Electrochemical Push-Pull Scanner with Mass Spectrometry Detection

--Electronic Supporting Information--

Dmitry Momotenko,[a] Liang Qiao,[a] Fernando Cortés-Salazar,[a] Andreas Lesch,[b] Gunther Wittstock [b] and Hubert H. Girault [a,].*

[a] Laboratoire d'Electrochimie Physique et Analytique, Ecole Polytechnique Fédérale de Lausanne, Station 6, CH-1015 Lausanne, Switzerland

[b] Department of Pure and Applied Chemistry, Center of Interface Science, Faculty of Mathematics and Natural Sciences, Carl von Ossietzky University of Oldenburg, D-26111 Oldenburg, Germany

[*] CORRESPONDING AUTHOR FOOTNOTE

EMAIL: hubert.girault@epfl.ch

Telephone number: +41-21-693 3145

Fax number: +41-21-693 3667

SI-1. ESI-MS experimental details

Figure S-1 demonstrates the ESI emitter microchip consisting of two open microchannels (100 μm × 50 μm) for pumping analyte and buffer solution, and an electrode used as anode for mass-spectrometer. The key advantage of the microchip design is the proximity of the electrode to the tip of ESI microchip and the possibility to tune fluidic flowrates in order to circumvent intricacies in MS detection attributed to the presence of air bubbles. The stability of the electrospray was achieved by setting flow rate for pushing sheath buffer to 40 $\mu L \cdot h^{-1}$ while the analyte was infused at 20 $\mu L \cdot h^{-1}$.

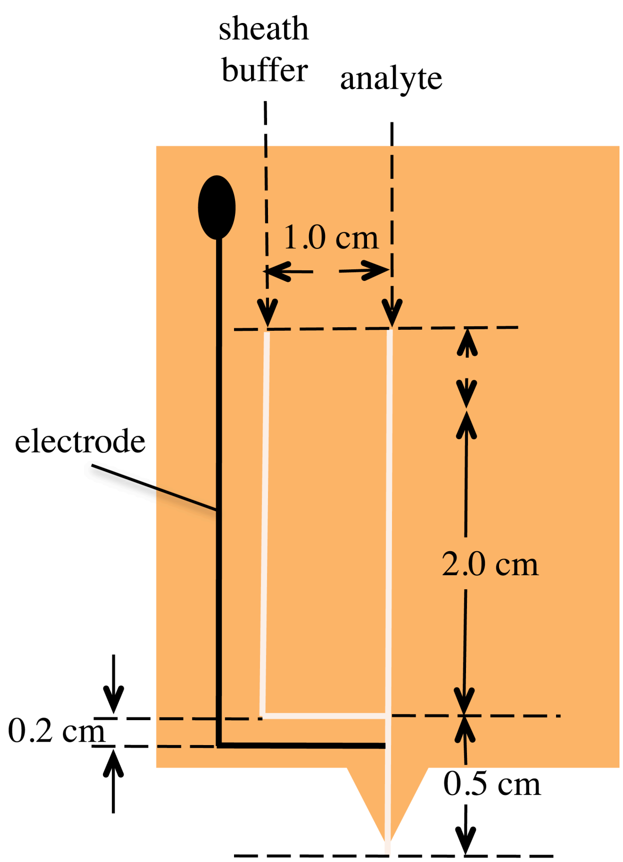


Figure S-1. Schematic representation of an ESI microchip.

In order to correlate amperometric and MS data during parallel SECM/ESI-MS experiments the substrate for enzymatic reaction PAPP was delivered to the probe tip along with lysine (Lys) that worked as internal standard with constant concentration in the microfluidic block for MS quantification of PAP since the two compounds have very close isoelectric point (9.47 for Lys and estimated at 9.6 for PAP) and molecular weight (146.19 and 109.13 for Lys and PAP, respectively) giving similar ionization efficiency under ESI conditions. PAP generated at SECM probe was delivered with Lys to the ESI-MS by the push-pull scanner. The peak intensity ratio between PAP and Lys in the mass spectrum is proportional to the amount of PAP and then relates to the SECM probe current. The starting and the end points for ESI-MS line scans were identified by monitoring the ion current attributed to protonated form of Lys because the delivery of Lys was started and finished immediately before and after the scanning, respectively. Following at the same time the ion current for target analyte PAP the SECM and ESI-MS data were correlated.

SI-2. Finite element simulations of SECM/MS line scans with push-pull microfluidic probe

The computational model assumes the probe (parallelepiped with dimensions 125 μm × 500 μm × 2128 μm) in a box-shaped domain (3000 μm × 3000 μm × 2000 μm) that represents a solution bulk (Figure S-2a). The active area of the microelectrode was approximated to a quarter-moon shape (*i.e.* 20 μm depth and 40 μm width) and the simulated microchannels had a shape of equilateral triangle with side length of 20 μm (Figure S-2b). The probe was in a contact with the substrate at an inclination angle equal to 70 degrees.

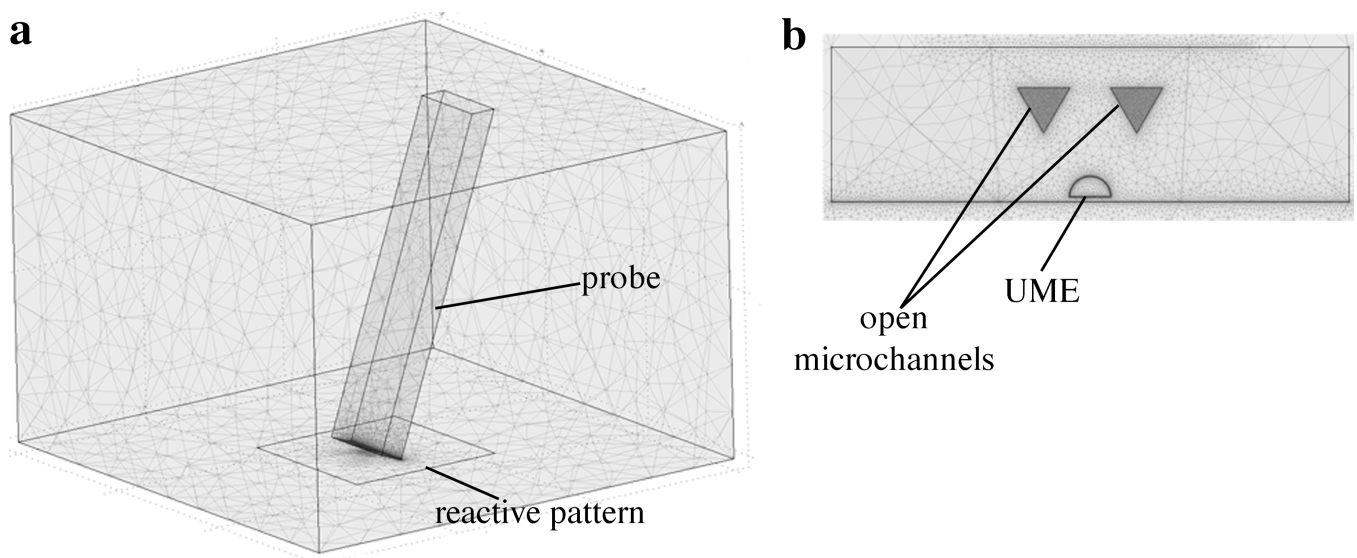


Figure S-2. General representation of a computational domain with mesh (a) and magnification of an exposed tip area (b).

The mesh size was refined down to the value of 300 nm at the edges of the microelectrode and to 700 nm at the microchannel opening boundary. Typical mesh consisted of ≈ 60,000 mesh points corresponding to approximately 340,000 tetrahedral mesh elements.

In this work we were solving Navier-Stokes and diffusion-convection steady-state equations (neglecting migration under electric field contribution) in sequential manner, assuming the electrochemical reaction of redox mediator *p*-aminophenol *PAP* to *p*-quinonimine PQI which takes place at the tip

$$PAP - e^{-} \xrightarrow{k_1} PQI$$

with kinetic rate constant $k_1 = 10^6$ m s^{-1}. These redox active species PAP were generated at the active area on a substrate (1 mm^2 squared region, with the heterogeneous rate constant $k_2 = 10^{-3}$ m s^{-1}) from PAPP molecules delivered from a pushing microchannel

$$PAPP \xrightarrow{k_2} PAP$$

All these chemical species are initially absent in the bulk electrolyte solution and are assumed to have the same value of diffusion coefficient $D = 7.1\ 10^{-10}$ m^2 s^{-1}. The fluid's properties (density $\rho = 1000$ kg m^{-3}, dynamic viscosity $\eta = 1$ mPa s) in these simulations are taken as of pure water and are simulated as independent from changes of species concentrations. The pushing flowrate was set to a moderate value of 12 µL h^{-1}. The boundary conditions used in these simulations are listed in the Table S-1.

Table S-1. Boundary conditions for FEM simulations (**n** denotes the vector normal to the surface).

Surface	**Boundary condition: Navier-Stokes**	**Boundary condition: diffusion-convection PAP**	**Boundary condition: diffusion-convection PAPP**
Active surface of electrode	Wall, no slip, $v_f = 0$	Flux, $-\mathbf{n} \bullet (D\nabla c_{PAP} - v_f\, c_{PAP}) = -k_1\, c_{PAP}$	Insulation, $-\mathbf{n} \bullet (D\nabla c_{PAPP} - v_f\, c_{PAPP}) = 0$
Body of the probe	Wall, no slip, $v_f = 0$	Insulation, $-\mathbf{n} \bullet (D\nabla c_{PAP} - v_f\, c_{PAP}) = 0$	Insulation, $-\mathbf{n} \bullet (D\nabla c_{PAPP} - v_f\, c_{PAPP}) = 0$
Box planes: top and sides	Wall, no slip, $v_f = 0$	Concentration, $c_{PAP} = 0$	Concentration, $c_{PAPP} = 0$
Box planes: bottom (except reactive pattern)	Wall, no slip, $v_f = 0$	Insulation, $-\mathbf{n} \bullet (D\nabla c_{PAP} - v_f\, c_{PAP}) = 0$	Insulation, $-\mathbf{n} \bullet (D\nabla c_{PAPP} - v_f\, c_{PAPP}) = 0$

Box planes: reactive pattern	Wall, no slip, $v_f = 0$	Flux, $-\mathbf{n} \bullet (D\nabla c_{PAP} - v_f\, c_{PAP}) = k_2\, c_{PAPP}$	Flux, $-\mathbf{n} \bullet (D\nabla c_{PAPP} - v_f\, c_{PAPP}) = -k_2\, c_{PAPP}$
Pushing microchannel	Inlet, fluid velocity $v_f = -\mathbf{n}\, v_{f0}$	Insulation, $-\mathbf{n} \bullet (D\nabla c_{PAP} - v_f\, c_{PAP}) = 0$	Concentration, $c_{PAPP} = 0$
Aspiration microchannel	Outlet, pressure $p = 0$;	Convective flux, $\mathbf{n} \bullet D\nabla c_{PAP} = 0$	Convective flux, $\mathbf{n} \bullet D\nabla c_{PAPP} = 0$

Herein D, v_f, v_{f0}, c_{PAP}, c_{PAPP} denote diffusion coefficient, fluid velocity (as variable), fluid velocity (as constant parameter), concentrations of PAP and PAPP, respectively.

Numerical solution of the system of differential equations was made using direct linear system solver UMFPACK with a relative error tolerance of 1×10^{-8}, using "stored solution options". This significantly reduces the RAM amount required for simulation and allows the numerical solution to converge, which is particularly difficult with coupled Navier-Stokes and diffusion-convection equations. The numerical description of FEM simulations is summarized in relevant COMSOL report file (SI-5).

SI-3. Simulation of a mixing processes in a capillary

These simulations were aimed to show the influence of convection and diffusion on the mixing process inside a 100 μm ID capillary of 5 cm length. This mixing process is extremely undesired during transport of analyte from the substrate into detection unit during push-pull scanning experiments as it leads to the loss of spatial resolution.

In this simulation we used a similar strategy as in the previous section, *i.e.* the computation of numerical solution of transient diffusion-convection equation on top of presolved steady-state Navier-Stokes equation using "stored solution " option available in COMSOL 3.5a. Typically, boundary conditions were setting inlet and outlet boundary conditions at the extremes of the capillary (simulated in 2D axisymmetric mode), no slip condition at the wall and insulation conditions for convection-diffusion (except convective flux condition assuming absence of diffusion at the outlet). The numerical description of FEM simulations is summarized in relevant COMSOL report file (SI-6).

Two plugs of equal concentration (c_0 = 1 mM) of analyte with $D = 1\ 10^{-9}\ m^2\ s^{-1}$ were located at the inlet of a capillary. Each plug was simulated as a subdomain of 1 mm length, the plugs were separated by 1 mm of pure aqueous solution (Figure S-3a).

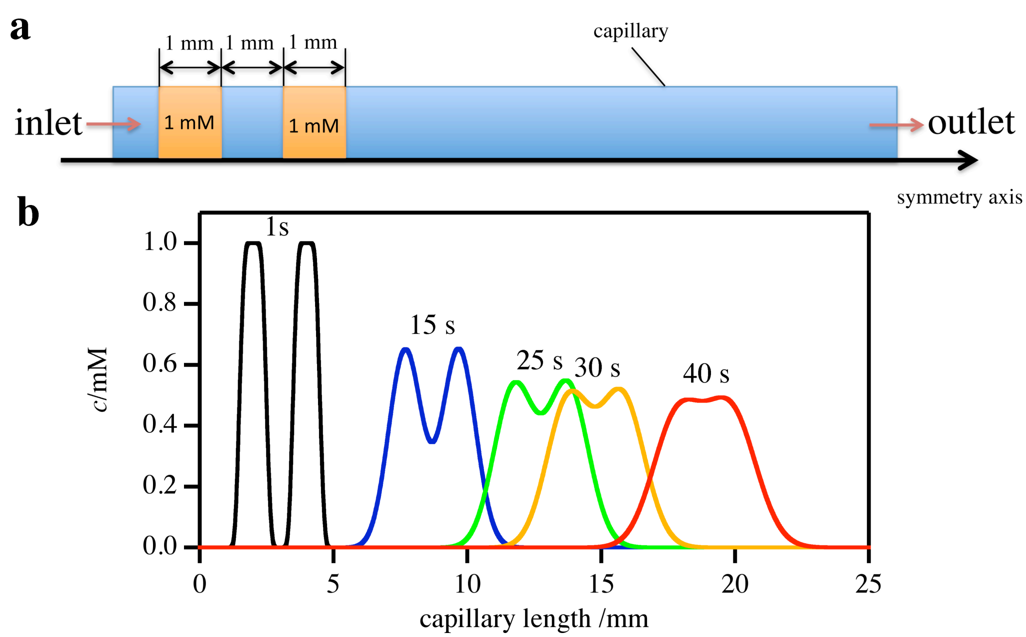


Figure S-3. Convection-diffusion mixing in the capillary. a) Schematic representation of a computational domain at the initial (t = 0) conditions. b) The concentration profiles of two analyte plugs. The movement of plugs is represented as overlay of graphs demonstrating the concentration profile along symmetry axis at specified times.

Figure S-3b demonstrates the result of numerical computations showing the evolution of plug concentration along the capillary. As can be seen, when using given parameters and even at moderate flowrates the parabolic flow profile within microcapillary leads to a very fast loss of spatial resolution. For example, when plugs cross a path of only 2 cm, the two equiconcentration zones could not be distinguished anymore.

SI-4. Push-pull scanning experiments over delicate samples

Figure S-4 demonstrates the advantages of a push-pull probes for SECM investigations over delicate samples. The image on the left shows the 40 nm Cu on glass substrate with a developed fingerprint after scanning with push-pull probe (remains unchanged) and the one on the right demonstrates the substrate destruction during SECM scanning under a thick electrolyte layer. As can be seen, the thin Cu layer was removed from a glass slide most likely due to oxidation of copper in the presence of dissolved oxygen.

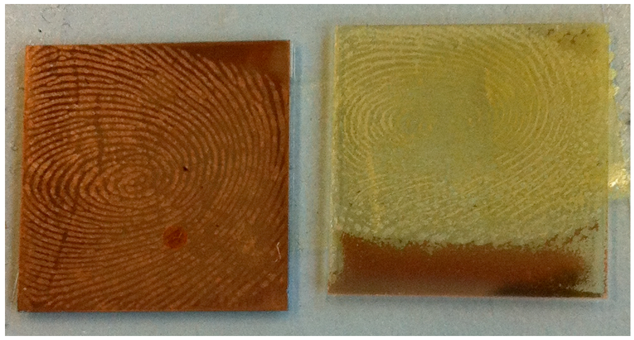
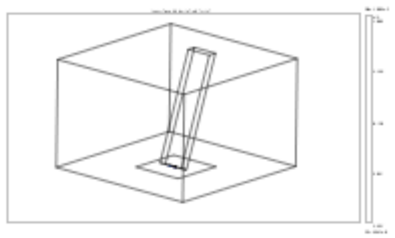


Figure S-4. Cyanoacrylate fumed human fingerprints on 40 nm Cu on a glass substrate. Untreated (left) and after immersion in 2 mM $FcCH_2OH$ and 40 mM KNO_3 solution for 1 h (right) fingerprints.

SI-5. COMSOL report file for finite element simulations of SECM/MS line scans with push-pull microfluidic probe

The generated COMSOL report file includes extensive details of numerical model used in the FEM simulations.

COMSOL Model Report



1. Table of Contents

2. Model Properties

Property	Value
Model name	
Author	
Company	
Department	
Reference	
URL	
Saved date	Mar 22, 2012 2:39:44 PM
Creation date	Feb 13, 2012 12:06:49 AM
COMSOL version	COMSOL 3.5.0.603

File name: /home/dmitry/Desktop/Fluidics TEST/PAPP/LineScan/x scan new/1500.mph

Application modes and modules used in this model:

- Geom1 (3D)
  - Incompressible Navier-Stokes
  - Convection and Diffusion
  - Convection and Diffusion

3. Constants

Name	Expression	Value	Description
c0	10[mmol/l]		bulk concentration of Ox
k1	10^6[m/s]		rate constant at UME
Vv	0.2[uL/min]		Volumic inlet flowrate
S	0.5*3.14*20[um]*20[um]		Surface
Visc	1[mPa*s]		Viscosity
DiffPAP	7.1e-10[m^2/s]		diffusion constant of PAP
k2	10e-3[m/s]		reaction rate const at substrate

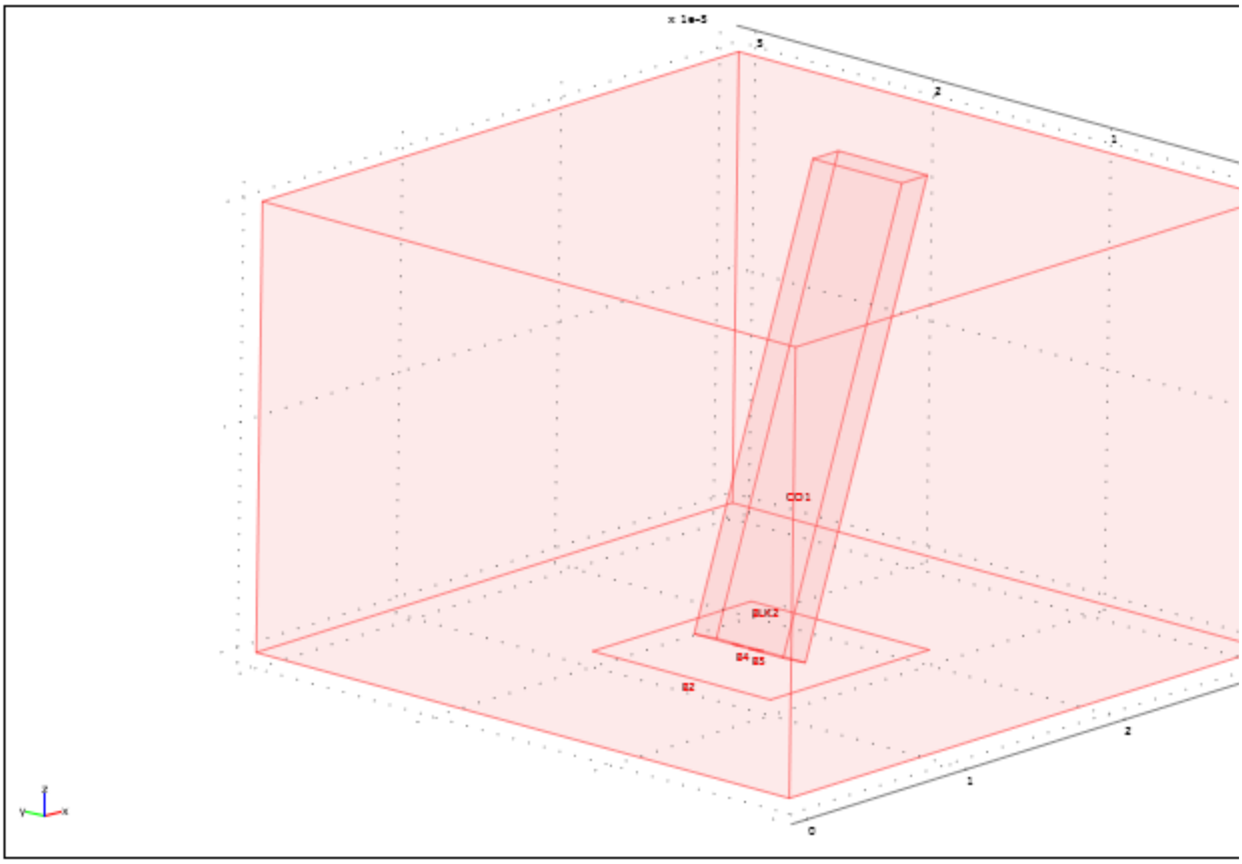
4. Global Expressions

Name	Expression	Unit	Description
vreact	k1*cPAP	mol/(m^2*s)	reaction at UME

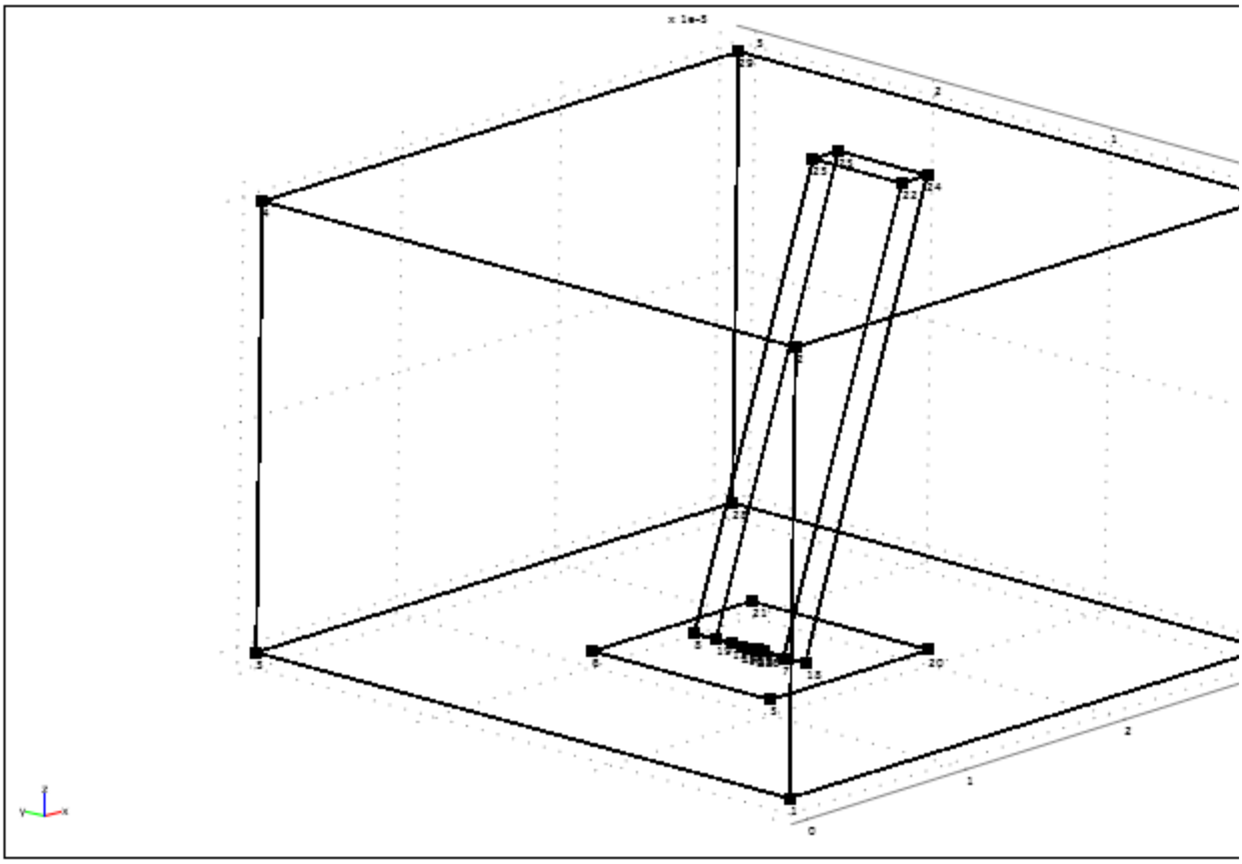
5. Geometry

Number of geometries: 1

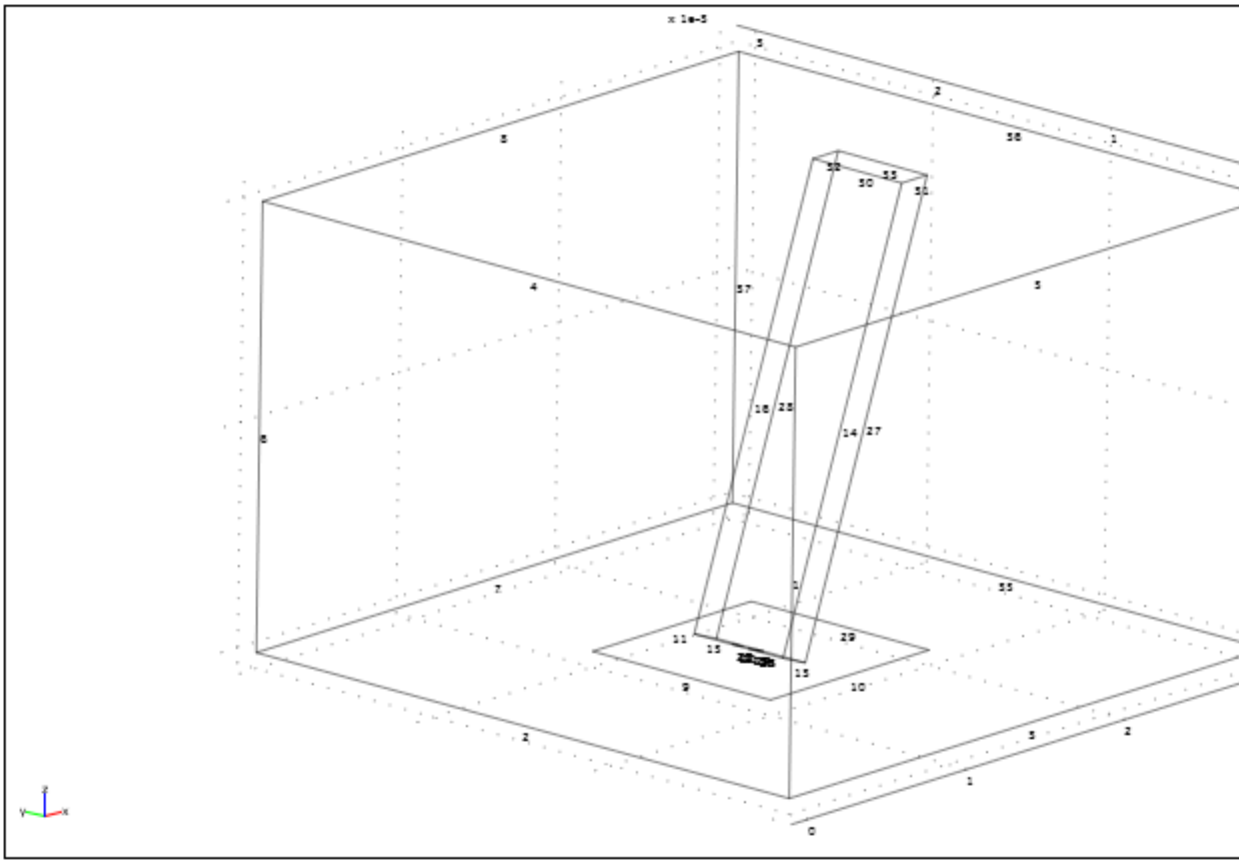
5.1. Geom1



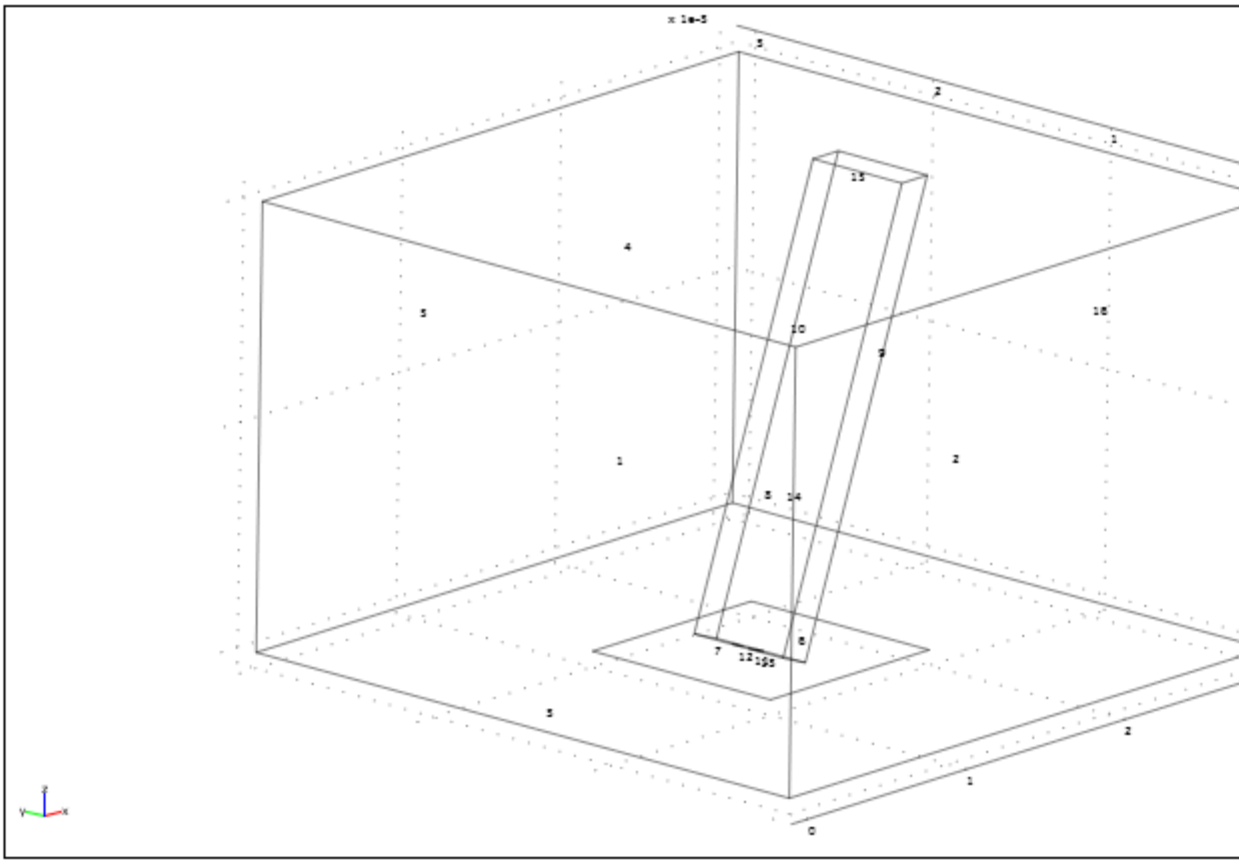
5.1.1. Point mode



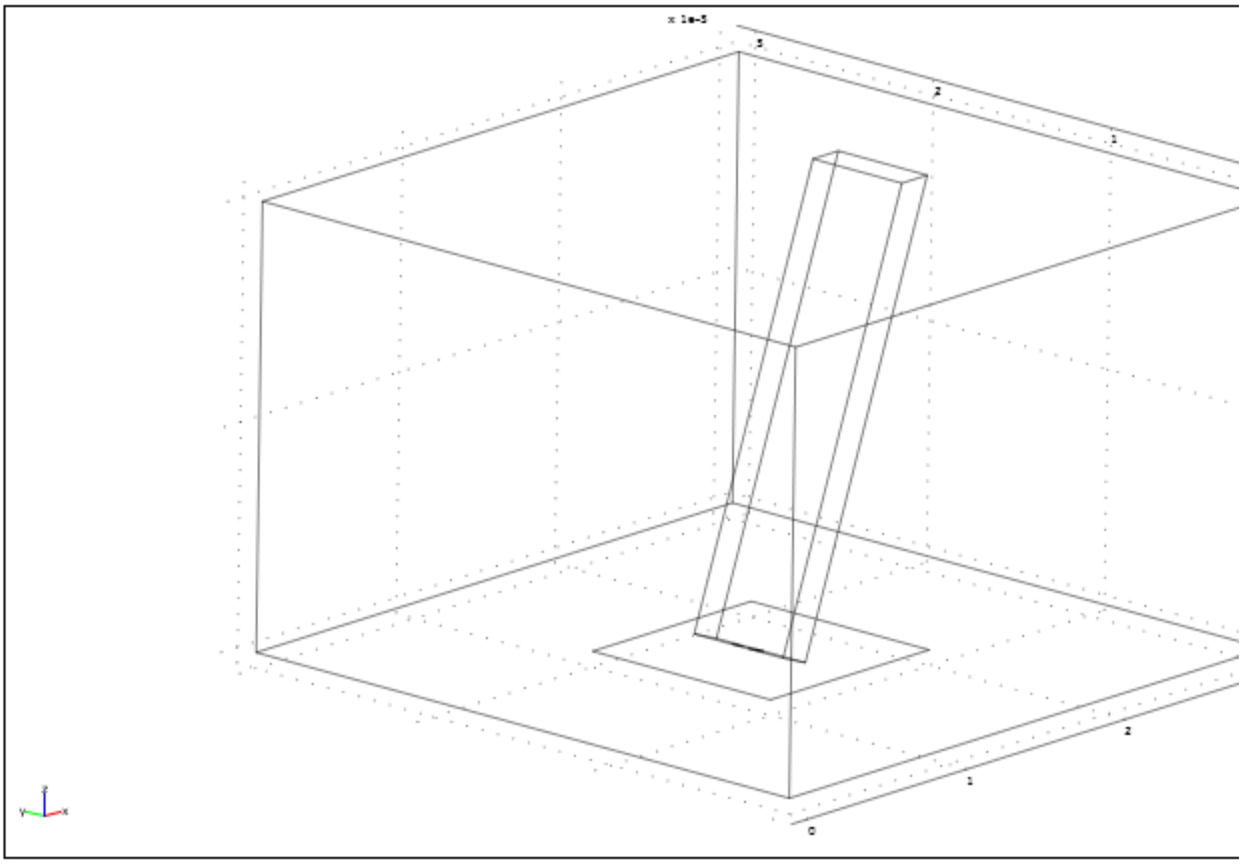
5.1.2. Edge mode



5.1.3. Boundary mode



5.1.4. Subdomain mode



6. Geom1

Space dimensions: 3D

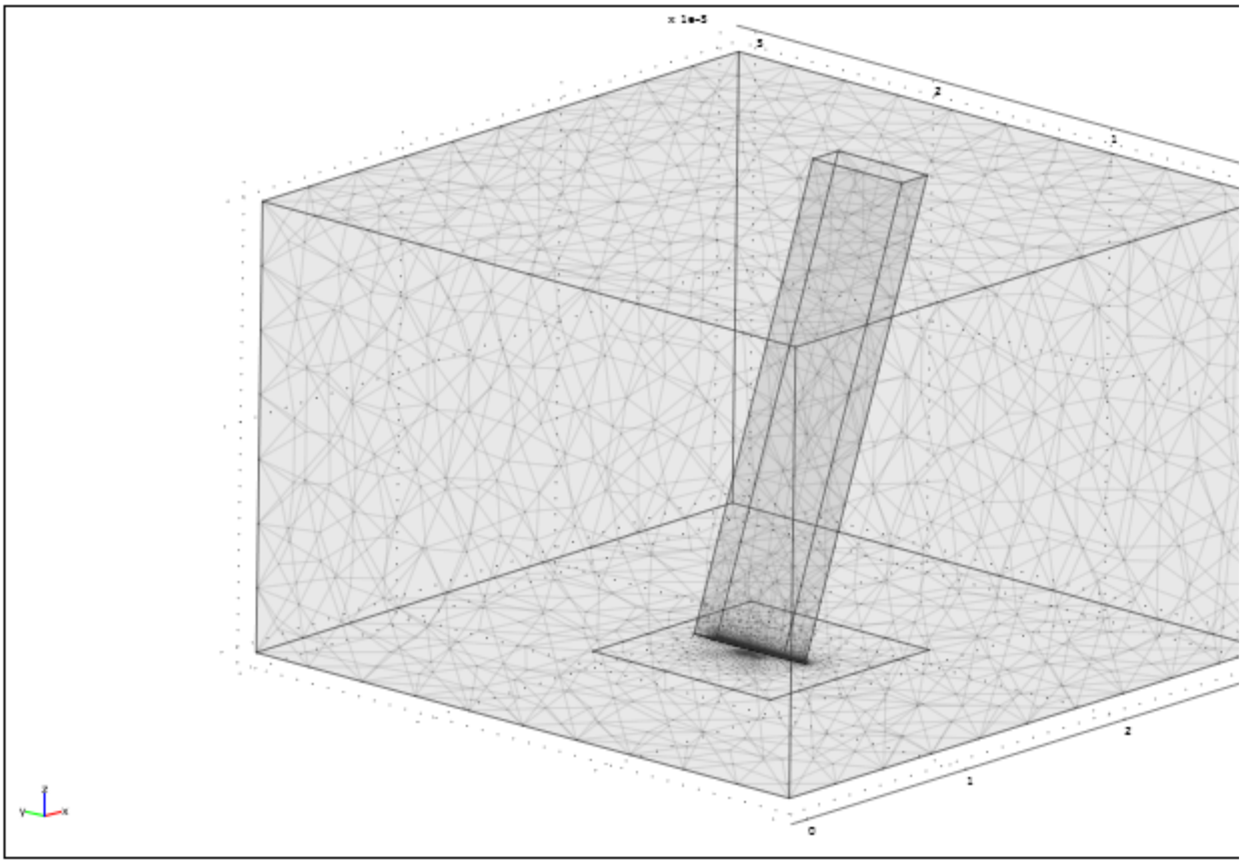
Independent variables: x, y, z

6.1. Mesh

6.1.1. Mesh Statistics

Number of degrees of freedom	1435827
Number of mesh points	58554
Number of elements	334186
Tetrahedral	334186
Prism	0
Hexahedral	0
Number of boundary elements	42148

Triangular	42148
Quadrilateral	0
Number of edge elements	1605
Number of vertex elements	29
Minimum element quality	0.016
Element volume ratio	0



6.2. Application Mode: Incompressible Navier-Stokes (ns)

Application mode type: Incompressible Navier-Stokes

Application mode name: ns

6.2.1. Scalar Variables

Name	Variable	Value	Unit	Description
visc_vel_fact	visc_vel_fact_ns	10	1	Viscous velocity factor

6.2.2. Application Mode Properties

Property	**Value**
Default element type	Lagrange - P_2 P_1
Analysis type	Stationary
Corner smoothing	Off
Frame	Frame (ref)
Weak constraints	Off
Constraint type	Ideal

6.2.3. Variables

Dependent variables: u, v, w, p, nxw, nyw, nzw

Shape functions: shlag(2,'u'), shlag(2,'v'), shlag(2,'w'), shlag(1,'p')

Interior boundaries not active

6.2.4. Boundary Settings

Boundary		1-10, 13-14	11	12
Type		Wall	Outlet	Inlet
Normal inflow velocity (U0in)	m/s	1	1	**Vv/S**

Boundary		16
Type		Wall
Normal inflow velocity (U0in)	m/s	**20e-6**

6.2.5. Subdomain Settings

Subdomain		1
Integration order (gporder)		**4 4 4 2**
Constraint order (cporder)		**2 2 2 1**
Density (rho)	kg/m^3	**1000**
Dynamic viscosity (eta)	Pa·s	**Visc**

6.3. Application Mode: Convection and Diffusion (cd)

Application mode type: Convection and Diffusion

Application mode name: cd

6.3.1. Application Mode Properties

Property	**Value**
Default element type	Lagrange - Quadratic
Analysis type	Stationary

Equation form	Non-conservative
Frame	Frame (ref)
Weak constraints	Off
Constraint type	Ideal

6.3.2. Variables

Dependent variables: cPAP

Shape functions: shlag(2,'cPAP')

Interior boundaries not active

6.3.3. Boundary Settings

Boundary		1-2, 4-5, 16	3, 7-10, 14	6
Type		Concentration	Insulation/Symmetry	Flux
Inward flux (N)	$mol/(m^2 \cdot s)$	0	0	**cPAPP*k2**

Boundary		11	12	13
Type		Convective flux	Insulation/Symmetry	Flux
Inward flux (N)	$mol/(m^2 \cdot s)$	0	**c0*U_ns**	**-vreact**

6.3.4. Subdomain Settings

Subdomain		1
Diffusion coefficient (D)	m^2/s	**DiffPAP**
x-velocity (u)	m/s	**u**
y-velocity (v)	m/s	**v**
z-velocity (w)	m/s	**w**

6.4. Application Mode: Convection and Diffusion (cd2)

Application mode type: Convection and Diffusion

Application mode name: cd2

6.4.1. Application Mode Properties

Property	**Value**
Default element type	Lagrange - Quadratic
Analysis type	Stationary
Equation form	Non-conservative
Frame	Frame (ref)
Weak constraints	Off
Constraint type	Ideal

6.4.2. Variables

Dependent variables: cPAPP

Shape functions: shlag(2,'cPAPP')

Interior boundaries not active

6.4.3. Boundary Settings

Boundary		1-2, 4-5, 16	3, 7-10, 13-14	6
Type		Concentration	Insulation/Symmetry	Flux
Inward flux (N)	$mol/(m^2 \cdot s)$	0	0	**-cPAPP*k2**
Concentration (c0)	mol/m^3	0	0	0

Boundary		11	12
Type		Convective flux	Concentration
Inward flux (N)	$mol/(m^2 \cdot s)$	0	**c0*U_ns**
Concentration (c0)	mol/m^3	0	**c0**

6.4.4. Subdomain Settings

Subdomain		1
Diffusion coefficient (D)	m^2/s	**DiffPAP**
x-velocity (u)	m/s	**u**
y-velocity (v)	m/s	**v**
z-velocity (w)	m/s	**w**

7. Solver Settings

Solve using a script: off

Analysis type	Stationary
Auto select solver	On
Solver	Stationary
Solution form	Automatic
Symmetric	auto
Adaptive mesh refinement	Off
Optimization/Sensitivity	Off
Plot while solving	Off

7.1. Direct (UMFPACK)

Solver type: Linear system solver

Parameter	Value
Pivot threshold	0.1

Memory allocation factor	0.7

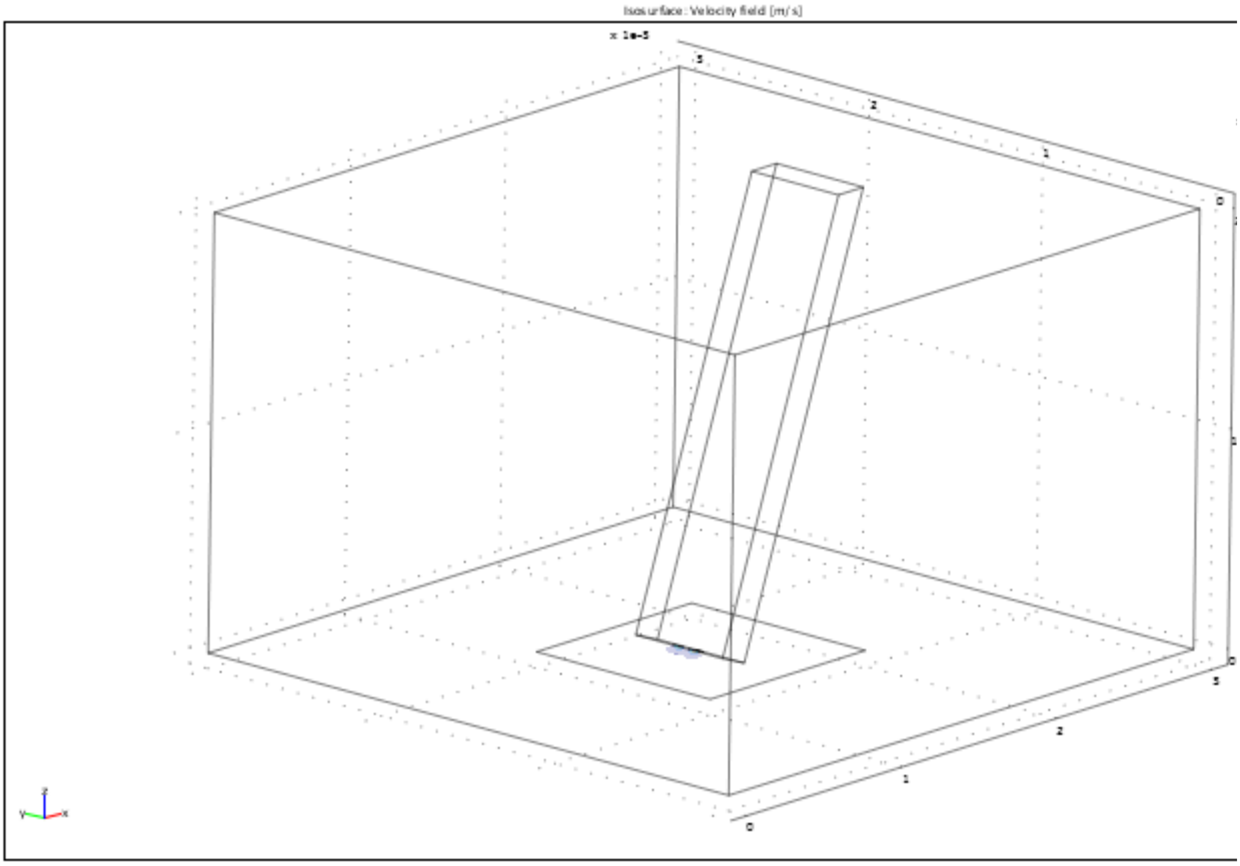
7.2. Stationary

Parameter	Value
Linearity	Automatic
Relative tolerance	1.0E-8
Maximum number of iterations	25
Manual tuning of damping parameters	Off
Highly nonlinear problem	Off
Initial damping factor	1.0
Minimum damping factor	1.0E-4
Restriction for step size update	10.0

7.3. Advanced

Parameter	Value
Constraint handling method	Elimination
Null-space function	Automatic
Automatic assembly block size	On
Assembly block size	1000
Use Hermitian transpose of constraint matrix and in symmetry detection	Off
Use complex functions with real input	Off
Stop if error due to undefined operation	On
Store solution on file	Off
Type of scaling	Automatic
Manual scaling	
Row equilibration	On
Manual control of reassembly	Off
Load constant	On
Constraint constant	On
Mass constant	On
Damping (mass) constant	On
Jacobian constant	On
Constraint Jacobian constant	On

8. Postprocessing



9. Variables

9.1. Boundary

9.1.1. Boundary 1-14, 16

Name	Description	Unit	Expression
K_x_ns	Viscous force per area, x component	Pa	eta_ns * (2 * nx_ns * ux+ny_ns * (uy+vx)+nz_ns * (uz+wx))
T_x_ns	Total force per area, x component	Pa	-nx_ns * p+2 * nx_ns * eta_ns * ux+ny_ns * eta_ns * (uy+vx)+nz_ns * eta_ns * (uz+wx)
K_y_ns	Viscous force per area, y component	Pa	eta_ns * (nx_ns * (vx+uy)+2 * ny_ns * vy+nz_ns * (vz+wy))

T_y_ns	Total force per area, y component	Pa	-ny_ns * p+nx_ns * eta_ns * (vx+uy)+2 * ny_ns * eta_ns * vy+nz_ns * eta_ns * (vz+wy)
K_z_ns	Viscous force per area, z component	Pa	eta_ns * (nx_ns * (wx+uz)+ny_ns * (wy+vz)+2 * nz_ns * wz)
T_z_ns	Total force per area, z component	Pa	-nz_ns * p+nx_ns * eta_ns * (wx+uz)+ny_ns * eta_ns * (wy+vz)+2 * nz_ns * eta_ns * wz
ndflux_cPAP_cd	Normal diffusive flux, cPAP	mol/(m^2*s)	nx_cd * dflux_cPAP_x_cd+ny_cd * dflux_cPAP_y_cd+nz_cd * dflux_cPAP_z_cd
ncflux_cPAP_cd	Normal convective flux, cPAP	mol/(m^2*s)	nx_cd * cflux_cPAP_x_cd+ny_cd * cflux_cPAP_y_cd+nz_cd * cflux_cPAP_z_cd
ntflux_cPAP_cd	Normal total flux, cPAP	mol/(m^2*s)	nx_cd * tflux_cPAP_x_cd+ny_cd * tflux_cPAP_y_cd+nz_cd * tflux_cPAP_z_cd
ndflux_cPAPP_cd2	Normal diffusive flux, cPAPP	mol/(m^2*s)	nx_cd2 * dflux_cPAPP_x_cd2+ny_cd2 * dflux_cPAPP_y_cd2+nz_cd2 * dflux_cPAPP_z_cd2
ncflux_cPAPP_cd2	Normal convective flux, cPAPP	mol/(m^2*s)	nx_cd2 * cflux_cPAPP_x_cd2+ny_cd2 * cflux_cPAPP_y_cd2+nz_cd2 * cflux_cPAPP_z_cd2
ntflux_cPAPP_cd2	Normal total flux, cPAPP	mol/(m^2*s)	nx_cd2 * tflux_cPAPP_x_cd2+ny_cd2 * tflux_cPAPP_y_cd2+nz_cd2 * tflux_cPAPP_z_cd2

9.1.2. Boundary 15

Name	Description	Unit	Expression
K_x_ns	Viscous force per area, x component	Pa	
T_x_ns	Total force per area, x component	Pa	
K_y_ns	Viscous force per area, y component	Pa	
T_y_ns	Total force per area, y component	Pa	
K_z_ns	Viscous force per area, z component	Pa	
T_z_ns	Total force per area, z component	Pa	
ndflux_cPAP_cd	Normal diffusive flux, cPAP	mol/(m^2*s)	
ncflux_cPAP_cd	Normal convective flux, cPAP	mol/(m^2*s)	
ntflux_cPAP_cd	Normal total flux, cPAP	mol/(m^2*s)	
ndflux_cPAPP_cd2	Normal diffusive flux, cPAPP	mol/(m^2*s)	
ncflux_cPAPP_cd2	Normal convective flux, cPAPP	mol/(m^2*s)	
ntflux_cPAPP_cd2	Normal total flux, cPAPP	mol/(m^2*s)	

9.2. Subdomain

9.2.1. Subdomain 1

Name	Description	Unit	Expression
U_ns	Velocity field	m/s	sqrt(u^2+v^2+w^2)
Vx_ns	Vorticity, x component	1/s	wy-vz
Vy_ns	Vorticity, y component	1/s	uz-wx
Vz_ns	Vorticity, z component	1/s	vx-uy
V_ns	Vorticity	1/s	sqrt(Vx_ns^2+Vy_ns^2+Vz_ns^2)
divU_ns	Divergence of velocity field	1/s	ux+vy+wz
cellRe_ns	Cell Reynolds number	1	rho_ns * U_ns * h/eta_ns
res_u_ns	Equation residual for u	N/m^3	rho_ns * (u * ux+v * uy+w * uz)+px-F_x_ uxx+uyy+vxy+uzz+wxz))
res_v_ns	Equation residual for v	N/m^3	rho_ns * (u * vx+v * vy+w * vz)+py-F_y_ vyy+vzz+wyz))
res_w_ns	Equation residual for w	N/m^3	rho_ns * (u * wx+v * wy+w * wz)+pz-F_z (wxx+uzx+wyy+vzy+2 * wzz))
beta_x_ns	Convective field, x component	kg/(m^2*s)	rho_ns * u
beta_y_ns	Convective field, y component	kg/(m^2*s)	rho_ns * v
beta_z_ns	Convective field, z component	kg/(m^2*s)	rho_ns * w
Dm_ns	Mean diffusion coefficient	Pa*s	eta_ns
da_ns	Total time scale factor	kg/m^3	rho_ns
taum_ns	GLS time-scale	m^3*s/kg	nojac(1/max(2 * rho_ns * sqrt(emetric(u,
tauc_ns	GLS time-scale	m^2/s	0.5 * nojac(if(u^2+v^2+w^2
res_p_ns	Equation residual for p	kg/(m^3*s)	rho_ns * divU_ns
grad_cPAP_x_cd	Concentration gradient, cPAP, x component	mol/m^4	cPAPx
dflux_cPAP_x_cd	Diffusive flux, cPAP, x component	mol/(m^2*s)	-Dxx_cPAP_cd * cPAPx-Dxy_cPAP_cd *
cflux_cPAP_x_cd	Convective flux, cPAP, x component	mol/(m^2*s)	cPAP * u_cPAP_cd

tflux_cPAP_x_cd	Total flux, cPAP, x component	mol/(m^2*s)	dflux_cPAP_x_cd+cflux_cPAP_x_cd
grad_cPAP_y_cd	Concentration gradient, cPAP, y component	mol/m^4	cPAPy
dflux_cPAP_y_cd	Diffusive flux, cPAP, y component	mol/(m^2*s)	-Dyx_cPAP_cd * cPAPx-Dyy_cPAP_cd *
cflux_cPAP_y_cd	Convective flux, cPAP, y component	mol/(m^2*s)	cPAP * v_cPAP_cd
tflux_cPAP_y_cd	Total flux, cPAP, y component	mol/(m^2*s)	dflux_cPAP_y_cd+cflux_cPAP_y_cd
grad_cPAP_z_cd	Concentration gradient, cPAP, z component	mol/m^4	cPAPz
dflux_cPAP_z_cd	Diffusive flux, cPAP, z component	mol/(m^2*s)	-Dzx_cPAP_cd * cPAPx-Dzy_cPAP_cd *
cflux_cPAP_z_cd	Convective flux, cPAP, z component	mol/(m^2*s)	cPAP * w_cPAP_cd
tflux_cPAP_z_cd	Total flux, cPAP, z component	mol/(m^2*s)	dflux_cPAP_z_cd+cflux_cPAP_z_cd
beta_cPAP_x_cd	Convective field, cPAP, x component	m/s	u_cPAP_cd
beta_cPAP_y_cd	Convective field, cPAP, y component	m/s	v_cPAP_cd
beta_cPAP_z_cd	Convective field, cPAP, z component	m/s	w_cPAP_cd
grad_cPAP_cd	Concentration gradient, cPAP	mol/m^4	sqrt(grad_cPAP_x_cd^2+grad_cPAP_y_
dflux_cPAP_cd	Diffusive flux, cPAP	mol/(m^2*s)	sqrt(dflux_cPAP_x_cd^2+dflux_cPAP_y_
cflux_cPAP_cd	Convective flux, cPAP	mol/(m^2*s)	sqrt(cflux_cPAP_x_cd^2+cflux_cPAP_y_
tflux_cPAP_cd	Total flux, cPAP	mol/(m^2*s)	sqrt(tflux_cPAP_x_cd^2+tflux_cPAP_y_c
cellPe_cPAP_cd	Cell Peclet number, cPAP	1	h * sqrt(beta_cPAP_x_cd^2+beta_cPAP_

Dm_cPAP_cd	Mean diffusion coefficient, cPAP	m^2/s	(Dxx_cPAP_cd * u_cPAP_cd^2+Dxy_cP/ u_cPAP_cd * w_cPAP_cd+Dyx_cPAP_c v_cPAP_cd^2+Dyz_cPAP_cd * v_cPAP_ u_cPAP_cd+Dzy_cPAP_cd * w_cPAP_c w_cPAP_cd^2)/(u_cPAP_cd^2+v_cPAP_
res_cPAP_cd	Equation residual for cPAP	mol/(m^3*s)	-Dxx_cPAP_cd * cPAPxx-Dxy_cPAP_cd u_cPAP_cd-Dyx_cPAP_cd * cPAPyx-Dy cPAPyz+cPAPy * v_cPAP_cd-Dzx_cPAF Dzz_cPAP_cd * cPAPzz+cPAPz * w_cP/
res_sc_cPAP_cd	Shock capturing residual for cPAP	mol/(m^3*s)	cPAPx * u_cPAP_cd+cPAPy * v_cPAP_c
da_cPAP_cd	Total time scale factor, cPAP	1	Dts_cPAP_cd
grad_cPAPP_x_cd2	Concentration gradient, cPAPP, x component	mol/m^4	cPAPPx
dflux_cPAPP_x_cd2	Diffusive flux, cPAPP, x component	mol/(m^2*s)	-Dxx_cPAPP_cd2 * cPAPPx-Dxy_cPAPF
cflux_cPAPP_x_cd2	Convective flux, cPAPP, x component	mol/(m^2*s)	cPAPP * u_cPAPP_cd2
tflux_cPAPP_x_cd2	Total flux, cPAPP, x component	mol/(m^2*s)	dflux_cPAPP_x_cd2+cflux_cPAPP_x_cd
grad_cPAPP_y_cd2	Concentration gradient, cPAPP, y component	mol/m^4	cPAPPy
dflux_cPAPP_y_cd2	Diffusive flux, cPAPP, y component	mol/(m^2*s)	-Dyx_cPAPP_cd2 * cPAPPx-Dyy_cPAPF
cflux_cPAPP_y_cd2	Convective flux, cPAPP, y component	mol/(m^2*s)	cPAPP * v_cPAPP_cd2
tflux_cPAPP_y_cd2	Total flux, cPAPP, y component	mol/(m^2*s)	dflux_cPAPP_y_cd2+cflux_cPAPP_y_cd
grad_cPAPP_z_cd2	Concentration gradient, cPAPP, z component	mol/m^4	cPAPPz
dflux_cPAPP_z_cd2	Diffusive flux, cPAPP, z component	mol/(m^2*s)	-Dzx_cPAPP_cd2 * cPAPPx-Dzy_cPAPF

cflux_cPAPP_z_cd2	Convective flux, cPAPP, z component	mol/(m^2*s)	cPAPP * w_cPAPP_cd2
tflux_cPAPP_z_cd2	Total flux, cPAPP, z component	mol/(m^2*s)	dflux_cPAPP_z_cd2+cflux_cPAPP_z_cd
beta_cPAPP_x_cd2	Convective field, cPAPP, x component	m/s	u_cPAPP_cd2
beta_cPAPP_y_cd2	Convective field, cPAPP, y component	m/s	v_cPAPP_cd2
beta_cPAPP_z_cd2	Convective field, cPAPP, z component	m/s	w_cPAPP_cd2
grad_cPAPP_cd2	Concentration gradient, cPAPP	mol/m^4	sqrt(grad_cPAPP_x_cd2^2+grad_cPAPF
dflux_cPAPP_cd2	Diffusive flux, cPAPP	mol/(m^2*s)	sqrt(dflux_cPAPP_x_cd2^2+dflux_cPAPI
cflux_cPAPP_cd2	Convective flux, cPAPP	mol/(m^2*s)	sqrt(cflux_cPAPP_x_cd2^2+cflux_cPAPF
tflux_cPAPP_cd2	Total flux, cPAPP	mol/(m^2*s)	sqrt(tflux_cPAPP_x_cd2^2+tflux_cPAPP_
cellPe_cPAPP_cd2	Cell Peclet number, cPAPP	1	h * sqrt(beta_cPAPP_x_cd2^2+beta_cPAPF
Dm_cPAPP_cd2	Mean diffusion coefficient, cPAPP	m^2/s	(Dxx_cPAPP_cd2 * u_cPAPP_cd2^2+Dx v_cPAPP_cd2+Dxz_cPAPP_cd2 * u_cP/ v_cPAPP_cd2 * u_cPAPP_cd2+Dyy_cP/ v_cPAPP_cd2 * w_cPAPP_cd2+Dzx_cP. u_cPAPP_cd2+Dzy_cPAPP_cd2 * w_cP. w_cPAPP_cd2^2)/(u_cPAPP_cd2^2+v_c
res_cPAPP_cd2	Equation residual for cPAPP	mol/(m^3*s)	-Dxx_cPAPP_cd2 * cPAPPxx-Dxy_cPAP cPAPPxz+cPAPPx * u_cPAPP_cd2-Dyx_ cPAPPyy-Dyz_cPAPP_cd2 * cPAPPyz+c cPAPPzx-Dzy_cPAPP_cd2 * cPAPPzy-D w_cPAPP_cd2-R_cPAPP_cd2
res_sc_cPAPP_cd2	Shock capturing residual for cPAPP	mol/(m^3*s)	cPAPPx * u_cPAPP_cd2+cPAPPy * v_cF R_cPAPP_cd2
da_cPAPP_cd2	Total time scale factor, cPAPP	1	Dts_cPAPP_cd2

9.2.2. Subdomain 2

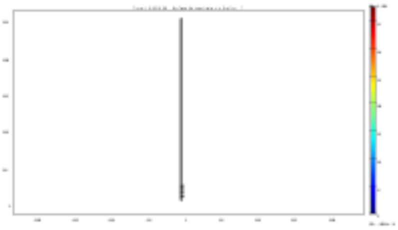
Name	Description	Unit	Expression
U_ns	Velocity field	m/s	
Vx_ns	Vorticity, x component	1/s	

Vy_ns	Vorticity, y component	1/s	
Vz_ns	Vorticity, z component	1/s	
V_ns	Vorticity	1/s	
divU_ns	Divergence of velocity field	1/s	
cellRe_ns	Cell Reynolds number	1	
res_u_ns	Equation residual for u	N/m^3	
res_v_ns	Equation residual for v	N/m^3	
res_w_ns	Equation residual for w	N/m^3	
beta_x_ns	Convective field, x component	kg/(m^2*s)	
beta_y_ns	Convective field, y component	kg/(m^2*s)	
beta_z_ns	Convective field, z component	kg/(m^2*s)	
Dm_ns	Mean diffusion coefficient	Pa*s	
da_ns	Total time scale factor	kg/m^3	
taum_ns	GLS time-scale	m^3*s/kg	
tauc_ns	GLS time-scale	m^2/s	
res_p_ns	Equation residual for p	kg/(m^3*s)	
grad_cPAP_x_cd	Concentration gradient, cPAP, x component	mol/m^4	
dflux_cPAP_x_cd	Diffusive flux, cPAP, x component	mol/(m^2*s)	
cflux_cPAP_x_cd	Convective flux, cPAP, x component	mol/(m^2*s)	
tflux_cPAP_x_cd	Total flux, cPAP, x component	mol/(m^2*s)	
grad_cPAP_y_cd	Concentration gradient, cPAP, y component	mol/m^4	
dflux_cPAP_y_cd	Diffusive flux, cPAP, y component	mol/(m^2*s)	
cflux_cPAP_y_cd	Convective flux, cPAP, y component	mol/(m^2*s)	
tflux_cPAP_y_cd	Total flux, cPAP, y component	mol/(m^2*s)	
grad_cPAP_z_cd	Concentration gradient, cPAP, z component	mol/m^4	
dflux_cPAP_z_cd	Diffusive flux, cPAP, z component	mol/(m^2*s)	
cflux_cPAP_z_cd	Convective flux, cPAP, z component	mol/(m^2*s)	
tflux_cPAP_z_cd	Total flux, cPAP, z component	mol/(m^2*s)	
beta_cPAP_x_cd	Convective field, cPAP, x component	m/s	
beta_cPAP_y_cd	Convective field, cPAP, y component	m/s	
beta_cPAP_z_cd	Convective field, cPAP, z component	m/s	
grad_cPAP_cd	Concentration gradient, cPAP	mol/m^4	
dflux_cPAP_cd	Diffusive flux, cPAP	mol/(m^2*s)	
cflux_cPAP_cd	Convective flux, cPAP	mol/(m^2*s)	
tflux_cPAP_cd	Total flux, cPAP	mol/(m^2*s)	
cellPe_cPAP_cd	Cell Peclet number, cPAP	1	
Dm_cPAP_cd	Mean diffusion coefficient, cPAP	m^2/s	
res_cPAP_cd	Equation residual for cPAP	mol/(m^3*s)	
res_sc_cPAP_cd	Shock capturing residual for cPAP	mol/(m^3*s)	
da_cPAP_cd	Total time scale factor, cPAP	1	
grad_cPAPP_x_cd2	Concentration gradient, cPAPP, x component	mol/m^4	
dflux_cPAPP_x_cd2	Diffusive flux, cPAPP, x component	mol/(m^2*s)	
cflux_cPAPP_x_cd2	Convective flux, cPAPP, x component	mol/(m^2*s)	

tflux_cPAPP_x_cd2	Total flux, cPAPP, x component	mol/(m^2*s)	
grad_cPAPP_y_cd2	Concentration gradient, cPAPP, y component	mol/m^4	
dflux_cPAPP_y_cd2	Diffusive flux, cPAPP, y component	mol/(m^2*s)	
cflux_cPAPP_y_cd2	Convective flux, cPAPP, y component	mol/(m^2*s)	
tflux_cPAPP_y_cd2	Total flux, cPAPP, y component	mol/(m^2*s)	
grad_cPAPP_z_cd2	Concentration gradient, cPAPP, z component	mol/m^4	
dflux_cPAPP_z_cd2	Diffusive flux, cPAPP, z component	mol/(m^2*s)	
cflux_cPAPP_z_cd2	Convective flux, cPAPP, z component	mol/(m^2*s)	
tflux_cPAPP_z_cd2	Total flux, cPAPP, z component	mol/(m^2*s)	
beta_cPAPP_x_cd2	Convective field, cPAPP, x component	m/s	
beta_cPAPP_y_cd2	Convective field, cPAPP, y component	m/s	
beta_cPAPP_z_cd2	Convective field, cPAPP, z component	m/s	
grad_cPAPP_cd2	Concentration gradient, cPAPP	mol/m^4	
dflux_cPAPP_cd2	Diffusive flux, cPAPP	mol/(m^2*s)	
cflux_cPAPP_cd2	Convective flux, cPAPP	mol/(m^2*s)	
tflux_cPAPP_cd2	Total flux, cPAPP	mol/(m^2*s)	
cellPe_cPAPP_cd2	Cell Peclet number, cPAPP	1	
Dm_cPAPP_cd2	Mean diffusion coefficient, cPAPP	m^2/s	
res_cPAPP_cd2	Equation residual for cPAPP	mol/(m^3*s)	
res_sc_cPAPP_cd2	Shock capturing residual for cPAPP	mol/(m^3*s)	
da_cPAPP_cd2	Total time scale factor, cPAPP	1	

SI-6. COMSOL report file for simulation of a mixing processes in a capillary

COMSOL Model Report



1. Table of Contents

2. Model Properties

Property	Value
Model name	
Author	
Company	
Department	
Reference	
URL	
Saved date	Mar 14, 2012 11:38:16 AM
Creation date	Mar 13, 2012 6:11:42 PM
COMSOL version	COMSOL 3.5.0.603

File name: /home/dmitry/Desktop/Mixing.mph

Application modes and modules used in this model:

- Geom1 (Axial symmetry (2D))
  - Convection and Diffusion
  - Incompressible Navier-Stokes (Chemical Engineering Module)

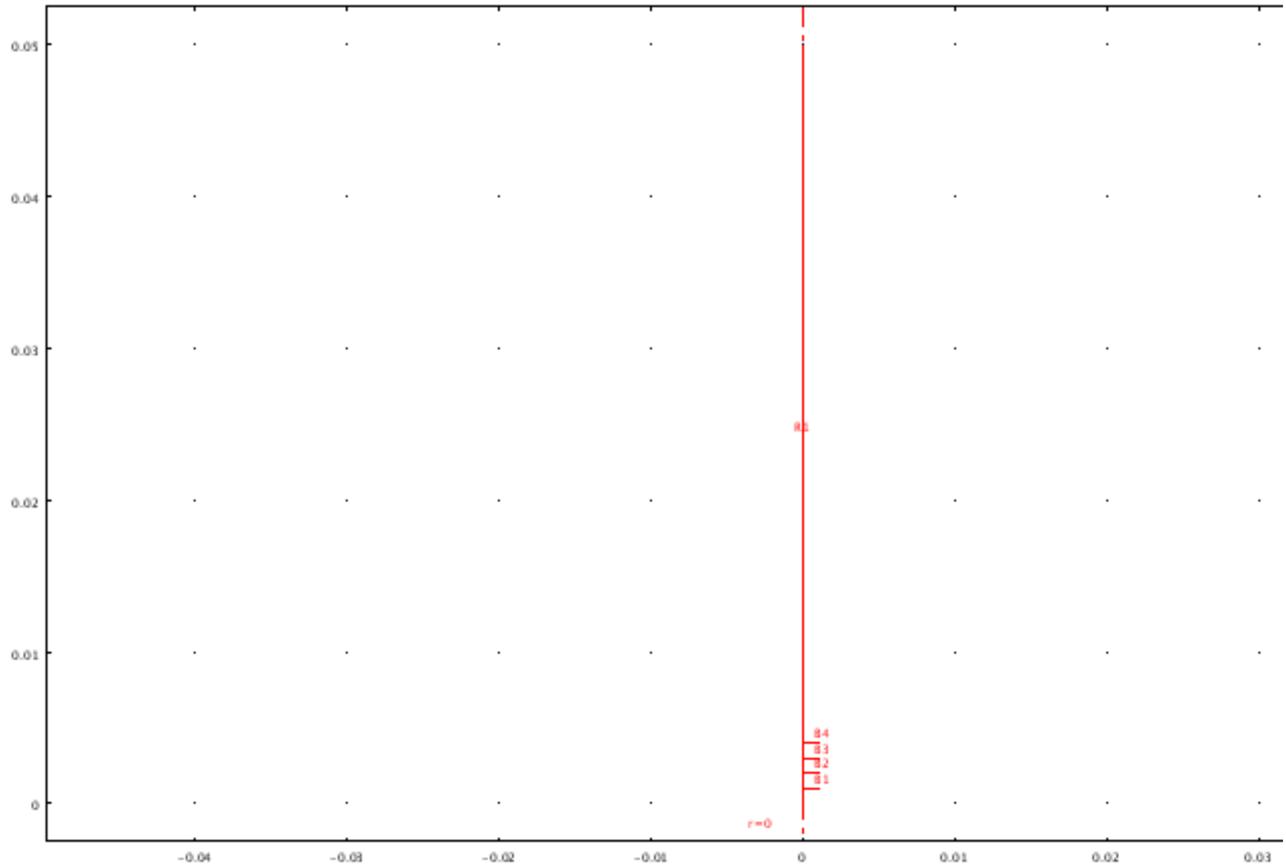
3. Constants

Name	Expression	Value	Description
Vv	0.20[uL/min]		
S	pi*rad*rad		
rad	50e-6[m]		
time	0.05[m]/(Vv/S)		

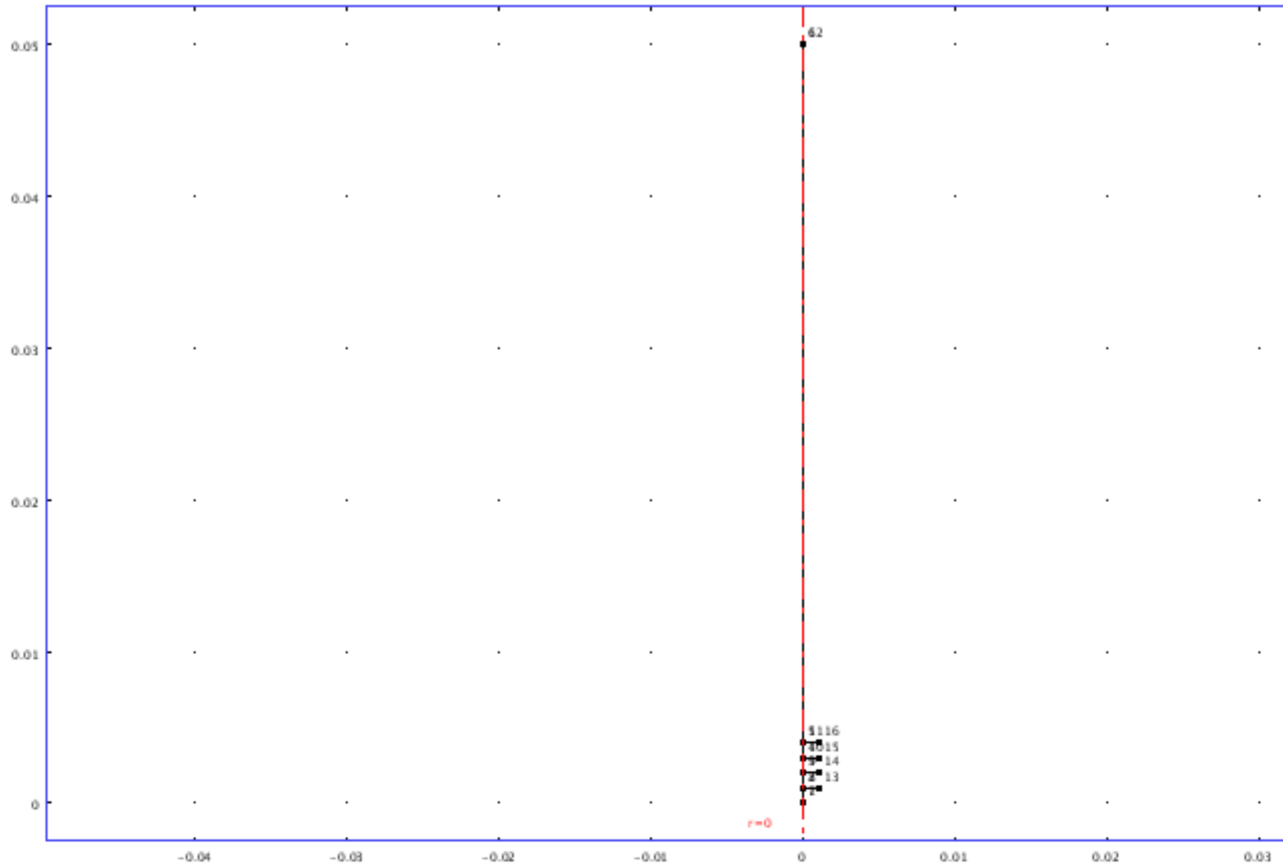
4. Geometry

Number of geometries: 1

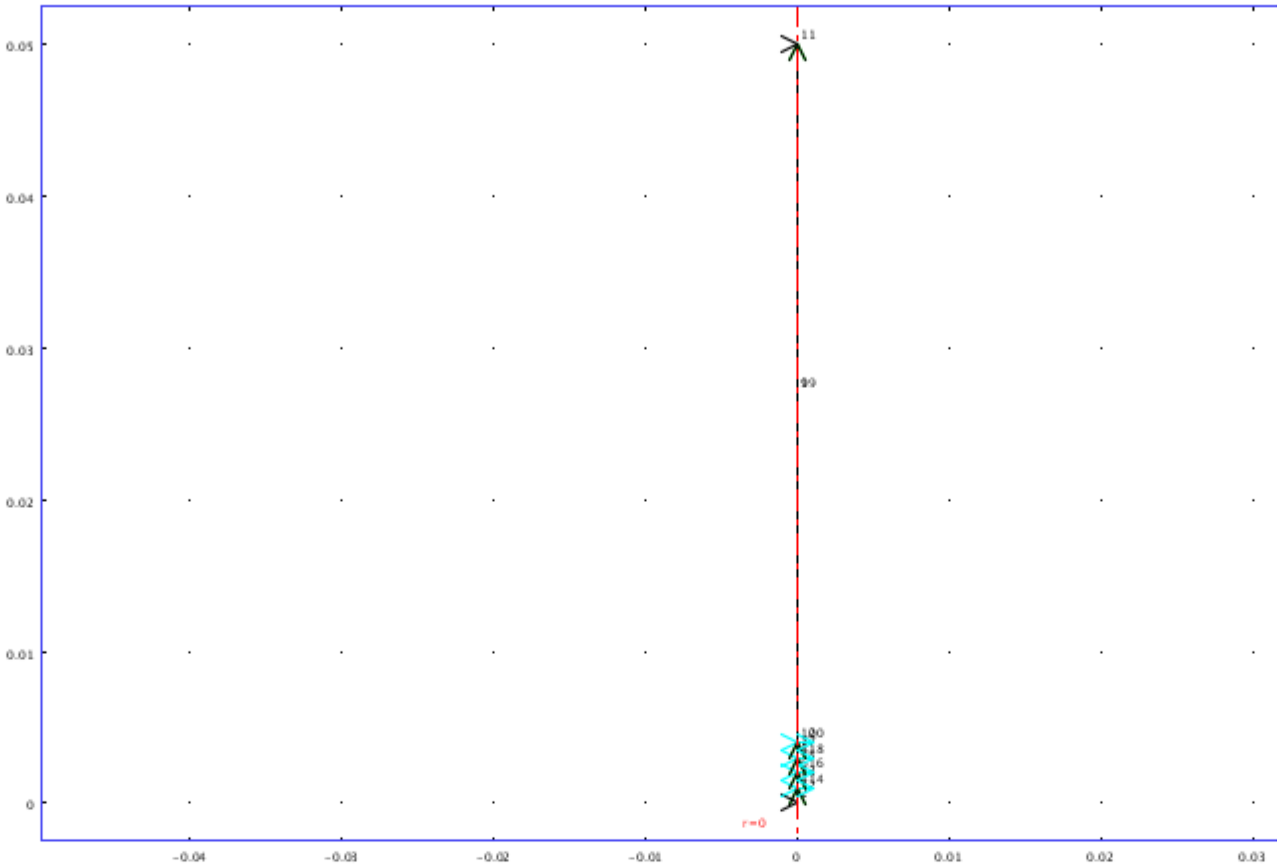
4.1. Geom1



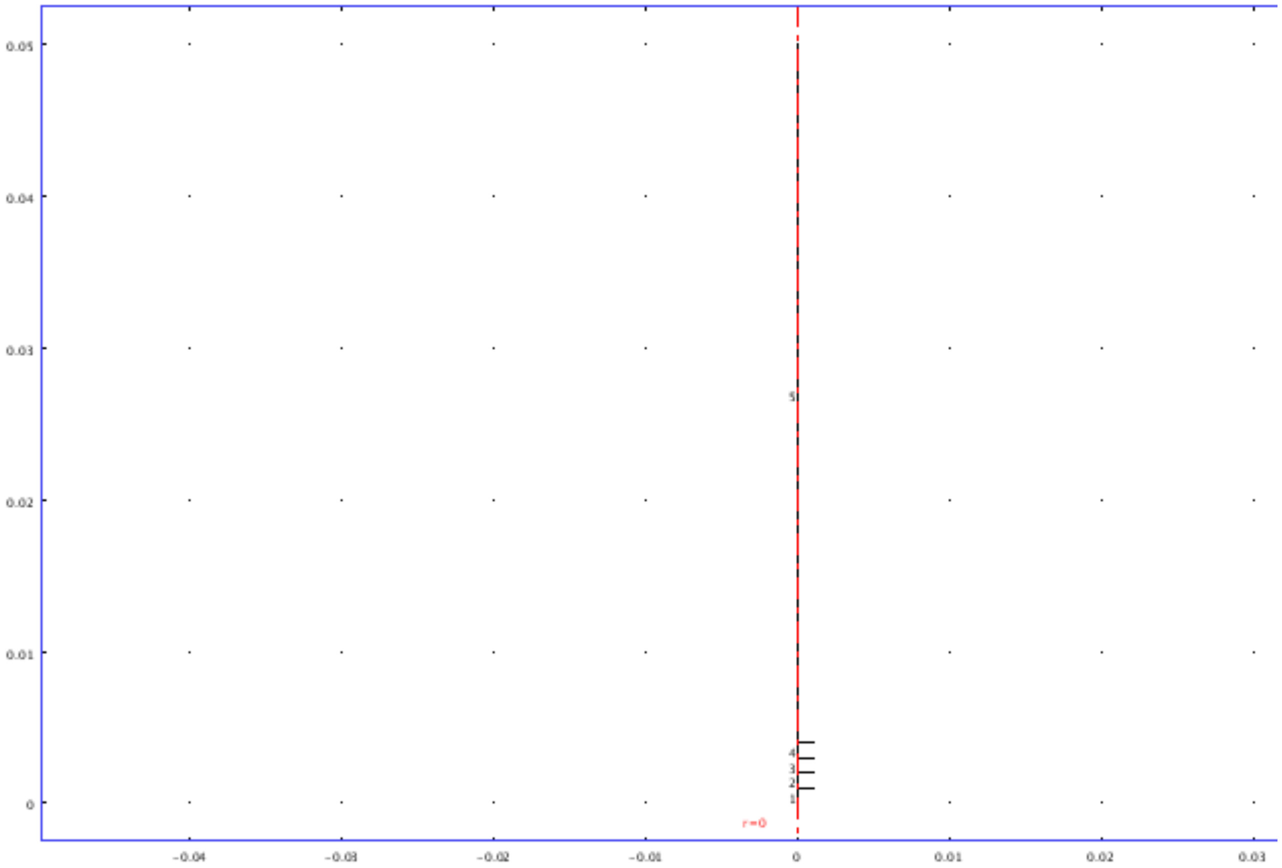
4.1.1. Point mode



4.1.2. Boundary mode



4.1.3. Subdomain mode



5. Geom1

Space dimensions: Axial symmetry (2D)

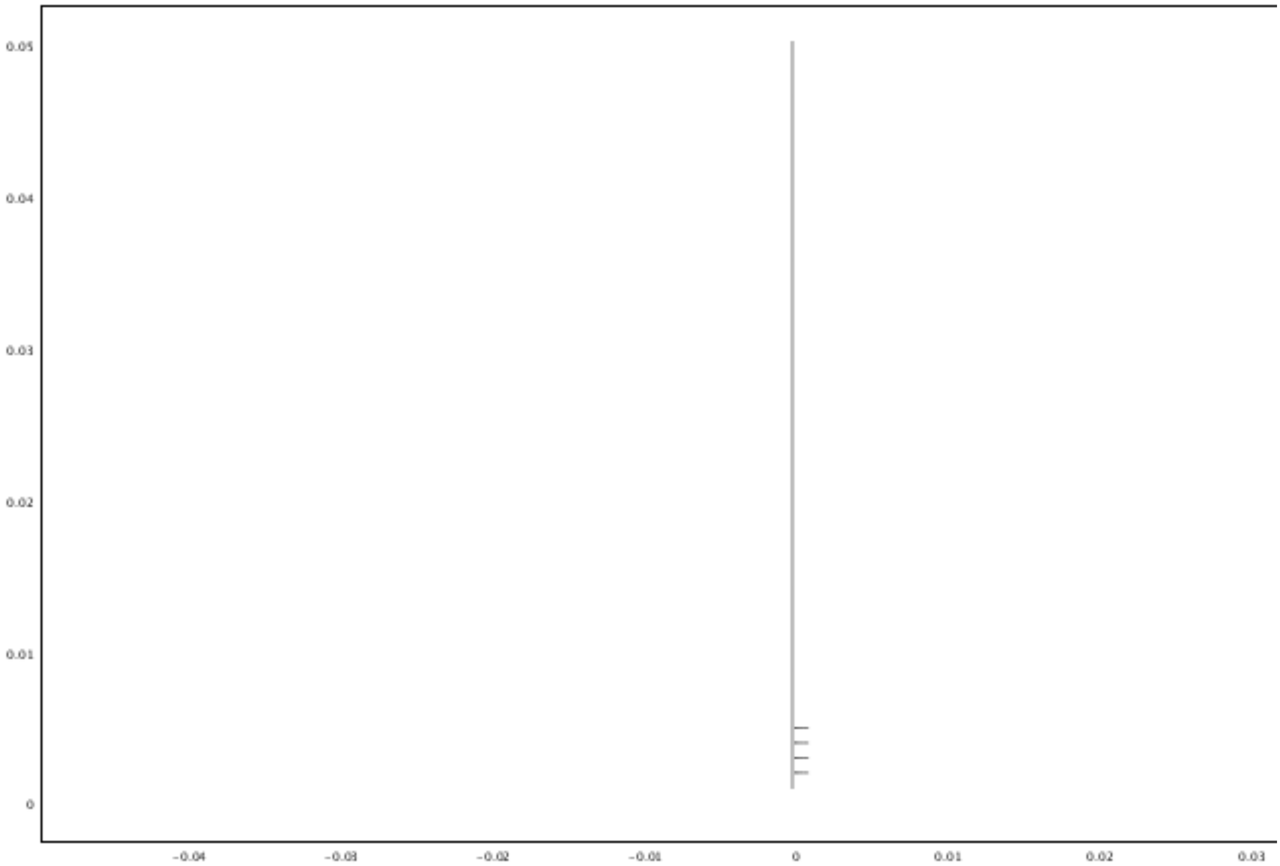
Independent variables: r, phi, z

5.1. Mesh

5.1.1. Mesh Statistics

Number of degrees of freedom	213116
Number of mesh points	18059
Number of elements	29014
Triangular	29014
Quadrilateral	0
Number of boundary elements	7066
Number of vertex elements	16

Minimum element quality	0.841
Element area ratio	0.111



5.2. Application Mode: Convection and Diffusion (cd)

Application mode type: Convection and Diffusion

Application mode name: cd

5.2.1. Application Mode Properties

Property	Value
Default element type	Lagrange - Quadratic
Analysis type	Transient
Equation form	Non-conservative
Frame	Frame (ref)
Weak constraints	Off

Constraint type	Ideal

5.2.2. Variables

Dependent variables: c

Shape functions: shlag(2,'c')

Interior boundaries not active

5.2.3. Boundary Settings

Boundary		1, 3, 5, 7, 9	2, 11-13, 15, 17, 19
Type		Axial symmetry	Insulation/Symmetry

5.2.4. Subdomain Settings

Subdomain		1, 3, 5	2, 4
Diffusion coefficient (D)	m^2/s	**1e-9**	**1e-9**
r-velocity (u)	m/s	**u**	**u**
z-velocity (v)	m/s	**v**	**v**

Subdomain initial value		1, 3, 5	2, 4
Concentration, c (c)	mol/m^3	0	1

5.3. Application Mode: Incompressible Navier-Stokes (chns)

Application mode type: Incompressible Navier-Stokes (Chemical Engineering Module)

Application mode name: chns

5.3.1. Scalar Variables

Name	Variable	Value	Unit	Description
visc_vel_fact	visc_vel_fact_chns	10	1	Viscous velocity factor

5.3.2. Application Mode Properties

Property	**Value**
Default element type	Lagrange - P_2 P_1
Analysis type	Stationary
Corner smoothing	Off
Weakly compressible flow	Off
Turbulence model	None
Realizability	Off
Non-Newtonian flow	Off
Brinkman on by default	Off

Two-phase flow	Single-phase flow
Swirl velocity	Off
Frame	Frame (ref)
Weak constraints	Off
Constraint type	Ideal

5.3.3. Variables

Dependent variables: u, v, w, p, logk, logd, logw, phi, psi, nrw, nzw

Shape functions: shlag(2,'u'), shlag(2,'v'), shlag(1,'p')

Interior boundaries not active

5.3.4. Boundary Settings

Boundary		1, 3, 5, 7, 9	2	11
Type		Symmetry boundary	Inlet	Outlet
symtype		**Axial symmetry**	Symmetry	Symmetry
Normal inflow velocity (U0in)	m/s	1	**Vv/S**	1

Boundary		12-13, 15, 17, 19
Type		Wall
symtype		Symmetry
Normal inflow velocity (U0in)	m/s	1

5.3.5. Subdomain Settings

Subdomain		1-5
Integration order (gporder)		**4 4 2**
Constraint order (cporder)		**2 2 1**

6. Solver Settings

Solve using a script: off

Analysis type	Transient
Auto select solver	On
Solver	Time dependent
Solution form	Automatic
Symmetric	auto
Adaptive mesh refinement	Off
Optimization/Sensitivity	Off
Plot while solving	Off

6.1. Direct (UMFPACK)

Solver type: Linear system solver

Parameter	Value
Pivot threshold	0.1
Memory allocation factor	0.7

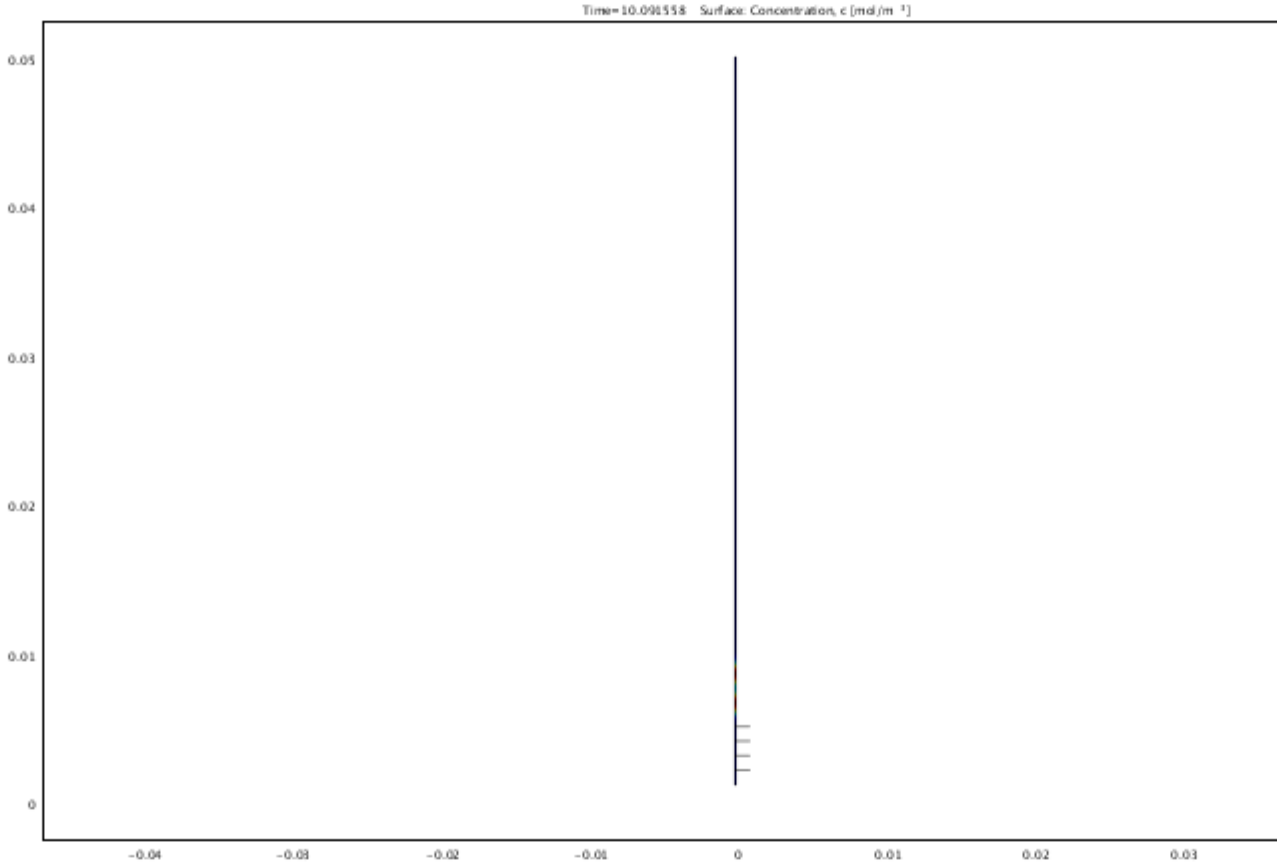
6.2. Time Stepping

Parameter	Value
Times	range(0,0.1,118)
Relative tolerance	1e-5
Absolute tolerance	1e-6
Times to store in output	Time steps from solver
Time steps taken by solver	Free
Maximum BDF order	5
Singular mass matrix	Maybe
Consistent initialization of DAE systems	Backward Euler
Error estimation strategy	Include algebraic
Allow complex numbers	Off

6.3. Advanced

Parameter	Value
Constraint handling method	Elimination
Null-space function	Automatic
Automatic assembly block size	On
Assembly block size	1000
Use Hermitian transpose of constraint matrix and in symmetry detection	Off
Use complex functions with real input	Off
Stop if error due to undefined operation	On
Store solution on file	Off
Type of scaling	Automatic
Manual scaling	
Row equilibration	On
Manual control of reassembly	Off
Load constant	On
Constraint constant	On
Mass constant	On
Damping (mass) constant	On
Jacobian constant	On
Constraint Jacobian constant	On

7. Postprocessing



8. Variables

8.1. Boundary

8.1.1. Boundary 1-13, 15, 17, 19

Name	Description	Unit	Expression
ndflux_c_cd	Normal diffusive flux, c	mol/(m^2*s)	nr_cd * dflux_c_r_cd+nz_cd * dflux_c_z_cd
ncflux_c_cd	Normal convective flux, c	mol/(m^2*s)	nr_cd * cflux_c_r_cd+nz_cd * cflux_c_z_cd
ntflux_c_cd	Normal total flux, c	mol/(m^2*s)	nr_cd * tflux_c_r_cd+nz_cd * tflux_c_z_cd
K_r_chns	Viscous force per area, r component	Pa	eta_chns * (2 * nr_chns * ur+nz_chns * (uz+vr))
T_r_chns	Total force per area, r component	Pa	-nr_chns * p+2 * nr_chns * eta_chns * ur+nz_chns * eta_chns * (uz+vr)

K_z_chns	Viscous force per area, z component	Pa	eta_chns * (nr_chns * (vr+uz)+2 * nz_chns * vz)
T_z_chns	Total force per area, z component	Pa	-nz_chns * p+nr_chns * eta_chns * (vr+uz)+2 * nz_chns * eta_chns * vz

8.1.2. Boundary 14, 16, 18, 20

Name	Description	Unit	Expression
ndflux_c_cd	Normal diffusive flux, c	mol/(m^2*s)	
ncflux_c_cd	Normal convective flux, c	mol/(m^2*s)	
ntflux_c_cd	Normal total flux, c	mol/(m^2*s)	
K_r_chns	Viscous force per area, r component	Pa	
T_r_chns	Total force per area, r component	Pa	
K_z_chns	Viscous force per area, z component	Pa	
T_z_chns	Total force per area, z component	Pa	

8.2. Subdomain

Name	Description	Unit	Expression
grad_c_r_cd	Concentration gradient, c, r component	mol/m^4	cr
dflux_c_r_cd	Diffusive flux, c, r component	mol/(m^2*s)	-Drr_c_cd * cr-Drz_c_cd * cz
cflux_c_r_cd	Convective flux, c, r component	mol/(m^2*s)	c * u_c_cd
tflux_c_r_cd	Total flux, c, r component	mol/(m^2*s)	dflux_c_r_cd+cflux_c_r_cd
grad_c_z_cd	Concentration gradient, c, z component	mol/m^4	cz
dflux_c_z_cd	Diffusive flux, c, z component	mol/(m^2*s)	-Dzr_c_cd * cr-Dzz_c_cd * cz
cflux_c_z_cd	Convective flux, c, z component	mol/(m^2*s)	c * v_c_cd
tflux_c_z_cd	Total flux, c, z component	mol/(m^2*s)	dflux_c_z_cd+cflux_c_z_cd
beta_c_r_cd	Convective field, c, r component	m^2/s	r * u_c_cd
beta_c_z_cd	Convective field, c, z component	m^2/s	r * v_c_cd
grad_c_cd	Concentration gradient, c	mol/m^4	sqrt(grad_c_r_cd^2+grad_c_z_cd^2)

dflux_c_cd	Diffusive flux, c	mol/(m^2*s)	sqrt(dflux_c_r_cd^2+dflux_c_z_cd^2)
cflux_c_cd	Convective flux, c	mol/(m^2*s)	sqrt(cflux_c_r_cd^2+cflux_c_z_cd^2)
tflux_c_cd	Total flux, c	mol/(m^2*s)	sqrt(tflux_c_r_cd^2+tflux_c_z_cd^2)
cellPe_c_cd	Cell Peclet number, c	1	h * sqrt(beta_c_r_cd^2+beta_c_z_cd^2)/Dm_c_cd
Dm_c_cd	Mean diffusion coefficient, c	m^3/s	r * (Drr_c_cd * u_c_cd^2+Drz_c_cd * u_c_cd * v_c_cd+Dzr_c_cd * v_c_cd * u_c_cd+Dzz_c_cd * v_c_cd^2)/(u_c_cd^2+v_c_cd^2+eps)
res_c_cd	Equation residual for c	mol/(m^2*s)	r * (-Drr_c_cd * crr-Drz_c_cd * crz+cr * u_c_cd-Dzr_c_cd * czr-Dzz_c_cd * czz+cz * v_c_cd-R_c_cd)
res_sc_c_cd	Shock capturing residual for c	mol/(m^2*s)	r * (cr * u_c_cd+cz * v_c_cd-R_c_cd)
da_c_cd	Total time scale factor, c	m	r * Dts_c_cd
U_chns	Velocity field	m/s	sqrt(u^2+v^2)
V_chns	Vorticity	1/s	uz-vr
divU_chns	Divergence of velocity field	1/s	ur+vz+u/r
cellRe_chns	Cell Reynolds number	1	rho_chns * U_chns * h/eta_chns
res_u_chns	Equation residual for u	Pa	r * (rho_chns * (u * ur+v * uz)+pr-F_r_chns)+2 * eta_chns * (u/r-ur)-eta_chns * r * (2 * urr+uzz+vrz)
res_v_chns	Equation residual for v	Pa	r * (rho_chns * (u * vr+v * vz)+pz-F_z_chns)-eta_chns * (r * (vrr+uzr)+2 * r * vzz+uz+vr)
beta_r_chns	Convective field, r component	Pa*s	r * rho_chns * u
beta_z_chns	Convective field, z component	Pa*s	r * rho_chns * v
Dm_chns	Mean diffusion coefficient	kg/s	r * eta_chns
da_chns	Total time scale factor	kg/m^2	r * rho_chns
taum_chns	GLS time-scale	m^3*s/kg	nojac(1/max(2 * rho_chns * sqrt(emetric(u,v)),48 * eta_chns/h^2))
tauc_chns	GLS time-scale	m^2/s	0.5 * nojac(if(u^2+v^2
res_p_chns	Equation residual for p	kg/(m^2*s)	rho_chns * r * divU_chns