

# Flow Characteristics of a Laminar Flow Interface for LC/MS/MS

## Introduction

Simulation using sophisticated modeling techniques has become a powerful tool for mass spectrometry design. In particular, such techniques are very well suited to ion sampling in the interface region of mass spectrometers where pressure ranges are such that flow dynamics can accurately be modeled. Previous studies<sup>1,2</sup> have been done for gas flows in moderate pressure devices, specifically the HSID™ (Hot Surface Induced Desolvation) interface. Various design changes to the HSID interface have been introduced, with the goal of improving performance and increasing versatility. In this work, the characteristics of the new HSID designs have been modeled to better understand their characteristics, and to suggest further improvements to the design. The scope of the simulations has been expanded to include droplet trajectories in addition to the flow field calculations conducted previously. Simulations with the addition of droplets and charged particles can aid in the design of relatively complex ion sampling geometries. A major challenge is to design an interface to direct as many ions as possible into the mass spectrometer low pressure regions, without extracting droplets or solvated clusters. Simulation allows the control of droplet trajectories and evaporation rates. A parametric study takes into account the flow and temperature fields for optimal droplet/particle motion and evaporation.

## Theoretical Methods

Flow field calculations were performed using three dimensional computational fluid dynamics (CFD) modeling. The gas was assumed to behave ideally and was under adiabatic conditions at ambient temperature. The standard k-epsilon models of turbulence was applied for the flow field calculations. The volume was divided into sub-volumes to give better resolution and accuracy for the calculations in each flow region. Each

sub-volume was meshed separately, using unstructured hexahedral/wedge or tetrahedral/hybrid mesh elements. A finite – volume analysis with a second order discretization scheme was used for the calculations. A segregated solver was used. The boundary condition was set by velocity at the walls, which is equal to zero. Droplets trajectories were calculated using the Discrete Phase Model. Turbulent dispersion effects for the droplet trajectories were taken into account using stochastic tracking with a discrete random walk model. The three dimensional calculations were performed using the commercially available ANSYS FLUENT<sup>3</sup> software package.

## Results

### Flow Simulations for Open and Closed Interfaces

Calculations were done for two interface configurations. Each configuration has a common initial path. For the open case, Figure 1a, a pump connected to the outlet side of the interface maintains it at an intermediate pressure and removes the neutral gas. About 80% of the gas flux goes straight out instead of through the skimmer and into the mass spectrometer. The entrained ions are blocked by a voltage on the deflector, and are selectively directed through the skimmer and into mass spectrometer.

For the closed case (Figure 1b), the ions and the neutrals alike are transmitted directly to the first ion guide region, which is maintained at an intermediate pressure. The first supersonic region for both interfaces is elongated relative to the analogous region for a free jet expansion due to the presence of walls which contain and direct the flow.

The droplets inside HSID are charged. Therefore, for droplet motion analysis, one should take into account droplet interactions with the outer electrical field as well as space charge effects created by the ions and other droplets. During droplet motion, the process of fission occurs. As discussed in<sup>4</sup>, droplet mass loss is predominantly via evaporation. Note that in the case of the closed HSID configuration there is no outer electrical field due to the absence of the charged deflector plate.

The influence of space charge effects can be estimated. As a first order approximation, the electrical current inside HSID is  $I \sim 2$  nA. The mass gas flow rate is approximately  $\dot{m} \approx 2 \times 10^{-5}$  kg/s. The typical size and flight times of the droplets which reach the exit of the HSID, as calculated per the next section, are  $d \sim 3$   $\mu$ m and  $\tau_h \sim 0.5$  ms. Using Gauss' law, and assuming the droplets are charged to the Rayleigh limit, it is possible to estimate the possible displacement caused by electrostatic interactions between ions and other droplets:

$$\Delta \approx \frac{3}{2} \sqrt{\frac{\gamma}{\epsilon_0}} \frac{\rho_g}{\rho_l} \frac{I}{f} \frac{1}{r_d^{3/2}} r \tau_h^2$$

Here  $\gamma$  is the coefficient of surface tension,  $\epsilon_0$  is the permittivity constant,  $\rho_g$  and  $\rho_l$  are the gas and droplet densities respectively, and  $r$  is the droplet distance from the center line of the HSID. Substituting representative values results in a displacement of  $\Delta \sim 0.02$  mm. This is much less than the scale of the HSID and may be neglected when considering droplet trajectories. Thus, for the closed HSID configuration (Figure 1b) one may treat the droplets as uncharged.

### Droplet Transmission Calculations

The first effect for droplet removal is evaporation, illustrated in Figure 2 by a droplet which decreases in size as it travels through the HSID. The diameter  $d$  of a droplet that completely evaporates in time  $\tau$  can be estimated within an order of magnitude by  $d \sim 0.0024 \tau_h$ . [4]. If  $\tau_h$  is the time taken for a droplet to travel through the HSID, a critical droplet diameter  $d_{lc} \sim 0.0024 \tau_h$  therefore exists. When  $d \sim d_{lc}$ , some droplet pass through the HSID while some evaporate. If  $d \gg d_{lc}$ , essentially all the droplets pass through HSID, while if,  $d \ll d_{lc}$  essentially all droplets evaporate before leaving the HSID. Taking into account the geometry and flow field characteristics of the HSID results in a residence time  $\tau_h$  of approximately 0.00064 s, giving a first droplet critical diameter of 1.5  $\mu$ m.

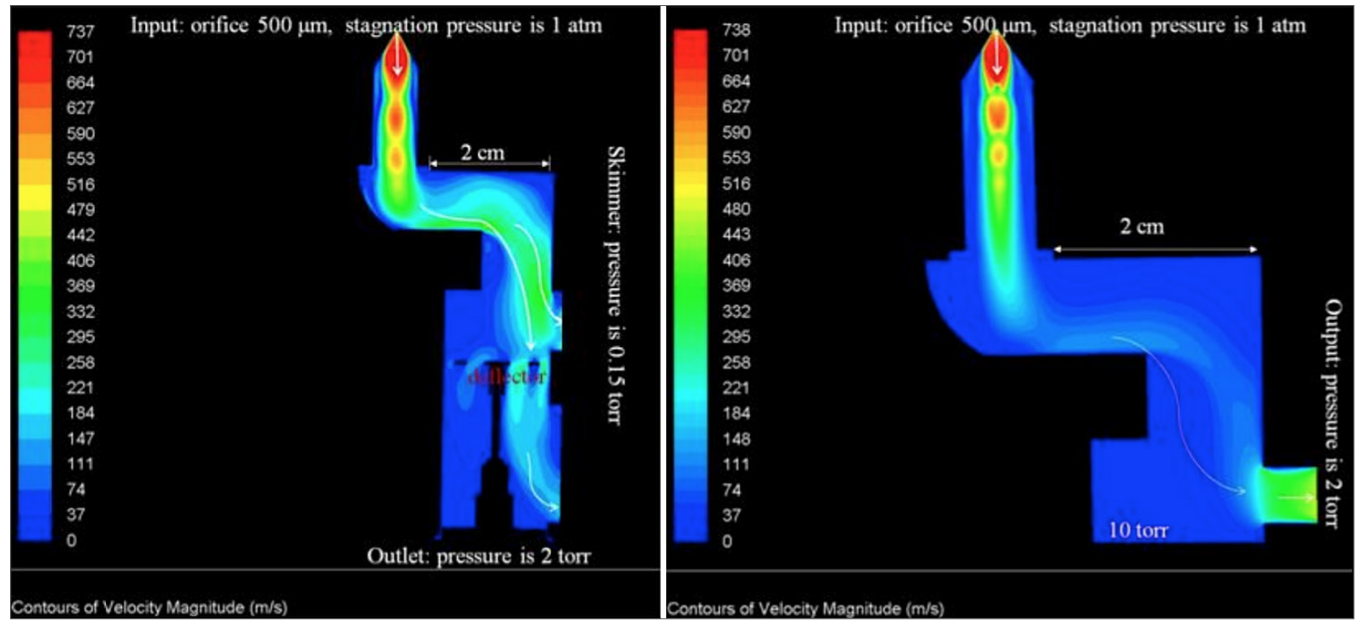


Figure 1a. Open HSID.

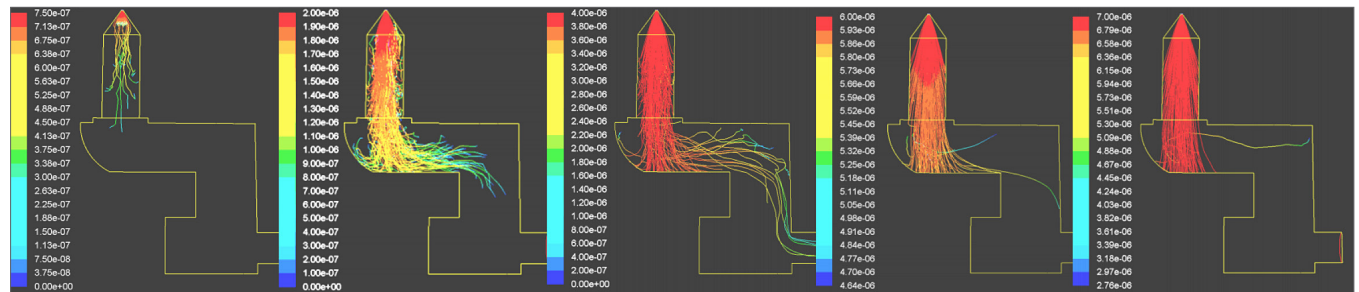


Figure 1b. Closed HSID.

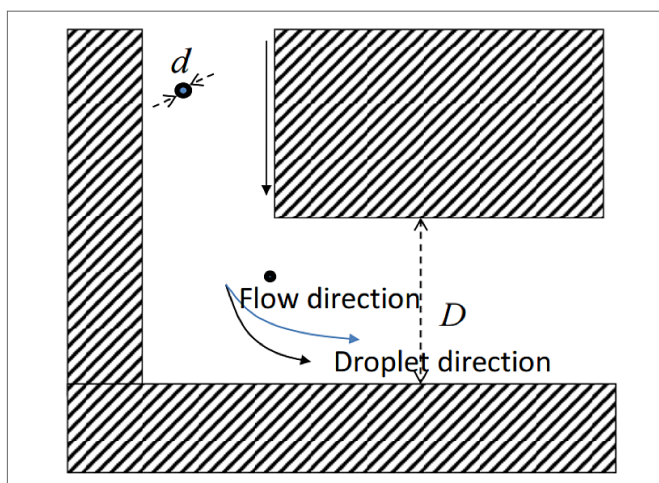


Figure 2. Droplet trajectories through HSID.

The second mechanism of droplet removal is inertia, or the so called "corner effect". At each corner, inertia causes droplets to continue towards the wall, deviating from the direction of flow, as illustrated in Figure 2. Sufficiently large droplets will impact the wall and be lost. This second critical droplet diameter can be estimated within an order of magnitude from Stoke's law:

$$d_{2c} = \sqrt{18 \frac{\mu D}{\rho V}}$$

Where  $\mu$  is the dynamic viscosity,  $\rho$  is the droplet mass density,  $D$  is the downstream channel diameter, and  $V$  is the upstream flow and droplet velocity. For the HSID described here,  $d_{2c} \sim 2.4 \mu\text{m}$ .

When  $d \sim d_{1c}$ , some droplets pass through the HSID. If  $d \ll d_{2c}$ , essentially all the droplets pass through HSID, while if,  $d \gg d_{2c}$  essentially all droplets impact the wall. Evaporation is thus responsible for the removal of small droplets, while the corner effect removes larger droplets. Droplets which are actually transmitted are therefore expected, as an order of magnitude estimate, to have diameters in the range of 1.5 – 2.4 microns. The calculations presented here use a droplet size distribution from 0.2 to 10 microns.

### Numerical Simulations of Droplet Trajectories

These calculations were conducted for water droplets (above), and for methanol (not shown). In both cases, the droplets with large initial diameters hit the wall. Droplets with small initial diameters avoid collision with the wall, but evaporate. Small quantities of intermediate sized droplets are transmitted, as expected.

More realistically, a distribution of initial droplet sizes might be expected. Calculations were performed for a distribution with initial droplet diameters of 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5 and 6.0 microns, assuming 2090 of droplets of each size. Because turbulence causes some chaotic contribution to the motion, different simulations are not expected to produce identical results for the final number and size distribution of droplets passing through HSID. For quantitative analysis, a large number of runs are required. The transmitted droplet distribution is illustrated in Figure 4 for water. Results indicate that only a small fraction of the droplets are transmitted. Calculations were performed for water and for methanol and generally indicated total transmission of not more than 1.4% for water and 0.3% for methanol.

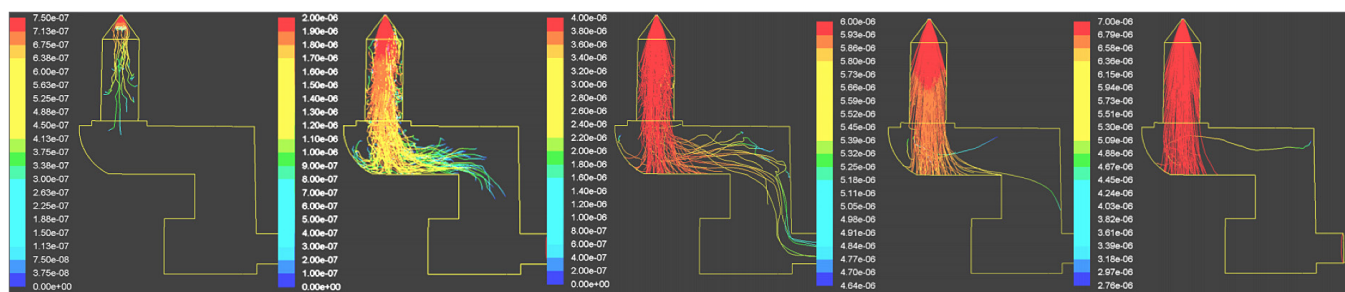


Figure 3. Trajectories of the water droplets. Each individual picture shows calculations for 209 droplets with a given initial diameter. The initial diameter of the droplets increases (left to right), from 0.75 to 7 microns.

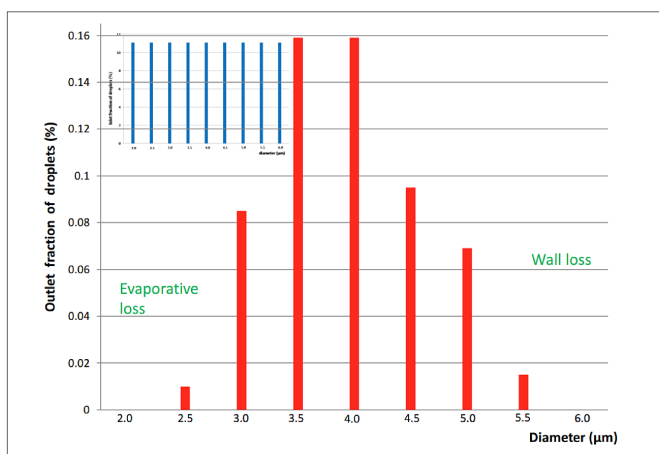


Figure 4. Diameter distribution of water droplets transmitted through HSID. The main (red) histogram shows the inlet diameters of the droplets, which are transmitted. The small (blue) histogram shows the initial inlet droplet distribution

### Summary and Conclusion

These estimations and numerical simulations show that HSID efficiently removes droplets. Small diameter droplets evaporate while larger droplets are removed by inertial effects. The percentage of droplets that is transmitted is very small, and depends on the initial droplet size distribution and on the nature of the solvent. The specific geometry of the HSID can be tailored, but in general is very efficient at preventing excess solvent from entering the mass spectrometer.

## References

1. S. Savtchenko, L. M. Cousins, Ch. Jolliffe, G. Javahery, Modeling of a Laminar Flow Interface with Multiple Bends for LC/MS/MS, ASMS Conference, Seattle, WA, 2006.
2. S. Savtchenko, L. M. Cousins, G. Javahery, I. Tomski, Ch. Jolliffe,, N. Ashgriz, 3-Dimensional Computation of a Laminar Flow Interface for LC/MS/MS, ASMS Conference, Indianapolis, IN, 2007.
3. ANSYS, Inc., 3255 Kifer Road, Santa Clara, CA 95051, USA.
4. P. Kebarle and L. Tang, From Ions in Solution to Ions in the Gas Phase (the Mechanism on Electrospray Mass Spectrometry) Report, Analytical Chemistry, v. 65, 1993; 22: 972-986.