A mixed Computational Fluid Dynamics and Direct Simulation Monte Carlo model of the intermediate pressure regions of a miniature ESI-MS

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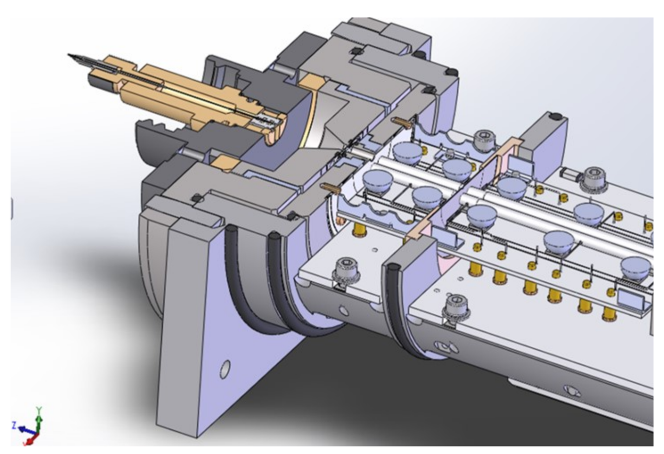
Overview

- Development of a Simion ion trajectory model incorporating results from both Navier Stokes based (NS) and Direct Simulation Monte Carlo (DSMC) solvers within openfoam.
- Experimental work to assess of models validity.
- Comparison of the results from a commercial instrument (4500 MiD®) and new development prototype.

Introduction

The recent development of miniaturized electrospray mass spectrometers (ESI-MS) has led to efforts to maintain high sensitivity whilst minimizing foot-print. Due to the experimental difficulties accessing these small and complex spaces, computational studies have increasingly become a useful compliment to empirical study. During development of a new, lower pressure ion optic a review of the coupling between the interface and analytical chambers within our ESI-MS products (Microsaic MiD®) was undertaken. Computational models of the outflow from new prototype and standard optics were undertaken to assess whether the local flow properties in the ionguide has been maintained with a simple scaling of components. Rough analysis of global Knudsen numbers imply transition from continuum flow within the setup resulting in the breakdown of the Navier-Stokes (NS) approach.



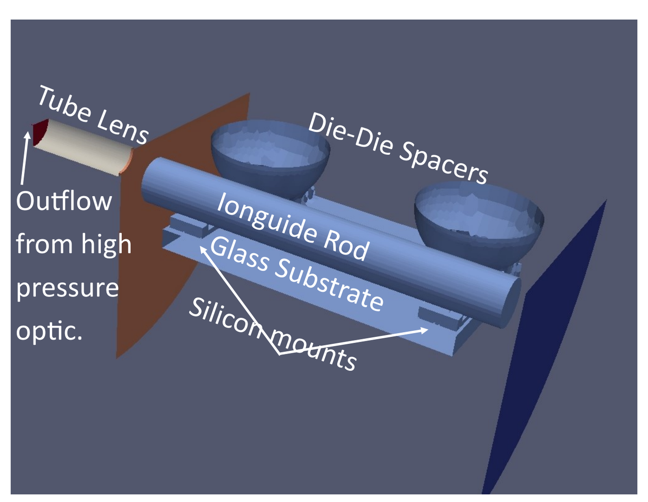


Figure 1:

Top left) The Microsaic MiD® 4500

Top right) A section of the instrument from ion source to analytical quadrupole.

Right) The domain of modelled here from the exit of the vacuum interface optic (vac-chip) to the quadrupole ionguide.

NS Breakdown

A number of different criteria for determining the applicably of NS to rarefied sonic flows have been suggested in the literature. Such as the gradient local length (GLL) based on a local Knudsen number for a flow property Q [1]:

$$Kn_{GLL} = \frac{\lambda_m}{Q}\left|\frac{\partial Q}{\partial x}\right| > 0.05$$

Or the validity of assumption underlying the derivation of the NS equations themselves [1].

$$B = \max\left(|q_i^*|, |\tau_{ij}^*|\right) > 0.2$$

Programable python filters in Paraview were developed to allow calculation of these parameters as fields over the domain. Contour plots of these criteria are shown in figure 2a) along with the more traditional Knudsen number ($Kn = \lambda/L$ where L is the tube diameter). All surfaces in the domain had Knudsen numbers > 0.01 so were to be assumed to be NS-slip

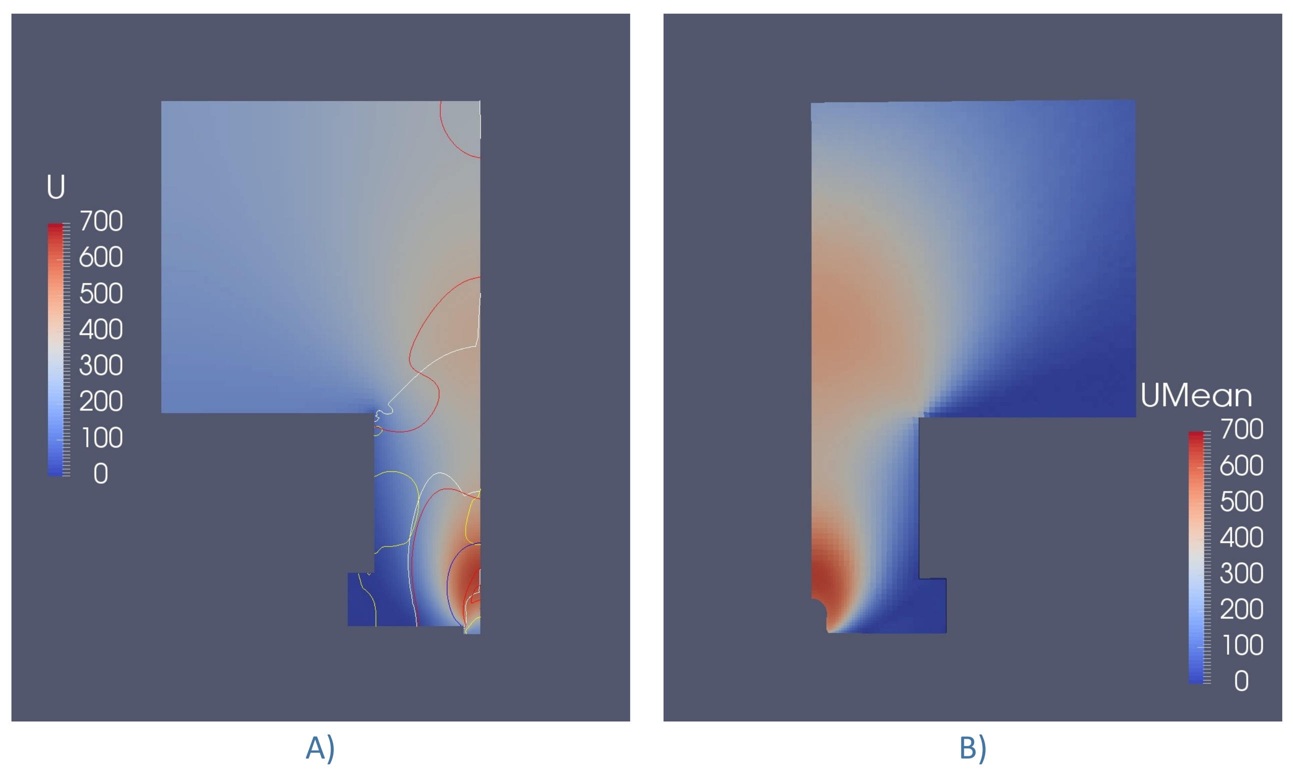


Figure 2: A) mag(U) with Breakdown parameter contours B = 0.2 (white), Knudsen Number = 0.05 (blue), Kn_GLL_T =0.05 (red) and Kn_GLL_Rho =0.05 (yellow). Artefacts at the centre line are probably due to the change in the final cell geometry at the wedge edge. B) The DSMC solution for the same cases based on a cut at B=0.2.

Method

Work station: Linux 24 core intel 3GHz Xeon.

1. Compute 2D wedge with slip continuum physics of the inlet/tube lens (figure 2.A).
   - RhoCentralFoam[2]: Laminar - Compressible - Parallel.
   - Diffuse smoluchowskiJumpT, maxwellSlipU walls
   - Empirically estimated mass flow rate inlet.
   - waveTransmissive outlet.
2. Export a contour with breakdown parameter B = 0.2 in post processing.
3. Convert contour to stl file and use in meshing inlet in 2D DSMC wedge (dsmcFoamPlus [3]).

   Conditions U, overallT, NumberDensity mapped from contour.

   Diffuse walls

   Fixed pressure outlet
4. Identify within the tube lens where gradient of U and T ~0 in the axial direction.
5. Use this location an inlet for a 3D DSMC simulation ¼ of the of the ionguide region.
6. Merge all 3 simulations into Simion [5] Pas (p, Ux, Uy, Uz and T).
7. Run trajectories in parallel via early access mode - incorporating simion HS1 collision model [6] with cross-sections taken from [7].

Results

Figure 3 compares experimental data with model output for adjusting the tube and lens at fixed ionguide voltage (1V). As all values below 1V are a retarding field transmission must incorporate viscous forces. Experimentally with approximately 1/3 the inflow there is negligible transmission below 1V and all 3 species behave identically.

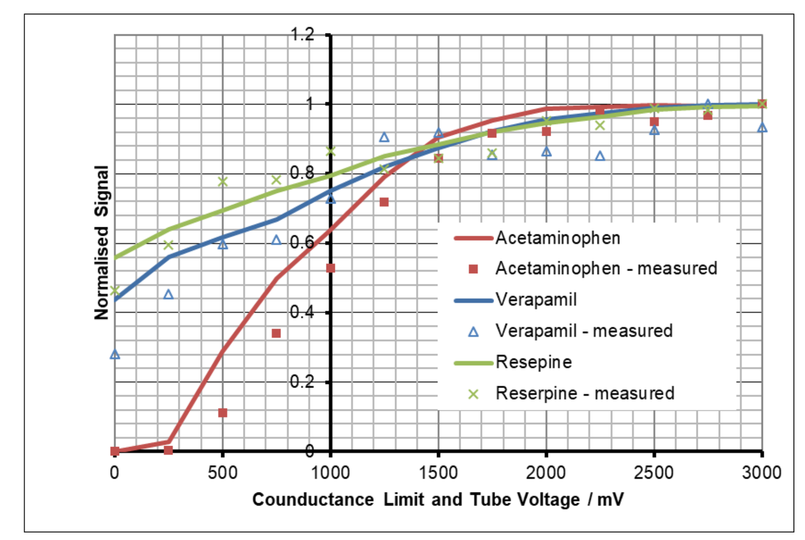


Figure 3: Comparison of simulation results and direct infusion experiments for the new prototype.

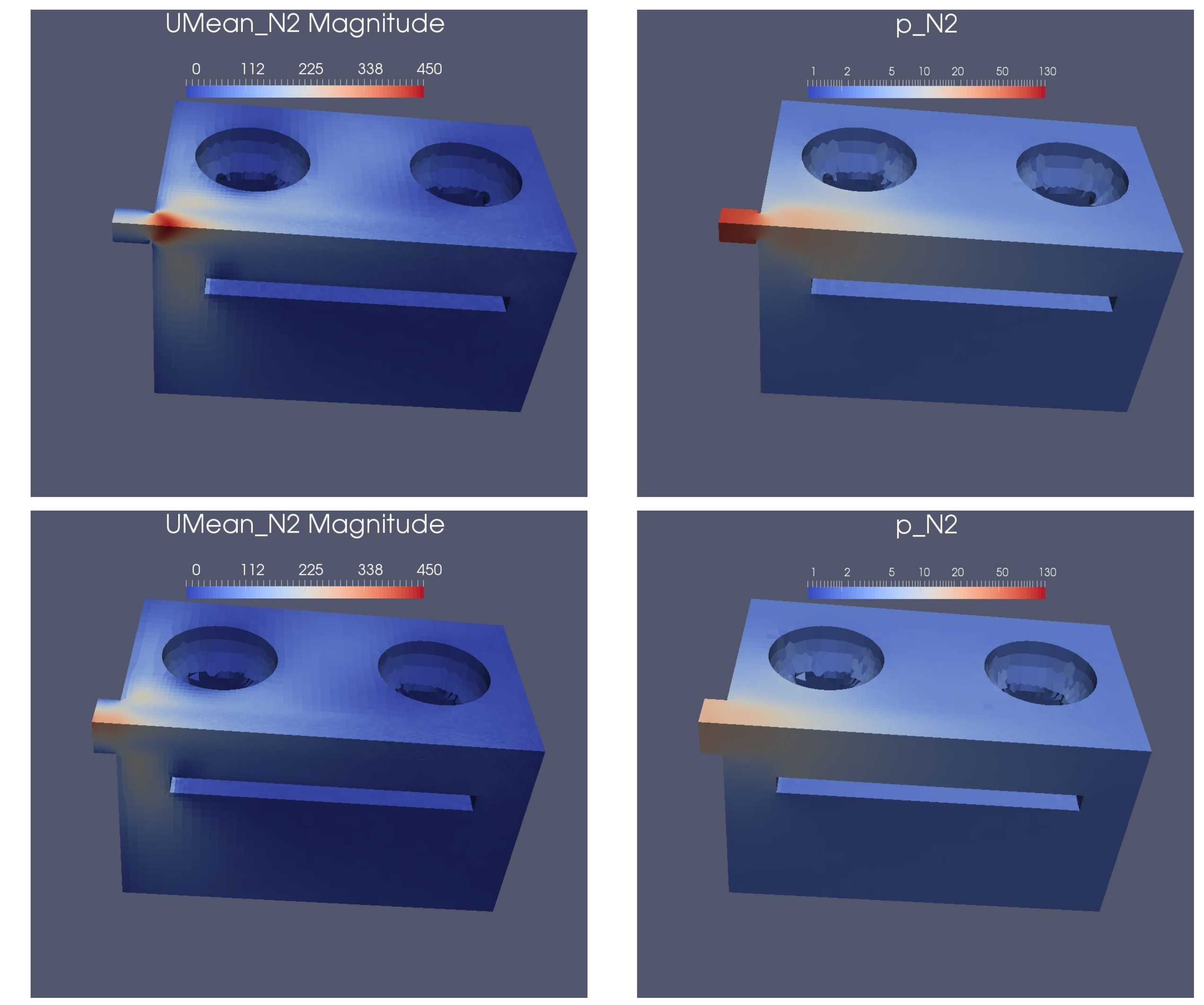


Figure 4 : Top) 4500 MiD®, Bottom) New interface each with left) mag(U) and right) log(p)

Computed fields for U and p are displayed in figure 4 for both the standard 4500 MiD® and the new setup for a typical gauge pressure of ~2 Pascals. For much of the inscribed radius the pressure is significant above this as predicted previously [8].

Figure 5 compares the 4500 MiD® under typical operation employing collision induced dissociation (CID) to improve S/N with the same three species as above. The relatively high pressures in the 4500 tube lens appear to re-thermalize ions within this optic. The shorter more open optic in the new prototype leads to lower local pressure so energetic ions reach the gap between tube and ionguide. However both cases show collisional focussing and high transmission efficiency. Much of this cooling is occurring in the upstream fringing fields suggesting the ionguide length could probably be significantly shortened.

It is quite likely that that within the new interface CID will be more energetic and so for a given application less volts will be required.

Simulations showed we could raise this CID voltage to 100 V without any change in the final ion energy. This was verified experimentally up to 40V with verapamil with no measurable change in resolution above which fragmentation prevented measurable transmission of $[M+H]^+$.

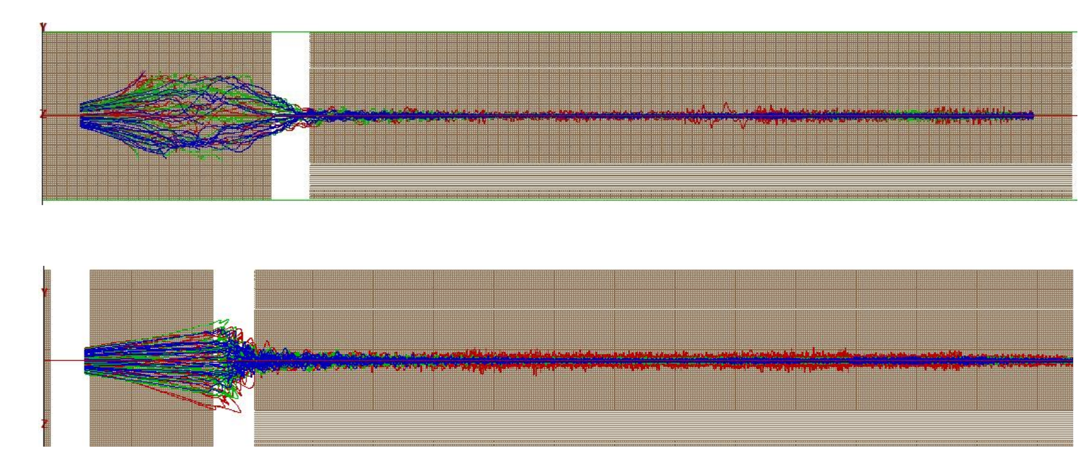


Figure 5 : Top) 4500 MiD® case (50V, 10V, 10V, 1V, 1V) and Bottom) New interface (50V, 10V, 1V, 1V)) with Acetaminophen (red) , Verapamil (Green) and Reserpine (Red).

Conclusions

- A reliable model of the ion trajectories within the slip to transition region of a MEMS based mass spectrometer has been developed.
- Previously reported [8] operating regime based on local properties has been confirmed in the model of the 4500 MiD®.
- Similar local effects have been observed in the new case and are substantive enough to provide collisional cooling of ions at energies relevant to 'in source' CID.

References

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