Supplementary Material (ESI) for Chemical Communications


# Electronic Supplementary Information for "Simulation of Atmospheric Transport and Droplet-Thin Film Collisions in Desorption Electrospray Ionization"

Anthony B. Costa and R. Graham Cooks
*Department of Chemistry, Purdue University, West Lafayette, IN, USA*

## Spray Simulation

The simulation of sprays in the DESI geometry relies on a complex mesh of approximately 380,000 cells generated in the 3D mesh element generator *Gmsh*. Areas of specific importance (i.e., near the spray source and at the substrate surface) are given increased cell density from those far away from the region of interest. Figures reported in the current work are 2D slices through this 3D volume. This is done in order to simplify the interpretation of the results, though all discretization is run in 3D. The mesh is imported into *OpenFOAM* where the *dieselFoam* solver for compressible laminar flow of Lagrangian particles is used to evolve the motion of droplets and surrounding fluid. Boundary conditions are generally simple. Atmospheric pressure (1 atm) is used as the internal pressure field. Atmospheric boundary conditions are set for the flat faces surrounding the simulation volume, where the normal component of the velocity magnitude $\mathbf{U}$ is evaluated from the flux. When $\mathbf{U}$ changes, the pressure $p$ is adjusted according to a fixed (1 atm) total pressure $p_0 = p + \frac{1}{2}\rho|\mathbf{U}|^2$. These are the standard *fluxCorrectedVelocity* and *totalPressure* types available in *OpenFOAM*. Nebulizing gas is directed away from the sprayer at a fixed velocity of 300 m/s and the normal gradient of the pressure is set to 0. All other simulation boundaries are set as wall boundaries, where the velocity is set explicitly to 0 and the normal gradient of the pressure is 0. These are the *fixedValue* and *zeroGradient* types available in *OpenFOAM*. Droplet collisions with walls are treated as fully elastic. Gravity is included, though insignificant on this time scale. A hollow cone injector model is used for droplet creation with an inner cone angle of 0 degrees and an outer cone angle of 20 degrees. Thermodynamic and heat/mass transfer aspects of the simulation are not yet reported, though these features are included in the implementation of the *dieselFoam* solver. Simulation control and stability is achieved via the Courant-Friedrichs-Lewy condition, where the Courant number is set to 0.2 and the simulation control algorithm adjusts the time step accordingly.

## Droplet-Thin Film Collision Simulation

The simulation of droplet-thin film collisions is achieved in two dimensions with a structured rectangular grid of approximately 150,000 cells. The cell density is uniform through the simulation surface. The multi-phase solver *multiphaseInterFoam* included in *OpenFOAM* for an arbitrary number of incompressible fluids, capturing the interface using a Volume-of-Fluid (VOF) method, is used to evolve the motion of the fluid phases. The cell occupation number $\gamma$ is set to 0 for air and 1 or 2 for liquid (water) phases, therefore the interface between the two fluids is not exact, though the cell density used here provides for reasonable interpretation of the boundary. Two boundary conditions are set: atmosphere for the left, right and top boundary and a solid wall for the lower boundary. The lower boundary is set in the same fashion as in the spray simulation, in which the velocity is set to 0 and the normal gradient of the pressure is 0 (*fixedValue* and *zeroGradient*). Atmospheric conditions are treated as inlet/outlet for all fluids, such that droplets and air may exit the simulation volume. The value of $\gamma$ is set to 0 for all fluid entering the simulation volume, though very little of this occurs during the course of the simulation. This is the *inletOutlet* and *pressureInletOutletVelocity* types included in *OpenFOAM*. Values for the velocity magnitude $\mathbf{U}$ and $\gamma$ are mapped onto the simulation surface at time 0 and allowed to evolve under the constraint of the Courant-Friedrichs-Lewy condition with the Courant number set at 0.2. Like the spray case, the simulation control algorithm adjusts the time step in order to maintain a constant Courant number.