# Multi-Species Fluxes for the Parallel Quiet Direct Simulation (QDS) Method

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**Abstract.** Fluxes of multiple species are implemented in the Quiet Direct Simulation (QDS) scheme for gas flows. Each molecular species streams independently. All species are brought to local equilibrium at the end of each time step. The multi species scheme is compared to DSMC simulation, on a test case of a Mach 20 flow of a xenon/helium mixture over a forward facing step. Depletion of the heavier species in the bow shock and the near-wall layer are seen. The multi-species QDS code is then used to model the flow in a pulsed-pressure chemical vapour deposition reactor set up for carbon film deposition. The injected gas is a mixture of methane and hydrogen. The temporal development of the spatial distribution of methane over the substrate is tracked.

## THE QUIET DIRECT SIMULATION SCHEME

Quiet Direct Simulation (QDS), developed by Albright et al. [1,2] as a first order flow solver for plasma simulations, and by Smith et al. [3] as a second order scheme for unsteady compressible flows, is a kinetic theory based method for the simulation of gas flows. In the basic scheme, the Maxwellian equilibrium distribution of molecular velocities is assumed to hold everywhere. At each time step, this distribution is discretised into a small number (typically 3 or 4) of discrete speeds each with a corresponding weight representing the fraction of molecules travelling at this speed. The speeds $u_i$ are determined individually in each cell according to

$$u_i = \bar{u} + \sqrt{2RT}q_i$$

(1)

Where $\bar{u}$ is the local bulk velocity, $R$ the gas constant, $T$ the local temperature and $q_i$ the $i$th abscissa of the Gauss Hermite quadrature.

In each time step, in each cell, the distance moved by molecules travelling at each speed $u_i$ during the time step is determined. The flux occurs over a regular Cartesian or cylindrical polar mesh. The fraction entering the neighbouring cell is calculated and credited to that cell. When all speeds in all cells are fluxed, the mass, momentum and energy in each cell are totalled and the Maxwellian recalculated for each cell before the next time step begins. For multidimensional simulations the molecular speeds in each direction are combined to produce true direction fluxes [3,4]. The time step is adjusted so that no flux streams further than a specified fraction of one grid spacing.

The fraction of molecules entering the neighbouring cell are calculated using typically piecewise constant, piecewise linear, or higher order spatial reconstruction, and a slope limiter to limit numerical dissipation.

The solution is advanced with explicit Euler time stepping. Boundary conditions are implemented with ghost cells which participate in the flux stage and have appropriately chosen properties. Local thermal equilibrium is

assumed, and it is also assumed that the streaming step occurs without collisions. The method has been validated in hypersonic flows where thermal fluctuations are small compared to the bulk velocity. Validation against Sod's shock tube problem and a Mach 3.0 forward facing cylinder flow are described in [3].

## PULSED PRESSURE CHEMICAL VAPOUR DEPOSITION (PP-CVD)

Pulsed Pressure CVD (PP-CVD) is a novel CVD technique conceived by Versteeg *et al.* [5] which has demonstrated improved film quality and substrate conformity over traditional CVD methods [6], as well as demonstrating high precursor conversion efficiency [7]. A heavy reactive molecule at low mole fraction in an inert carrier vapour is injected into an evacuated chamber (Figure 1). The injected vapour flows over a heated substrate. The heavy reactive molecule decomposes on the surface to leave the film material, and gaseous waste products which are drawn off with the carrier gas by a vacuum pump. Periodic injection and continuous evacuation results in a cycling of pressure from typically 1-1000Pa minimum to 10-100,000Pa maximum. The injection of gaseous precursor is typically done with an underexpanded jet. In this highly unsteady, highly compressible flow, some inertial separation of the heavy and light species is expected.
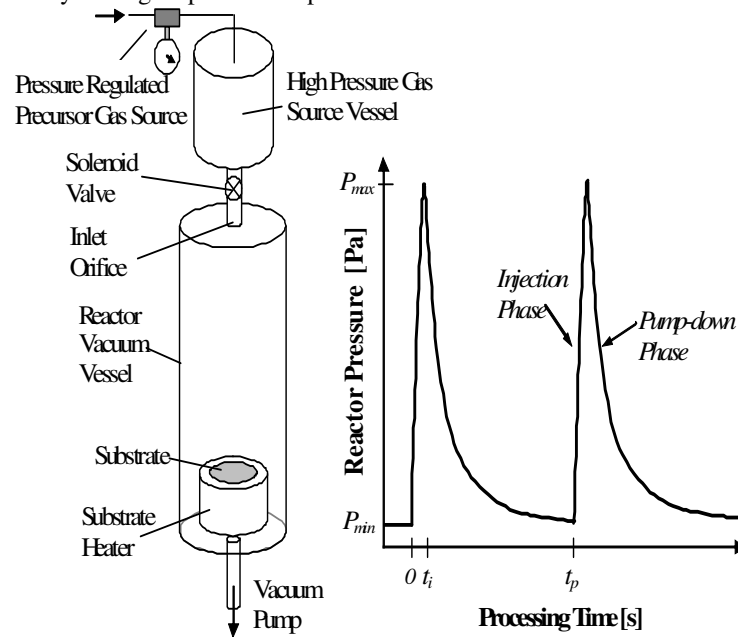


**FIGURE 1:** Schematic of the PP-CVD reactor and pressure history.

## MULTIPLE SPECIES IN GAS FLOWS

Flows of reactive mixtures are frequently modelled with conventional Navier-Stokes PDE solvers using a further equation modelling the transport of species fraction for each additional species. This was not used in the present case due to the difficulty of obtaining converged solutions in the highly unsteady, highly compressible flow in PP-CVD.

It is straightforward to model the transport of separate species with Direct Simulation Monte Carlo (DSMC) [8]. However the rarity of collisions between molecules of different species means that obtaining statistically significant trace species distributions can incur extremely high computational cost.

The flux of multiple species is trivial to implement in QDS and no statistical fluctuations arise.

## MULTIPLE SPECIES FLUXES IN QDS

During the flux phase, each species is fluxed separately using the appropriate single species gas constant. After the fluxes are computed, all species are brought to local thermodynamic equilibrium using an effective gas constant $R_{eff}$ determined from the properties of the mixture in each cell:

$$R_{eff} = \frac{\sum\limits_{i=0}^{i} R_i f_i}{\sum\limits_{i=0}^{i} f_i}$$

(2)

Where $R_i$ is the gas constant of species $i$ at mole fraction $f_i$

## VALIDATION OF MULTIPLE SPECIES QDS AGAINST DSMC

This implementation of multiple species fluxes in QDS was validated against DSMC in a simulation of the bow shock in a Mach 20 flow over a forward facing step. At the inlet the mixture was 50% xenon, 50% helium by mole fraction (97.04% Xe by mass). The conditions at inlet were $\rho$=1.0 kgm$^{-3}$, $T$=1.0K, and $u_x$=286.3ms$^{-1}$. Slip wall boundary conditions were used.

The QDS simulation used four speeds in each direction, piecewise constant (1$^{st}$ order) spatial reconstruction, and the kinetic CFL number was limited to <0.5. Four processors were used and the simulation required 31s of wall clock time. The direct simulation used ~ 1.5M particles with VHS collision models, a forced average of 4 collisions per particle per time step. Particle positions within each cell were randomised at the end of each time step to achieve effective piecewise constant spatial reconstruction equivalent to the QDS simulation. A constant time step was set to ensure CFL < 0.5 and the flow was allowed to equilibrate for the time taken for an average free stream particle to move the length of the domain before sampling began The calculation required 13 hours wall-clock time for 10,000 time steps on a single processor of the same type used for the QDS. Both simulations used a 100x100 grid. Results are shown in Figure 2.
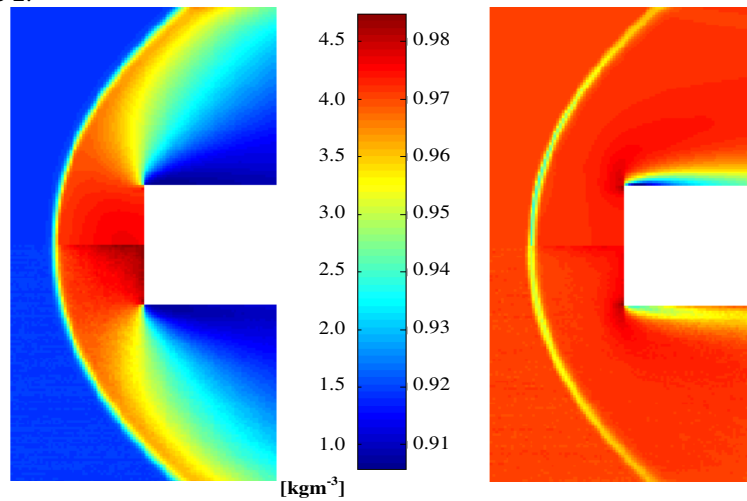


**FIGURE 2:** Flow over a forward facing step. Left: density contours. Right: Xenon mass fraction. Top: QDS; Bottom: DSMC

Both simulations predict the same shock position and the density contours are virtually identical (some statistical scatter is seen in the DS results). Both simulations also predict separation of the species, with the xenon becoming depleted in the shock (the heavier xenon has a lower residence time in the shock due to its higher momentum) and on the horizontal surface of the rectangular body (less of the heavier xenon being less carried around the corner into the near wall region on due to its greater momentum). The QDS simulation predicts greater depletion of xenon in than the DSMC, perhaps due to the different collision treatments.

## MODELLING OF THE DIAMOND-LIKE CARBON (DLC) PP-CVD REACTOR

PP-CVD has been used to deposit diamond films and carbon nano-fibres by Lebedev (results summarised in [9]). In these experiments, a mixture of 1 to 5 vol% methane in hydrogen was injected into the reactor. A tungsten

filament heated to approximately 2000°C was suspended just above the deposition surface in order to decompose the methane. The pulse pressure range was maintained between 30Pa and 800Pa with 20s between injections. It was found that concentrations of methane of around 5 vol% resulted in the production of nano-fibres, whereas lower concentrations produced diamond-like films.

The reactor modeled with QDS was 345 mm long with a radius of 50mm and an inlet orifice of diameter of 1mm. The initial reactor pressure was 30Pa with a supply pressure of 100kPa resulting in a choked inlet condition. The initial temperature of the reactor volume and the supply vessel was set at 293K and the concentration of methane was set at 1.0vol% (equivalent to 7.453% by mass). A regular cylindrical polar grid with cells of width 0.1mm resulted in a total of 1,957,298 flow field cells. The first 5ms of the injection phase were simulated using a parallel axisymmetric second-order QDS code on 32 processors which required approximately 15.5 hours of wall-clock time. The quiescent gas in the chamber at the start of injection is 100% hydrogen. The heating wire, and the surface deposition process, were not modelled.

An axisymmetric QDS solver using piecewise linear (2nd order) spatial reconstruction and implementing the multi-species method described above was used. A 32 processor PC cluster required approx. 5 wall clock hours for each 1ms of flow time. Figure 3 shows contours of methane concentration for the first 3.0ms following the start of injection.
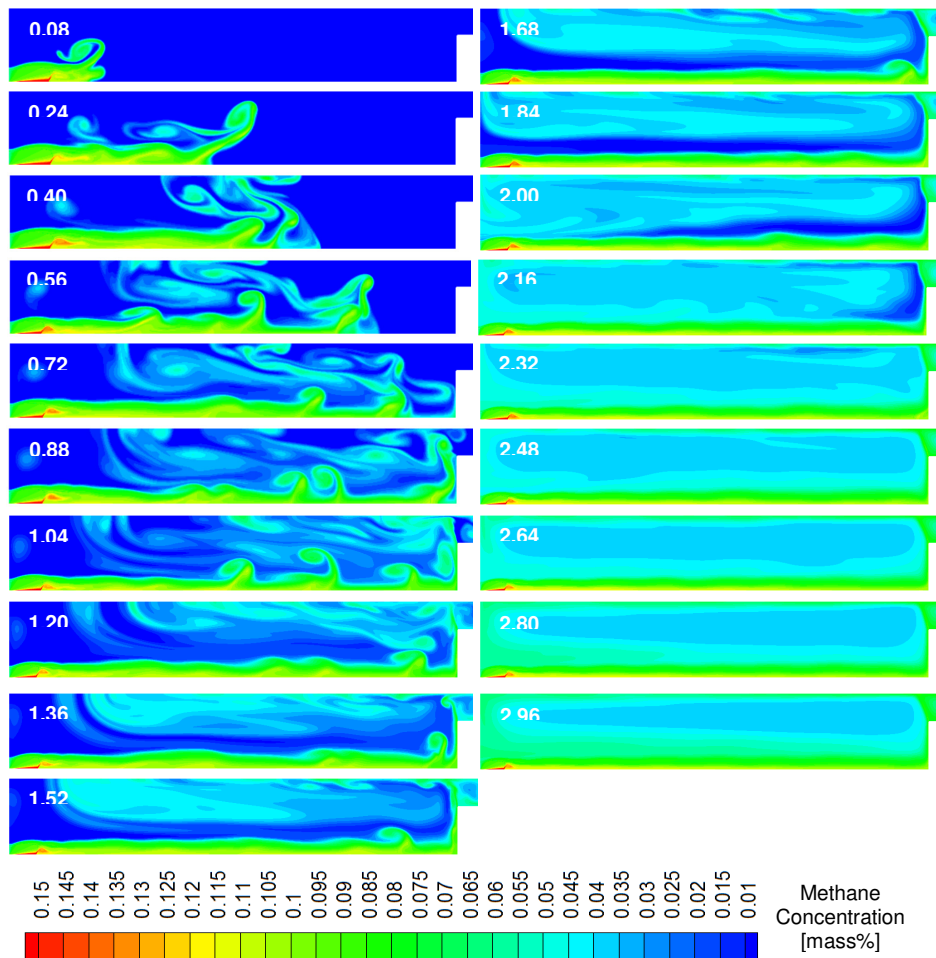


**FIGURE 3:** Contours of methane concentration (in mass percentage) during the first 3.0ms of the injection phase in a PP-CVD reactor used for the deposition of carbon films.

In Figure 3 the injector is at left hand side. Half of the reactor volume is shown. Times indicated are from the beginning of the injection pulse. The Mach disk forms early in the injection, and the jet develops toward the substrate until it impinges between 0.72 and 0.88ms. The jet then spreads out over the substrate and exits the chamber at the vacuum ports to the side. The concentration of methane is higher at the core of the jet because the heavier methane molecules maintain their momentum as they move down stream (whereas the lighter hydrogen

molecules diffuse out of the core of the jet). As can be seen, a quasi-steady flowfield is set up after approximately 2.5ms and the methane becomes quite well mixed outside of the jet core. Eddies are seen in the jet shear layer which are due to the inherent viscosity in the scheme. The numerical viscosity of this scheme is discussed in a companion paper at this conference by the same authors.

It was hypothesised by Cave [9] that soon after the orifice shuts at the end of injection the jet structure will completely breakdown leaving an approximately even concentration of methane throughout the reactor volume. To test this hypothesis, an additional simulation was carried out to show the evolution of the flow immediately after the jet shuts off and the pump-down phase begins. Here the jet was allowed to reach a steady state by simulating the flow from a starting pressure of 740Pa for 5ms, resulting in a reactor pressure of approximately 800Pa at the end of the injection phase. Otherwise, the simulation conditions were identical to those mentioned above.

Figure 4 shows contours of mass density (including both species) during the 0.6 ms after the jet shuts down. Note that the contour range has been restricted to better illustrate the flow phenomena during the collapse of the jet.
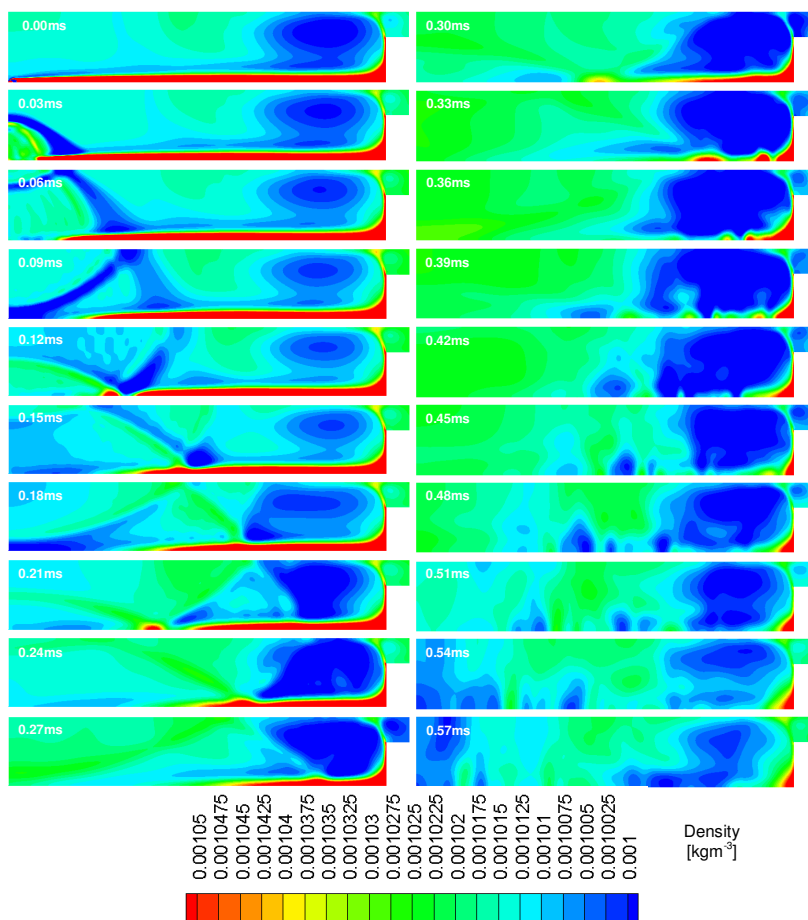


**FIGURE 4:** Density contours during the 0.6ms immediately following jet shutoff.

The jet and the reflected shock structure is seen to dissipate, beginning at the nozzle, and dissipating last at the substrate.

Later still, at 1.25 ms after the end of injections, the variation in methane mass fraction is everywhere within 3% of the concentration at injection (data not shown). This state is expected to persist for the remainder of the pressure cycle, typically of order 10-20s. This uniformity is beneficial for even film deposition.

# CONCLUSIONS

Fluxes of multiple species, with independent fluxes of individual species and equilibration between all species at the end of the time step, were implemented in QDS. The implementation is straightforward. The method was validated against DSMC in He/Xe flow at Mach 20 over a forward facing step . Inertial separation was seen in the bow shock and near wall layer. Agreement was good except for a slightly higher concentration of Xe in the aforementioned regions. The code was used to model a methane/hydrogen mixture in a PP-CVD reactor. Shear layer eddies were observed due to the inherent numerical viscosity of the scheme. The jet dissipates within 1ms of the end of injection. Methane mass fraction is within 3% of the average value in the feedstock everywhere by 1.25ms after injection.

Flow-field chemistry are expected to be simple to implement in codes using this multiple species flux model.

# ACKNOWLEDGMENTS

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