 690 m s^{-1} and oriented coaxial to the beam axis, as derived from the literature [20]. To initialize the domain with close to steady-state values, the voids of the interface were set to a pressure of 100 Pa, both for the section between sampler and skimmer, as well as downstream of the skimmer. As fixed pressure outlets are not implemented in *dsmcFoam*, this was mimicked by a constant temperature of 10^{-1} K at those boundaries. This unphysically low temperature causes all particles hitting the boundary to be removed from the simulation domain. Therefore, these boundaries act as if they are ideal vacuum pumps. Each simulator particle represents 2×10^7 real atoms, the time steps between collision evaluations were chosen to be 1×10^{-9} s. This leads to approximately 1.2×10^7 particles in the system, resulting in $\approx 2 \times 10^5$ collisions per time step. A list of the physical parameters employed for the species utilized in the simulation is summarized in Table 1. The reference diameter for the collision selection is represented by d_{ref}, ω is the viscosity coefficient in the utilized variable hard sphere model [13]. These parameters are of particular importance for the collision selection process in the DSMC simulation.

At the start of the simulation, only a few particles are in the system, based on the initial pressure condition. Once the simulation is running,[1] the particles populate the domain through the inlet and eventually leave the domain once they hit the outlet boundary (Fig. 2). At the time the inflow approximately matches the outflow, the simulation is considered in steady-state and stopped for a change in modeling parameters. Up to this point, all deduced data for the flow field have been discarded after each time step. The system reached equilibrium after 25 ms flow time. The data were averaged for an additional time slot of 50 ms to obtain a good representation of the flow field.

2.2. Type of simulations

As described before, the situation was simulated for four combinations, defined by the selection of commercially available cone types. The particular focus was put on the shock waves forming behind the sampler. Next to the shock waves, also the fraction of particles transmitted through the skimmer was investigated. The flow field data were sampled along the beam axis and across the skimmer tip in order to qualitatively compare the results obtained with the different cone combinations. In a final set of simulations, an attempt was made to derive the extent of mass discrimination between the two cones, affecting the transmitted matter. For this type of simulation, the particle type was altered from pure Ar to a mixture of Ar, Kr and Xe, with 80%, 10% and 10% particle abundance, respectively. Additionally, the number of

[1] Video available as electronic supplement.